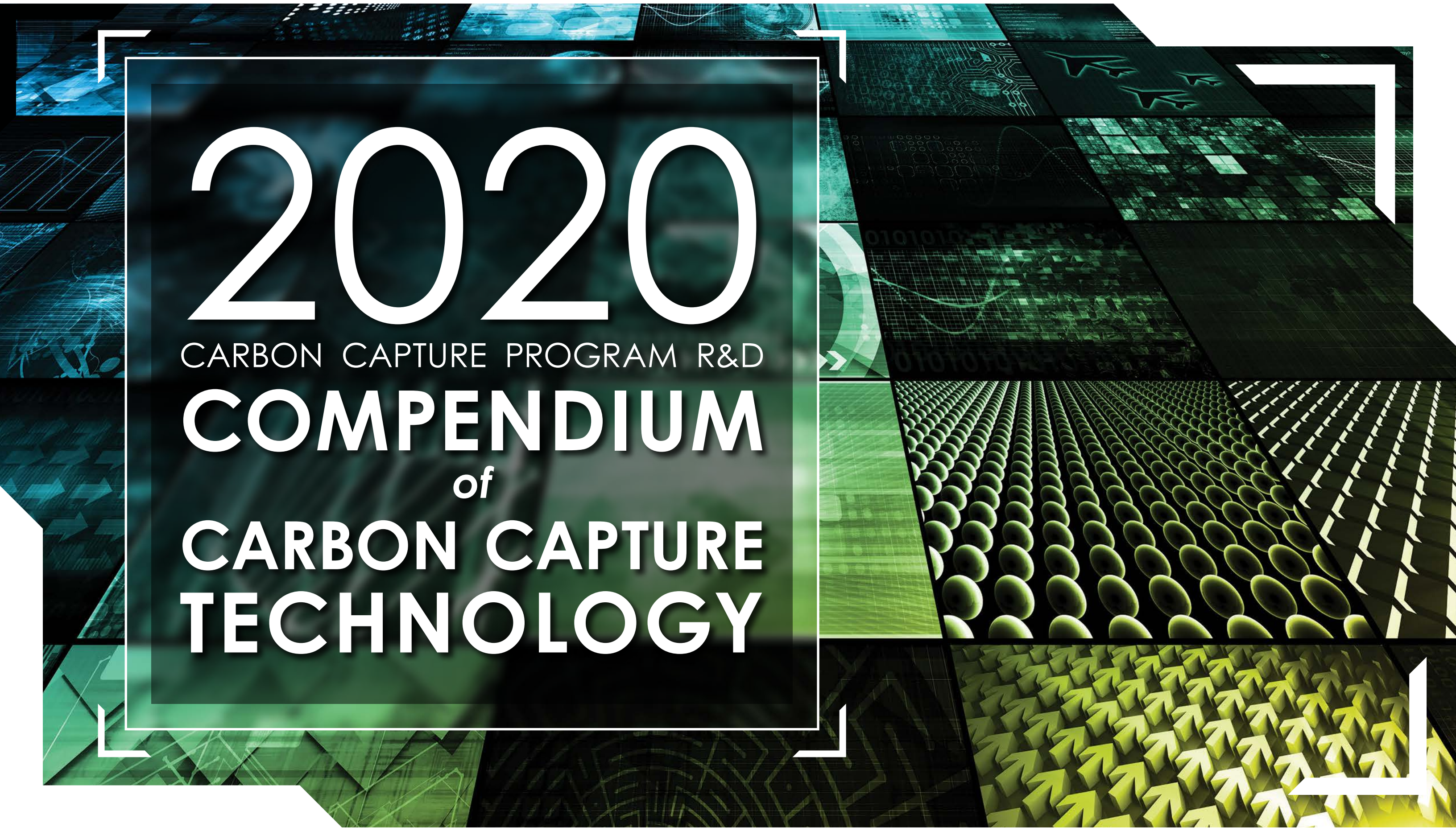

2020
CARBON CAPTURE PROGRAM R&D
COMPENDIUM
of
CARBON CAPTURE TECHNOLOGY

MAY 2020

U.S. DEPARTMENT OF ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

05.2020–1000

DISCLAIMER

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COMPENDIUM OF CARBON CAPTURE TECHNOLOGY

OVERVIEW

The U.S. Department of Energy's (DOE) Fossil Energy Program has adopted a comprehensive, multi-pronged approach to the research and development (R&D) of advanced carbon dioxide (CO_2) capture technologies for today's fossil fuel-based power platforms, as well as for industrial systems. The National Energy Technology Laboratory (NETL) is implementing the Carbon Capture R&D Program to develop the next generation of advanced CO_2 capture concepts. The success of this research will enable cost-effective implementation of carbon capture and storage (CCS) technologies throughout the power generation sector and ensure the United States will continue to have access to safe, reliable, and affordable energy from fossil fuels.

DOE's CCS R&D effort is conducted as part of the CCS and Power Systems Program under the Office of Clean Coal and Carbon Management (OCCM). OCCM is implemented by NETL through contracted research activities and onsite research at NETL. Research projects are carried out under various award mechanisms — including partnerships, cooperative agreements, and financial assistance grants — with corporations, small businesses, universities, nonprofit organizations, and other national laboratories and government agencies.

DOE/NETL's Carbon Capture Program consists of two core research areas — Post-Combustion Capture and Pre-Combustion Capture — composed of projects with Technology Readiness Levels (TRLs) ranging from conceptual engineering and materials design (i.e., TRL 2) to 25-megawatt-electrical (MWe) equivalent pilot testing (i.e., TRL 5-7). These two core areas are focused on creating technological improvements providing a step-change in both cost and performance as compared to current state-of-the-art solvent-based capture systems. Post-combustion systems separate CO_2 from the flue gas stream produced by conventional fossil fuel-fired power plants after fuel combustion in air. In this approach, CO_2 is separated from nitrogen (N_2), the primary constituent of the flue gas. Pre-combustion systems are designed to separate CO_2 and hydrogen (H_2) from the syngas stream produced by the gasifier in integrated gasification combined cycle (IGCC) power plants. In both cases, R&D is underway to develop technologies based on advanced solvents, sorbents, membranes, hybrid systems, and other novel concepts.

This Technology Compendium provides a technical summary of DOE/NETL's Carbon Capture Program, assembling CO_2 capture technology R&D descriptions for 132 projects in a single document. As of October 1, 2019, there were 80 active projects and 52 completed projects. Active projects listed were active at some point between September 1, 2017, and October 1, 2019, some of which may have ended during that time frame. Descriptions of the completed projects are provided in Appendix A. It should be noted that some of the previously completed projects may differ slightly in format as they were developed for a prior version of the compendium. The following tables list the CO_2 capture technologies summarized in this Compendium as developed under DOE/NETL's onsite and external R&D projects.

National Energy Technology Laboratory – Research and Innovation Center Technologies

Onsite research at NETL in CO_2 capture leverages cutting-edge research facilities, world-class scientists and engineers, state-of-the-art computational modeling and simulation tools, and strategic collaborations to foster the discovery, development, and testing of transformational materials and high-throughput computational tools. Through the Carbon Capture Simulation for Industry Impact (CCSI^2), DOE's core strengths in modeling and simulation are partnered with industry to scale-up new and innovative carbon capture technologies.

Project Focus	Participant	Performance Period
ACTIVE		
Transformational Solvents	National Energy Technology Laboratory – Research and Innovation Center Technologies	04.01.2019 – 03.31.2022
Microwave Assisted Sorbent Regeneration	National Energy Technology Laboratory – Research and Innovation Center Technologies	04.01.2019 – 03.31.2022
Transformational Membranes	National Energy Technology Laboratory – Research and Innovation Center Technologies	04.01.2019 – 03.31.2022
Systems Engineering & Analysis	National Energy Technology Laboratory – Research and Innovation Center Technologies	04.01.2019 – 03.31.2022
Carbon Capture Simulation for Industry Impact	National Energy Technology Laboratory – Research and Innovation Center Technologies	04.01.2019 – 03.31.2022

Post-Combustion Solvent Technologies

High levels of CO_2 capture are possible with chemical solvent-based systems, but these systems also require significant amounts of energy for regeneration, which involves a temperature swing to break the absorbent-CO_2 chemical bond. Advanced solvents that have lower regeneration energy requirements, lower volatility, and lower degradation rates than commercially available amine systems, combined with high CO_2 capture capacity and tolerance to flue gas impurities, are being developed through DOE/NETL-sponsored research. Water-lean solvents are particularly promising for CO_2 capture processes, providing significant reductions in energy requirements, corrosion, and solvent losses.

Project Focus	Participant	Performance Period
ACTIVE		
Piperazine Solvent with Flash Regeneration	URS Group	10.01.2010 – 12.31.2018
Advanced Solvents, Heat Integration, and Membrane Separation	University of Kentucky	10.01.2011 – 03.31.2019
Microencapsulated CO_2 Capture Materials	University of Notre Dame	10.01.2015 – 03.31.2019
Direct Air Capture from Dilute CO_2 Sources	Carbon Engineering LTD	09.19.2016 – 06.30.2019
CO_2-Binding Organic Liquid Solvents	Pacific Northwest National Laboratory	07.01.2017 – 03.31.2021
Electrochemical Regeneration of Amine Solvents	Massachusetts Institute of Technology	08.01.2017 – 07.31.2020
Linde/BASF CO_2 Capture Process	University of Illinois at Urbana-Champaign	04.04.2018 – 12.31.2020
Biphasic Solvents for CO_2 Absorption	University of Illinois at Urbana-Champaign	04.06.2018 – 04.05.2021
Molecular Refinement of Water-Lean Solvents	Pacific Northwest National Laboratory	05.01.2018 – 01.31.2021
Advanced Mixed-Salt Solvent Process	SRI International	06.01.2018 – 11.30.2021
Pre-FEED Study for Retrofit	University of North Dakota Energy and Environmental Center	06.25.2018 – 12.31.2019
Ammonia- and Potassium Carbonate-Based Mixed Salt Solvent	SRI International	07.01.2018 – 07.31.2021
Water-Lean Solvent	Research Triangle Institute	08.08.2018 – 06.30.2021
CO_2-Binding Organic Liquid Solvents	Pacific Northwest National Laboratory	10.01.2018 – 09.30.2020
Rotating Packed Bed with Advanced Solvent	Gas Technology Institute	10.01.2018 – 03.31.2021
Novel Additives for Water-Lean Amines	Liquid Ion Solutions, LLC	10.01.2018 – 09.30.2021
Water-Lean Solvent Emissions Mitigation	Research Triangle Institute	10.01.2018 – 09.30.2021
Fog and Froth Solvent Process	University of Kentucky	05.01.2019 – 04.30.2021
Water-Lean Amine-Based Solvent for CO_2 Capture	ION Clean Energy, Inc.	06.01.2019 – 05.31.2021
Advanced KM CDR Process FEED	University of Illinois at Urbana-Champaign	09.30.2019 – 09.30.2021
FEED Study for Carbon Capture System Retrofit	ION Clean Energy, Inc.	10.01.2019 – 03.31.2021
Econamine FG Plus (EFG+) Retrofit to NGCC FEED	Electric Power Research Institute, Inc.	10.01.2019 – 03.31.2021
Piperazine Solvent with Advanced Stripper FEED	University of Texas at Austin	10.01.2019 – 06.30.2021
Fluor's Econamine FG Plus Technology FEED	Minnkota Power Cooperative, Inc.	10.01.2019 – 09.30.2020
Amine-Based Capture Retrofit to NGCC FEED	Bechtel National, Inc.	10.01.2019 – 09.30.2020
Linde-BASF Amine Solvent-Based Technology Retrofit for NGCC	Southern Company Services, Inc.	10.01.1029 – 09.30.2021
KM CDR Process FEED	Enchant Energy LLC	10.15.2019 – 03.31.2021
COMPLETED (in Appendix)		
Phase-Changing Absorbent	GE Global Research	11.01.2014 – 09.30.2017
CO_2-Binding Organic Liquid Solvents	Pacific Northwest National Laboratory	04.01.2014 – 09.30.2017

Project Focus	Participant	Performance Period
Aminosilicone Solvent	GE Global Research	10.01.2015 – 06.30.2017
Waste Heat Integration	Southern Company Services, Inc.	10.01.2011 – 03.31.2017
Amine-Based Solvent and Process Improvements	Southern Company Services, Inc.	10.01.2015 – 03.31.2017
Slipstream Novel Amine-Based Post-Combustion Process	Linde LLC	12.01.2011 – 11.30.2016
Chilled Ammonia Process Improvements	GE Power	10.01.2015 – 09.30.2016
Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution (“Solvents”)	Akermin, Inc.	10.01.2013 – 09.30.2016
Carbon Absorber Retrofit Equipment	Neumann Systems Group	01.02.2012 – 12.31.2015
Novel Absorption/Stripper Process	William Marsh Rice University	10.01.2011 – 12.31.2015
Gas-Pressurized Stripping	Carbon Capture Scientific LLC	10.01.2011 – 06.30.2015
Solvent + Enzyme and Vacuum Regeneration Technology	Novozymes North America, Inc.	10.01.2011 – 06.30.2015
Optimized Solvent Formulation	Babcock & Wilcox	10.01.2011 – 04.30.2014
Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping	University of Illinois at Urbana-Champaign	01.01.2011 – 03.31.2014
Self-Concentrating Amine Absorbent	3H Company, LLC	10.01.2010 – 01.31.2013
Ionic Liquids	University of Notre Dame	03.01.2007 – 09.30.2012
Novel Integrated Vacuum Carbonate Process	Illinois State Geological Survey	10.01.2008 – 04.30.2012
POSTCAP Capture and Sequestration	Siemens Energy Inc.	10.01.2010 – 02.29.2012
Chemical Additives for CO_2 Capture	Lawrence Berkeley National Laboratory	06.01.2008 – 09.30.2011
Reversible Ionic Liquids	Georgia Tech Research Corporation	10.01.2008 – 09.30.2011
Phase Transitional Absorption	Hampton University	06.15.2005 – 06.30.2009

Post-Combustion Sorbent Technologies

DOE/NETL’s R&D objectives for post-combustion sorbents include development of low-cost, durable sorbents that have high selectivity, high CO_2 adsorption capacity, and can withstand multiple regeneration cycles with little to no attrition.

Project Focus	Participant	Performance Period
ACTIVE		
Alkalized Alumina Solid Sorbent	TDA Research, Inc.	02.03.2014 – 01.31.2020
Fluidizable Solid Sorbents	Research Triangle Institute	10.01.2015 – 06.30.2018
Pressure Swing Adsorption Process with Novel Sorbent	Georgia Tech Research Corporation	10.01.2015 – 09.30.2019
Porous Polymer Networks	Texas A&M University	10.01.2015 – 03.31.2019
Structured Sorbent-Based Process for Low-Concentration Sources	InnoSepra, LLC	02.22.2016 – 04.09.2019
High Efficiency Post Combustion Carbon Capture System	Precision Combustion, Inc.	02.21.2017 – 05.20.2020
Amine-Appended Metal-Organic Framework Sorbent	Lawrence Berkeley National Laboratory	08.31.2017 – 07.31.2021
Amine-Functionalized Resin Sorbent	TDA Research, Inc.	07.02.2018 – 08.18.2021
Membrane-Sorbent Hybrid System	TDA Research, Inc.	08.15.2018 – 08.14.2021
Bi-Layer Structured Sorbent	Electricore, Inc.	05.01.2019 – 04.30.2021
Microporous Sorbent	InnoSepra, LLC	05.01.2019 – 04.30.2022

Project Focus	Participant	Performance Period
Metal-Organic Framework (MOF)-Based Sorbent	TDA Research, Inc.	06.01.2019 – 05.31.2022
Size-Sieving Sorbent Integrated with Pressure Swing Adsorption	Rensselaer Polytechnic Institute	10.01.2019 – 09.30.2022
COMPLETED (in Appendix)		
Novel Solid Sorbent	SRI International	10.01.2013 – 09.30.2018
Advanced Aerogel Sorbents	Aspen Aerogels, Inc.	10.01.2013 – 12.31.2016
Temperature Swing Adsorption with Structured Sorbent	NRG Energy Inc.	10.01.2015 – 09.30.2016
Rapid Pressure Swing Adsorption	W.R. Grace and Co.	10.01.2011 – 07.31.2016
Cross-Heat Exchanger for Sorbent-Based CO_2 Capture	ADA-ES, Inc.	10.01.2013 – 12.31.2015
Advanced Solid Sorbents and Processes for CO_2 Capture	RTI International	10.01.2011 – 12.31.2015
Low-Cost, High-Capacity Regenerable Sorbent	TDA Research, Inc.	10.01.2011 – 09.30.2015
Rapid Temperature Swing Adsorption	Georgia Tech Research Corporation	10.01.2011 – 03.31.2015
Hybrid Sorption Using Solid Sorbents	University of North Dakota	10.01.2011 – 12.31.2014
Metal Monolithic Amine-Grafted Zeolites	University of Akron	02.21.2007 – 03.31.2011
CO_2 Removal from Flue Gas Using Microporous MOFs	UOP	03.12.2007 – 06.30.2010
Dry Sorbent-Based Post Combustion CO_2 Capture Process	Research Triangle Institute	03.07.2007 – 12.31.2009

Post-Combustion Membrane Technologies

DOE/NETL's R&D objectives for post-combustion membrane technologies include the development of low-cost, durable membranes that have improved permeability and selectivity, thermal and physical stability, tolerance to contaminants in combustion flue gas, and are integrated into low pressure drop modules.

Project Focus	Participant	Performance Period
ACTIVE		
Sub-Ambient Temperature Membrane	American Air Liquide, Inc.	10.01.2015 – 12.31.2019
Selective Membranes for <1% CO_2 Sources	Ohio State University	03.01.2016 – 08.31.2019
Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes	Luna Innovations	02.21.2017 – 05.20.2020
Large Pilot Polymer Membrane System	Membrane Technology and Research, Inc.	04.01.2018 – 12.31.2020
Polymeric Membrane-Based Post Combustion Engineering Design	Electric Power Research Institute, Inc.	04.06.2018 – 03.31.2020
Polymeric Membranes	Membrane Technology and Research, Inc.	06.01.2018 – 09.30.2021
Graphene Oxide Membranes	Gas Technology Institute	06.01.2018 – 09.30.2021
Polaris™ Membrane CO_2 Capture System	Membrane Technology and Research, Inc.	08.01.2018 – 07.31.2021
Mixed Matrix Membranes	State University of New York	07.01.2019 – 06.30.2020
Inorganic/Polymer Composite Membranes	Ohio State University	07.01.2019 – 06.30.2022
Polaris Membrane Technology FEED	Membrane Technology and Research, Inc.	10.01.2019 – 09.30.2021
COMPLETED (in Appendix)		
Inorganic/Polymer Composite Membrane	Ohio State University	10.01.2011 – 12.31.2015
Composite Hollow Fiber Membranes	GE Global Research	10.01.2011 – 12.31.2014
Low-Pressure Membrane Contactors (Mega-Module)	Membrane Technology & Research, Inc.	10.01.2011 – 09.30.2014

Project Focus	Participant	Performance Period
Hollow-Fiber, Polymeric Membrane	Research Triangle Institute	09.26.2008 – 09.30.2011
Biomimetic Membrane	Carbozyme	03.28.2007 – 07.31.2009
Dual Functional, Silica-Based Membrane	University of New Mexico	08.23.2004 – 04.30.2009

Post-Combustion Novel Concepts

DOE/NETL is evaluating various post-combustion novel concepts for large-scale CO_2 capture or compression. Novel concepts include hybrid systems that combine attributes from multiple technologies, electrochemical membranes, and advanced manufacturing to enable enhanced processes. Several concepts were evaluated using computational fluid dynamics and laboratory testing, leading to prototype development and field testing.

Project Focus	Participant	Performance Period
ACTIVE		
Encapsulation of Solvents in Permeable Membrane for CO_2 Capture	Lawrence Livermore National Laboratory	03.01.2015 – 04.30.2019
Integrated Temperature and Pressure Swing Carbon Capture System	Altex Technologies Corporation	06.08.2015 – 08.18.2018
ICE Membrane for Post-Combustion CO_2 Capture	Liquid Ion Solutions LLC	10.01.2015 – 09.30.2018
Supersonic Compression	Dresser-Rand Company	03.01.2016 – 06.30.2018
Cryogenic Carbon Capture Process	Sustainable Energy Solutions, LLC	10.01.2016 – 06.30.2019
Additive Manufacturing for CO_2 Capture	Oak Ridge National Laboratory	07.01.2017 – 09.20.2019
Additively Manufactured High-Efficiency Reactors for Sorbents, Solvents, and Membranes	Lawrence Livermore National Laboratory	08.01.2017 – 07.31.2021
Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture	ION Clean Energy, Inc.	01.19.2018 – 05.31.2020
Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer	University of Kentucky	05.01.2018 – 04.30.2021
Aerosol Flue Gas Pretreatment	Linde, LLC	06.01.2018 – 02.28.2021
Corrosion-Resistant Coated Carbon Steel Components in CO_2 Capture Processes	LumiShield Technologies Incorporated	10.01.2018 – 09.30.2020
Solvent Enabling Techniques	University of Kentucky	10.01.2018 – 09.30.2021
COMPLETED (IN APPENDIX)		
Supersonic Inertial CO_2 Extraction System	Orbital ATK, Inc.	10.01.2013 – 03.31.2017
Evaluation of Compression Efficiency Improvements	Southwest Research Institute	10.01.2005 – 06.30.2014

Pre-Combustion Solvent Technologies

Pre-combustion solvent R&D activities focus on addressing solvent technology challenges, including increasing CO_2-loading capacity and reaction kinetics coupled with decreasing regeneration energy.

Project Focus	Participant	Performance Period
COMPLETED (in Appendix)		
CO_2 Capture Using AC-ABC Process	SRI International	10.01.2009 – 09.30.2016

Pre-Combustion Sorbent Technologies

DOE/NETL is developing solid sorbents for pre-combustion CO_2 capture aimed at improving the cost and performance of IGCC CO_2 separation. These sorbents must maintain a high adsorption loading capacity, be resistant to attrition over multiple regeneration cycles, and exhibit good performance at the high temperatures encountered in IGCC systems to avoid the need for syngas cooling and reheating.

Project Focus	Participant	Performance Period
ACTIVE		
High Capacity Regenerable Sorbent	TDA Research, Inc.	10.01.2013 – 03.31.2021
COMPLETED (in Appendix)		
Sorbent Development for WGS	URS Group, Inc.	01.01.2010 – 09.30.2013

Pre-Combustion Membrane Technologies

Several advanced membrane technology options are under development by DOE/NETL to separate CO_2 and H_2 in coal-derived syngas. Membrane designs include metallic, polymeric, or ceramic materials operating at elevated temperatures and using a variety of chemical and/or physical mechanisms for separation. Successful membranes must have high permeability and selectivity with low pressure drop, tolerance to contaminants (e.g., sulfur), and be capable of operation at system temperatures up to 500°F.

Project Focus	Participant	Performance Period
ACTIVE		
Zeolite Membrane Reactor	Arizona State University	10.01.2015 – 12.31.2018
Mixed Matrix Membranes	State University of New York, Buffalo	10.01.2015 – 09.30.2018
WGS Catalytic Membrane Reactor	Bettergy Corporation	07.02.2018 – 08.18.2021
Composite Polymeric Membranes for H_2 Separation from Coal Syngas	Membrane Technology and Research, Inc.	10.01.2018 – 09.30.2021
PBI Polymer Membrane	SRI International	10.01.2018 – 09.30.2021
Ceramic-Carbonate Membrane Reactor	Arizona State University	10.01.2018 – 09.30.2021
Amine-Containing Polymeric Membrane	Ohio State University	10.01.2018 – 09.30.2021
Carbon Molecular Sieve Hollow Fiber Membranes	State University of New York, Buffalo	10.01.2018 – 09.30.2021
COMPLETED (in Appendix)		
Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane	Media and Process Technology, Inc.	10.01.2013 – 09.30.2017
High-Temperature Polymer-Based Membrane	Los Alamos National Laboratory	03.01.2013 – 03.31.2016
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	10.01.2009 – 09.30.2014
Pd-Alloys for Sulfur/Carbon Resistance	Pall Corporation	10.01.2009 – 09.30.2014
Hydrogen-Selective Zeolite Membranes	University of Minnesota	10.01.2009 – 09.30.2014
Pressure Swing Membrane Absorption Device and Process	New Jersey Institute of Technology	10.01.2009 – 03.31.2013
Nanoporous, Superhydrophobic Membrane Contactor Process	Gas Technology Institute	10.01.2009 – 03.31.2012

Pre-Combustion Novel Concepts

DOE/NETL is developing various novel concepts for the integration of CO_2 removal processes with other systems, including water-gas shift and adsorption reactors, to efficiently and cost-effectively separate CO_2 from produced syngas streams.

Project Focus	Participant	Performance Period
ACTIVE		
Combined CMS Membrane/WGS Reactor and Adsorption Reactor	University of Southern California	06.01.2019 – 05.31.2022
Combined CO_2 Sorbent/WGS Reactor	Southern Research Institute	10.01.2015 – 09.30.2018

R&D Collaborations

DOE/NETL also participates in R&D collaborations exploring multiple approaches to CO_2 capture for coal-based power plants and modeling the economic and emissions reduction impact of carbon capture R&D.

Project Focus	Participant	Performance Period
ACTIVE		
Carbon Capture Testing Center	Southern Company	06.06.2014 – 05.31.2020
COMPLETED (in Appendix)		
Partnership for CO_2 Capture	University of North Dakota Energy and Environmental Research Center	09.28.2011 – 12.31.2014
Analysis of CCS Technology Adoption	Argonne National Laboratory	02.01.2011 – 03.31.2014

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CARBON CAPTURE TECHNOLOGY SHEETS

RESEARCH AND INNOVATION CENTER TECHNOLOGIES

Transformational Solvents

primary project goals

The National Energy Technology Laboratory's (NETL) Research and Innovation Center (RIC) is developing advanced solvents for pre-combustion carbon dioxide (CO_2) capture that can reduce both the energy penalty and the cost of CO_2 separation compared with conventional technologies. Novel advanced solvents are optimized through designing, synthesizing, characterizing, modeling, and performance-testing these materials.

technical goals

- Design and synthesize low-cost hydrophobic solvents with high CO_2 uptake, low hydrogen (H_2) uptake, low viscosity, and low vapor pressure.
- Measure the crucial properties of these solvents, which are needed in order to conduct economic comparisons with commercially available physical solvents.
- Measure corrosion rates for both commercially available solvents and NETL-designed solvents. Generally, hydrophobic physical solvents have significantly lower corrosion rates compared with aqueous and hydrophilic solvents under acidic conditions inside a pre-combustion CO_2 capture absorber and flash tanks.
- Develop a method for operating the existing continuous stirred tank reactor (CSTR) under mixed gas conditions. While quantifying gas uptake into solvents under mixed gas conditions is challenging compared with measuring gas uptake under pure gas conditions, such data are crucial for predicting the real-world performance of a pre-combustion carbon capture solvent, especially water absorption from the gas stream effects on CO_2 and H_2 solubilities.
- Conduct economic comparisons for 30 different physical solvents, which will include both commercially available solvents and NETL-synthesized solvents.
- Conduct long-term experimental testing at the University of North Dakota's Energy and Environment Research Center (UNDEERC) on the most promising physical solvent based on economic comparisons of 30 physical solvents.
- Conduct a hybrid solvent-membrane test at UNDEERC, demonstrating the synergies of a hybrid solvent-membrane system at modular-scale gasifiers.

technical content

Liquid solvent processes are the most well-developed technology for CO_2 separation. In these processes, a liquid solvent circulates between an absorption column and a series of desorption flash tanks. The energy required to separate CO_2 from the gas stream can either come in the form of electricity or low-grade/waste heat.

The current state-of-the-art pre-combustion CO_2 capture solvents are Selexol® (Union Carbide, Houston, Texas, United States) and Rectisol® (Lurgi AG, Frankfurt am Main, Germany). Unfortunately, both solvents are hydrophilic, have high vapor pressure, and can cause significant corrosion at elevated temperatures. To avoid water uptake and solvent evaporation, the syngas temperature for both processes

technology maturity:

Laboratory-Scale; Pilot-Scale, Actual Syngas

project focus:

Pre-Combustion Solvents

participant:

National Energy Technology Laboratory – Research and Innovation Center

project number:

FWP-1022402

predecessor project:

2018 Carbon Capture FWP

NETL technical portfolio lead:

David Hopkinson
david.hopkinson@netl.doe.gov

NETL principal investigator:

Nicholas Siefert
nicholas.siefert@netl.doe.gov

partners:

University of Pittsburgh,
University of North Dakota Energy & Environmental Research Center (UNDEERC),
Carbon Capture Scientific

is typically lowered to sub-ambient conditions (10°C for Selexol and -10°C for Rectisol) and then raised back up to roughly 200°C for combustion. This process is both inefficient and costly. Instead, hydrophobic solvents with low vapor pressures could be operated at higher temperatures to avoid the energy and cost penalties associated with cooling the syngas to below ambient conditions. The ideal pre-combustion carbon capture solvent would be operated above room temperature and regenerated using waste heat, which would minimize the electricity and cost penalties associated with CO_2 separation from syngas.

Accordingly, this research is focused on finding materials that are hydrophobic so that they can be operated at temperatures between 40 and 150°C and in the presence of water vapor and contaminants. A particular focus has been placed on the testing solvents to determine their CO_2 solubility, kinetics, mass transfer, regeneration energy, stability, and corrosion rates on common steels. Each of these properties is a parameter that may be tuned in solvent development, so their effect on CO_2 separation energetics, and ultimately cost, serves to guide materials development. Equally important, system and economic studies are being conducted to determine how these material properties affect the overall performance of the pre-combustion capture system. NETL-RIC is currently conducting economics comparisons on 30 solvents (both commercially available and NETL-synthesized). Subsequently, a regression analysis will be conducted to determine the ideal combination of these properties (i.e., the trade-offs between viscosity, CO_2 uptake, H_2 uptake, and vapor pressure).

Improvements in material performance can be achieved through modifications to the structure or formulation of the solvent material. When appropriate, computational methods have been used to guide structure and formulation modifications. For example, NETL has developed several hydrophobic physical solvents with promising performance for pre-combustion CO_2 capture by combining high absorption capacity of polyethylene glycol (PEG) and the hydrophobicity and low viscosity of poly(dimethylsiloxane) (PDMS). Using hydrophobic solvents avoids the necessity to remove water vapor from the syngas stream, which increases efficiency and decreases capital cost. To date, several solvents that were invented by NETL show improvements, and one in particular, PEGPDMS-3, has shown exceptional performance for low energy and low capital cost of CO_2 removal from fuel gas. Another exciting solvent, which came from a computational screening of more than 100,000 physical solvents, is titled CASSH-1. This solvent is extremely low cost and hydrophobic, and has reasonably low vapor pressure, high CO_2 uptake, and high CO_2/H_2 selectivity.

NETL has tested both PEGPDMS-3 and CASSH-1 under real syngas generated at a fluidized-bed gasifier at UNDEERC. Both solvents performed well compared against the two commercially available solvents, which were also tested at UNDEERC under the same operating conditions. (See references below for experimental results.)

technology advantages

NETL's PEGPDMS-3 and CASSH-1 solvents have several advantages for pre-combustion CO_2 capture:

- Simple synthesis procedure using low-cost reagents.
- Hydrophobic nature allows pre-combustion capture at higher temperatures when water vapor is present in syngas, eliminating the need to lower the syngas temperature to below 40ºC to remove the water vapor and minimizing the energy and cost penalties of cooling the syngas.
- High CO_2/H_2 selectivity.
- No foaming tendency.
- Can operate above room temperature due to lower vapor pressure, reducing energy penalty for chilling syngas.

R&D challenges

Challenges for physical solvent process for pre-combustion CO_2 capture include:

- Achieving balance between required physical properties, such as viscosity, density, vapor pressure, CO_2 capacity, CO_2/H_2 selectivity, and cost.

- Identifying chemical functionalities for the optimal mix of physical properties and performance.
- Increasing the CO_2/H_2 selectivity of the solvent, increasing hydrophobicity, decreasing viscosity, and optimizing solvents for temperature, pressure, and gas mixture conditions specific to its application.
- Measuring uptake of gases into the solvent phase under real/mixed gas conditions (CO_2, H_2, water [H_2O], and other impurities)

status

In previous work, NETL developed several promising physical solvents based on PEG/PDMS with comparable CO_2 capacity, higher CO_2/H_2 selectivity, and improved vapor pressure compared to Selexol, along with improved hydrophobicity and lower viscosity. Two NETL-developed solvents were tested in actual syngas at UNDEERC.

available reports/technical papers/presentations

Siefert, N. and Hopkinson, D., "*Physical Solvent Development for Pre -Combustion Carbon Capture*," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019.

Shi, W., Thompson, R., Macala, M., Resnik, K., Steckel, J., Siefert, N., Hopkinson, D., "*Molecular Simulations of CO_2 and H_2 Solubility, CO_2 Diffusivity, and Solvent Viscosity at 298 K for 27 Commercially Available Physical Solvents*," Journal of Chemical & Engineering Data, 2019, 64, 9, 3682-3692.

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Microwave-Assisted Sorbent Regeneration

primary project goals

The objective of this project is to evaluate microwave-assisted sorbent regeneration for carbon dioxide (CO_2) capture processes as an alternative for the current state-of-the-art methods. A novel sorbent material that is optimal for electromagnetic fields will be designed, synthesized, optimized, and evaluated.

technical goals

- Develop a novel microwave-assisted slurry process for post-combustion carbon capture that has a CO_2 desorption flux 10 times faster in comparison with thermal heating and consumes much less energy for CO_2 desorption, even at process temperatures of 65 to 85°C.
- Assess microwave-assisted sorbent regeneration for some known in-house sorbent materials.
- Develop highly active, thermally and chemically stable materials to achieve sorbent regeneration at relatively lower temperatures (i.e., as low as 85°C) than the conventional processes.
- Provide a fundamental understanding of phenomena leading to the development of novel materials and processes for carbon capture technologies.
- Develop and optimize a novel reactor system for carbon capture technologies.

technical content

Carbon capture using solid sorbents has many benefits compared to state-of-the-art solvent systems, including the inherent ability to circulate less moisture than solvent systems, which results in lower heat duties. However, solid sorbents are more difficult to heat than solvents and generally require direct heating, in which the use of steam or recirculated CO_2 for regeneration results in slow kinetics. Regeneration temperatures can be reached at extremely fast rates using the method of rapid heating through microwave radiation. This rapid regeneration leads to a smaller size regenerator, potentially reducing capital costs. Sorbent regeneration rates can be enhanced by applying high-frequency electromagnetic fields to the sorbent regeneration zone, which can selectively stimulate targeted sites on the sorbent through dielectric and magnetic interactions without increasing the bulk gas temperature and solid medium. These conditions result in significantly higher sorbent regeneration rates at relatively lower temperatures than predicted by thermodynamics, which can provide savings in both energy and feed costs. Further, due to the selective input of energy, microwave heating is more efficient and more rapid than conventional heating, which requires heating of the entire reactor system and is limited by conventional heat transfer mechanisms. The basis of these effects lies in the fundamental physics by which radiation at microwave frequencies interact with matter.

technology maturity:

Laboratory/Bench-Scale, Simulated Flue Gas

project focus:

Microwave-Assisted Sorbent Regeneration for Carbon Capture

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402

predecessor project:

2018 Carbon Capture FWP

NETL technical portfolio lead:

David Hopkinson
david.hopkinson@netl.doe.gov

NETL principal investigators:

Dushyant Shekhawat
Dushyant.Shekhawat@netl.doe.gov
McMahan Gray
Mac.Gray@netl.doe.gov

partners:

N/A

The National Energy Technology Laboratory's (NETL) basic immobilized amine sorbent (BIAS) slurry has demonstrated the removal of CO_2 from a dry or humidified post-combustion flue gas, along with fast CO_2 desorption kinetics. The adsorption data shown in Figure 1 verify that the amount of CO_2 adsorbed by sorbent-1 is the same as the amount of CO_2 adsorbed by a slurry of the same sorbent dispersed in solvent-1 (when normalized to the mass of sorbent in the slurry). The equal uptake in the sorbent and slurry verify that the silicone oil dispersant does not interfere with CO_2 uptake in the suspended sorbent. The microwave desorption data showed a regeneration time of only a few minutes for releasing a CO_2 gas stream from the slurry compared to several hours using the conventional thermal regeneration method. As Figure 2 shows, microwave (MW) irradiation delivered up to 10 times more accumulated CO_2 than thermal heating (TH) within the first 20 minutes. The enhanced CO_2 desorption rate under microwave heating is especially pronounced during the first few minutes of microwave Time on Stream (mTOS) due to the lag in the thermal heating ramp resulting from the thermal inertia of the system. Thermal images, as shown in Figure 3, also demonstrated that microwave energy can be selectively absorbed by polarized components with a high dielectric loss factor (i.e., CO_2-adsorbed BIAS) in slurry. The other major advantage is a high-pressure pure CO_2 product, as indicated in Table 1 – as high as 30 pounds per square inch gauge (psig) of pressure was observed.

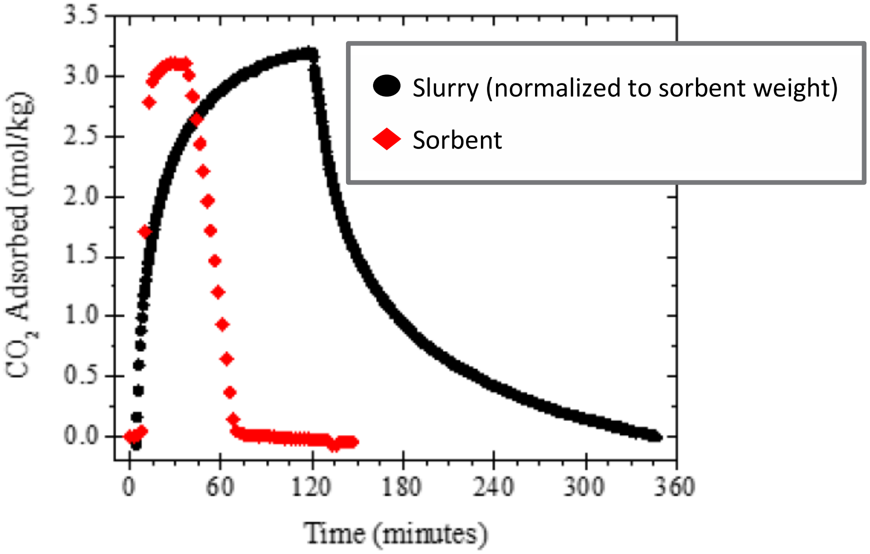

Figure 1: Comparing CO_2 uptake normalized to the mass of sorbent for the pure sorbent-1 (red) and a slurry of the same sorbent dispersed in solvent-1 (black).

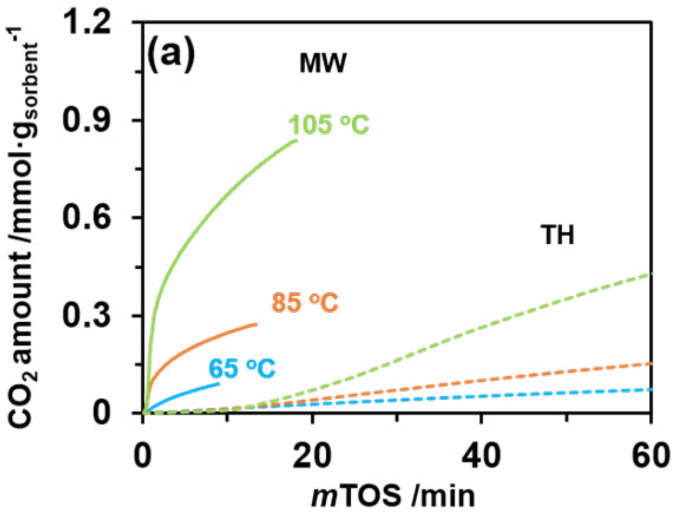

Figure 2: Comparison of microwave and thermal regeneration of the basic immobilized amine slurry.

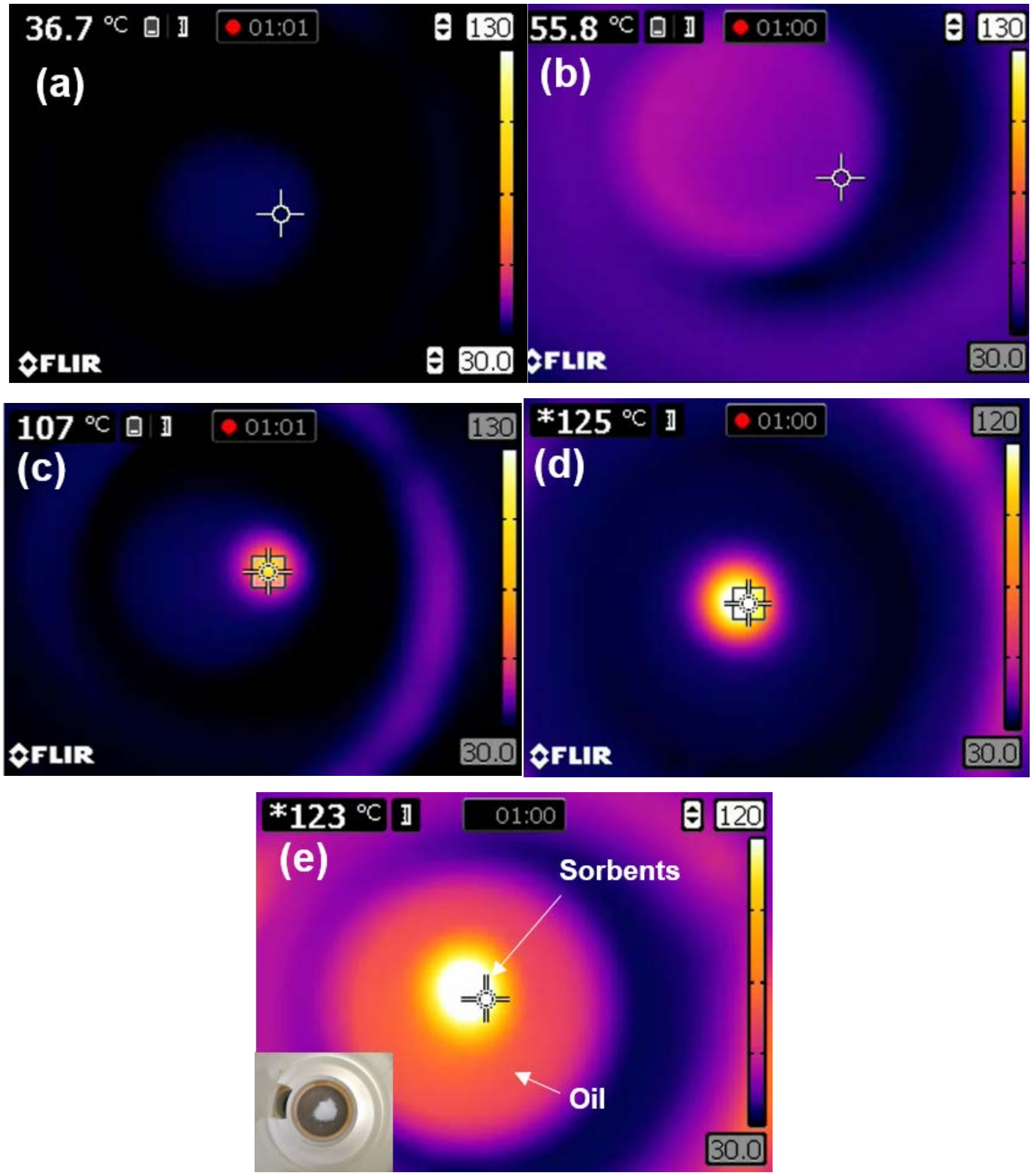

Figure 3. Thermal images of (a) silica, (b) silicone oil, (c) fresh BIAS, (d) CO_2-loaded BIAS, and (e) CO_2-adsorbed BIAS in silicone oil, respectively, at 1 min mTOS under 200-W microwave irradiation.

TABLE 1: MICROWAVE REGENERATION OPERATION PARAMETERS

Temp., °C	TOS, min	Pressure, psig	Pulsed MW output, W
40	2	n/a	-
40	2	n/a	-
60	2	*3*	-
60	5	*9*	-
100	2	*26*	13-20
100	2	*26*	13-20
100	60	*30*	13-20
100	2	*25*	13-20

Since traditional carbon capture materials may not be optimal for electromagnetic field regeneration, there is a need for proof-of-concept runs on proven sorbents that are also active in an electromagnetic field. Zeolite-based sorbents have been shown to absorb microwave radiation, and when properly functionalized, zeolite can capture CO_2. Using zeolite-based material as a capture material also allows for high surface area and tunable surface chemistry. In this project, zeolite-based materials are being investigated and optimized to improve regeneration using a semi-continuous fixed-bed microwave reactor. As microwave interactions with materials depend on the particle geometry, zeolite-based materials can be optimized by adjusting physical properties, including particle size, pore size, number of active surface sites, etc. Proof-of-concept testing on microwave-assisted regeneration of zeolite 13X have shown rapid regeneration rates with greater than 50% faster regeneration times compared to conventional regeneration (Figure 4). Zeolite 13X is an excellent microwave absorber and heats to a desorption temperature of 100°C in 30 seconds under microwave irradiation. Conventionally, heating times are on the order of 15 minutes.

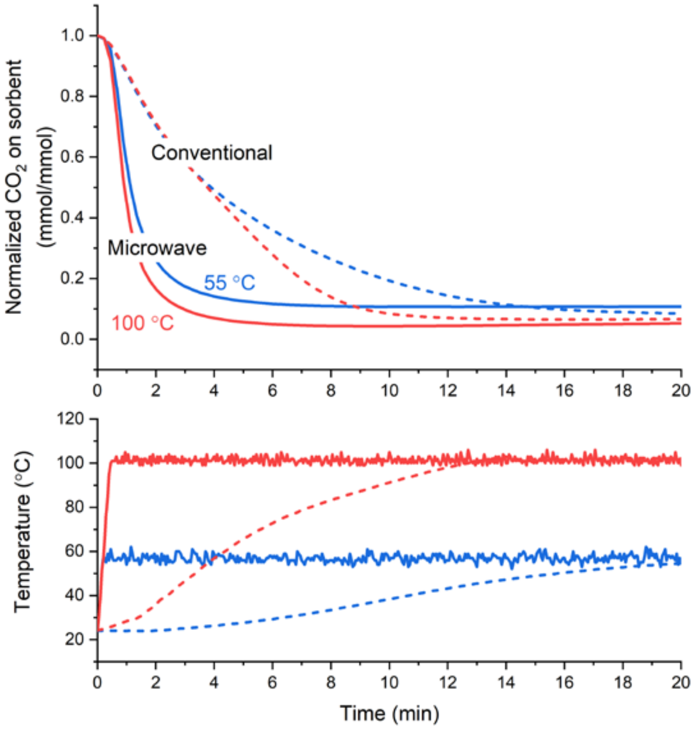

Figure 4. CO_2 desorption curves and temperature profiles during microwave and conventional regeneration of zeolite 13X.

In addition, computational modeling techniques, such as a finite difference time domain (FDTD), are being used to optimize interactions between the microwave field and material and to minimize any thermal losses in the system. Poor interaction between the microwave field and material, thermal losses, and coupling with interior features of the reactor cavity versus material contribute in making microwave technology inefficient for certain materials; therefore, it is important to target sorbent materials that can heat efficiently under microwave irradiation. In addition to zeolites, amine-based materials or carbon hybrid materials that can be heated with microwaves can also be evaluated. A basic kinetic study on the regeneration of CO_2 using these materials is required to confirm rapid release of CO_2. Furthermore, a system study will determine the energy savings associated with the process and will reveal what type of reactor is suitable for larger-scale application.

In this project, new formulas of microwave-stable slurry are being designed, synthesized, optimized, and evaluated in electromagnetic fields for carbon capture. The effects of reaction conditions (regeneration temperature; microwave power, pulse, and frequency) on slurry regeneration are being investigated. The formulated slurry is being tested in a laboratory environment (absorption at 60°C and desorption at no more than 100°C) at NETL using a Discover SP microwave reactor with simulated flue gas. Promising materials are further investigated in a bench-scale environment. In parallel to the slurry studies, an optimal sorbent material is also being designed, characterized, and evaluated for the microwave-assisted carbon capture technologies. A systems engineering and analysis assessment for microwave-assisted regeneration process is being prepared based on experimental results, including an evaluation of kinetics and activation energy of desorption, to determine the energy and cost savings compared to using steam for regeneration. A survey will be performed to explore the application of microwave technology used for any industrial scaled-up processes and the scalability of the technology.

The scale-up of the microwave-assisted slurry process for carbon capture involves testing in a slurry reactor (1-liter scale) with a microwave regeneration unit and the establishment of operating conditions and procedures to further commercialize the process. Computational efforts focus on screening and optimizing non-aqueous solvents and sorbents for use of microwave regeneration. This involves studying the interactions between CO_2 and the non-aqueous solvent or sorbent under microwave conditions and then determining the materials that will be most responsive to microwaves at certain wavelengths. Information gathered from experimental tests and modeling is used to design and improve microwave-assisted slurry carbon capture systems that can be scaled-up and tested with a slipstream of flue gas at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama.

technology advantages

- Selective heating via microwave radiation is extremely rapid, allowing regeneration temperatures to be attained at very fast rates.
- Rapid regeneration allows for smaller regenerator size in a commercial application, lowering capital costs.
- Applying electromagnetic fields to sorbent or slurry regeneration zone enhances sorbent regeneration rates at relatively low temperature (i.e., at 85°C), providing energy and cost savings.
- Microwave regeneration of sorbent and non-aqueous slurry are steam-free processes, which substantially lowers the cooling and regeneration energy duties while eliminating the need for reboilers and steam extractors.
- NETL is established as a premier institute in the microwave area and has commissioned a variable frequency microwave reactor that is a one-of-a-kind system that does not exist in any other research laboratories in the world.

R&D challenges

- Addressing issues associated with microwave technology, such as poor interaction between the microwave field and material, thermal losses, and coupling with interior features of the reactor cavity versus material.
- Scale-up of microwave-based slurry or sorbent regeneration process.

status

NETL's Research and Innovation Center (RIC) has demonstrated significantly higher sorbent regeneration rates (at least 50% faster) for releasing a CO_2 gas stream from a zeolite sorbent or BIAS slurry compared to using the conventional thermal regeneration method (steam). A conceptual systems engineering and analysis assessment for the microwave-assisted regeneration process was also performed based on the measured regeneration kinetics. The scalability of the microwave-assisted slurry process is being evaluated.

available reports/technical papers/presentations

Patents

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F. Shi, J. Culp, M. Gray, etc., Regenerable Non-Aqueous Basic Immobilized Amine Slurries for Removal of CO_2 from a Gaseous Mixture and a Method of Use Thereof, 2018, 16/110,352.

Technical Paper

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Presentations

F. Shi, T. Ji, H. Paudel, Y. Duan, J. Culp, C. Marin, M. Gray, Novel Microwave-Accelerated Regeneration of a Non-aqueous Slurry (MARS) for Post-combustion Carbon Capture, 2019 AIChE meeting, Orlando, FL, Nov. 10, 2019.

F. Shi, T. Ji, Y. Soong, M. Gray, A study of ultra-fast CO_2 desorption kinetics for Microwave-Enhanced Regeneration Process, 2019 Carbon Management Technology Conference, Houston, TX. July 2019.

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Transformational Membranes

primary project goals

The National Energy Technology Laboratory's (NETL) Research and Innovation Center (RIC) is developing new, ultra-high-performance membranes and membrane modules for post-combustion carbon dioxide (CO_2) capture. Membrane types under investigation include polymer membranes and mixed matrix membranes (MMMs); also, high-permeance flat sheet and hollow fiber supports are being fabricated on which thin-film coatings of the polymers can be demonstrated. Development efforts are consistent with overall goals of reducing the energy penalty and cost of CO_2 separation relative to conventional technologies.

technical goals

- For polymer membranes, selectivity/permeability performance for CO_2/nitrogen (N_2) gas separations lying on or above the Robeson upper bound.
- Polymeric materials must overcome the practical difficulty of poor mechanical properties that are often associated with high-performance experimental polymers.
- Viable membrane module performance given the low-pressure driving force available in post-combustion flue gas.
- Progression from proven performance in simulated flue gas to validation on actual flue gas slipstream at pilot scale.
- Determination of cost effectiveness of membranes/modules for post-combustion CO_2 capture in techno-economic analyses (TEAs), consistent with approach to a cost of carbon capture at $30/tonne CO_2 by 2030.

technical content

Membrane technology poses an exciting option for large-scale gas separations due to the small footprint, simplicity of the device and process, ease of operation, modularity and bolt-on installation, and typically low parasitic energy requirements. Industrially, polymer-type membranes have a well-established role in gas separation technology, and are commonly used in applications such as separation of hydrogen from gas mixtures, purifying natural gas, etc. However, extremely high-permeability membrane materials are needed to make this technology an economically viable option for post-combustion CO_2 capture. While there are multiple experimental membranes reported in the literature that appear to meet the performance requirements, most have practical drawbacks, such as poor mechanical strength, poor thin film forming ability, reduced performance with aging, or complex and expensive synthesis procedures. Therefore, there is a need to develop new membranes that have high performance but also meet the practical requirements of post-combustion CO_2 capture.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Post-Combustion Membrane Materials

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022402

predecessor project:

2018 Carbon Capture FWP

NETL technical portfolio lead:

David Hopkinson
david.hopkinson@netl.doe.gov

NETL principal investigator:

David Hopkinson
david.hopkinson@netl.doe.gov

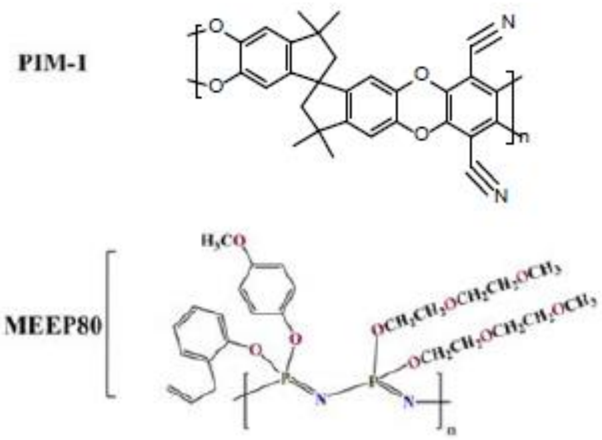
partners:

Compact Membrane Systems, University of Pittsburgh, Penn State University, Texas A&M

Advanced Polymer Membranes

Fundamentally, polymer membranes are bounded by their performance, known as the Robeson upper bound (gas permeability must be sacrificed for species selectivity and vice versa). This intrinsic trade-off between permeability and selectivity is a significant limitation of using polymer membranes in the challenging application of capture of relatively dilute CO_2 from flue gas. Incremental improvements in polymer performance continue to advance the trade-off curve towards more selective, more permeable materials, but a step-change over current technology would facilitate wider implementation of membrane technology.

Recently, NETL-RIC has been investigating two polymers of interest for CO_2 capture: PIM-1 and MEEP80-polyposphazene (MEEP80-PPZ), as illustrated in Figure 1. PIM-1 has high permeability, but has low selectivity, forms brittle films, and aging tends to reduce its permeability. MEEP-PPZ has only moderate permeability but has high selectivity and forms gummy films.



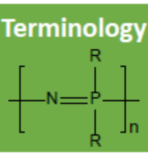
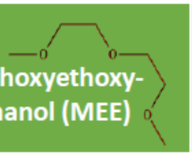
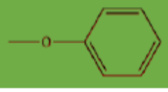
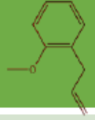
Terminology 	methoxyethoxy-ethanol (MEE) 	4-methoxyphenol (4-MEOP) 	phenoxy 	2-allylphenol (2-AP) 
MEEP80-PPZ	80%	15%	0%	5%
PPOP-PPZ	0%	0%	97%	3%

Figure 1: High-performance polymers.

NETL has found that blends of PIM-1/MEEP-PPZ have high permeability and excellent mechanical properties in terms of forming strong and flexible films. The performance of the neat polymers and the better performing blends are shown in Figure 2.

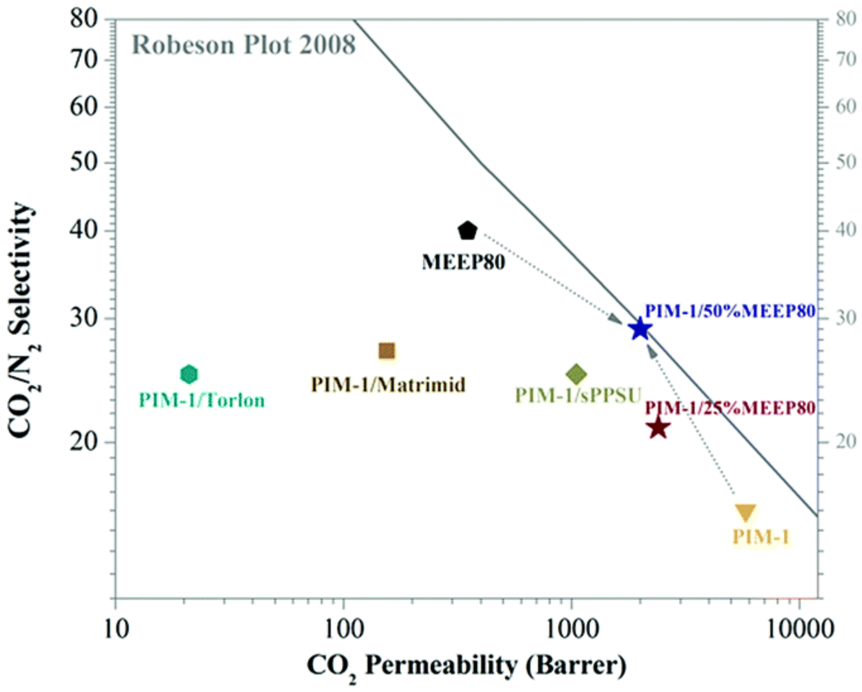


Figure 2: Polymer blend performance.

Also, in the area of advanced polymers, NETL has been combining MEEP-PPZ and PPOP-PPZ and adding a crosslinking agent to form crosslinked MEEP (XL MEEP). MEEP-PPZ has excellent gas separation performance, but is a flowing semi-solid material, while PPOP-PZ has poor gas separation performance but excellent mechanical robustness. The resultant XL MEEP has excellent gas separation performance and is a solid with good mechanical robustness. NETL testing and analyses have shown that crosslinking of MEEP dramatically improves film durability with some decrease in gas permeability, and that crosslinked MEEP gas separation performance can be optimized based on composition and crosslinker. Crosslinked MEEP is stable in real flue gas, shows little performance degradation in the presence of humidity, and thin films suffer no significant degradation from aging.

Mixed Matrix Membranes

MMMs are a technology that could potentially achieve a step-change in gas separation performance. MMMs are composite structures that make use of a polymer matrix and a porous filler particle. Metal-organic frameworks (MOFs) are commonly used as the filler particle because of their high CO_2 uptake and the tunability of their pores for achieving selective mass transfer of CO_2 relative to the other species in post-combustion flue gas (primarily N_2). In general, MOFs will have more desirable gas transport properties than a polymer but are very difficult to form into a free-standing and defect-free membrane film. By integrating MOFs into a polymer film, the selectivity and permeance of the film are enhanced. This makes the system more capable of dealing with a low partial pressure driving force than conventional polymers, while also retaining the processability of a polymer. The MMM concept, challenges, and development are depicted in Figure 3.

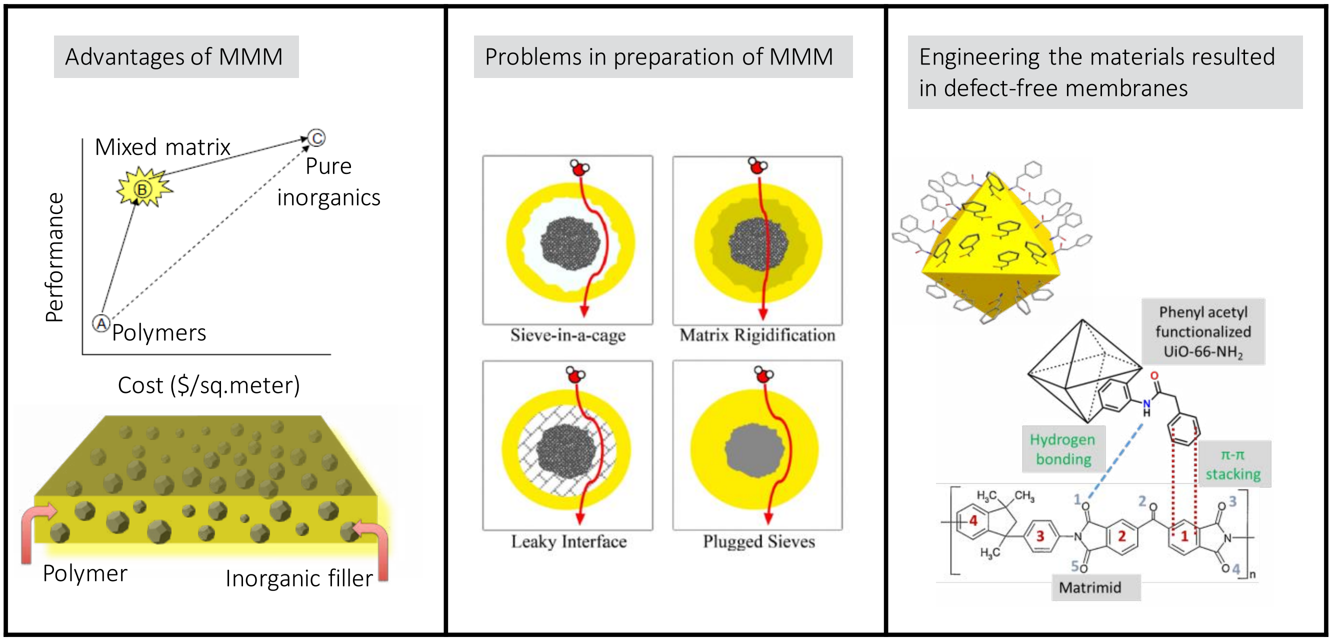


Figure 3: MMMs characteristics and development.

MMMs often suffer from poor contact between the polymer matrix and MOF crystallites. This phenomenon, known as the sieve-in-a-cage effect, can cause gas streams to bypass the MOFs without separation, thus dramatically reducing selectivity. Overcoming this problem and identifying a polymer-MOF pair with the capability to form a highly permeable and selective membrane is a technology development focus.

Figure 4 shows the performance of various MMMs on the Robeson plot, showing their potential to exceed the characteristic performance limits of ordinary polymeric membranes.

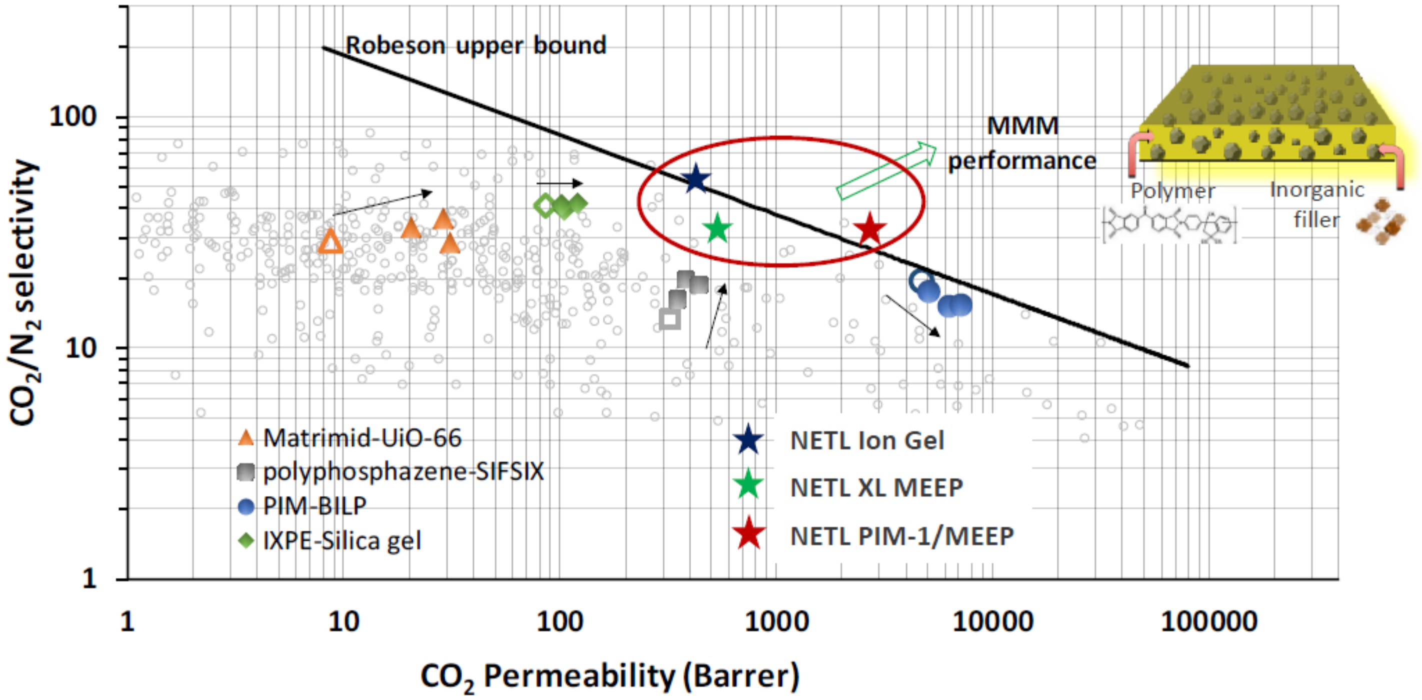


Figure 4: MMMs performance.

Most recently, NETL has taken a unique approach to MMM design by using high-throughput computational tools to predict the gas permeability of a large database of MOF materials and make predictions of the gas permeation behavior of more than a million hypothetical MMMs. The model was expanded by coupling it with process analysis tools to calculate the cost of capture for the hypothetical MMMs. This represents the first known attempt at a true rational design of MMMs for post-combustion carbon capture. It was found that a well-designed MMM can lead to dramatic improvement of performance over a neat polymer and reduce the cost of capture by $15/tonne.

Several screened candidates were experimentally demonstrated, showing excellent agreement with model results. Figure 5 shows these candidates, which exceed the Robeson upper bound.

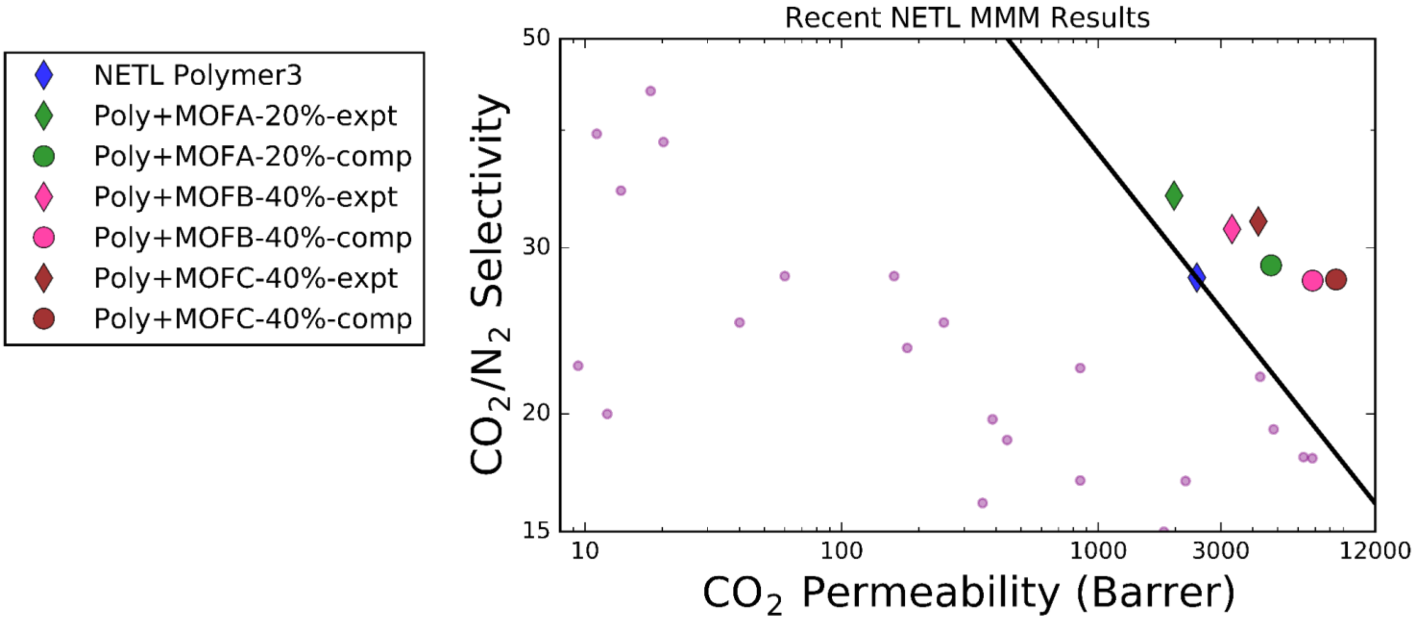


Figure 5: NETL's recent MMM results.

NETL has investigated incorporating MOFs into the already high-performance advanced polymers PIM-1/MEEP and XL MEEP, as discussed previously. The MMMs formed show improved performance over the base advanced polymers, as illustrated in Figure 6.

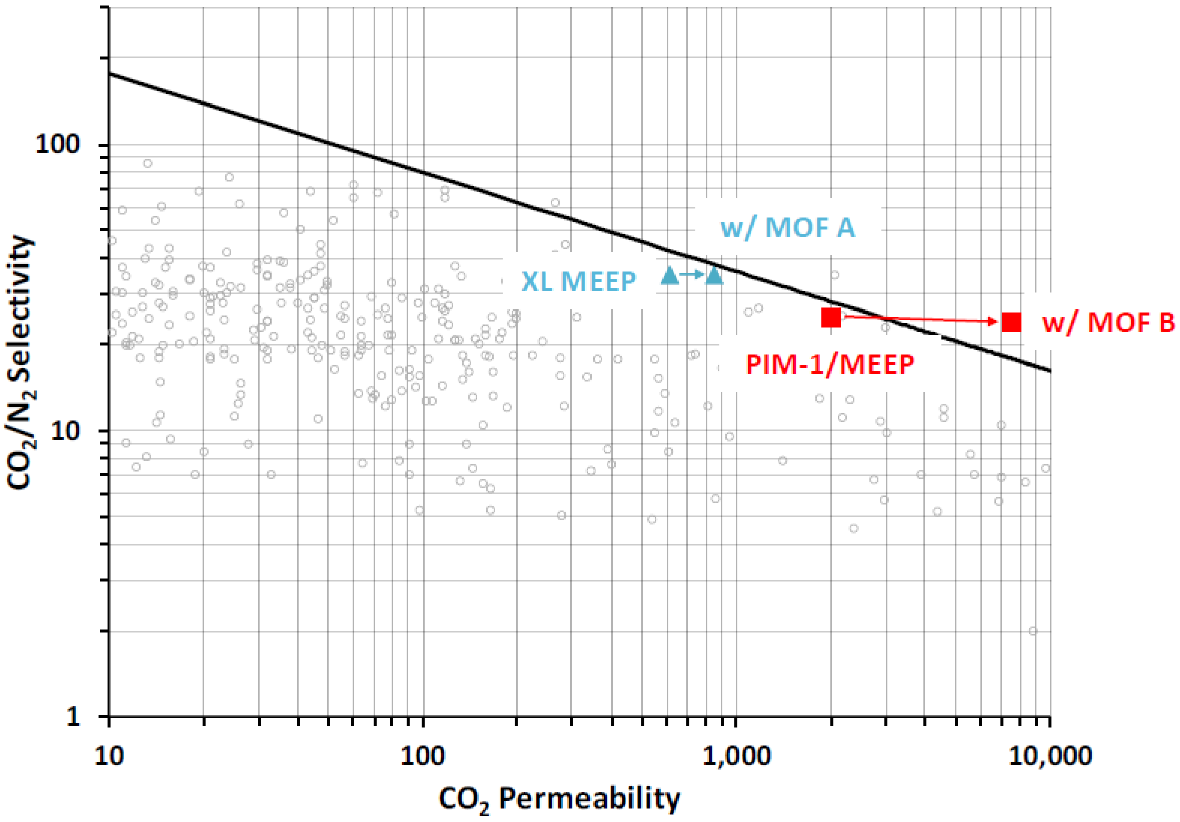


Figure 6: Improved performance of NETL MMMs from XL MEEP and PIM-1/MEEP advanced polymers.

Supports and Thin-Film Coatings

Carbon capture using membranes depends on much more than the development of an effective selective layer. The selective layer must be extremely thin, and thus it must be reinforced by a strong, highly permeable support layer. In order to prevent the selective material from flowing into the pores of the support layer, a thin "gutter" layer can be introduced between the support and the thin selective layer. The combination of these various layers is called a thin-film composite (TFC). NETL has recently made significant advances in TFC membranes, particularly in the development of high-flux porous supports. NETL's current hollow fiber membrane supports have N_2 permeance greater than 100,000 gas permeation units (GPU), CO_2/N_2 selectivity ~0.8 (Knudsen diffusion), surface pore size ~20 nm, and are resistant to mild solvents. These have been fabricated as both high-flux hollow fiber supports and high-flux flat sheet supports. The two panels on the top of Figure 7 show PIM-1/MEEP/10% MOF MMM selective layer on a hollow fiber support, while the bottom two panels show a XL MEEP selective layer on a flat sheet support.

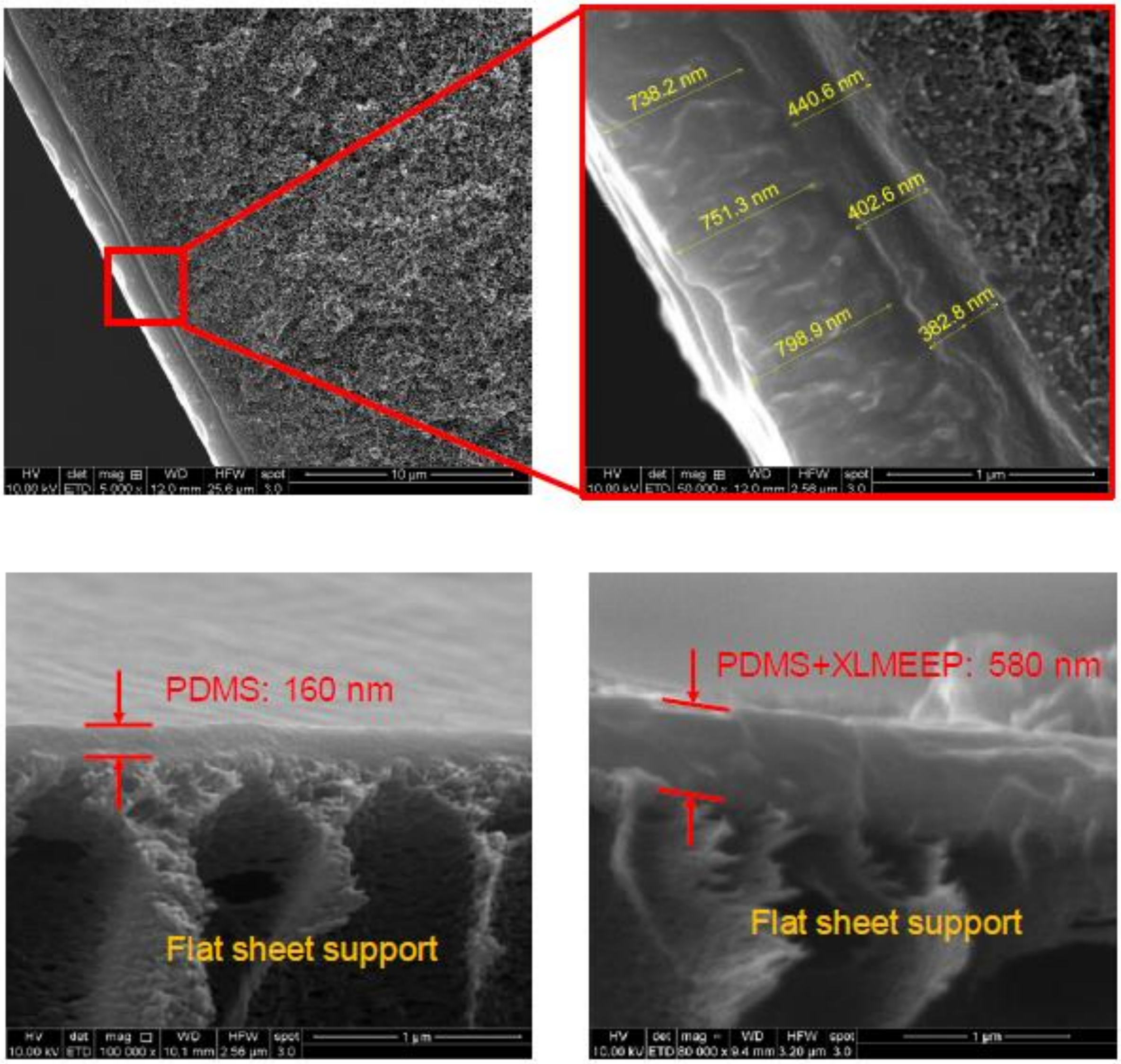


Figure 7: PIM-1/MEEP MMMs and XL MEEP in thin-film composites.

technology advantages

- Membranes separate mixed gas streams according to differences in gas permeability across a membrane film, enabling steady-state operation with no energy-intensive regeneration step required. This creates potential for energy savings using this technology.
- Higher-permeability membranes lead to a reduced membrane area requirement, smaller capital cost, and a smaller equipment footprint.
- NETL-developed polymers have enhanced mechanical stability.
- High-throughput computational methods have identified MMMs capable of breaking the Robeson upper bound.

R&D challenges

- Increasing membrane permeability and selectivity for CO_2.
- Identifying compositions that have durable mechanical properties and good thin-film forming properties.
- Maintaining low cost of fabrication, particularly in membranes that involve complex synthesis procedures.
- Maintaining robust performance under harsh operating conditions, such as elevated temperature or pressure.

- Increasing the resistance of membranes and membrane materials to contaminants including water, sulfur species, or particulates.
- Increasing the compatibility between composite membrane materials.
- Realizing good membrane separation performance, even under low driving forces for separation associated with energy-saving configurations.
- Achieving defect-free thin-film selective layer coatings that are less than 1 µm in thickness.

available reports/technical papers

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Carbon Capture Retrofit Database – v.2019.1

primary project goals

The U.S. Department of Energy's (DOE) National Energy Technology Laboratory (NETL) has developed three carbon capture retrofit database (CCRD) tools that provide high-level analysis on the incremental cost for retrofitting point sources with carbon dioxide (CO_2) capture and/or compression systems. The tools also provide options to include the cost of implementing other plant emissions reduction technology improvements that may be required to comply with various regulations (e.g., Mercury and Air Toxic Standards [MATS][1] and New Source Performance Standards [NSPS][2]) when installing CO_2 scrubbing technology, or aid in maximizing the efficiency of the installed CO_2 removal technology.

technical goals

- Provide a tool that allows for the quick approximation of the cost to retrofit an existing power or industrial plant with CO_2 capture equipment, grounded in sound techno-economic analysis (TEA) fundamentals and methodology approaches.
- Provide sufficient technology options for selection, upstream of the capture system, to maximize the applicability of the tool.
    - For example, if a candidate plant for retrofit does not remove sulfur from the flue gas at adequate levels to meet the inlet flue gas specifications of the capture system to be added, the tool provides additional technology options for selection and inclusion to frame all requirements for the addition of CO_2 capture.

technical content

Techno-economic evaluation of the impacts that post-combustion CO_2 capture systems impart on power and industrial plants is key to determination of technology viability. Performing a TEA of an individual technology can provide insights into the key process parameters for a given capture system and identify areas for improvement that offer the most return by way of performance improvement and cost reduction. Practitioners of TEAs generally operate using their preferred set of assumptions, modeling and cost estimating methodologies, and sensitivity analysis approaches, and these standards may vary across organizations. In addition, there may be limitations regarding data availability and approaches for filling these gaps may vary widely. These factors can contribute to assessments that may or may not be developed on equivalent bases, and thus may not be comparable without sufficient definition of all assumptions and methodologies.

At NETL, systems analysis of power and power-related technologies, particularly post-combustion carbon capture, has been a focus for many years, and a key output of that work has been publicly available guidelines for conducting a TEA

technology maturity:

Systems Engineering and Analysis

project focus:

Carbon Capture Retrofit Database Tools

participant:

National Energy Technology Laboratory – Research and Innovation Center

project number:

FWP-1022402

predecessor projects:

N/A

NETL technical portfolio lead:

Alexander Zoelle
alexander.zoelle@netl.doe.gov

NETL principal investigator:

Timothy Fout
timothy.fout@netl.doe.gov

partners:

N/A

that are normalized, consistent, and transparent. However, even with the detailed guidance available for technology developers seeking to assess their systems, differences can still arise that lead to incompatible studies and results. To alleviate this issue, NETL has developed numerous tools for public use that build on the extensive systems analysis guidelines developed by NETL and simplify the process of systems analysis to allow for a broader range of engineers and scientists to take advantage of techno-economic evaluations.

NETL has developed three separate CCRD tools:

- Two power-related tools:
  - One assessing coal-fired pulverized coal (PC) and atmospheric fluidized bed (AFB) units (the PC CCRD) and another assessing natural gas units (the natural gas combined cycle [NGCC] CCRD).
- A third focused on industrial source (IND) sectors.

The IND CCRD contains data on facilities from the ammonia, cement, ethanol, hydrogen, and natural gas processing industries. The tools allow for a user to quickly screen, at a high level, the impact of adding carbon capture to a plant by calculating the incremental cost for retrofitting point sources with CO_2 capture and/or compression systems.

The reference costs for all CCRDs are predicated on baseload operation, so no cost or performance considerations are rendered for turn-down capability. In addition, the reference cost data sourced from NETL reports, and applied in the CCRDs, has been developed for a target plant size; therefore, scaling cost and performance data to units of significantly differing sizes, compared to the reference data, will introduce inaccuracies due to the nature of process design. Calculation of cost results follows NETL's guidance[3] and utilizes capital charge factors that will be contingent on a number of financial parameter assumptions, including interest rate, return on equity, economic life of the plant, debt and equity split, debt term, and others.

Similar to reference costs, the performance basis for the reference systems considered in the CCRD were developed for International Organization for Standardization (ISO) ambient conditions[4][5], and no cost or performance adjustments are made in the CCRD to account for the operating ambient conditions.

In order to reflect the expected but undefined costs associated with the retrofit of existing plants, a retrofit cost factor is applied to all sites with no consideration given to the amount of retrofit equipment required, the available space, or other site-specific conditions. As the plant configuration will have a significant impact on the actual installation costs and design (and therefore equipment costs) of each system, the site-specific retrofit factor would be expected to deviate significantly from the average value applied in the CCRDs.

The PC and NGCC CCRDs do not provide a library of existing U.S. fleet power plants for which calculations may be applied to. If this type of analysis is desired, the individual user must obtain and import this data into the CCRD. The CCRD does come pre-populated with cases that derive from legacy NETL systems analysis studies of representative coal and natural gas power plants. These cases can be used without further adjustment if appropriate for the analysis desired.

In the case of a user importing U.S. fleet plant data, the CCRD offers several options to allow the user to bring the plant into compliance with air emissions regulations, such that the plant is suitable for the addition of post-combustion capture equipment. For example, if an existing unit does not meet the nitrogen oxides (NO_X) environmental regulatory limit, a selective catalytic reducer (SCR) can be included in the retrofit configuration, and the cost of adding the SCR unit is calculated by the CCRD based on the CO_2 capture rate. There are cost result accuracy considerations given the approach employed by the CCRD to include addition of the SCR. The scaling approach of CO_2 flow rate provides a short-cut method reasonable for a screening-level assessment to approximate costs, but does not take into account site-specific considerations of the existing plant, such as boiler type, coal type, removal efficiency requirements, and other factors, and thus could result in an over- or under-sized SCR. Similar to NO_X, if an existing unit does not meet the sulfur dioxide (SO_2) regulatory limit, wet flue gas desulfurization (FGD) can be included in the retrofit configuration, and the cost of FGD is calculated by the CCRD based on the CO_2 capture rate. The same cost result accuracy considerations listed for addition of SCR apply to the addition of FGD.

While scaling the CO_2 removal system on the rate of CO_2 captured is significantly more accurate than for either FGD or SCR (discussed above) for similarly designed plants, regardless of coal type, considerable deviations can occur due to various process design choices, such as excess air to the boiler, infiltration air, air leakage, efficiency of existing gas cleanup systems, and operating temperature and pressure. Using solvent-based CO_2 removal systems as an example, additional air in the flue gas will not only increase the volumetric flow rate, but will also have a diluting effect on the CO_2 concentration of the flue gas. These factors will affect the sizing of both the pre-scrubber and absorption columns (impacting capital costs), as well as the solvent circulation rate (impacting the operating and maintenance [O&M] costs, capital cost, and auxiliary load). The same cost result accuracy considerations listed for addition of SCR and FGD apply to the retrofit of the CO_2 removal system, and the user should take these considerations into account when interpreting the results.

The reference CO_2 compression system considered in the CCRD is an integrally geared centrifugal type, designed for baseload operation[4], which may not be suitable for all unit sizes. For small units, reciprocating compressors may be more appropriate, but the current CCRD does not offer this technology selection option.

In instances where the user provides U.S. plant fleet data, the CCRD charting tools allow for generation of an array of scenario results plots. In Figure 1, the fleet-of-entries level view is presented for the breakeven CO_2 sales price. In this scenario, which is based on a particular user-defined set of assumptions, the plot shows that 80% of the total plant capacity input into the CCRD tool and retrofitted could return a cost of $125/tonne or less. Figure 2 presents a different scenario, where the nameplate capacity of the unit retrofitted, based on the user-defined fleet data, is plotted against the calculated breakeven CO_2 sales price. The trend shows that as the unit size increases, the breakeven CO_2 sales price decreases.

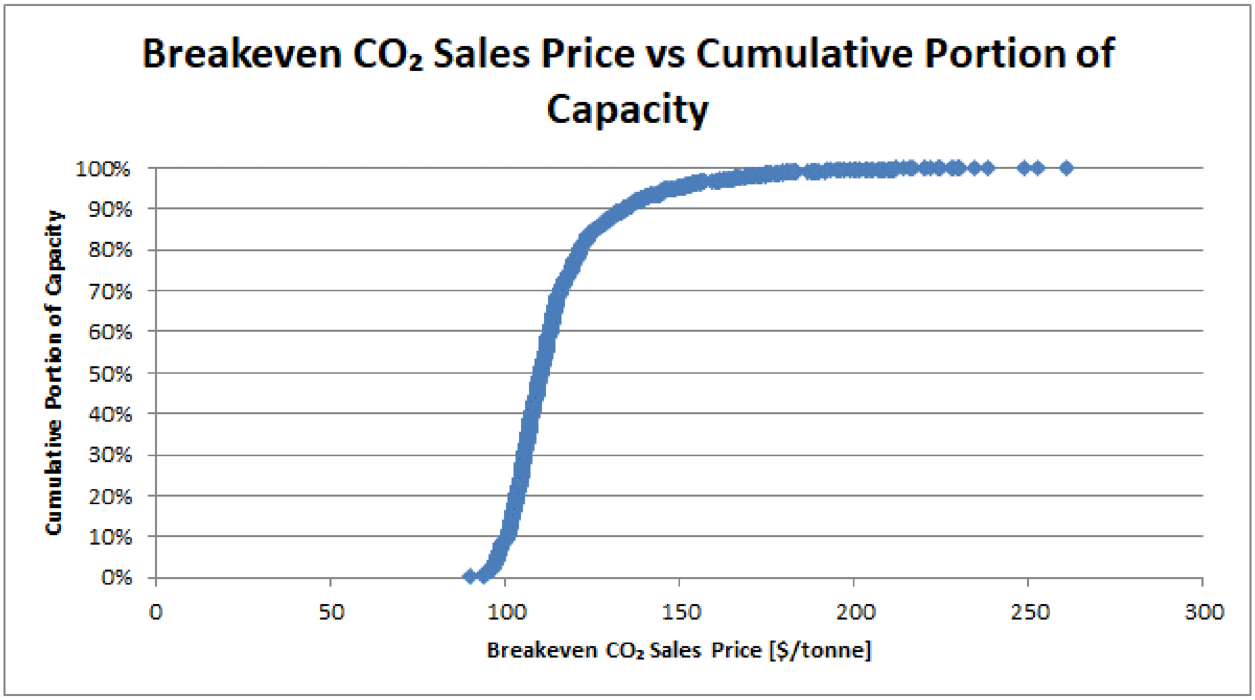

Figure 1: Breakeven CO_2 sales price versus cumulative portion of capacity retrofitted.

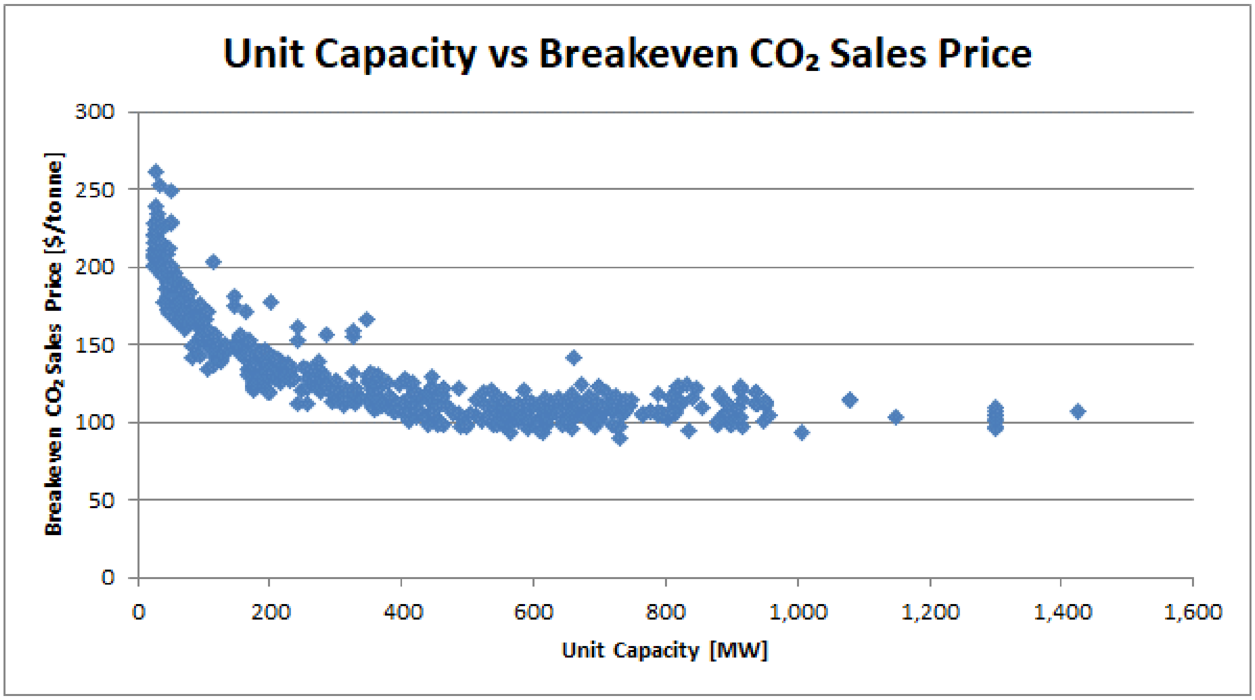

Figure 2: Unit capacity retrofitted versus breakeven CO_2 sales price.

technology advantages

- The tool allows for a first-cut screening of the potential impact of technology options, ranging from developing to commercially available CO_2 capture technologies, on the existing fleet of coal and gas power plants (when fleet data is provided by the user), as well as industrial sources.

R&D challenges

- Lack of detailed energy and mass balance diagrams for each plant in the U.S. fleet reduces absolute accuracy of single point results.
- Lack of comprehensive publicly available U.S. fleet plant data for pre-population of the tool database.
- The user must provide their own plant data or use the pre-populated cases that derive from legacy NETL systems analysis studies of representative coal and natural gas power plants.
- The individual plant level accuracy of results is subject to the underlying performance and cost approximation methodologies and plant data. While the underlying methodologies are sound, an individual plant-level model and capital cost estimate is not developed for each case. Thus, the most useful application of the tool results is to compare case outputs based on varying user inputs (e.g., power plant inputs, capture technology inputs, etc.) rather than assessing an individual case's absolute result.

status

NETL has developed three CCRD tools that allow for a quick approximation of the cost to retrofit an existing power or industrial plant with CO_2 capture equipment.

available reports/technical papers/presentations

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Carbon Capture Simulation For Industry Impact (CCSI²)

primary project goals

The primary project goals are to utilize the computational tools and models developed under the Carbon Capture Simulation Initiative (CCSI), in partnership with industry, to scale-up new and innovative carbon capture technology. The Carbon Capture Simulation for Industry Impact (CCSI^2) operates in conjunction with and in support of the U.S. Department of Energy's (DOE) Office of Fossil Energy's (FE) Carbon Capture Program to focus on advancing promising technologies.

In 2010, DOE initiated CCSI to help reduce the amount of time that it historically takes to develop and scale-up new technologies in the energy sector, which traditionally takes up to 15 years to move from the laboratory to pre-deployment, and another 20 to 30 years for mature, industrial-scale deployment. Advanced modeling and simulation is developed and applied to enable more rapid and lower-cost capture technology development at reduced risk during the commercialization process.

technical goals

The team assists the Carbon Capture Program and technology developers by:

- Providing more detailed understanding of capture materials through system performance under parametric uncertainty.
- Enabling improved designs for high performance and intensified unit operations.
- Indicating synthesis of processes optimized for novel materials.
- Characterizing dynamic system behavior.
- Providing more informed design, operating, and control decisions.
- Optimizing processes with intrinsic uncertainty.
- Providing a framework for intelligent design of experiments at all Technology Readiness Levels (TRLs) for model refinement and system optimization.

CCSI^2 has released the CCSI Toolset to the public as open-source and continues to maintain the tools, including document capabilities and instructions for use, as well as the public repository. In addition, CCSI^2 also continues to provide improvements to better support the Carbon Capture Program. The CCSI^2 website can be found at: *https://www.acceleratecarboncapture.org/* and the CCSI Toolset is available at: *https://github.com/CCSI-Toolset/*.

CCSI^2 is led by the National Energy Technology Laboratory (NETL) and leverages the DOE national laboratories' core strengths in modeling and simulation. CCSI^2 integrates the best modeling and simulation capabilities at NETL and complements them with relevant, world-class expertise at Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), Pacific Northwest National Laboratory (PNNL), and Oak Ridge National Laboratory (ORNL) in pursuit of the overarching vision of CCSI^2.

technology maturity:

Practical Application of Modeling to all TRLs

project focus:

Carbon Capture Simulation

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP-1022422

predecessor project:

2018 Carbon Capture FWP

NETL project leads:

Parrish Galusky
parrish.galusky@netl.doe.gov

Michael Matuszewski
michael.matuszewski@netl.doe.gov

NETL technical portfolio lead:

Benjamin Omell
benjamin.omell@netl.doe.gov

partners:

Los Alamos National Laboratory, Lawrence Berkeley National Laboratory, Pacific Northwest National Laboratory, Lawrence Livermore National Laboratory, Oak Ridge National Laboratory, West Virginia University, University of Texas-Austin, University of Toledo, University of Notre Dame, University of Pittsburgh

technical content

Carbon capture is critical to significantly reducing domestic and global carbon dioxide (CO_2) emissions. However, the energy and capital cost associated with carbon capture systems is prohibitive for deployment. Today's cost to capture CO_2 using state-of-the-art carbon capture technologies must be reduced to competitive levels more rapidly and at lower risk. FE goals are for technologies under development to be ready for commercial deployment by 2030 and must be on a pathway to achieve a price of $30/tonne of CO_2 captured, or a reduction in cost of electricity (COE) of a state-of-the-art supercritical pulverized coal plant with carbon capture and storage (CCS; excluding transportation and storage) by 30%. Balancing capital cost reduction and performance improvements with a level of CO_2 capture meaningful enough to contribute to climate change mitigation is critical in this approach, yet this balance introduces a great deal of additional complexity. CCSI^2, with world-class expertise in process modeling and proven cost-performance optimization frameworks, is ideally positioned to provide well-informed perspective on the most impactful areas of research and development (R&D) to most cost-effectively mitigate CO_2 in electrical and industrial sectors.

The CCSI^2 team provides fundamental analysis, modeling, and optimization of carbon capture technology by working closely with industry partners. The CCSI^2 team efficiently identifies data collection needs, characterizes carbon capture materials, designs and optimizes devices and processes, and fully propagates uncertainty in model predictions for a complete perspective on model accuracy.

The work is organized under several tasks, including the Discovery of Carbon Capture Substances and Systems (DOCCSS) Support, the Computational Support for the Capture Portfolio, and the Open-Source Toolset Community Support.

The DOCCSS Initiative has three projects that explore the integrated development and optimization of devices and systems for the following transformational concepts:

- LBNL Metal-Organic Framework (MOF) Sorbent Materials
- PNNL CO_2-Binding Organic Liquids (CO_2BOL)
- LLNL Advanced Device Manufacturing

The Computational Support for the Capture Program task focuses on increasing the impact of R&D across the Carbon Capture Program by generating and applying computational frameworks to support carbon capture technology research. The subtasks for this task include:

- Sequential Design of Experiments
- Multi-Scale Modeling and Optimization
- Guiding R&D for Carbon Capture in the Industrial Sector

An Open-Source Toolset Community Support task manages the open-source CCSI Toolset, which was released March 30, 2018. A centralized open-source repository was created and is maintained to facilitate public access to the CCSI Toolset. Prior to release, the CCSI computational tools were conditioned and documented to reduce the need for ongoing support of the public release. This task developed a software and management framework for interoperability of the underlying simulation tools, ongoing development of the software and management of public tools for CCSI^2, and information access (i.e., CCSI^2 website management).

technology advantages

CCSI developed and deployed a suite of multi-scale computational tools that find use in multiple carbon capture technology development applications. Overall, this CCSI Toolset: (1) enables promising concepts to be more quickly identified through rapid computational screening of processes and devices; (2) reduces the time to design and troubleshoot new devices by using detailed, device-scale models to better understand and improve the internal behavior of complex equipment; (3) streamlines process design by using state-of-the-art optimization techniques that focus development on the best overall operating conditions and process configurations; and (4) provides quantitative predictions of device and process performance during scale-up based on rigorously validated simulations that take into account model and parameter uncertainty.

With open-source licensing of the CCSI Toolset available, the CCSI^2 team is poised to rapidly engage carbon capture technology developers for direct and widespread support within the Capture Program. Moreover, the CCSI^2 team is also currently in multiple negotiations/agreements with technology developers outside the FE Carbon Capture Program; some are interested in complementary R&D via Cooperative Research and Development Agreements (CRADAs) for maximum collaborative impact, and others are interested in directly funding the CCSI^2 team via Contributed Funds Agreements (CFAs) to apply their expertise to specific problems of interest. Both mechanisms will strengthen CCSI^2 capabilities and ability to extend application of the developed knowledge to future capture technology development efforts.

R&D challenges

Identification and rigorous quantification of scale-up uncertainty and model enhancement to reduce such uncertainties.

status

The tasks of CCSI^2 have four thrusts:

1. Provide direct, low-TRL support to the projects awarded under the DOCCSS Initiative. The DOCCSS Initiative integrates contributions from national laboratory developers and industrial stakeholders to accelerate the commercialization process of advanced carbon capture materials, requiring a multi-hierarchical characterization that embodies materials through systems-level performance. Specifically, this work ensures advanced materials development efforts are integrated with advanced systems design, analysis, and optimization. Work first focused on CO_2BOL and MOF-based modeling frameworks to enable multi-scale, integrated materials and device and process optimization. Work continues to address generalized solvent and sorbent frameworks for execution year (EY) 2020 and beyond.
2. Develop a formalized Sequential Design of Experiments (SDoE) methodology that strives for data generation at all TRLs that is optimized for a variety of objectives, including model refinement, process optimization, etc. In EY 2018, this thrust worked towards developing a methodology to optimize the experimentation required at any scale, maximizing learning while reducing the time and cost of experimental testing at lab- through pilot-scale. In EY 2019, to reduce time and personnel required to implement SDoE, the project teams worked to build additional capability for computational Design of Experiments into the Framework for Optimization and Quantification of Uncertainty and Sensitivity (FOQUS)—a validated computational fluid dynamics (CFD) model to wetted area in a packed column—which covered computational experimental design, maximizing learning while reducing the time and computational cost of generating results from computationally-intense simulations; developed constrained Design of Experiments to consider operational and/or safety restrictions in the Design of Experiments; and investigated the feasibility of Design of Experiments generation based on output-based requirements. In EY 2020, the initiative will work to implement dynamic Design of Experiments, which will substantially increase the speed and amount of data that can be generated at pilot-scale.
3. Inform R&D efforts in projects supported by the Carbon Capture Program through fundamental modeling, analysis, and optimization, including an Advanced Flash Stripper (AFS) modeling framework capable of rapid design and operational optimization to minimize COE, and demonstration of an Advanced Process Control (APC) strategy predicted to reduce settling time by 80%. The efforts expanded in EY 2019 to work on accurate wetted area framework for estimating advanced packing and generic solvents to inform device performance, as well as the support of large-scale pilots through modeling and uncertainty quantification. The EY 2020 focus will shift to advance solvent system configurations by developing models for packed-column intensification and optimization, a framework for techno-economic analysis (TEA) taking into account flexibility of solvent-based capture systems, and reducing emissions from industrial sources.
4. Prepared and released the full CCSI Toolset to the open domain, namely to complete a fully operational toolset release and launch of a repository for both open-source and internal CCSI^2 modeling products. Then focus shifted to launch of the system for evaluation, testing, and release management of open-source contributions to the CCSI Toolset. In EY 2020, the project seeks to improve the toolset for continued Carbon Capture Program support. The CCSI^2 team continues to work to develop the management system as a fully operational open-source community with toolset revision evaluation and distributed toolset management in EY 2020.

available reports/technical papers/presentations

CCSI^2 Website: *https://www.acceleratecarboncapture.org*.

CCSI Toolset: *https://github.com/CCSI-Toolset/*.

CCSI^2 Publications List: *https://www.acceleratecarboncapture.org/publications*.

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION SOLVENT TECHNOLOGIES

Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas

primary project goals

URS Group, Inc. (URS) investigated the use of a concentrated aqueous piperazine (PZ) solvent combined with novel solvent regeneration systems to capture carbon dioxide (CO_2) from coal-fired flue gas more economically. Methods for measurement, generation, and control of amine aerosols were also explored. Pilot tests and analyses were conducted at the 0.1-megawatt-electric (MWe) scale, and then scaled to the 0.5-MWe scale for testing at the National Carbon Capture Center (NCCC). Results were used to evaluate the technical and economic feasibility of a full-scale implementation of this process.

technical goals

- Quantify and demonstrate the robustness of concentrated PZ with coal-fired flue gas in an integrated absorption/stripping system with solvent regeneration at 150°C.
- Optimize equipment design and energy performance for the innovative solvent regeneration configurations.
- Identify and resolve other potential operational and design issues, including amine aerosol emissions, process control, corrosion, foaming, and solids precipitation.
- Evaluate the technical and economic feasibility of a full-scale implementation of this process.

technical content

URS, in collaboration with the University of Texas (UT) and Trimeric Corporation, studied the use of concentrated PZ as a solvent for absorbing CO_2 from coal-fired power plant flue gas. Concentrated PZ has a faster CO_2 absorption rate, higher CO_2 capacity, lower volatility, and negligible thermal and oxidative degradation compared with conventional amine solvents. Evaluations of concentrated PZ for CO_2 removal have previously been performed through laboratory investigations, process modeling, and short-term testing in a 0.1-MWe unit with synthetic flue gas. Results indicated greater than 90% CO_2 capture. This project continued the development of the PZ-based CO_2 absorption process through a series of four test campaigns at pilot scale to gain operational experience with the solvent in coal-fired flue gas, while employing a novel, high-temperature flash regeneration design. The process parameters of the PZ solvent are listed in Table 1.

The project team addressed the project objectives in two phases. In the first phase, the PZ absorption process was combined with a novel regeneration scheme—a high-temperature two-stage flash (2SF), shown in Figure 1. This configuration was

technology maturity:

Pilot-Scale (0.5 MWe), Simulated Flue Gas and Coal-Derived Flue Gas Slipstream

project focus:

Piperazine Solvent with Flash Regeneration

participant:

URS Group, Inc.

project number:

FE0005654

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Gary T. Rochelle
The University of Texas at Austin
gtr@che.utexas.edu

partners:

University of Texas at Austin, Trimeric Corporation

start date:

10.01.2010

percent complete:

100%

installed in UT's Separations Research Program (SRP) plant and tested at 0.1-MWe scale with synthetic flue gas using PZ in the SRP plant absorption column.

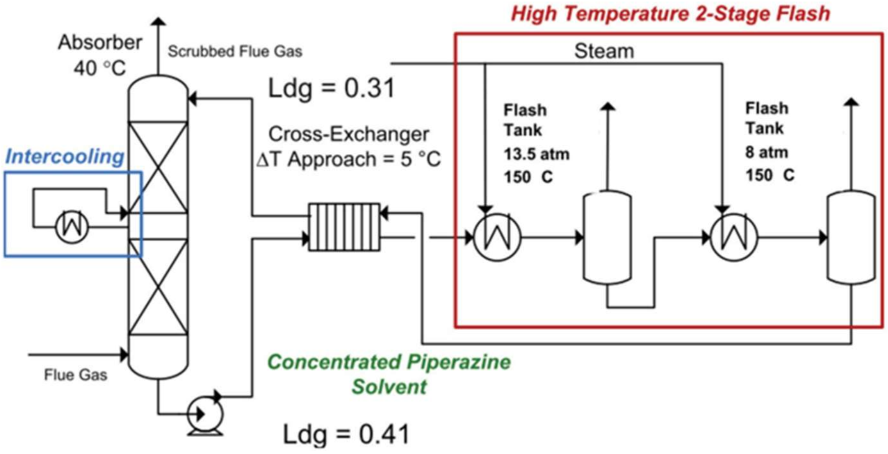

Figure 1: Diagram of PZ CO_2 absorption process with high-temperature two-stage flash.

The results from the SRP test program and the techno-economic analysis (TEA) demonstrated the benefits of using PZ as a solvent-of-choice for CO_2 capture. The results from the SRP test program revealed that 2SF regeneration is a viable alternative regeneration process to simple stripping; however, the TEA showed only a marginal economic benefit of the 2SF process. Therefore, additional testing at the 0.1-MWe scale was performed on an advanced flash stripper (AFS) (Figure 2) regeneration design to validate a significant reduction in energy requirement and capital cost. The improvement in energy performance is achieved through use of the cold rich bypass and warm rich bypass streams in the AFS configuration. Compared to previous campaigns with the 2SF, the AFS reduced the heat duty by more than 25%. Testing at the SRP plant also confirmed that PZ with a 5 molal concentration is a superior solvent to PZ with an 8 molal concentration. The reduced viscosity of 5 molal PZ results in an enhanced CO_2 absorption rate in the absorber and improved heat transfer performance in the cross-exchanger, which reduces heat duty. Combining the 5 molal PZ solvent with the AFS, as shown in Figure 2, decreases the cost of CO_2 capture to less than $40/tonne.

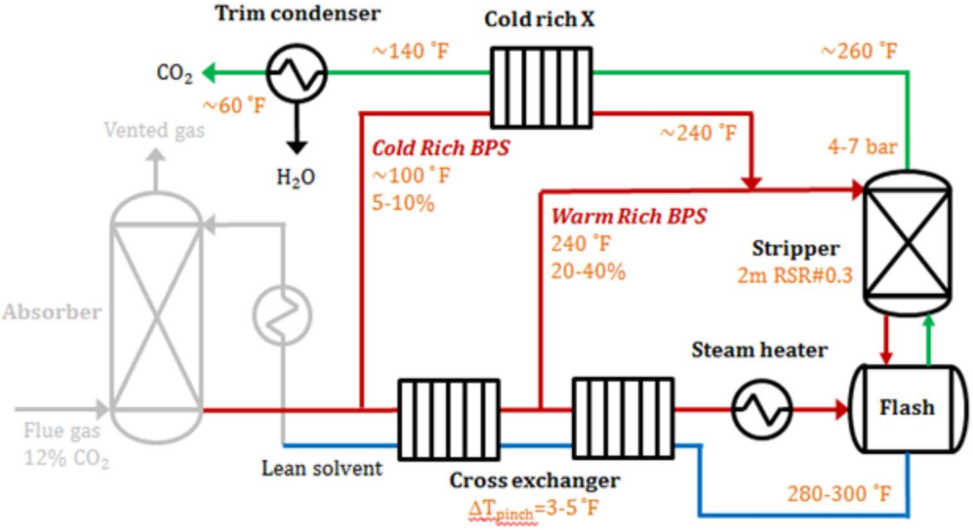

Figure 2: 5 molal PZ CO_2 absorption with the advanced flash stripper.

Since one of the main objectives of this project was to address operational and design issues of the PZ process, the project team recommended to the U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) that project resources be allocated toward investigating and solving critical solvent management issues that are common to amine solvents, particularly the formation and control of aerosols. DOE/NETL approved the project team to use the project resources remaining in Phase I to study aerosol formation in the absorber. Aerosols have been implicated in high amine emissions from absorbers at several pilot plants. The project team conducted further tests at UT's SRP facility to investigate possible mechanisms for aerosol formation and concluded that aerosol and solid precipitation could be managed with 5 molal PZ.

In Phase II, the optimized technology including the AFS and 5 molal PZ was scaled to 0.5-MWe scale for a single test campaign at the NCCC with coal-fired flue gas. The existing NCCC Pilot Solvent Test Unit (PSTU) system was modified to change the existing lean solvent storage tank to a rich solvent storage tank. The second bed intercooler was not used, and the third bed was piped so that it could be used as an additional stage of water wash during a portion of testing.

Testing at the NCCC provided operational experience with PZ in coal-fired flue gas and demonstrated that the AFS process configuration provides significant improvements in energy performance over the conventional simple stripper (SS) configuration with PZ and has the potential to improve the energy performance of other solvents. Additionally, the campaign investigated the effect of flue gas sulfur trioxide (SO_3) concentration on amine aerosol emissions and evaluated the technology for other operational and design issues, such as the solvent stability, degradation, and corrosion.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	86.14	86.14
Normal Boiling Point	°C	146	146
Normal Freezing Point	°C	106	106
Vapor Pressure @ 15°C	bar	0.000206	0.000206
Manufacturing Cost for Solvent	$/kg	$60/lb	$60/lb
Working Solution			
Concentration	kg/kg	30%	30%
Specific Gravity (15°C/15°C)	—	1.02	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2
Viscosity @ STP	cP	7	7
Absorption			
Pressure	bar	0.05	0.05
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.8	0.8
Heat of Absorption	kJ/mol CO_2	70	70
Solution Viscosity	cP	3.2	3.2
Desorption			
Pressure	bar	6	6
Temperature	°C	150	150
Equilibrium CO_2 Loading	mol/mol	0.44	0.44
Heat of Desorption	kJ/mol CO_2	70	70

Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		2,662,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	153
Absorber Pressure Drop	bar		0.013	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction of PZ with CO_2 involves formation of the following four PZ species:

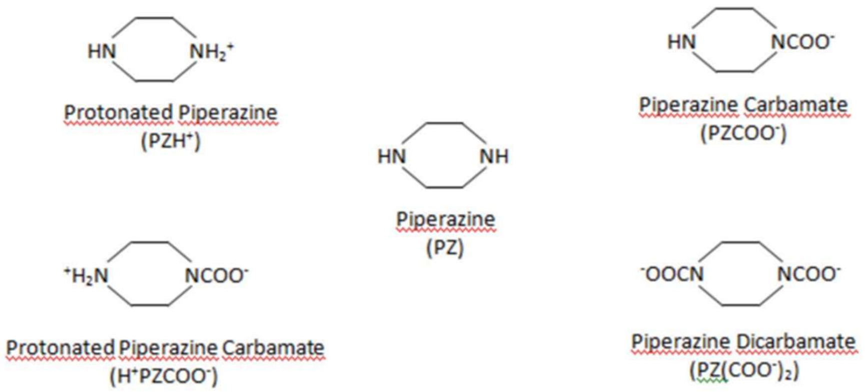

Figure 3: Molecular structure of piperazine species.

These reactions are as follows:

1. $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
2. $PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
3. $H_2O + H^+PZCOO^- \leftrightarrow H_3O^+ + PZCOO^-$
4. $PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

TABLE 2: EQUILIBRIUM CONSTANTS FOR ABOVE REACTIONS

Eq. No	Equilibrium Constant	In K = A + B/T + C InT		
		A	B	C
1	$K_1 = \frac{x_{PZ}x_{H3O+}}{x_{H2O}x_{PZH+}}$	-11.91	-4,351	—
2	$K_2 = \frac{x_{H3O+}x_{PZCOO-}}{x_{PZ}x_{CO2}x_{H2O}}$	-29.31	5,615	—
3	$K_3 = \frac{x_{H3O+}x_{PZCOO-}}{x_{H+PZCOO-}x_{H2O}}$	-8.21	-5,286	—
4	$K_4 = \frac{x_{H3O+}x_{PZ(COO-)2}}{x_{PZCOO-}x_{CO2}x_{H2O}}$	-30.78	5,615	—

This speciation and solubility model has been used to predict the partial pressure of CO_2 and mole fraction of species in solution as a function of PZ loading; the results show a good match between the model and the experimental data.

Solvent Contaminant Resistance – 5 molal PZ is thermally stable at 150°C with negligible oxidative (Freeman, 2011) degradation. The total amine loss is estimated to be 0.5% per week when stripping at 150°C. At 135°C, the estimated total amine loss of PZ is 0.3% as compared to 3.0% in the case of an MEA solvent. PZ forms nitrosamines and other nitro products with nitrogen dioxide (NO_2). Both pilot-scale flue gas testing and bench-scale testing have confirmed that nitrosamines decompose at temperatures of 150°C and greater. The main degradation products of PZ are formate (0.04 mM/hr) and ammonia (0.09 mM/hr) (Freeman, 2011).

Solvent Foaming Tendency – Pilot plant tests of PZ with two different sources of coal-fired flue gas and with air/CO_2 have experienced no persistent problems with foaming. However, bench-scale experiments have shown the possibility for PZ to foam under certain conditions (e.g., after undergoing oxidation degradation). In the bench-scale tests, foaming of PZ was greatly reduced with use of an oxidation inhibitor or with use of 1 part per million (ppm) of silicone antifoam (Chen, 2011).

Flue Gas Pretreatment Requirements – Tests at UT's SRP plant were performed on synthetic flue gas composed of air and CO_2. NCCC tests were conducted on medium-sulfur bituminous coal flue gas cleaned by FGD. Commercial applications would likely need sulfur oxides (SO_X) to be removed to levels below 10 ppm.

Solvent Makeup Requirements – Including an estimate for additional amine lost in the reclaiming process, the required makeup rate is estimated to be 0.76 kg of 30 wt% PZ per metric ton (MT) of CO_2 captured for PZ regenerated at 150°C. The estimated makeup rate for 30 wt% MEA at 120°C is approximately 2.0 kg/MT CO_2.

Waste Streams Generated – The major amine solid/liquid waste streams come from reclaimer waste. There could be fugitive liquid amine emissions, which can be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Gas-phase amine emissions from the absorber can be minimized by controlling aerosol formation and aerosol emissions from the absorber. Gas-phase amine emissions from the stripper can be minimized by controlling temperature of the CO_2 outlet gas and via operating conditions of the condenser.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 2.

Proposed Module Design – The design is based on the flue gas assumptions stated above.

technology advantages

As compared to conventional amine solvents, the advantages of PZ are:

- Faster CO_2 absorption rate, higher working capacity, higher thermal stability, and less oxidative degradation—all of which point toward 10 to 20% less energy use.
- Lower capital costs due to reduced energy use, greater stripper pressure (reduced compressor size), and faster kinetics.
- Additional savings in cost of electricity (COE) may be achieved by optimization of absorber packing, flue gas pre-treating, compressors, heat exchangers, and design improvements realized as part of this project.

R&D challenges

- Similar to other amines, PZ may absorb on aerosols in flue gas leading to poor amine collection in the water wash after CO_2 absorption and thus high amine emissions. Aerosol formation needs to be managed.
- PZ reacts with dissolved or entrained oxygen (O_2) at temperatures exceeding 150°C, potentially leading to greater than expected solvent makeup, but still less than MEA.
- PZ forms as a solid phase with water ($PZ \cdot 6H_2O$) and also with CO_2 ($H{+}PZCOO{-} \cdot H_2O$). Process robustness to excursions in CO_2 loading, temperature, and water balance is being demonstrated by quantifying their effects on solids precipitation and plant operation.

status

Testing was conducted on synthetic flue gas at the UT's SRP facility to investigate CO_2 capture with 5 and 8 molal PZ and 2SF and AFS regeneration designs. The testing showed that the AFS represents an optimized amine regeneration system with superior energy performance and simple operability over the 2SF or a simple stripper, that 5 molal PZ provides an economic and operability advantage over 8 molal, and that phase doppler interferometry can provide useful particle size information on amine aerosol. An extended test campaign resulted in more than 2,000 hours of operation at 0.5-MW scale on coal-fired flue gas at the NCCC to investigate CO_2 capture with 5 molal PZ and the AFS. The pilot plant testing verified reliable long-term operation of the novel regeneration technology and solvent combination. Results were used to evaluate the technical and economic feasibility of the full-scale implementation of this process.

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UKy-CAER Heat-Integrated Transformative CO_2 Capture Process for Pulverized Coal Power Plants

primary project goals

The University of Kentucky Center for Applied Energy Research (UKy-CAER) team is developing a post-combustion carbon dioxide (CO_2) capture technology using advanced solvents and incorporating innovative heat integration methods to utilize heat typically rejected to the environment via a two-stage solvent regeneration configuration, thereby ultimately improving power plant efficiency.

UKy-CAER has prepared a pre-front-end engineering design (pre-FEED) study for a 10-megawatt-electric (MWe) large pilot plant (FE0026497) based on the technology demonstrated at the 0.7-MWe scale.

UKy-CAER is performing the design, construction, and operation of a 10-MWe capture system based on the UKy-CAER heat-integrated transformational CO_2 capture technology at a coal-fired power plant. Phase I has been completed and consisted of: (1) selection of a host site for Phases II and III; (2) creation of Aspen Plus® model simulation; (3) completion of an environmental information volume (EIV); and (4) determination of Phase II team and cost-share commitments. Phase II efforts are underway, consisting of a detailed FEED study, National Environmental Policy Act (NEPA) permitting and documentation, and Phase III cost-share commitments. If selected for Phase III, the project will support construction and operation of the large-scale pilot facility. The Fossil Fuel Large-Scale Pilots effort supports the design, construction, and operation of large test facilities for transformational CO_2 capture technologies aimed at enabling step-change improvements in coal-powered system performance, efficiency, and cost of electricity (COE).

technical goals

Phase I objectives were to:

- Reinforce the formation of a cohesive project team covering technology development; solvent development; environmental, health, and safety (EH&S); engineering design, fabrication, and construction management; technology commercialization; and end-user utilities.
- Select and secure a host site and carbon capture system location.
- Update heat and material balances with the most recent small-scale experimental data and chemical composition to complete and improve accuracy of an EIV and process design package for the proposed UKy-CAER CO_2 capture technology, including the cost and schedule.
- Secure commitments from an engineering design firm, NEPA contractor, technology partners, and vendors.
- Update preliminary costs and schedules for Phases II and III.
- Secure commitments for Phases II and III cost share.

technology maturity:

Large Pilot-Scale, Actual Flue Gas (10 MWe)

project focus:

Transformative Process Using Advanced Solvents, Heat Integration, and Membrane Separation

participant:

University of Kentucky Research Foundation

project number:

FE0031583

predecessor projects:

FE0007395
FE0012926
FE0026497

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Kunlei Liu
University of Kentucky
kunlei.liu@uky.edu

partners:

Carbon Clean Solutions, USA (CCSUS), Smith Management Group (SMG), Carbon Management Research Group (CMRG), Electric Power Research Institute (EPRI), Huaneng Clean Energy Research Institute (HCERI), Koch Modular Process Systems (KMPS), Worley, Membrane Technology Research (MTR), University of Texas at Austin (UTA), Trimeric Corporation, Louisville Gas and Electric and Kentucky Utilities (LG&E and KU), Integrated Test Center (ITC), Carnegie Mellon University (CMU)

start date:

04.01.2018

percent complete:

55%

Phase II objectives are to:

- Complete a FEED study for the proposed large-scale pilot, including a detailed cost and schedule estimate for Phase III for the installation of the 10-MWe pilot at the host site, followed by commissioning, start-up, testing, operations, and data collection for performance validation.
- Complete the NEPA process at the host site.
- Submit permitting documentation to appropriate authorities and obtain the air permits for the steam generator and carbon capture system units.
- Document secured cost share for Phase III.
- Secure commitments for all necessary Phase III team members, including an engineering, procurement, and construction (EPC) vendor or equivalent to complete construction.
- Update the techno-economic analysis (TEA) for the UKy-CAER technology integrated with a 550-MWe net supercritical pulverized coal power plant based on the most recent system design and cost information.

technical content

UKy-CAER's four-pronged CO_2 capture approach that includes process intensification, two-stage solvent regeneration, heat integration, and an advanced solvent has evolved over a series of projects in recent years. Currently, the proposed capture process system incorporates several energy-saving and performance-increasing features, among which the most notable are as follows:

- A two-stage solvent regeneration configuration, consisting of a steam-driven, first-stage primary stripper removing most of the CO_2, followed by a secondary stage designed as an air stripper powered by recovered heat from the carbon capture system block, CO_2 compressor intercoolers, and the primary stripper overhead stream. The two-stage stripping reduces the carbon loading in the lean solvent to very low levels, and the exiting CO_2-laden air is fed into the boiler as secondary combustion air to boost CO_2 concentration at the absorber inlet. The system integration and heat recovery scheme has been demonstrated through experimentation and simulation. The secondary stripper also provides direct cooling to the lean solution returning to the absorber, significantly reducing the duty of the indirect-cooled lean solvent polishing exchanger; therefore, the additional capital cost of the second stripping column is offset by heat exchanger and cooling tower savings. Another advantage of the two-stage solvent regeneration scheme is that ion-free water carried by saturated air from the up-stream water evaporator is added to the solvent loop in the secondary stripper, eliminating the complexity, equipment, chemicals, and power needed to produce de-ionized water for amine loop makeup.
- Applied process intensification technologies, including:
    - Three discrete packing sections in the absorber with random packing included as in-situ gas-liquid distributors at every 5 to 10 feet of structured packing for high volumetric effectiveness and less gas-liquid channel flow.
    - Membrane CO_2 pre-concentration prior to the absorber inlet applied as needed to boost carbon loading in the rich solvent. Outputs from membrane consist of retentate enriched in CO_2 and permeate depleted in CO_2. These two flue gas streams are introduced at different levels in the absorber column, with the lean stream injected higher in the column where fresher solvent is present, and the rich stream injected farther down.
    - A split rich feed to the primary stripper to reduce the reboiler steam requirement and decrease the water content in the exit gas stream. The rich amine stream is split with a portion being heated to ~175 to 180°F (solvent- and stripping-dependent), and fed to the top of the stripper packing, acting as a heat sink to condense the water vapor and reduce the exit gas water (H_2O)/CO_2 ratio. The remaining rich flow is further heated to 220 to 239°F past the vaporization point, and two-phase flow is fed to the middle of the stripper packing, acting as a second source of carrier gas for CO_2 stripping.
    - Extracted steam exergy loss minimization through splitting of the feed water after the boiler feed water pump into two streams. While the main portion of the feed water maintains the normal flow path, 20 to 25% of the flow is heated to the same parameters as the boiler economizer in a split, last-stage feed water heater powered by steam extracted for the carbon capture system reboiler.
    - Solids incorporated in the absorber exit gas wash stream to minimize solvent entrainment and aerosols. By adding particles (up to 2 wt%) within the water wash stream, the solvent emission at the exhaust of the solvent recovery system is demonstrated to be less than the instrument detection limit.

- Has been demonstrated with various advanced solvents at the bench- and pilot-scales. Notably, the commercial Hitachi H3-1 and Carbon Clean Solutions, USA (CCSUS) CDRMax solvents have been under investigation and have figured prominently in small-pilot testing. Corporate restructuring has resulted in H3-1 becoming commercially unavailable, but CCSUS is partnering with UKy-CAER at the large-pilot scale. To balance the cost of commercial solvents and the gain in performance benefits, the advisable approach to solvent development focuses on striking a good balance of moderate solvent cost with CO_2 absorption performance and kinetics, including, but not limited to, cyclic capacity, solvent emissions, and degradation. This can be achieved by blending amines that are functionalized to prevent the formation of nitrosamine, and using additives with catalytic kinetic function and inhibitors to reduce solvent degradation and corrosion.
- Advanced process controls; UKy-CAER has developed two computing blocks, integrated with process control software such as Emerson DeltaV, to determine the alkalinity and carbon loading of the solvent first by using conventional instrumentation such as temperature and density signals, and then to manipulate the most effective control variables, such as lean solution circulation rate, lean loading, and liquid/gas temperature, in prompt response to external changes while ensuring minimum stream extraction is maintained.

Figure 1 depicts the general process arrangement of the UKy-CAER technology (most of these features are depicted here).

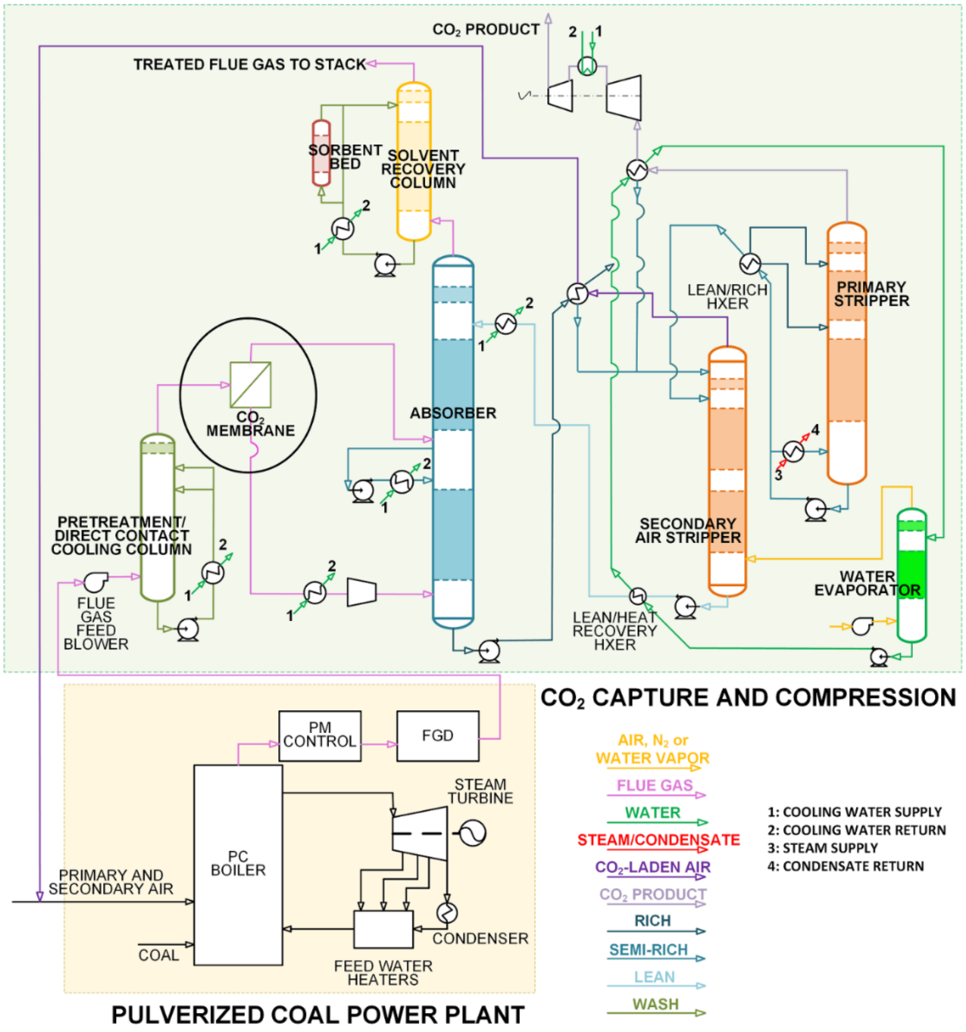

Figure 1: UKy-CAER carbon capture system process flow diagram.

Note: Black oval indicates the CO_2 pre-concentrating membrane unit investigated in FE0012926, which is not included in the large-pilot carbon capture system.

UKy-CAER's Advanced Solvents

UKy-CAER solvent development focuses on low-cost, enhanced CO_2 absorption kinetics; low emissions; and low degradation, considering both chemical and physical properties and the interactions between amine components of solvent blends and the additives. The overwhelming majority of research and development (R&D) in CO_2 capture solvents has focused on the amine chemistry, with little thought to the impact of additives on gas-liquid interface characterization. Understanding the impact of additives on key solvent properties – including surface tension and elasticity, wettability, and whether these impacts play a significant role in CO_2 capture characteristics such as adsorption rate, degradation, and aerosol formation – are an important focus of R&D in this context.

The UKy-CAER novel catalytic amine solvents utilize organometallic homogeneous catalyst chemistry to enhance CO_2 absorption kinetics. Mass transfer rate increases of 15 to 40% are possible by using a catalytic advanced amine solvent over an uncatalyzed amine solvent, resulting in more efficient absorption of CO_2, increased rich stream CO_2 concentration, and decreased absorber size requirements. Improved solvent thermal stability allows the solvent to be used in the high-temperature stripper conditions utilized in this process. Additional improvements from the catalytic solvent include increased cyclic capacity, reduced solvent loss and makeup requirements, and lower energy regeneration demand.

UKy-CAER designates catalytic solvents currently under investigation with codes to maintain confidentiality, reflecting permutations of proprietary commercial amine solvents (Solvent A, Solvent B, etc.). One of the solvents much investigated of late is CAER-B3.

Discretized Packing in Absorber

For any advanced solvent, the absorber temperature bulge typically occurs 10 to 15% from the top of a uniformly packed section when operated under a low liquid/gas ratio. UKy-CAER bench experimental data has shown that with a discretized packing arrangement, the temperature profile is modified, moving the bulge down the column and resulting in a 5 to 11% increase in rich loading for the same heights of packing, depending on the solvent lean loading. With an ideal column temperature profile, significant CO_2 absorption rate improvements (2 to 4x) will result in a small absorber (25 to 50% size reduction).

Pressurized Primary Stripper with Split Rich Solvent Feeds

UKy-CAER developed a rich solvent split configuration using the traditional lean/rich heat exchanger with one additional warm rich solvent extraction port. During operation, up to 50% of the total rich flow is extracted at a temperature of approximately 170°F (solvent- and stripping-dependent) and fed to the top of the stripper packing. This acts as a heat sink to condense the water vapor and reduce the exit gas H_2O/CO_2 ratio. The remaining rich flow is further heated past the vaporization point and a two-phase flow, with 5 to 6% vapor concentration, enters the middle of stripper packing at a temperature of 220 to 239°F depending on stripper pressure and solvent properties. The produced vapor acts as a second source of carrier gas for CO_2 stripping. Combined with solvent regeneration under pressure, UKy-CAER modelling results indicate the H_2O/CO_2 ratio in the stripper exhaust is significantly reduced from conventional 0.8 to 1.0, to 0.3 to 0.4 at 45 pounds per square inch (psi) stripper pressure, resulting in a steam consumption reduction of ~26%. This feature, in combination with CO_2 recycling, will result in a reboiler-specific energy of 950 British thermal units (Btu)/lb (2.2 gigajoules [GJ]/tonne) CO_2 captured for advanced solvents.

CO_2 Pre-Concentrating Membrane

Experimental results show that using a CO_2 pre-concentrating membrane to split the absorber gas feed into two streams (the permeate stream, with an enriched CO_2 concentration of 30 vol %, and the rejection stream, with a CO_2 concentration of ~10 vol %) yields a 30% energy savings compared to the conventional non-membrane configuration. Figure 2 shows the membrane separator for enriching CO_2 in the flue gas, and an actual polymeric membrane unit produced by Membrane Technology and Research (MTR), which was used in pilot-scale testing.

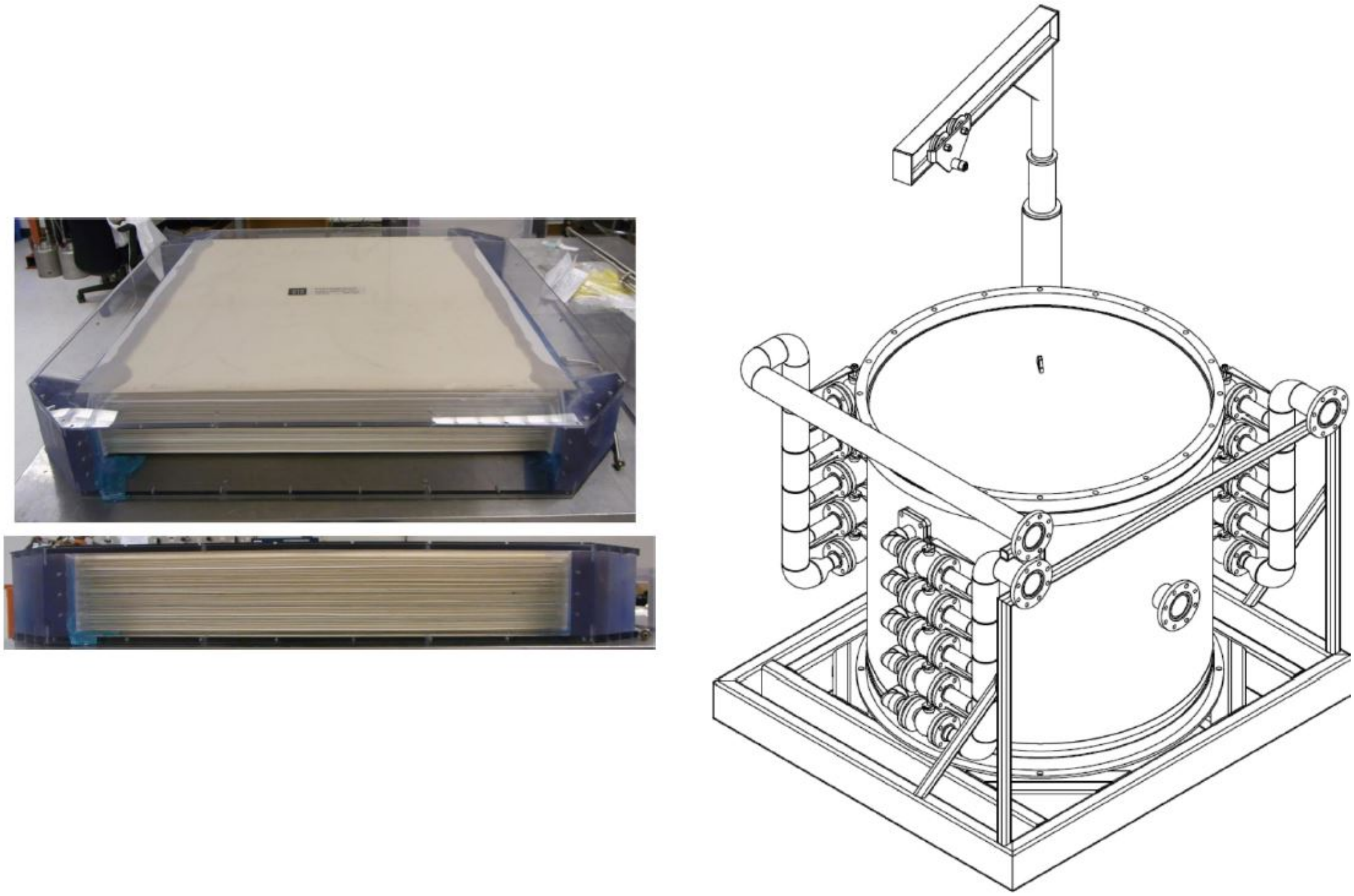

Figure 2: MTR CO_2 pre-concentrating membrane, internals on left and housing on right.

Membrane-Based Dewatering of Rich Amine Solvent

Related bench-scale project work (FE0012926) has extended the technology to include a membrane dewatering unit installed in the solvent rich stream. This feature is an integrated membrane concentrator unit intended to provide dewatering of the CO_2-rich amine solvent/solution exiting from the CO_2 absorber, either before or after the lean/rich heat exchanger. The membrane separator would selectively permeate water from the stream for recycle to the absorber through a zeolite-based membrane, as shown in Figure 3, effectively concentrating the CO_2-rich stream and increasing the CO_2 partial pressure, which can further reduce process energy demand. This membrane should be designed to maximize water permeability and carbon/amine rejection while maintaining stable performance over time. UKy-CAER has investigated zeolites as the material of choice for this membrane. Currently, given the membrane surface area required and the high cost of zeolite membranes, it is not practical to include it in process scenarios as envisioned. However, through the use of lower-cost hollow fiber support materials and increasing the packing density of the active membrane surface area up to >200 m^2/m^3, the economics of this enrichment process can be improved. In addition, through modifications to the active membrane layer and the permeability of the support layer, water flux through the membrane can be enhanced to further reduce the cost and implementation of this system in a CO_2 capture process.

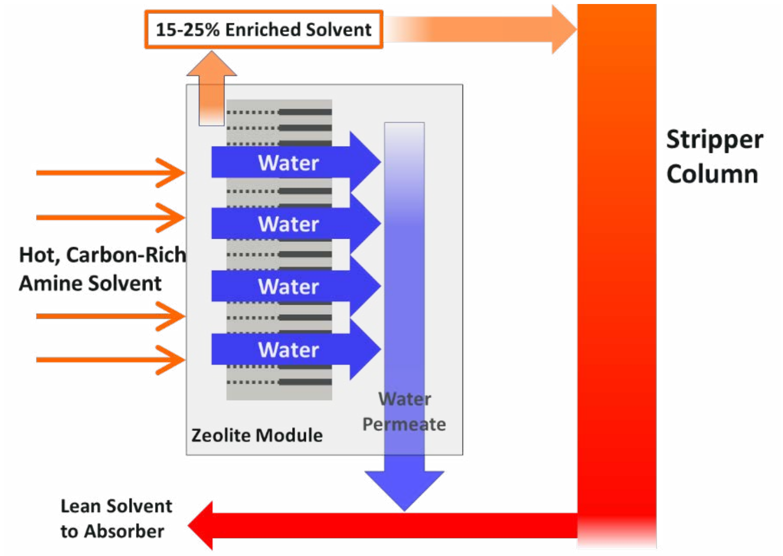

Figure 3: Solvent membrane dewatering for CO_2 enrichment.

Findings from Slipstream Testing

Small pilot testing at 0.7 MWe has been performed at the Kentucky Utilities E.W. Brown Generating Station in Harrodsburg, Kentucky, using a process configuration including much of the scheme depicted in Figure 1. Performance of the capture system was baselined using a generic 30-wt% monoethanolamine (MEA) solvent to obtain data for direct comparison with the National Energy Technology Laboratory (NETL) Reference Case 10 (RC10). Also, Hitachi's proprietary solvent H3-1, CCSUS' proprietary solvent CDRMax, and the CAER blended solvent were tested. Parametric test campaigns, system transient dynamic studies, and long-term continuous verification tests of the heat integration process enabled characterization of the system response in terms of load-demand following, varying flue gas conditions, and individual component operation. Evaluation of solvent degradation, process emissions, and corrosion studies of materials in the circulating solvent were accomplished. See below, and also in the Other Parameters section following Table 2 for findings in these areas. Data were collected to support a full techno-economic and EH&S analysis for a 550-MW commercial-scale carbon capture plant.

Notable findings are as follows:

- The process can easily capture 90% of CO_2 in flue gas using either MEA, H3-1, CDRMax, or CAER solvent as the working capture solvent.
- MEA solvent regeneration energy was determined to be 1,200 to 1,750 Btu/lb CO_2 captured, ~13% lower than RC10.
- H3-1 solvent regeneration energy was determined to be 900 to 1,600 Btu/lb CO_2 captured,~36% lower than RC10. Overall, low-regeneration energies are possible over a range of solvent concentrations.
- CDRMax solvent regeneration energy was determined to be 1,150 to 1,400 Btu/lb CO_2 captured,~8 to 25% lower than RC10.
- The secondary air stripper is capable of regenerating >10% of the CO_2 captured, as depicted in Figure 4. At the commercial scale, the exhaust CO_2-laden air (8 to 12 vol% CO_2, dry) will be recycled back to the boiler as combustion secondary air, yielding a higher absorber inlet CO_2 concentration (15 to 17 vol%), which has been observed to always correspond to a low-solvent regeneration energy.
- A high rich carbon loading (2.3 to 2.4 mol/kg solution), corresponding to a low-solvent regeneration energy, can be achieved with a pump around to the bottom section of the absorber packing with assistance of interstage cooling.

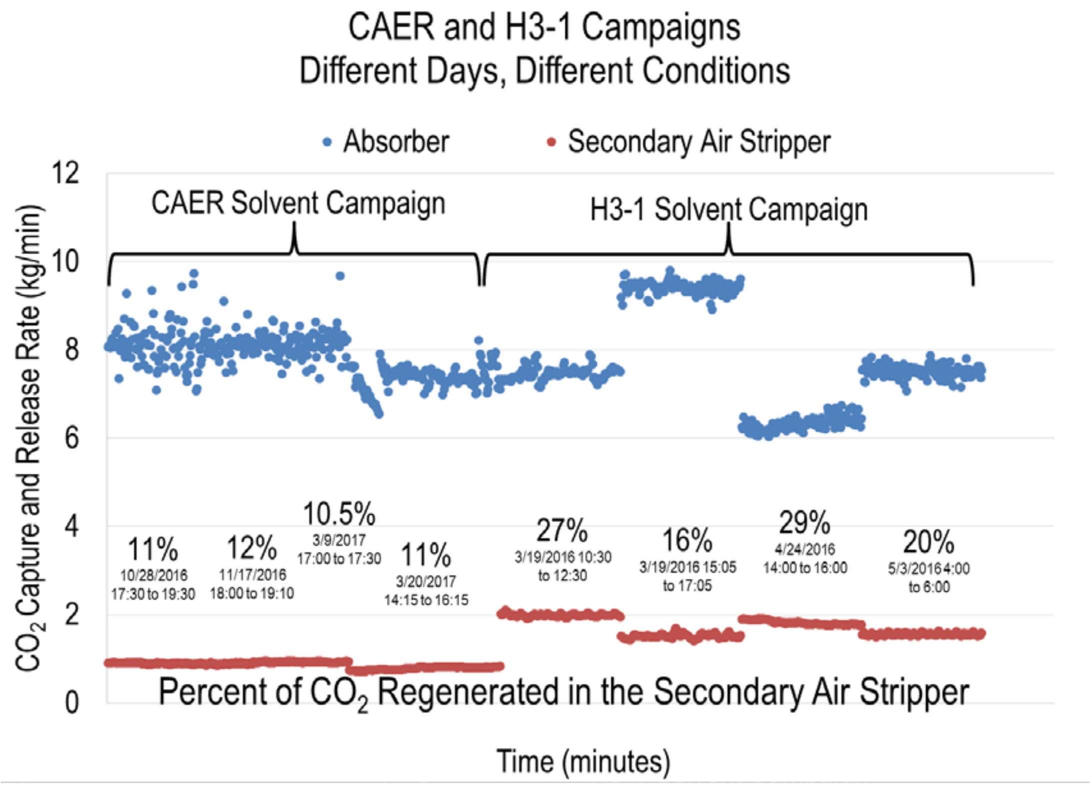

Figure 4: UKy-CAER secondary air stripper CO_2 regeneration.

- Varying ambient conditions have an impact on CO_2 capture, attributable to cooling water temperature variations that impact the capture system process stream temperatures at any point where heat exchange with cooling water is involved, including flue gas temperature, lean solvent return, and absorber interstage cooling.
- Adequate absorber liquid/gas distribution is required to maintain high absorber efficiency.
- Lean/rich exchanger performance is critical to the energy efficiency of the cycle: if the approach temperature in the exchanger is not kept low, the efficiency suffers. This is depicted in Figure 5, showing that an increase in approach temperature to 35°F from 20°F increases the solvent regeneration energy demand by about 400 Btu/lb CO_2.

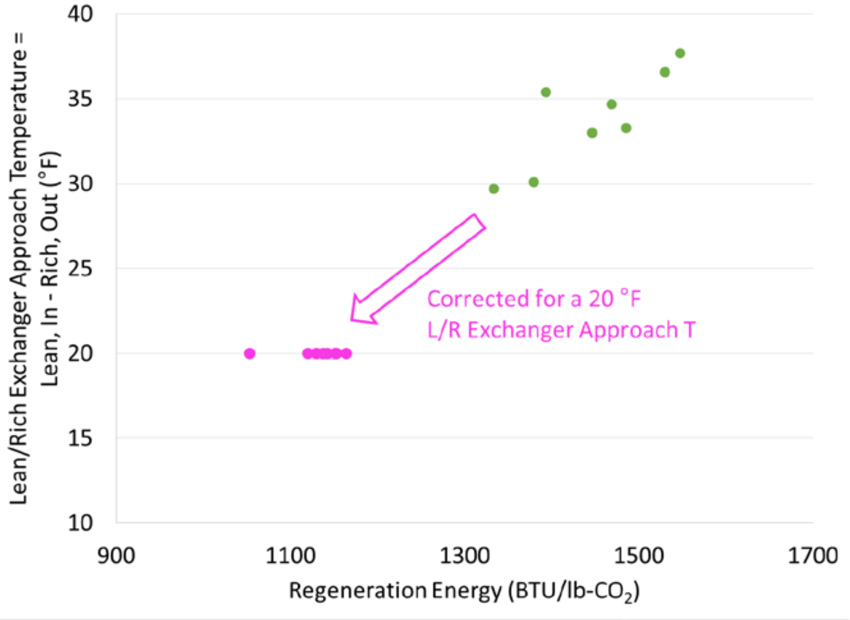

Figure 5: Effect of lean/rich heat exchanger approach temperature on solvent regeneration energy demand.

- Use of deionized water for makeup is not necessary in the UKy-CAER two-stage stripping technology when scrubbing coal combustion flue gases, helping to reduce the cost and complexity of constructing and operating CO_2 capture systems. The measured accumulation of chloride from the service water and heat-stable salt (HSS) contaminants from coal flue gas is depicted in Figure 6. While elemental accumulation in the solvent still needs to be monitored, this shows that the majority of accumulating contaminants originate in the coal flue gas, not the service water source. Because accumulating species can cause various deleterious impacts, including solvent degradation and loss of absorption performance, corrosion of materials in the process circuit, etc., this is an area to continue investigating in future technology scale-up.

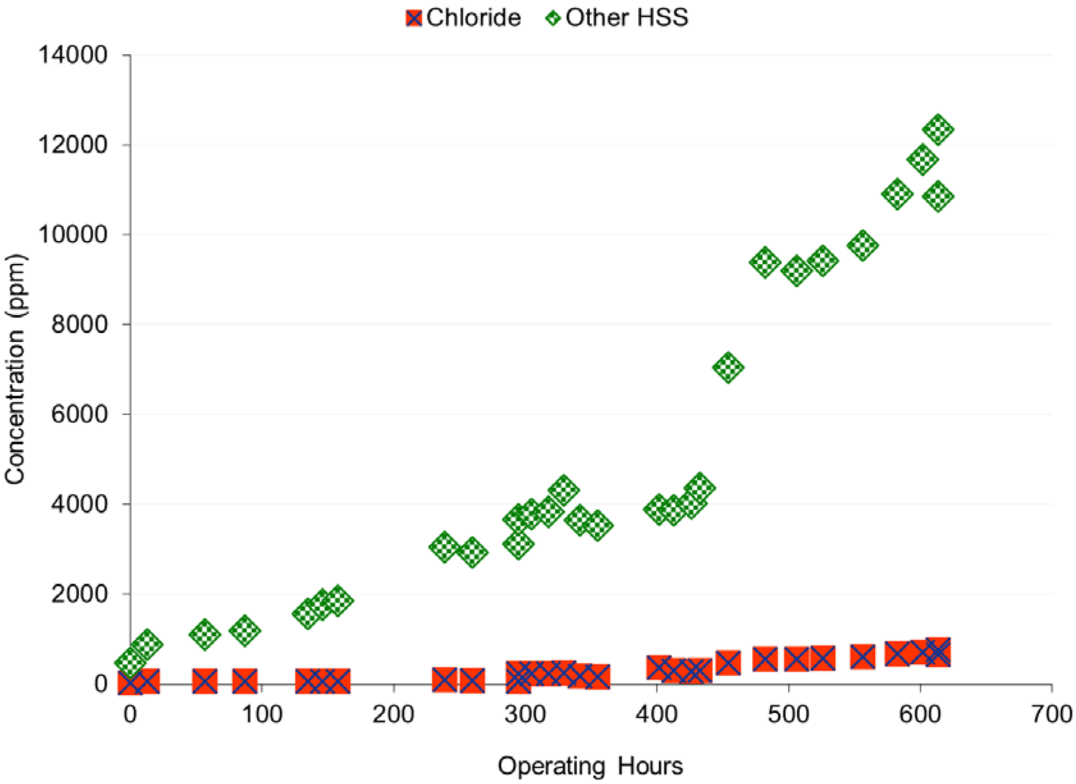

Figure 6: Accumulation of contaminants in solvent.

- Process emissions in the scrubbed flue gas from solvent degradation (as ammonia) were found to be related to increasing iron content in the solvent from corrosion, as depicted in Figure 7. Corrosion and solvent degradation can be controlled by adding a proprietary multi-functional additive to the solvent. Figure 8 shows that when the multi-functional additive concentration in the solvent is above the operating level of 100 parts per million (ppm), the ammonia emissions are low, but when the additive is depleted, solvent degradation and ammonia emissions increase.

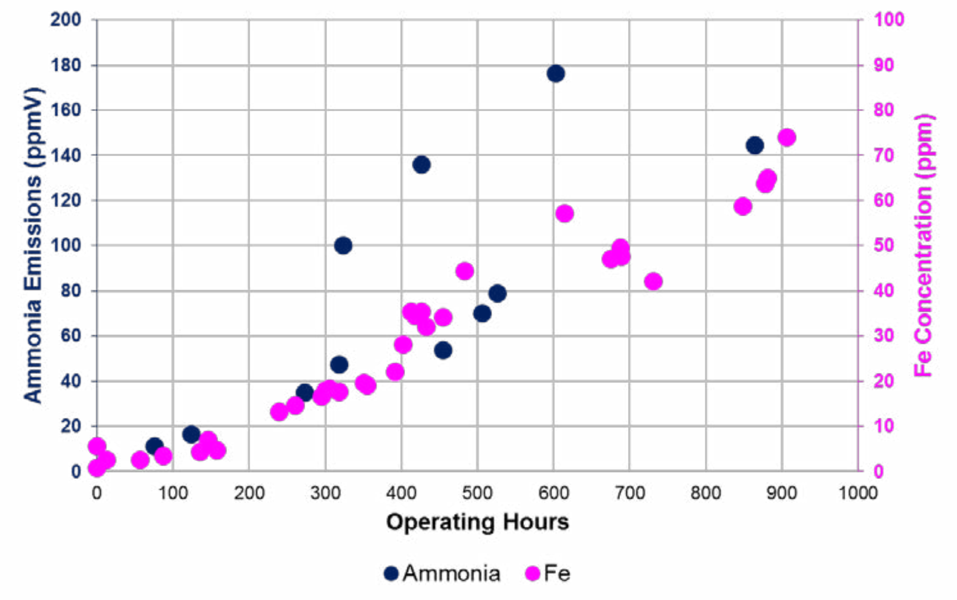

Figure 7: Ammonia emissions and iron.

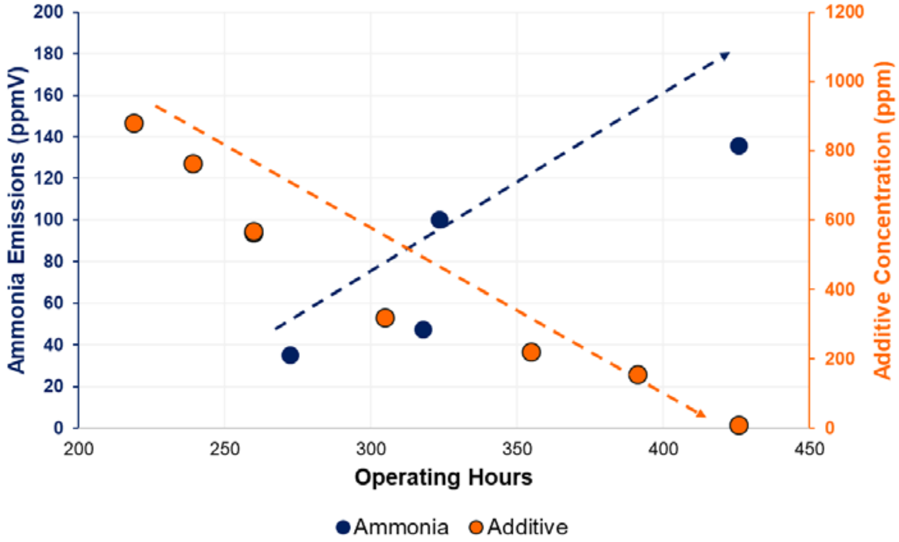

Figure 8: Ammonia emissions versus additive in the solvent.

Techno-Economic Analysis Findings

The preliminary TEA conducted and experimentally validated under FE0007395 shows that application of the improved process cycle (with MEA as the solvent) would reduce the COE by about 8% over the conventional 90% capture case, and that use of H3-1 in the improved process cycle would reduce COE 12%. The TEA was updated to include discretized packing for absorber temperature control, a solids-incorporated solvent recovery system, split rich primary stripper feeds to reduce H_2O/CO_2 ratio in the stripper outlet, and de-superheating the carbon capture and storage (CCS) extracted steam with a feed water heater. In this case, the overall reduction in COE is 19%. Figure 9 shows that the cost of CO_2 capture (excluding transportation, storage, and monitoring) is reduced from $56.52 to $34.51 per tonne of CO_2 captured, a reduction of 38.9% with coal being the sole energy source. The cost of CO_2 capture could be further reduced to $25.26 per tonne of CO_2 captured when all auxiliary electricty and steam required for the carbon capture system are from natural gas-fuel by taking advantage of the low capital cost of natural gas combined electricity and heat unit.

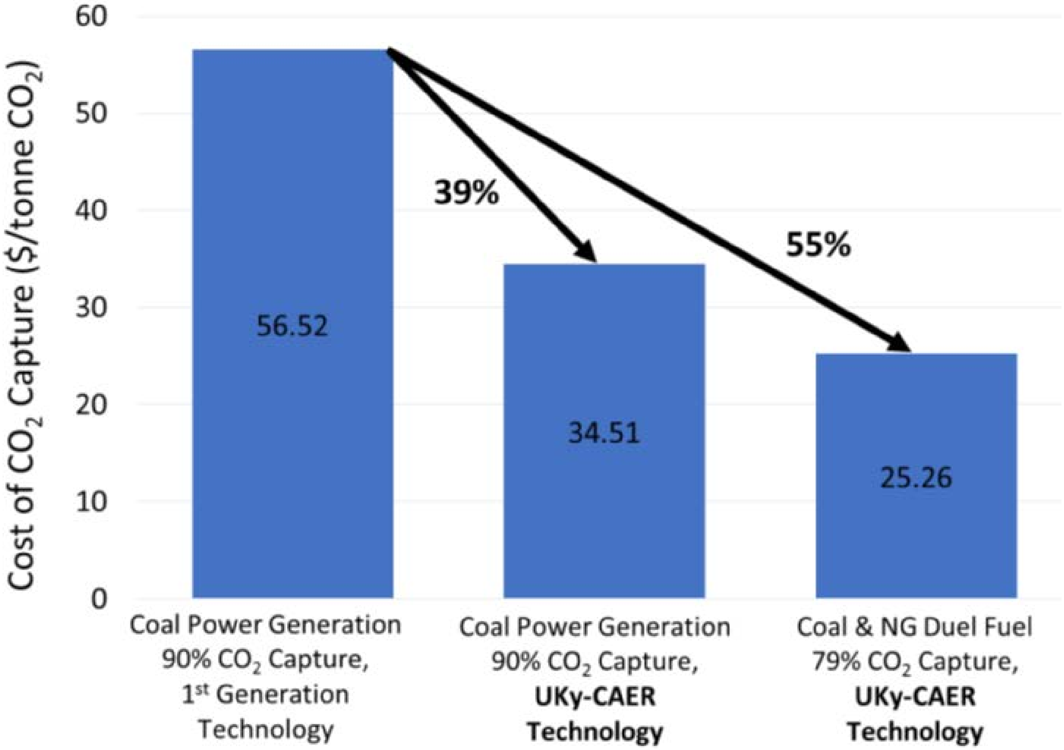

Figure 9: Cost of CO_2 capture estimates from techno-economic analysis.

However, additional cost reductions will be necessary to attain ultimate U.S. Department of Energy (DOE) program targets. For this, UKy-CAER estimates that a combination of a further-improved third-generation solvent will be critical, combined with absorption enhancement technologies via optimal absorber temperature profile and gas-liquid interface mixing. To illustrate the issue, the current second-generation solvents are simply too expensive compared to conventional MEA, as shown in Table 1 (Solvent B is 10 times the cost of MEA on a unit basis). In these cases with solvents A and B being commercially available, the energy savings are less than the additional solvent makeup cost.

TABLE 1: SOLVENT COST COMPARISON

	30 wt% MEA	Solvent A	Solvent B
Make-up Rate (kg/ton CO_2)	1.5	0.5	0.5
Energy Consumption Compared to 30 wt% MEA		30% less	40% less
Unit Cost (\$/kg)	1.5	9	15
Solvent Cost (\$/tonne CO_2 Captured)	2.25	4.5	7.5
COE (\$/MWh)	106.5	93.3	91.2

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	<90	<90
Normal Boiling Point	°C	160–165	160–220
Normal Freezing Point	°C	-2	-2–5
Vapor Pressure @ 15°C	bar	6.3×10^{-4}	6.3×10^{-4}-6.3×10^{-3}
Manufacturing Cost for Solvent	\$/kg	4–6 (estimated)	3–5

Working Solution				
Concentration	kg/kg	<0.4		<0.45
Specific Gravity (15°C/15°C)	-	1.01		1.01
Specific Heat Capacity @ STP	kJ/kg-K	3.7		3.7
Viscosity @ STP	cP	3.04		3.5
Surface Tension @ STP	dyn/cm	<55		<55
Absorption				
Pressure	bar	1		1
Temperature	°C	40		40
Equilibrium CO$_2$ Loading	mol/mol	0.42		0.51–0.65
Heat of Absorption	kJ/mol CO$_2$	74		<60
Solution Viscosity	cP	4.88		8-10
Desorption				
Pressure	bar	3.1		3.0
Temperature	°C	125		120
Equilibrium CO$_2$ Loading	mol/mol	0.23		0.30
Heat of Desorption	kJ/mol CO$_2$	84		<75
Proposed Module Design		*(for equipment developers)*		
Flue Gas Flowrate @ 10 MWe equivalent	kg/hr	43,000		
CO$_2$ Recovery, Purity, and Stripper Pressure	%/%/bar	90	99.9	3.0
Absorber Pressure Drop	bar	<0.1–0.15		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	~200		

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO$_2$ absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO$_2$-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Surface Tension – The tension of the surface film of a liquid caused by the attraction of the particles in the surface layer by the bulk of the liquid, which tends to minimize surface area. This is measured in force per unit length (dyn/cm).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO$_2$ partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO$_2$ partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO$_2$ in equilibrium with the solution. If the vapor phase is pure CO$_2$, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO$_2$. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted otherwise, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption reactions for any amine-based system can be broken into two primary reactions, as depicted in Figure 10. The absorption of CO_2 is primarily dictated by the reactions of primary amine (SC) to form carbamates. The reaction second order rate constant for these species can vary, but is generally on the order of (10^3 l/mol·s), with similar rate constants observed for CAER-B3. The SC reaction generates a mole of proton for each mole of CO_2 capture, leading to primary amines being generally limited on a molar basis to 0.5 CO_2:1N. The CAER-B3 amine solvent utilizes a primary amine as the main component. Additionally, another minor component is added to the solvent to principally act as a proton receiver (PC) in the solution to balance the bicarbonate formation. The pKa of this proton receiver is higher (more basic) than that of the main component. The reaction from the proton receiver to directly form bicarbonate is much slower (100x). It is expected to function similarly to those enzymes in directly catalyzing the reaction of dissolved CO_2 in solution to form bicarbonate. A third reaction to form bicarbonate directly from hydroxide present in solution can generally be excluded from consideration despite the fast rate constant (10^4 l/mol·s) because hydroxide concentration is limited by the base dissociation constant in typical amine solutions (<1 x 10^{-4}).

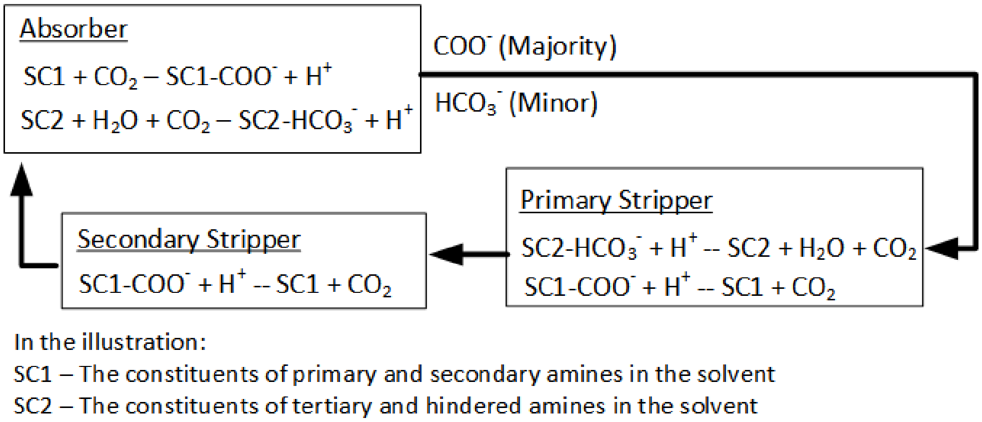

Figure 10: Schematic for reactions occurring in the CO_2 capture cycle.

Solvent Contaminant Resistance – The CAER-B3 solvent shows behavior analogous to MEA towards oxidation and flue gas components. Similar levels or less of oxidation and degradation due to flue gas components are anticipated.

Solvent Foaming Tendency – The addition of anti-foam to solvent can help control foaming tendencies by lowering the solvent surface tension. Any new solvent additive will need to be evaluated for its foaming potential and any that may increase foaming tendency should be avoided. The CAER-B3 solvent has very low foaming tendencies (less than 30% MEA) due to a low surface tension of <40 dyn/cm.

Flue Gas Pretreatment Requirements – At the UKy-CAER bench-scale CO_2 capture facility, flue gas from the boiler goes through a solid separator where particulate matter is initially removed before being treated in a wet desulfurization process to lower sulfur dioxide (SO_2) concentration typically below 100 ppm using conventional limestone-based wet flue gas desulfurization (WFGD). After SO_2 removal, the flue gas goes through a knock-out drum for final particulate and liquid droplet removal before it is sent to the CO_2 capture unit. In practice, power generation flue gas exiting from existing environmental controls is further polished to below 10 ppm SO_2 through an additional pretreatment step to slow the accumulation of sulfate in the solvent. Sulfate is an HSS, meaning it cannot be thermally removed from the solvent. Its accumulation will slowly reduce the CO_2 capture capacity of the solvent.

Solvent Makeup Requirements – Long-term stability is an ever-present concern of all solvent developers. The CAER solvent is composed of amines that are inherently more stable than MEA and has a higher thermal stability than MEA. As seen in Figure 11, a 50 to 70% decrease in rate-of-amine loss as a percent of initial is observed at the high temperatures associated with stripper conditions over a two-week period. Regression of the data compared to reference MEA predicts a thermal degradation rate similar to MEA at a 10°C higher stripper operating temperature. It is expected that the makeup requirements will be similar to that of MEA under the proposed process conditions of a higher stripper temperature/pressure.

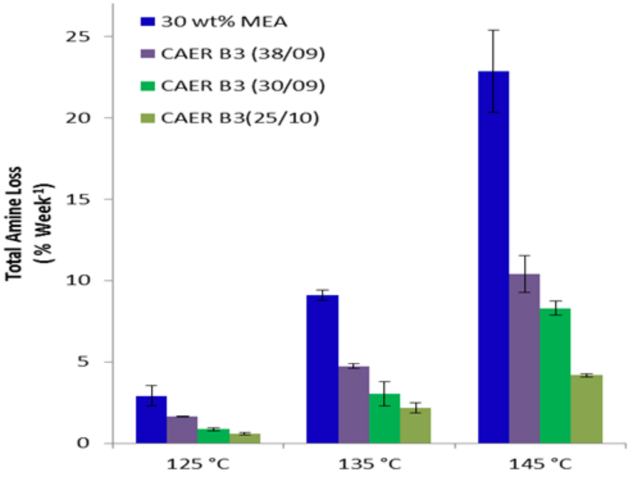

Figure 11: Rate of amine loss as total percent amine under stripper conditions of 30 wt% MEA (blue) and various combinations of CAER-B3.

Waste Streams Generated – The waste streams generated from the process are the spent soda ash solution and CAER-B3 solvent, used for SO_2 removal and the absorption of CO_2, respectively. The loss of performance and how quickly the solvent is spent is impacted by the rate of degradation and HSS formation in the solvent. In practice, the solvent will be treated in a thermal reclaimer to remove HSSs and metal species, which will also produce a waste that is likely hazardous in nature.

Process Design Concept – The process flow is shown in Figure 1. In brief, the SO_2-polished flue gas (from the pretreatment tower) enters the CO_2 pre-concentrating membrane to produce two streams that are injected into the CO_2 absorber at separate locations. After gaseous CO_2 is converted into aqueous carbon species, the carbon-rich solution exits the absorber bottom, is pressurized, and sent to the rich-lean solution heat exchanger (Crossover HXER) with split rich outlets to primary stripper or the hot rich stream from lean/rich heat exchanger entering to the dewatering membrane unit for solution pre-concentration, which is not shown in Figure 1. The permeate stream of the dewatering membrane unit with low amine concentration combines with the regenerated lean solution stream exiting at the outlet of the stripper. The reject stream, which has higher carbon loading than the feed stream, is sent to the middle of pressurized stripper for solvent regeneration. This stage will require an energy source to drive the reboiler. At the stripper exit, the gas stream consists primarily of CO_2 and water vapor at a pressure of approximately 3 bar. After exiting the heat recovery unit at the top of stripper, the CO_2 gas stream has a purity of 99.9% and will be pressurized to about 135 bar and intercooled for downstream utilization or storage. The carbon-lean solution exiting the primary stripper is sent to the Crossover EHX, where heat will be recovered with the carbon-rich solution. After the Crossover EHX, this heat depleted stream will be cooled to approximately 40°C and recycled to the absorber.

technology advantages

- The two-stage stripping unit, including the deployment of an air-based secondary stripper, will regenerate an exceptionally CO_2-lean solvent, increasing the rate of CO_2 absorption and solvent cyclic capacity, will eliminate the need for deionized water for amine loop makeup, and will provide a direct cooling effect on lean solvent prior to returning to the absorber.

- Low capital cost resulting from a discretized packing arrangement and in-situ gas-liquid distribution to minimize the liquid maldistribution.
- High system efficiency resulting from carbon capture system internal heat integration, rich solvent split to the primary stripper, and de-superheating extracted steam by splitting the feed water.
- The solvent recovery column, at the outlet of the gas stream leaving the CO_2 absorber, with solid particle assistance to minimize the solvent emissions, minimizing solvent makeup requirements.
- The advanced solvent used in this system has: (1) a higher mass-transfer flux; (2) a higher net cyclic carbon capacity; (3) less energy demand for CO_2 stripping; and (4) lower corrosion rates than a 30 wt% MEA solution, leading to lower capital and operational costs.
- The advanced solvent also has a 15 to 20% lower degradation rate compared to 30 wt% MEA, leading to lower solvent makeup volume.
- Potential for reduced capital cost for post-combustion CO_2 capture, chiefly through increased absorption kinetics that allow for a smaller absorber and regeneration columns coupled with a lower solvent circulation rate and smaller associated equipment (blowers, pumps, and piping systems).
- Potential for reduced energy consumption compared to conventional MEA-based scrubbing, chiefly attributable to:
    - High cyclic capacity.
    - High stripper pressure: the primary CO_2 stripper can be operated at approximately 3 bar in order to maximize the energy benefit while minimizing system capital and solvent degradation, which could lead to low compressor capital and operating costs.
    - Heat integration to power air-based secondary stripper.

R&D challenges

To achieve the targets set forth by DOE/NETL, several R&D challenges remain to be met.

- Due to the low CO_2 absorption driving force in utility flue gas and the highly viscous nature of second-generation + solvents, the low-pressure drop structured packing suffers from a lack of macro-mixing/turbulence between the bulk solvent and the gas-liquid interface, which results in localized channel flow and significantly reduces column effectiveness. The application of short sections (3 to 6 inches) of high-pressure drop random packing could re-adjust the pressure and redistribute the liquid within a section of structured packing.
- Two-stage solvent regeneration has been successfully demonstrated at the small pilot scale, but intensification in the absorber and strippers can be applied to reduce the column height and steam requirement.
- The UKy-CAER solvent recovery from the absorber exit gas stream has been demonstrated at lab, bench, and pilot scale.
- Use of a CO_2 pre-concentrating membrane in the absorber flue gas feed has been demonstrated at bench scale, and been tested at the pilot scale.
- Implementation of a smart process control scheme needs to be demonstrated to reduce the solvent regeneration energy while also responding quickly to the dynamic load and ambient conditions.
- Waste minimization techniques need to be demonstrated at the large pilot scale. Accumulation of elements such as selenium (Se) and arsenic (As) in the CO_2 capture solvent can result in a hazardous classification of the material.
- The relationship between thermal compression and lean/rich heat exchanger size needs to be understood and included when reporting solvent and process performance. It is generally accepted that the stripper is equilibrium-controlled, and in-situ thermal compression via high-temperature operation will drop the H_2O/CO_2 ratio at the stripper outlet, lowering the specific reboiler duty. The 0.7-MWe small pilot experimental data indicate this holds true only for systems with a relatively large lean/rich heat exchanger (low ΔT between hot lean from stripper and hot rich to stripper).
- Long-term, low-cost advanced solvent performance needs to be demonstrated. While several solvents are currently in use at the commercial scale, they are costly, and improved performance may not justify this cost.
- Lower-cost corrosion-resistant materials of construction need to be demonstrated. In general, most amine solvents have the tendency to corrode metal surfaces, especially in high carbon loading and/or high temperature locations. Sections of the CCS that are specifically impacted are the absorber bottom, lean/rich heat exchanger, and the top

of the stripper. Currently, most CCS systems deployed in the utility environment use stainless steel for locations where wetted surfaces are expected, while some are using concrete with a plastic/polymer or ceramic liner for the CO_2 absorber, which results in a higher capital investment.

status

Small pilot-scale (0.7-MWe) testing results and identification of process improvements have shown the promise of UKy-CAER's process-intensified and heat-integrated post-combustion CO_2 capture technology to attain DOE program goals. Additional advancement to meet ultimate performance and cost goals will rely on identification of a third-generation advanced solvent that can be produced at reasonable cost, and subsequent large-pilot demonstration at the proposed 10-MWe plant scale.

UKy-CAER is designing a pilot-scale (10-MWe) post-combustion carbon capture system for installation at the Wyoming Integrated Test Center (ITC). The ITC is located at Basic Electric Power Cooperative's Dry Fork Station near Gillette, Wyoming, wherein flue gas from the plant is diverted to the testing facility. In Phase I, Wyoming ITC coal-fired power plant in Gillette, Wyoming, was selected as the host site for the large capture pilot and cost-share commitments were finalized. Preliminary engineering and cost estimates were prepared for the equipment inside the battery limit (ISBL) and outside the battery limit (OSBL). A NEPA contractor was also selected as part of the Phase I effort. A plan was developed for securing cost-share commitments for Phase III. Phase II efforts are underway and will conclude with completion of a FEED study, NEPA process, permitting documentation, and team member commitments.

available reports/technical papers/presentations

FE0031583

Liu, K., et. al., UKy-CAER Heat-integrated Transformative CO_2 Capture Process in Pulverized Coal Power Plants," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/K-Liu-UKY-CAER-Heat-Integrated-Capture_r1.pdf*.

Nikolic, H., et. al., "UKy-CAER Heat-integrated Transformative CO_2 Capture Process in Pulverized Coal Power Plants," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKCAER-Heat-Integrated-CO2-Capture.pdf*.

"UKy-CAER Heat-integrated Transformative CO_2 Capture Process in Pulverized Coal Power Plants," Project kickoff meeting presentation, May 2018. *https://www.netl.doe.gov/project-information?p=FE0031583*.

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Nikolic, H., et. al., "Application of a Heat Integrated Post-Combustion Carbon Dioxide Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKY-CAER-Integrated-Postcombustion-Capture.pdf*.

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Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture

primary project goals

The University of Notre Dame, in collaboration with Lawrence Livermore National Laboratory (LLNL) and colleagues at the University of Texas, has been developing technology for hybrid encapsulated ionic liquid (IL) and phase-change ionic liquid (PCIL) materials for post-combustion carbon dioxide (CO_2) capture. Although ILs have many favorable properties as CO_2-absorbing solvents, their typically high viscosities directly correlate with poor mass transfer rates and prohibit their practicable application in large-scale commercial operation when configured in conventional absorption/regeneration systems. Researchers' work in identifying ILs and PCILs with high capacity and low regeneration energy that, when combined with their technology for microencapsulation of the ILs or PCILs in polymer shells, may enable synthesis of high surface area IL- and PCIL-based materials well-suited for CO_2 capture from post-combustion flue gas. The goal of the project is successful synthesis of the microencapsulated ILs and/or PCILs and validated CO_2 removal from simulated flue gas in a laboratory-scale unit, with demonstration of dramatically improved mass transfer rates.

technical goals

- Encapsulated ILs/PCILs structural integrity: microcapsules in fluidized beds able to contain the ILs without leaking.
- Uptake of CO_2 by encapsulated ILs/PCILs: greater than 50% CO_2 absorption from a humid nitrogen (N_2)-CO_2 gas mixture in laboratory-scale testing.
- Durability/recyclability of the encapsulated ILs/PCILs: less than 20% decline in absorption capacity of CO_2 after five cycles in humid N_2-CO_2 gas mixture.
- Solvent regeneration: at least 80% of the absorbed CO_2 removed by hot vapor (steam) without significant damage to the particles.
- Substantial technology progress towards a capture system enabling 90% CO_2 capture with 95% CO_2 purity at a cost of electricity 30% less than baseline aqueous amine technologies.

technical content

Conventional solvent-based carbon capture methods typically employ amines such as monoethanolamine (MEA) as the capture solvent. However, amines are corrosive, degrade over time, and have relatively high vapor pressures, making their leakage into the environment more likely. ILs are a class of ionic salts tending to have large nitrogen or phosphorous-bearing cations with alkyl chain substituents. ILs are anhydrous, liquid at ambient temperatures, have low vapor pressures, are thermally stable and relatively non-corrosive, and certain ILs have a considerable affinity for absorption of CO_2 and selectivity towards CO_2 in gas mixtures. For example, the hexafluorophosphate (PF_{6-}) and tetrafluoroborate (BF_{4-}) anions have been shown to be amenable to CO_2 capture.

ILs might be used in a similar process to amine gas treating to effect carbon capture from flue gas, where the flue gas is contacted with the solvent in an absorption column, and the rich solvent is regenerated in a stripper column at

technology maturity:

Laboratory-Scale, Simulated Flue Gas (3.3 liters per minute)

project focus:

Microencapsulated CO_2 Capture Materials

participant:

University of Notre Dame

project number:

FE0026465

predecessor projects:

DE-FC26-07NT43091
DE-AR0000094

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Mark McCready
University of Notre Dame
mjm@nd.edu

partners:

University of Texas at Austin
Lawrence Livermore National Laboratory

start date:

10.01.2015

percent complete:

100%

higher temperature through use of steam heating. ILs consistently show CO_2 absorption behavior of decreasing solubility with increasing temperature, enabling conventional temperature swing absorption cycling. Because they have increasing CO_2 solubility with increasing pressure, ILs could also be stripped using pressure swing or swept with inert gases, possibly reducing the process energy requirement.

A current issue with ILs for carbon capture is that they have a lower working capacity than amines. Another pressing concern with their use is their high viscosity compared with that of commercial solvents. ILs that employ chemisorption depend on a chemical reaction between solute and solvent for CO_2 separation. The rate of this reaction is dependent on the diffusivity of CO_2 in the solvent and is thus inversely proportional to viscosity. The self-diffusivity of CO_2 in ILs is generally on the order of 10^{-10} m^2/s, approximately an order of magnitude less than similarly performing commercial solvents used for CO_2 capture. This represents a problematic mass transfer barrier for ILs and overcoming it would constitute a significant advance in IL-based carbon capture technology.

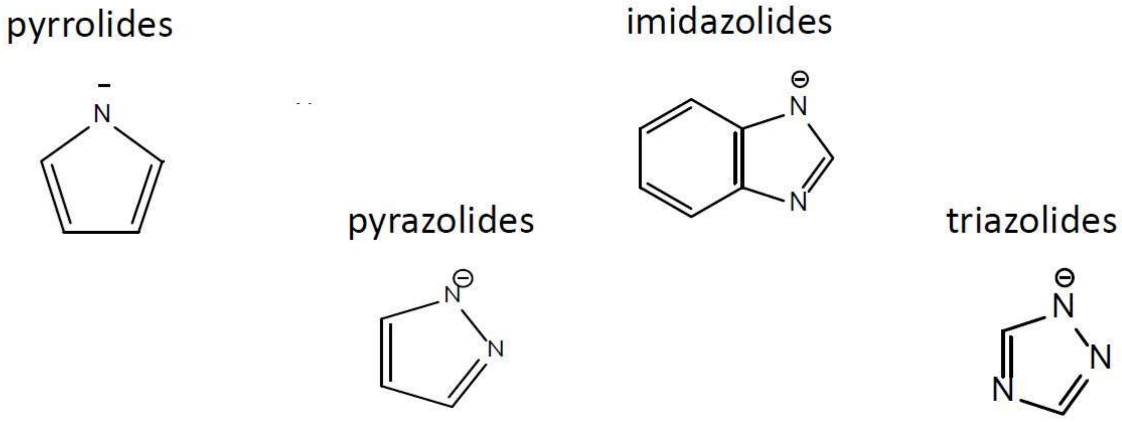
However, encapsulating ILs/PCILs in small spherical shells and suspending these in a low-viscosity medium would create a high-surface area IL/PCIL-based material into which CO_2 could much more easily diffuse and react, potentially overcoming the mass transfer barriers caused by the inherently high viscosities of the stand-alone ILs/PCILs. Therefore, the technologic development approach being explored here involves combining IL and PCIL materials having high CO_2 absorption capacity and low regeneration energy, and microencapsulation of these in polymer shells, with significant potential for resulting in high surface area materials to be very well-suited for CO_2 capture from post-combustion flue gas.

Selection of Suitable ILs and PCILs

Strongly performing ILs and PCILs would have several favorable properties/characteristics, such as:

- Chemical complexation strong enough to increase capacity and to decrease required IL circulation rates.
- Chemical complexation weak enough to keep regeneration energies (and temperatures) down.
- High equimolar absorption capacity: value of 1 mol CO_2/mol IL at absorption conditions is favorable.
- No viscosity increases of the IL upon reaction with CO_2. Such increases occur because of the formation of hydrogen bonding networks.

It has been observed that ILs containing aprotic heterocyclic anions are favorable on these points. They enable relatively high absorption capacity. It is possible to tailor/tune heat of reaction of these ILs, guided by experience and previous density functional theory, in order to enable an optimal chemical complexation strength (this happens to be between about -45 and -60 kJ/mole enthalpy of reaction with CO_2). Also, they retain amine in the ring structure, and further reduction of free hydrogens to reduce hydrogen bonding is possible, avoiding the viscosity increase problem. Figure 1 depicts some types of these aprotic heterocyclic anions.


pyrrolides

imidazolides

pyrazolides

triazolides

Figure 1: Several types of aprotic heterocyclic anions.

The researchers have evaluated a number of possibilities for ILs and PCILs prepared by LLNL, and settled on one IL and one PCIL for continued development in this technology. The IL (NDIL0230) is triethyl(octyl)phosphonium 2-cyanopyrrolide ($[P_{2228}]$[2CNPyr]), and the PCIL (NDIL0309) is tetraethylphosphonium benzimidazolide ($[P_{2222}]$[BnIm]), which was developed in an Advanced Research Projects Agency-Energy (ARPA-E) project. The PCIL will undergo a phase change to and from liquid and solid at the varying temperatures it experiences during regeneration and absorption. This is expected to confer certain energy efficiency advantages as discussed below in process implementation.

Microencapsulation

The central innovation of this developmental technology involves encapsulating ILs and PCILs in thin CO_2-permeable polymeric shells to produce particles of approximately 100 to 600 µm in diameter. It is thought that this approach will create a high volumetric surface area material that can put ILs within easy diffusion range of CO_2-containing flue gas in a fluidized-bed or moving-bed absorber in a post-combustion CO_2 capture cycle. This idea is depicted in Figure 2. The typical tower packing in amine absorption columns is either structured packing or random packing fill, which in either case establishes a surface area for liquid-gas contacting in the range of hundreds of m^2 surface per m^3 of column volume. However, note the microcapsules would generally establish surface areas near or above 10,000 m^2 per m^3.

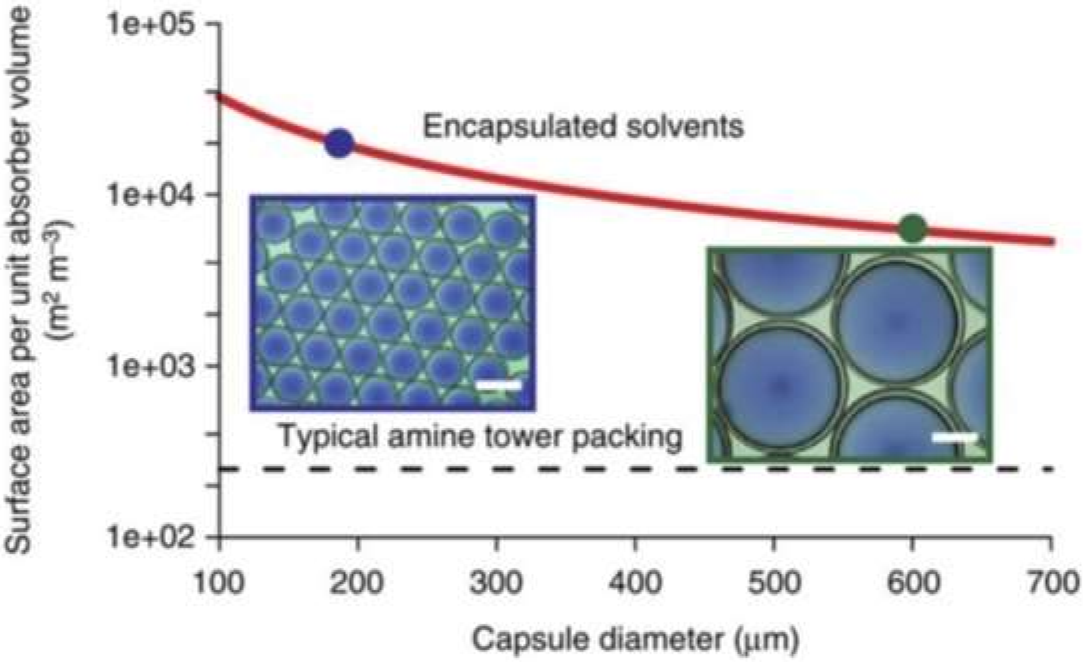


Figure 2: Surface area benefit of microencapsulation.

The technology for creating polymer-shell-encased IL microcapsules is now well established by LLNL. The microcapsules are produced in a microfluidic device where the solvent and uncured shell material are flowed together in a third, inert carrier fluid through a junction to create double emulsions – drops of solvent inside drops of shell material precursor, suspended in the carrier fluid. The apparatus is diagrammed in Figure 3. The shell material is subsequently cured by exposure to ultraviolet (UV) light. In project work, capsules are produced in single-junction devices assembled from glass capillaries, but the process can be parallelized for large-scale production.

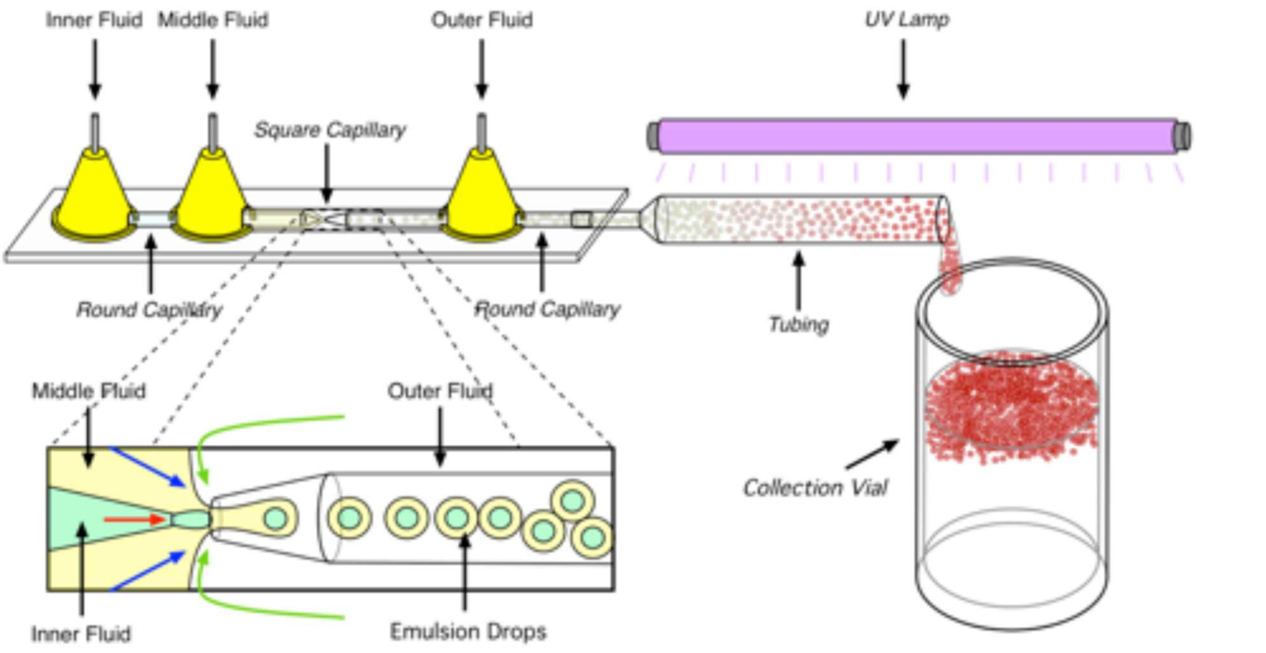


Figure 3: Diagram of the capsule production apparatus (Inner Fluid is the IL; Middle Fluid is the shell material precursor; and Outer Fluid is an aqueous, inert, carrier solution).

The polymer shell of the microcapsules must satisfy several conditions, including ability to reliably contain the IL contents and maintain general physical stability, provide negligible diffusion resistance to CO_2, and to not adversely affect the IL absorption reaction. Initially, issues were experienced with incompatibility of the ILs with the polymer material forming the polymer shell, but these have since been overcome. LLNL settled on their in-house developed and refined Thiolene-Q shell material formulation for NDIL0309, given its chemical compatibility and for which an alternative crosslinker for improved microcapsule production and in-air production was found. Figure 4 depicts this formulation. For NDIL0230, a different polymer SiTRIS was found to be compatible; Figure 5 is a magnified image of the microcapsules that have been successfully fabricated using these combinations.

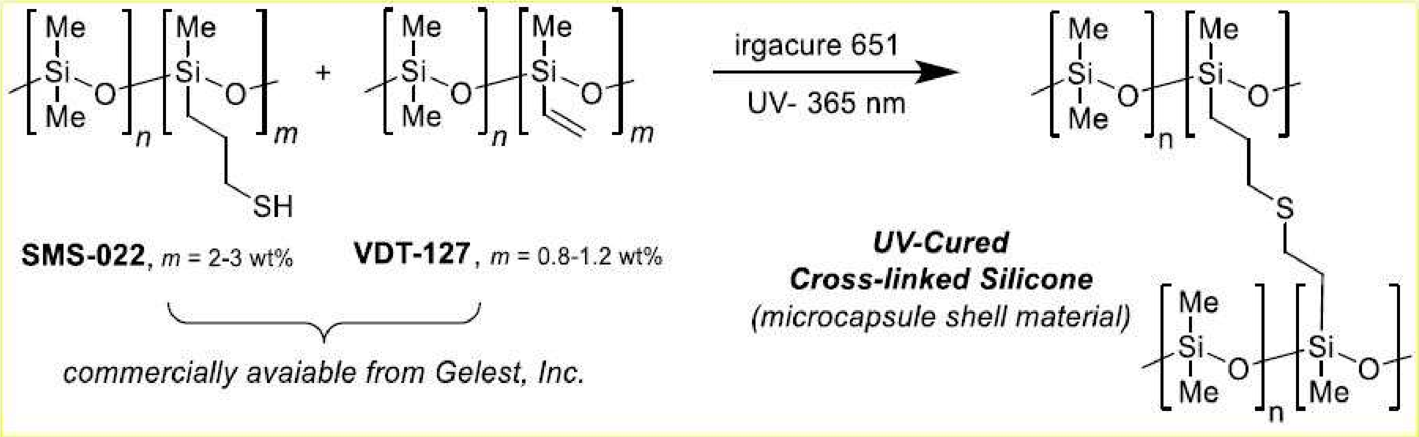


Figure 4: Thiolene-Q shell material.

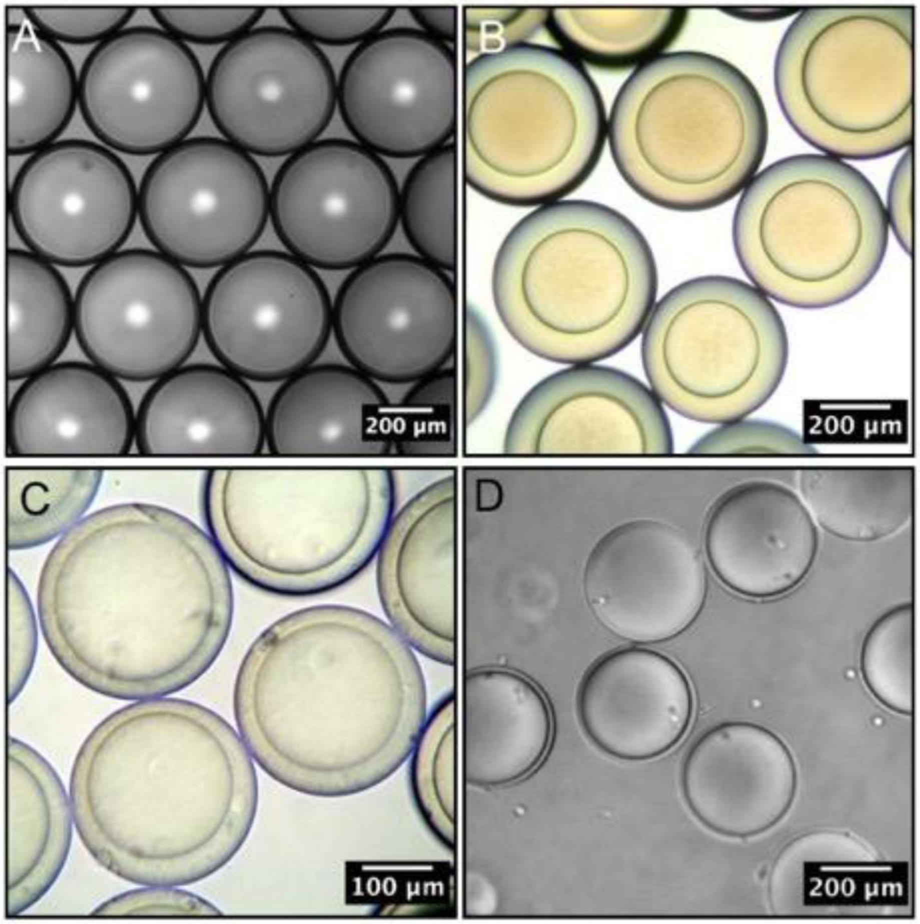


Figure 5: Successful microcapsules: A: NDIL0231/water-in-SiTRIS; B: NDIL0230/water-in-SiTRIS; C: NDIL0309/water-in-Thiolene-Silica; D: NDIL0309/water-in-Thiolene-Q.

Testing of the encapsulated ILs/PCILs in simulated flue gas showed the following:

- Effects of impurities: the IL and PCIL under consideration both react irreversibly with sulfur dioxide (SO_2) and nitrogen oxides (NO_X), whether free or encapsulated. Accordingly, CO_2 capture with these would need to follow the flue gas desulfurization (FGD) and NO_X reduction units in the flue gas cleanup system.
- Reaction of water with the IL or PCIL in the presence of CO_2 is completely reversible and recyclable. Therefore, water does not need to be excluded from the cores of the microcapsules. This is greatly advantageous given the inevitable presence of water vapor in flue gas.

PCIL Process Implementation

Process advantages result from the inherent characteristics of PCILs in temperature swing absorption cycles, as depicted in Figure 6. In the absorption column on the left, a PCIL slurry containing encapsulated PCILs at low temperature (at which the PCILs are in the solid phase) is contacted counter-currently with CO_2-containing flue gas passing up the column. The PCIL reacts exothermically with CO_2, creating heat that is absorbed by the PCIL particles, causing them to melt. The PCIL-CO_2 liquid leaving the column is sprayed into a dryer shown on the right, which serves as the regenerator in this process cycle. The PCIL is heated in the dryer, causing it to release CO_2 in relatively pure gaseous form, which is withdrawn and compressed for transport or storage. The heat duty of the stripper is reduced somewhat by the heat of fusion of the PCIL as it goes from liquid to solid phase. Also, the cooling duty of the PCILs on the absorption side is reduced by the phase change from solid to liquid phase.

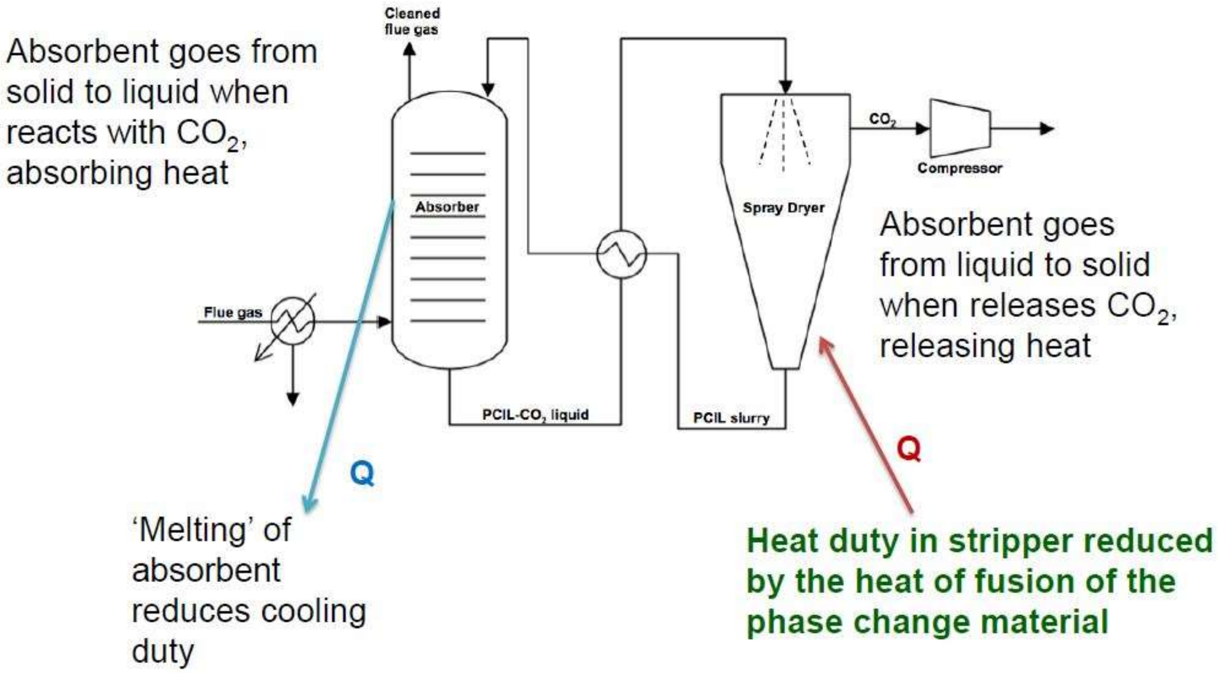


Figure 6: CO_2 capture cycling with phase-change material.

The result of this is that the overall heat duties on either side of the process cycle are moderated somewhat by the phase changes occurring. This is more clearly depicted in Figure 7, which accounts how the phase changes of the PCILs reduce the total molar heat duty on either side by 20 kJ/mol. Instead of needing to supply the entire 50 kJ/mol by external heating of the dryer/regenerator, only the net amount of 30 kJ/mol needs to be supplied; the other 20 kJ/mol being contributed by the PCIL phase-changes. This should lessen the parasitic energy demand for operating the process relative to a non-phase-change scenario.

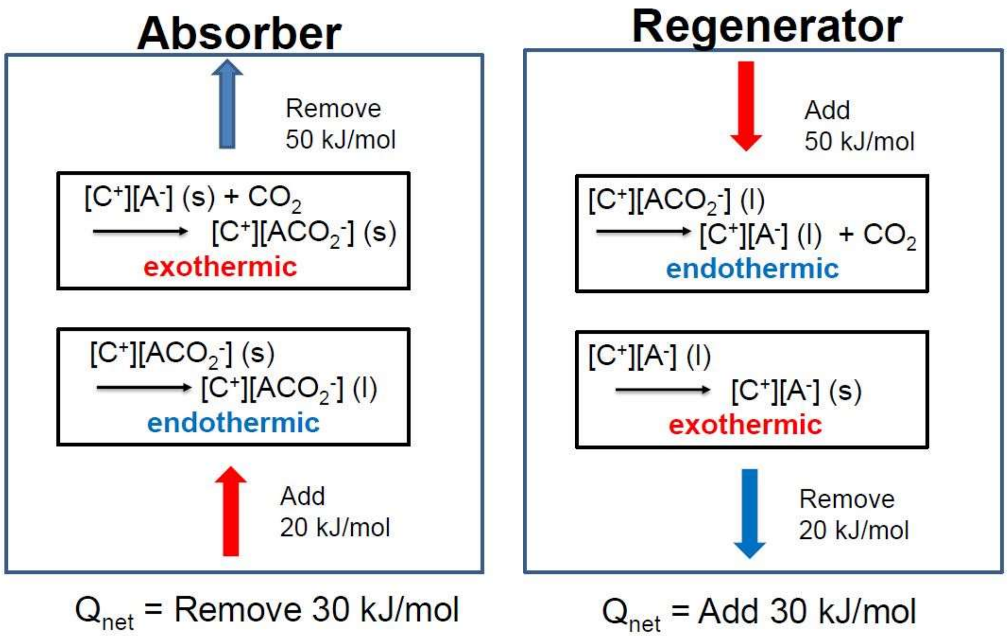


Figure 7: Heat duties for CO_2 capture with PCILs.

Project Summary Findings

Small quantities (~1 g) of microcapsules with good integrity of both the IL and the PCIL have been successfully produced. The CO_2 uptake by these capsules is the same as for the free IL and PCIL and the capacity of the capsules decreases only slightly after five absorption and desorption cycles. Over five cycles of absorption and regeneration, the CO_2 capacity has been consistently measured at 0.64 to 0.68 moles CO_2/mol PCIL.

Large samples (~70 g and 100 g) of encapsulated PCIL were produced in a parallel microfluidic device and in an in-air device, respectively. These capsules have been tested in a laboratory-scale unit (LSU) at 3.3 liters per minute simulated flue gas flow rate to demonstrate uptake capacity in a fluidized bed. The LSU also allowed determination of recyclability and mass transfer coefficients. Equivalent experiments with the IL were not possible due to difficulties with producing large samples of the encapsulated IL. This IL encapsulation "scale-up" problem was not solved during the course of the project. Nonetheless, testing of the PCIL microcapsules verified that the mass transfer is internally controlled. In concert with a new rate-based model of a microcapsule fluidized-bed absorber, it was found that productivity is increased by a factor of 4.75 in the microcapsule fluidized-bed absorber compared to a conventional liquid-gas packed-bed absorber.

An initial techno-economic model (assuming a process design as depicted in Figure 8) shows that the capital cost for the microcapsule IL continuous fluidized-bed process is similar to that of an aqueous amine process (specifically, the Econamine FG Plus technology). However, the stripping heat requirements are about 35% less for the model IL microcapsule case compared to the MEA case. Thus, encapsulated ILs/PCILs in a continuous fluidized-bed absorber for post-combustion CO_2 capture are a significant improvement over the free IL/PCIL case and represent a major reduction in the parasitic energy requirements compared to an aqueous amine process.

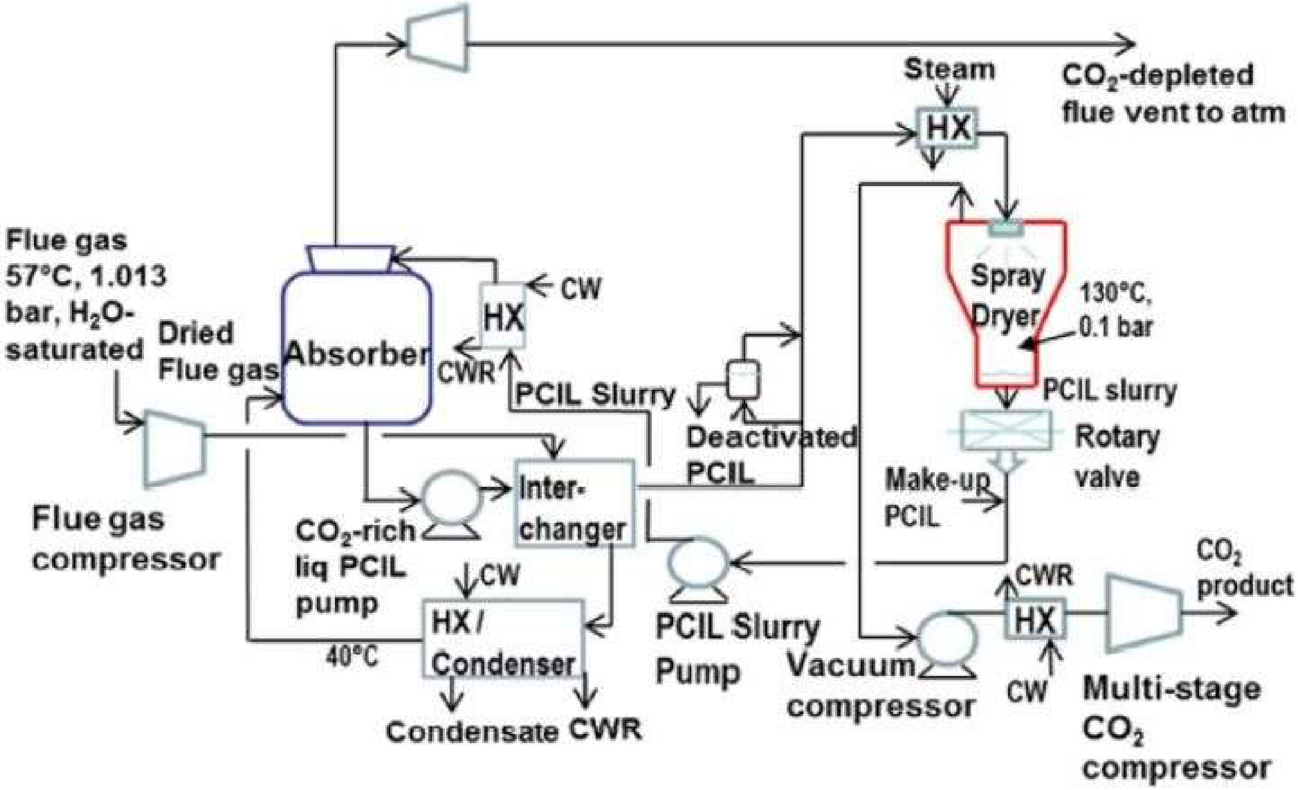


Figure 8: Process flow diagram for CO_2 capture in a full-scale plant using PCILs.

technology advantages

- The encapsulation of ILs and PCILs in micrometer-sized shells is projected to increase the mass transfer area by an order of magnitude or more.
- Significant reduction of the capital costs of the absorber and regenerator in CO_2 capture systems.
- Lowered energy demands to operate absorption/regeneration cycle with the encapsulated solvents.

R&D challenges

- IL absorption capacities decrease with lower partial pressures of CO_2, and CO_2 concentration in flue gas is low at only about 0.15 bar.
- Viscosities of ILs generally increase upon reaction with CO_2, occurring because of the formation of hydrogen bonding networks.
- ILs tend to degrade strongly in the presence of typical flue gas contaminants, such SO_2 and SO_X.
- Encapsulation of ILs in polymer shells: getting sufficiently high loadings of the IL/PCIL in the shells, possible compatibility issues or unfavorable effects of the IL and polymer material on each other, and viscosity and surface tension issues in microencapsulation.
- Solids handling issues that arise from encapsulating liquids in shells, essentially turning a liquid into a finely granular solid material, and the necessity of reliably circulating this material around a complicated absorption-regeneration cycle.
- The shells themselves must withstand damage and reliably contain the ILs; leakage of the IL/PCIL if shell polymeric cross-linking is insufficient.

status

The project has been completed.

available reports/technical papers/presentations

Final Scientific/Technical Report, "Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture," June 29, 2019.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture*," presented by Mark McCready, University of Notre Dame, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August, 2018.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture*," presented by Mark McCready, University of Notre Dame, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August, 2017.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide (CO_2) Capture*," Topical Report, November 2016.

"*Hybrid Encapsulated Ionic Liquids for Post-Combustion CO_2 Capture*," presented by Joan Brennecke, University of Notre Dame, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Hybrid Encapsulated Ionic Liquids for Post Combustion CO_2 Capture*," Project kickoff meeting presentation, November 2015.

Dilute-Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions

primary project goals

Carbon Engineering Ltd. is developing advancements for their Direct Air Capture (DAC) technology to capture carbon dioxide (CO_2) from dilute CO_2 sources, including evaluating DAC for other coal-relevant sources, such as post-carbon capture and storage (CCS) flue gas, and to re-capture legacy atmospheric coal-based emissions. The DAC process uses a wet scrubbing air contactor, along with chemical processing steps, to produce pure CO_2 and remake the capture solution. The project will focus on applied research and development (R&D) at their pilot facility, along with a commercial readiness and cost-estimation evaluation.

technical goals

- Use Carbon Engineering's existing research pilot facility to perform component testing, sensitivity analysis, and sub-system optimization of the DAC technology.
- Conduct performance analysis and technology optimization based on laboratory, simulated, and pilot operations.
- Develop key engineering inputs for scale-up of DAC technology.
- Perform a techno-economic assessment (TEA) and applicability to coal stream study.

technical content

Carbon Engineering Ltd. has been developing this dilute-source CO_2 capture technology since 2009 to scrub CO_2 from atmospheric air present at concentrations of 400 parts per million (ppm). This project is aimed to further advance this DAC technology for atmospheric CO_2 concentrations, as well as evaluating the system's performance as applied to other coal-relevant dilute CO_2 sources, including post-CCS flue gas and re-capturing legacy atmospheric coal-based emissions.

The DAC process, shown in Figure 1, is based on the use of a wet scrubbing air contactor followed by several chemical processing steps. The chemistry of the process is shown in Figure 2. The aqueous potassium hydroxide (KOH) used in the air contactor is converted into aqueous potassium carbonate (K_2CO_3) when reacted with the CO_2 from the air. In the pellet reactor, the aqueous K_2CO_3 reacts with solid calcium hydroxide ($Ca(OH)_2$) from the slaker to regenerate the aqueous hydroxide, which is sent back to the air contactor, and calcium carbonate ($CaCO_3$) to be used in the calciner. In the calciner, at elevated temperature, the $CaCO_3$ decomposes into solid calcium oxide (CaO), releasing pure CO_2 from the process.

technology maturity:

Pilot-Scale

project focus:

Direct Air Capture from Dilute CO_2 Sources

participant:

Carbon Engineering Ltd.

project number:

FE0026861

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Jenny McCahill
Carbon Engineering Ltd.
jmccahill@carbonengineering.com

partners:

N/A

start date:

09.19.2016

percent complete:

100%

The CaO goes to the slaker where water is introduced, forming the $Ca(OH)_2$, which is sent to the pellet reactor, completing the cycle.

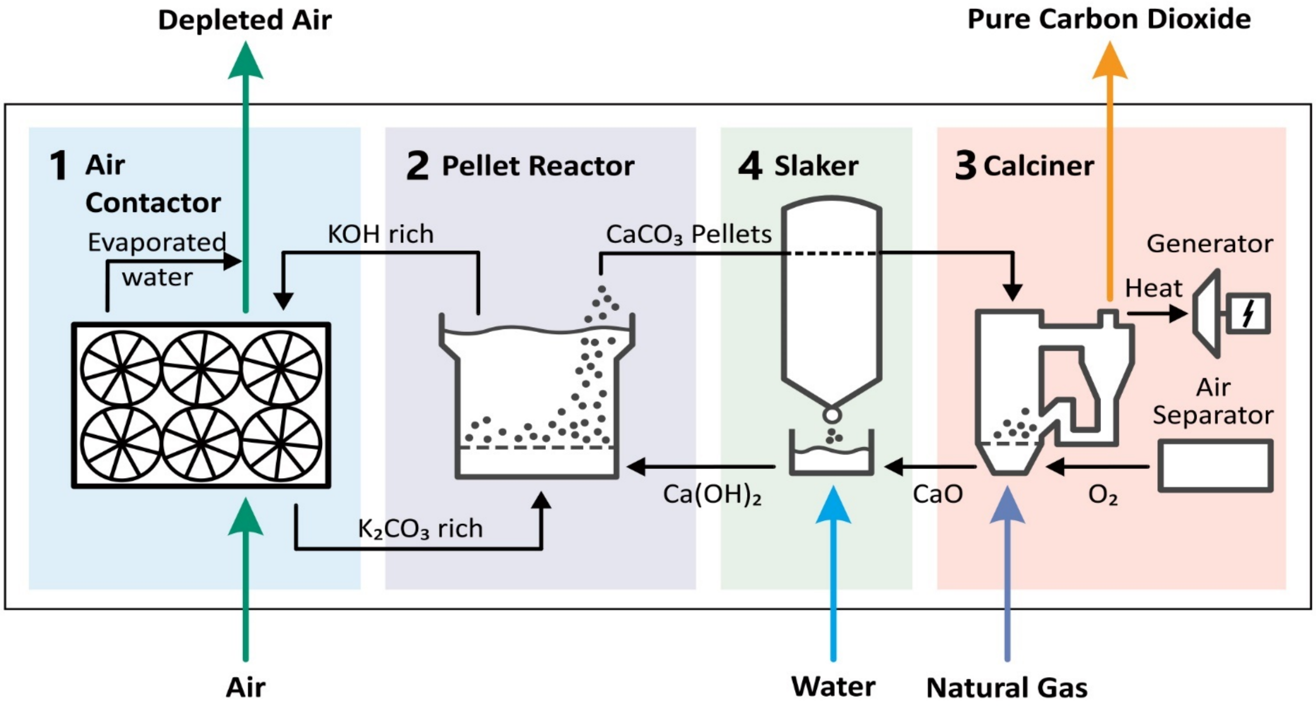


Figure 1: Schematic of the DAC process.

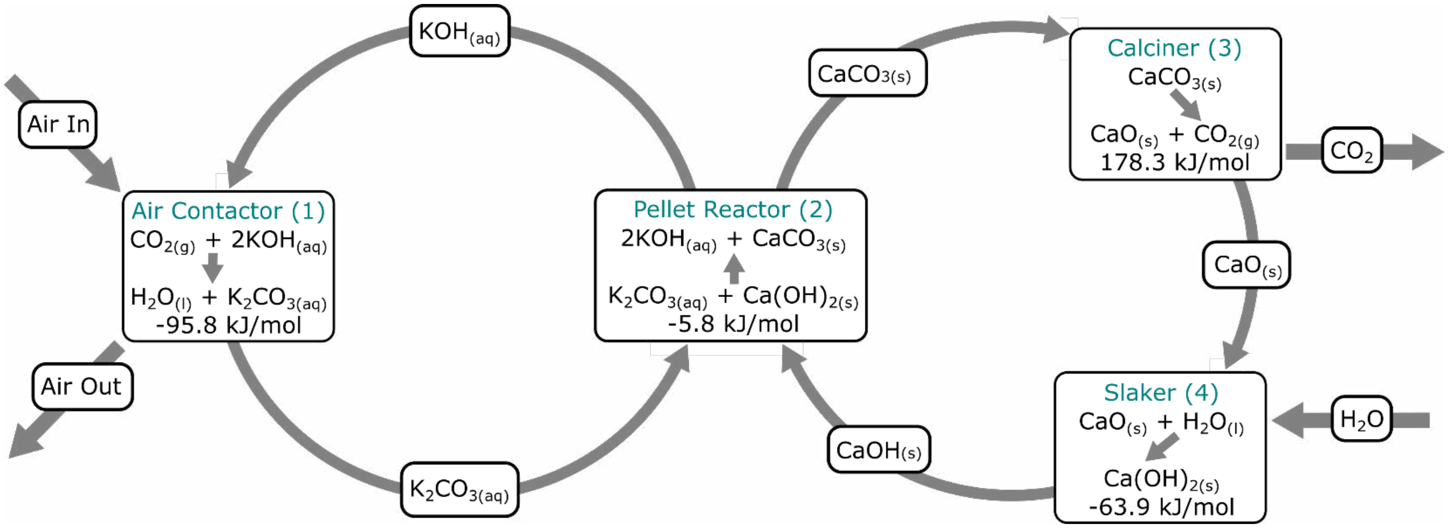


Figure 2: Chemistry of the DAC process.

Carbon Engineering has a DAC research pilot facility in Squamish (British Colombia, Canada), which has been used to support the testing in this project (Figure 3).

Figure 3: Pilot plant in Squamish, British Columbia.

The project team formulated a heat and mass balance for an industrial-scale plant scrubbing CO_2 directly from ambient air. Carbon Engineering's process scales-up to plant sizes capable of capturing 1,000,000 tonnes/year (t/yr) of CO_2, which are the most cost-effective due to economies of scale. Carbon Engineering's efforts were focused on taking results from the research pilot in Squamish, British Columbia, and utilizing them to design a first-of-a-kind plant that is expected to capture on order of 1,000,000 t/yr. The key items in the heat and mass balance are:

- All the power required by the equipment in the DAC plant is provided by a turbine.
- Steam to drive this turbine is partially generated by the hot flue gasses and CaO pellets leaving the calciner, and partially from the combustion of natural gas.
- All the CO_2 produced by the combustion of natural gas is also captured and delivered as product CO_2.
- Only fugitive emissions of CO_2 are lost to the atmosphere.
- The amount of CO_2 delivered is 50% larger than the CO_2 that was captured from the air, with the extra from the combustion of natural gas.
- The water that enters the system and is used to wash the pellets and fines is balanced by the amount of water that the absorber evaporates into the atmosphere.

The scope of work for the TEA included a design and cost estimate of a modified Carbon Engineering DAC plant used as a polishing unit on a modern commercial supercritical pulverized coal power plant that already removed 90% of the CO_2 produced using a conventional liquid amine-based CCS system.

The TEA indicates that using DAC technology to remove an additional 1 Mt/yr CO_2 (~9% of total CO_2 emitted) from the point source stack gases of a conventional coal-fired power plant equipped with a CO_2 removal (CDR) system increases the total cost of electricity (COE) by 16%.

TABLE 1: PROCESS PARAMETERS

Capture Solution	Units	Value
Nominal Concentrations – $K^+/OH^-/CO_3^{2-}$	mol/L	2.0/1.0/0.5
CO_2 Capture		
Delivered Feedstock (Upstream Air) (CO_2)	ppm	400
Downstream Air (CO_2)	ppm	~100
Air Contactor Mass Transfer Rate	mm/sec	1.0-1.3
Pressure Drop	Pa	~130
Air Velocity	m/s	1.4-1.7
CO_2 Release		
Pressure	bar	1
Temperature (Calcination)	°C	~900

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

CO_2 Laden Air (feed) Assumptions – Unless noted, gas pressure, temperature, and composition of feed (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	32–68	0.04	Variable	78.09	20.95	0.93	trace	trace

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Strong aqueous hydroxide solution reacts with large volumes of atmospheric CO_2 across an extremely large, dispersed air contactor. The reaction forms K_2CO_3 in an aqueous, liquid solution that can easily be transported from the contactor to a central processing location. In addition, strong hydroxide solutions have fast reaction kinetics with CO_2, are robust against fouling, and have negligible volatility, meaning there is little risk when using it with atmospheric air.

Gas Pretreatment Requirements – No treatment of atmospheric air required.

Solvent Makeup Requirements – $CaCO_3$ (seed material) and small quantities of KOH makeup.

Waste Streams Generated – Minimal quantities of lime mud ($CaCO_3$) as fines and inerts.

Proposed Module Design – The DAC plant draws air through an air contactor, where it contacts a strong aqueous KOH solution. The CO_2 in the air reacts with the KOH to form a solution of K_2CO_3 and water, absorbing about three-quarters of the available CO_2.

The carbonate solution is transferred to a pellet reactor, where it contacts $Ca(OH)_2$, also known as hydrated lime, and precipitates $CaCO_3$ pellets through a process known as causticization.

The pellets are fed into a circulating fluidized bed and treated at ~900°C through a process known as calcination. The heat releases the CO_2 as a pure, gaseous stream, leaving CaO as byproduct. Heat for the calciner is provided by combusting natural gas with oxygen (known as "oxy-firing"), so that the combustion exhaust is pure CO_2 and water vapor, which can be combined with the CO_2 stream leaving the calciner. The resultant CaO from the calciner is fed into the slaker, where it combines with water to regenerate hydrated lime, which is then fed into the pellet reactor for reuse.

technology advantages

- Negative emission technology.
- Technology can manage CO_2 emissions from any dilute source.
- Highly scalable technology.

R&D challenges

- Compared to standard CCS, there is a higher thermodynamic barrier for dilute-source capture.
- Compared to standard CCS, a larger air volume must be processed for dilute-source capture.
- Controlling/minimizing aerosol emissions is a challenge.

status

Carbon Engineering has concluded TEA activities by working closely with BBA (Engineering company), and an external consultant (Keith Patch). The project has concluded.

available reports/technical papers/presentations

McCahill, J., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," Final Briefing, Pittsburgh, PA, September 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=16805&filename=FE0026861_Final%20Briefing_09-27-19.pdf*.

Souza, R., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13378&filename=R-Souza-CarbonEng-Dilute-Source-CO2-Capture.pdf*.

Ritchie, J., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," Project Continuation Application Review Meeting Presentation, September 2017.

Kahn, D., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/D-Kahn-Carbon-Engrg-Dilute-Source-Carbon-Capture.pdf*.

Ritchie, J., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," Project Kick-Off Meeting Presentation, March 2017.

Low-Viscosity, Water-Lean CO_2-Binding Organic Liquids (CO_2BOL) with Polarity-Swing Assisted Regeneration (PSAR)

primary project goals

This project is an extension to the Pacific Northwest National Laboratory's (PNNL) initial Discovery of Carbon Capture Substances and Systems (DOCCSS) project, which is aimed at advancing the promising Carbon Dioxide-Binding Organic Liquid (CO_2BOL) single-component derivative N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA) to assess this solvent's viability towards meeting the U.S. Department of Energy's (DOE) cost and performance targets for carbon capture. This DOCCSS extension will allow programmatic involvement by industrial participants to evaluate the CO_2BOL derivative on a bench-scale platform and to aid in the development of a novel system. The final process design, along with the solvent, will include integrated (simultaneous absorption and regeneration) testing at the bench-scale on synthetic flue gas at an industrial participant facility. The participants will also lead key techno-economic analyses (TEAs), targeted testing, and broader industry outreach to assure subsequent transfer of the technology to industry.

technical goals

- Test the DOCCSS CO_2BOL solvent EEMPA using an integrated (simultaneous absorption and regeneration) carbon capture system at bench-scale on synthetic flue gas at an industrial participant facility.
- Perform independent solvent durability testing.
- Provide inputs of viability of laboratory-scale testing to acquire adequate data for a quantitative TEA to assess full-scale performance and project process costs at or below DOE's cost and performance targets.
- Provide guidance on scale-up routes; help engage with other industrial entities that represent key scale-up pathways.

technical content

PNNL is performing this project to test their most advanced single-component water-lean CO_2BOL solvent, EEMPA. This solvent was developed through discrete placement and orientation of hydrogen bonds at the molecular level. The control over hydrogen bond orientation and strength resulted in the development of a derivative that is greater than 90% lower in viscosity than the reference compound. The low regeneration temperature of EEMPA provides a solvent system with potential for a minimal temperature swing between absorption and regeneration cycles. This project was designed to measure the critical data needed to project performance of EEMPA for post-combustion carbon dioxide (CO_2) capture, ultimately enabling slip stream testing and subsequent industry adoption. Key

technology maturity:
Bench-Scale, Simulated Flue Gas

project focus:
CO_2-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-70924

predecessor project:
FE0007466

NETL project manager:
Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:
David Heldebrant
Pacific Northwest National Laboratory
david.heldebrant@pnnl.gov

partners:
Carbon Capture Simulation for Industry Impact

start date:
07.01.2017

percent complete:
60%

efforts include comprehensive data collection and process modeling, as well as engagement with collaborators from Carbon Capture Simulation for Industry Impact ($CCSI^2$) and industry to determine viability of EEMPA for slip stream testing and subsequent industry handoff.

The project team performed chemical durability measurements with individual components, CO_2, water (H_2O), oxygen (O_2), sulfur dioxide (SO_2), and nitric oxide (NO). These tests showed that EEMPA is stable under thermal, oxidative, and hydrolysis test conditions. In the presence of sulfur oxides (SO_X) and nitrogen oxides (NO_X), EEMPA forms heat-stable salts similar to other amine-based solvents.

Forty hours of continuous operation on PNNL's laboratory continuous flow system (LCFS) test loop at greater than 90% CO_2 capture was completed with a simulated flue gas and EEMPA in a configuration without Polarity-Swing Assisted Regeneration (PSAR). The LCFS test system was configured with an absorber column loaded with Pro-Pak packing, a high surface area laboratory random packing. A compact absorber section was used (7.62 cm x 50.8 cm). A forced circulation reboiler was used for the stripper.

Before the flue gas enters a CO_2 capture unit, it is typically passed through a pre-scrubber and/or direction contact cooler to reduce SO_2 and NO_X levels and reduce temperature. In the current CO_2BOL-based capture unit, the flue gas is chilled to about 16°C to reduce water content. It is assumed that a pre-scrubber will also be used to reduce SO_2 and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively. For the LCFS flue gas simulant, NO_X was delivered in form of NO. In some preliminary work (routine testing), a simpler simulant without the O_2/SO_2/NO components was also used. In all tests, the simulated flue gas was humidified to a 16°C dew point. The target simulated flue gas compositions are summarized in Table 1.

TABLE 1: TARGET SIMULATED FLUE GAS COMPOSITION

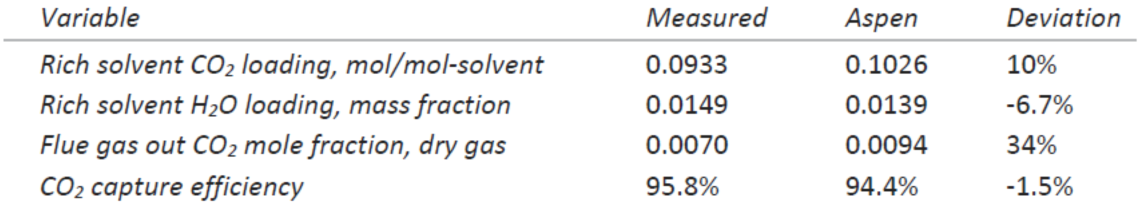
composition	component	Baseline (NETL B11A)	Routine testing	LCFS 40 hr
Mole fraction	N_2	0.8016	0.8493	0.8164
(dry gas basis)	CO_2	0.1506	0.1507	0.1440
	O_2	0.0380	-	0.0370
	Ar[3]	0.00959	-	0.0026
	SO_2	43.1 ppm	-	4.50
	NO_x	60.1 ppm	-	51.9
Dew point		56°C	15.6°C	15.6°C

For the 40-hour duration testing, the dry flue gas rate was chosen as 12.5 standard liters per minute (slm) to target a greater than 90% capture efficiency. The remaining test conditions chosen were 0.24 liters per minute (L/min) for solvent circulation, 40°C absorber column temperature, and 115°C reboiler temperature.

An Aspen simulation of the LCFS test loop was performed at the measured absorber and stream conditions. The Pro-Pak absorber section was specified according to manufacturer-provided data, such as specific area, void fraction, and Stichlmair correlation parameters for pressure drop. The packing-specific area was scaled from manufacturer data based on the actual packed mass to account for the wall effects of the relatively small diameter of the LCFS absorber column. The EEMPA solvent properties were calculated using the same thermodynamic package developed from vapor liquid equilibrium (VLE) and wetted-wall column (WWC) data for the process flowsheet and TEA.

The Aspen simulation was compared with the measured outlet stream properties and the capture efficiency in Table 2. The data are close to the Aspen prediction. The largest relative error is seen on the flue gas outlet CO_2 mole fraction, which is expected because this quantity is very small in absolute value. The deviation in capture efficiency, 1.5%, is small. Considering the uncertainties in the Aspen thermodynamic package, as well as in the effective area of the packing section, there is good agreement between the Aspen simulation and experimental data.

TABLE 2: COMPARISON OF LCFS 40-HOUR TEST AND ASPEN SIMULATION RESULTS



Variable	*Measured*	*Aspen*	*Deviation*
Rich solvent CO_2 loading, mol/mol-solvent	0.0933	0.1026	10%
Rich solvent H_2O loading, mass fraction	0.0149	0.0139	-6.7%
Flue gas out CO_2 mole fraction, dry gas	0.0070	0.0094	34%
CO_2 capture efficiency	95.8%	94.4%	-1.5%

EEMPA showed no visible evidence of degradation, foaming, or solid precipitation during the LCFS testing for the 40 hours on stream. The solvent maintained its ability to capture CO_2 and be regenerated thermally as expected, indicating EEMPA can proceed to larger-scale testing.

The project team has been revising the TEA. The best system configuration as modeled is a combination of an inter-heated column (IHC), advanced heat integration (AHI), and lean-vapor compression (LVC) together, giving a heat rate of 2.0 gigajoules (GJ)/tonne CO_2, and a CO_2 capture cost of $50.6/tonne CO_2. These results are still preliminary based on the thermodynamic package developed on previously collected VLE. Additional data from PTxy and reboiler heat duty will further refine the energetics of EEMPA, while formal costing from Fluor will provide a more rigorous costing analysis for the final process configuration.

The project team has started a preliminary assessment on how the units of operation for EEMPA with and without a PSAR would be incorporated into RTI International's slip stream test system. Engineers are assessing whether, how, and where units such as a two-stage flash stripper, intercooling, and PSAR infrastructure would be incorporated. Preliminary discussions have started on sizing and configurations for each unit.

TABLE 3: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	-
Normal Boiling Point	°C	181.0	-
Normal Freezing Point	°C	<0	-
Vapor Pressure @ 15°C	bar	5E-5	-
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	-
Specific Gravity (15°C/15°C)	-	0.94	-
Specific Heat Capacity @ STP	kJ/kg-K	1.95	-
Viscosity @ 15°C	cP	11.3	-
Absorption			
Pressure	bar	1	-
Temperature	°C	40	-
Equilibrium CO_2 Loading	mol/mol	0.29	-
Heat of Absorption	kJ/mol CO_2	75	-
Solution Viscosity	cP	25	-
Desorption			
Pressure	bar	1.8	-
Temperature	°C	117	-
Equilibrium CO_2 Loading	mol/mol	0.05	-
Heat of Desorption	kJ/mol CO_2	75	-

Proposed Module Design			(for equipment developers)	
Flue Gas Flowrate	kg/hr		2.6E6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	150
Absorber Pressure Drop	bar		<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		pending	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – EEMPA appears to be relatively stable towards oxidative and thermal degradation and hydrolysis in the absence of steel, while SO_X and NO_X form heat-stable salts.

Solvent Foaming Tendency – EEMPA showed no evidence of foaming during 40 continuous hours of testing with simulated flue gas.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce SO_2 and NO_X to about 5 ppm and 50 ppm, respectively.

Solvent Makeup Requirements – Solvent makeup rates are expected to be at worst comparable to 5M MEA, though preliminary degradation studies indicate higher chemical durability of EEMPA under absorber and stripper conditions.

Waste Streams Generated – Sulfur oxides and NO_X form heat-stable salts, which will need treatment to recover EEMPA in a working process. Preliminary results indicate the addition of PSAR can facilitate regeneration of heat-stable salts, releasing NO_X and SO_X from EEMPA at 60°C and 130°C, respectively.

Process Design Concept –

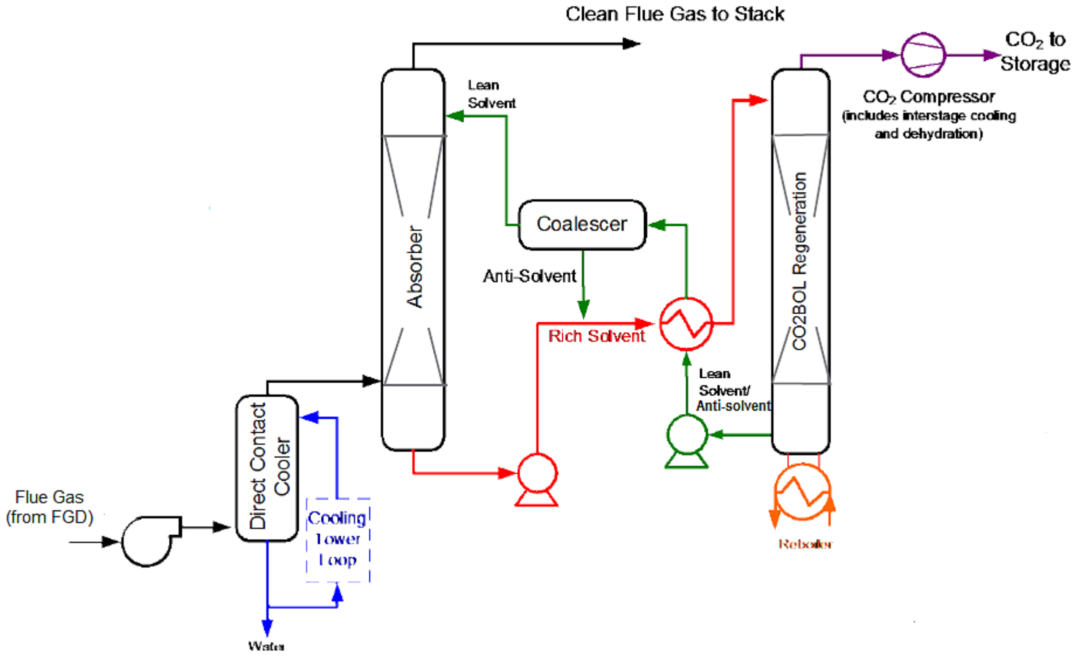


Figure 1: CO_2BOL/PSAR conceptual configuration.

technology advantages

- No diluent: 100% active solvent.
- Low solvent volatility.
- Lower CO_2-rich viscosity than early versions of CO_2BOL solvents.
- PSAR decreases the regeneration temperature by destabilizing the acid gas carrier.
- Significantly lower regeneration energy compared to aqueous amines.

R&D challenges

- PSAR regeneration of heat-stable salts as part of solvent reclamation process.
- Reducing the cost of solvent.

status

The project team has continued its efforts in testing EEMPA for CO_2 capture from simulated flue gas. The primary focus of FY19 Q4 was continuous flow testing of EEMPA. Other efforts included revising the TEA with industrial partners and $CCSI^2$ collaborators. The project team successfully completed 40 hours steady-state performance of CO_2 capture on simulated flue gas. The project team has also identified the chemical tolerance of EEMPA towards heat-stable salt formation, oxidative degradation, thermal degradation, and hydrolysis.

The project team upgraded and retrofitted the PVT cell to enable PTxy capability. The project team installed a chilled mirror and CO_2 sensor within the cell to enable gas-phase analysis during isotherm measurements. These upgrades will enable CO_2 and water partial pressures to be measured, enabling more accurate and robust thermodynamic models that will provide higher-fidelity modeling results of solvent performance. The cell will be used to analyze EEMPA at varied loadings of water.

available reports/technical papers/presentations

Heldebrant, D. "Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.

Heldebrant, D. "Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," project kickoff meeting, Pittsburgh, PA, September 2017. *https://www.netl.doe.gov/sites/default/files/netl-file/FWP-70924-PNNL-DOCCSS-kickoff.pdf*.

D. Malhotra, D. C. Cantu, P. K. Koech, D. J. Heldebrant, A. Karkamkar, F. Zheng, M. D. Bearden, R. Rousseau, and V. A. Glezakou, "Directed Hydrogen Bond Placement: Low Viscosity Amine Solvents for CO_2 Capture." ACS Sustainable Chem. Eng., (2019), 7 (8), pp 7535–7542.

D. Malhotra, J. P. Page, M. E. Bowden, A. Karkamkar, D. J. Heldebrant, V. A. Glezakou, R. Rousseau, P. K. Koech. "Phase change aminopyridines as carbon dioxide capture solvents." Ind. Eng. Chem. Res., (2017), 56, (26), 7534-7540.

D. Malhotra, P. K. Koech, D. J. Heldebrant, D. C. Cantu, F. Zheng, V. A. Glezakou, R. Rousseau, "Reinventing design principles for developing low-viscosity carbon dioxide binding organic liquids (CO_2BOLs) for flue gas clean up." ChemSusChem. (2017), 10, 636 –642.

Electrochemically Mediated Amine Regeneration in CO_2 Scrubbing Processes

primary project goals

The Massachusetts Institute of Technology (MIT) is advancing a novel carbon dioxide (CO_2) capture technology using traditional amine-based solvents, but with the key innovation of using electrochemical regeneration of the solvent instead of conventional thermal regeneration. By utilizing cost-effective reduction/oxidation of metal ions to electrochemically enable the capture and release of CO_2 by traditional amine sorbents and thereby eliminating the demand for steam characteristic of conventional amine regeneration technology, the parasitic power requirement for operating the process is expected to be markedly less than that of conventional methods. This should enable substantial savings in the cost of electricity (COE) for carbon capture process scenarios, with promise to meet programmatic U.S. Department of Energy (DOE) carbon capture goals.

technical goals

- Develop an optimized electrochemical cell configuration/design and size, allowing best efficiency and cost performance for scalable carbon capture processes for commercial-scale coal-fired plants.
- Validate system using electrochemically mediated amine regeneration in a CO_2 scrubbing cycle for capture of at least 90% of CO_2 from coal-derived flue gas while demonstrating significant progress toward achievement of the DOE target of less than 35% increase in levelized cost of electricity (less than \$40/tonne CO_2).
- Reduce energy requirements 20 to 40% relative to that of baseline monoethanolamine (MEA) capture. Achieve specific regeneration energy of 0.91 gigajoules (GJ)/tonne CO_2.
- Demonstrate electrochemical cell stability over 15 days continuous operation, at simulated flue gas flow rate enabling capture of 0.01 kg CO_2 per day.

technical content

MIT terms their technology as Electrochemically Mediated Amine Regeneration (EMAR). In conventional amine regeneration-based capture processes, a standard amine solvent such as MEA is contacted in countercurrent flow with CO_2-containing flue gas in an absorption column at relatively low temperature (less than 60°C). At lower temperatures, CO_2 readily reacts with the amine forming an amine-CO_2 complex, and given suitable contact time and solvent flow in the absorption column, high levels of CO_2 removal (greater than 90%) can be attained. The rich amine solvent (containing elevated levels of absorbed CO_2) exiting the absorber column is preheated in a countercurrent heat exchanger and introduced into the desorber column, where it is further heated with low-pressure steam

technology maturity:

Laboratory-Scale, Simulated Flue Gas (0.01 kg/day CO_2 captured)

project focus:

Electrochemical Regeneration of Amine Solvents

participant:

Massachusetts Institute of Technology

project number:

FE0026489

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Trevor A. Hatton
Massachusetts Institute of Technology
tahatton@mit.edu

partners:

N/A

start date:

08.01.2017

percent complete:

70%

withdrawn from the power plant's steam cycle, to reach temperatures greater than 110°C. At elevated temperatures, the CO_2 is released from the solvent as a relatively pure stream of CO_2 that can be recovered. Hot lean solvent is cooled and returned to the absorption column. This conventional thermal regeneration-based process is depicted in the top half of Figure 1.

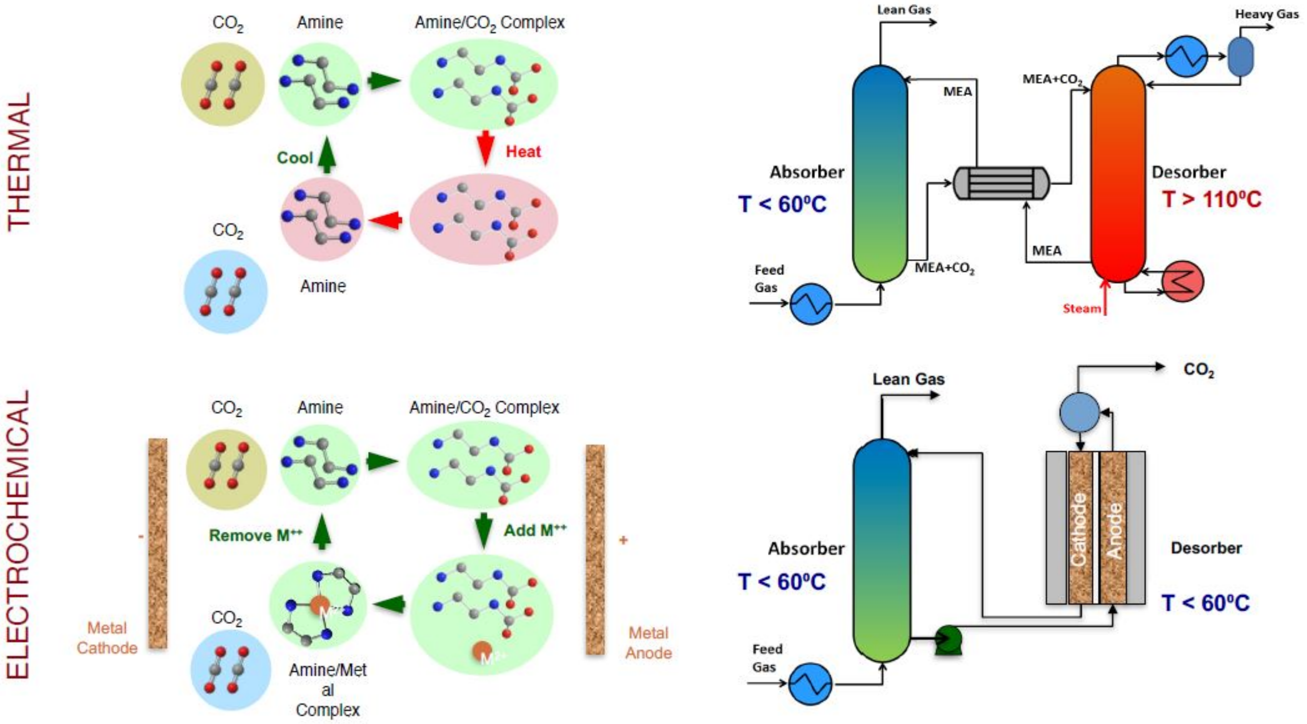


Figure 1: Electrochemically mediated versus thermal amine regeneration.

In EMAR (depicted in the bottom half of Figure 1), the process uses the same type of absorption column and operating conditions therein. However, the rest of the process is significantly different. Instead of regenerating the rich solvent by increasing its temperature, the solvent passes sequentially through the anodic and cathodic sides of an electrochemical cell. On the anodic side, certain metal ions enter solution and react with the amine/CO_2 complexes in the rich solvent. If the metal ions have sufficiently strong binding with the amines, they displace the CO_2 and cause it to be liberated in pure gaseous form, enabling its separation. On the cathodic side, the amine metal compound remaining behind is stripped of the metal ions, resulting in lean amine solvent ready to return to the absorber. Temperature remains essentially constant throughout the process, eliminating heat exchange operations and their associated energy losses and capital costs.

Because the EMAR process requires only a limited amount of electrical power to operate the electrochemical processes in the cells, it avoids the need to use steam withdrawn from the power plant's steam cycle, minimizing parasitic energy consumption. This is depicted in Figure 2, which compares the amounts of CO_2 capture work (units of kilojoule [kJ_e]/mol CO_2 captured) associated with the EMAR system, and those of comparative thermal amine systems. Note the EMAR system advantage in respect of steam withdrawals.

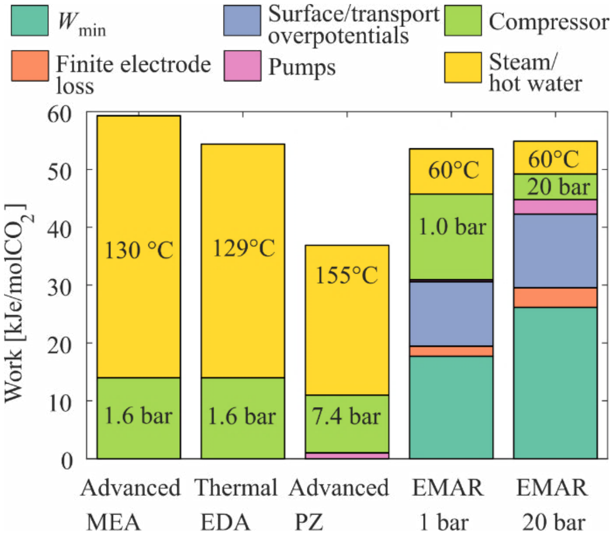


Figure 2: Comparison of capture work of thermal amine systems and EMAR systems.

This process concept has been proven at lab-scale, and ongoing work has been refining/optimizing the technology in terms of optimal selection of amine and metal ions, improving electrochemical kinetics, and optimizing cell design as discussed below.

Amine Selection—Binding energies of metal ions with amines are specific to the amine. The binding energies must be strong enough to overcome the amine/CO_2 complexation, but higher binding energies demand high power consumption in the electrochemical cell to remove metal ions from the amine/metal complexes. Therefore, amine selection is important in optimizing the process. Adequate amine stability in the process is required. Candidate amines evaluated have included the following:

- MEA
- Diethanolamine (DEA)
- Diethylenetriamine (DETA)
- 2-Amino-2-methyl-1-propanol (AMP)
- Ethylenediamine (EDA)
- Pentamethyldiethylenetriamine (PMDTA)
- Aminoethylethanolamine (AEEA)
- Triethylenetetramine (TETA)
- Piperazine (PZ)

Metal Ions—Ion species, including Co^{2+}, Fe^{3+}, Fe^{2+}, Cr^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+}, have been evaluated as possibilities for the optimal choice for metal/amine complex according to the following essential criteria:

- No precipitation in alkaline solvent.
- Redox active on metal electrode.
- Stability.

Screening of amine/metal complexes considering the candidates above has been performed. The screening methodology considered metal/amine stability in EMAR operating conditions, measurement of CO_2 capacity, testing of electrochemical reversibility, and validation of the CO_2 separation via electrolysis in batch reactors. Via the stability measurement, MIT concluded that only copper (Cu), zinc (Zn), and nickel (Ni) are plausible candidates to form metal-ligand complexes using off-the-shelf aqueous amine solvents. Nevertheless, only Cu-EDA can be modulated with electrochemical methods without incurring hydrogen evolution (i.e., water splitting). Therefore, MIT concluded that Cu-EDA is the most suitable candidate to be integrated into the envisioned EMAR process.

Electrochemical Kinetics—Rapid reaction rates of the complexes in the electrochemical cells are needed to accommodate the high solvent throughputs typical of large-scale post-combustion capture process scenarios. The EMAR cathode ideally operates in the absence of CO_2, but in practice CO_2 is present and tends to hinder the kinetics. Chlorides in solution have been found to improve performance significantly.

MIT investigated the thermodynamic potential of Cu-EDA and provided detailed speciation modeling of the Cu-EDA-water (H_2O) electrolyte. Results are informing modeling of the EMAR process, which will enable estimates of the energy consumption of an EMAR process in context of a post-combustion carbon capture cycle. The kinetics of the electrochemical reactions have been examined via deposition and dissolution experiments performed with rotating disk electrodes. The cathodic deposition of Cu is the slower process of the two Faradaic reactions and would require higher overpotential to drive out the desired reaction rate (i.e., current density). Suitable electrolyte combinations (with supporting salt) to decrease ohmic resistances and to minimize unwanted reactions have been identified. Both the Cu-EDA-H_2O-sodium (Na)-sulfate (SO_4) and Cu-EDA-H_2O-Na-chloride (Cl) systems were identified as stable electrolyte formulations. These electrolyte combinations have been further implemented in a bulk electrolysis setup that validates the electrochemical-thermal separation of CO_2. Results from systematic study and experimental validation of the CO_2 solubility constants have aided ongoing revision/improvement of the proposed thermodynamic cycle.

Cell Design—Ongoing work is optimizing cell architectures for fluid flow configuration and operational efficiency. Because CO_2 bubbles are formed in the cells, the design needs to efficiently accommodate removal of the gas. Prototype architectures are being developed for continuous CO_2 gas removal by utilizing gas/liquid separation membranes. In addition, cell stacking strategies to optimize volumetric efficiency and fluid flow will be investigated. Figure 3 gives an idea of the present configuration of cell engineering, showing metallic electrodes, channels, seals, etc. Figure 4 depicts a cell stacking concept.

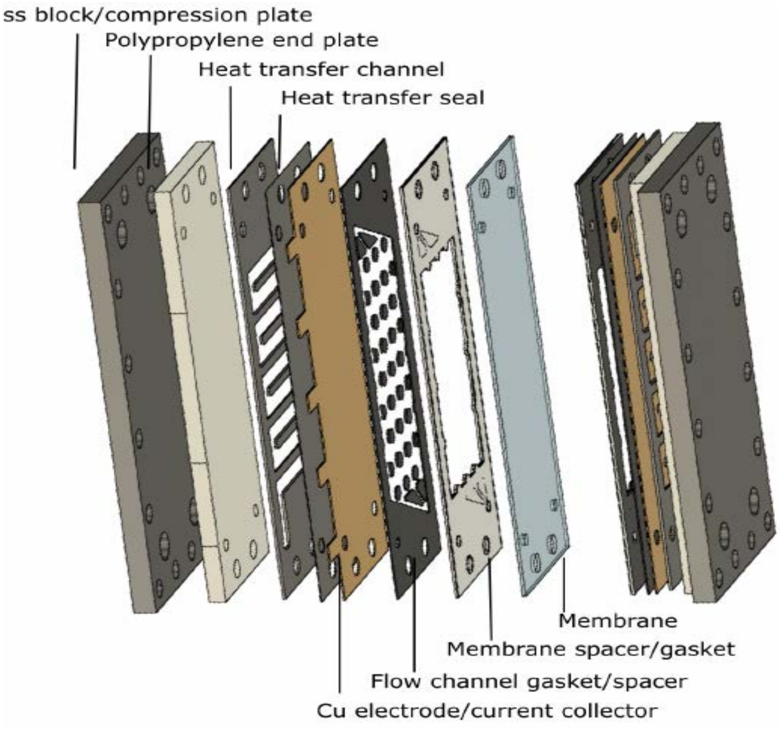


Figure 3: Electrochemical single-cell engineering.

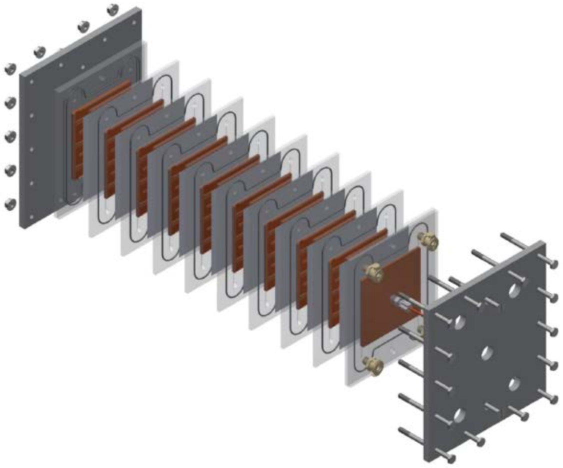


Figure 4: Cell stacking.

Process and Costs—MIT has created a process model accounting for all process unit operations (e.g., absorbers, heat exchangers, compressors), as well as additional energy efficiency losses (e.g., kinetic overpotentials) associated with an EMAR system in a full-scale power plant context. Figure 5 depicts the flowsheet for this model.

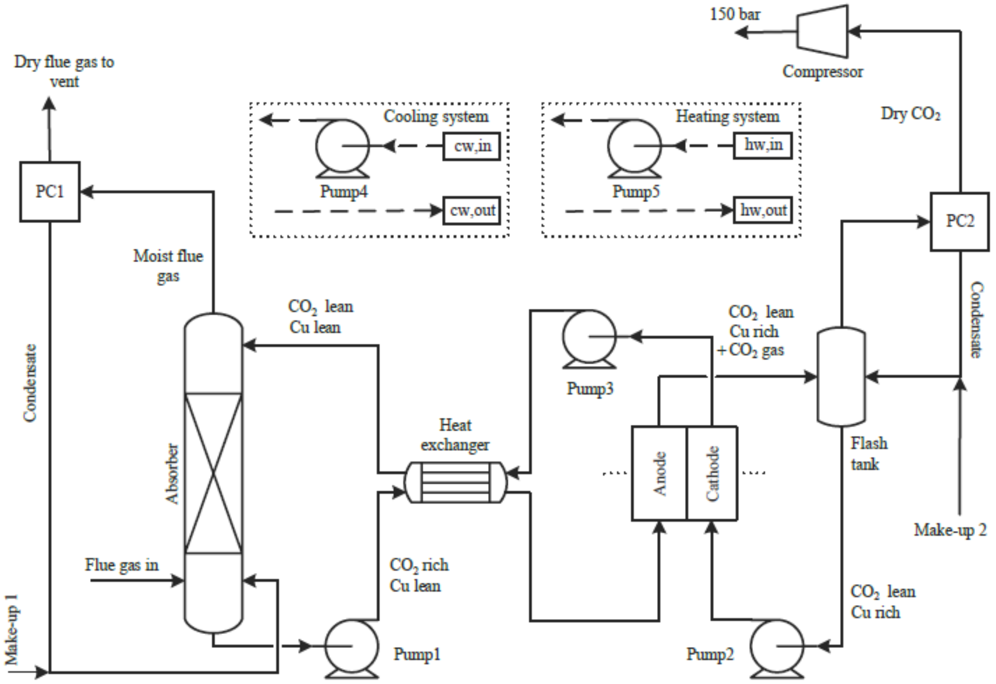


Figure 5: Detailed flowsheet simulated for EMAR process for carbon capture.

A range of operating conditions and operation schemes were varied parametrically to identify reasonable overall energetics in the EMAR system process. Interesting findings of the process simulations include the realization that net energy demands can be significantly reduced if waste heat is available at temperatures below 90°C, and that the EMAR process is able to desorb CO$_2$ at pressures up to 20 bar with negligible additional energy penalty. Preliminary cost analysis of a full-scale EMAR process indicates a cost of around $60 per ton of CO$_2$ avoided ($40 per ton of CO$_2$ captured) in capture from post-combustion flue gas from a 550-megawatt (MW) coal-fired power plant. It is postulated that further reduction in cost should emerge from advanced process design, process optimization, and improved solvent formulation.

MIT has preliminary estimates of capital and operating costs of an EMAR system, as well as comparisons to baselines. Figure 6 shows the expected breakdown of equipment costs and offers COE comparisons to a no-capture case and conventional amine-based capture cases.

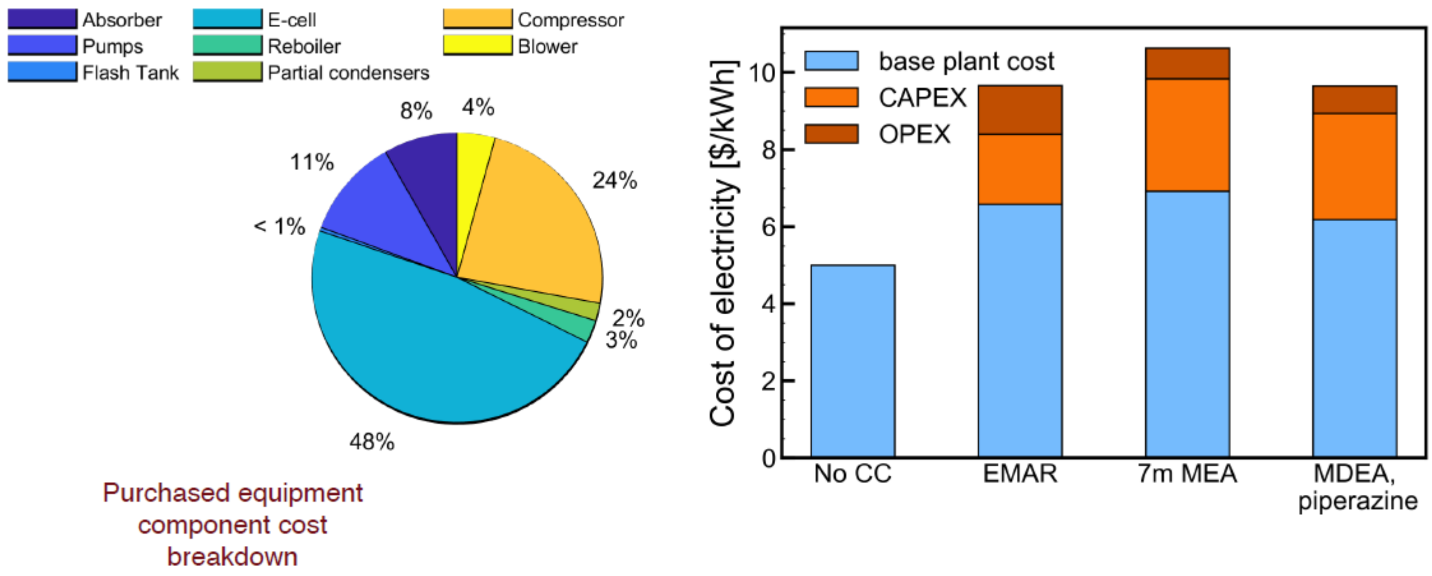


Figure 6: Capital cost breakdown and COE estimates/comparisons.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g mol^{-1}	60.2172	60.2172
Normal Boiling Point	°C	116	116
Normal Freezing Point	°C	11	11
Vapor Pressure @ 15°C	bar	0.037	0.037
Manufacturing Cost for Solvent	$/kg	<50	<50
Working Solution			
Concentration	kg/kg water	0.06	0.24
Specific Gravity (15°C/15°C)	-	1	<1
Specific Heat Capacity @ STP	kJ/kg-K	4	4
Viscosity @ STP	cP	1.3	
Absorption			
Pressure	bar	1	1
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	1	1
Heat of Absorption	kJ/mol CO_2	85	85
Solution Viscosity	cP	1.3	
Desorption			
Pressure	bar	1	1-10
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	<0.2	<0.2
Heat of Desorption	kJ/mol CO_2		89

Proposed Module Design		*(for equipment developers)*
Flue Gas Flowrate	kg/hr	466
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%/99%/1–10bar
Absorber Pressure Drop	bar	<0.1
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column (or in the case of EMAR, at the exit of the electrochemical cell). Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted otherwise, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					Ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – EDA readily forms carbamate upon contact with CO_2 in water. The solvent exhibits a strong affinity to CO_2 in the absence of chelating metal ions, and no affinity for CO_2 in the presence of these metal ions.

Flue Gas Pretreatment Requirements – Sulfur removal.

Process Design Concept – See Figures 1 and 5 above.

technology advantages

- Amine scrubbing with electrochemically mediated amine regeneration offers a combination of fast kinetics, low parasitic energy requirements, and process flexibility.
- CO_2 gas recovered from the regenerator is at elevated pressure (up to 20 bar), lessening downstream compression requirements and saving energy.
- An initial techno-economic analysis (TEA) indicates that the electrochemically mediated capture technology could have a significant economic advantage over state-of-the-art thermal amine processes, cutting capture costs by 30 to 60%.

R&D challenges

- Possible sensitivity of the process to disturbances and long-term operation viability. Since the system needs to switch the polarity of the electrodes and the corresponding process stream, this requires implementation of an automation system that can accomplish both tasks for long-term operation stability.
- Validation of the basis for scale-up of the process to commercial-scale capability.
- Cell fluid flow channeling. Gas trapping in the fluid channel will reduce effective ionic conductivity, leading to reduced CO_2 separation. High velocities of liquid on the surface of the electrode will need to be ensured to minimize boundary layer thickness.

status

MIT's electrochemically mediated amine regeneration technology has been previously developed from concept to a proof-of-concept lab-scale device, validating the feasibility and potential of the approach. Additional lab-scale work has been underway to further optimize the performance of the technology, with a Cu-EDA amine/metal complex identified as preferred. Cell architecture, cell operation and kinetics, and process optimization are being worked on currently.

available reports/technical papers/presentations

"*Electrochemically Mediated Amine Regeneration in CO_2 Scrubbing Processes*," Budget Period 2 project review presentation by T. Alan Hatton of MIT, at NETL Pittsburgh on November 14, 2019.

"*Electrochemically Mediated Amine Regeneration in CO_2 Scrubbing Processes*," presented by T. Alan Hatton, 2019 NETL CCUS Integrated Project Review Meeting, August 2019.

"*Electrochemically-Mediated Sorbent Regeneration in CO_2 Scrubbing Processes*," presented by T. Alan Hatton, Kickoff meeting presentation, December 2017.

"*Electrochemically-Mediated Sorbent Regeneration in CO_2 Scrubbing Processes*," presented by T. Alan Hatton, Massachusetts Institute of Technology, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

Wang, M.; Rahimi, M.; Kumar, A.; Hariharan, S.; Choi, W.; Hatton, T. A. Flue Gas CO_2 Capture via Electrochemically Mediated Amine Regeneration: System Design and Performance. *Applied Energy* **2019**, 255, 113879.

Wang, M.; Hariharan, S.; Shaw, R. A.; Hatton, T. A. Energetics of Electrochemically Mediated Amine Regeneration Process for Flue Gas CO_2 Capture. *International Journal of Greenhouse Gas Control* **2019**, 82, 48–58.

Large Pilot Testing of Linde-BASF Advanced Post-Combustion Carbon Dioxide Capture Technology at a Coal-Fired Power Plant

primary project goals

The University of Illinois is evaluating the design, construction, and operation of a 10 megawatt-electric (MWe) capture system based on the Linde-BASF advanced amine-based post-combustion capture technology at a coal-fired power plant. The project consists of three phases. Phase I has been completed and consisted of a feasibility study that (1) outlined preliminary engineering designs; (2) conducted preliminary analysis of National Environmental Policy Act (NEPA)-related issues; and (3) concluded selection of a host site for Phases II and III. Phase II efforts are underway, consisting of a detailed front-end engineering design (FEED) study, NEPA permitting and documentation, and cost-share commitments. If selected for Phase III, the project will support construction and operation of the large-scale pilot facility. The Fossil Fuel Large-Scale Pilots effort supports the design, construction, and operation of large test facilities for transformational carbon dioxide (CO_2) capture technologies aimed at enabling step-change improvements in coal-powered system performance, efficiency, and cost of electricity (COE).

technical goals

Phase I objectives were to:

- Establish the feasibility of installing a 10-MWe capture facility at one of three potential pilot host sites.
- Select a host site based on the feasibility studies.
- Complete an Environmental Information Volume for each potential host site.
- Obtain necessary commitments from the selected site.
- Update the preliminary cost and schedule estimates provided in this Phase I proposal.
- Secure cost-share commitments for Phase II (Design) and develop a plan for securing cost-share commitments for Phase III (Construction/Operation).

Phase II objectives are to:

- Complete a FEED study for the proposed large-scale pilot, including a detailed cost and schedule estimate for Phase III for the installation of the 10-MWe pilot plant at the host site, followed by commissioning, start-up, operations, testing, and data collection for performance validation.
- Complete NEPA process at the host site.

technology maturity:

Large Pilot-Scale (10 MWe), Actual Flue Gas Slipstream

project focus:

Linde-BASF CO_2 Capture Process

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031581

Predecessor projects:

FE0026588
FE0007453

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Kevin O'Brien
University of Illinois at Urbana-Champaign
kcobrien@illinois.edu

partners:

Linde, LLC, Affiliated Construction Services, Affiliated Engineers, Inc.

start date:

04.04.2018

percent complete:

55%

- Draft permitting documentation to be submitted to appropriate authorities to initiate the permitting process and develop a clear understanding of timelines that will support Phase III.
- Document secured cost share for Phase III.
- Secure commitments for all necessary Phase III team members, including an engineering, procurement, and construction (EPC) firm to complete construction.
- Update the techno-economic analysis (TEA) for the Linde-BASF technology integrated with a 550-MWe net supercritical pulverized coal power plant based on the most recent system design and cost information.

technical content

The Linde-BASF advanced CO_2 capture process incorporating BASF's novel amine-based solvent, OASE® blue, with Linde's process and engineering innovations allows for a significant increase in energy efficiency and reduced cost for CO_2 recovery from coal-based power plants. In addition to a reduction in regeneration energy and a lower solvent circulation rate enabled by the BASF solvent, Linde has achieved significant improvements in process design, as shown in Figure 1, featuring an advanced stripper inter-stage heater design to optimize heat recovery in the process. This results in lower capital and operating costs for the CO_2 capture system. The Linde-BASF technology addresses all the major challenges for solvent-based carbon capture, including: (1) high specific energy for regeneration, (2) lack of stability due to thermal and oxidative degradation, (3) increased corrosiveness with increased CO_2 loading, and (4) lack of tolerance to impurities from coal combustion products.

Previous testing of a 0.45-MWe pilot plant incorporating the Linde-BASF technology and utilizing lignite-fired power plant flue gas has shown that the OASE® blue solvent is stable, with little degradation observed over 55,000 hours, whereas the reference monoethanolamine (MEA) solvent started to degrade appreciably under the same conditions after 2,000 hours. The Linde-BASF CO_2 capture process was also previously tested at 1.5-MWe-scale at the National Carbon Capture Center (NCCC) under project DE-FE0007453, supported by the U.S. Department of Energy (DOE). The study validated solvent stability and demonstrated a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact. This project leverages work done previously through a DOE Phase I grant (DE-FE0026588), in which a 15-MWe pilot plant of the Linde-BASF advanced CO_2 capture technology was designed to be integrated with the University of Illinois' Abbott Power Plant on the campus of the University of Illinois at Urbana-Champaign (UIUC), with the goal of capturing ~300 tonnes per day (tpd) of CO_2 at a 90% capture rate. The 15-MWe pilot project aimed to optimize the process at larger scale and gather performance data under realistic conditions to enable a robust commercial design. Phase I of the project resulted in the completion of a preliminary plant design with basic engineering and cost estimates; establishment of permitting needs; identification of approaches to address environmental, health, and safety concerns related to pilot plant installation and operation; and completion of a detailed TEA, demonstrating that the implementation of Phase II (Detailed Design, Construction, and Operation) of the project is feasible. The project also established strategies for workforce development for the operation and maintenance of carbon capture systems based on the Linde-BASF technology that are retrofitted to existing power plants.

The design and costing of the 10-MWe capture plant for installation at the selected host site – City, Water, Light, and Power (CWLP) coal-fired power plant in Springfield, Illinois – was based on the estimate for the 15-MWe pilot in the previous DOE-funded project and established industry-scaling factors. The capture system would be installed in the Dallman 4 unit, which is a nominal 200-MWe pulverized coal-fired unit that became operational in 2009. The unit employs a Foster Wheeler front and rear wall-fired pulverized coal boiler equipped with low-nitrogen oxide (NO_X) burners; a selective catalytic reduction (SCR) unit for NO_X removal; a hydrated lime injection (HLI) system for sulfur trioxide (SO_3) removal; a fabric baghouse to capture particles; a flue gas desulfurization (FGD) system to mitigate sulfur dioxide (SO_2) emissions; and a wet electrostatic precipitator (ESP) to remove liquid droplets, such as sulfuric acid mist. For the 10-MWe capture pilot, a slipstream flue gas from the Dallman 4 unit will be utilized as a feed gas for CO_2 capture.

Based on results from small pilot studies and the TEA, the technology will achieve high CO_2 capture (~90%) and generate high-purity (greater than 99.9%) captured CO_2 in a cost-effective manner. TEA results indicated that when the proposed advanced Linde-BASF technology is integrated with a 550-MWe net supercritical pulverized coal power plant there will be an increase in power plant efficiency of approximately 3% (relative), a nominal 11.4% reduction in COE, and an 18% reduction in capital costs compared to the latest DOE/National Energy Technology Laboratory (NETL) base case (Case B12B reference).

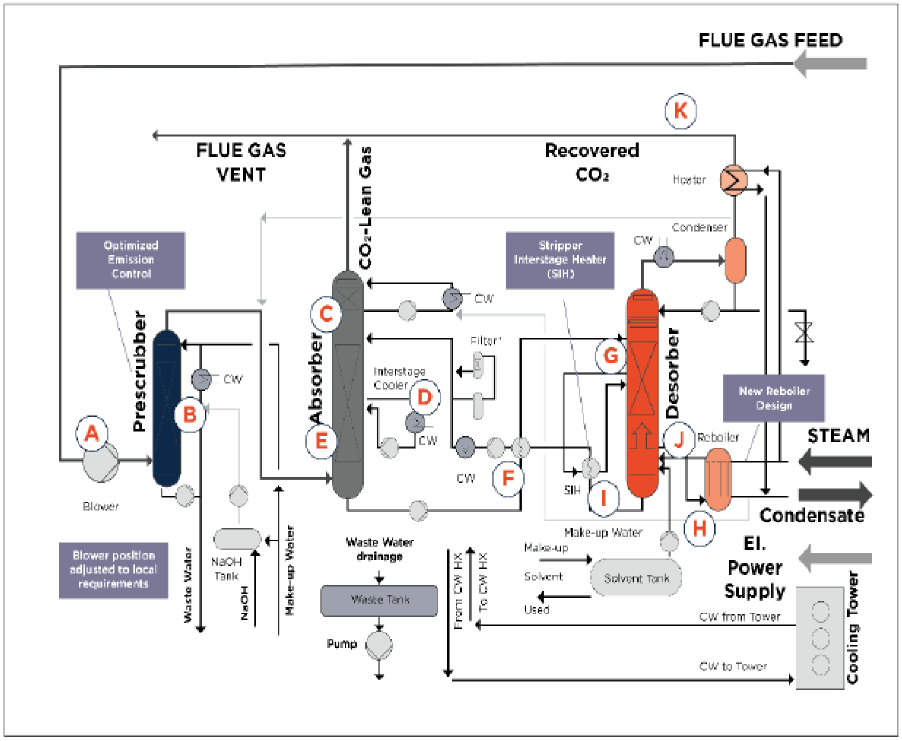


Figure 1: Large pilot process configuration for Linde-BASF technology with highlighted design improvements.

A. Flue gas blower provides enough pressure to overcome the pressure drop across the pre-scrubber and absorber. The blower location will be adjusted to host site-specific equipment in the most cost-effective manner.

B. Integrated pre-scrubber and direct contact cooler to reduce SO_X content below 5 ppm and simultaneously cool the flue gas stream to ~35 -40°C.

C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols.

D. A gravity-driven inter-stage cooler for the absorber that eliminates the pump and the controls.

E. High capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction.

F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.

G. Regenerator designed for operation at pressures up to 3.4 bar(a), significantly reducing CO_2 compression energy and eliminating the bulky first stage of the CO_2 compressor train, resulting in capital cost savings.

H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to power plant load changes.

I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.

J. Variations of the stripper-reboiler flashing configuration, which are being evaluated for an ultimate reduction of solvent regeneration energy.

K. Optional CO_2 recycle stream, provided to evaluate the effect of plant loading and variable CO_2 concentration in the flue gas on overall energy consumption, and to limit the effects of power plant loading

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	proprietary	proprietary
Vapor Pressure @ 15°C	bar(a)	proprietary	proprietary
Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15°C/15°C)	—	proprietary	proprietary
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	proprietary	proprietary

Absorption			
Pressure	bar(a)	1.0	0.9-1.1
Temperature	°C	30-70	30-60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	proprietary	proprietary
Desorption			
Pressure	bar(a)	1.6-3.4	1.6-3.4
Temperature	°C	124-140	124-140
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary	proprietary
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	% / % / bar(a)	90%, 99.98% (dry), 3.4 bar(a)	90%, 99.98% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary	

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero, i.e. not taking into account atmospheric pressure.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

		Composition						
		mol%					ppmv	
Pressure psig	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
0	135	9.8	17	67	5.3	0.80	34	30

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – CO_2 in the flue gas chemically binds to the OASE blue® aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE® blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operation, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 parts per million (ppm) in order to limit solvent degradation and is implemented in a direct contact cooler in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE blue® solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the direct contact cooler where SO_X and NO_X are removed; this stream is typically handled in the power plant waste water treatment facility. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – See Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

technology advantages

- Significant reduction in specific regeneration steam consumption (24 to 40% lower), electrical power (14 to 26% lower), and cooling water duty (32 to 43% lower) compared to a reference MEA plant.
- Increased higher heating value efficiency (HHV) for power production (up to ~31.7% efficiency) and lower thermal load compared to a reference MEA plant (28.4% efficiency) due to a combination of advanced solvent and process improvements, including integrated pre-scrubber and direct contact cooler, downstream gas blower, higher desorber pressure, and interstage gravity-flow cooler.
- The total plant costs are ~20% lower compared to a reference MEA plant, with significantly lower post-combustion capture plant capital costs.

- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is the producer of the OASE blue® solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue® solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.
- The Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant EPC, commercial deployment, and long-term, continuous operations.

R&D challenges

- Scale-up of absorber column at low cost, maintaining uniform vapor and liquid distribution.
- Optimizing operation of the stripper to reduce steam utilization and increase energy efficiency of the CO_2 capture process using advanced stripper configurations and stripper inter-stage heating.
- Managing flue gas impurities and aerosol formation to reduce amine losses.
- Testing of new process units for energy optimization.
- Integration with operations at the CWLP host site.

status

In Phase I, the CWLP coal-fired power plant in Springfield, Illinois, was selected as the host site for the large pilot (10 MWe) capture plant and Phase II cost-share commitments were finalized. Preliminary engineering and cost estimates were prepared for the equipment inside the battery limit (ISBL) and outside the battery limit (OSBL). A NEPA contractor (ICF Jones & Stokes, Inc.) was also selected as part of the Phase I effort. A plan was developed for securing cost-share commitments for Phase III. Phase II efforts are underway and will conclude with completion of a FEED study, NEPA process, permitting documentation, and team member commitments.

available reports/technical papers/presentations

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Development and Bench-Scale Testing of a Novel Biphasic Solvent-Enabled Absorption Process for Post-Combustion Carbon Capture

primary project goals

The University of Illinois at Urbana-Champaign (UIUC) will advance the development of a novel biphasic carbon dioxide (CO_2) absorption process (BiCAP) and validate its technical advantages by testing an integrated system at a 40-kilowatt-electric (kWe) bench scale with actual coal-derived flue gas. The proposed novel water-lean biphasic solvents have previously demonstrated (FE0026434) the desired vapor-liquid equilibrium (VLE) behavior, rapid absorption kinetics, and high stability in lab-scale characterization experiments, and individual major process steps have been tested on the lab-scale equipment or assessed by modeling studies. This project will move the technology development forward via fully integrated bench-scale testing in a relevant flue gas environment.

technical goals

- To develop process simulations using an Aspen Plus model to determine the optimal process configuration and operating conditions.
- Investigate biphasic solvent losses, emission control, and reclamation of the degradation products.
- Design, fabricate, and test a 40-kWe integrated bench-scale biphasic solvent-based capture unit with simulated flue gas. A subsequent test will use a flue gas slipstream from a coal-fired power plant.
- Assess the techno-economic performance of the technology integrated into a net 550-megawatt-electric (MWe) coal-fired power plant.
- Analyze technology gaps and potential environmental, health, and safety (EH&S) risks to advance the technology toward further scale-up and commercialization.

technical content

The BiCAP utilizes biphasic solvents, which are water-lean solvent blends, that can form and develop dual liquid phases, with the absorbed CO_2 highly enriched in one of the phases and lean solvent in the other. The phase transition behavior of a biphasic solvent is illustrated in Figure 1. The process features multiple stages of liquid-liquid phase separation (LLPS) during CO_2 absorption to maximize the CO_2 absorption kinetics and minimize the increase in solvent viscosity.

technology maturity:

Bench-Scale (40 kWe), Simulated Flue Gas and Actual Flue Gas Slipstream

project focus:

Biphasic Solvents for CO_2 Absorption

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031600

predecessor project:

FE0026434

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Yongqi Lu
Illinois State Geological Survey, University of Illinois at Urbana-Champaign
yongqilu@illinois.edu

partners:

Trimeric Corporation

start date:

4.06.2018

percent complete:

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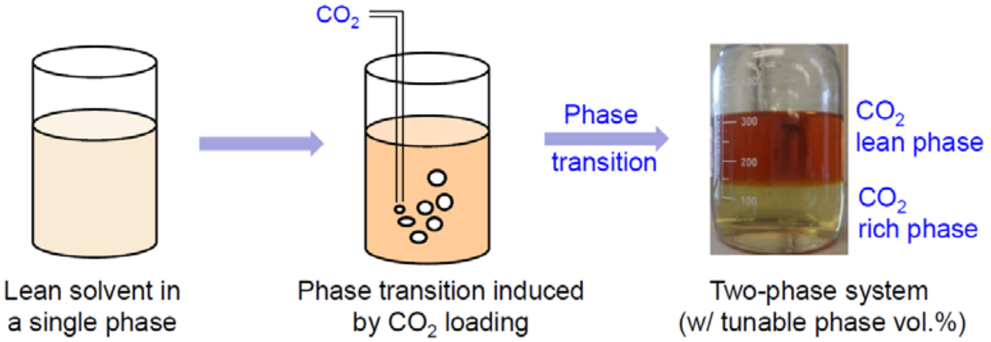

Figure 1: Phase transition behavior of a biphasic solvent.

A schematic diagram of the BiCAP is shown in Figure 2. The flue gas, after the desulfurization and sulfur dioxide (SO_2) polishing stages, enters the absorption column, which contains multiple stages of packed beds, and the CO_2 is absorbed into a biphasic solvent. At each stage, upon CO_2 loading, the biphasic solvent undergoes a phase transition and forms dual liquid phases. The CO_2-enriched phase is separated and collected in a rich solvent tank. The CO_2-lean phase then flows to a heat exchanger to reduce the solvent temperature before entering the next stage of the packed bed. At the last stage, the solvent exiting the absorber is sent to an LLPS tank, in which the CO_2-enriched phase is pumped into the rich solvent tank. Both the hot and cold rich solvents are fed to a flash/stripper to remove CO_2, while the CO_2-lean phase is mixed with the regenerated solvent from the CO_2 stripper before recycling to the absorber. The CO_2 product streams from both the flash and stripper are cooled and compressed.

Key features of the BiCAP include: (1) a unique process configuration of multi-stage CO_2 absorption and phase transition allows continual separation and removal of the CO_2-enriched liquid phase, maintaining rapid kinetics and low solvent viscosity throughout CO_2 absorption; (2) only the CO_2-enriched liquid phase is used for CO_2 desorption, thus lowering the mass flow of solvent required for regeneration; (3) a combination of flash and CO_2 stripping operations allows the high pressure of CO_2 desorption to further improve the energy efficiency; and (4) a portion of cold feed stream enters the stripping column bypassing the cross heat exchanger further reduces the stripping heat requirement.

In a previous U.S. Department of Energy (DOE)-funded project (FE0026434), the BiCAP was tested at laboratory scale (10 kWe) and exhibited a 34% reduction in parasitic power requirements and twice the CO_2 working capacity for desorption when compared with a process using the amine-based solvent, monoethanolamine (MEA). After determining the optimal process configuration and operating conditions, the team will design and fabricate the 40-kWe integrated bench-scale capture unit. Parametric testing for two of the best performing biphasic solvents identified from previous research (FE0026434) will be conducted with simulated flue gas at UIUC's Abbott power plant. One selected solvent will be further evaluated with a slipstream of coal-derived flue gas at the power plant. The team will use the test results to prepare a techno-economic analysis (TEA), as well as an analysis of the technology gaps and potential EH&S risks, to advance the technology for further scale-up and commercialization.

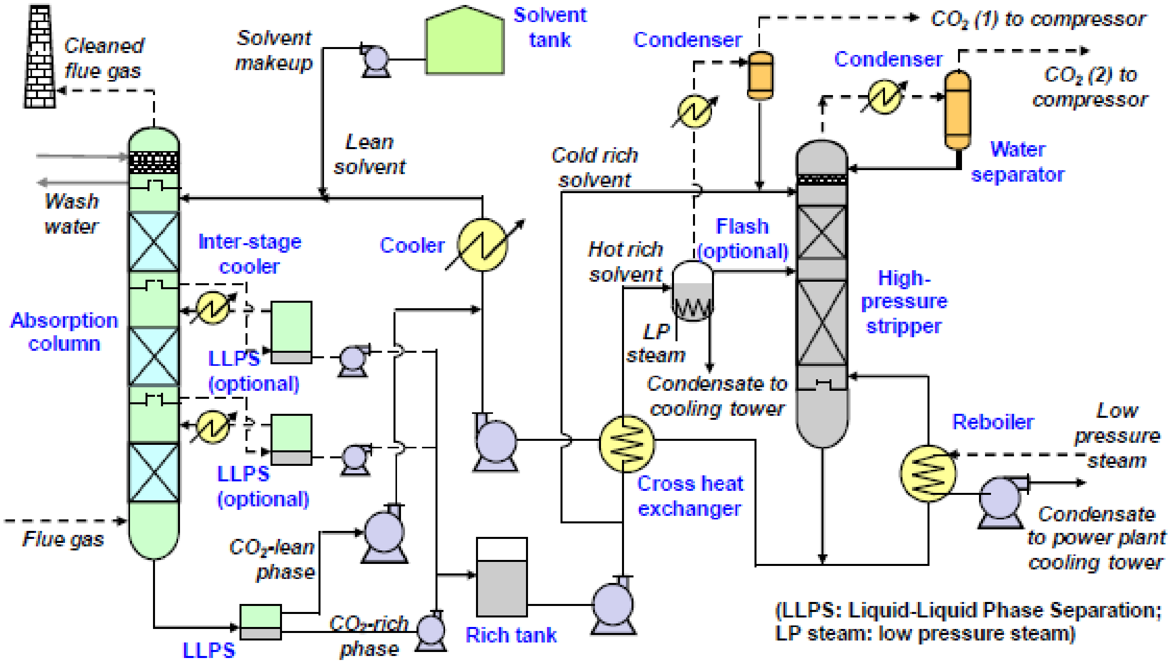

Figure 2: Schematic diagram of the BiCAP with multiple stages of LLPS.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	60-240	<230
Normal Boiling Point	°C	140-300	>140
Normal Freezing Point	°C	-30 to 110	<20
Vapor Pressure @ 20 °C	bar	1 x 10^{-5} to 4 x 10^{-3}	<1.0 x 10^{-3}
Manufacturing Cost for Solvent	$/kg	3-10	<15
Working Solution			
Concentration	kg/kg	0.6-0.8	>0.5
Specific Gravity (15 °C/15 °C)	-	~1.0	0.9–1.4
Specific Heat Capacity @ STP	kJ/kg-K	2.5–3.5	<3.5
Viscosity @ STP	cP	2-15	<20
Absorption			
Pressure*	bar	0.05 (equilibrium P_{CO2} at absorber bottom)	<0.07
Temperature	°C	40	30–50
Equilibrium CO_2 Loading	mol/mol	0.375-0.625 (0.7-1.0 in rich phase)	>0.375
Heat of Absorption	kJ/mol CO_2	65-85	~75
Solution Viscosity	cP	5–10/30–50 (upper/lower phases)	<100 (CO_2-enriched phase)
Desorption			
Flash			
Pressure**	bar	4-9 (5-11 in total)	≥7 (10 in total)
Temperature	°C	100-140	<140

Equilibrium CO_2 Loading	mol/mol	0.4-0.7	
Stripping (lean solution)			
Pressure***	bar	2-5 (3-7 in total)	≥3 (≥4 in total)
Temperature	°C	120-150	<150
Equilibrium CO_2 Loading	mol/mol	0.05-0.35	<0.25
Heat of Desorption (flash + stripping)	kJ/mol CO_2	65-85	~75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	not available	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >99% / >4	
Absorber Pressure Drop	Bar	0.14	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	not available	

*CO_2 partial pressure in the flue gas; **CO_2 partial pressure exiting flash; ***CO_2 partial pressure exiting stripper

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The developed solvent belongs to a new class of biphasic solvents. The solvent is a blend of amines or the like and is a water-lean system containing less than 30 wt% water. The solvent absorbs CO_2 through chemical reactions between amines and CO_2. The solvent undergoes a phase transition to form dual liquid phases based on the difference of hydrophobicity between different species.

Solvent Contaminant Resistance – The developed biphasic solvent is highly resistant to oxygen and heat. Experiments revealed that the oxidative degradation of the biphasic solvent was eight times slower than the benchmark MEA under similar absorption conditions and its thermal stability at 150°C was comparable to the benchmark MEA at 120°C.

Solvent Foaming Tendency – No foaming issue was observed for the biphasic solvent, either in a gas bubbler tested continually for two weeks or in a laboratory absorption column operated intermittently for several months.

Flue Gas Pretreatment Requirements – The flue gas leaving the FGD needs be further polished to reduce the content of SO_2 below 10 parts per million volume (ppmv).

Solvent Makeup Requirements – Laboratory solvent stability experiments indicate that the makeup requirement of the biphasic solvent is lower than the benchmark MEA (i.e., less than 2 kg/ton CO_2 captured).

Waste Streams Generated – Waste streams from the BiCAP are similar to those from amine-based processes, including flue gas condensate, water wash blowdown, cooling water blowdown, heat stable salts, spent solvent wastes, and spent solvent reclamation materials (e.g., activated carbon).

Process Design Concept – See Figure 2.

technology advantages

- BiCAP maintains rapid kinetics throughout the CO_2 absorption process and thus can reduce the footprint and cost of absorption equipment compared with either MEA or other biphasic solvent-based processes.
- BiCAP is able to maintain the solvent at a lower viscosity and thus retain rapid mass transfer in the absorber, potentially increasing the CO_2 working capacity of the solvent and reducing the footprint and capital cost of the absorber.
- The combination of flash and stripping operations achieves high-pressure CO_2 desorption and thus lowers the energy use for CO_2 separation and compression.
- BiCAP desorption configuration with a cold rich solvent stream directly fed to the top of the stripper results in reduced water vapor in the CO_2 stream and thus further reduces the stripping heat duty.
- The energy efficiency advantages of the BiCAP coupled with reduced equipment sizes when scaled-up for commercial systems leads to reductions in both capital and operating expenses compared with the benchmark MEA process.

R&D challenges

- Develop methods for controlling solvent losses caused by volatility of the selected biphasic solvents.
- Identifying the optimal process design and operating conditions for the proposed BiCAP.
- Developing methods for solvent reclamation with high efficiency and low environmental impact.

- Demonstrating reliable operation and stable performance of the bench-scale unit in an actual power plant environment.

status

The solvent volatility and losses studies on the two biphasic solvents were completed, and a preliminary assessment of water wash option and performance completed to provide inputs for equipment design. The host site agreement was finalized with Abbot Power. Also, the 40-kWe bench-scale capture equipment design was completed with the optimal process identified. The design calculations show that the unit can meet the performance targets (e.g., heat duty less than or equal to 2,100 kJ/kg of CO_2 and stripping pressure greater than or equal to 4 bar). The experimental studies of solvent degradation reclamation were conducted, and a suitable method for biphasic solvent reclamation was identified. The bench-scale unit fabrication process is underway, with multiple vendors under consideration.

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Molecular Refinement of Transformational Solvents for CO_2 Separations

primary project goals

Pacific Northwest National Laboratory (PNNL) aims to perform molecular refinement of third-generation water-lean solvents during this project. The objectives are to reduce volatility while retaining desirable physical and thermodynamic properties, study the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation), design new molecules that are resistant to these chemical degradations, and decrease infrastructure capital expenditures (CAPEX) while increasing longevity by replacing steel with cheaper and more durable plastics. This proposal builds on PNNL's integrated solvent development approach, with an integrated effort combining the elements of computation, advanced synthesis and testing capabilities, and comprehensive material property testing to refine advanced solvent performance while also reducing the CAPEX of these third-generation solvents.

technical goals

- Refine third-generation carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) solvents (aminopyridines [APs], diamines [DAs]) to reduce volatility while retaining favorable viscosity and CO_2 bonding enthalpy.
- Learn the molecular underpinnings of chemical degradation and develop strategies to mitigate or remove solvent decomposition with flue gas impurities, such as sulfur oxides (SO_X), nitrogen oxides (NO_X), oxygen (O_2), and hydrolysis.
- Measure the contact angles of water-lean solvents at varied CO_2 and water loadings on plastic surfaces and assess whether plastic infrastructure could be used in place of steel.
- Assess the reduction in CAPEX by substituting steels with fiber-reinforced plastic to determine progress towards $30/tonne CO_2 target.
- Disseminate all findings to the U.S. Department of Energy (DOE), Carbon Capture Simulation for Industry Impact ($CCSI^2$), and peer-reviewed publications.

technical content

The PNNL team aimed to refine the secondary and tertiary properties that are limiting for water-lean CO_2BOL solvents. It was anticipated that the vapor pressure of third-generation solvents, such as APs or DAs, would be reduced to sub-parts-per-million (ppm) levels, effectively negating evaporative losses of solvent. PNNL expected to learn the reaction mechanisms of chemical degradations of carbamate and alkylcarbonate solvent molecules and learn how to redesign new molecules that are resistant to oxidation, nitration, and hydrolysis. PNNL aimed to demonstrate that new formulations will exhibit an increase in solvent lifetime by two to four times. PNNL also expected that water-lean solvents under operating conditions (~ less

technology maturity:
Laboratory-Scale

project focus:
Molecular Refinement of Water-Lean Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-72396

predecessor project:
FWP-65872

NETL project manager:
Isaac Aurelio
Isaac.aurelio@netl.doe.gov

principal investigator:
David Heldebrant
Pacific Northwest National Laboratory
david.heldebrant@pnnl.gov

partners:
N/A

start date:
05.01.2018

percent complete:
55%

than 10 wt% water, 40°C, 0 to 50 mol% CO_2 loading) will be able to adequately wet plastics, enabling the substitution of cheaper and more chemically durable plastic to be used in place of steel. The removal of steel will effectively cease corrosion, improving solvent lifetime while negating the need for costly corrosion inhibitors. The substitution for fiber-reinforced plastics like polyethylene or polypropylene are estimated to provide an estimated 50% reduction in CAPEX for absorbers, strippers, and piping. These cost reductions are anticipated to help reduce CAPEX of carbon capture and storage (CCS) to enable third-generation solvents to meet DOE's prior $40/tonne cost metric, with the potential to achieve the revised $30/tonne metric.

PNNL was tasked with resolving three key problems associated with aminosilicone solvents: (1) susceptibility to disproportionation and hydrolysis; (2) significantly high CO_2-rich viscosity of the solvents; and (3) the need for co-solvent, thereby leading to increased capital and operational costs. To address all these challenges, the team has been working towards developing a novel DA-based system. In order to overcome the hydrolysis and disproportionation issues related to amino silicones, the silicone moiety was replaced with alkyl chains; however, these solvents solidified upon standing when CO_2 was loaded. It was hypothesized that two secondary amines were providing too much hydrogen bonding, so tertiary amine moieties were incorporated to reduce viscosity and solidification. The team started by designing a library for secondary/tertiary amines. The challenge was to down-select hundreds of molecules to a few candidate derivatives that would have a low viscosity. PNNL applied its previously developed reduced-order model to a library (Figure 1) to down-select to final derivatives. Their CO_2 uptake capacities were also evaluated. Several other analogues of DAs are in the process of being synthesized, as shown in Figure 1 (in the pipeline), in order to fully develop the structure activity relationship.

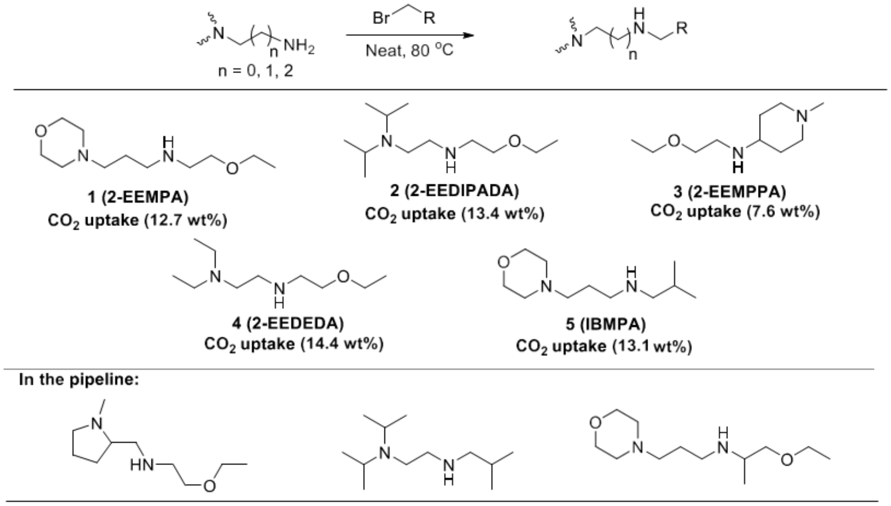


Figure 1: Selected library for non-volatile, low-viscosity secondary/tertiary diamines.

In order to address the volatility issue associated with the second-generation aminopyridine class of CO_2 capture solvents, two low-vapor pressure derivatives were prepared from modeling efforts to synthesize. These third-generation APs were functionalized with ether and morpholine motifs to promote high internal hydrogen bonding, but to also reduce vapor pressure. The synthetic approach for these two derivatives involved the condensation of 2-pyridinecarboxaldehyde with the corresponding amines to in situ generate imines, which were reduced by the treatment with sodium borohydride to yield 8a 3-methoxy-N- (pyridin-2-ylmethyl)propan-1-amine and 8b 2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine in 70% and 68% yields, respectively (Figure 2).

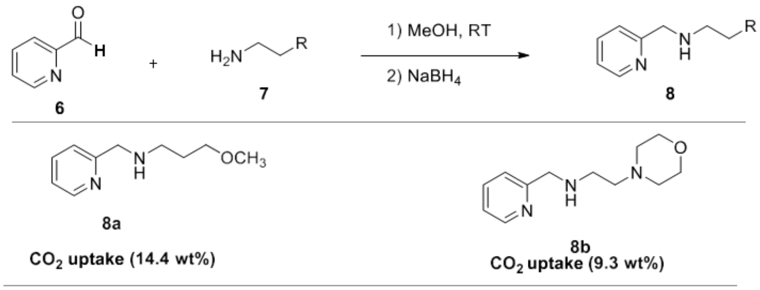


Figure 2: Synthetic methodology for the synthesis of third-generation aminopyridine derivatives.

Once the AP and DA screenings were completed, the synthesis team started designing synthesis routes and began synthesis of the viable derivatives for comprehensive material property testing. For the testing, 50 grams (g) of the candidate derivatives were synthesized, and their physical and thermodynamic properties were evaluated using the in-house built pressure-volume-temperature (PVT) cell. Based on the results, PNNL recommends further testing on 8a as the final candidate AP for larger-scale testing, as it is cheaper, has lower molecular weight while having a lower CO_2-rich viscosity, and has stronger CO_2 sorption as compared to other AP derivatives. PNNL recommends 2-EEDEDA as the final DA candidate, as it has a low molecular weight, comparable CO_2 sorption as compared to other DA derivatives, while having the lowest CO_2-rich viscosity of any known water-lean solvent ever developed.

PNNL performed large-scale molecular simulations to assess wetting properties and surface energies of a representative CO_2BOL alkanolguanidine (1-IPADM-2-BOL) adhered to 316 stainless steel and polyethylene interfaces. The goal was to determine what molecular-level interactions occur on either interface to determine how organics can wet stainless steel almost as well as plastic. Further, a second goal was to determine any reactions between the solvent molecules and the interface, to provide a better understanding of solvent durability. The simulations showed negligible interactions between 1-IPADM-2-BOL and a model polyethylene surface, whereas strong interactions were observed on a steel interface. It was noted that the iron (Fe) atoms appeared to catalyze a reaction between two solvent molecules through mediated proton transfer, suggesting a potential mechanism of degradation (i.e., hydrolysis) that would occur for water-lean and aqueous formulations. The solvent at the interface was observed to partially degrade, leaving an organic coating on the steel interface. These simulations suggest that a steel interface could be catalytic with respect to decomposition reactions of the solvent, such as hydrolysis. They also shed light as to why organics can wet steel interfaces almost as well as plastic. This phenomenon was not observed on the polyethylene plastics, suggesting the solvent would not degrade by these means on a plastic interface, indicating that solvent lifetime would be higher on plastic packings than on stainless as hypothesized.

PNNL has continued contact angle measurements to determine the wettability of water-lean solvents on different surfaces. PNNL has continued using ASTM standard (current version: ASTM D7334-08 [2013]), which requires at least six measurements at 23 ± 2°C on drops with consistent size. The contact angle measurements are especially important when determining the material composition of the reactors and their interactions with liquid reactants.

In the experimental approach, four surfaces cut in 2-inch by 2-inch pieces were used: Teflon®, Ultra High Molecular Weight Polyethylene (UHMWPE), polyetheretherketone (PEEK), and 314 stainless steel. The plastics were chosen due to their chemical and temperature resistance, while the 314 stainless steel is a material currently used in the industrial installations and serves as a benchmark. The results can be seen in Table 1.

TABLE 1: CONTACT ANGLE MEASUREMENTS OF SOLVENTS ON VARIOUS SURFACES

		Teflon®	UHMWPE	PEEK	Stainless (314)
1	1-IPADM-2-BOL/0% CO_2	avg. 72	avg. 40	avg. 30.5	avg. 42.5
2	1-IPADM-2-BOL/**48**% CO_2	avg. 78	avg. 55	avg. 48.5	avg. 55.5
3	2-EEMPA/0% CO_2	avg. 48	avg. 34	avg. 10	avg. 46
4	2-EEMPA/**43**% CO_2	avg. 69	avg. 39.5	avg. 20.5	avg. 35
5	2-EEMPA/**48**% CO_2, **4.3**% H_2O	avg. 60	avg. 30.5	avg. 22	avg. 35.5
6	2-EEMPA/**49.5**% CO_2, **4.3**% H_2O	avg. 62	avg. 31	avg. 20	avg. 30
7	H_2O (RO)	avg. 106	avg. 81	avg. 82	avg. 89.5
8	H_2O (tap)	avg. 115	avg. 88	avg. 95	avg. 90

*Teflon® and UHMWPE are considered hydrophobic, while 314 Stainless Steel is considered a hydrophilic surface.

The current data indicates that the best wettability of the surface is achieved in case of the PEEK surface. The results obtained for this batch of experiments indicate superiority of the plastic over the commercially used steel. This result is encouraging, as by removing steel from the system, one can slow down decomposition of the solvents and corrosion of equipment.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	-
Normal Boiling Point	°C	181.0	-
Normal Freezing Point	°C	<0	-
Vapor Pressure @ 15°C	bar	5E-5	-
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	-
Specific Gravity (15°C/15°C)	-	0.94	-
Specific Heat Capacity @ STP	kJ/kg-K	1.95	-
Viscosity @ 15°C	cP	11.3	-
Absorption			
Pressure	bar	1	-
Temperature	°C	40	-
Equilibrium CO_2 Loading	mol/mol	0.29	-
Heat of Absorption	kJ/mol CO_2	75	-
Solution Viscosity	cP	25	-
Desorption			
Pressure	bar	1.8	-
Temperature	°C	117	-
Equilibrium CO_2 Loading	mol/mol	0.05	-
Heat of Desorption	kJ/mol CO_2	75	-

Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2.6E6		
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	90
Absorber Pressure Drop	bar	<0.1		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	pending		

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – Oxidative degradation and hydrolysis studies indicate solvents are more durable than 5M MEA under comparable oxidation and hydrolysis testing.

Solvent Foaming Tendency – Solvent has shown no propensity to foam under operating conditions.

Flue Gas Pretreatment Requirements – Small up-stream cooling is required to reduce water accumulation.

Solvent Makeup Requirements – Not yet available.

Waste Streams Generated – Not yet available.

Process Design Concept – Not yet available.

technology advantages

- Oxidation, foaming, aerosol formation, and corrosion issues are mitigated.
- The solvent volatility is reduced while still maintaining a favorable viscosity.
- The solvent lifetime is increased.
- Adequate wettability of solvents on plastic surfaces enables possible replacement of steel process infrastructure, reducing CAPEX and eliminating need for corrosion inhibitors.

R&D challenges

- There is potential for the nitration of solvents by NO_X potentially making nitrosamines.
- The chemical and physical durability of plastics in presence of solvents and the pressure, temperatures, and stresses of the system must be proved.
- Manufacturing costs for the solvents must be acceptable.

status

All remaining third-generation DA and AP solvents have been synthesized and tested for vapor liquid equilibrium (VLE), viscosity, and mass transfer measurements in the PVT cell. There is one derivative that appears to have comparable CO_2 bonding strength to that of 1-BEIPADIPA-2-BOL, while also exhibiting the lowest CO_2-rich viscosity (29 cP) of any solvent to come from any of the three solvent classes in the laboratory.

Solvent decomposition findings indicate CO_2BOLs such as 1-IPADM-2-BOL (and aqueous amines) are likely to degrade on steel, suggesting plastics are a better choice for solvent longevity in addition to cost.

The theory team has now started calculations to derive contact angles and surface energies to further shed light on the wetting behavior of solvents on stainless steel versus plastics. This knowledge will help shed light as to which packing material will perform best with water-lean solvents as compared to aqueous solvents. Lastly, the experimental team has nearly completed contact angle measurements for varied water-lean solvents on PEEK plastic using ASTM D7334-08.

available reports/technical papers/presentations

Freeman, C. “Molecular Refinement of Transformational Solvents for CO_2 Separations,” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/C-Freeman-PNNL-Molecular-Refinement.pdf*.

Mixed-Salt-Based Transformational Solvent Technology for CO_2 Capture

primary project goals

SRI International is developing a novel, water-lean, mixed-salt-based transformational solvent technology to provide a step-change reduction in the cost and energy penalties of post-combustion carbon dioxide (CO_2) capture.

technical goals

- Demonstrate that the advanced mixed-salt process (A-MSP) can:
  - Operate as a solvent-rich system with a very high cyclic CO_2-loading capacity (greater than 0.10 kilogram [kg] CO_2/kg of solvent).
  - Regenerate CO_2 at greater than 10 bar at temperatures less than 120°C.
  - Operate continuously in an integrated absorber-regenerator using simulated flue gas with 13 to 15% CO_2 and balance air.
- Perform thermodynamic modeling and vapor-liquid equilibrium (VLE) measurements of multi-component systems.
- Conduct kinetic measurements of CO_2 absorption of select compositions.
- Conduct solvent degradation and aerosol formation studies.
- Perform bench-scale testing of integrated absorber-regenerator system.
- Develop a rate-based model and process flowsheet and perform a techno-economic analysis (TEA) to aid identification of development pathways for technology advancement.

technical content

SRI International, in collaboration with SINTEF, Technical University of Denmark (DTU), OLI Systems, Inc., and Trimeric Corporation, are utilizing the knowledge gained during a U.S. Department of Energy (DOE)-funded project (FE0012959) in the design of a mixed-salt process (MSP) that uses a solvent formulation comprised of ammonium (NH_4) and potassium (K) salt solutions to develop a transformational technology that achieves further improvements in performance. An analysis conducted by SRI indicates that inclusion of a tertiary amine to the mixed-salt formulation will yield a high CO_2-loading capacity and high-pressure solvent regeneration at low temperature, thus further reducing the energy penalty of CO_2 capture.

Bench-scale testing of SRI's first-generation MSP under FE0012959 showed that the two-component system has significant advantages over single-component systems. In the MSP chemistry, ammonia (NH_3) plays a dual role – the role of catalyst and the role of the absorbent due to its high mobility and reactivity with CO_2. Ammonia absorbs large amounts of CO_2 at low temperature and releases CO_2 at high temperature and pressure, making it a highly useful chemical in CO_2 absorption formulations. By blending NH_3 with other low-capacity and low-reactivity components to suppress the undesirable high vapor pressure of NH_3, SRI has identified a next-generation A-MSP formulation that can provide a step-change reduction in CO_2 capture costs. Based on preliminary examinations,

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Advanced Mixed-Salt Solvent Process

participant:

SRI International

project number:

FE0031597

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Palitha Jayaweera
SRI International
palitha.jayaweera@sri.com

partners:

OLI Systems, Inc., SINTEF, Technical University of Denmark, Trimeric Corporation

start date:

06.01.2018

percent complete:

45%

adding methyl diethanolamine (MDEA) into the MSP formulation significantly improves the capture performance, yielding a regeneration energy of 1.5 to 1.8 megajoules (MJ)/kg-CO_2 while operating with less than 50% water. The solvent and process parameters are provided in Table 1.

The A-MSP concept includes two isothermal absorbers, a selective regenerator, and auxiliary equipment, as shown in Figure 1. Absorber 1 operates with high NH_3/(MDEA+K) solvent composition and absorber 2 operates with low NH_3/(MDEA+K) solvent composition, resulting in efficient absorption and minimum NH_3 slip. In the range of 60 to 80% of the CO_2 in the flue gas stream is absorbed in absorber 1 and the remaining CO_2 is absorbed in absorber 2. The dual-stage absorber system reduces NH_3 carryover, resulting in less than 10 parts per million (ppm) NH_3 in the clean flue gas stream exiting the water wash. Both absorbers operate with liquid recycle using heat exchangers to remove the heat of reaction. The bottom stage operates with the highest CO_2 loading (up to 0.7 mol/mol). The CO_2-rich solutions from the absorbers are then sent to the regenerator through crossflow heat exchangers, which recover the heat from returning lean solutions. The A-MSP uses a selective regenerator to produce two CO_2-lean salt streams with high and low NH_3 content, drawn from the lower-middle and bottom stages of the regenerator. The regenerator is operated under high-pressure isobaric conditions (10 to 20 bar) and has a temperature gradient in the column (top ~30°C and bottom ~110°C). At high temperature, the NH_3 at the bottom of the regenerator is vaporized along with CO_2, making a lean, low-NH_3/(MDEA+K) ratio solution to be used in absorber 2. Vaporized NH_3 gets re-absorbed as the vapor moves up the regenerator column, thereby creating a high-NH_3/(MDEA+K) ratio solution in the mid-section of the regenerator for use in absorber 1. In the A-MSP design, operating the regenerator at relatively low temperature and high pressure eliminates the water stripping, thus generating an almost-dry CO_2 stream ($H_2O_{vap}/CO_2 < 0.02$) at high pressure. Figure 2 shows equilibrium modeling data comparing MSP and A-MSP systems, illustrating the high-CO_2 regeneration pressure advantage (almost doubled for 0.55 mol/mol CO_2 loading) of A-MSP with the inclusion of MDEA to the solvent. This results in a reduction of regeneration and CO_2 compression energy costs (operating cost reduction) and removal of the expensive first stage of CO_2 compression (capital cost reduction). In addition, the lower regeneration temperature and lower reboiler duty significantly reduce power plant energy loss due to steam extraction, improving the net power output of the plant (Figure 3).

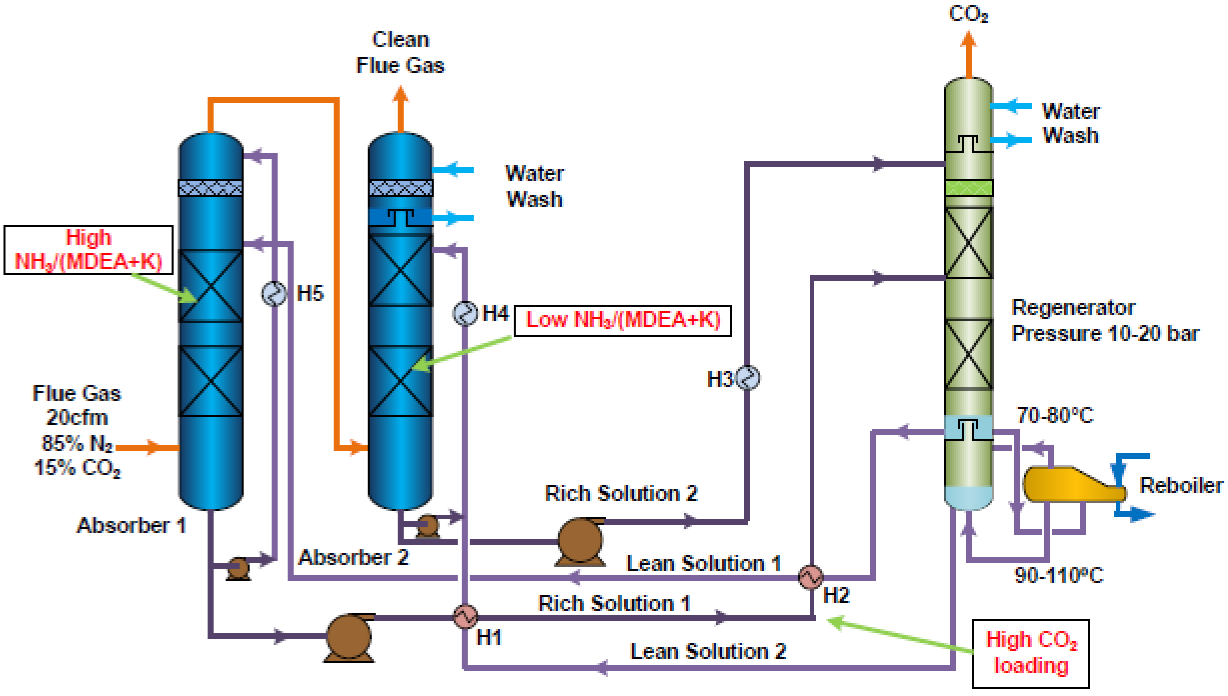


Figure 1: Conceptual process flow diagram for the A-MSP.

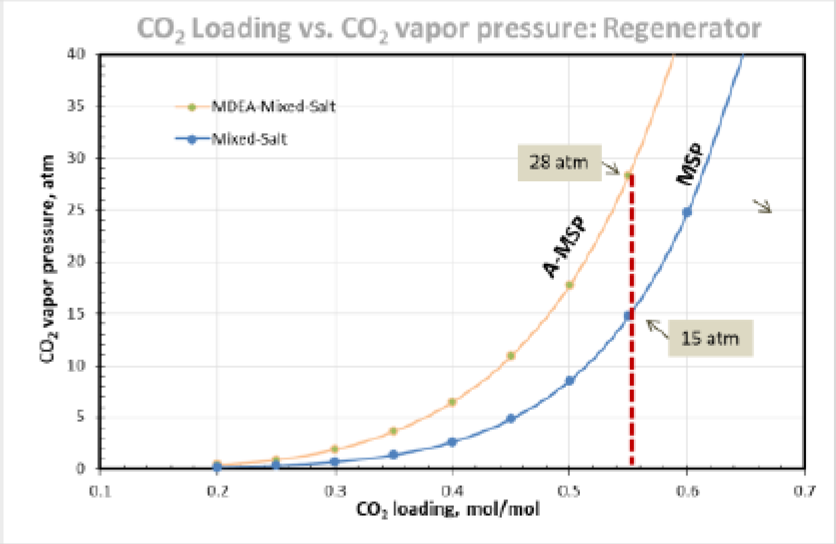


Figure 2: CO_2 loading versus CO_2 pressure at 100°C for (i) 10 molal mixed-salt and (ii) 10 molal MDEA-mixed-salt formulations.

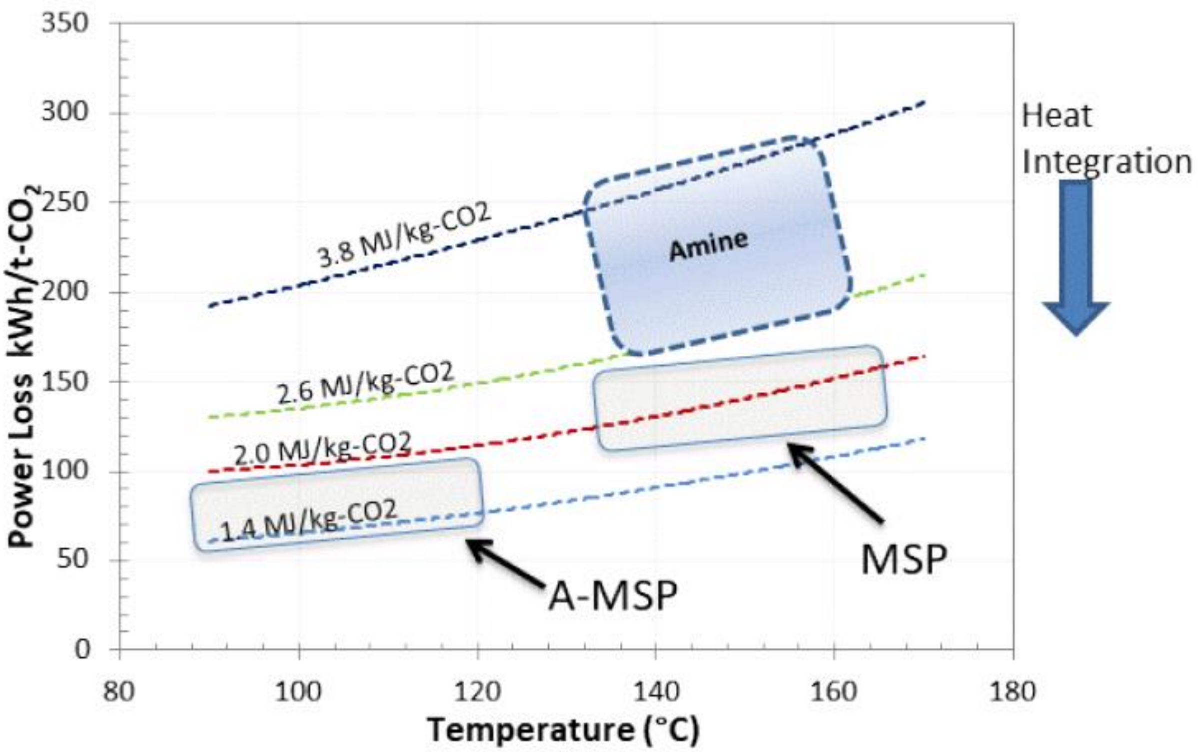
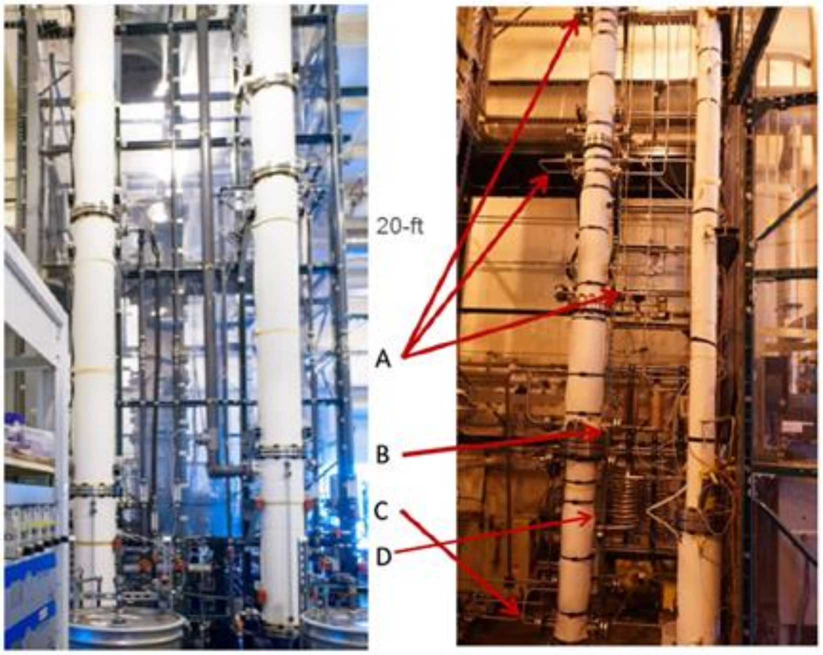


Figure 3: Power plant energy loss due to steam extraction.

Following lab-scale and small bench-scale testing, SRI's large bench-scale integrated CO_2 absorber-regenerator system (Figure 4), originally built for testing the MSP, will be used without any modifications for dynamic and steady-state testing.



A: Rich solution inlet locations
B: Discharge locations for high NH$_3$/K solution
C: Discharge locations for low NH$_3$/K solution
D: Heat exchangers (Cold rich↔Hot lean)

Figure 4: SRI's large bench-scale integrated absorber-regenerator system (gas flow rates up to 400 standard liters per minute).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.17	0.17
Manufacturing Cost for Solvent	$/kg	--	--
Working Solution			
Concentration	kg/kg	0.20-0.55	0.30-0.55
Specific Gravity (15°C/15°C)	—	1.37	1.37
Specific Heat Capacity @ STP	kJ/kg-K	3.2	3.2
Viscosity @ 20°C	cP	1.6-35	1.6-35
Surface Tension @ STP	dyn/cm	73.4	73.4
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	20-40
Equilibrium CO_2 Loading	gmol CO_2/kg	1.5-3.5	2.5-3.5
Heat of Absorption	kJ/kg CO_2	795-1,136	<1,100
Solution Viscosity	cP	1.5-3.0	1.5-3.0
Desorption			
Pressure	bar	>10	10-15
Temperature	°C	120-180	140-160
Equilibrium CO_2 Loading	gmol CO_2/kg	0.2-1	0.2-0.5
Heat of Desorption	kJ/kg CO_2	1,500-2,200	<2,000

Proposed Module Design *(for equipment developers)*

Flue Gas Flowrate	kg/hr		--	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	--
Absorber Pressure Drop	bar		--	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		--	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction involves chemical absorption of CO_2 through gas/liquid phase mass transfer followed by chemical reactions in the liquid phase.

These reactions are as follows:

1. $CO_2\ (g) \leftrightarrow CO_2\ (aq)$
2. $NH_3\ (aq) + CO_2\ (aq) + H_2O\ (liq) \leftrightarrow (NH_4)HCO_3\ (aq)$
3. $(NH_4)_2CO_3 + 2CO_2\ (aq) + H_2O\ (liq) \leftrightarrow 2(NH_4)HCO_3\ (aq)$

4. $2NH_3$ (aq) + CO_2 (aq) ↔ $(NH_4)NH_2CO_2$
5. $(NH_4)NH_2CO_2$ (aq) + CO_2 (aq) + $2H_2O$ (liq) ↔ $2(NH_4)HCO_3$ (aq)
6. K_2CO_3 (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $2KHCO_3$ (aq) + catalyst
7. R1R2R3N (aq) + CO_2 (aq) + H_2O (liq) + catalyst ↔ $(R1R2R3NH)HCO_3$ (aq) + catalyst
   where $R1=R2=CH_2CH_2OH$ and $R3=CH_3$

Solvent Contaminant Resistance – High.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – The process is installed downstream of the FGD unit.

Solvent Makeup Requirements – To be determined.

Waste Streams Generated – To be determined.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

technology advantages

- Low NH_3 emissions.
- High CO_2 absorption rate and high CO_2 loading capacity.
- Reduced reboiler energy demand.
- Addition of tertiary amine to NH_4-based mixed-salt solvent reduces regeneration energy need and water use.
- Lower reboiler duty and regeneration temperature improves net power output, increasing net plant efficiency.
- Low-temperature, high-pressure regeneration of greater than 99% pure dry CO_2 reduces compression requirements.

R&D challenges

- Precipitation of solids in the absorber during cold weather conditions.
- Residual amine and/or NH_3 in exit gas stream.
- Solvent interaction with acid gases.
- Thermal management of absorber columns and regenerator.
- Volatility and corrosiveness of MDEA.

status

The project team conducted VLE measurements of various CO_2 loading levels and compositions for the regenerator side and is conducting lab-scale absorber tests to investigate reaction kinetics and CO_2 absorption capacity. SRI completed the refurbishment of the existing absorber bench-scale unit and has performed parametric testing in the unit with simulated flue gas to determine the rate of CO_2 absorption in the A-MSP solutions as a function of temperature, gas flow rate, solution composition, CO_2 loading, and liquid/gas ratio. After testing 11 different MSP solvent formulations, it was determined that a 9 molal (total) formulation comprised of potassium carbonate (K_2CO_3), NH_3, and MDEA exhibited the highest overall carbon capture efficiency. The existing MSP process model was updated to include MDEA in the solvent formulation and VLE data will be used to inform model refinements and process design. DTU has assembled a thermodynamic modeling program for the process to aid with predicting CO_2 and NH_3 isotherms under various test conditions and solvent compositions. Oxidative and thermal degradation studies, integrated absorption/desorption testing, further development of the process flowsheet model, and a TEA will be completed in Budget Period 2.

available reports/technical papers/presentations

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Jayaweera-SRI-Mixed-Salt-Solvent.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," Project Kick-Off Meeting, September 2018. *https://www.netl.doe.gov/projects/files/FE0031597-Kickoff-Presentation-090418.pdf*.

Jayaweera, P., "Mixed-Salt Based Transformational Solvent Technology for CO_2 Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/P-Jayaweera-SRI-Mixed-Salt-Based-Transformational-Solvent.pdf*.

Initial Engineering, Testing, and Design of a Commercial-Scale, Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit

primary project goals

The University of North Dakota (UND) Energy and Environmental Research Center (EERC), in partnership with the North Dakota Industrial Commission, ALLETE Clean Energy, Minnkota Power Cooperative, Mitsubishi Heavy Industries (MHI), and Burns & McDonnell, will perform a pre-front-end engineering and design (pre-FEED) analysis and cost estimate for retrofitting MHI's Kansai Mitsubishi Carbon Dioxide Recovery (KM-CDR™) amine-based post-combustion carbon dioxide (CO_2) capture process with an existing coal-fired generating unit.

technical goals

The goal of the project is to determine retrofit costs for a post-combustion CO_2 capture system on an existing coal-fired electric generating unit. Specific objectives to support this goal include the following:

- Design a fully integrated post-combustion CO_2 capture system for Milton R. Young Unit 2 (MRY2).
- Evaluate KS-1™ solvent on lignite coal-derived flue gas to refine critical design parameters.
- Complete a techno-economic assessment (TEA) in accordance with the U.S. Department of Energy's (DOE) bituminous baseline study (B12B).
- Complete a pre-FEED analysis of the specified post-combustion CO_2 capture system at MRY2.

technical content

The commercially available KM-CDR™ process uses an advanced amine solvent, KS-1™, that exhibits less solvent degradation, a higher working capacity and lower solvent circulation rate, and reduced steam consumption for regeneration compared to monoethanolamine (MEA). The solvent technology has shown to be reliable, routinely achieving 90% CO_2 removal, while capturing approximately 1.6 million tonnes of CO_2 per year from a 240-megawatt-electric (MWe) sub-bituminous coal-derived flue gas stream at the W.A. Parish Plant in Thompsons, Texas, through a DOE-funded project with Petra Nova Parish Holdings, LLC. Through the development, several improvements to the process have been implemented, including a novel flue gas quencher and absorber design for lower capital costs and ease of construction and an amine wash section for minimizing aerosol emissions from treated flue gas. The team will design a fully integrated

technology maturity:

Commercial-Scale Design

project focus:

KM-CDR™ Process Retrofit

participant:

University of North Dakota
Energy and Environmental
Research Center (UNDEERC)

project number:

FE0031602

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
Andrew.opalko@netl.doe.gov

principal investigator:

Jason Laumb
UNDEERC
jlaumb@undeerc.org

partners:

North Dakota Industrial Commission, ALLETE Clean Energy, Minnkota Power Cooperative, Mitsubishi Heavy Industries (MHI), and Burns & McDonnell

start date:

06.05.2018

percent complete:

89%

KM-CDR™ system for installation at MRY2 near Center, North Dakota; perform testing with EERC's slipstream baghouse installed at MRY2 to evaluate aerosol emissions; evaluate the KS-1™ solvent on lignite coal-derived flue gas to refine critical design parameters; complete a TEA in accordance with DOE's bituminous baseline study; and complete a pre-FEED analysis and cost estimate of the system at MRY2.

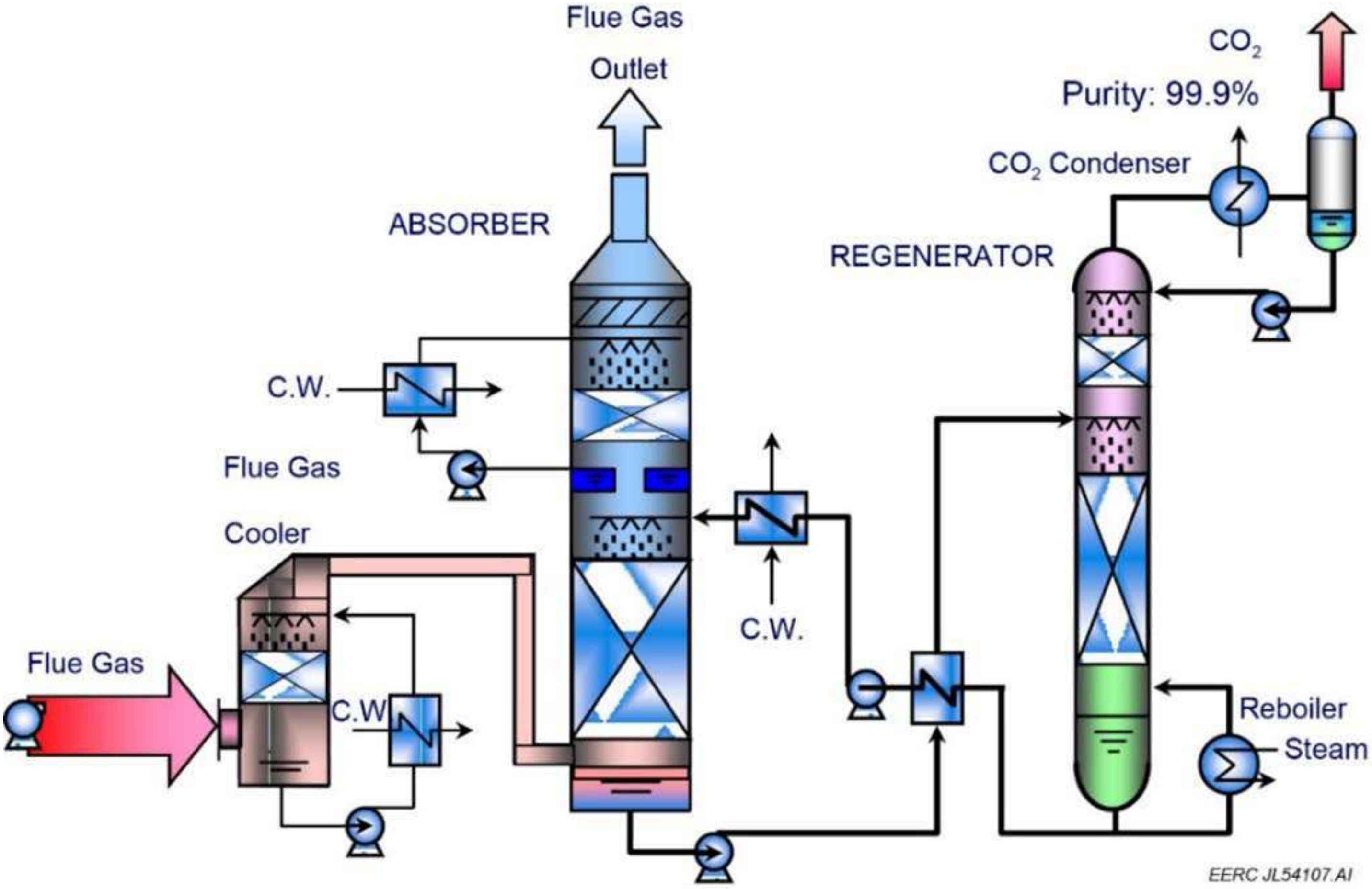


Figure 1: MHI's KM-CDR™ process.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary data	proprietary data
Normal Boiling Point	°C	proprietary data	proprietary data
Normal Freezing Point	°C	proprietary data	proprietary data
Vapor Pressure @ 15°C	Bar	proprietary data	proprietary data
Manufacturing Cost for Solvent	$/kg	proprietary data	proprietary data
Working Solution			
Concentration	kg/kg	proprietary data	proprietary data
Specific Gravity (15°C/15°C)	-	proprietary data	proprietary data
Specific Heat Capacity @ STP	kJ/kg-K	proprietary data	proprietary data
Viscosity @ STP	cP	proprietary data	proprietary data
Absorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data

Heat of Absorption	kJ/mol CO_2	proprietary data	proprietary data
Solution Viscosity	cP	proprietary data	proprietary data
Desorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data
Heat of Desorption	kJ/mol CO_2	proprietary data	proprietary data
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,938,700	
CO_2 Recovery, Purity, and Pressure	% / % / bar	95% / 99.9%+ / 158.6	
Absorber Pressure Drop	Bar	proprietary data	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary data	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%-wet					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_2	NO_x
13.68	150	10.45	20.5	62.9	5.3	0.79	44	149.7

Chemical/Physical Solvent Mechanism – CO_2 is captured by chemical absorption.

Solvent Contaminant Resistance – KS-1™ solvent is highly resistant to contaminant compared to conventional solvent MEA.

Solvent Foaming Tendency – KS-1™ solvent has low foaming tendency compared to conventional solvent MEA.

Flue Gas Pretreatment Requirements – Flue gas cooling and sulfur oxide (SO_X) removal unit may be required depending on flue gas conditions.

Solvent Makeup Requirements – Solvent makeup rate depends on the impurity levels in the flue gas but is generally lower than conventional solvent MEA.

Waste Streams Generated – Solvent reclaiming waste is the main waste stream generated.

Process Design Concept – KM-CDR™ process is equipped with a proprietary amine emissions reduction system, energy-saving system, and amine purification system, which maximize the capture efficiency while minimizing the energy consumption and environmental impact.

Proposed Module Design –Not applied.

technology advantages

The combination of the state-of-the-art KM-CDR™ technology with refined design criteria and optimized thermal integration will improve performance of the CO_2 capture system and maximize overall system efficiency.

R&D challenges

This project will address challenges associated with a full-scale system, such as the use of lignite coal, effects from cold climate, treating higher quantities of flue gas, and application of heat integration.

status

Field testing at MRY2 was completed, including long-term stable operation and aerosol mitigation testing. The project design basis was completed, including utility requirements, flow diagrams, balance of plant, permitting strategy, and optimization studies. The TEA is underway and the pre-FEED cost estimate is near completion. The project final report nearing completion will include the pre-FEED cost estimate, system layout, a hazard and operability study (HAZOP), constructability, the steam integration report, the transportation study, and the technology maturation plan.

available reports/technical papers/presentations

Laumb, J., Initial Engineering, Testing, and Design of a Commercial-Scale Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit, Aug 2018, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://www.netl.doe.gov/sites/default/files/netl-file/J-Laumb-UNDEERC-Engineering-Testing-and-Design.pdf*.

Laumb, J., Initial Engineering, Testing, and Design of a Commercial-Scale Post-Combustion CO_2 Capture System on an Existing Coal-Fired Generating Unit, Aug 2019, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://netl.doe.gov/sites/default/files/netl-file/J-Laumb-UND-EERC-Postcombustion-Coal-Plant-Capture.pdf*.

Engineering-Scale Demonstration of the Mixed-Salt Process for CO_2 Capture

primary project goals

SRI International is developing a novel ammonia (NH_3) and potassium carbonate (K_2CO_3)-based mixed-salt solvent carbon dioxide (CO_2) capture process. Large bench-scale and engineering-scale (~10 megawatt-electric [MWe]) testing is being performed to validate enhanced CO_2 capture efficiency, high loading capacity, and reduced energy consumption.

technical goals

- Demonstrate the individual absorber and regenerator processes for NH_3 and K_2CO_3 solvent systems with high efficiency, low NH_3 emission, and reduced water use compared to the state-of-the-art NH_3-based technologies.
- Establish a rate-based thermodynamic modeling database for the potassium- and NH_3-based system heat and mass balance evaluations.
- Demonstrate the completely integrated absorber-regenerator CO_2 capture system at the bench-scale and optimize the system operation.
- Test two alternative flowsheets for process optimization, test system at highest possible CO_2 loadings, and determine steam usage for regeneration.
- Test the continuous operation of the process in an integrated absorber-regenerator system.
- Field test the mixed-salt process (MSP) at engineering scale to determine process operability under both dynamic and steady-state conditions using actual flue gas.
- Test the process with advanced heat integration for improved process efficiency and determine optimal regeneration energy requirement.
- Optimize the engineering-scale operation of the MSP to achieve high capture rate, high cyclic CO_2 loading, and high-purity CO_2 stream at high pressure.
- Evaluate solvent and water management strategies.
- Collect data to perform the detailed techno-economic analysis (TEA) of CO_2 capture process integration to a full-scale power plant.

technical content

SRI International is developing a novel mixed-salt solvent-based technology for post-combustion CO_2 capture using a non-degradable solvent that combines readily available, inexpensive potassium and NH_3 salt solutions and employs a novel flow configuration that is optimized to improve absorption kinetics, minimize NH_3 emissions, and reduce water use compared to state-of-the-art NH_3-based and amine technologies. The solvent and process parameters are provided in Table 1.

A singular NH_3-based process, such as chilled NH_3, has several advantages: very high CO_2 loading capacity, reduced reboiler duty due to high-pressure regeneration, and fast absorption kinetics. Challenges of this process include the need for a large water wash to reduce NH_3 emissions, requirement to chill the solvent, and energy usage for solid dissolution. A singular K_2CO_3-based process

technology maturity:

Large Pilot-Scale (~10 MWe), Actual Flue Gas

project focus:

Ammonia and Potassium Carbonate-Based Mixed Salt Solvent

participant:

SRI International

project number:

FE0031588

predecessor project:

FE0012959

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Indira Jayaweera
SRI International
indira.jayaweera@sri.com

partners:

Technology Center Mongstad (TCM), Baker Hughes (BH), Politechnico di Milano (PoliMi), OLI Systems Inc., Aqueous Solutions Aps (ASAps)

start date:

07.01.2018

percent complete:

50%

offers several advantages: no emissions, long-term industrial use, and simple permitting. However, this process has lower efficiency and CO_2 loading, as well as energy requirements for solid dissolution and vacuum water stripping. By combining these two solvent technologies, SRI capitalizes on the advantages of each while minimizing the drawbacks. The MSP maintains the high CO_2 loading and enhanced absorption kinetics, delivering high-pressure CO_2 in a solids-free system. The rate of CO_2 absorption is enhanced by having NH_3 act as a promoter that shuttles the CO_2 to the carbonate ion in the solution across the gas/liquid interface and increases the partial pressure of CO_2 in the dissolved phase. This increases the rate of CO_2 collision with carbonate ion and results in an increase in the rate of CO_2 absorption. Furthermore, by combining the salts, the capture system experiences reduced reboiler and auxiliary electricity loads, reduced NH_3 emission, reduced water usage, and a reduced system footprint.

Taking into consideration the key advantages discussed above, the regenerator energy requirement was estimated and compared to monoethanolamine (MEA)-based and pure K_2CO_3-based processes. Figure 1 shows a significant reduction in regenerator heat requirement for the MSP. In the MSP, the sensible heat is lower than that of MEA-based technology because the MSP is operated with very high CO_2 loading and lean regeneration; thus, a lower volume of solvent is required to carry the CO_2. In addition, since the regenerator operates at a higher pressure in the MSP, the reflux ratio is very low (water [H_2O]/CO_2 less than 0.01); therefore, the heat of evaporation is insignificant. The heat of reaction is considerably lower for MSP compared to amine processes, leading to further reduction in reboiler heat duty. Another key difference in the MSP is that, unlike chilled NH_3 or a neat K_2CO_3-based process, the MSP is designed to operate without solids in the absorber, eliminating additional heat requirement for solid dissolution in the regenerator or heat exchangers.

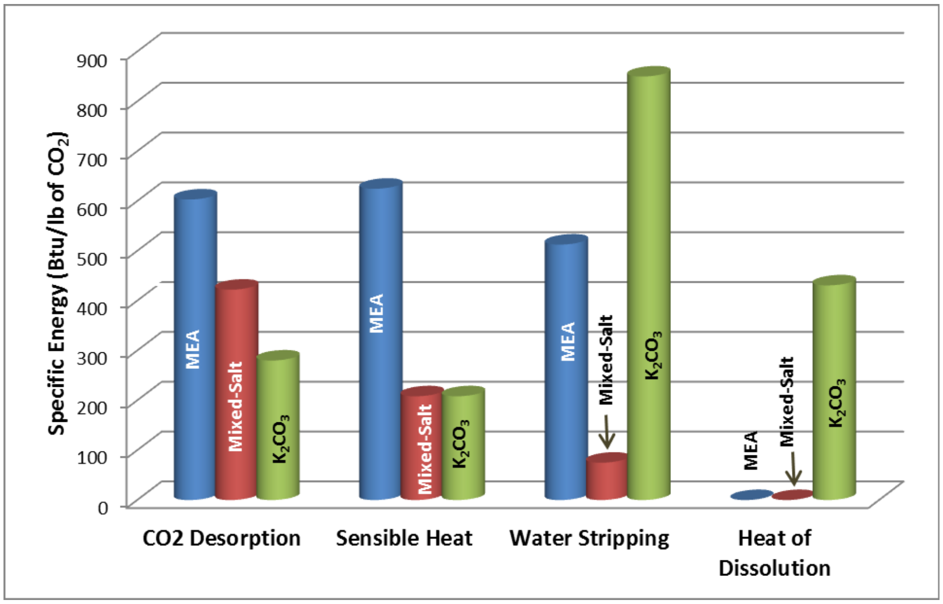


Figure 1: Estimated regenerator heat requirement for mixed-salt system with 0.2 to 0.6 cyclic loading of CO_2.

The MSP system, shown in Figure 2, comprises two isothermal absorbers, a selective regenerator, and auxiliary equipment. The absorbers operate with different ammonia to potassium ratio (NH_3/K) solutions formulated to maximize the absorption and minimize the NH_3 loss. The absorber system is designed to integrate downstream of a flue-gas desulfurization (FGD) unit in a pulverized coal power plant. The CO_2 in the flue gas stream is absorbed in the absorber columns, which are operated with liquid recycle and heat exchangers to remove the heat of reaction and keep the solution at the optimum temperature for efficient absorption and minimum NH_3 slip. The CO_2-rich solutions from the absorbers are sent to the regenerator for CO_2 stripping and solvent regeneration. The MSP uses a selective regenerator to regenerate two CO_2-lean salt streams with different NH_3/K ratios. These streams are drawn from a lower-middle stage and the bottom stage of the regenerator. The regenerator is operated at high-pressure, isobaric conditions, and has a temperature gradient along the height of the column. The key advantage of the MSP regenerator design is to capture the latent heat within the regenerator before the stream exits the vessel, thus generating almost dry CO_2 stream (H_2Ovap/CO_2 less than 0.2) at high pressure, reducing both operational and capital CO_2 compression costs. The overall benefit of MSP is a significant reduction in the cost of the CO_2 capture.

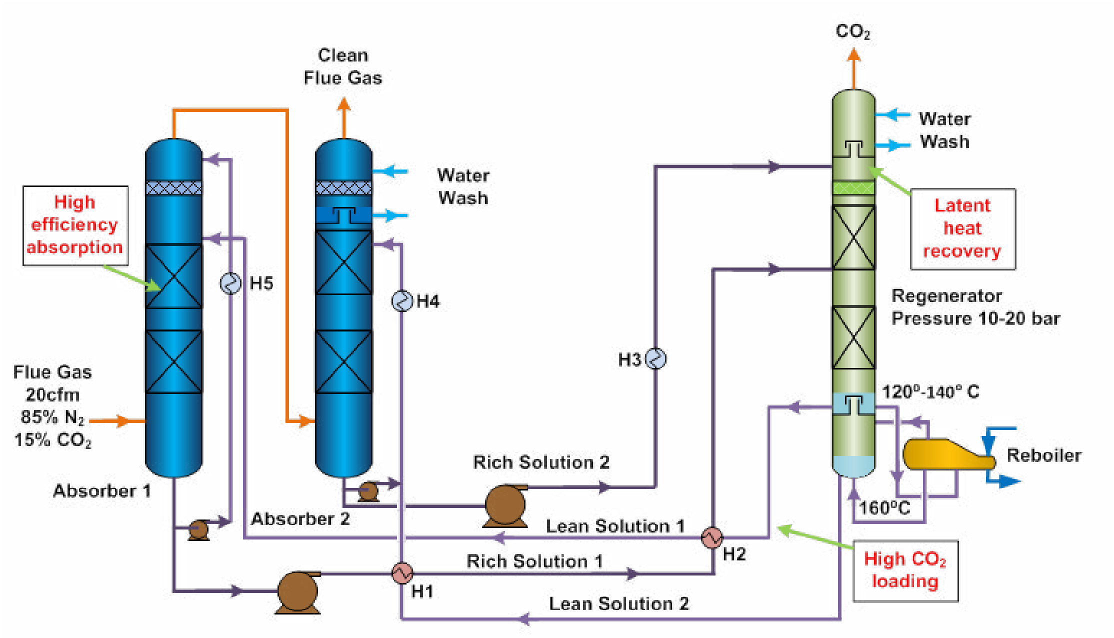


Figure 2: SRI mixed-salt simplified process diagram.

Bench-scale operation of the individual absorber and regenerator units provided optimized process parameters prior to the design and testing of the large bench-scale integrated absorber-regenerator system. The absorber was operated near ambient temperature and the regenerator was operated up to 160°C. The absorber system (Figure 3) has two absorber columns (8-inch diameter) that are designed to operate independently with different absorption solutions, and the gas stream passes through them in series. The dual absorber system operates with a high NH_3/K ratio solution in the first absorber and low NH_3/K ratio solution in the second absorber, which results in a reduction in NH_3 loss from the absorbent solution compared with a single solution approach, as shown in Figure 4. The data from the mixed-salt absorber system testing also demonstrated that it was possible to reach greater than 90% CO_2 capture even using a solution that has fairly high CO_2 loadings (e.g., in the 0.4 to 0.6 range).

Figure 3: Close-up view of two absorber columns.

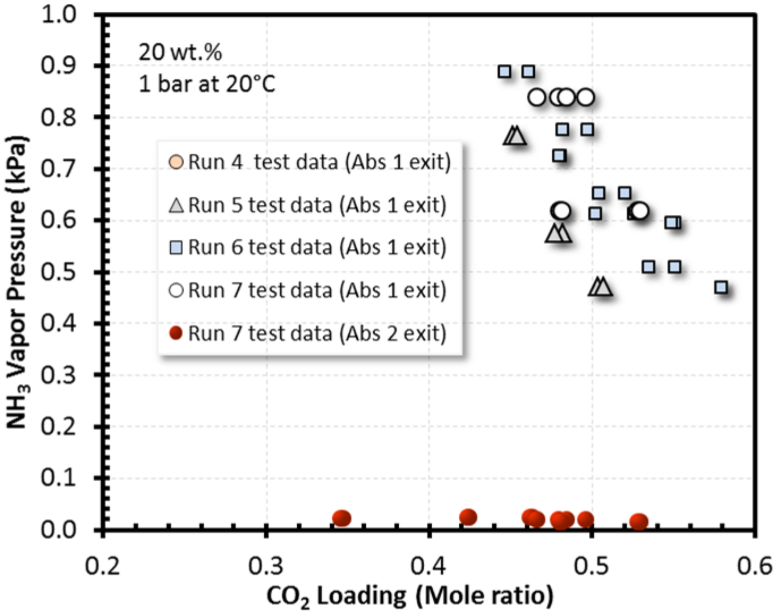


Figure 4: Measured NH_3 vapor pressure at various CO_2 loadings for tests conducted with a single absorber (Runs 4, 5, and 6) and for the test conducted with the dual absorber (Run 7).

Regenerator tests were performed with 20 and 30 wt.% mixed-salt compositions in a semi-continuous mode. Figure 5 is a photograph of the large bench-scale regenerator showing solution inlets, outlets, and heat exchangers. Figure 6 shows the number of moles of CO_2 stripped in a series of runs in the pressure ranges of 6 to 7 and 11 to 12 bar in the temperature range of 120 to 160°C for 20 wt% mixed-salt solutions with 0.49 CO_2 loading.

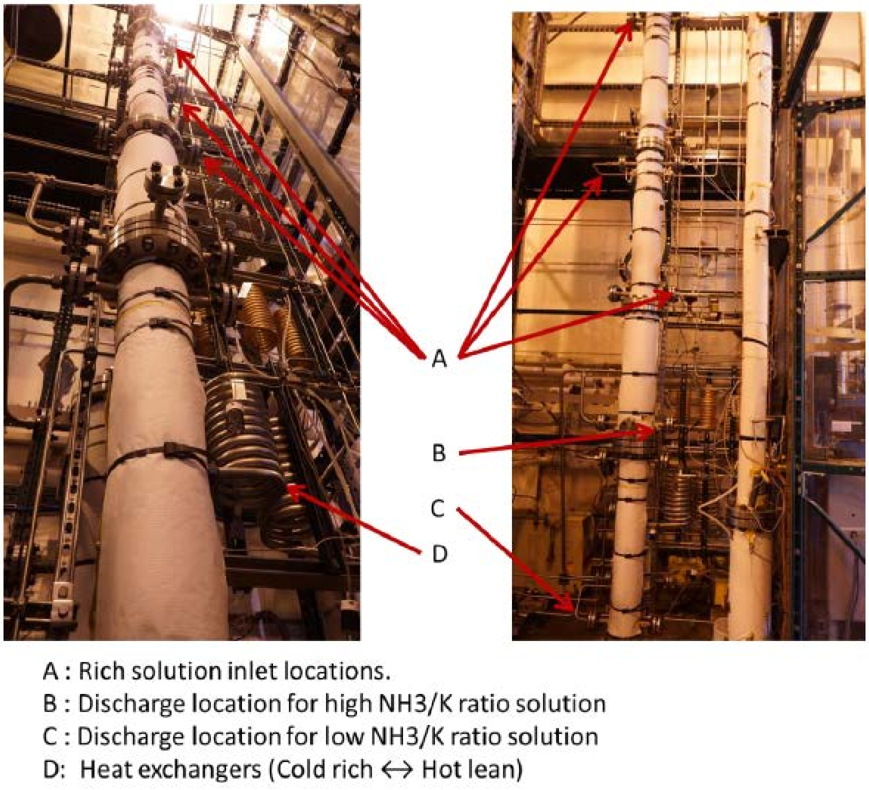


Figure 5: Large bench-scale regenerator.

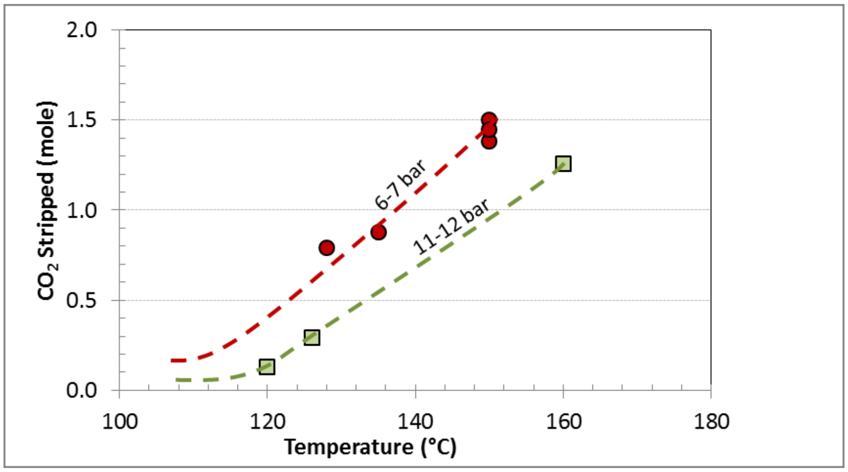


Figure 6: CO_2 stripping as a function of regeneration temperature and pressure.

The integrated bench-scale CO_2 capture and regeneration system, as depicted in Figure 2, was operated for 60 hours. The rich liquid flow from absorber 1 was split and pumped into the column at two stages with ~20% going to an upper stage. The rich solution from absorber 2 was cooled to ~15°C and pumped to the top stage of the regenerator column to reduce the NH_3 emission from the regenerator. As a polishing step, the high-pressure water wash was mounted at the very top of the regenerator such that the emitted CO_2 gas has less than 10 parts per million (ppm) NH_3 content. The lean stream with high NH_3/K ratio for absorber 1 was drawn from a lower-middle stage of the regenerator column, which was at ~130°C. The lean solution with low NH_3/K ratio for absorber 2 was drawn from the bottom stage of the regenerator column, and the temperature of this stage was about 160°C. The regenerator was operated under isobaric conditions with a temperature gradient, ~30 to 50°C at the top and 155 to 160°C at the bottom. Two main heat exchangers recovered the sensible heat from the regenerated solution to heat the incoming rich solution. The outgoing lean streams from heat exchangers were ~40°C, and thus they needed to be cooled to about 15 to 20°C before they were fed to the absorber columns. For the continuous operation of the regenerator, the input rich-solution flows and exit lean-solution flows were balanced, and the liquid levels of draw stages were carefully controlled to avoid flooding or dry-up of regenerator stages. The integrated system performed as designed with excellent absorption and regeneration cycles and demonstrated more than 90% CO_2 capture. Two variants of the MSP were tested to further decrease the NH_3 loss and water usage. In variant 1, the length of absorber 2 was increased and solvent flow recirculation was slightly modified. A water wash was also installed, with larger surface area and recirculation than the original MSP design. These changes reduced the NH_3 in the absorber exit from ~3,000 ppm to ~1,000 ppm and the NH_3 in the water wash exit to less than 10 ppm. In addition, the raw water consumption was reduced by a factor of six. In the variant 2 configuration, the CO_2-rich solution was introduced at the exit of the second absorber to reduce the NH_3 content in the gas stream leaving the absorbers. In this case, the system took longer to reach steady-state and needed higher flow rate of water in the water wash to control the NH_3 emission; thus, variant 2 was not pursued for more detailed testing.

Using the bench-scale experimental data, a rate-based model for detailed mass-balance and heat-balance calculations for a flue gas feed equivalent to a 550-MWe flue gas stream was developed and validated in OLI System's Environmental Simulation Program. Initially, OLI conducted the mass and heat balance determination for various regenerator options. The reboiler duty requirement for the best layout with 0.2 to 0.5 cyclic CO_2 loading operation was 2.0 (± 0.2) MJ/kg-CO_2. The technology was modeled for the CO_2 recovery facility, in which 90% percent of the CO_2 from the flue gas was captured from a supercritical pulverized coal plant with a nominal net output of 550 MWe (U.S. Department of Energy [DOE] Case 11). The other fixed parameters were regeneration of high-pressure CO_2 at 99% purity and an NH_3 release from the absorber that was less than 10 ppm. The study showed the technology offers much lower energy penalty than Fluor Econamine FG Plus^{SM} technology, which uses a formulation of MEA and a proprietary corrosion inhibitor to recover CO_2 from the flue gas.

A field test of the MSP at engineering-scale is being conducted using the existing Chilled Ammonia Process (CAP) infrastructure at Technology Center Mongstad (TCM) in Norway. Re-commissioning of the CAP system is required prior to conducting the field test, followed by a hazard and operability (HAZOP) evaluation. Modeling of the modified flowsheet is being performed to identify the optimal configuration for MSP implementation at TCM. The process involves modeling of individual systems blocks (absorber, regenerator, and NH_3 recovery block) separately and then integrating them with the inclusion of flow stream. The absorber block includes three absorbers. In these studies, the NH_3 emission from the water wash tower (less than 10 ppm) and the CO_2 capture efficiency (greater than 90%) were set as fixed parameters.

Figure 7 shows the comparison between the CO_2 capture efficiency profiles in each of the absorbers for configurations A and B as predicted by the model.

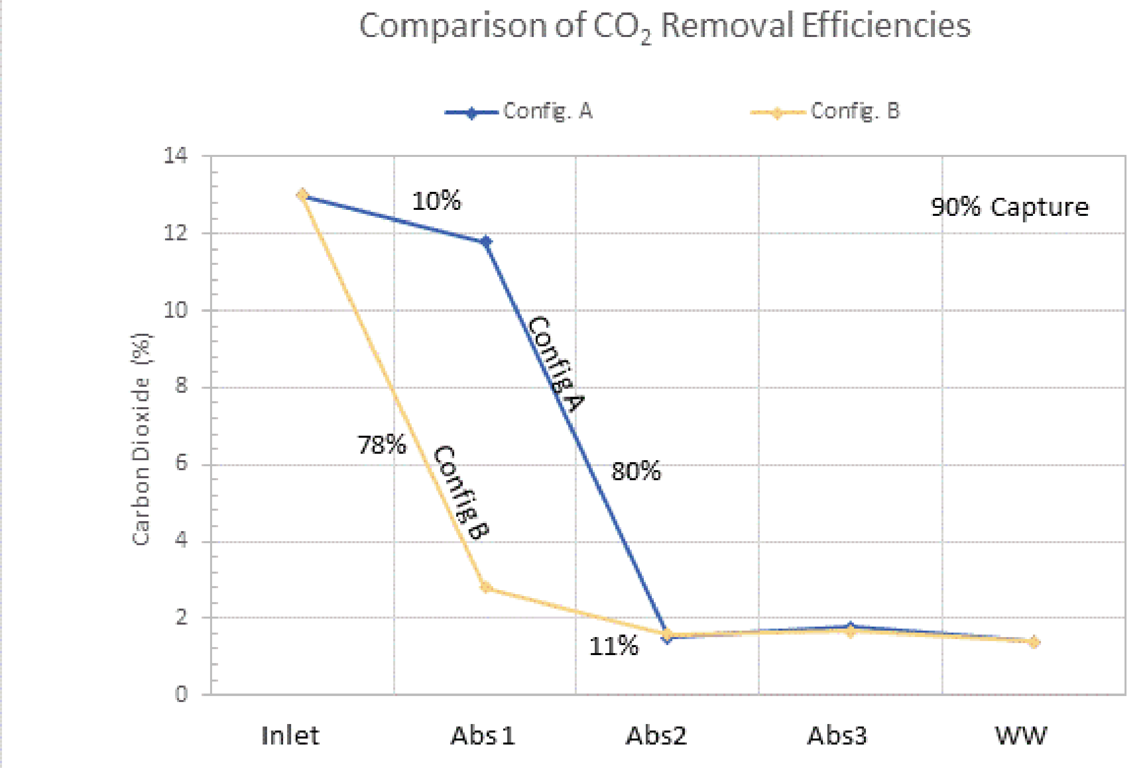


Figure 7: CO_2 capture efficiency profiles for configurations A and B (total of 90% capture in both cases).

Testing of the integrated system, along with process modeling, provided parametric optimization to update the TEA and determine costs associated with the use of this system in a 550-MWe power plant. The cost of electricity (COE) found in the analysis of the mixed-salt technology was 126.1 \$/MWh, yielding a reduction of 11.7% compared to the National Energy Technology Laboratory (NETL) Case 12B COE of 142.8 \$/MWh.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15°C	bar	0.17	0.17
Manufacturing Cost for Solvent	\$/kg	-	-
Working Solution			
Concentration	kg/kg	0.27-0.35	0.35
Specific Gravity (15°C/15°C)	-	1.1-1.3	1.1-1.3
Specific Heat Capacity @ STP	kJ/kg-K	3.0-4.0	3.0-4.0
Viscosity @ 15°C	cP	1.6	1.6
Absorption			
Pressure	bar	1	1
Temperature	°C	20-40	25-40
Equilibrium CO_2 Loading	mol/mol	0.6 (rich)	0.6 (rich)
Heat of Absorption	kJ/mol CO_2	1,000–1,200	<1,200
Solution Viscosity	cP	1.5-1.8	<1.9

Desorption				
Pressure	bar	10-15		10
Temperature	°C	120-170		120-170
Equilibrium CO_2 Loading	mol/mol	0.2 (lean)		<0.2 (lean)
Heat of Desorption	kJ/mol CO_2	1,000-1,200		<1,200
Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		-	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	~20
Absorber Pressure Drop	bar		<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – In the MSP, CO_2 is captured by a chemical absorption that involves a series of ionic chemical reactions among CO_2, NH_3, K_2CO_3, and H_2O. The mechanism of CO_2 capture by chemical absorption using various chemical formulations has been studied extensively. The MSP chemistry comprises gas/liquid-phase mass transfer, followed by a series of chemical reactions in the liquid phase. The overall process chemistry can be summarized as:

$$K_2CO_3 - NH_3\text{-}xCO_2\text{-}H_2O \leftrightarrow K_2CO_3 - NH_3\text{-}yCO_2\text{-}H_2O$$

Where $y > x$

Solvent Contaminant Resistance – The solvent is expected to be resistant to several contaminants, such as sulfur oxides (SO_X) and nitrogen oxides (NO_X), nominally present in a flue gas stream. Sulfur dioxide (SO_2) reacts with the solvent, but it can be removed in the direct contact cooler section as sulfates. The resistance of the solvent to trace metals is not yet known.

Solvent Foaming Tendency – Solvent foaming tendency was not observed in the bench-scale tests.

Flue Gas Pretreatment Requirements – Unlike in an MEA system, a mixed-salt system does not require deep FGD; 200-ppm level SO_2 is acceptable.

Solvent Makeup Requirements – Mixed-salt is a mixture of NH_3 and K_2CO_3 and it is inexpensive and readily available. The loss of the solvent is expected to be less than 0.2 kg/tonne of CO_2 captured.

Waste Streams Generated – Water wash with trace ammonium sulfate from the SO_2 captured by the direct contact cooler.

Process Design Concept – See Figure 2.

technology advantages

- Low heat of reaction (35 to 50 kJ/mol) and low reboiler duty (~2 MJ/kg of CO_2).
- High temperature (20 to 40°C) absorber operation without solvent chilling.
- High CO_2 loading capacity (10 wt%).
- High-pressure regeneration of greater than 99% pure dry CO_2, resulting in reduced compression costs.
- Low sensitivity to impurities.
- Non-degradable solvent uses inexpensive, industrially available materials.
- Low NH_3 emissions using two-stage absorber approach.
- Low water usage.
- Requires no feed stream polishing.
- No hazardous waste generation.
- Uses known process engineering.
- Operates with no solids in the absorber.
- Reduced energy consumption compared to MEA.
- Reduced auxiliary electricity loads.

R&D challenges

- Residual NH_3 in the exit gas stream.
- Reduction of NH_3 evaporation at higher reaction rates.
- High-pressure drop in absorber column.

status

SRI has completed bench-scale testing of the integrated two-stage absorber system with the regenerator using simulated flue gas, indicating cyclic operation with greater than 90% CO_2 capture (at ~0.3 ton/day) with cyclic CO_2 lean and rich loading between 0.2 and 0.59 mol/mol (maximum cyclic CO_2 loading achieved is ~10 wt%). Lean solutions with two compositions, NH_3-rich and potassium-rich, were generated using a two-stage regenerator. The two-stage absorber approach showed a reduction in NH_3 emissions. Overall, long-term operability of the integrated system was shown over 2.5 years. The TEA for the mixed-salt technology showed a reduction in heat duty (compared to the Fluor Econamine FG Plus^{SM} baseline technology) from 3.56 to 2.0 MJ/kg CO_2 and a cost of CO_2 captured of approximately $38/tonne CO_2. In preparation for field testing of the MSP at TCM, SRI has completed the HAZOP evaluation of the CAP system and reconfigured MSP pilot system and has conducted flowsheet modeling to determine the process configuration that is best suited for MSP implementation at TCM.

available reports/technical papers/presentations

Jayaweera, I., “Engineering-Scale Demonstration of Mixed-Salt Process (MSP) for CO_2 Capture,” presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/I-Jayaweera-SRI-Mixed-Salt-Capture-Process.pdf*.

Jayaweera, I., “Engineering-Scale Demonstration of Mixed-Salt Process (MSP) for CO_2 Capture,” Project Kick-off and BP1 Review Meeting, October 2018. *https://netl.doe.gov/projects/files/Engineering%20Scale%20Demonstration%20of%20Mixed-Salt%20Process%20for%20CO2%20Capture%20Oct%202018.pdf*.

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Engineering-Scale Testing of Transformational Non-Aqueous Solvent-Based Carbon Dioxide Capture Process at Technology Centre Mongstad

primary project goals

Research Triangle Institute (RTI) is developing and testing at large pilot-scale a non-aqueous solvent (NAS; i.e., water-lean solvent) carbon dioxide (CO_2) capture process to confirm the potential to reduce the parasitic energy penalty associated with the capture of CO_2 from flue gas; demonstrate the long-term process operational reliability at static and dynamic conditions; and verify the solvent degradation rate, emissions, solvent loss, and corrosion characteristics of the solvent at engineering scale.

technical goals

- Evaluate water-lean solvent degradation and material compatibility.
- Measure water-lean solvent performance over static and dynamic operating conditions.
- Design/procure water-lean solvent-specific components for implementation in the host site facility.
- Confirm a reduction in parasitic energy penalty to less than 2.1 gigajoules (GJ)/tonne CO_2 captured.
- Complete a techno-economic analysis (TEA) to confirm RTI's NAS process can reduce CO_2 capture costs.

technical content

RTI is advancing the development of a water-lean solvent-based CO_2 capture process that was previously developed and tested at lab- and bench-scale (~10 kilowatts [kW]) with simulated flue gas under the U.S. Department of Energy (DOE)-funded project FE0013865. Water-lean solvents have the potential to significantly reduce the cost of CO_2 capture from coal-fired flue gas when compared to aqueous amine-based solvent processes by reducing the energy required for solvent regeneration. RTI's water-lean solvent is a hydrophobic, sterically hindered, carbamate-forming amine with low-water solubility solubilized in a diluent having low vapor pressure and low viscosity. It is characterized by low heats of absorption and generation of high CO_2 partial pressures at low temperatures and has the potential to reduce the regeneration energy to less than 2.1 GJ/tonne CO_2. The overall reboiler heat duty, or thermal regeneration energy, is made up of the sensible heat, heat of vaporization of water, and heat of absorption. The heat of vaporization, due to the lack of water, is significantly less for water-lean solvents than for aqueous amine-based processes. Also, water-lean solvents overcome the foaming issues that are often associated with aqueous

technology maturity:

Large Pilot-Scale (~10 MWe), Actual Flue Gas

project focus:

Water-Lean Solvent

participant:

Research Triangle Institute

project number:

FE0031590

predecessor projects:

FE0026466
FE0013865

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Marty Lail
Research Triangle Institute
mlail@rti.org

partners:

Technology Centre Mongstad (TCM), Electric Power Research Institute, Inc., Linde, SINTEF

start date:

08.08.2018

percent complete:

55%

solvents, as shown in Figure 1. RTI's CO_2-rich water-lean solvent has a viscosity of less than 30 cP and is non-foaming.

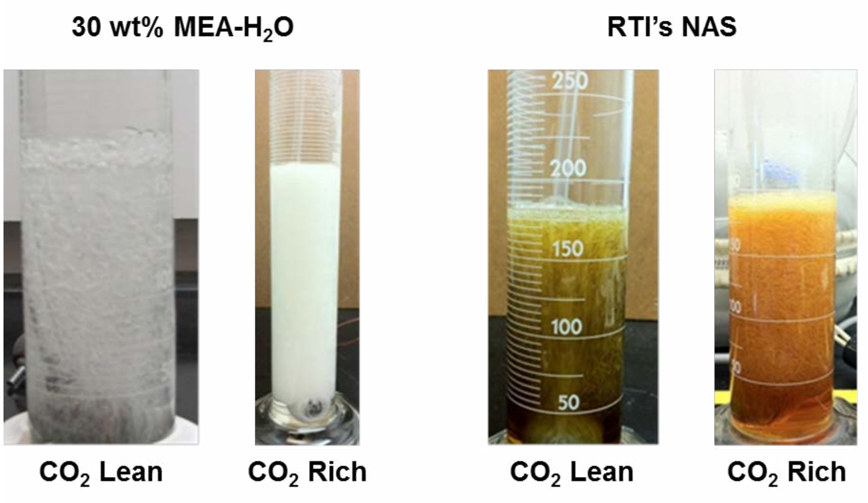

Figure 1: Comparison of foaming in aqueous and RTI's water-lean solvents.

The NAS CO_2 capture process includes a solvent regenerator design specifically for water-lean solvents that combines heat delivery and gas release in a single-step process unit to maintain lower regeneration temperatures. The process, as shown in Figure 2, is similar to conventional solvent scrubbing systems with key novel design features:

- NAS solvent recovery and wash section—similar to water washing, but water-lean solvents have low water-solubility.
- Solvent regenerator—lack of low-boiling component (conventional reboilers are not applicable).

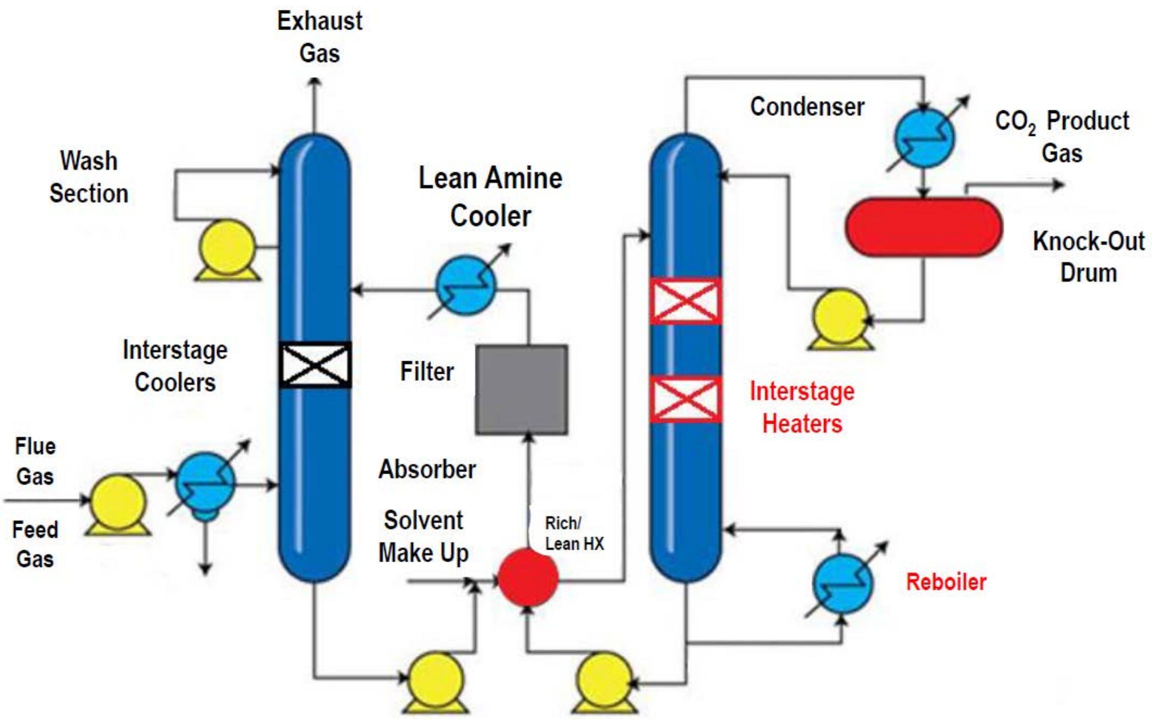

Figure 2: NAS CO_2 capture process diagram.

Under DOE-funded project DE-FE0026466, RTI used the bench-scale test unit (up to 60 kW) at SINTEF's Tiller plant to experimentally show that the water-lean solvent is capable of achieving 90% CO_2 capture and generating a high-purity CO_2 product (greater than 95% CO_2), as well as to evaluate the effectiveness of the developed NAS recovery/wash section and solvent regenerator design. Bench-scale testing at SINTEF's Tiller plant was first performed using the monoethanolamine (MEA) control and the water-lean solvent in an unmodified configuration of the test unit. Baseline testing of the water-lean solvent using propane and coal-fired flue gas was performed over a period of approximately four months, showing a CO_2 capture rate of approximately 90%. Heat stable salts (HSS) and metals analyses were used to determine the solvent stability and corrosion. The HSS level was relatively constant and low during the test campaign. The results also indicate that the corrosion rate of NAS is quite low and stable, confirming previous test results that showed much lower corrosion rate for NAS as compared with MEA.

As the CO_2 capture system at Tiller was designed specifically to achieve the optimum performance for an aqueous-based solvent, it is not an ideal setup to realize the energy reduction benefit by using the water-lean solvent. Based on the knowledge acquired throughout the testing in RTI's gas absorption system (BsGAS) with various process configurations, the following modifications (Figure 3) to the existing absorption system at the Tiller plant were made:

- Addition of two interstage coolers between existing sections of packing in the absorber.
- Replacement of three existing packing sections in the regenerator column with three new sections consisting of an electric/steam heating portion located at the top-half of the section and a high surface area packing portion located at the bottom-half of the section.
- Expansion of lean-rich heat exchanger by adding a second crossover plate-and-frame heat exchanger in series.
- Addition of coal-fired burner.
- Rich solvent preheater installed at regenerator inlet.
- Addition of an acid wash/water wash section.

Result Highlights:

- Interstage heaters: 2.19 (all) to 2.86 (none) GJ/tonne-CO_2
- Interstage coolers: 2.19 (all) to 3.23 (none) GJ/tonne-CO_2
- The use of preheater (HX-305) lowers the SRD

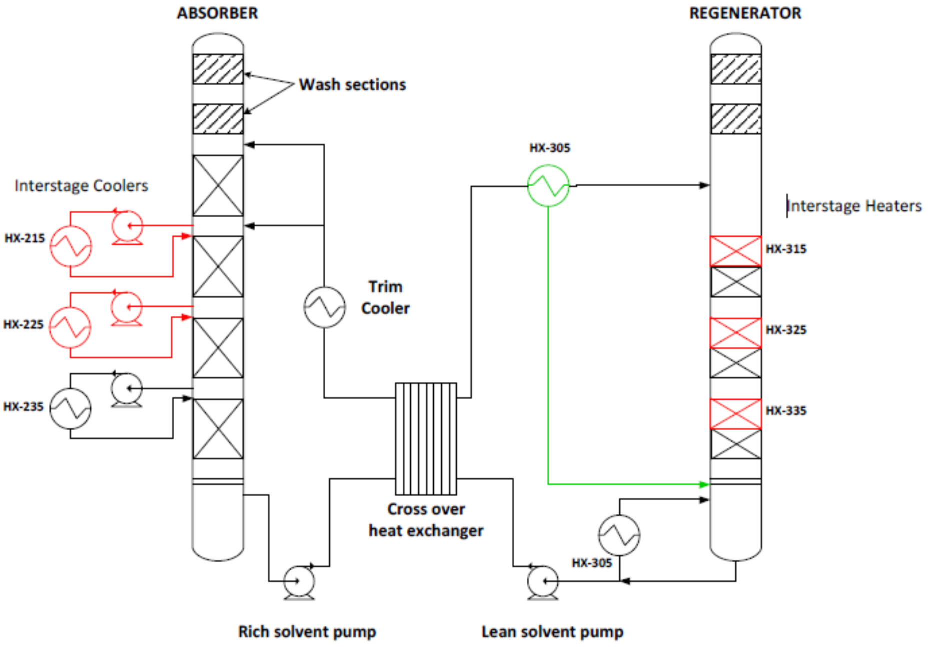

Figure 3: Design improvements for NAS-based process.

The solvent formulation was also refined to increase CO_2 loading and working capacity and to reduce the reboiler heat duty required for solvent regeneration. The improved formulation (NAS-5) results in an increase in CO_2 working capacity from ~0.45 $\text{mol}_{CO2}/\text{mol}_{amine}$ to ~0.48 $\text{mol}_{CO2}/\text{mol}_{amine}$, and a decrease in heat of absorption from ~82 kilojoules (kJ)/mol_{CO2} to ~75 kJ/mol_{CO2}, and is expected to reduce the reboiler heat duty by decreasing the liquid/gas (L/G) ratios and the heat of absorption at higher temperatures. Through testing in RTI's bench-scale BsGAS, it was found to be advantageous to use two interstage coolers in the absorber column (with one at the bottom and one at the top) to achieve a heat duty near 2 MJ/kg-CO_2. The coolers play an essential role in lowering the temperature in the absorber column to maintain a high CO_2 loading in the solvent. A wash column was added to RTI's BsGAS to allow for testing different conditions to reduce amine losses for the technology, demonstrating that the wash section could effectively remove 92 to 93% of the amine emissions from the absorber.

Following the installation of the NAS-specific components into the Tiller plant, including a new particulate filter, updated coal-burner control software, additional absorber intercoolers, additional water wash section, regenerative "inter-heaters," and one additional crossflow heat exchanger, parametric testing was performed with NAS-5 to allow optimal operating conditions to be identified and long-term testing to be completed. Test results showed an average CO_2 capture rate of 90% and the lowest reboiler heat duty obtained was 2.3 GJ/tonne CO_2 when the rich solvent pre-heater was used.

Additional baseline testing of the new water-lean solvent formulation was performed at the National Carbon Capture Center (NCCC) to investigate solvent degradation, corrosion, and emissions using the Slipstream Solvent Test Unit (SSTU) with long-term exposure to coal-derived flue gas from the Gaston Power Plant in Wilsonville, Alabama. The NCCC system was operated for 580 hours with flue gas with intermittent delays. The effects of flue gas velocity, CO_2 capture efficiency, and aerosols on amine emissions were studied during the test campaign. Preliminary testing has indicated that the water-lean solvent displays minimal corrosion; therefore, the materials of construction for some of the equipment could be replaced with lower cost options. A TEA and environmental, health, and safety (EH&S) assessment of the NAS process based on test data obtained from SINTEF's Tiller plant and from the SSTU at NCCC show that the NAS technology has the potential to meet DOE's $40/tonne CO_2 capture target when it is fully developed and poses little EH&S risk.

In RTI's current DOE-funded project, engineering-scale tests are being performed using the existing large pilot infrastructure at the Technology Centre Mongstad (TCM) in Norway. The test campaign includes baseline testing with the water-lean solvent in TCM's 12-megawatt-electric (MWe) pilot plant in the configuration designed for aqueous-amine solvents, a hardware revamp of the plant to implement NAS-specific components, and follow-on NAS testing under optimized conditions. Based on the findings realized during the evaluation of RTI's BsGAS and SINTEF's Tiller plant under various process configurations, the following modifications to the existing system at TCM are being made:

- Addition of one or two interstage coolers between existing sections of packing in the absorber.
- Rich solvent preheater installed between rich outlet of rich/lean heat exchanger and regenerator inlet.
- Expansion of lean-rich heat exchanger by adding a second crossover plate and frame heat exchanger in series.

In addition, strategies for reducing the amine emissions to less than 1 part per million (ppm) are being implemented to meet TCM's emissions requirements, including modifying the existing water wash section of the TCM unit, lowering the gas flow rate, and adding an intercooler to the absorber. Large pilot-scale test results will be used to demonstrate the applicability of the water-lean solvent as a drop-in replacement solvent in conventional capture systems and the process scalability and commercial potential of RTI's transformational NAS CO_2 capture process for pulverized coal power plants.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	$/kg	30	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38
Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/kg CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28
Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45–1.13*	0.45

Heat of Desorption	kJ/kg CO_2	2,100*	2,045

* Experimentally measured data.
** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxides (SO_X) and nitrogen oxides (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2 to 0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

technology advantages

- Low water solubility.
- Reduced regeneration energy.
- High solvent regeneration pressure at low regeneration temperatures, such that desorbed CO_2 can go directly to second stage of compression.
- Favorable thermodynamics.
  - Low heat of absorption.
  - High working capacity based on vapor-liquid equilibrium (VLE).
- Excellent thermal and oxidative stability; no formation of HSS.
- Low vapor pressure (less than 0.3 kPa [40°C], less than 10 ppm emissions in treated flue gas).
- Low conductivity; low corrosion rates.
- Low oxygen solubility.

R&D challenges

- Implementation of NAS-specific components into host site facility.
- Effective control of water content in both the rich and lean water-lean solvent solution to minimize regeneration energy required.
- Minimizing the rise in absorber temperature.
- Operating TCM plant within emission requirements.
- Obtaining sufficient heat exchange for optimal performance.
- Improving the working capacity of the solvent.
- Solvent emissions control.

status

RTI has tested multiple water-lean solvent formulations and identified an improved formulation (NAS-5). Experimental testing of NAS-5 in RTI's BsGAS showed that the lowest regeneration of 2.15 MJ/kg CO_2 was achieved when the system operated at L/G of 4.2. The team performed 405 hours of NAS baseline testing at the SINTEF Tiller plant in an unmodified configuration, revealing that the energy required for solvent regeneration is 15% lower for NAS than that for MEA, even though NAS was run under less-than-optimal conditions. Parametric testing and a cumulative 1,200 hours of long-term testing of NAS-5 in the Tiller plant were conducted following installation of NAS-specific components to determine optimal operating parameters and validate reduced reboiler duty. The lowest specific reboiler heat duty of 2.3 GJ/tonne CO_2, water balance, and operational stability were maintained during about 1,600 hours of testing using the NAS-5 formulation. Additional water-lean solvent baseline testing using coal-fired flue gas at NCCC showed that 90% CO_2 capture is consistently observed under varying test conditions. In preparation for large pilot-scale testing, RTI initiated design and engineering of TCM facility modifications, and a front-end engineering design (FEED) study to determine the cost of modifications is underway. In addition, solvent qualification testing is underway at SINTEF to demonstrate performance of the manufactured solvent.

available reports/technical papers/presentations

Lail, M., "Engineering Scale Testing of Transformational Non-Aqueous Solvent-Based CO_2 Capture Process at Technology Centre Mongstad," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Lail-RTI-Testing%20at%20TC%20Mongstad.pdf*.

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Zhou, S. James, “Engineering Scale Testing of Transformational Non-Aqueous Solvent-Based CO_2 Capture Process at Technology Centre Mongstad,” presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/projects/files/Engineering%20Scale%20Testing%20of%20Transformational%20Non-Aqueous%20Solvent-Based%20CO2%20Capture%20Process%20at%20Technology%20Centre%20Mongstad%20(Aug%202018).pdf*.

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Zhou, S., “Large Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants Utilizing Real Coal Derived Flue Gas,” Budget Period 1 Project Review Meeting, Pittsburgh, PA, April 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026466-BP1-Review.pdf*.

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Zhou, S. James, et. al., “Non-Aqueous Solvent CO_2 Capture Process,” November 14 - 18, 2016, GHGT 13, Lausanne, Switzerland.

Lail, M., “Bench-Scale Development of a Non-Aqueous Solvent CO_2 Capture Process for Coal-Fired Power Plants,” 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *http://netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/M-Lail-RTI-Non-Aqueous-Solvent-CO2-Capture.pdf*.

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Alkanolamines for Acid Gas Removal in Gasification Processes

primary project goals

Pacific Northwest National Laboratory (PNNL) is performing this project to identify candidate molecules that have high carbon dioxide (CO_2) selectivity compared to other components of syngas (carbon monoxide [CO], hydrogen [H_2], and water [H_2O]). This is being done by conducting high-pressure nuclear magnetic resonance (NMR) measurements using PNNL's custom high-pressure NMR cells. Candidate molecules will be identified by conducting vapor-liquid equilibria (VLE) measurements of anhydrous tertiary alkanolamines with individual components of syngas (CO, CO_2, H_2, and H_2O) and simulated syngas. Two-dimensional (2D) NMR measurements are being used to measure diffusion coefficients for CO_2 and the solvent molecules, which can then be used to calculate the viscosity of the solutions. A preliminary techno-economic assessment (TEA) will be made to determine energy savings over activated methyldiethanolamine (aMDEA) for CO_2 capture from syngas.

technical goals

- Identify candidate molecules that have high CO_2 selectivity compared to other components of syngas (CO, H_2, and nitrogen [N_2]).
- Obtain VLE measurements of anhydrous tertiary alkanolamines with individual components of syngas (CO, CO_2, H_2, and N_2).
- Measure diffusion coefficients of CO_2 and the solvent molecules using 2D NMR.
- Perform a preliminary TEA.
- Optimize solvent formulations and measure viscosities using a high-pressure viscometer.
- Design, construct, and shakedown a high-pressure pressure-volume-temperature (hp-PVT) cell with validation against known solvent standards, such as aMDEA or Selexol.
- Perform comprehensive property testing (VLE, viscosity, density, and mass transfer coefficients) for the best solvent or blend using hp-PVT cell.
- Perform final TEA and process performance projections.
- License intellectual property and transfer it to industrial partner.

technical content

To begin this effort, PNNL performed screening for CO_2-binding organic liquid (CO_2BOL) solvents suitable for removal of CO_2 from syngas. Three alkanolamine pressure-swing regeneration solvents were selected for screening: EDEA, DMEA, and PSA-1 (Figure 1). Additionally, four thermal regeneration solvents were evaluated for this application: three aminopyridines (2-MAMP, 2-EAMP, and AP) and a diamine

technology maturity:

Laboratory-Scale, Simulated Syngas

project focus:

CO_2-Binding Organic Liquid Solvents

participant:

Pacific Northwest National Laboratory

project number:

FWP-72564

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Phillip Koech
Pacific Northwest National Laboratory
phillip.koech@pnnl.gov

partners:

Susteon Inc

start date:

10.01.2018

percent complete:

54%

(DA; Figure 1). The specific names and structures of PSA-1, AP, and DA are currently proprietary. EDEA and DMEA solvents have shown promising CO_2 uptake capacity with both chemical and physical absorption, but the performance dropped significantly in mixed gases. The aminopyridines (2-MAMP, 2-EAMP, and AP) and DA bind CO_2 chemically at ambient pressure with potential additional physical absorption under elevated pressures.

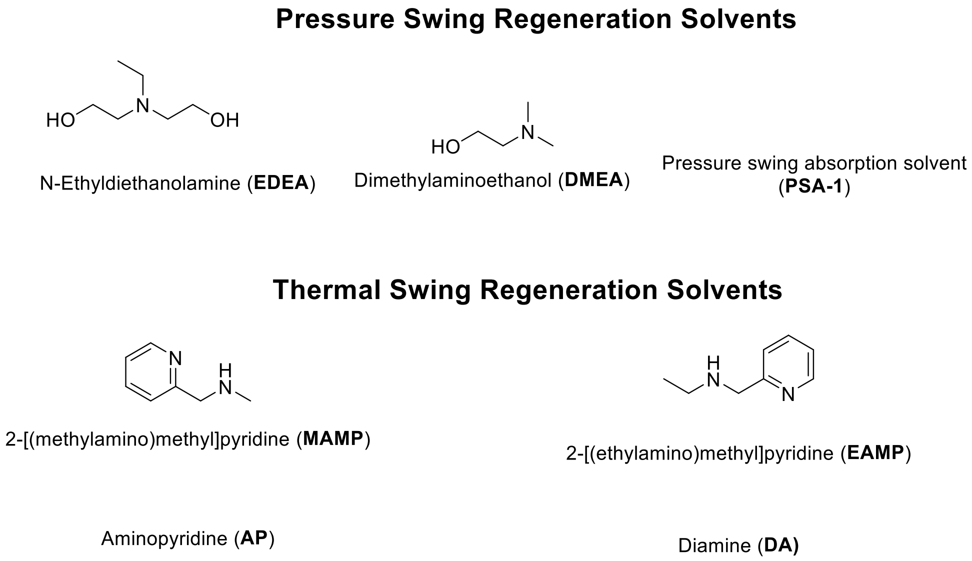

Figure 1: Amine solvents tested for CO_2 capture.

In order to improve the CO_2 solubility of pressure-swing absorption (PSA) solvents such as EDEA and DMEA, a new solvent designated as PSA-1 was designed using learnings from past post-combustion CO_2 capture work to increase CO_2 solubility while lowering viscosity. VLE measurements for the PSA-1 solvent showed the highest physical solubility (42.22 mol% of CO_2) compared to all CO_2BOL solvents. It also showed minimal chemical absorption of 1.38 mol% as carbonate, resulting into a total uptake capacity 43.6 mol%. PSA-1 exhibited similar drop in CO_2 capacity in mixed gases as EDEA and DMEA.

Thermal-swing solvents, DA and AP, exhibited excellent CO_2 uptake capacity without significant drop in mixed gases, but they suffered from increased viscosity under syngas conditions. It was hypothesized that a blend of the best thermal- and pressure-swing solvents would result in a formulation with high CO_2 capture capacity and low viscosity. To evaluate this concept, controlled blends of DA (the best thermal-swing solvent) and PSA-1 (the best pressure-swing solvent) were made, and the VLE data of these blends were measured. The gravimetric CO_2 uptake capacity of the DA:PSA-1 blends shows a good uptake capacity under both pure CO_2 and mixed gas containing CO_2 and H_2. These solvent formulations have negligible H_2 uptake under gravimetric conditions.

A blend of the 1:1 mole ratio of DA and PSA-1 was selected for VLE studies using a redesigned high-pressure NMR cell. Figure 2 shows VLE data for 1:1 DA:PSA-1 for CO_2:H_2 (1:1) gas mixture at 35 bar. This figure shows high CO_2 uptake and VLE as a function of temperature follows the expected trend of decreasing uptake with increased temperature.

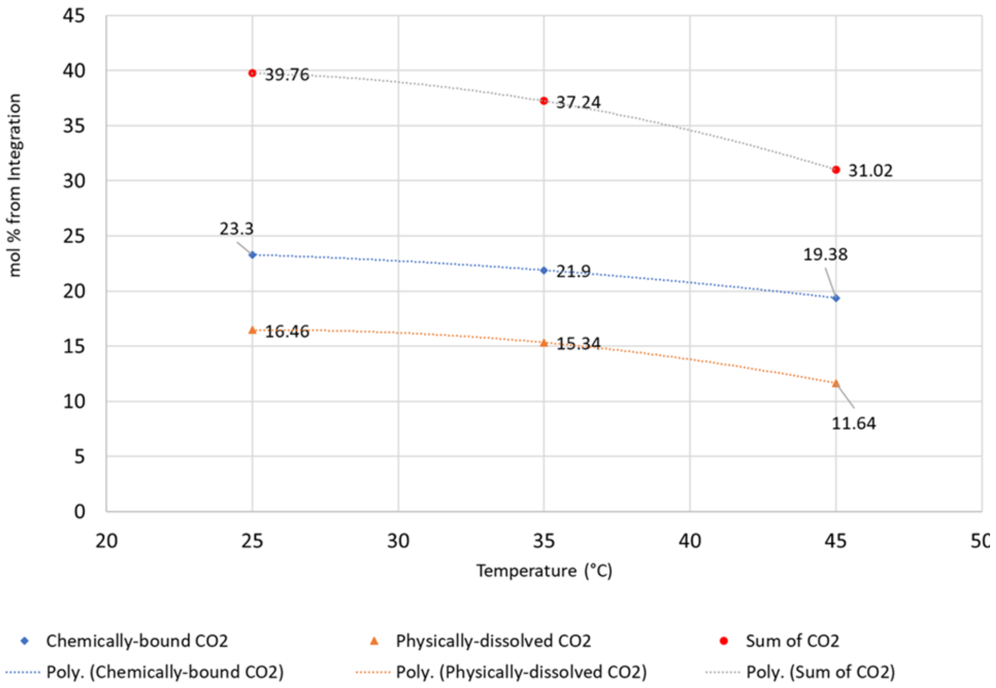

Figure 2: VLE for 50:50 DA:PSA-1 for CO_2:H_2 (1:1) gas mixture at 35 bar.

Low viscosity of the CO_2-rich solvent is critical for both low capital and operation cost of the plant. To understand the viscosity of the promising formulation, the viscosity was measured at a CO_2 pressure of 500 pounds per square inch (psi). Figure 4 shows the viscosity of DA:PSA-1 (1:1) as a function of temperature. The highest viscosity measured for this formulation at 25°C was ~16 cP, which decreased to 4.2 cP when the temperature increased to 45°C, which is comparable to the viscosity of the aMDEA solvent.

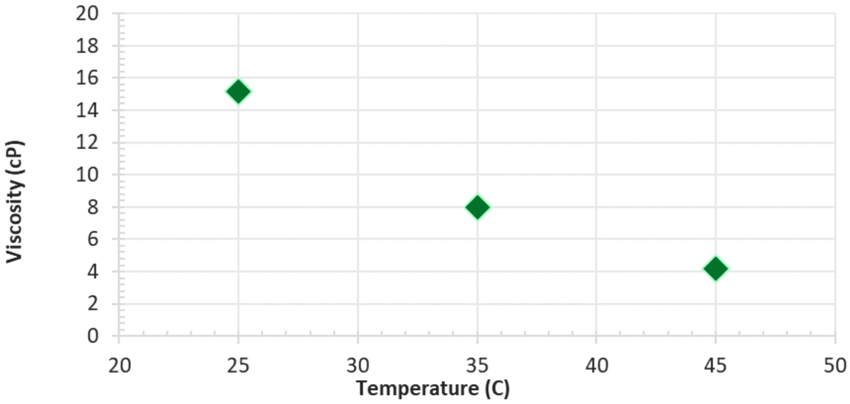

Figure 3: Viscosity versus temperature DA:PSA-1 (1:1) under 500 psi CO_2.

Susteon developed a series of process configurations to maximize the CO_2 capture efficiency of the solvent, while minimizing the overall energy requirement and capital cost of the process. This analysis led to a regeneration scheme with a combination of a flash pressure-reduction and a small reboiler. Preliminary results from this analysis indicated a total energy requirement between 0.64 to 0.69 gigajoules (GJ)/tonne of CO_2 compared to about 1 GJ/tonne of CO_2 for the current state-of-the-art process technologies. These values show that there is a strong potential to achieve up to a 28% improvement in the total energy for CO_2 capture from high-pressure syngas mixtures using the new mixed solvent as a replacement or drop-in solvent in existing commercial aMDEA plants.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	TBD	-
Normal Boiling Point	°C	TBD	-
Normal Freezing Point	°C	TBD	-
Vapor Pressure @ 15°C	bar	TBD	-
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	TBD	-
Specific Gravity (15°C/15°C)	-	TBD	-
Specific Heat Capacity @ STP	kJ/kg-K	-	-
Viscosity @ 15°C	cP	~16	~16
Absorption			
Pressure	bar	-	-
Temperature	°C	25-45	-
Equilibrium CO_2 Loading	mol/mol	TBD	-
Heat of Absorption	kJ/mol CO_2	TBD	-
Solution Viscosity	cP	-4	-
Desorption			
Pressure	bar	-	-
Temperature	°C	-	-
Equilibrium CO_2 Loading	mol/mol	TBD	-
Heat of Desorption	kJ/mol CO_2	TBD	-
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 -	
Absorber Pressure Drop	bar	-	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Combination of physical and chemical.

Solvent Contaminant Resistance – Currently unknown.

Solvent Foaming Tendency – Currently unknown.

Flue Gas Pretreatment Requirements – Currently unknown.

Solvent Makeup Requirements – Currently unknown.

Waste Streams Generated – Currently unknown.

Process Design Concept – The DA:PSA-1 mixed solvent can be used as a drop-in replacement solvent in a commercial aMDEA CO_2 capture process.

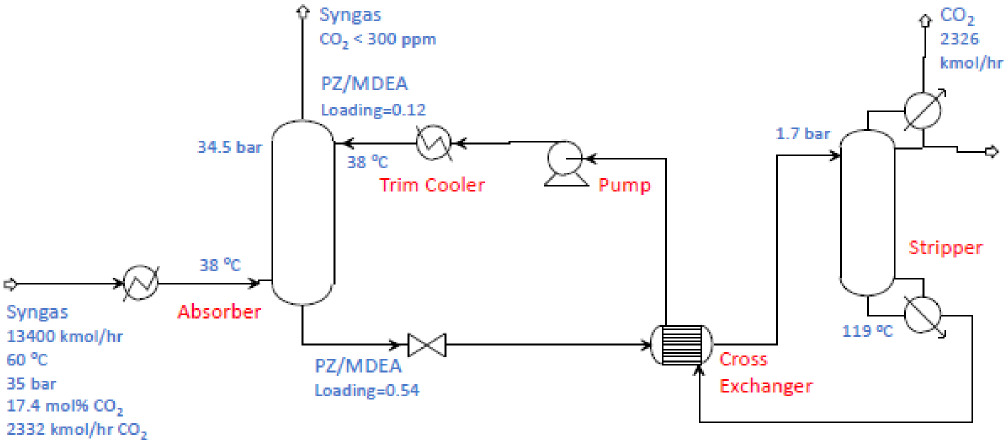

Figure 4: Configuration and operating conditions of the aMDEA process.

technology advantages

- Low regeneration energy requirements (less than 0.7 GJ/tonne CO_2).
- Lower capital cost from small equipment resulting from higher CO_2 capacity and CO_2 selectivity.
- Mixed DA:PSA-1 solvent can be used as a drop-in replacement in an aMDEA process.

R&D challenges

- Resource risks, including availability of equipment and staff availability.
- Effect of flue gas contaminants is currently unknown.
- Improving performance in mixed gases versus pure CO_2.

status

A new PSA solvent was developed, PSA-1, which was designed to improve CO_2 solubility without increasing viscosity. This new solvent had the highest physically absorbed CO_2 of all CO_2BOLs (about 44 mol%), but similar to the other PSA solvents, the CO_2 uptake capacity significantly dropped in mixed gases. Thus, it is not able to achieve greater than 90% CO_2 capture from syngas streams.

The TSA solvents, namely 2-MAMP, 2-EAMP, DA, and AP, had high-gravimetric CO_2 uptake capacity (up to 129 mol% for DA), but also had high viscosity in the NMR cell, which prevented further evaluation.

It was found that VLE for blends of DA and PSA-1 showed the best CO_2 uptake with a combination of both chemical and physical absorption of CO_2 without significant drop-in uptake in binary and ternary gas mixtures. The viscosity of CO_2-rich DA:PSA-1 (1:1 mole ratio) was measured at 16 cP at 25°C under 500 psi CO_2, and decreased to 4.2 cP at 45°C. The Aspen simulation results showed that the preliminary mixed solvent (DA:PSA-1) process uses lower overall energy.

available reports/technical papers/presentations

Koech, P. "Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration," NETL Carbon Capture Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Koech-PNNL-Syngas%20Purification.pdf*.

ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds

primary project goals

Gas Technology Institute (GTI), with Clean Carbon Solutions Ltd. (CCSL), will develop and validate a transformational carbon dioxide (CO_2) capture technology (ROTA-CAP) using novel rotating packed-bed (RPB) absorbers and regenerators combined with an advanced solvent.

technical goals

- Design, construct, and commission the ROTA-CAP equipment at GTI.
- Develop a preliminary process model and perform an initial fabrication feasibility study for commercial process.
- Test the ROTA-CAP system with simulated flue gases and natural gas burner flue gas at GTI to determine key operating parameters.
- Calibrate the process model and measure solvent carryover.
- Perform long-term reliability and operability testing at the National Carbon Capture Center (NCCC) on coal-fired flue gas.
- Verify the process model.
- Determine scale-up challenges, solvent degradation, and aerosol formation.
- Complete a high-level techno-economic analysis (TEA).

technical content

The RPB contactor design comprises a rotating disk of packing material that generates a high gravity centrifugal force, which distributes solvent radially toward the outer edge of the disk, providing a high surface area for mass transfer to occur as countercurrent flue gas contacts the solvent droplets. An integrated absorber-regenerator bench-scale test skid for the ROTA-CAP system will be designed, constructed, and operated at GTI using simulated flue gas and natural gas burner flue gas to determine key operating parameters. See Figure 1 for a schematic of RPBs in gas-liquid contactor operation. CCSL will provide an advanced solvent for the test, such as its proprietary amine-promoted buffer salt (APBS) solvent. To compare the performance of ROTA-CAP to the conventional process using commercial monoethanolamine (MEA) solvent, the team is utilizing the Slip Stream Test Unit (SSTU) at NCCC. See Figure 2 for a general bench-scale ROTA-CAP skid process flow diagram. Long-term (1,000-hour) stability testing of the integrated ROTA-CAP CO_2 capture system will be conducted on a coal-fired flue gas slipstream at NCCC at a scale of 1 tonne CO_2 per day, and the collected data will be used to determine solvent degradation and aerosol formation. A simulation process model will be developed for integrated RPB carbon capture systems and will be used to aid in larger-scale deployment of the ROTA-CAP technology, such

technology maturity:

Bench-Scale, Small-Pilot (simulated, natural gas burner and coal-fired flue gases)

project focus:

Rotating Packed Bed with Advanced Solvent

participant:

Gas Technology Institute

project number:

FE0031630

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
Andrew.opalko@netl.doe.gov

principal investigator:

Osman Akpolat
Gas Technology Institute
osman.akpolat@gastechnology.org

partners:

Clean Carbon Solutions Ltd. (CCSL), National Carbon Capture Center

start date:

10.01.2018

percent complete:

48%

as integration with coal-fired power plants. A high-level TEA of the process will be performed based on experimental data and the capture process model verified with the long-term operation data.

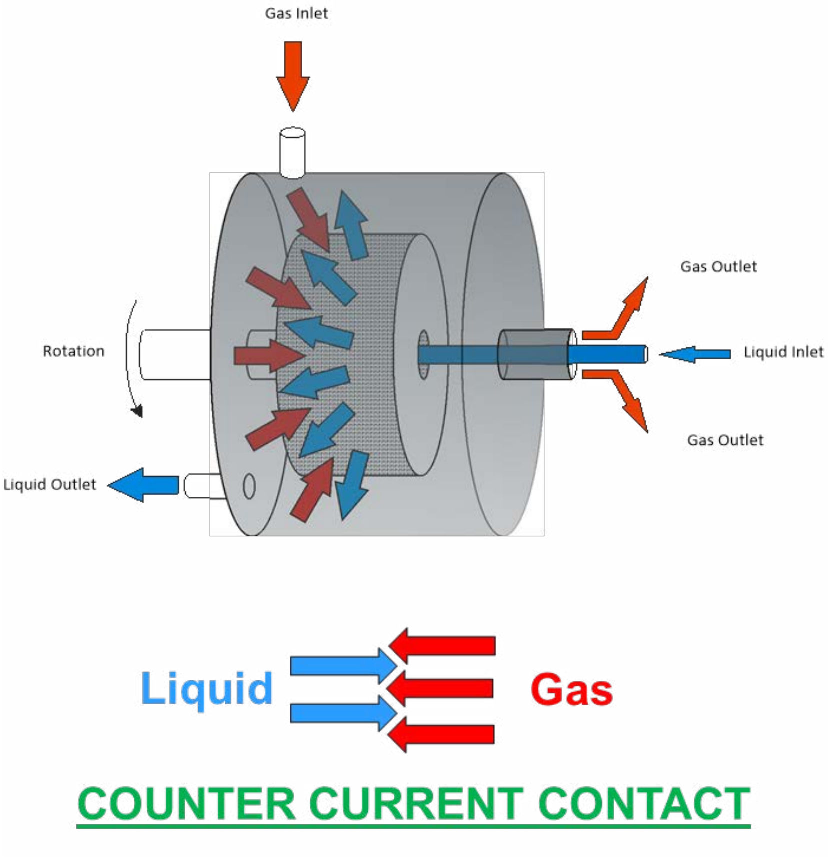

Figure 1: RPB gas liquid contactor.

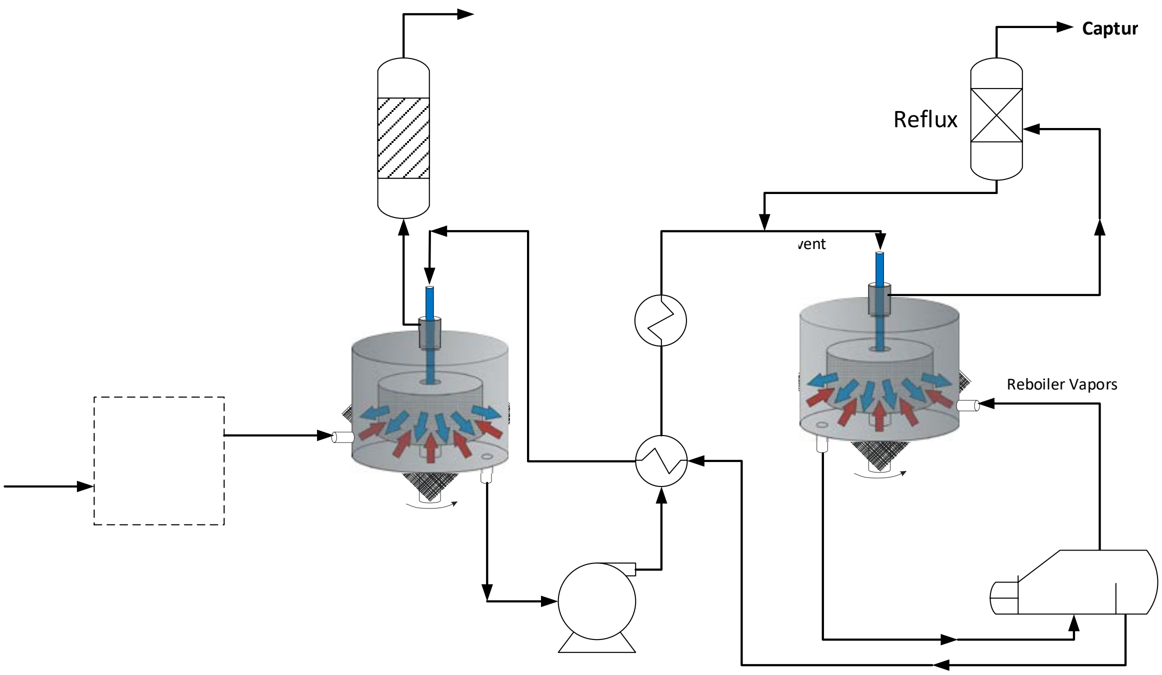

Figure 2: ROTA-CAP bench-scale test skid process flow diagram.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	57.29	57.29
Normal Boiling Point	°C	104-220	104-220
Normal Freezing Point	°C	N/A	N/A
Vapor Pressure @ 15°C	bar	18.2	18.2
Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	0.425	0.425-0.55
Specific Gravity (15°C/15°C)	-	1.007	>1.007
Specific Heat Capacity @ STP	kJ/kg-K	3.344	>3.344
Viscosity @ STP	cP	2.839	>2.839
Absorption			
Pressure	bar	0.1	0.1
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	3.3	>3.3
Heat of Absorption	kJ/mol CO_2	75.2	>75.2
Solution Viscosity	cP	4.4	>4.4
Desorption			
Pressure	bar	0.07	0.07
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.7	>0.7
Heat of Desorption	kJ/mol CO_2	2.7-3.0	2.55-2.85

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The solvent utilizes a chemical reaction with acid gases to remove them from the feed gas stream. The reaction is reversed in the stripper unit operation through the application of heat to the solvent.

Solvent Contaminant Resistance – Besides physical contamination (e.g., feed gas solids), the main contaminant expected in the solvent is heat-stable salts (HSSs). HSSs are a byproduct of heat and solvent reaction with components in the feed gas (e.g., oxygen [O_2], nitrogen oxide [NO_X], sulfur oxide [SO_X]). In long-term testing by CCSL, the solvent has superior resistance to HSS generation when compared to other commercial solvents.

Solvent Foaming Tendency – Foaming has not been reported in any test campaign or commercial operation of the solvent to date.

Flue Gas Pretreatment Requirements – Pretreatment would include:

- Reduction of particulate matter, NO_X, and SO_X to current U.S. Environmental Protection Agency (EPA) limits.
- Cooling and water saturation of the feed gas to approximately 110°F.

Solvent Makeup Requirements – Solvent makeup is minimal as HSS generation and physical loses should be low. It is expected that less than 0.35 kg solvent per tonne of CO_2 should be added intermittently.

Waste Streams Generated – A water bleed is expected from the regenerator reflux to maintain the solvent concentration and remove any trapped ammonia salt species. During long-term testing, HSSs could be removed through reclaiming. The HSS sludge would need to be disposed. However, with only a 1,000-hour target for the long-term testing, reclaiming is not anticipated during this test campaign.

technology advantages

- The RPB technology provides intense micromixing and internal mass transfer, thereby facilitating significant size reductions in the absorber and regenerator relative to conventional columns, resulting in lower capital costs.
- The use of a highly concentrated solvent, such as CCSL's APBS solvent, reduces the regeneration energy and leads to greater process efficiency.
- Reduced oxidative and thermal degradation.
- Decreased solvent top-up requirements by approximately 77%.
- Reduced waste handling and disposal cost by up to 92%.
- A simulation process model for integrated RPB carbon capture systems will be developed, which can be used in future larger-scale deployments.
- TEA will evaluate the value of the ROTA-CAP technology in the carbon capture market.
- RPB reactors are non-selective to the solvent used.

- RPB reactors offer higher efficiencies and are non-selective to the solvent used.

R&D challenges

- The integrated use of RPBs as both absorber and regenerator in a single system.
- The mechanical design parameters of rotating equipment.
- Solvent performance during operation.
- Integrating and achieving required solvent regeneration using an RPB regenerator.
- During testing, GTI will determine the solvent performance and modify it as needed to achieve a 90% CO_2 removal rate. The optimum CO_2 removal rate to achieve the lowest cost of removal will be calculated.
- Scale-up limitations exist with rotating equipment. Modular design may be useful to overcome size limitations of RPBs for larger systems. Capital cost and added complexity of the system will need to be managed.

status

GTI designed and costed the bench-scale ROTA-CAP test skid, a 50-kilowatt-electric (kWe) (1,000-kg/day CO_2 removal) equivalent-scale integrated carbon capture skid. The skid will have a flue gas cooling and filtration section available to be used when necessary.

The key variables will include:

- RPB rotational speed of 200 to 1,000 RPM.
- Absorber liquid/gas ratio of 0.5 to 5.0 kg/m^3.
- Solvent circulation rate of 30 to 150 kg/h.
- Solvent concentration/viscosity of 40 to 80 wt% (5 to 100 cP).
- Regenerator operating pressure/temperature of 0.0 to 1.0 bar(g) (100 to 130°C).
- Flue gas composition (synthetic, natural gas-fired, coal-fired).

The task duration for testing of the bench-scale ROTA-CAP skid at GTI is planned to be five months. This includes three months for simulated gas testing and one month natural gas burner flue gas testing, with an additional month of testing that can be used for either. Long-term testing at NCCC is planned to be a cumulative 1,000-hour test.

available reports/technical papers/presentations

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA. . *https://netl.doe.gov/sites/default/files/netl-file/O-Akpolat-GTI-ROTA-CAP.pdf*.

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/sites/default/files/2018-12/O-Akpolat-GTI-Rotating-Packed-Beds.pdf*.

Akpolat, O., "ROTA-CAP: An Intensified Carbon Capture System Using Rotating Packed Beds," Project Kick-Off Meeting, Pittsburgh, PA, Dec 2018. *https://www.netl.doe.gov/sites/default/files/2019-01/FE0031630-kickoff-presentation-121418.pdf*.

Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors

primary project goals

Liquid Ion Solutions LLC, along with Carnegie Mellon University (CMU) and Carbon Capture Scientific, will develop and evaluate novel additives that lower the viscosity of water-lean amine solvents for post-combustion carbon dioxide (CO_2) capture. The project will focus on developing a solvent additive that minimizes the formation of long-range hydrogen bonding (HB) networks, in turn decreasing the solvent viscosity and improving the process economics. Three model solvents will be prepared using amines that encompass the characteristics of most amines used in water-lean solvents, and the solvents will be studied computationally and experimentally to benchmark the behavior of the solvents' viscosity in the presence of CO_2. The project team will then use simulation models to understand the molecular interactions in water-lean solvents and identify additives that disrupt HB networks effectively, measure solvent viscosity reduction with additives at lab-scale, optimize the combination of additive/solvent and test the optimized system in synthetic flue gas, and perform a cost-benefit analysis to examine the advantage of using additives for solvent viscosity reduction.

technical goals

The goal of the project is to evaluate, at lab-scale, the effectiveness of ether and ester HB disruptor additives in lowering solvent viscosity without having an adverse impact on CO_2 capture capacity. Objectives include:

- Computer simulation to understand the molecular interactions in water-lean CO_2 capture solvents.
- Synthesis and characterization of HB disrupter molecules with the specific goal of significantly reducing the viscosity of water-lean carbon capture solvents in the presence of CO_2.
- Proof-of-concept performance testing to demonstrate the effectiveness of HB disrupters in lowering viscosity.
- Optimization of HB disruptor chemical structure based on insights gained from computational modeling and experimental proof-of-concept studies.
- Demonstration of the effectiveness of the optimized HB disrupters in the presence of synthetic flue gas.

technical content

Liquid Ion Solutions, in partnership with CMU and Carbon Capture Scientific, is developing and evaluating novel additives that minimize the formation of long-range HB networks and thus decrease the viscosity of water-lean amine solvents for post-combustion CO_2 capture by 50% upon CO_2 uptake. Three different

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Novel Additives for Water-Lean Amines

participant:

Liquid Ion Solutions LLC

project number:

FE0031629

predecessor projects:

N/A

NETL project manager:

Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:

Xu Zhou
Liquid Ion Solutions LLC
zhou@liq-ion.com

partners:

Carbon Capture Scientific,
Carnegie Mellon University

start date:

10.01.2018

percent complete:

45%

amines—2-(methylamino)ethanol (NMAE), 2-methoxyethylamine (MOEA), and bis(2-methoxyethyl)amine (BMOEA) — are being used for this study.

The project work includes development of computer simulation to understand the molecular interaction in water-lean CO_2 capture solvents; design, synthesis, and performance testing of HB disrupters as additives to reduce solvent viscosity; optimization of the HB disrupter; and performance testing of the optimized additive in the presence of synthetic flue gas.

The computational study will include a detailed analysis of viscosity and size distribution of HB clusters of three amine solvents as a function of ammonium/carbamate ion concentration: NMAE, MOEA, and BMOEA. Initial calculations will be made to determine force field parameters, partial charges of ammonium, and carbamate ions. Molecular dynamics simulations will allow for study of viscosity, HB structures, and kinetics of HB formation and breaking. Disruptor additives under consideration to include oxy-dibenzene, pyran, crown-ethers, and dimethyl sulfoxide like moieties. Quantitative portions of the computational study will investigate the effects of HB disrupting additives, including influence of 3D HB structures of the absorbents, as well as their HB cluster lifetime; how the additives modulate viscosity; and what key factors govern the disruption of HB structures.

HB disruptor synthesis and testing will also be conducted, including a proof-of-concept study, additive screening, and optimization and synthetic flue gas testing. For the proof-on-concept, candidate disruptors will be selected and viscosity tested at uncharged, CO_2-charged, and after desorption states. Then the concentration of the additive will be optimized, including evaluation of working capacity and viscosity. The optimized additive and solvent will be tested at lab-scale with synthetic flue gas, evaluating working capacity and viscosity after multiple cycles.

An engineering analysis will also be conducted, examining the impacts of viscosity on momentum, heat and mass transfer in carbon capture systems, and conducting a preliminary cost-benefit analysis.

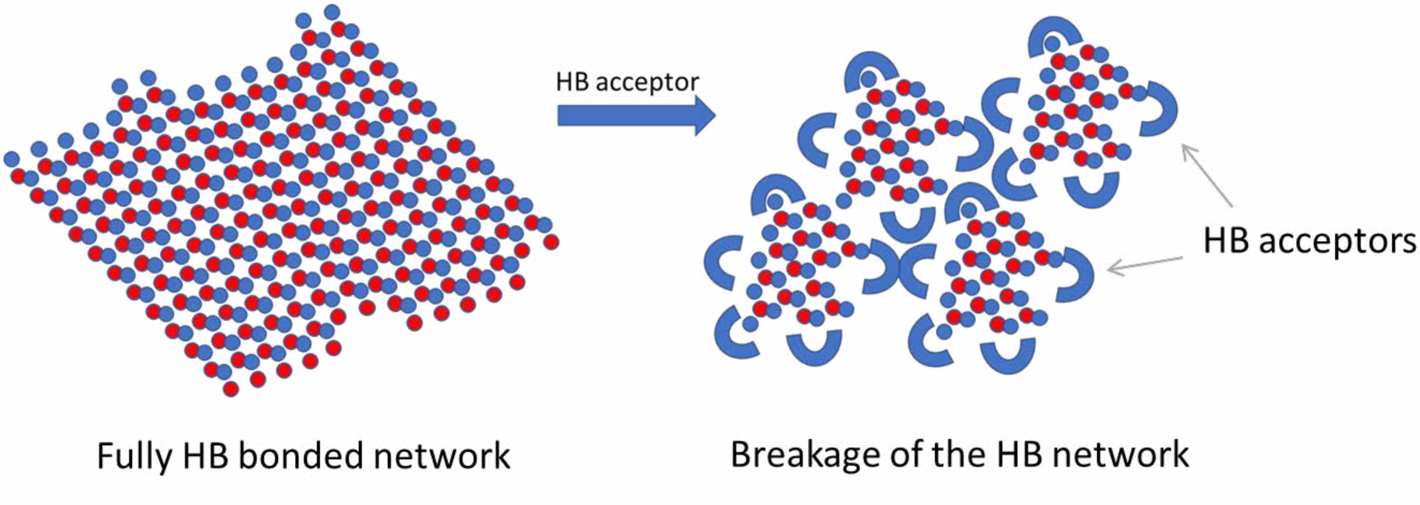

Figure 1: Illustration of fully HB network (left) and the breakage of the HB network by addition of HB acceptors (right).

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	80-140	112.4
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15°C	Bar	<0.01	<0.01
Manufacturing Cost for Solvent	$/kg	N/A	2
Working Solution			
Concentration	kg/kg	100	50/100
Specific Gravity (15°C/15°C)	-	1.02-1.07	1.05
Specific Heat Capacity @ STP	kJ/kg-K	3.0-3.5	3.3
Viscosity @ STP	cP	2-6	12.5
Absorption			
Pressure	Bar	1.01	1.01
Temperature	°C	40	30
Equilibrium CO_2 Loading	mol/mol	0.48	0.48
Heat of Absorption	kJ/mol CO_2	unknown	57
Solution Viscosity	cP	2-6	5.3
Desorption			
Pressure	Bar	1	1
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.10	0.33
Heat of Desorption	kJ/mol CO_2	Unknown	57.0
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,716,229	
CO_2 Recovery, Purity, and Pressure	% / % / bar	80/10/0.10	
Absorber Pressure Drop	Bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	160	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverize coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hour of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – Chemical (Additive).

Solvent Contaminant Resistance – N/A.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – N/A.

Solvent Makeup Requirements – N/A.

Waste Streams Generated – CO_2.

Process Design Concept – Standard absorption/desorption column.

technology advantages

The development of an HB disruptor additive capable of significantly reducing the viscosity of any water-lean chemical solvent will allow for increased heat exchanger and mass transfer efficiency, thus lowering the capital and operating costs for CO_2 capture.

R&D challenges

HB networks in capture solvents result in an increase in viscosity. In order to break down the overall size of the HB network, additives can be introduced that disrupt the overall network, forming smaller segmented networks.

status

The simulation of relationship between HB and viscosity and quantitative analysis of co-solvent and mixture effects was completed. The team has completed the proof-of-concept viscosity testing using the rheometer testing system. Initial additives screening based on viscosity testing has shown up to 50% viscosity reduction in the amine systems upon addition of up to 10 wt. % additives. The preliminary engineering analysis is still underway. The quantitative assessment of impact on operating costs has been completed.

available reports/technical papers/presentations

Nulwala, H., "Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors," Poster at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/H-Nulwala-LIon-Solutions-Solvent-Viscosity-Reduction.pdf*.

Zhou, X., Brown, D., Nulwala, H., Liu, J., Li, Y., Kim, H., Chen, S., "Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors," Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/X-Zhou-LIS-Solvent-Viscosity.pdf*.

Nulwala, H., "Universal Solvent Viscosity Reduction Via Hydrogen Bonding Disruptors," *Project Kickoff Meeting*. *https://www.netl.doe.gov/projects/files/FE0031629_Kickoff%20meeting_10-12-2018.pdf*.

Emissions Mitigation Technology for Advanced Water-Lean Solvent-Based CO_2 Capture Processes

primary project goals

Research Triangle Institute (RTI) will develop a comprehensive solvent emission mitigation tool set for reducing the solvent and aerosol emissions from carbon dioxide (CO_2) capture systems using water-lean solvents (WLSs). Due to their low energy requirement for solvent regeneration, lower regeneration temperature, low corrosivity, and low vapor pressure, WLS systems are rapidly being developed for CO_2 capture. RTI's tool set is specifically designed for WLS systems, implementing an advanced organic solvent wash system in conjunction with water wash, acid wash, and other commercially available, state-of-the-art emission reduction technologies.

technical goals

- Characterize and understand the emission produced by WLSs while capturing CO_2.
- Develop an empirically derived emission model based on the solvent physical properties and on critical operating parameters from the absorber and wash section.
- Evaluate suitable process arrangement for emission-reduction devices.
- Demonstrate the effectiveness of these emission mitigation devices on the bench-scale CO_2 capture system optimized for WLSs.

technical content

RTI is advancing development of an effective tool set to reduce amine emissions for WLSs by means of reducing the vapor loss, liquid entrainment, and aerosol formation altogether. The project team will characterize the emissions produced by WLSs while capturing CO_2; develop a model that predicts the emissions based on the solvent's physical and chemical properties on critical operating parameters from the absorber and wash section; develop a process tool set for emission reduction over a range of solvent systems; evaluate the effectiveness of these emission mitigation devices in a bench-scale (6-kilowatt-electric [kWe]) CO_2 capture system by testing with RTI's current WLS formulation, NAS-5, and a second selected WLS under actual flue gas conditions; and complete a techno-economic analysis (TEA) to determine the contribution of the emission control technologies to the overall CO_2 capture cost.

technology maturity:

Bench-Scale (6 kWe), Actual Flue Gas

project focus:

Water-Lean Solvent Emissions Mitigation

participant:

Research Triangle Institute (RTI)

project number:

FE0031660

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
Sai.gollakota@netl.doe.gov

principal investigator:

Jak Tanthana
Research Triangle Institute
jtanthana@rti.org

partners:

Technology Centre Mongstad (TCM), Linde

start date:

10.01.2018

percent complete:

50%

The results obtained in this study will assist in process scalability, mitigate the technology's risk associated with emissions, improve the economic potential, and aid in the commercial adoption of WLSs.

The project tasks will determine RTI's Non-Aqueous Solvent (NAS) and selected WLS emissions characteristics from the absorber column; develop an empirical emission model based on critical operating parameters; screen organic solvents and amine adsorbents; and determine, implement, and evaluate the effectiveness of the emissions control technologies (ECTs) at RTI's Bench-Scale Gas Absorption System (BsGAS). Figure 1 shows the potential ECTs for WLS systems to be incorporated at a CO_2 capture plant. Also, the team will carry out the modifications based on RTI's findings and evaluate the amine emissions using NAS-5 and a selected WLS and refine the empirical emission model/determine the impact of the ECTs to the CO_2 capture cost.

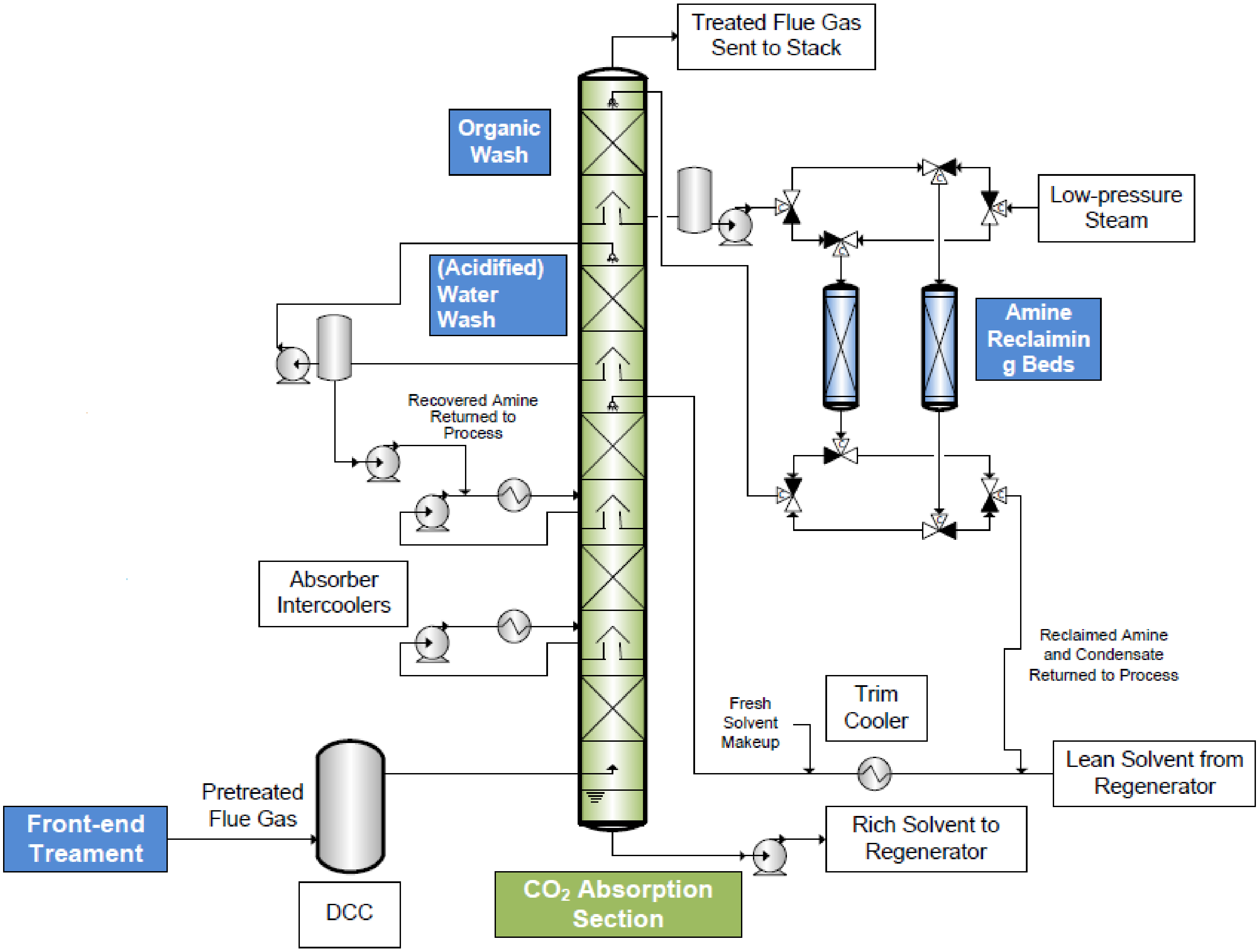

Figure 1: Potential emissions control technologies for WLS systems to be incorporated at a CO_2 capture plant.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	95–115**	99
Normal Boiling Point	°C	185–243**	200
Normal Freezing Point	°C	(-6 to -24)**	-9.15
Vapor Pressure @ 15°C	bar	4.47e–4**	4.47e–4
Manufacturing Cost for Solvent	$/kg	30	5
Working Solution			
Concentration	kg/kg	0.5–0.6*	0.55
Specific Gravity (15°C/15°C)	-	0.9–1.035*	1.035
Specific Heat Capacity @ STP	kJ/kg-K	2.78*	2.78
Viscosity @ STP	cP	4.38–4.7*	4.7
Absorption			
Pressure	bar	0.133*	0.133
Temperature	°C	35–45*	38
Equilibrium CO_2 Loading	mol/mol	2.04–2.22*	2.04
Heat of Absorption	kJ/mol CO_2	1,700–2,000*	1,931
Solution Viscosity	cP	4–30*	28
Desorption			
Pressure	bar	2–7.8*	2
Temperature	°C	90–110*	105
Equilibrium CO_2 Loading	mol/mol	0.45-1.13*	0.45
Heat of Desorption	kJ/mol CO_2	2,100*	2,045
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

* Experimentally measured data.

** Calculated data for different concentrations and conditions using standard mixing rules from pure components data.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical

Solvent Contaminant Resistance – More resistant than MEA to sulfur oxide (SO_X) and nitrogen oxide (NO_X).

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_X control.

Solvent Makeup Requirements – 0.2 to 0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – Absorber with interstage coolers coupling with regenerator with interstage heaters.

technology advantages

- WLS system has a low energy requirement for solvent regeneration and other added benefits, which reduce cost of CO_2 capture.
- Project to provide a model that predicts the amine emissions using the solvent properties, key process parameters, and the recommended emissions mitigation devices required for solvents specific to the developers.

R&D challenges

- Aerosol particle generation.
- Development of aerosols and particle counts technique for WLSs.
- Quantification and speciation of the emissions from WLSs.
- Emissions model development.
- Solvent screening for organic wash section.

- Process arrangement for amine extraction.
- Parametric and long-term testing.
- TEA.

status

Under development are various components of the prototype emissions control system for using water-lean solvents for CO_2 capture. Solvent degradation testing systems were constructed to determine the oxidative degradation and chemical pathways for the formation of nitrosamines (NA) and amine component thermal degradation products. Various solid adsorbents were tested for their amine absorption capacity and ability to regenerate to identify potential sorbent candidates to be used for the amine recovery unit.

RTI's NAS-5 has been tested to evaluate the impact of various process parameters that affect the overall amine emissions and aerosols formation using BsGAS. The key parameters that may impact the emissions are water wash temperature, liquid-to-gas ratio, CO_2 capture rate, the bulge temperature in the absorber.

Additional water wash, advanced demister, CO_2 acidification tanks, and particulate filters were added to BsGAS in late 2019. The effectiveness of these devices in controlling the amine emissions are being evaluated.

RTI has developed a Principle Component Analysis (PCA) framework for an empirical model to predict aerosol-based emissions utilizing BsGAS. This model correlates the process parameters of a water-lean solvent CO_2 capture system that is based on BsGAS testing of a water-lean solvent.

available reports/technical papers/presentations

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Project kickoff meeting presentation, Nov 2018. *https://www.netl.doe.gov/projects/files/FE0031660-kickoff.pdf*.

Tanthana, J., "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Poster presentation by Jak Tanthana, RTI International, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, *https://www.netl.doe.gov/projects/files/J-Tanthana-RTI-Solvent-Emissions-Mitigation.pdf*.

Tanthana, J., " "Emissions Mitigation Technology for Advanced Water-Lean Solvent Based CO_2 Capture Processes," Presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Tanthana-RTI-Solvent-Emissions-Mitigtion.pdf*.

Fog- and Froth-Based Post Combustion CO_2 Capture in Fossil Fuel Power Plants

primary project goals

The University of Kentucky Center for Applied Energy Research (UKy-CAER) is developing a transformational compact carbon dioxide (CO_2) absorber with internal fog and froth formation, for use in a solvent-based post-combustion CO_2 capture process, to surmount the limitations of packed-bed CO_2 absorption columns and to lower the capital cost of carbon capture.

technical goals

- Design and fabricate a compact absorber with internal fog and froth sections.
- Develop and finalize the atomizing nozzle and froth generating screens and operation conditions for fog and froth formation and destruction.
- Evaluate the fog and froth sections performance in a cold test unit.
- Complete a bench-scale parametric testing campaign followed by a long-term campaign to assess performance and investigate the effects of solvent degradation on fog and froth formation.
- Prepare a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

UKy-CAER is developing an open-tower compact absorber with internal fog and froth for enhanced solvent-based CO_2 capture, as shown in Figure 1. In the process, the flue gas enters the bottom of the absorber and contacts the solvent in a counter-current flow through a section containing structured packing, capturing approximately 30% of the total CO_2 before passing through a riser to the top of the fog/froth capture section. In this section, the gas first contacts a lean amine mist in a co-current flow in a temperature-controlled environment, with up to five times the liquid/gas contact area. Both the gas and liquid exiting from the fog section are forced through froth generating and propagating screens in the froth section. Here, also a temperature-controlled environment, the mass transfer is increased because a thin (target of ~10 µm) liquid film virtually eliminates the CO_2-amine diffusion resistance that typically impedes mass transfer in the conventional capture technologies. By greatly increasing the liquid/gas contact area and minimizing the diffusion resistance, the absorber column size can be reduced by up to 70% compared to a standard absorber design. Combining this fog-froth process with other UKy-CAER CO_2 capture technologies could potentially reduce the CO_2 capture capital cost by 57%.

technology maturity

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Fog and Froth Solvent Process

participant:

University of Kentucky Center for Applied Energy Research

project number:

FE0031733

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Heather Nikolic
University of Kentucky
heather.nikolic@uky.edu

partners:

Industrial Climate Solutions, Inc., Nexant, Smith Management Group

start date:

05.01.2019

percent complete:

15%

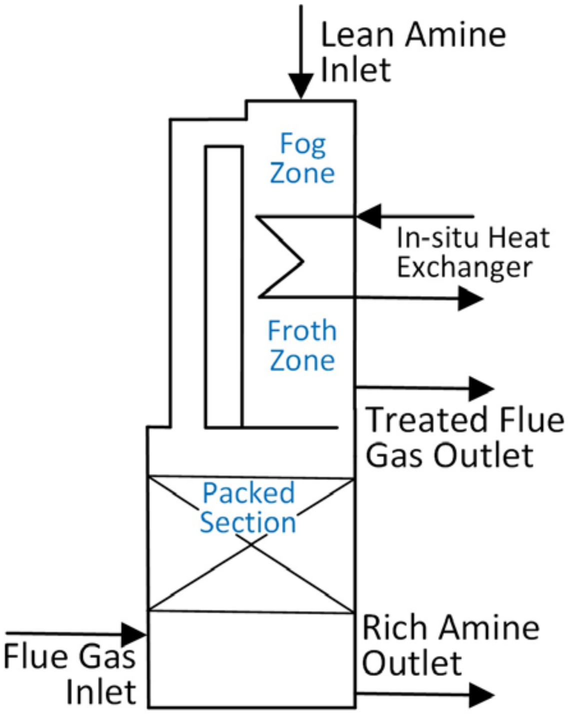

Figure 1: Schematic of University of Kentucky's compact absorber.

The project is designing and fabricating the complete compact absorber including the atomizing nozzle, froth generating and propagating screens, and in-situ heat removal. The frothing screens, as shown in Figure 2, are optimized for froth generation and propagation. They are designed and supplied by Industrial Climate Solutions. Fog generation includes spray nozzle selection and optimization of the nozzle arrangement, as well as mist size distribution in the column, via liquid supply parameters and solvent properties. Individual testing of the fog section and froth section will be followed by parametric and long-term testing of the compact absorber integrated in UKy-CAER bench-scale post-combustion capture facilities using simulated and actual flue gas. Data from testing supports development of a TEA and EH&S assessment for the process.

Figure 2: Froth generating and propagation screens.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g/mol	Amine	Amine
Normal Boiling Point	°C	155-170	155-170
Normal Freezing Point	°C	-2	-2
Vapor Pressure @ 20°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	$/kg (pure chemical, small batch)	14.74	14.74
Working Solution			
Concentration	kg/kg	0.35 to 0.45	0.35 to 0.45
Specific Gravity (15°C/15°C)	-	~1.0	~1.0
Specific Heat Capacity @ 40°C	kJ/kg-K	2.7-3.3	2.7-3.3
Viscosity @ STP	cP	5-7	5-7
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5	0.45
Heat of Absorption	kJ/mol CO_2	~-65	~-70
Solution Viscosity	cP	3-5	3-5
Desorption			
Pressure	bara	3-5	3-5
Temperature	°C	110-130	110-130
Equilibrium CO_2 Loading	mol/mol	0.20	0.20
Heat of Desorption	kJ/mol CO_2	~85	~85
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	24	
CO_2 Recovery, Purity, and Pressure	% / % / bara	90 / >95% / 1.65	
Absorber Pressure Drop	bar	<20"WC	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$	$36K	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, **T**, and carbon loading, **C/N**, can be expressed as: $\mathbf{R(T, C/N) = k_G \cdot a \cdot (P_{CO2} - P^*_{CO2})}$ where $\mathbf{k_G}$ is mass transfer coefficient, **a** is effective wetted surface area, and $\mathbf{(P_{CO2} - P^*_{CO2})}$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via $\mathbf{k_G}$ and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the proposed aqueous system compared to any 2nd-gen technology because there is an order of magnitude greater effective wetted surface area n in the top of the absorber.

Solvent Contaminant Resistance – UKy-CAER analysis show the solvent is more resistant to degradation, 40 to 50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – Unstable froth formation (not persistent foaming) is a key aspect to the proposed compact absorber. Surfactant is added to reduce the surface tension and therefore control the frothing behavior. Initial CO_2 capture experiments on solvent physical properties were performed in a packed column (2-inch internal diameter [ID] mini-scrubber). Adding surfactant to change the solvent surface tension led to a CO_2 capture efficiency increase of 15 to 20% throughout the carbon loading range. The key reason for this enhancement is the presence of fine froth (bubbles) that increase surface area with the addition of surfactant. It was also found that as carbon loading increases, the tendency to form bubbles decreases due to increased viscosity and surface tension. For an unstable froth, the dispersion rate is also important. A surfactant was chosen with the faster dispersion rate compared to others considered.

Flue Gas Pretreatment Requirements – The flue gas pretreatment requirement is sulfur dioxide (SO_2) removal to less than 5 ppm to minimize heat stable salt formation. This can be done with a standard counter-current pretreatment column with a circulating solution of either of soda ash (Na_2CO_3) or sodium hydroxide (NaOH). The solvent used is a hindered primary amine and does not form stable nitrosamine species, therefore no additional NO_X removal is required. No additional moisture removal required, as it is for ionic liquids.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UKy-CAER analysis show the solvent has degradation rates less than 30 wt% MEA and when the UKy-CAER developed solvent recovery technology is applied, the solvent emission will be about 0.5 ppm. The anticipated solvent makeup rate is less than 0.5 kg/tonne CO_2 captured.

Waste Streams Generated – The waste streams of the post-combustion CO_2 capture process using the proposed compact absorber are the same as any other post-combustion CO_2 capture process. There will be a blowdown stream from the SO_2 pretreatment column and a reclaimer waste stream from the solvent loop.

Process Design Concept – The proposed concept is shown in Figure 3. A 3-inch column is used for the fogging and frothing section where the flue gas and solvent flow in a co-current fashion. The bottom section contains typical structured packing with the flue gas and solvent moving in a counter-current fashion.

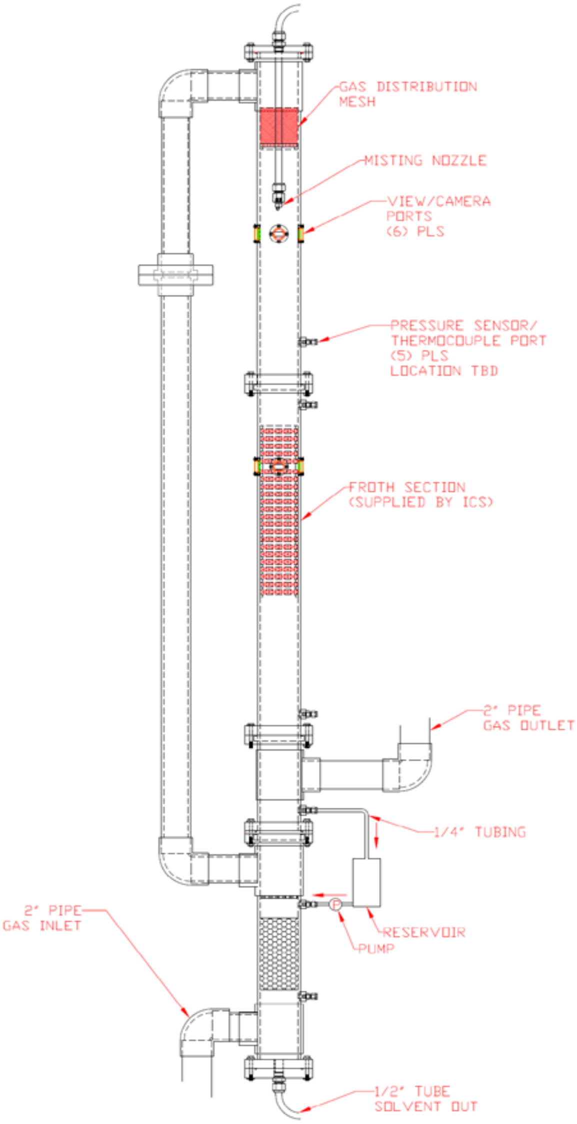

Figure 3: Compact absorber design concept.

Proposed Module Design – The proposed absorber would be modular with a natural divide between the bottom packed section and the top fog and froth section.

technology advantages

- Up to five times increase in liquid/gas contact area over structured packing.

- Up to four times increase in mass transfer over conventional columns due to a thin (target of ~10 µm) liquid film, eliminating the CO_2-amine diffusion resistance that can impede the overall mass transfer of a capture technology.
- Up to 70% reduction in absorber height.
- Up to 50% reduced pump power requirement.
- Maintain carbon loading as close as achieved with conventional column containing structured packing.
- Potential, when combined with other University of Kentucky CO_2 capture features, for a 57% reduction in capital cost for carbon capture.

R&D challenges

- Demonstration at the bench scale due to wall effects in the small column.
- Controlling the froth size.

status

The University of Kentucky has compared and selected options for the atomizing nozzle and frothing screens for their system. The initial design and construction of the fog and froth sections has been completed.

available reports/technical papers/presentations

Nikolic, H. "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Nikolic-UKY-CAER-Fog-Froth-Capture.pdf*.

Nikolic, H. "Fog+Froth-based Post-Combustion CO_2 Capture in Fossil-Fuel Power Plants," Presented at the Project Kickoff Meeting, Pittsburgh, PA, May 2018. *https://www.netl.doe.gov/projects/files/Fog%20Froth-Based%20CO2%20Capture%20Kickoff_May%202019.pdf*.

Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability

primary project goals

ION Clean Energy, Inc. (ION) is developing a novel amine-based solvent (ICE-31) with transformational stability and excellent carbon dioxide (CO_2) capture performance. The project, designated by ION as "Apollo," aims to scale-up the solvent technology from bench-scale to pilot-scale (0.6 megawatt-electric [MWe]).

technical goals

- Develop an understanding of breakdown pathways and confirm the revolutionary stability of the new solvent using various laboratory techniques.
- Develop and validate a ProTreat® process simulation model for design at a commercial scale.
- Determine values for key performance indicators through testing on coal-fired or natural gas-fired flue gas: minimum energy consumption, emissions profile, solvent degradation rates, and washing section efficiency.
- Perform parametric tests to understand the impact of dynamic operations and operational upsets beyond design parameters, followed by long-term, steady-state (at least 1,500 hours) testing for solvent stability assessment.
- Develop a techno-economic assessment (TEA) to compare against commercial technologies.

technical content

After conducting an extensive screening of both commercially available amines and designer amines, ION has identified a transformational water-lean amine-based solvent (ICE-31). ICE-31 exhibits exceptional regeneration energy, working capacity, kinetics, material compatibility, stability under both oxidative and thermally challenging environments, and a minimal environmental impact.

ION's current solvent technology, ICE-21, has demonstrated significant reductions in the cost of CO_2 capture by reducing the parasitic load resulting from the CO_2-stripping process, enhancing reaction kinetics, expanding solvent carrying capacity, lowering the corrosion rate, and lowering emissions relative to the base case 30 wt% monoethanolamine (MEA) solvent. The novel ICE-31 solvent properties are superior to traditional MEA and even ICE-21 regarding energy consumption, emissions, and thermal and oxidative degradation.

ICE-31's revolutionary stability reduces the solvent makeup rate and associated costs, such as pre-treatment and reclaimer operations. The fast capture kinetics of the solvent, coupled with low water content, further enhance the carrying capacity and drive down the regeneration energy. A 2017 TEA of ICE-21 performed by Sargent & Lundy, using the U.S. Department of Energy's (DOE) Bituminous Baseline Case 12, based on incorporating ICE-21 in the process simulation model ProTreat for a greenfield net-550 MW coal-fired power plant with

technology maturity:

Pilot-Scale (0.6 MWe),
Actual Flue Gas

project focus:

Water-Lean Amine-Based
Solvent for CO_2 Capture

participant:

ION Clean Energy, Inc.

project number:

FE0031727

predecessor projects:

N/A

NETL project manager:

Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:

Erik Meuleman
ION Clean Energy, Inc.
erik.meuleman@ioncleanenergy.com

partners:

Commonwealth Scientific & Industrial Research Organisation (CSIRO), Optimized Gas Treating, National Carbon Capture Center, Sargent & Lundy

start date:

06.01.2019

percent complete:

40%

CO_2 capture, reported that the capture cost for ICE-21 is in the range of \$39 to \$45/tonne of CO_2.

In this project, the project team is conducting comprehensive lab-scale research to understand the chemical properties of the solvent ICE-31. Optimized Gas Treating (OGT) is using lab-scale results to develop a rate-based model of the solvent in ProTreat that can simulate operations at a commercial scale for conducting the TEA. The empirical data includes the operation of the Commonwealth Scientific & Industrial Research Organisation's (CSIRO) 0.01-MWe Process Development Facility (PDF) on simulated flue gas for initial performance studies. Other empirical data for the model will come from the operation of CSIRO's Solvent Degradation Rig (SDR) to forecast long-term solvent stability through accelerated degradation under harsh conditions. ION is also further validating the performance of the solvent through testing with actual flue gas at the National Carbon Capture Center's (NCCC) pilot-scale (0.6-MWe) pilot solvent test unit (PSTU) in Wilsonville, Alabama. The test campaign includes parametric studies to determine optimal operating conditions and validate the new ProTreat simulation model; dynamic operations studies to evaluate the impact of variations in flue gas flow rates due to load fluctuations from the power station and other process upsets; emissions studies under steady-state and dynamic conditions; and long-term, steady-state testing to evaluate solvent stability. The results from the trials at the PSTU provide additional data to validate the new ProTreat module and produce a stronger TEA at the end of the project for a large-scale capture facility.

The objectives in the test plan at NCCC include:

- Validating the instrumentation and equipment performance.
- Conducting parametric testing to develop a dataset for identifying the optimum performance, operating window, and validation of the ProTreat model for ICE-31.
- Conducting accelerated oxidative and thermal degradation experiments in the PSTU.
- Evaluating dynamic operation conditions, including the determination of maximum safe ramp rates and optimal ramp rates.
- Simulating potential system upsets, including flue gas desulfurization (FGD) and direct contact cooler (DCC) outages (hot/dry flue gas, sulfur dioxide [SO_2] concentration spikes) that mimic real conditions found in a commercial system.
- Demonstrating the viability of continuous operation on aging solvent.

The combination of the ICE-31 solvent's performance and lower solvent replacement results in a significant improvement from DOE's Bituminous Baseline Case 12B (\$58/tonne of CO_2 captured) and estimated values for ION's solvent technology, ICE-21 (\$39/tonne of CO_2 captured [2017]). Since 2017, further reduction in the cost of capture has been realized through incorporating heat recovery from the compression system. ION intends to follow a similar development path for ICE-31 to the accelerated scale-up of ION's ICE-21 solvent, consisting of testing at Technology Centre Mongstad (TCM; 12 MWe), followed by front-end engineering design (FEED), and then demonstration at commercial scale.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	80 – 150	100 – 150
Normal Boiling Point	°C	220 – 250	220 – 250
Normal Freezing Point	°C	<-15	<-20
Vapor Pressure @ 15°C	bar	<0.0001	<0.0001
Manufacturing Cost for Solvent	$/kg	-	-
Working Solution			
Concentration	kg/kg	650 – 800	650 – 800
Specific Gravity (15°C/15°C)	-	0.8 – 1.1	0.8 – 1.1
Specific Heat Capacity @ STP	kJ/kg-K	~1.5 – 2.5	1.3 – 2.0
Viscosity @ STP	cP	<10	<10
Surface Tension @ STP	dyn/cm	<50	<50
Absorption			
Pressure	bar	1.0	1.0
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5 – 1.0	0.5 – 1.0

Heat of Absorption	kJ/mol CO_2	-1,600 to -1,750	-1,600 to -1,750
Solution Viscosity	cP	<20	<20
Desorption			
Pressure	bar	1.5 – 2.0	1.5 – 4.5
Temperature	°C	110 – 125	110 – 140
Equilibrium CO_2 Loading	mol/mol	0.05 – 0.20	0.05 – 0.20
Heat of Desorption	kJ/mol CO_2	<1,800	<1,800

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption/desorption of CO_2 to/from working solution.

Solvent Contaminant Resistance – Sulfur oxide (SO_x) and nitrogen oxide (NO_x) are manageable. Extremely stable towards oxygen (O_2).

Solvent Foaming Tendency – No issues (more than 3,000 hours experience).

Flue Gas Pretreatment Requirements – As for any stable amine-based solvent.

Solvent Makeup Requirements – Aimed at less than 0.010 kg/tCO_2.

Waste Streams Generated – Similar profile, but estimated to be less than other stable amine-based solvents.

Process Design Concept – Similar to stable amine-based solvents, just a smaller footprint.

Proposed Module Design – N/A.

technology advantages

- Fast kinetics, coupled with low water content, enhances the carrying capacity and reduces regeneration energy.
- Environmentally benign (i.e., low parasitic load, near-zero emissions, and negligible solvent makeup).
- Low thermal and oxidative degradation rates result in revolutionary solvent stability, reducing solvent makeup rates and associated operating costs (OPEX).
- Low Specific Reboiler Duty (SRD) and solvent stability result in smaller capture plant equipment, reducing capital expenditure (CAPEX).
- Field-testing with coal-derived and natural gas-derived flue gas at NCCC will expand the critical knowledge base for ICE-31.
- The output from the field test campaign, supporting laboratory work, and process modeling will facilitate continued scale-up of the technology.
- The ICE-31 solvent is currently available from commercial chemical manufacturers.

R&D challenges

- Implementation of heat-integration strategies.
- Verification of long-term solvent performance in coal- or natural gas-fired flue gas environment.

status

Initial testing using CSIRO’s 0.01-MWe PDF test rig and simulated flue gas is underway to evaluate the ICE-31 solvent’s performance. The data collected will feed forward into the test plan development by ION for small-scale pilot testing using real flue gas at NCCC’s PSTU, a 0.6-MWe scale. The collected data from the PSTU serves to indicate the exactness of the process model being developed by OGT for a new module in the ProTreat simulation software. Collaborating with OGT and refining the internal parameters and calculations of the process model, the compilation of the data from the PSTU will support the creation of a TEA for a large-scale facility using ICE-31.

available reports/technical papers/presentations

Meuleman, E., Fine, N., Silverman, T., “Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Apollo),” Project kickoff meeting presentation, Pittsburgh, PA, December 2019. *https://netl.doe.gov/projects/files/DE-FE-0031727-Apollo-Kickoff%20Public.pdf*.

Meuleman, E., Fine, N., Silverman, T., “Validation of Transformational CO_2 Capture Solvent Technology with Revolutionary Stability (Apollo),” presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Meuleman-ION-Transformational-Solvent.pdf*.

Full-Scale FEED Study for Retrofitting the Prairie State Generating Station with an 816-MWe Capture Plant Using Mitsubishi Heavy Industries America Post-Combustion CO_2 Capture Technology

primary project goals

The University of Illinois and its partners will perform a front-end engineering design (FEED) study for the retrofit of the Prairie State Generation Company's (PSGC) coal-fired power station with post-combustion carbon capture. The University of Illinois and the team will produce a FEED study that uses Mitsubishi Heavy Industries' (MHI) Advanced Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ carbon dioxide (CO_2) capture technology to retrofit one of PSGC's two generating units (approximately 816 megawatt-electric [MWe]) in Marissa, Illinois, to become the largest post-combustion capture plant in the world.

technical goals

- The purpose of the FEED study is to complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at PSGC.
- The team will perform multiple feasibility and design studies based on project-specific details in preparation for developing engineering deliverables. These studies will help define the scope of the retrofit project, based on project-specific decisions, technology-specific performance, site-specific requirements, and client-specific needs.
- Once the scope has been defined, detailed design will commence for the CO_2 capture system and its integration with the existing facility. Various design and engineering deliverables will be developed that will help define commodity quantities, equipment specifications, and labor effort required to execute the project.

technical content

The overall project goal is a full FEED study on a carbon capture system for Unit #2 (816 MWe) at the PSGC Energy Campus in Marissa, Illinois, based upon on the KM CDR Process CO_2 capture technology from MHI. This capture technology represents the current state-of-the-art and employs an improved solvent from that used at the 240-MWe Petra Nova capture plant in Thompsons, Texas. The capture technology will be scaled-up to 816 MWe.

Work on this FEED study will produce detailed engineering designs, costing, and timelines for the construction. It will also designate permitting agencies and timelines in order to execute the follow-on build and operate project. Lessons

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Advanced KM CDR Process Retrofit

participant:

University of Illinois at Urbana-Champaign

project number:

FE0031841

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Kevin O'Brien
University of Illinois at Urbana-Champaign
kcobrien@illinois.edu

partners:

Mitsubishi Heavy Industries, Ltd., Prairie State Generating Company, Kiewit Corporation, Sargent & Lundy

start date:

10.01.2019

percent complete:

10%

learned during the FEED study will be documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

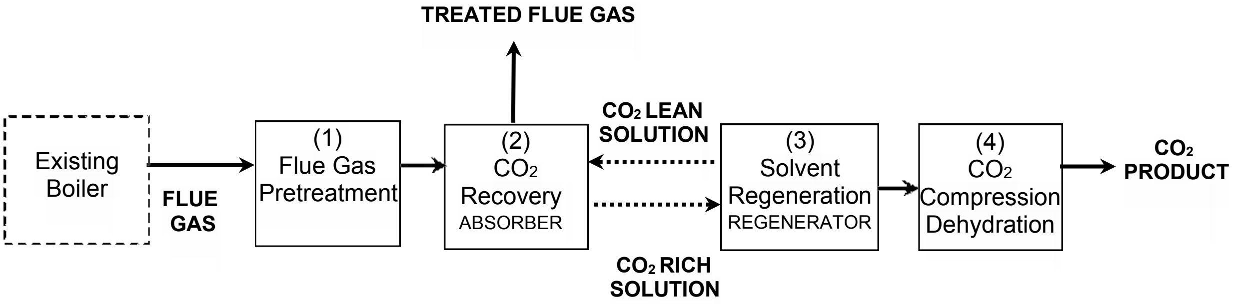

Figure 1: Block flow diagram of the CO_2 recovery plant.

The KM CDR Process is an improvement upon MHI's original KM CDR Process and is an amine-based CO_2 capture process that uses a newly developed solvent known as KS-21. The CO_2 capture system will recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of sulfur dioxide (SO_2) in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

In solvent regeneration, cool rich solvent is heated by the hot lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines.

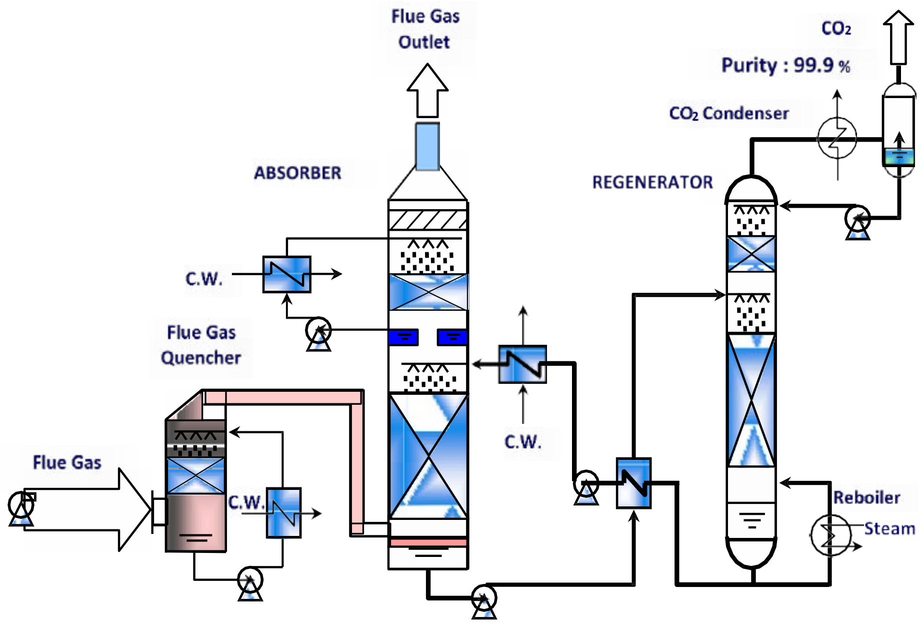

Figure 2: Carbon capture basic process flow diagram.

technology advantages

- Uses an improved, newly developed proprietary solvent known as KS-21. This solvent's properties translate into reduced capital costs.
    - Has less volatility, which reduced the height of the water wash section of the CO_2 absorber, lowering capital cost.
    - Has improved thermal stability, allowing the regenerator to be operated at a higher pressure and temperature, thereby reducing the equipment size and the power consumption for CO_2 compression, resulting in lowering operating and capital costs.
    - More resistance to oxidative degeneration, which reduces solvent loss.
    - Has lower heat of absorption, which allows higher circulation rate and therefore slightly less steam consumption.
- Will recover 95% of the CO_2 from the flue gas and compress and treat the CO_2 to adequate pipeline conditions.
- The capture system will be scaled-up using multiple trains so that it can standardized, modularized, and overall project cost can be reduced.

R&D challenges

- To deploy the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large-scale (19,000 to 25,000 short tons per day).

status

This project has commenced.

available reports/technical papers/presentations

None.

Commercial Carbon Capture Design and Costing: Part Two (C3DC2)

primary project goals

ION Clean Energy, Inc. (ION), Nebraska Public Power District (NPPD), and their partners are conducting a front-end engineering design (FEED) study for a carbon capture system designed for retrofit onto Unit 2 of NPPD's Gerald Gentleman Station (GGS2), a 700-megawatt (MW) coal-fired power station located in Western Nebraska. For the proposed project, a 700-MW-equivalent (two parallel 350 megawatt-electric [MWe] capture units) commercial-scale carbon dioxide (CO_2) capture plant will be designed and costed for GGS2. The team is leveraging work performed during a previously awarded commercial carbon capture design and costing project (FE0031595).

technical goals

The overall objective of the proposed project is to conduct a FEED study for a commercial-scale CO_2 capture system retrofitted onto an existing coal-fueled power station. With this approach, the team strives to decarbonize as much of Unit 2 as possible utilizing ION's ICE-21 solvent technology. This project will leverage prior U.S. Department of Energy (DOE) project award FE0031595, which conducted a design and costing study for a 300-MW slipstream carbon capture system for GGS2.

technical content

The project team will design the capture system and produce a capital cost estimate that will cover both engineering design for the carbon capture process and the balance of plant. The engineering design will be performed at a level consistent with an Association for the Advancement of Cost Engineering (AACE) Class 2 estimate, which would result in accuracy ranges of -15 to +20% for the capital cost estimate. The FEED study development will include process flow diagrams, utility flow diagrams, piping and instrument diagrams, heat and material balances, a 3D model, plot plans, final layout drawings, complete engineered process and utility equipment lists, one-line diagrams for electrical, electrical equipment and motor schedules, vendor quotations, detailed project execution plans, and resourcing and workforce plans developed by the project team. Balance of plant engineering design will include specifications for utilities, such as compression, cooling water, and waste treatment, as well as the sources of energy, electricity, and/or steam necessary to power the capture process. Civil and structural engineering tasks will also be incorporated throughout the design to include the proper stormwater runoff and spill containment, as well as geological assessments to support foundation design.

Additionally, the team will conduct a series of studies and investigations to aid in the design of the carbon capture facility, including steam sourcing, cooling water system, solvent materials compatibility, wastewater treatment, permitting and regulatory review, reagent handling, constructability review, overpressure relief, and project execution and operations management planning.

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Water-Lean Solvent Technology Retrofit

participant:

ION Clean Energy, Inc.

project number:

FE0031840

predecessor project:

FE0031595

NETL project manager:

Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:

Erik Meuleman
ION Clean Energy, Inc.
erik.meuleman@ioncleanenergy.com

partners:

Nebraska Public Power District, Sargent & Lundy, Koch Modular Process Systems, Siemens

start date:

10.01.2019

percent complete:

10%

The final report will summarize project results from the FEED study, including a systems and benefits analysis, summarize the results from the technical and economic feasibility analysis of scale-up, and make recommendations for future research and development.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	75–95
Normal Boiling Point	°C	150–210
Normal Freezing Point	°C	-15–2
Vapor Pressure @ 15°C	bar	$1\text{-}2 \times 10^4$
Manufacturing Cost for Solvent	$/kg	Proprietary
Working Solution		
Concentration	kg/kg	0.6–0.85
Specific Gravity (15°C/15°C)	-	0.9–1.2
Specific Heat Capacity @ STP	kJ/kg-K	2–3
Viscosity @ STP	cP	<5
Absorption		
Pressure	bar	1.0–1.15
Temperature	°C	20–50
Equilibrium CO_2 Loading	mol/mol	0.4–1.0
Heat of Absorption	kJ/mol CO_2	50–100
Solution Viscosity	cP	<20
Desorption		
Pressure	bar	1.1–1.8
Temperature	°C	80–150
Equilibrium CO_2 Loading	mol/mol	0.01–0.40
Heat of Desorption	kJ/mol CO_2	50–100

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – Estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	150	10.5	20.5	66.4	5.3	0.80	44	150

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The physico-chemical properties of ION's solvent system allow for a unique mechanism that combines fast kinetics with low energy consumption.

Solvent Contaminant Resistance – Sulfur oxides (SO_X) and nitrogen oxides (NO_X), other than nitric oxide (NO), are absorbed into the solvent and lower the carrying capacity of CO_2. Oxidative and thermal degradation are manageable. To date, ION's solvent system has not been limited by contaminant concentration.

Solvent Foaming Tendency – No foaming issues have been seen during either of ION's solvent pilot test campaigns.

Flue Gas Pretreatment Requirements – It is preferred that the flue gas be saturated with water vapor and can include any concentration of CO_2. Pretreatment to levels of SO_X less than 10 to 30 parts per million (ppm) (spikes are manageable) and NO_X less than 100 to 200 ppm is also favored.

Solvent Makeup Requirements – Proprietary.

Waste Streams Generated – Proprietary.

Process Design Concept – ION's solvent-based process steps include pre-scrubbing to remove SO_X, several other gases, and most of the particles; a direct contact cooling unit to control the inlet flue gas temperature and humidity; an absorber consisting of a packed column with counter-flow for removal of CO_2 into the proprietary solvent; and water wash to remove solvent droplets and vapors from the exhaust gas. Following the absorption step, the final unit operation is a regenerator to produce the CO_2, recover the solvent, and recycle the solvent back to the absorber.

technology advantages

As part of the FEED study, the proprietary ION ICE-21 solvent technology will be utilized. Relative to aqueous MEA technology and other commercial capture systems, ION's ICE-21 solvent technology offers the following benefits to lower operating and capital costs for CO_2 capture:

- Reduction in regeneration energy requirements.
- Higher CO_2 loading capacities.
- Reduced corrosion and solvent losses.
- Faster absorption kinetics.
- Less water used by the process.

The carbon capture plant will be designed to take full advantage of these benefits, which will result in a smaller physical plant, reduced energy requirements, less solvent degradation, lower emissions, and lower capital costs relative to systems built with DOE Bituminous Baseline Study (BBS) case benchmark solvents.

R&D challenges

In the project, ION will look to optimize the operating costs versus the capital costs, which will be defined by some design basis decisions such as sparing philosophy, process robustness, and maintenance.

status

The project has commenced.

available reports/technical papers/presentations

Meuleman, E., Awtry, A., Atcheson, J., "Commercial Carbon Capture Design & Costing: Part Two," Project Kick-off Meeting, December 5, 2019. *https://netl.doe.gov/projects/files/DE-FE0031840%20-%20C3DC2%20DOE%20Kickoff%20Meeting%20-%20PUBLICUSE.pdf*.

Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant

primary project goals

Electric Power Research Institute (EPRI) and its partners Fluor Corporation and California Resources Corporation (CRC) are conducting a front-end engineering design (FEED) study to determine the technical and economic feasibility of a retrofit, post-combustion, carbon capture technology on a commercially operating, natural gas-fired combined cycle (NGCC) power plant.

technical goals

Conduct a FEED study for 75% overall capture (90% capture on 83% slipstream) at CRC's 550-megawatt-electric (MWe) NGCC Elk Hills Power Plant (EHPP) using Fluor's proprietary Econamine FG Plus^{SM} (EFG+) aqueous amine technology. The captured 4,000 tonnes of carbon dioxide (CO_2) per day will be used by CRC for enhanced oil recovery (EOR) in fields adjacent to the power plant.

technical content

The FEED study will examine the cost and engineering requirements for installing a plant to capture CO_2 produced by the 550-MWe NGCC unit located in the Elk Hills Oil Field in Kern County, California. Fluor is the design engineering contractor and Fluor's EFG+ technology will be used for the carbon capture system design. CRC is the owner and operator of the host site, EHPP. Fluor's EFG+ technology is a post-combustion CO_2 capture technology with proven process for removal of CO_2 from flue gases, with the CO_2 product used for EOR and other applications.

The FEED study deliverables are to include a design basis, process flow diagrams, piping and instrument diagrams, equipment datasheets, a plot plan, bulk material takeoffs, and a capital cost estimate. For the design basis of the FEED study, the completed and ongoing details include: consolidated historic performance and run history of the power plant, evaluating various operating scenarios and conditions; results from flue gas testing review and validation of solvent performance through FEED; historic construction details from surrounding facilities to incorporate site requirements; ongoing review and optimization of energy use and waste streams; and ongoing evaluation of construction practices and contracting strategies to optimize cost, schedule, and risk.

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Econamine FG Plus^{SM} (EFG+) Retrofit to NGCC

participant:

Electric Power Research Institute, Inc.

project number:

FE0031842

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Abhoyjit Bhown
EPRI
abhown@epri.com

partners:

Fluor Corporation, California Resources Corporation

start date:

10.01.2019

percent complete:

10%

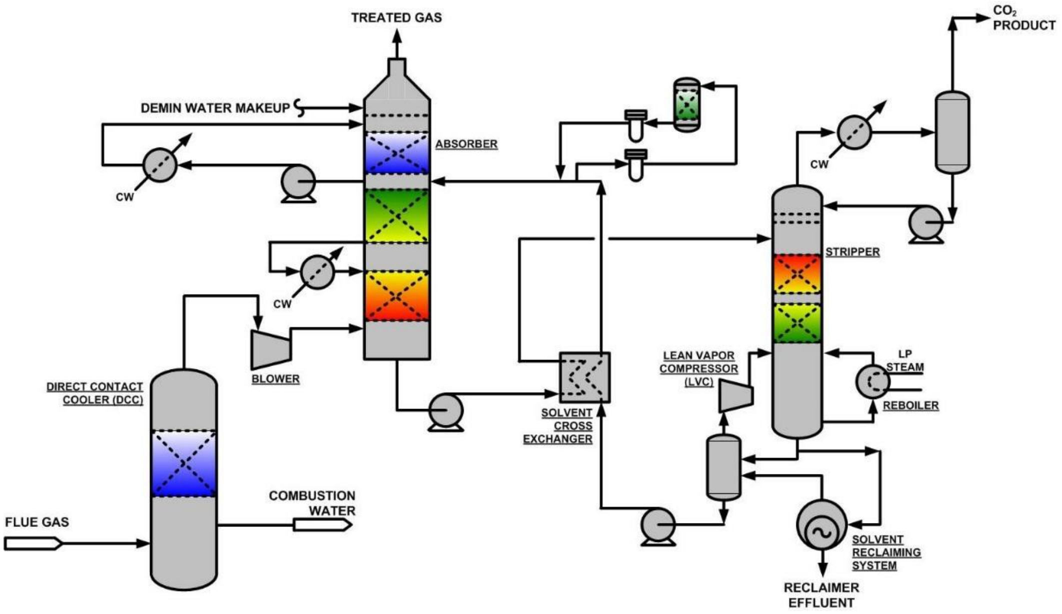

Figure 1: Simplified schematic of Fluor Corporation's Econamine FG Plus™ CO_2 capture process.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the NGCC unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	205	4.54	9.30	72.95	12.34	0.88	0.7	1.7

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is by chemical reaction.

Solvent Contaminant Resistance – The solvent has high resistance to contaminants in the flue gas due to the solvent maintenance system's ability to maintain the solvent in pristine condition.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – None.

Solvent Makeup Requirements – 0.42 kg/tonne CO_2.

Waste Streams Generated – Solvent maintenance system waste.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Proposed Module Design – To be prepared after logistics/route study.

technology advantages

- FEED studies for carbon capture systems at actual sites such as this will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.

- This FEED study could lead to the world's first commercial deployment of carbon capture on a natural gas-fired power plant, and could be duplicated at other power plants across the world.
- Fluor's latest version of its EFG+ technology has several key features, including enhanced solvent formulation that has a high resistance to degradation, reduced amine circulation rate, a solvent maintenance system that keeps the solvent in pristine condition, low waste production, very low absorber vent emissions, and load-following capability. These features are proven on both gas turbine exhaust and coal flue gas. The enhanced dual-cell column and absorber design enables a large flue gas throughput, which reduces capital costs.

R&D challenges

- Targeting not just operating expenses, but also capital expenses in this FEED study to minimize the overall cost of CO_2 capture, via utilization of various technology and process synergies.
- Optimizing cooling water usage as California and the Bakersfield area's ongoing challenge of water availability for power production.

status

The project has commenced.

available reports/technical papers/presentations

"Front-End Engineering Design Study for Retrofit Post-Combustion Carbon Capture on a Natural Gas Combined Cycle Power Plant," DOE Project Kick-off Meeting, October 30, 2019. *https://www.netl.doe.gov/projects/files/FE0031842%20Kickoff%20Meeting.pdf*.

Piperazine Advanced Stripper Front-End Engineering Design

primary project goals

The University of Texas at Austin (UT-Austin) is performing a front-end engineering design (FEED) study of the piperazine advanced stripper (PZAS) process for carbon dioxide (CO_2) capture from the natural gas combined cycle (NGCC) power plant at Golden Spread Electric Cooperative's (GSEC) Mustang Station in Denver City, Texas.

technical goals

- To develop a comprehensive estimate for the total installed cost of PZAS with CO_2 compression on an NGCC power plant.
- To provide cost details to be used in the economic optimization of the process features of PZAS and other second-generation amine scrubbing processes.
- To provide the host site and cost-share partners with the information necessary to determine whether a commercial project to capture and use CO_2 for enhanced oil recovery (EOR) can be justified.
- To provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application.

technical content

The PZAS process is a second-generation amine scrubbing process with advanced solvent regeneration for post-combustion CO_2 capture. Figure 1 shows the flow and operating conditions for PZAS as tested at the National Carbon Capture Center (NCCC) pilot plant and reflects the planned design for Mustang Station. The NGCC at Mustang Station is comprised of a combined cycle facility, which consists of two gas turbines with two heat recovery steam generators (HRSGs) and a steam turbine with a total rating of 464 megawatt-electric (MWe).

The system uses 5 molal piperazine (PZ) solvent that absorbs CO_2 two and half times faster than 30 wt% monoethanolamine (MEA), requiring only 30 feet of absorber packing height to achieve 90% CO_2 removal. Flue gas from the NGCC is contacted with PZ solvent at a lean loading of 0.24 mol CO_2/gram-equivalent PZ to remove 90% of the CO_2. The hot flue gas leaving the HRSG is cooled in the bottom section of the absorber by recirculation of rich solvent through an exchanger using cooling water at the heat sink, mostly eliminating the temperature bulge of the absorber. Gas leaving the middle section of the absorber is contacted with cooled wash water in the top section of structured packing.

Rich PZ solvent is pumped through the cold cross-exchanger, the hot cross-exchanger, and the steam heater to the sump of the stripper. A fraction of the rich solvent (5 to 10%) is heated in the cold bypass exchanger. A fraction of the warm rich solvent (10 to 30%) is bypassed at its bubble point after the cold cross-exchanger. The two bypass streams are combined and fed to the top of the

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Piperazine Solvent with Advanced Stripper Retrofit to NGCC

participant:

University of Texas at Austin

project number:

FE0031844

NETL project manager:

Isaac Aurelio
Isaac.aurelio@netl.doe.gov

principal investigator:

Gary T. Rochelle
The University of Texas at Austin
gtr@che.utexas.edu

partners:

Trimeric Corporation

start date:

10.01.2019

percent complete:

10%

stripper. The flows of the bypassed streams are optimized to minimize the steam duty. Heat is recovered from the hot lean solvent as it is returned through the hot cross-exchanger and the cold cross-exchanger and then further cooled in the trim cooler. The stripper sump is maintained at 150°C and 6.3 bar(a). Vapor from the stripper sump flows through two sections of random packing. Heat is recovered from the vapor leaving the stripper in the cold bypass exchanger. The CO_2 product is further cooled in a condenser and the water is separated and returned to the absorber water wash. The advanced stripper configuration results in a heat duty less than 2.1 gigajoules (GJ)/tonne CO_2, compared to values of 2.4 to 2.7 GJ/tonne CO_2 for six other solvents tested at NCCC with the simple stripper under coal and NGCC operations. The improvement in energy performance is achieved through use of the cold rich bypass and warm rich bypass streams in the advanced stripper configuration.

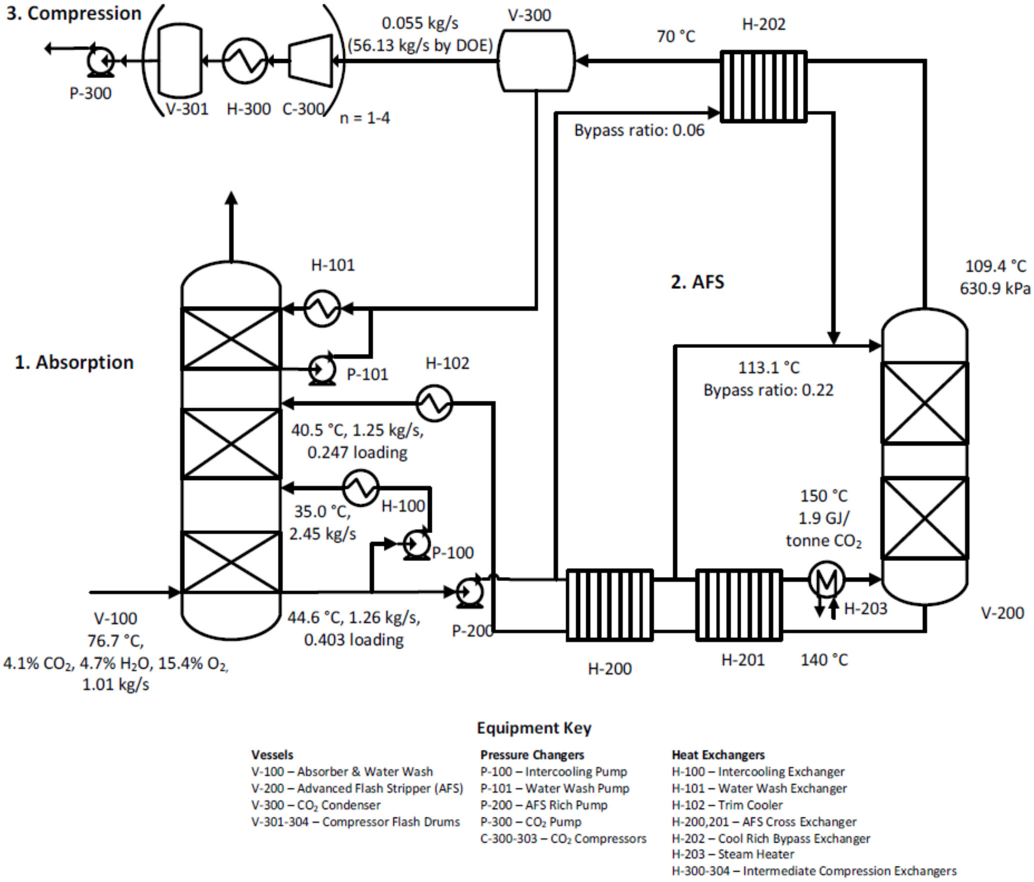

Figure 1: PZAS process flowsheet.

The PZAS process has evolved from bench-scale experiments to pilot-scale test campaigns, including testing at UT-Austin's Separations Research Program (SRP) pilot plant using simulated coal and natural gas flue gas and testing at NCCC using flue gas derived from fossil fuels at both coal and NGCC conditions. Previous testing has confirmed that PZ with a 5 molal concentration is a superior solvent to PZ with an 8 molal concentration. The reduced viscosity of 5 molal PZ results in an enhanced CO_2 absorption rate in the absorber and improved heat transfer performance in the cross-exchanger, reducing the heat duty in the advanced flash stripper (AFS) steam heater. Combining the 5 molal PZ solvent with the AFS decreases the cost of CO_2 capture to less than $40/tonne.

The details of the techno-economic analysis (TEA) that was prepared for the PZAS process in the previous DOE-funded project DE-FE0005654 are being utilized to determine equipment sizes and to develop an approximate capital cost estimate for installing PZAS at Mustang Station. The PZAS process is estimated to require a capital investment roughly two-thirds that of other second-generation amine scrubbing processes, which is largely attributable to a significant decrease in absorber column size and modest decrease in stripper column size.

The FEED study will allow the project team to develop detailed estimates for these direct capital cost components and provide a more accurate estimate of total plant costs for a PZAS installation at Mustang Station. The resulting estimates can be used to arrive at a more accurate Lang factor for developing future cost estimates for carbon capture on NGCC plants. The project team will interface directly with vendors to obtain detailed design and cost estimates for individual pieces of equipment for a full-scale capture facility. Operating costs can be estimated based on PZAS experience at the NCCC pilot plant and the resulting TEA. Parasitic loads are calculated based on developed thermodynamic properties of PZAS and the design of heat exchangers and other equipment requiring either electricity or steam energy. An appropriate source of steam will be identified that results in maximum efficiency. The FEED will also examine the benefits and economics of integrating CO_2 captured from a power station directly into an existing CO_2 pipeline network and possibly direct use by local CO_2-EOR end-users in the area.

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

Molal Concentration (Molality) – The amount (in moles) of solute, divided by the mass (in kilograms) of the solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The reaction of PZ with CO_2 involves formation of the following four PZ species:

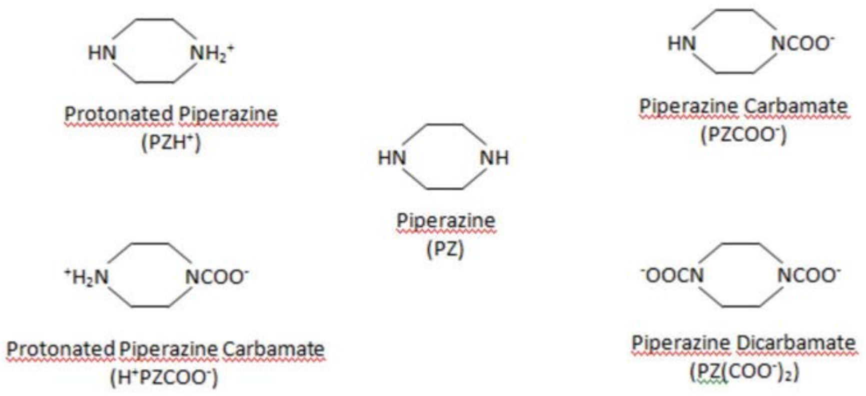

Figure 2: Molecular structure of piperazine species.

These reactions are as follows:

1. $PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
2. $PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
3. $H_2O + H^+PZCOO^- \leftrightarrow H_3O^+ + PZCOO^-$
4. $PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

TABLE 1: EQUILIBRIUM CONSTANTS FOR ABOVE REACTIONS

Eq. No	Equilibrium Constant	ln K = A + B/T + C lnT		
		A	B	C
1	$K_1 = \frac{x_{PZ} x_{H3O+}}{x_{H2O} x_{PZH+}}$	-11.91	-4,351	—
2	$K_2 = \frac{x_{H3O+} x_{PZCOO-}}{x_{PZ} x_{CO2} x_{H2O}}$	-29.31	5,615	—
3	$K_3 = \frac{x_{H3O+} x_{PZCOO-}}{x_{H+PZCOO-} x_{H2O}}$	-8.21	-5,286	—
4	$K_4 = \frac{x_{H3O+} x_{PZ(COO-)2}}{x_{PZCOO-} x_{CO2} x_{H2O}}$	-30.78	5,615	—

This speciation and solubility model has been used to predict the partial pressure of CO_2 and mole fraction of species in solution as a function of PZ loading; the results show a good match between the model and the experimental data.

Solvent Contaminant Resistance – 5 molal PZ is thermally stable at 150°C with negligible oxidative (Freeman, 2011) degradation. The total amine loss is estimated to be 0.5% per week when stripping at 150°C. At 135°C, the estimated total amine loss of PZ is 0.3%, as compared to 3.0% in the case of an MEA solvent. PZ forms nitrosamines and other nitro products with nitrogen dioxide (NO_2). Both pilot-scale flue gas testing and bench-scale testing have confirmed that nitrosamines decompose at temperatures of 150°C and greater. The main degradation products of PZ are formate (0.04 mM/hr) and ammonia (0.09 mM/hr) (Freeman, 2011).

Solvent Foaming Tendency – Pilot plant tests of PZ with two different sources of coal-fired flue gas and with air/CO_2 have experienced no persistent problems with foaming. However, bench-scale experiments have shown the possibility for PZ to foam under certain conditions (e.g., after undergoing oxidation degradation). In the bench-scale tests, foaming of PZ was greatly reduced with use of an oxidation inhibitor or with use of 1 part per million (ppm) of silicone antifoam (Chen, 2011).

Solvent Makeup Requirements – Including an estimate for additional amine lost in the reclaiming process, the required makeup rate is estimated to be 0.76 kg of 30 wt% PZ per metric ton of CO_2 captured for PZ regenerated at 150°C. The estimated makeup rate for 30 wt% MEA at 120°C is approximately 2.0 kg/MT CO_2.

Waste Streams Generated – The major amine solid/liquid waste streams come from reclaimer waste. There could be fugitive liquid amine emissions, which can be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Due to the low fly ash concentration of natural gas combustion gas, the heavy metal concentration in the solvent is not expected to trigger a hazardous waste classification with this technology. Gas-phase amine emissions from the absorber can be minimized by controlling aerosol formation and aerosol emissions from the absorber. Although amine aerosol emissions, which require sulfur trioxide (SO_3) or other sources of aerosol nuclei, are not expected to be problematic with natural gas combustion, careful measurement of PZ emissions from the NCCC pilot plant with NGCC conditions have established that the PZAS process will produce less than 1 ppm PZ in the clean flue gas.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

technology advantages

As compared to conventional amine solvents, the advantages of PZ are:

- Faster CO_2 absorption rate, higher working capacity, higher thermal stability, and less oxidative degradation—all of which point toward 10 to 20% less energy use.

- Advanced stripper configuration minimizes steam heater heat duty required for regeneration, limiting equipment sizes for major process equipment.
- Elevated regeneration pressure allows for elimination of lean solvent pump and elimination of two initial stages of CO_2 compression, resulting in capital cost savings.
- High absorption rate leads to smaller absorber size, reducing capital cost.
- PZ is resistant to oxidative degradation in the absorber.
- Five molal PZ is less corrosive than MEA at typical absorber temperatures, allowing less expensive and more readily available materials of construction to be used.
- No direct contact cooler or inlet booster fan are required.

R&D challenges

- Like other amines, PZ may absorb on aerosols in flue gas, leading to high amine emissions. Aerosol formation needs to be managed.
- PZ reacts with dissolved or entrained oxygen (O_2) at temperatures exceeding 150°C, potentially leading to greater than expected solvent makeup, but still less than MEA.
- PZ forms as a solid phase with water (PZ • $6H_2O$) and also with CO_2 (H+PZCOO- • H_2O). Process robustness to excursions in CO_2 loading, temperature, and water balance is being demonstrated by quantifying their effects on solids precipitation and plant operation.

status

The project team has begun establishing the project design basis for the FEED, taking into account site-specific characteristics and design specification, potential permitting requirements, and process targets for CO_2 capture and CO_2 product purity. Process modeling efforts have been initiated; process simulations will be used to arrive at a baseline heat and mass balance.

available reports/technical papers/presentations

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Front-End Engineering and Design: Project Tundra Carbon Capture System

primary project goals

Minnkota Power Cooperative is performing a front-end engineering and design (FEED) study to install a post-combustion carbon dioxide (CO_2) capture system at Square Butte Electric Cooperative's Milton R. Young Station, Unit 2 (MRY2), located near Center, North Dakota. Based on the results of pre-FEED studies of two leading commercial-ready carbon capture technologies, Fluor's Econamine FG Plus^{SM} (EFG+) technology has been selected for installation.

technical goals

- Complete a FEED study for constructing the carbon capture system at MRY2, including balance of plant (BOP).
- Address final challenges to implementing CO_2 capture with studies to optimize plant efficiency.
- Finalize a permitting strategy for the overall project.
- Evaluate environmental, health, and safety (EH&S) concerns and mitigation approaches.
- Conduct a hazard and operability (HAZOP) review.
- Complete a FEED-level cost estimate and construction schedule.

technical content

Minnkota is executing a FEED study on the addition of Fluor's EFG+ technology to an existing power plant fueled by North Dakota lignite to deliver the engineering and design work needed to demonstrate the feasibility of a next-generation carbon capture system technology at world-scale. The FEED comprises a broader effort led by Minnkota, titled Project Tundra, which is an initiative to build the world's largest carbon capture facility in North Dakota and to implement carbon capture, utilization, and storage (CCUS) to preserve the use of lignite, support the CO_2 enhanced oil recovery (EOR) industry, and revitalize legacy oil fields.

The project team aims to substantiate the economics and engineering supporting the business case for construction and operation of Fluor's EFG+ technology to capture 90% (11,000 tonnes/day) of the CO_2 from the flue gas of the 477-megawatt-electric (MWe) MRY2, producing near "zero carbon" power with limited or no impact on the price of electricity.

Fluor's EFG+ technology is an advanced amine-based process tailored for removal of CO_2 from low-pressure, high-oxygen-containing flue gas (up to 15 vol%) and is used in more than 30 commercial plants worldwide to process flue gases derived from a variety of fuels. The basic plant configuration consists of a two-stage direct contact cooler (DCC) for flue gas cooling and sulfur dioxide (SO_2) removal, an

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Econamine FG Plus^{SM} (EFG+) Retrofit to Coal Plant

participant:

Minnkota Power Cooperative, Inc.

project number:

FE0031845

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gerry Pfau
Minnkota Power Cooperative, Inc.
gpfau@minnkota.com

partners:

Fluor Enterprises, Inc., Burns & McDonnell, David Greeson Consulting, Hunt International Energy Services, North Dakota Industrial Commission, Energy & Environmental Research Center, Golder Associates, AECOM, Square Butte Electric Cooperative

start date:

10.01.2019

percent complete:

10%

absorber, a regenerator, and a compression and dehydration system to generate pipeline-ready CO_2, as shown in Figure 1. As the conditioned flue gas flows up the absorber, CO_2 is chemically absorbed into a circulating solvent stream flowing down the column. The CO_2-loaded solvent is then pumped from the bottom of the absorber, through a heat recovery exchanger where it is heated against hot CO_2-lean solvent, and into the top of the regenerator. As the solvent flows down the regenerator, it is contacted by steam, which strips the CO_2 from the solvent, producing an overhead mixture of steam and CO_2. The steam/CO_2 product is cooled, and the steam is condensed and separated from the CO_2 product. Hot CO_2-lean solvent from the bottom of the regenerator is pumped back through the heat recovery exchanger where it is cooled against the cold CO_2-loaded solvent before being returned to the top of the absorber.

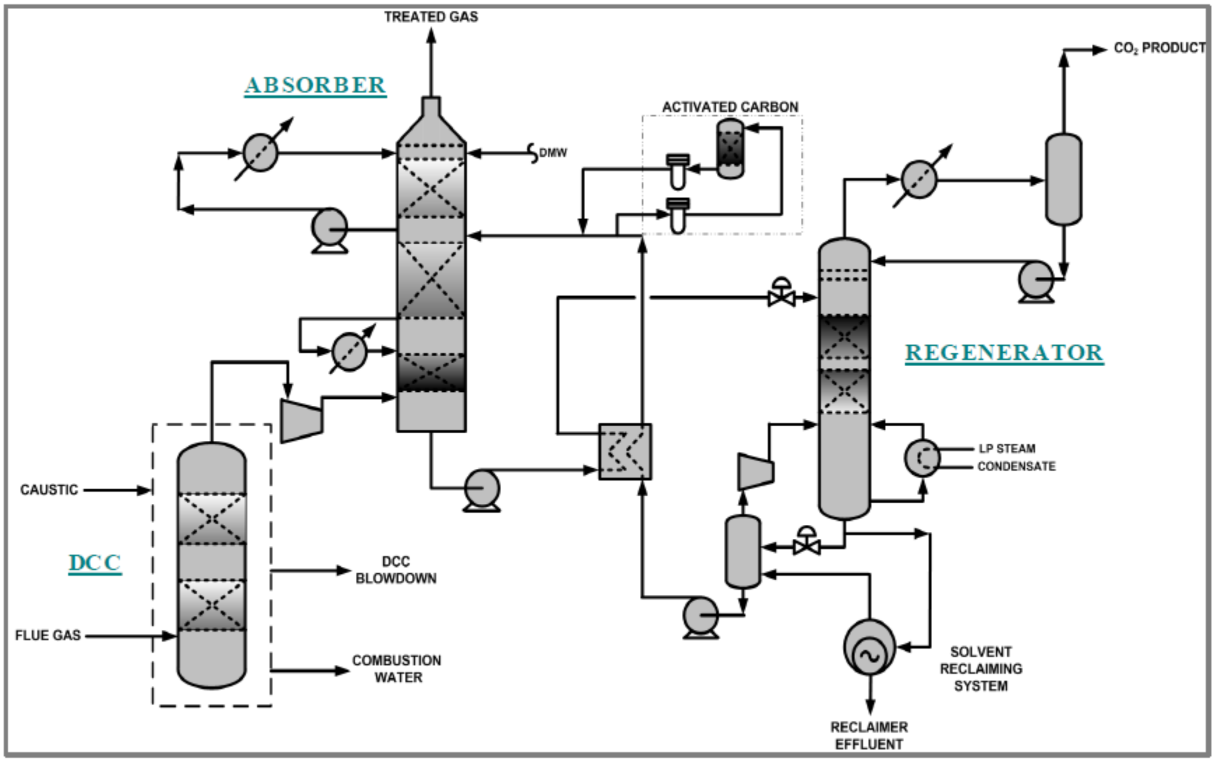


Figure 1: Schematic of Fluor's EFG+ CO_2 capture technology.

Advancements to progress the technology beyond the current state-of-the-art include steam cycle integration with advanced heat recovery to improve energy efficiency; methods for removing aerosols and a unique solvent maintenance system to minimize solvent degradation, thereby improving the environmental and cost profile; design of the world's largest capture facility (3.6 million tonnes/year, a twofold increase over any other facility) to capture greater economies of scale; optimization for cold climate performance; and establishment of the lowest levelized cost of capture attempted at world-scale.

Experience gained from Fluor's EFG+ demonstration plant in Wilhelmshaven, Germany, that captures 70 tonnes of CO_2 per day from a coal-fired power plant has enabled Fluor to make significant improvements to the process. Some of the unique features of the process design include:

- The EFG+ solvent is a proprietary formulation of primary amines with a regeneration steam requirement 30% lower than monoethanolamine (MEA).
- Fluor's patented two-stage DCC treats the flue gas in two sections, cooling the flue gas to harvest quality combustion knock-out water and removing SO_2 to single-digit part per million (ppm) levels.
- Fluor's patented absorber intercooling technology removes heat of absorption to increase the CO_2 carrying capacity of the solvent, reducing the net steam demand of the EFG+ process by 3 to 5%.

- A lean solvent flash/vapor compression configuration, in which the lean vapor compressor (LVC) recycles residual heat from the hot-lean solvent leaving the regenerator and transfers it back to the regenerator, resulting in a lower steam demand for the reboiler and reducing the total solvent regeneration energy requirement by ~10 to 15%.
- Minimized pressure drop in absorber due to advanced design of internals and packing in the DCC and absorber, thereby reducing the blower power by approximately 65% compared to conventional carbon capture plants.
- A solvent maintenance system (SMS) to remove heat-stable salts (HSSs) and other non-volatile degradation products in order to maintain solvent hygiene and performance.

Prior successful installations of the EFG+ process at a variety of facilities worldwide has prepared the project team for addressing new challenges, including processing a higher flue gas volume, effects from cold climate, and aerosols/solvent degradation concerns with using lignite coal-based flue gas.

The project team previously conducted a pre-FEED study to determine constructability, tie-in locations, preliminary pipe routings and interfaces, electrical interconnections, equipment specifications, capture system power requirements, geotechnical details, and control design. These components form the basis of the full FEED study, which will result in the following multidisciplinary design package:

- A FEED study report along with an electronic 3D model in SmartPlant® 3D.
- Material takeoffs (MTOs) exported from the 3D model for large-bore pipe lengths, fittings, flanges, valves, raceway, cables, and instrumentation; structural steel and concrete takeoffs developed from structural design software and sketches.
- An optimized general arrangement drawing.
- A tie-in list and location plan, with input from construction specialists during the detailed design phase; updates to process and instrumentation diagrams (P&IDs) with tie-in information.
- Detailed specifications for the major equipment packages.
- A Level 2 Process Hazard Analysis (i.e., HAZOP) report utilizing the overall P&IDs.
- A steam supply design.
- A fire protection study in accordance with National Fire Protection Agency codes and standards.
- An instrument control list with inputs and outputs and distributed control system (DCS) points, including cost specifications for all major instrument and control packages.
- Exploratory excavation plans and specifications to verify that proposed foundation and subsurface facilities are clear of obstructions.
- Preliminary foundation sketches to support equipment and ancillaries required for FEED cost estimates.
- Preliminary architectural drawings and sketches to support a cost specification for pre-engineered buildings and heating, ventilation, and air conditioning (HVAC), and obtaining budgetary quotes to support the FEED cost estimate.

Based on the pre-FEED study, a \$50/tonne 45Q tax credit for CO_2 storage or a \$35/tonne 45Q tax credit for EOR, plus projected CO_2 sales to oil companies for EOR operations, provides enough revenue to cover the capital, return on capital, and plant's operating costs, while yielding a near 10% return to tax equity. In addition, the cost of capture is expected to be \$49/tonne CO_2, which is a 20% reduction from the cost of CO_2 capture at the Petra Nova facility, the U.S.'s first commercial post-combustion carbon capture system at a coal-fired power plant. The FEED study is the next step in verifying and optimizing these costs and projections to reflect the higher level of engineering and design and cost-estimating certainty.

For the BOP items, operating cost estimates will be developed through detailed studies involving Fluor, owner's engineer Burns & McDonnell, and Minnkota. Both the operating and capital costs for an EFG+ plant are dependent on a number of variables, including, but not limited to, plant location, site conditions, plant capacity, final configuration, modularization versus field erected, flue gas conditions, air versus water cooling, and cost of utilities such as steam and electricity.

Although the EFG+ technology and the chemistry of the process are the same regardless of scale, the process equipment in the EFG+ process must be designed to ensure that the EFG+ chemistry occurs efficiently. Specifically, the scale-up challenge is construction of large-diameter columns and achieving good gas/liquid distribution in the packing.

As part of the pre-FEED, the team evaluated natural gas-fired auxiliary boiler and steam turbine extraction scenarios. Early stages of the FEED study will choose which steam source will be utilized.

In addition to removing ~3.6 million tonnes per year of CO_2, the carbon capture facility installed at MRY2 will also be designed to remove ~2,200 tonnes of SO_2 annually. However, significant concentrations of alkali-derived aerosols have been measured at MRY2 during previous studies, which can impact both amine solvent emissions and degradation rates. Also, solvent emissions from the absorber may include ppm levels of amine and degradation byproducts in the form of ammonia and aldehydes. The combination of the aldehydes/amine may constitute a new major source of VOCs, which requires a Title V permit under the Clean Air Act. In the FEED, Fluor will evaluate the cost-effectiveness of solutions for removal of aerosols upstream of the absorber, thereby eliminating/mitigating the challenge of aerosol-exacerbated emissions of amine from the absorber. Preliminary air dispersion modeling was performed in the pre-FEED study to determine appropriate stack height, parameters, and location. In order to confirm that the site will not exceed National Ambient Air Quality Standards (NAAQS), an additional air dispersion model will be required using the final FEED study parameters, emissions, and layout.

An SMS will also be included in the EFG+ plant design for MRY2 to maintain favorable solvent purity and produce a small waste effluent stream that is collected and periodically hauled offsite for disposal. Furthermore, by maintaining low impurity levels in the solvent, undesired VOC emissions are reduced dramatically.

Wastewater produced by the EFG+ plant includes blowdown from the DCC (knock-out water and SO_2 scrubbing solution). The condensed water vapor from cooled flue gas is of high quality and can be used as cooling water makeup at MRY2 after minor treatment. After investigating the compatibility of existing MRY Station wastewater treatment, Minnkota concluded that disposal via a Class I injection well is the likely method of disposal for some of the effluents. The FEED study will include design and costing of a Class I well. The proposed changes will require the MRY2 plant to modify its National Pollutant Discharge Elimination System (NPDES) permit for industrial wastewater discharges.

Any plant constructed in North Dakota requires a winterization plan, as temperatures can reach to -40°C or less. Through the pre-FEED effort, the project team identified best practices for ensuring the plant remains efficient and operational during the winter months, including specifications for building foundation depth, insulation and material specifications, cold process startup/shutdown, and buried fluid lines.

Modularization is a key component of the construction strategy for Project Tundra, which includes a transportation study to determine module size and onsite fabrication requirements. A construction-driven strategy is key to schedule certainty, risk reduction, and cost-effective execution and delivery of the project.

Flue Gas Assumptions – Unless noted, average flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.5	141	10.2	20.5	65.1	6.9	0.80	42.7	148.3

Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 is a chemical reaction.

Solvent Contaminant Resistance – The solvent has very good resistance to contaminants in the flue gas aided by the solvent maintenance system.

Solvent Foaming Tendency – None.

Flue Gas Pretreatment Requirements – SO_2 removal and temperature control is required prior to the absorber.

Solvent Makeup Requirements – Estimated at 0.25 kg/tonne.

Waste Streams Generated – Solvent maintenance system waste, water treatment waste, and cooling tower blowdown.

Process Design Concept – Flowsheet/block flow diagram shown above in Figure 1.

Proposed Module Design – Will be determined based on results of a logistics/route study.

technology advantages

- Advanced solvent formulation with high CO_2 capacity and high absorption rate.
- Low pressure-drop packing in DCC and absorber has the potential to lower the power consumption for the blower by 65%.
- Large diameter column design for absorber and DCC reduces the number of absorption trains required, thereby lowering capital costs.
- Novel absorber intercooler configuration increases solvent loading and lowers the overall solvent circulation rate, further reducing power consumption and solvent loss.
- An LVC unit reduces the steam demand for solvent regeneration by 10 to 15%.
- Fluor's proprietary SMS lowers overall solvent loss and makeup.
- Advanced reclaiming technology significantly reduces reclaimer waste.

R&D challenges

- Lignite coal-based flue gases, such as that produced at MRY2, contain alkali-derived aerosols and particulate matter that can have a detrimental impact on both amine solvent emissions and degradation rates.
- Integration into an existing facility poses many operating and plant layout challenges.
- Maintaining a proper water balance for the facility becomes a challenge.

status

The project team has developed a formal optimized design manual that establishes the common design basis for the project. The design of the carbon capture system, along with an analysis of integrating the carbon capture system with the plant's steam cycle or utilizing natural gas-fired auxiliary boilers, are underway. A preliminary meeting with the North Dakota Department of Environmental Quality (NDDEQ) was held to discuss the requirements for air emissions and water discharge permitting.

available reports/technical papers/presentations

"Front-End Engineering & Design: Project Tundra Carbon Capture System," DOE Kick-off Meeting, November 12, 2019. *https://netl.doe.gov/projects/files/Slides%20Minnkota%20FE0031845%20Kickoff%20Mtg%202019-11-12%20Non-Confidential.pdf.*

Front-End Engineering Design Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Gas Turbine Combined Cycle Power Plant

primary project goals

Bechtel National, Inc. is performing a comprehensive front-end engineering design (FEED) study for a carbon capture and compression plant retrofit to an existing natural gas-fired combined cycle (NGCC) power plant located in Texas. The capture plant is based on conventional technology comprising a non-proprietary aqueous solvent, monoethanolamine (MEA), an absorber-stripper cycle, and multi-stage centrifugal compressors.

technical goals

- Develop a project design basis to provide general project requirements that apply to the specific plant site, ambient conditions, fuel feedstock and flue gas characteristics, environmental requirements, and modularization design requirements.
- Develop process engineering documents for constructing the carbon capture system, including block flow diagrams, heat and mass balance diagrams, process flow diagrams for major components, and a water balance diagram.
- Conduct a preliminary hazard and operability (HAZOP) study and produce a report to document the results.
- Develop civil, structural, mechanical, electrical, and control systems engineering design packages.
- Develop a layout and design package that includes process plant arrangement drawings and piping and instrumentation diagrams.
- Summarize expected emissions and waste streams.
- Review various contracting and purchasing options for procuring a new process system and perform a constructability review to identify construction access, lay-down areas, and sequencing of construction work.
- Develop an overall project capital cost estimate within a ±15% accuracy.
- Prepare a final FEED study package.

technical content

Bechtel is executing a FEED study on retrofitting an existing NGCC power plant with an amine-based post-combustion carbon capture plant. The prospective end use for the captured carbon dioxide (CO_2) is enhanced oil recovery (EOR). Bechtel is aiming to develop a technology readiness level (TRL) 9 carbon capture, utilization, and storage (CCUS) concept for retrofitting an existing NGCC with mature and field-proven technology and equipment. Figure 1 illustrates a simplified process flow diagram of a conventional absorber-stripper scrubbing system with a non-proprietary solvent such as MEA.

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Amine-Based Solvent Technology Retrofit to NGCC

participant:

Bechtel National, Inc.

project number:

FE0031848

NETL project manager:

Naomi O'Neil
naomi.oneil@netl.doe.gov

principal investigator:

William Elliott
Bechtel National, Inc.
belliott@bechtel.com

partners:

Electric Power Research Institute, Inc., Nexant

start date:

10.01.2019

percent complete:

10%

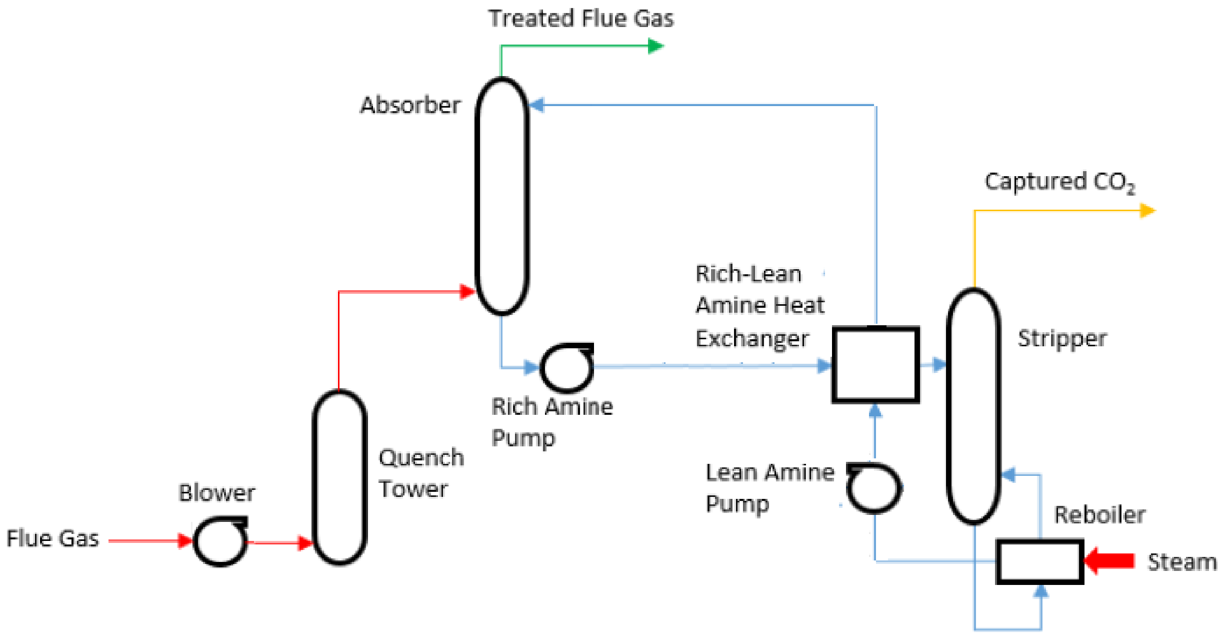


Figure 1: Generic simplified flowsheet for amine-based CO_2 capture from flue gas.

Bechtel is applying an "open access" and "open technology" methodology to the process and physical design of the facilities and the solvent used in the technology. An "open access" technology approach denotes that the owner/operators of a post-combustion carbon capture plant are in full control of the technology used in the plant. The post-combustion carbon capture hardware can be procured by competitive tendering against a non-proprietary specification, similar to conventional power plants. This allows the owner/operators to specify the post-combustion carbon capture plant hardware and solvent selection based on the latest published technology and operating experience. "Open access" technology utilizes a generic, non-proprietary solvent that is readily purchased on the open market from chemical manufacturers at a relatively low cost. These features facilitate lower capital and operating expenses and avoid royalty payments and technical restrictions associated with use of proprietary system designs and solvent selection.

The host site selected for the FEED study is the Sherman Generating Station, a 2x2x1 NGCC located in Sherman, Texas. The 758-megawatt-electric (MWe) power plant built by Bechtel is powered by two Siemens F class gas turbines. The selection of the site has several advantages, including:

- The NGCC plant was built by Bechtel; therefore, key project personnel have access to all design documents and are familiar with the facility.
- The plant includes F class gas turbines, a state-of-the-art technology.
- The location of the host plant is near oil-bearing formations favorable for EOR operation.

Lessons learned and experience gained from earlier FEED and FEED verification studies performed by Bechtel are being used as a basis for this FEED study. Bechtel prepared a FEED verification in 2015 under the direction of Shell for a proposed carbon capture retrofit to gas turbine Unit 13 at the Peterhead Power Station in Scotland. In 2009, Bechtel performed a FEED study for a CO_2 capture and compression facility designed to capture 85% of the CO_2 emissions from a 420-MWe gas-fired power plant in Norway. Both a proprietary solvent and MEA were used as bases of design. The plants involved in both FEED studies employ Siemens gas turbines, similar to the gas turbines in the Sherman facility; thus, much of the engineering work has already been completed by Bechtel for flue gas conditions very similar to the host site in Texas. Bechtel's FEED report will be based on these past design reports.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	61.08
Normal Boiling Point	°C	170
Normal Freezing Point	°C	10.3
Vapor Pressure @ 15°C	bar	<1
Manufacturing Cost for Solvent	$/kg	1 – 2
Working Solution		
Concentration	kg/kg	35
Specific Gravity (15°C/15°C)	-	1.02
Specific Heat Capacity @ STP	kJ/kg-K	3.6
Viscosity @ STP	cP	4
Absorption		
Pressure	bar	1.089
Temperature	°C	53.5
Equilibrium CO_2 Loading	mol/mol	0.4 – 0.49
Heat of Absorption	kJ/mol CO_2	TBD
Solution Viscosity	cP	2.56
Desorption		
Pressure	bar	2.31
Temperature	°C	130.8
Equilibrium CO_2 Loading	mol/mol	0.22 – 0.25
Heat of Desorption	kJ/mol CO_2	TBD
Module Design		
Flue Gas Flowrate	kg/hr	2.53×10^6
CO_2 Recovery, Purity, and Pressure	% / % / bar	80-90 / 99.0+ / 200
Absorber Pressure Drop	bar	0.076
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.5	194	3.82	7.74	74.78	12.81	0.85	10	370

Flue Gas Pretreatment Requirements – Flue gas is cooled to approximately 50°C before entering absorber towers through a fogging system that reduces temperature and saturates flue gas with water.

Solvent Makeup Requirements – To be detailed in the FEED report.

Chemical/Physical Solvent Mechanism – The chemical/physical solvent mechanism is primarily controlled by the solubility and alkalinity characteristics of the amine. MEA is fully water soluble and exhibits high alkalinity. MEA's low molecular weight permits higher solution capacity and its low boiling point allows higher recovery during reclamation of contaminated solution. Carbon dioxide solubility in MEA solutions is relatively high. Regeneration of MEA solutions is accomplished at reasonable temperatures with moderate heat input. Further discussion will be included in the FEED report.

Solvent Contaminant Resistance – To be detailed in the FEED report.

Solvent Foaming Tendency – To be detailed in the FEED report.

Waste Streams Generated – MEA and ammonia emissions from the absorber are reasonable and will be defined in the FEED report. Liquid and solid wastes from solvent maintenance and reclaiming will be defined in the FEED report.

Process Design Concept – The process overview under normal operation consists of the following systems:

- Flue gas diversion—The flue gas is directed from the existing stack to the plant.
- Flue gas cooling—The flue gas as supplied is too hot to process efficiently in the absorber and is cooled to its saturation temperature before entering the absorber.
- CO_2 absorption—Parallel absorbers use an amine solution to remove the CO_2 from the flue gas.
- Heat integration—Heat is recovered from internal streams to enhance plant energy efficiency.
- CO_2 stripping—The amine is regenerated for reuse by liberating the CO_2 from the amine solution.
- CO_2 compression and drying—The CO_2 is compressed, dried, further compressed, and liquefied to meet the CO_2 specifications.
- Amine reclamation—Heat stable salts (HSS) and degradation/oxidation products are removed from the amine solution.
- Amine storage—Fresh amine and lean amine are stored and injected into the absorption system to maintain the amine solution concentration.

Proposed Module Design – To be detailed in the FEED report.

technology advantages

- Use of generic solvent avoids restrictions and costs associated with proprietary solvents.
- An "open access" and "open technology" approach can accelerate CCUS deployment and reduce the costs of CCUS by facilitating efficient know-how exchange and competition within the fleet of plants that may be built over the next five to 10 years.
- "Open access" and "open technology" full-scale plants can facilitate the progression of post-combustion capture systems currently at TRL 9 to achieve a commercial readiness index of 6 within 10 years or less.
- Bechtel has extensive experience in carbon capture studies, plus detailed design, construction, and operation of NGCC power plants and CO_2 capture plants, including involvement in several previous FEED studies on CO_2 capture retrofits to NGCC plants.

R&D challenges

- Steam extraction complexity.
- Confirmation of carbon capture simulation software accuracy for generic amine solutions at high solvent strengths.

status

The project team is developing final engineering documents to include block flow diagrams, process flow diagrams, heat and mass balances, water balance diagrams, piping and instrument diagrams, and summary equipment specifications. Engineering design packages will be prepared for civil, structural, mechanical, electrical, automation, and environmental systems.

available reports/technical papers/presentations

"Front-End Engineering Design (FEED) Study for a Carbon Capture Plant Retrofit to a Natural Gas-Fired Turbine Combined Cycle Power Plant (2x2x1 Duct-Fired 758-MWe Facility with F Class Turbines)," DOE Kick-off Meeting, November 15, 2019. *https://netl.doe.gov/projects/files/Bechtel%20Kickoff%20DE-FE0031848%20r3%20PUBLIC.pdf*.

Front-End Engineering Design of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant

primary project goals

Southern Company Services, Inc. is conducting a front-end engineering design (FEED) study for a carbon dioxide (CO_2) capture system based on Linde-BASF's aqueous amine solvent-based technology installed at an existing Southern Company natural gas-fired combined cycle (NGCC) power plant. The CO_2 capture plant will be of commercial scale (at least ~375 megawatt-electric [MWe]) and designed to achieve a high removal of CO_2 from the flue gas feed stream.

technical goals

- Select an NGCC generating plant as the host site for the FEED study based on a set of defined criteria (performance of the gas turbines, availability of space to house a carbon capture system, availability of utilities to support the system, suitability of the surrounding geology for enhanced oil recovery [EOR] or storage).
- Produce a design basis for the carbon capture system based on the specific site requirements, including flue gas composition, environmental requirements, and requirements for modularization.
- Complete a conceptual design package for the process area of the post-combustion capture plant and assess the logistics for solvent delivery required for a commercial-scale carbon capture plant.
- Complete design packages for mechanical, electrical, structural, instrumentation and control, and facilities engineering and assess the cost and logistics for constructability and site security.
- Utilize the cost and schedule estimates of equipment vendors and contractors to derive a total project cost and schedule estimate within ±15% error.

technical content

Linde and BASF have been jointly developing, optimizing, and testing an advanced post-combustion CO_2 capture technology since 2007. The Linde-BASF technology for capturing CO_2 from flue gas using the BASF OASE® blue solvent is a mature technology that has been tested in two pilot plants with different flue gas sources covering a wide variety of flue gas compositions and impurities. The Linde-BASF aqueous amine solvent-based post-combustion CO_2 capture technology provides a solution for key challenges encountered by solvent-based carbon capture

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Linde-BASF Amine Solvent-Based Technology Retrofit to NGCC

participant:

Southern Company Services, Inc.

project number:

FE0031847

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Landon Lunsford
Southern Company
LDLUNSFO@southernco.com

partners:

Linde Gas North America LLC, BASF, Linde Engineering Dresden

start date:

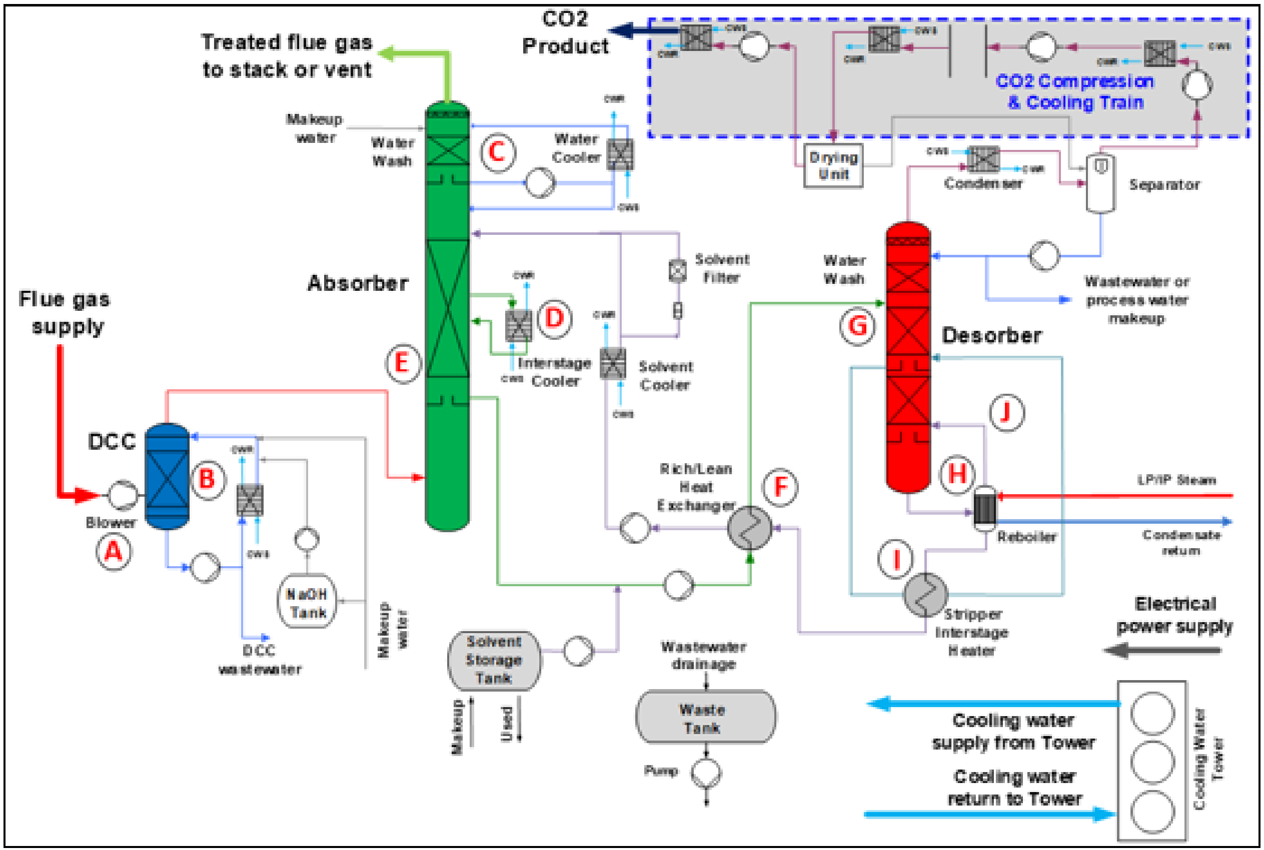
01.29.2020

percent complete:

10%

technologies, which include relatively high capital costs, significant parasitic energy requirements, and solvent stability and degradation issues.

The technology is based on a typical lean-rich solvent absorption/regeneration cycle for CO_2 capture, but leverages several key innovative features for both solvent and process optimization to reduce the cost of CO_2 capture from NGCC plants. The optimized properties of the OASE blue solvent lead to capital and operating cost reduction due to efficient CO_2 capture from low pressure sources through favorable reaction kinetics and reduced reboiler steam energy consumption; better stability than monoethanolamine (MEA); and a lower solvent circulation rate. In addition to advances in solvent design, Linde has achieved significant improvements in process design, as outlined in Figure 1.



A. Flue gas blower provides sufficient pressure to overcome pressure drop across the direct contact cooler (DCC)/pre-scrubber and absorber. The blower location can be adjusted to minimize cost based on arrangement of equipment and piping at the NGCC site.
B. Integrated DCC/pre-scrubber to reduce sulfur oxides (SO_X) content below 5 parts per million (ppm) and simultaneously cool the flue gas stream to ~35 to 40°C.
C. Innovative and patented water wash section at the top of the column to reduce amine losses, even in the presence of aerosols. Dry bed configuration helps mitigate aerosol-driven amine losses.
D. A gravity-driven inter-stage cooler for the absorber that eliminates the need for a pump and related controls.
E. High-capacity structured packing reduces the absorber diameter, thereby enabling a larger single-train plant construction and greatly reduced capital costs.
F. Solvent-based heat exchanger designed to operate over a wide range of temperature approaches, which provides the opportunity to optimize the performance and capital cost trade-off.
G. Regenerator designed for operation at pressures up to 3.4 bara significantly reduces CO_2 compression energy and eliminates the bulky first stage of the CO_2 compressor, resulting in capital cost savings.
H. Innovative plate and frame design of the reboiler minimizes thermal degradation of solvent and provides for a lower solvent inventory and faster dynamics to respond to flue gas load and composition changes.
I. Stripper Inter-Stage Heater (SIH) enhances energy-efficient CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.
J. Variations of the stripper-reboiler flashing configuration, which are being evaluated to further minimize solvent regeneration energy.

Figure 1. Process flow diagram of Linde-BASF OASE® blue post-combustion CO_2 capture technology.

A development timeline of the Linde-BASF technology is shown in Figure 2. Previous testing of a 0.45-MWe dry lignite-fired pilot plant incorporating the Linde-BASF technology has shown that the OASE blue solvent is more stable than MEA after 2,500 hours of testing. The process was also previously tested at 1.5-MWe-scale at the National Carbon Capture Center (NCCC) under the U.S. Department of Energy (DOE)-funded project DE-FE0007453, validating solvent stability and revealing a cyclic capacity 20% higher than MEA and regenerator steam consumption 25% lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact.

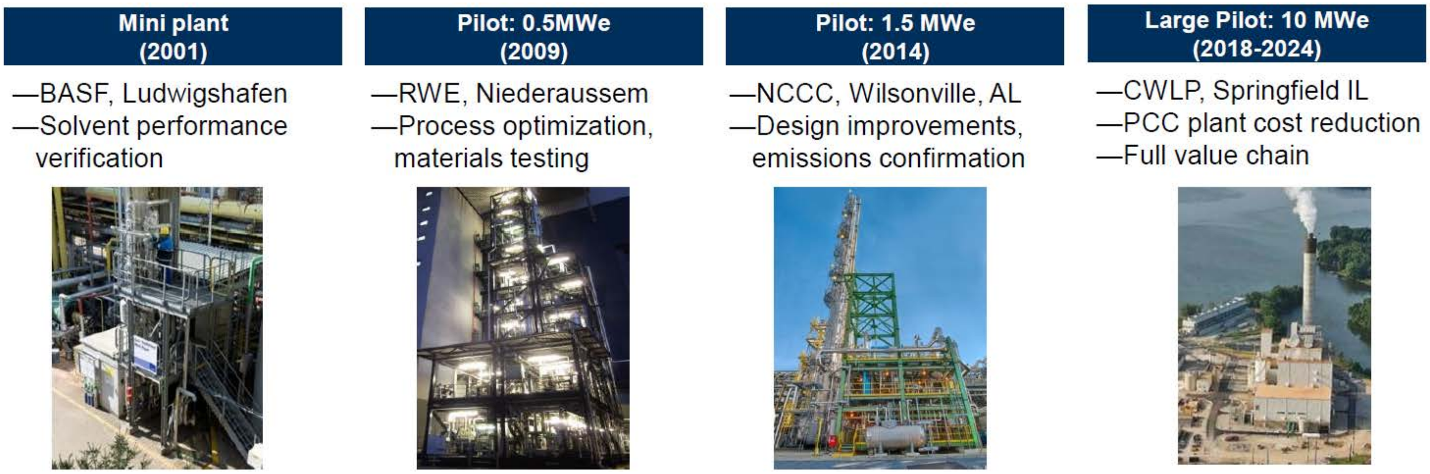


Figure 2. Linde-BASF post-combustion CO_2 capture technology development.

Milestones achieved thus far for the Linde-BASF post-combustion CO_2 capture technology applied to NGCC flue gas conditions are outlined in Figure 3. These include testing on an NGCC flue gas composition at the 0.45-MWe pilot-scale in Niederaussem, Germany; completion of a detailed FEED study on CO_2 capture from a 510-MWe NGCC power plant in 2011; and completion of a pre-FEED study for CO_2 capture at a 480-MWe NGCC power plant in 2018.

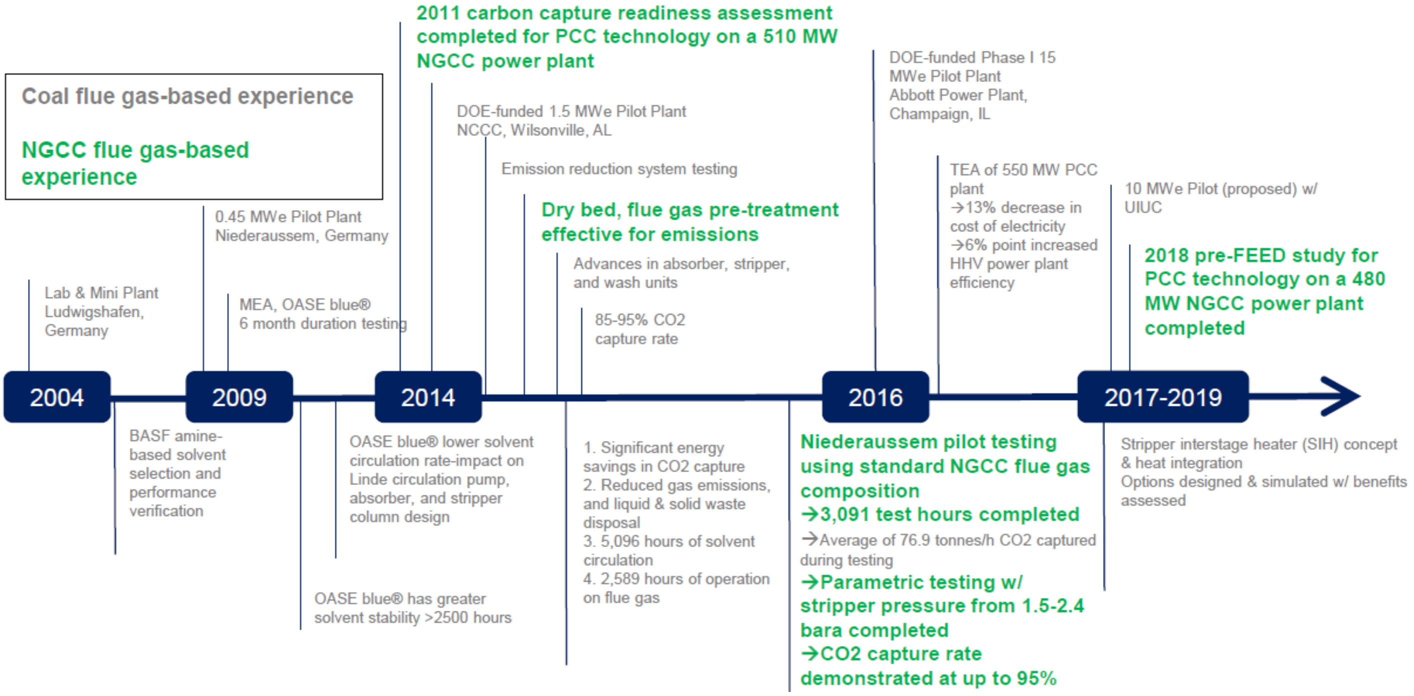
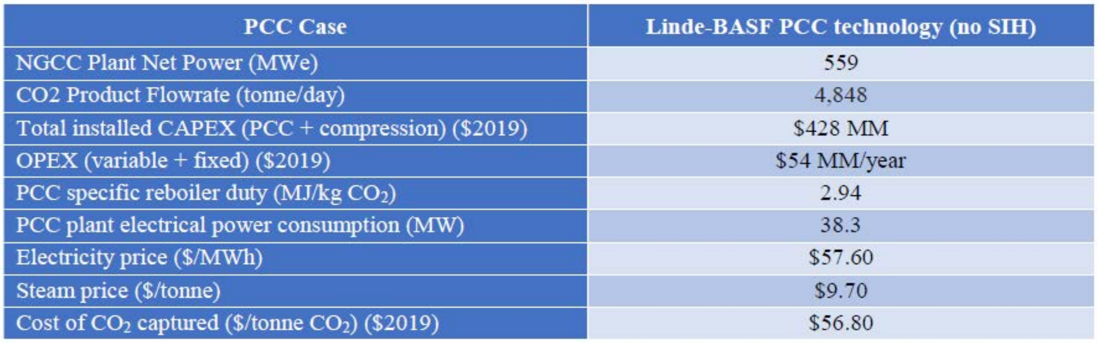


Figure 3. Milestones achieved by Linde-BASF post-combustion CO_2 capture technology.

The capital and operating costs determined from the previous pre-FEED and FEED studies are shown in Table 1. The studies were based on commercial Linde-BASF post-combustion CO_2 capture plants recovering 85 to 90% of the CO_2 in the flue gas supplied to the process from an NGCC power plant. All major process components were included in each study and the CO_2 product purity was specified at greater than 99 mol% (dry) with less than 100 parts per million (ppm) oxygen (O_2) content. Capital costs were estimated using Linde's proprietary cost estimation methodology for new commercial plants and were derived from databases of actual equipment quotes from vendors collected from recent projects. Capital costs for CO_2 capture plants integrated with NGCC plants are significantly higher compared to those integrated with coal-fired power plants due to the reduced flue gas CO_2 concentration in natural gas-derived flue gas (~4 mol% versus ~12% mol% CO_2 for coal-fired plants). This reduced flue gas CO_2 concentration necessitates a taller and larger diameter absorber column to achieve 90% CO_2 capture at low or ambient pressures. The optimum CO_2 capture rate at the host site will be defined in the FEED study to achieve an attractive cost option.

TABLE 1: ESTIMATED CAPEX, OPEX, AND COST OF CO_2 CAPTURED FOR LARGE-SCALE LINDE-BASF CO_2 CAPTURE AND COMPRESSION PLANT (550+ MWE) FOR NGCC BASED ON PAST LINDE STUDIES (COST YEAR=2019) (WITHOUT TRANSPORTATION AND STORAGE)



PCC Case	Linde-BASF PCC technology (no SIH)
NGCC Plant Net Power (MWe)	559
CO2 Product Flowrate (tonne/day)	4,848
Total installed CAPEX (PCC + compression) ($2019)	$428 MM
OPEX (variable + fixed) ($2019)	$54 MM/year
PCC specific reboiler duty (MJ/kg CO_2)	2.94
PCC plant electrical power consumption (MW)	38.3
Electricity price ($/MWh)	$57.60
Steam price ($/tonne)	$9.70
Cost of CO_2 captured ($/tonne CO_2) ($2019)	$56.80

The general approach for the FEED follows the methodology described in Figure 4.

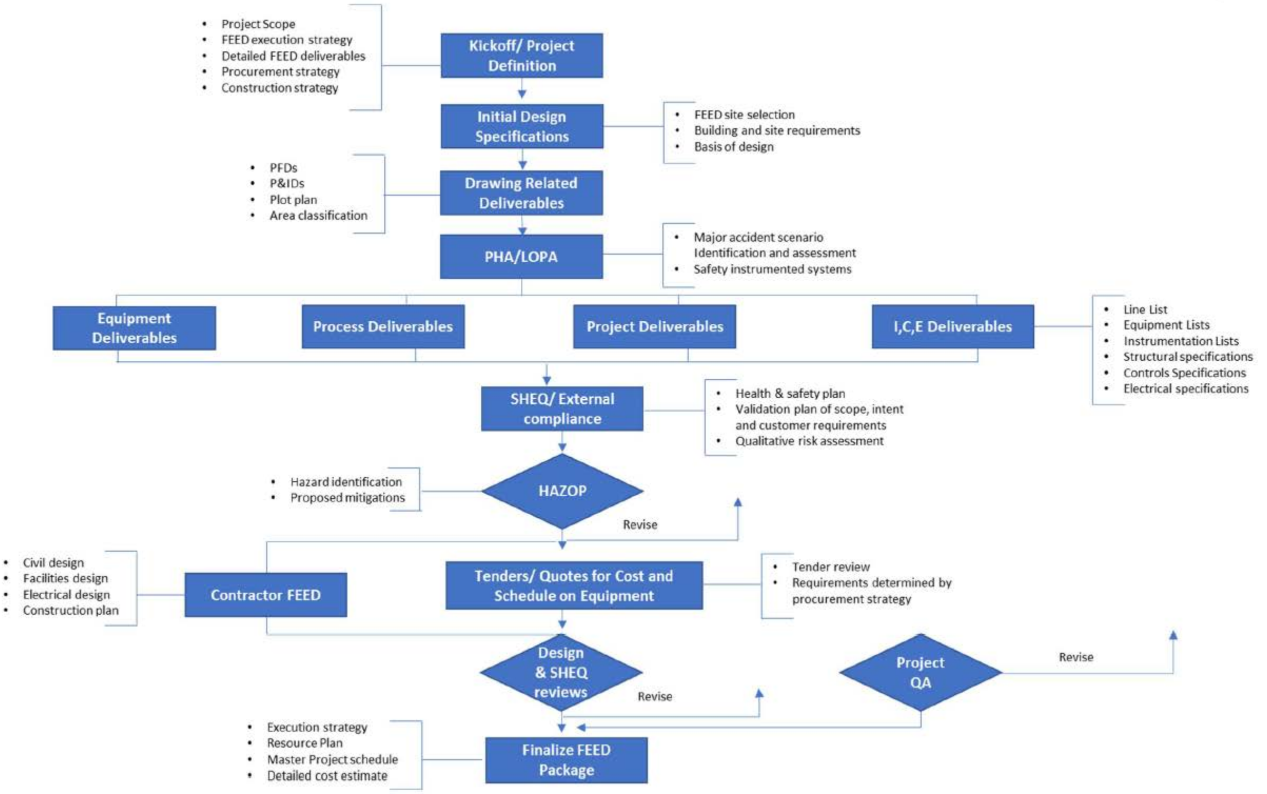


Figure 4. FEED approach.

Process designs that reduce the energy required for solvent regeneration through heat recovery integration are being optimized as part of the FEED study. Waste heat sources at the NGCC-fired host site can be leveraged to reduce the parasitic steam consumption of the CO_2 capture system and reduce the negative impact of the capture plant on power plant steam cycle efficiency or net electrical power generation. Sources include: (1) supplemental low- to medium-pressure steam from the power plant steam cycle in the range of 5 to 6 bara not currently used for electricity production can be redirected for use in the post-combustion CO_2 capture plant reboiler; (2) waste heat recovered from the hot flue gas upstream of the CO_2 capture plant after the heat recovery steam generator (HRSG) can be used to pre-heat CO_2-rich solvent entering the stripper column; or (3) external steam generation can reduce the steam input from the power plant. In addition, process optimization within the post-combustion CO_2 capture plant itself, including lean vapor compression (LVC) involving flashing of the CO_2-lean solution at the bottom of the stripper and redirecting the vapor after compression back to the bottom of the stripper, is an option that can substantially reduce the reboiler steam consumption for NGCC-fired CO_2 capture down to 2.4 gigajoules (GJ)/tonne CO_2 based on past FEED studies conducted for large Linde-BASF post-combustion CO_2 capture plants.

Linde has conducted extensive research on the management of flue gas aerosol particles that contribute to amine losses through the treated gas exiting the absorber, including literature studies and aerosol measurements taken during testing of the Linde-BASF post-combustion CO_2 capture technology at NCCC. Experimentally, Linde has determined that if aerosol concentrations are less than 10^7 particles/cm^3 for particles ranging from 70 to 200 nanometer (nm) in diameter, there is no need for pre-treatment beyond a direct contact cooler (DCC)/pre-scrubber and dry bed wash section in the absorber to manage the aerosols. Aerosol concentrations are expected to be much lower for NGCC-derived flue gas than for coal-fired flue gas; therefore, typical emission control measures have been integrated into the Linde-BASF CO_2 capture plant design.

Two Southern Company host sites are being evaluated in the first phase of the FEED study: Alabama Power Company's Plant Barry (Units 6 and 7), located in Bucks, Alabama, and Mississippi Power Company's Plant Daniel (Units 3 and 4), located in Moss Point, Mississippi. Each of the gas-fired combined cycle units (Units 6 and 7 at Plant Barry and Units 3 and 4 at Plant Daniel) produce a nominal 525 MWe (net). For either host site, equipment and operating modifications in the combined cycle to increase CO_2 concentration in the flue gas is a primary focus of the FEED study to minimize carbon capture costs. Cooling water capacity at both combined cycle plants is limited; therefore, evaluations of new cooling tower capacity versus air cooling are being performed in the FEED. For each site, steam supply to the carbon capture process may be available via extraction from the steam turbine, but the overall impact on the HRSG, steam cycle, and steam turbine is being evaluated during the FEED to determine the cost impact of extraction versus alternate steam production from a package boiler or cogeneration unit.

The FEED will provide a financial indicator of the costs of installation at an actual domestic NGCC power plant site and potentially illustrates that this capture system can be employed at operating commercial coal-fired power plants. The commercial FEED will provide a realistic framework for NGCC power plants to be built CO_2 capture-ready or to retrofit existing NGCC plants with an economical CO_2 capture system.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Design Value
Molecular Weight	mol^{-1}	proprietary
Normal Boiling Point	°C	proprietary
Normal Freezing Point	°C	-5 to 25
Vapor Pressure @ 15°C	bar(a)	proprietary
Manufacturing Cost for Solvent	$/kg	proprietary
Working Solution		
Concentration	kg/kg	proprietary
Specific Gravity (15°C/15°C)	-	1.0 – 1.2
Specific Heat Capacity @ STP	kJ/kg-K	proprietary
Viscosity @ STP	cP	1.5 – 7.0

Absorption		
Pressure	bar(a)	0.9 – 1.1
Temperature	°C	30 – 60
Equilibrium CO_2 Loading	mol/mol	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary
Solution Viscosity	cP	1.5 – 7
Desorption		
Pressure	bar(a)	1.6 – 3.4
Temperature	°C	125 – 140
Equilibrium CO_2 Loading	mol/mol	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary
Module Design		
Flue Gas Flowrate	kg/hr	Designed for >375 MWe slipstream
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, >99.9% (dry), 3.4 bar(a)
Absorber Pressure Drop	bar	proprietary
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary

Definitions:

Bar(a) – Unit used to indicate absolute pressure, where the reference pressure is absolute zero (i.e., not taking into account atmospheric pressure).

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the HRSG unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.8	231	4	9	74	12	1	0.08	2

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Carbon dioxide in the flue gas chemically binds to the OASE blue aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue solvent is highly resistant against many contaminants in the flue gas, as shown in both parametric and long-term continuous tests (see Electric Power Research Institute [EPRI] report[1] for additional information).

Solvent Foaming Tendency – During the pilot plant operations, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_X) in the flue gas to 2 to 5 ppm in order to limit solvent degradation and is implemented in a DCC in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_X present in the flue gas.

Solvent Makeup Requirements – The OASE blue solvent makeup rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low makeup rates were observed during long-term testing well below an operationally manageable threshold. Low solvent makeup is expected at scale when processing flue gas from power plants with a baghouse filter for particulate removal or with upstream flue gas pretreatment for aerosol mitigation.

Waste Streams Generated – The main waste liquid stream is from the DCC where SO_X and nitrogen oxide (NO_X) are removed; this stream is typically handled in the power plant wastewater treatment facility. A small amount of solid waste is removed using an activated carbon filter and mechanical cartridge filter that are replaced at regular intervals. Since the solvent degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – Flowsheet/process flow diagram shown in Figure 1.

Proposed Module Design – Free standing absorber and stripper columns will be tied into a modularized process skid. There will be associated containers for electrical equipment, analytical equipment, and process control.

technology advantages

- Exhibits a lower solvent circulation rate, reduced reboiler steam energy consumption compared to process using MEA solvent, reduced absorber diameter due to high efficiency packing, and lower downstream CO_2 compression cost due to the ability to operate at higher desorber pressures.
- BASF is the producer of the OASE blue solvent and the owner of the solvent technology. A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.

- The Southern Company-Linde-BASF partnership combines the necessary capabilities and experience to deliver the complete CO_2 capture technology value chain from solvent production to full-scale CO_2 capture plant engineering, procurement, and construction (EPC); commercial deployment; and long-term, continuous operations.

R&D challenges

- Carryover and emissions of amines and amine degradation products.
- Handling large volumes of process condensate from DCC.
- Disposal of spent activated carbon and filters can generate solid waste management.
- Designing for low liquid/gas ratios caused by lower CO_2 concentration in natural gas flue gas may result in below-target CO_2 capture rate or vapor and liquid maldistribution.
- Equipment scale-up associated with large vapor flows due to low CO_2 concentration.
- Engineering the liquid hydraulics and gas distribution in large manifolds needed for multiple absorbers.
- Integration of post-combustion CO_2 capture plant with host site.

status

The project team is evaluating the two potential host sites, Plant Barry in Alabama and Plant Daniel in Mississippi, for installation of the Linde-BASF CO_2 capture technology.

available reports/technical papers/presentations

Lundsford, Landon, "Front End Engineering Design of Linde-BASF Advanced Post-Combustion CO2 Capture Technology at a Southern Company Natural Gas-Fired Power Plant," DOE Kick-off Meeting, November 2019. *https://netl.doe.gov/projects/files/Slides%20SCS%20FE0031847%20Kickoff%20Mtg%202019-11-22%20public%20copy.pdf*.

Bostick, D., Krishnamurthy, K., "Final Testing Report to NCCC," January 27, 2017. *NCCC Technology Developer Reports*, National Carbon Capture Center, *https://static1.squarespace.com/static/566b0ac3df40f3a731712cf4/t/58f53329bebafb77565eda81/1492464428545/Linde-BASF+-+Slipstream+Pilot-Scale+Demonstration+of+a+Novel+Amine-Based+Post-Combustion+Technology+for+Carbon+Dioxide+Capture+from+Coal-Fired+Power+Plant+Flue+Gas.pdf*.

Bostick, D., Stoffregen, T., Rigby, S., "Final Techno-Economic Analysis of 550 MWe Supercritical PC Power Plant with CO_2 Capture using the Linde-BASF Advanced PCC Technology," January 9, 2017. *https://www.osti.gov/servlets/purl/1338328*.

O'Brien, K., "Large Pilot Testing of Linde-BASF Advanced Post-Combustion CO_2 Capture Technology at a Coal-Fired Power Plant," presented at 2018 NETL CO_2 Capture Technology Project Review Meeting, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/K-OBrien-ISTC-Linde-BASF-Post-Combustion-CO2-Capture.pdf*.

Moser, P., Schmidt, S., Stahl, K., Vorberg, G., Lozano, G., Stoffregen, T., Rösler, F., "Demonstrating Emission Reduction – Results from the Post-combustion Capture Pilot Plant at Niederaussem," GHGT-12. Energy Procedia 2014; 63: Pages 902-910. *https://www.sciencedirect.com/science/article/pii/S1876610214019158*.

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references

[1] BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

Large-Scale Commercial Carbon Capture Retrofit of the San Juan Generating Station

primary project goals

The overall goal of this project is to perform a front-end engineering design (FEED) study for the retrofit of the San Juan Generating Station (SJGS) with post-combustion carbon capture. The FEED study will document the initial engineering and cost estimates for the retrofit project, including the levelized cost of carbon capture on an existing plant, and provide estimates of the technical and economic viability of extending the life of the existing SJGS coal-fired power plant through the installation of Mitsubishi Heavy Industries' (MHI) Kansai Mitsubishi Carbon Dioxide Recovery (KM CDR) Process™ carbon dioxide (CO_2) capture technology. The FEED study will enable SJGS to move forward into detailed engineering, procurement, installation, and operation in future work.

technical goals

- The purpose of the FEED study is to complete preliminary engineering and design work to support developing a detailed cost estimate for the cost of retrofitting CO_2 capture at SJGS.
- The team will perform multiple feasibility and design studies based on project-specific details in preparation for developing engineering deliverables. These studies will help define the scope of the retrofit project, based on project-specific decisions, technology-specific performance, site-specific requirements, and client-specific needs.
- Once the scope has been defined, detailed design will commence for the CO_2 capture system and its integration with the existing facility. Various design and engineering deliverables will be developed that will help define commodity quantities, equipment specifications, and labor effort required to execute the project.

technical content

Enchant and its partners will perform a FEED study for retrofitting the host site with an advanced amine-based carbon capture technology. The FEED study will be performed for 847 megawatts-electric (MWe; Units 1 and 4 at SJGS in Waterflow, New Mexico). The coal is supplied by the adjacent mine, San Juan Coal Company, owned by Westmoreland Holdings. The current contract expires on June 30, 2022; however, San Juan Coal has offered SJGS a new contract for 3.2 million tons of coal per year from 2022 to 2033. Both operating units are equipped with state-of-the-art environmental controls that meet or exceed government-permitted levels of emissions for nitrogen oxide (NO_X), sulfur dioxide (SO_2), particulate matter (PM), and mercury (Hg), making the unit carbon capture-ready from an emissions perspective.

SJGS is currently owned by a group of public utilities and municipal power entities and is operated by Public Service of New Mexico (PNM), pursuant to the Amended San Juan Participation Agreement (ASJPA). The City of Farmington (Farmington), currently a part-owner and also sub-recipient under this award, has the right under the ASJPA to acquire the 95% interest in SJGS held by all the other owners

technology maturity:

Front-End Engineering Design (FEED)

project focus:

KM CDR Process™ Retrofit

participant:

Enchant Energy, LLC

project number:

FE0031843

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Jason Selch
Enchant Energy, LLC
jselch@enchantenergy.com

partners:

City of Farmington, Mitsubishi Heavy Industries America, Inc., Mitsubishi Heavy Industries Engineering, Ltd., Sargent and Lundy, LLC, Navigant Consulting, EJM Associates, LLC, Baker Tilly Virchow Krause, LLP

start date:

10.15.2019

percent complete:

N/A

effective at the termination of the existing coal contract on June 30, 2022. Prior to taking over ownership from the exiting owners on June 30, 2022, Enchant, who acquired Farmington's acquisition rights in August 2019, will manage the CO_2 capture retrofit process by virtue of the Agency Agreement with the City of Farmington. The ASJPA also provides Farmington and its agent, Enchant, the right to access the site immediately for purposes of completing this FEED study.

Work on this FEED study will produce detailed engineering designs, costing, and timelines for the construction. It will also designate permitting agencies and timelines in order to execute the follow-on build and operate project. Lessons learned during the FEED study will be documented to assist in future large-scale capture retrofit projects at coal-fired power plants.

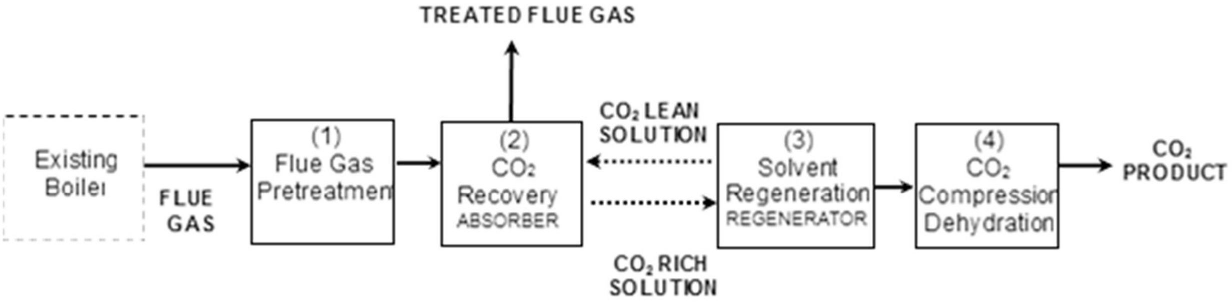

Figure 1: Block flow diagram of the CO_2 recovery plant.

The KM CDR Process has the following key features: (1) demonstrated performance on a large-scale (240 MWe); (2) high-performing amine solvent KS-1™ (high absorption capacity, low steam consumption, high resistance to oxidation and thermal degradation); and (3) key process technologies, such as an amine emission reduction system, solvent degradation reduction, automatic load adjustment control system, and amine purification system.

The CO_2 recovery facility consists of four main sections, as shown in Figure 1: (1) flue gas pretreatment, (2) CO_2 recovery, (3) solvent regeneration, and (4) CO_2 compression and dehydration. In flue gas pretreatment, the flue gas temperature is cooled in the flue gas quencher by direct contact with circulation water. The circulation water is injected with caustic soda to reduce the amount of SO_2 in the flue gas entering the amine system. A flue gas blower is installed downstream of the flue gas quencher to overcome the pressure drop across the flue gas quencher and the CO_2 absorber.

Figure 2 shows the process flow diagram for the CO_2 recovery and solvent regeneration steps. In CO_2 recovery, the cooled flue gas from the flue gas quencher is introduced at the bottom of the CO_2 absorber. The flue gas moves upward through the packing while the CO_2-lean solvent is supplied at the top of the absorption section where it flows down onto the packing. The flue gas contacts with the solvent on the surface of the packing, where 95% of the CO_2 in the flue gas is absorbed by the solvent. The CO_2-rich solvent from the bottom of the CO_2 absorber is sent to the regenerator. The CO_2-lean flue gas exits the absorption section of the CO_2 absorber and enters the flue gas washing section of the CO_2 absorber. The flue gas contacts with circulating water to reduce the carryover amine that is emitted from the top of the CO_2 absorber.

In solvent regeneration, cool-rich solvent is heated by the hot-lean solvent extracted from the bottom of the regenerator in a heat exchanger. The pre-heated rich solvent is then introduced at the top of the regenerator column and flows down over the packing, where it contacts with stripping steam. As it flows down the column, the rich solvent releases captured CO_2 and is regenerated back into lean solvent. The steam in the regenerator is produced by the reboiler, where low-pressure steam is used to heat the lean solvent. The lean solvent is then cooled to the optimum absorption temperature before being recycled back to the CO_2 absorber.

The overhead vapor leaving the regenerator is cooled, and the condensed liquid from this unit is then returned to the system. In CO_2 compression and dehydration, CO_2 is compressed through a multi-stage gas compressor. Treatment such as oxygen (O_2) removal or dehydration may be necessary to meet pipeline and storage guidelines.

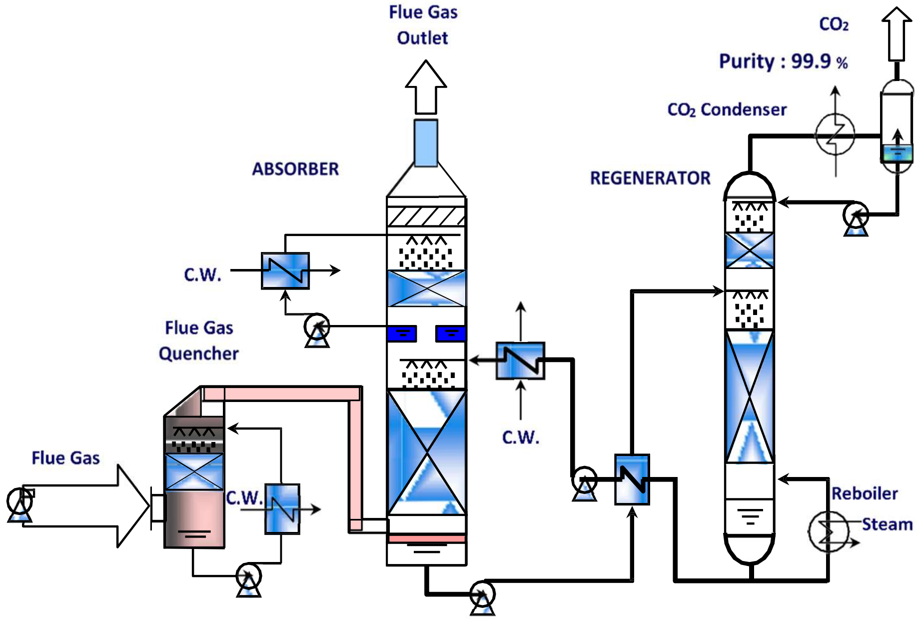

Figure 2: Carbon capture basic process flow diagram.

technology advantages

FEED studies for carbon capture systems at this site will provide the U.S. Department of Energy (DOE) with a more detailed understanding of carbon capture costs in a commercial application, thereby enabling DOE to better design its research and development (R&D) program to reduce those costs for similar carbon capture technologies being developed in its R&D portfolio.

R&D challenges

- To deploy the post-combustion amine technology on coal-fired gas while adequately managing accumulation of impurities in the exhaust without excessive cost.
- Ensuring reliable operation over a long period at large-scale.

status

Project has commenced.

available reports/technical papers/presentations

"Preliminary Assessment of Post-Combustion Capture of Carbon Dioxide at the San Juan Generating Station: An Independent Assessment of a Pre-feasibility Study Conducted by Sargent & Lundy for Enchant Energy,"12 December 2019, Los Alamos National Laboratory. *https://www.lanl.gov/science-innovation/science-programs/applied-energy-programs/_assets/docs/preliminary-technical-assessment-december2019.pdf*.

"Enchant Energy, San Juan Generating Station – Units 1 & 4, CO_2 Capture Pre-Feasibility Study, FINAL," July 8, 2019, Project No. 13891-001, Prepared by Sargent & Lundy. *https://www.enchantenergy.com/wp-content/uploads/2019/07/Enchant-Energy_SJGS-CO2-Pre-feasibility-Study_FINAL-Rev-0-7-8.pdf*.

CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION SORBENT TECHNOLOGIES

Sorbent-Based Post-Combustion CO_2 Slipstream Testing

primary project goals

TDA Research, Inc. is designing, constructing, and operating a slipstream 0.5-megawatt-electric (MWe) pilot-scale process for post-combustion carbon dioxide (CO_2) capture using their low-cost alkalized alumina sorbent to conduct parametric and long-term steady-state testing to demonstrate the effectiveness of the technology to reduce the cost of CO_2 capture and to develop scale-up conditions for the process.

technical goals

- Modify bench-scale unit to mimic proposed pilot plant configuration and conduct testing in bench unit to optimize process and collect data for pilot plant design.
- Characterize breakthrough performance and pressure drop for different sorbent pellet sizes.
- Design pilot plant unit based on developed low-cost alkalized alumina sorbent technology.
- Scale-up production of sorbent.
- Fabricate and install pilot plant unit at the National Carbon Capture Center (NCCC).
- Perform parametric and steady-state testing on pilot plant using actual flue gas.
- Update environment, health, and safety (EH&S) study and techno-economic analysis (TEA) based on pilot plant testing results.

technical content

TDA Research, Inc. is designing, constructing, and operating a slipstream 0.5-MWe pilot-scale process for post-combustion CO_2 capture. This technology is based on their novel dry alkalized alumina sorbent developed previously in a U.S. Department of Energy (DOE)-funded project (DE-NT0005497). The regenerable sorbent acts as a physical adsorbent for CO_2. The CO_2 capture process runs near isothermally at around 140 to 150°C in both adsorption and regeneration, requiring no heating or cooling between adsorption and regeneration steps. The sorbent is regenerated with low pressure (15.5 pounds per square inch absolute [psia]) steam. The sorbent shows excellent tolerance to contaminants, including sulfur dioxide (SO_2) and nitrogen oxides (NO_X).

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the adsorber/regenerator unit and (2) the CO_2 compression and purification unit. The process is designed for the sorbent to remove the CO_2 from the flue gas at intermediate temperature and near-ambient pressure, and then be regenerated with low-pressure superheated steam. A multiple fixed-bed design is used, providing counter-flow contact between solids and gases, where the beds cycle between adsorption and desorption. The flue gas flows in parallel through the adsorption beds and in series across regeneration beds. This setup has several advantages over moving beds, including a simple-

technology maturity

Pilot-Scale, Actual Flue Gas Slipstream (0.5 MWe)

project focus:

Alkalized Alumina Sorbent

participant:

TDA Research, Inc.

project number:

FE0012870

predecessor projects:

NT0005497

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Jeannine Elliott
TDA Research, Inc.
jelliott@tda.com

partners:

University of California at Irvine, Porocel, Babcock and Wilcox, Louisiana State University, Western Research Institute

start date:

02.03.2014

percent complete:

95%

bed design, basic ductwork, low construction cost, and the elimination of parasitic power required to move the sorbent, all of which result in a lower overall cost than moving beds.

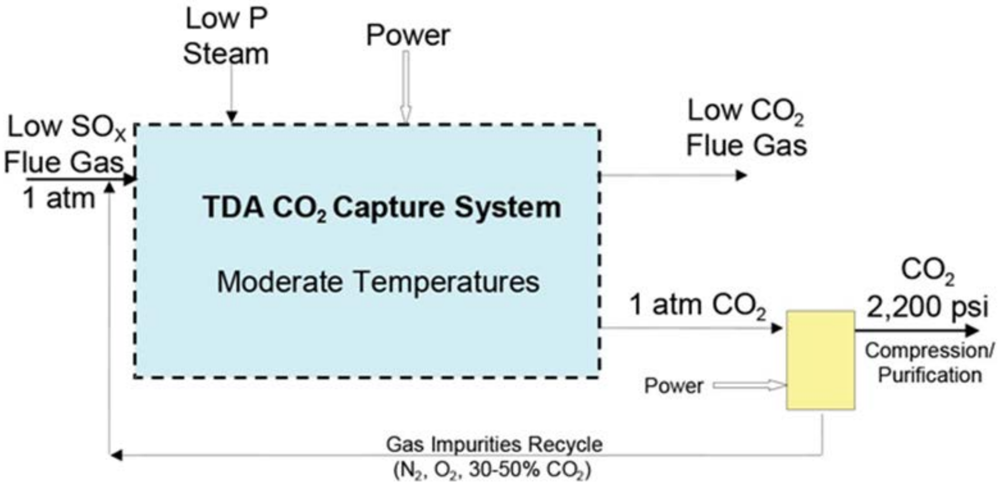

Figure 1: Block flow diagram of TDA's CO_2 capture system.

The slipstream pilot plant is a 0.5-MWe skid-mounted system (shown in Figure 2) installed at the NCCC. The adsorber/regeneration system is made up of multiple fixed beds containing the alumina sorbent that switch between adsorption, regeneration, and purge operations. The complete slipstream pilot unit includes adsorber/regeneration beds, heat exchangers, blowers, valving, and instrumentation.

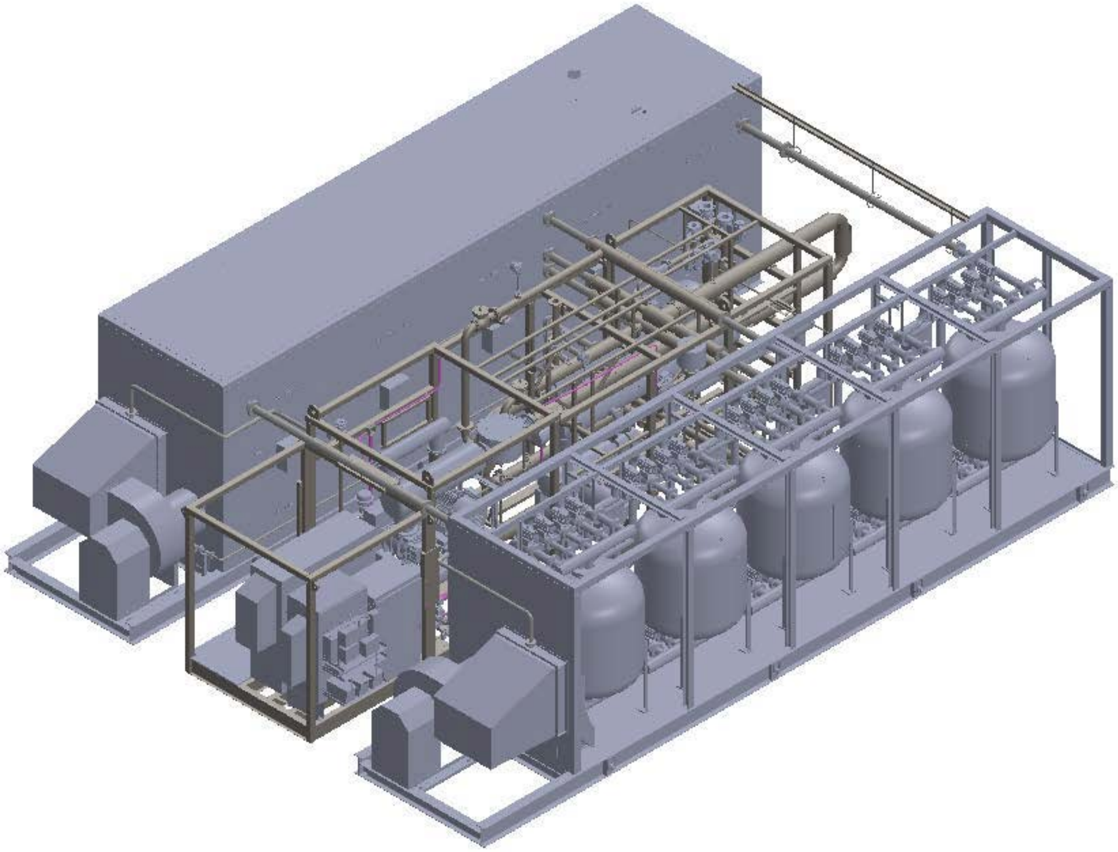

Figure 2: TDA's 0.5-MWe test skid.

Slipstream pilot unit testing under both parametric and steady-state conditions using actual coal-fired flue gas provides data and recommended operating conditions to update the TEA and EH&S assessment, as well as for definition of recommended scale-up conditions. The project aims to demonstrate the novel system for reduction in carbon capture cost.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	750	750
Bulk Density	kg/m^3	520	520
Average Particle Diameter	mm	1.5	3.175
Particle Void Fraction	m^3/m^3	0.55	0.55
Packing Density	m^2/m^3	9.4E+07	9.4E+07
Solid Heat Capacity @ STP	kJ/kg-K	0.72	0.72
Crush Strength	kg_f	8	8
Manufacturing Cost for Sorbent	$/kg	6.5	3
Adsorption			
Pressure	bar	1.12	1.12
Temperature	°C	140	140
Equilibrium Loading	g mol CO_2/kg	1.0	1.5
Heat of Adsorption	kJ/mol CO_2	-12.5 to -41.9	-12.5 to -41.9
Desorption			
Pressure	bar	1.17	1.17
Temperature	°C	150	150
Equilibrium CO_2 Loading	g mol CO_2/kg	0.93	1.0
Heat of Desorption	kJ/mol CO_2	12.5 to 41.9	12.5 to 41.9
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Multiple fixed bed	
Flue Gas Flowrate	kg/hr	2,273	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 / 95 / 1.013	
Adsorber Pressure Drop	bar	0.02	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent is an adsorbent and is regenerated with steam.

Sorbent Contaminant Resistance – Based on extended cycling 1,500 hours with simulated flue gas with 13.8% CO_2, 104 parts per million (ppm) SO_2, 3% oxygen (O_2), and 9% water (H_2O), sorbent life was calculated to be one year with 5 ppm of SO_2. No effect of NO_X on capacity was seen after 200 cycles with 739 ppm nitric oxide (NO) and 84 ppm nitrogen dioxide (NO_2).

Sorbent Attrition and Thermal/Hydrothermal Stability – None provided.

Flue Gas Pretreatment Requirements – Flue gas should have <5 ppm sulfur oxides (SO_X).

Sorbent Makeup Requirements – 15% per year.

Waste Streams Generated – None known.

Process Design Concept – See Figure 1 above.

Proposed Module Design – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module. TDA's CO_2 capture system is located downstream of the FGD unit. The adsorbent removes dilute CO_2 from the flue gas (10 to 14% CO_2, 8 to 10% H_2O, <5 ppm SO_2) at intermediate temperature (140°C) and near-ambient pressure.

technology advantages

- Inexpensive, durable sorbent.
- Low-pressure (17 psi) steam for sorbent regeneration, low regeneration energy.
- Near isothermal operation.
- No heat recovery from solids required.
- Rapid adsorption/regeneration kinetics due to surface-only adsorption.
- Low heat of adsorption.
- Counter-current operation maximizes capture efficiency and sorbent loading.

R&D challenges

- Minimize the parasitic demands from the sorbent system.
- Effectively produce a sorbent from low-cost raw materials with extensive regenerative life.

status

TDA Research, Inc. has designed and constructed the 0.5-MWe-scale pilot plant test unit and produced the sorbent needed for testing. The skid has been installed at the NCCC, to be followed by 1.5 months of parametric testing and two months of steady-state testing using an actual flue gas slipstream.

available reports/technical papers/presentations

Elliott, J. and Yi, F. “Update on Pilot Unit of Sorbent Based Post-Combustion CO_2 Capture,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Elliott-TDA-Sorbent-CO2-Capture.pdf*.

Elliott, J. and Yi, F. “Update on Pilot Unit of Sorbent Based Post-Combustion CO_2 Capture,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/J-Elliott-TDAR-Pilot-Unit-Sorbent-Based-Capture.pdf*.

Elliott, J. and Yi, F. “Sorbent Based Post-Combustion CO_2 Slipstream Testing,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/2-Tuesday/J-Elliott-TDA-Post-Combustion-CO2-Slipstream-Testing.pdf*.

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Lab- and Bench-Scale Applications for Research and Development of Transformational Carbon Dioxide Capture

primary project goals

Research Triangle Institute (RTI) is developing novel third-generation fluidizable solid sorbents for their sorbent-based carbon dioxide (CO_2) capture process. Two different types of sorbents are being developed, based on hybrid metal organic frameworks (MOFs) and hybrid phosphorus dendrimers (*P*-dendrimers), with long-term performance testing of the most promising sorbents in a fluidized-bed reactor.

technical goals

- Design, synthesize, and optimize two novel fluidizable CO_2 adsorbents based on hybrid MOFs and hybrid *P*-dendrimers.
- Demonstrate superior performance of these solid sorbents at lab-scale in a packed-bed reactor (PBR).
- Evaluate impact of flue gas contaminants such as sulfur oxides (SO_X), nitrogen oxides (NO_X), oxygen (O_2), and water (H_2O).
- Scale-up production of selected sorbents in fluidizable form.
- Complete performance testing in lab-scale fluidized-bed reactor.
- Conduct a high-level techno-economic analysis (TEA).

technical content

RTI is developing novel hybrid fluidizable sorbents for CO_2 capture based on hybrid MOFs and hybrid *P*-dendrimers. The hybrid MOF-based sorbents are based on impregnating polyethylenimine (PEI) on an MOF-silica support. For this sorbent, the silica provides attrition resistance, fluidizability, low cost, and acceptable density. The MOF has very high surface area and tunable pore sizes. The PEI is a polymer with a repeating amine unit, providing high amine content, high CO_2 affinity, and a relatively low cost. RTI has developed a new general approach to selectively grow well-dispersed MOF nanocrystals within mesoporous silica via novel "solid-state" synthesis, which will be used for preparing the novel MOF hybrid CO_2 sorbents. The ability to control and direct the growth of MOFs on confined surfaces (pores) paves the way for new prospective applications of such hybrid systems (i.e., CO_2 adsorption). As confirmed by a combination of different characterization techniques, an outstanding high loading of mesoporous cavities (up to 50 wt%) by the smallest MOF crystals yet reported (4.5±1 nm) leads to several improved properties, including diffusion, attrition resistance, handling, and, particularly for this project, fluidizability, which can approach, for the first time, MOFs to applications in a fluidized-bed reactor, in which MOFs have never been proposed.

Figure 1 shows the high MOF loading in the silica using a confocal microscope. Figure 2 shows the full characterization of the resulting hybrid material. Figure 2(a) shows the N_2 sorption isotherms at 77K (closed symbols correspond to adsorption branches while open symbols correspond to desorption branches, 20%MOF: green line, 40%MOF: blue line).

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Fluidizable Solid Sorbents

participant:

Research Triangle Institute

project number:

FE0026432

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

Mustapha Soukri
RTI
msoukri@rti.org

partners:

N/A

start date:

10.01.2015

percent complete:

100%

X-ray diffractograms (Cu Kα radiation) are shown in Figure 2(b). Figure 2(c) shows the pore-size distribution calculated from Barrett-Joyner-Halenda (BJH) adsorption pore volume versus pore diameter (dV/dD) plot (inset figure: pore diameter [nm] at X-axis and pore volume [cm3 g-1 nm-1] at Y-axis). Figure 2(d) shows the Fourier transform infrared spectroscopy (FTIR) spectra measured in attenuated total reflectance (ATR) mode [Reference lines: Pure MOF (black line, the FTIR intensity was divided by 3 for better comparison), Silica(A) (grey line) and MOF precursors loaded on Silica(A) (dark yellow line)].

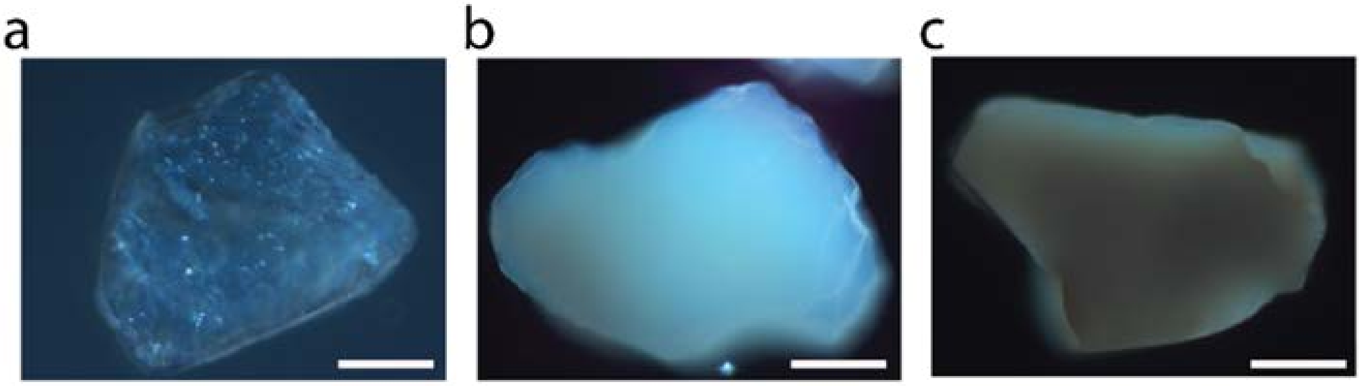

Figure 1: MOF loading in silica: (a) transparent amorphous silica; (b) 20% MOF; (c) 40% MOF.

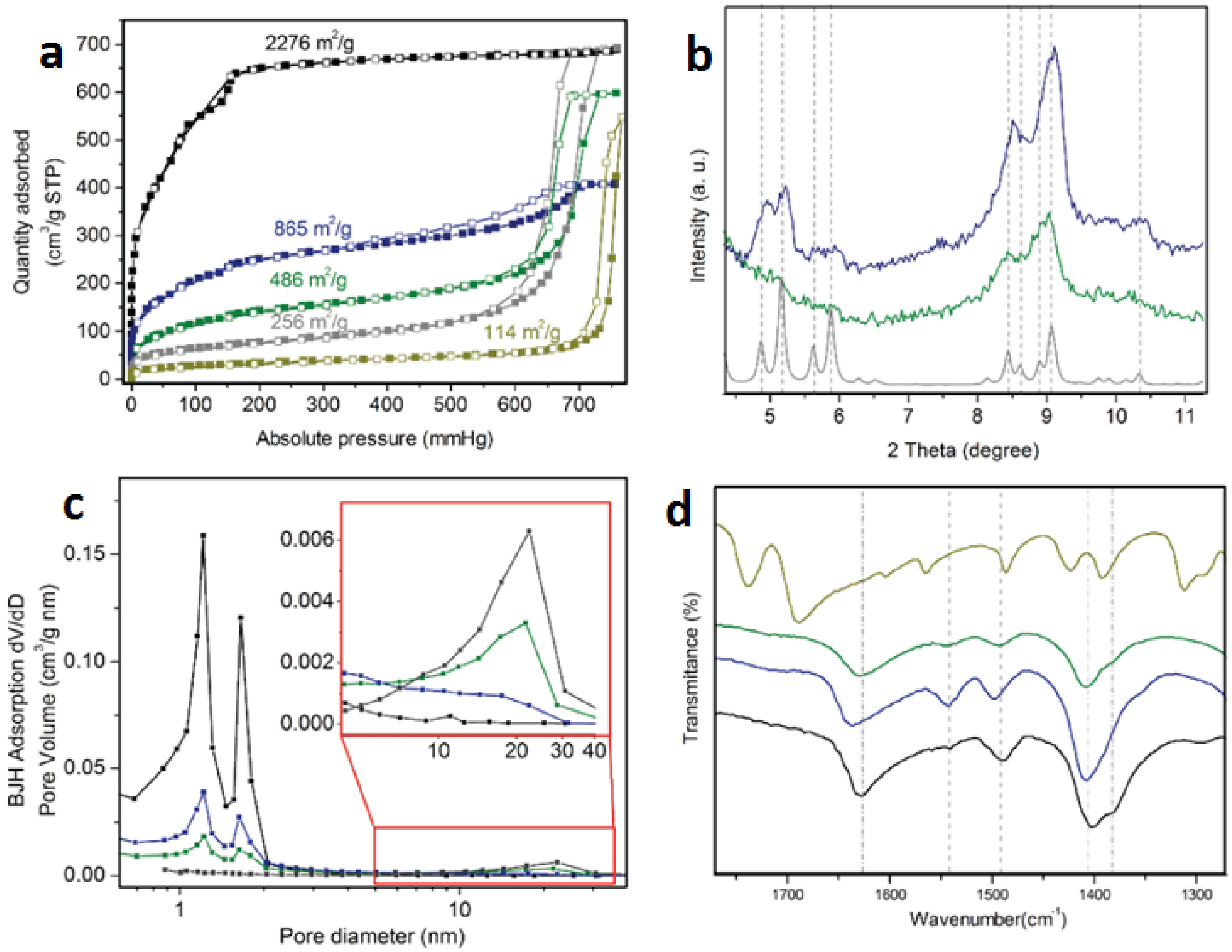

Figure 2: Characterization of the hybrid material: (a) N_2 sorption isotherms at 77K; (b) X-ray diffractograms; (c) pore-size distribution; (d) FTIR spectra measured in ATR mode.

In order to evaluate the utilization of these novel MOF hybrid materials prepared via solid-state synthesis for CO_2 capture from post-combustion flue gas, fluidized MOF/silicon dioxide (SiO_2) hybrid sorbents containing different polyamines and selected MOF nanocrystals have been systematically studied. Hybrid sorbents containing a moderate loading of (Zn)ZIF-8 are the most promising sorbents in terms of CO_2 capacity and long-term stability (250 cycles) and were successfully prepared at the kilogram scale. Two sorbents exhibited excellent stability for 250 cycles under simulated flue gas conditions, as shown in Figure 3.

These hybrid sorbents demonstrated excellent fluidizability and performance under the relevant process conditions in a visible fluidized-bed reactor.

Dendrimers are repeatedly branched, large spherical molecules. *P*-dendrimers provide a rigid scaffold, hydrophobic interior, and well-defined spatial location of the functional groups, along with high thermal stability. An example of a dendrimer structure is shown in Figure 4. RTI is developing an approach to produce sorbents by covalently grafting amine-functionalized *P*-dendrimers on solid supports, such as silica, to improve stability and fluidizability.

Extensive cyclic adsorption/desorption testing was conducted with the best performing *P*-dendrimer sorbent (1-G0/600PEI) produced in this study, revealing an average CO_2 capacity of 13.1 wt% from simulated flue gas over 350 cycles running for 700 contiguous hours. A heat of adsorption value of 103 kJ mol-1 was determined from CO_2 isotherms, providing evidence for chemisorption binding. The effect of common contaminants of flue gas (sulfur dioxide [SO_2], nitric oxide [NO], and nitrogen dioxide [NO_2]) were investigated with 1-G0/600PEI. The sorbent was significantly impacted by SO_2 exposure at low concentrations (50 parts per million [ppm]), binding the SO_2 irreversibly and blocking active amine sites. Like many solid amine sorbents, for 1-G0/600PEI to be utilized on a practical scale for post-combustion CO_2 capture, a desulfurization step would be required. The impact of NO_X contaminants, NO and NO_2, was less influential – with only a small decrease over 100 cycles presumably from the binding of NO_2 as a nitrite species. Extensive efforts were made to fluidize the 1-G0/600PEI sorbent so that it could be utilized in a fluidized-bed reactor. Unfortunately, this material was unable to reach high capacities and attain packed-densities greater than 0.6 g/mL required for fluidization. Alongside the poor physical properties for fluidization, the material also had much higher costs when projected for commercial-scale production in comparison to the MOF-based hybrid sorbents.

A PBR is used to screen the novel hybrid sorbents with multi-cycle adsorption-regeneration, measuring CO_2 loading and rate along with contaminant effects. A visual fluidized-bed reactor, shown in Figure 5, is utilized to verify the fluidizability of the sorbents under realistic process conditions and to test optimal fluidization conditions.

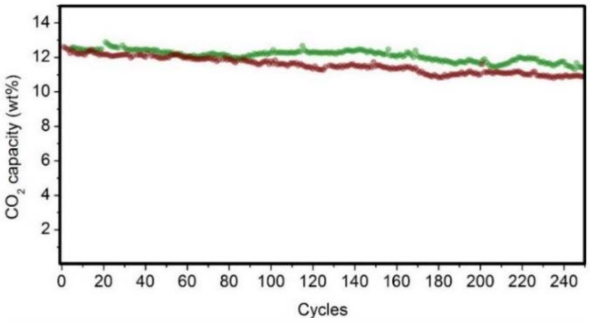

Figure 3: Long-term CO_2 adsorption performance stability for PEI/(Zn)ZIF-8/SiO_2 (green) and PEI/(Zn)ZIF-7/SiO_2 (dark red) under simulated flue gas conditions.

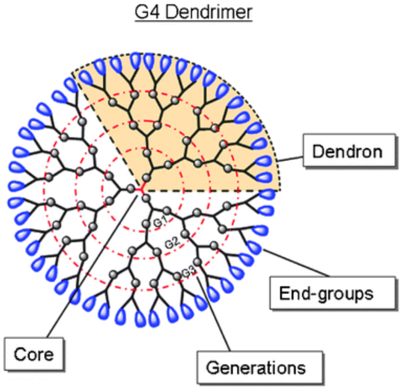

Figure 4: Dendrimer structure.

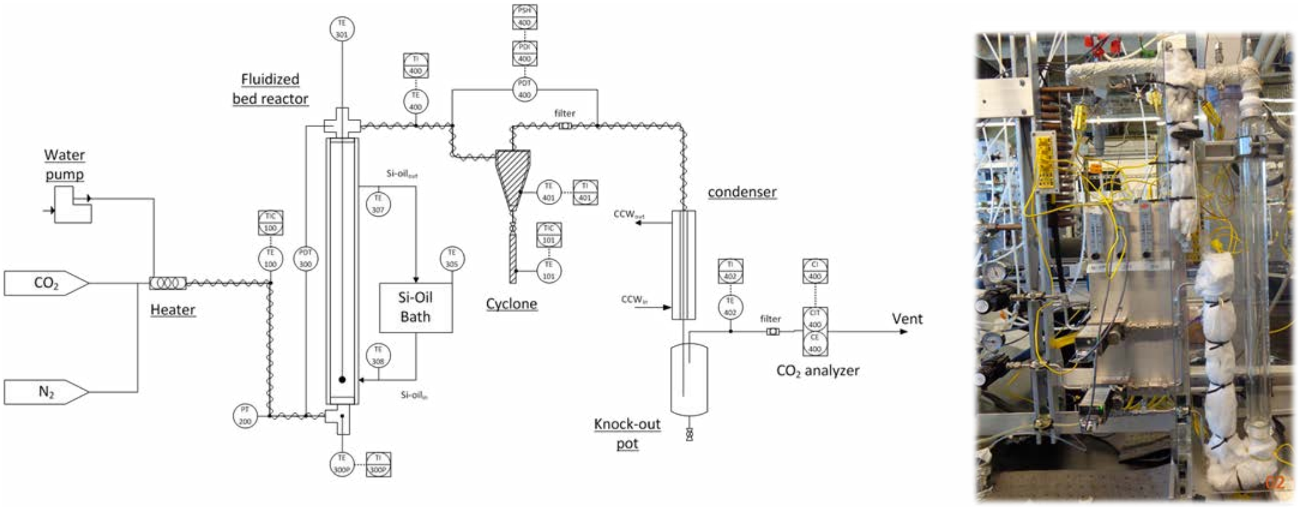

Figure 5: RTI visual fluidized-bed reactor.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	650-750	—
Average Particle Diameter	mm	165	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	1.5	—
Crush Strength	kg$_f$	10%	—
Manufacturing Cost for Sorbent	$/kg	15	—
Adsorption			
Pressure	bar	1-1.2	—
Temperature	°C	60-70	—
Equilibrium Loading	g mol CO$_2$/kg	12.5	—
Heat of Adsorption	kJ/mol CO$_2$	85-90	—
Desorption			
Pressure	bar	1.3-1.4	—
Temperature	°C	110-120	—
Equilibrium CO$_2$ Loading	g mol CO$_2$/kg	0.5-1	—
Heat of Desorption	kJ/mol CO$_2$	75-90	—

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO$_2$-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO$_2$ partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism **–** To provide insight regarding the influence that the presence of MOF nanocrystals causes on the CO_2 dynamics of impregnated PEI, the adsorption-desorption profiles for 35 wt% of PEI confined on 4.6 wt% of (Zn)ZIF-8/SiO_2 and bare SiO_2 at the tenth cycle are compared in Figure 6. The adsorption breakthrough profile for the MOF-containing solid sorbent shows a superior CO_2 adsorption compared with PEI/SiO_2. The characteristic adsorption-regeneration profiles for the PBR filled with inert silicon carbide SiC4 are represented by the red line, which determines the dead volume of the PBR. However, the regeneration profile shows an interesting difference in terms of CO_2 desorption for the composite incorporating MOF nanocrystals. Larger concentrations of early release adsorbate are measured for the MOF/SiO_2 hybrid sorbent, which is attributed to weakly adsorbed CO_2 via physisorption because the temperature required to release them is lower than 80°C.

PEI/SiO_2 also exhibited an early release, but it is mainly attributed to CO_2 trapped in the dead volume of the PBR, as suggested by comparison with the profile for the inert SiC4. In addition, PEI/MOF/SiO_2 exhibited higher CO_2 desorption between 80 and 100°C, which suggests slightly better use of the PEI amines for CO_2 chemisorption as well. This result highlights the unusual dual adsorption performance of our hybrid sorbents containing MOF nanocrystals compared with the pure silica counterpart.

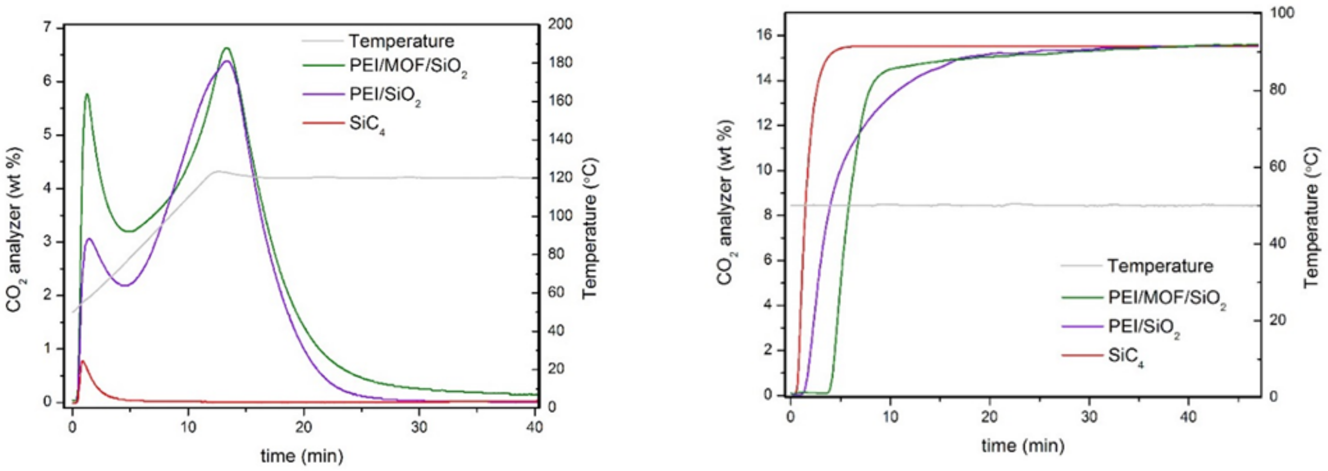

Figure 6: Adsorption (left) and regeneration (right) profiles for 35 wt% of PEI/4.6 wt% of (Zn)ZIF-8/SiO_2 and 35 wt% of PEI/SiO_2.

Sorbent Contaminant Resistance – Fluidized MOF/SiO_2 hybrid sorbents have demonstrated good CO_2 adsorption capacity under simulated flue gas conditions, since they exhibit 140% higher CO_2 capacity and similar deactivation (*ca* 10% after 250 cycles) than the reference PEI impregnated on bare mesoporous silica. As flue gas from coal-fired power plants typically contains other acid gas impurities, such as SO_2 and NO_X, that can dramatically influence the CO_2 capture efficiency. The results show a clear deactivation of the CO_2 adsorption capacity of the sorbents under the presence of SO_2. This deactivation is due to the irreversible reaction occurring during the adsorption step between SO_2 and PEI amines, which are not further active for the CO_2 capture. On the other hand, excellent stability has been observed under elevated concentration of NO_X. Therefore, the presence of MOF nanocrystals within the hybrid solid sorbent does not reduce the tendency of PEI amines to be deactivated by irreversible binding with SO_2, as similar deactivation has been measured for PEI/SiO_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – This work is the first example of CO_2 capture from simulated flue gas in a fluidized-bed configuration using an MOF-based CO_2 solid sorbent. The application of MOFs on this configuration have never been proposed due to the poor attrition, handling, and lack of fluidizability of bulk MOFs. By engineering MOFs within mesoporous silica, the final sorbent is demonstrating excellent fluidizability, handling, and improved attrition resistance (up to two to three times compared to SiO_2, and six to seven times compared to MOF). Very aggressive regeneration conditions (stream containing 80 volume/volume % H_2O balanced with nitrogen [N_2] at 100°C for one hour) were used to check the stability of this sorbent; the CO_2 adsorption capacity was practically maintained for PEI/MOF/SiO_2, whereas a significant drop was observed for the MOF-free sorbent.

Flue Gas Pretreatment Requirements – An additional unit should be included up-stream for scrubbing the SO_2 levels in the flue gas down to a single-digit ppm level prior to reaching the fluidized-bed reactor to elongate the life of the hybrid solid sorbents and reduce the makeup rate.

Sorbent Makeup Requirements – Fluidized MOF/SiO_2 hybrid sorbents demonstrate an excellent attrition resistance and therefore significantly reduced the makeup rate.

Waste Streams Generated – Two waste streams could be generated:

- Sorbent attrition fines could be reprocessed and used as sulfur guard-bed.
- Steam condensate from regenerator CO_2 capture steam usually has leached PEI. However, water-wash experiments of the sorbent showed no PEI leaching. This suggests that the condensed water will be easily processed and reused.

Process Design Concept – RTI proposes the use of a multi-stage, fluidized-bed, absorber-regenerator process for the capture and recovery of CO_2. By employing fluidized-bed reactors with heat transfer internals, the process temperature in each stage will be controlled precisely by removing heat during adsorption and adding heat in the regenerator. Multi-stage reactors are essential in maximizing sorbent-rich loading in the absorber and lean-loading in the regenerator, thereby maximizing working capacity.

technology advantages

- High theoretical CO_2 loading for *P*-dendrimers.
- MOF/silica fluidized hybrid materials offer several advantages:
    - High MOF loading (up to 50%).
    - Excellent MOF dispersion and homogeneity.
    - Good water and air stability.
    - Good chemical and thermal stability.
    - Tunable pore size distribution.
    - Elevated surface area (up to 900 m^2/g) and density (0.65 g/cm^3).
    - Enhanced attrition resistance.
    - Good fluidizability.
- High CO_2 capacity (≥12 wt%) and good stability of hybrid MOF-based adsorbents.

R&D challenges

- Reducing sorbent production costs, particularly for the *P*-dendrimer-based adsorbents.
- Transforming the *P*-dendrimer-based adsorbents to fluidizable form.

status

The project was completed on June 30, 2018. RTI has developed a novel technique to grow MOF inside the pores of silica supports. Testing of the three most promising PEI-impregnated silica-MOF sorbents has shown high (greater than 12%) CO_2 capacity with good MOF dispersion and homogeneity, good water and air stability, good chemical and thermal stability, enhanced attrition resistance, and excellent fluidizability. The sorbents exhibit better performance and long-term stability in a fluidized configuration. Production of the hybrid MOF-based sorbent has been scaled from 20-mg to 5-kg scale. Three *P*-dendrimer sorbents were evaluated and showed high (greater than 12.0 wt%) CO_2 capacities over at least 250 cycles. The project team has down-selected a PEI-impregnated silica-MOF sorbent, based on performance characteristics and the successful scale-up in a fluidized form to kilogram quantities, which was then tested in RTI's lab-scale fluidized moving-bed reactor prototype. This hybrid MOF sorbent was capable of achieving 90% CO_2 capture.

available reports/technical papers/presentations

Soukri, M., et al. "Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/M-Soukri-RTI-Solid-Sorbent.pdf*.

Soukri, M., et al. "Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/M-Soukri-RTI-Lab-scale-Sorbent.pdf*.

Novel Process that Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process

primary project goals

The Georgia Institute of Technology is developing prototype fiber sorbent modules containing polymeric fibers embedded with metal organic framework (MOF) for use in a sub-ambient rapid-cycle pressure swing adsorption (RCPSA) post-combustion carbon capture process.

technical goals

- Scale-up the MOF sorbent.
- Experimentally determine sub-ambient sorption isotherms.
- Spin fibers containing the MOF.
- Construct the RCPSA system and complete testing of fiber sorbent modules and fiber sorbent modules with phase-change materials.
- Model and optimize fiber module operation, as well as flue gas conditioning optimization.
- Prepare an overall system techno-economic analysis (TEA).

technical content

Georgia Tech Research Corporation is developing a process to achieve 10 mole/kg sorbent swing capacity using an RCPSA process. The sorbent system includes novel polymeric fibers embedded at high loadings with MOF materials. An example of the fibers is shown in Figure 1. MOFs are known to have good carbon dioxide (CO_2) capacity and rapid adsorption/desorption kinetics if kept isothermal. The team is developing a scalable, modular contactor for the sorbents with high surface area, low pressure drop, and low mass transfer resistance. An encapsulated, stationary phase-change material is incorporated in the hollow fiber sorbents (Figure 2) to maintain isothermal adsorption/desorption. This material has a melting/freezing point equivalent to the system operating temperature. It will melt as heat is released upon CO_2 adsorption and freeze as CO_2 is desorbed; therefore, steam and cooling water are not necessary. The system consists of modules containing the hollow fibers.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Pressure Swing Adsorption Process with Novel Sorbent

participant:

Georgia Tech Research Corporation

project number:

FE0026433

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Ryan Lively
Georgia Tech Research Corporation
ryan.lively@chbe.gatech.edu

partners:

Inmondo Tech, Inc.

start date:

10.01.2015

percent complete:

100%

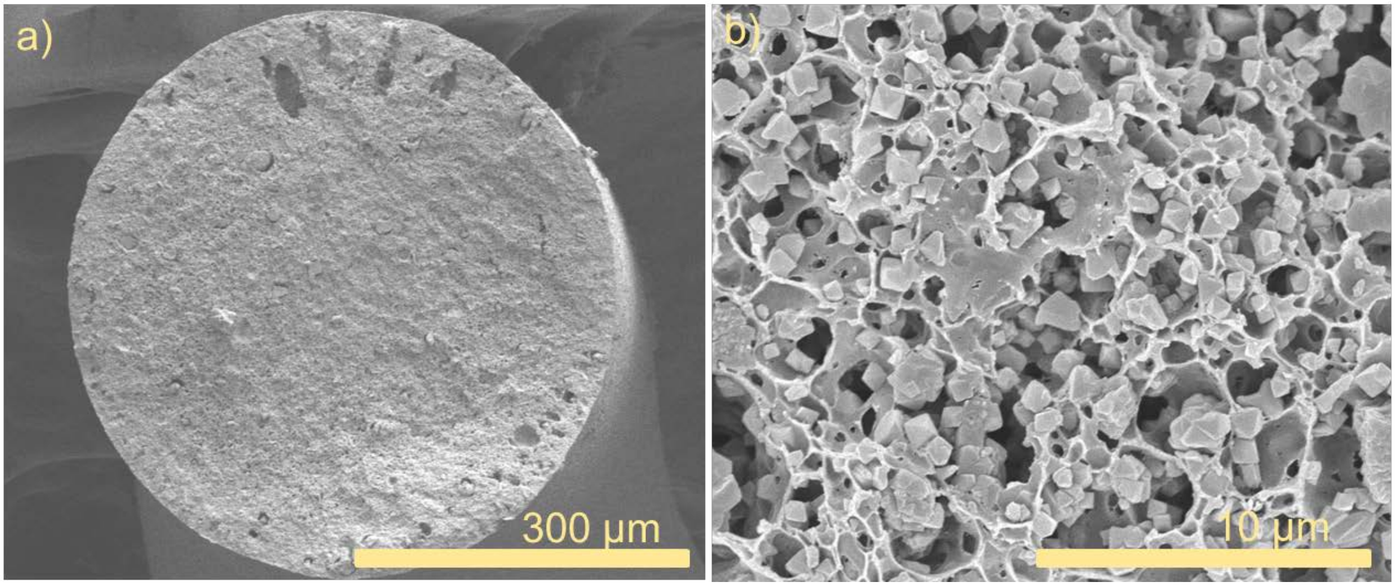

Figure 1: MIL-101(Cr)/cellulose acetate fiber sorbents: ~50 wt% MIL-101(Cr); (a) low magnification fiber, (b) Zoomed in sub-structure.

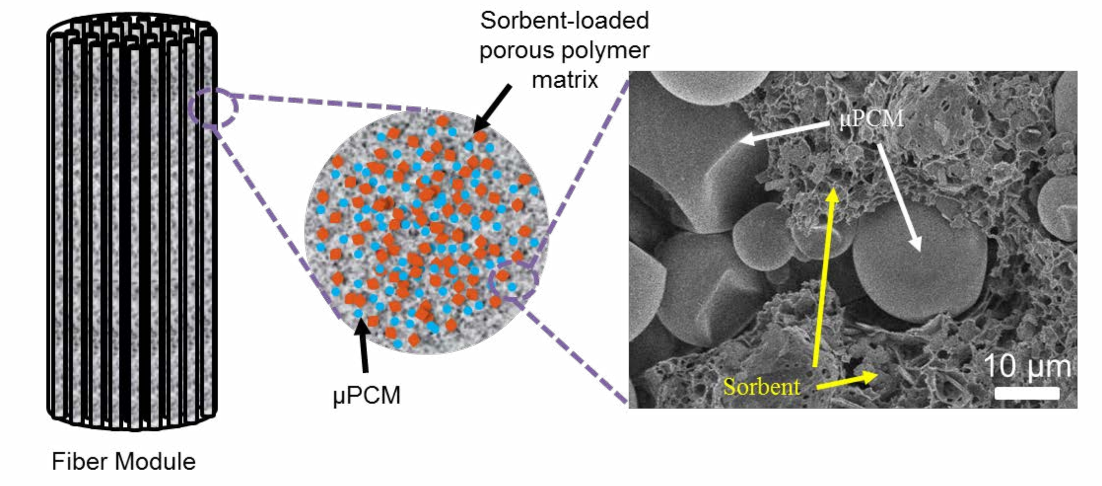

Figure 2: Phase-change material in hollow fiber sorbents.

A simplified schematic of the overall CO_2 capture process is shown in Figure 3. The conditioned flue gas is passed through a sub-ambient heat exchanger before entering the PSA unit containing the hollow fiber sorbent modules. The steps of the RCPSA process (pressurization, adsorption, depressurization, desorption) are shown in Figure 4. Sub-ambient conditions increase adsorption selectivity and working capacity.

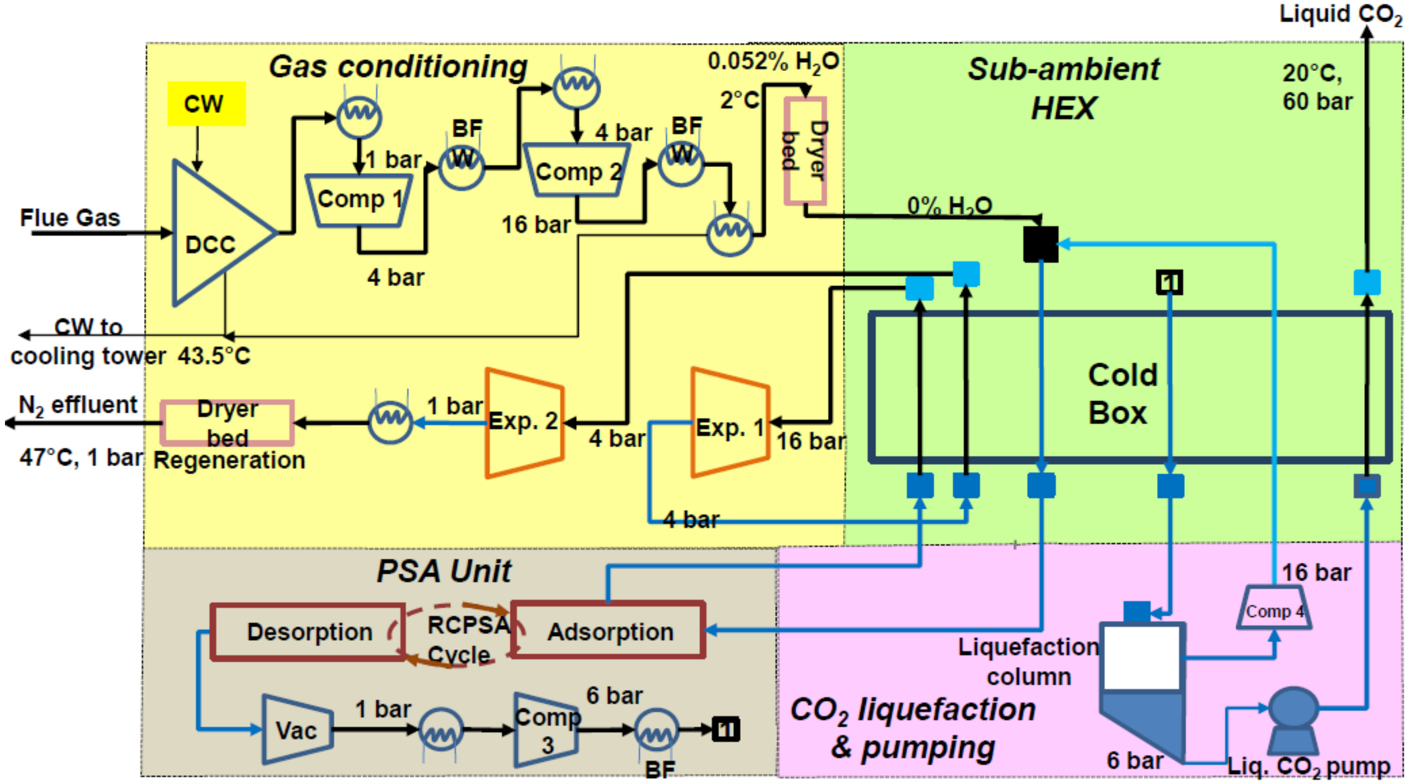

Figure 3: Process flow diagram.

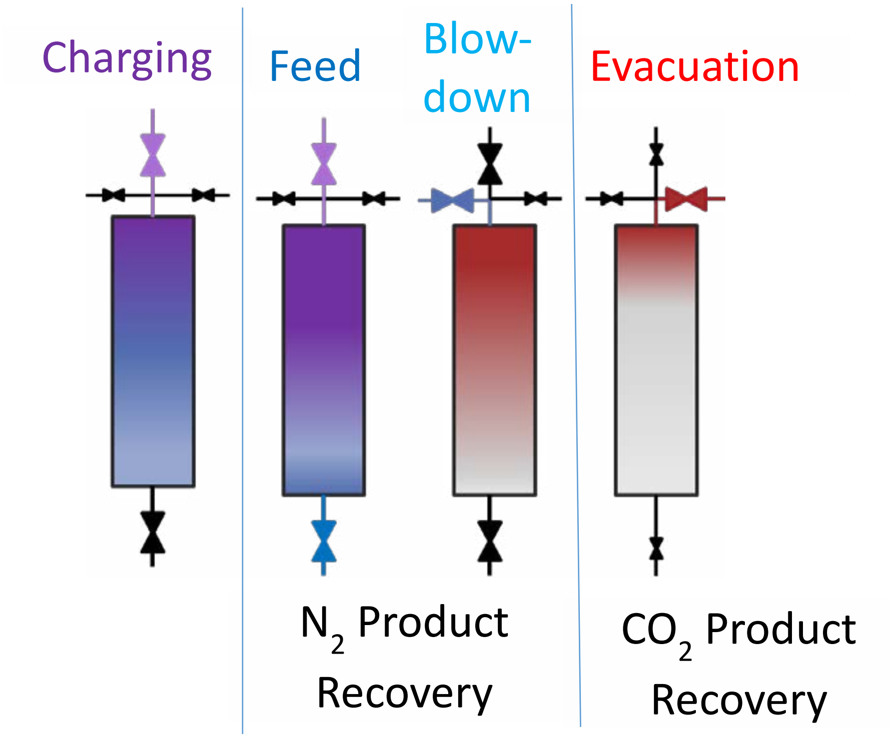

Figure 4: Pressure swing adsorption process.

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	1,200	1,200
Average Particle Diameter (diameter of fiber)	mm	0.8	0.8
Particle Void Fraction (void fraction of the fiber bed)	m^3/m^3	0.4	0.35
Packing Density	m^2/m^3	1,000	2,000
Solid Heat Capacity @ STP	kJ/kg-K	1,600	1,600
Crush Strength	kg_f	unknown	not specified
Manufacturing Cost for Sorbent	$/kg	unknown	30
Adsorption			
Pressure	bar	2	2
Temperature	°C	-30	-30
Equilibrium Loading	g mol CO_2/kg	10.2	delta (ads-des) =10
Heat of Desorption	kJ/mol CO_2	21.5	< 35
Desorption			
Pressure	bar	0.3	0.3
Temperature	°C	-30	-30
Equilibrium CO_2 Loading	g mol CO_2/kg	1.2	Delta (ads-des) =10
Heat of Adsorption	kJ/mol CO_2	21.5	< 35
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed fiber/parallel flow/cyclic	
Flue Gas Flowrate	kg/hr	—	
PSA CO_2 Recovery, Purity, and Pressure [from PSA] (from total process)	%/%/bar	[92/80/1] (90/99.5/60)	[92/95/1] (90/99.9/60)
Adsorber Pressure Drop	bar	0.1	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	390-480 (process)	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High, resistant to humid sulfur dioxide (SO_2) at 50 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – Irreversible sorption of SO_2 and nitrogen dioxide (NO_2) with little effect on CO_2 capacity

Flue Gas Pretreatment Requirements – Pressurization, dehydration, cooling.

Sorbent Makeup Requirements – None.

Waste Streams Generated – Clean (100% RH) nitrogen (N_2).

Process Design Concept – Discussed above.

technology advantages

- High working capacity of MOF sorbents.
- High contact area, low pressure drop, and low mass transfer resistance for the modules.
- Sub-ambient conditions increase adsorption selectivity and working capacity.
- The efficiency of the pressure swing cycle is boosted by installing a stationary phase-change material in the fiber sorbents that will isothermally melt upon release of sorption enthalpy and conversely isothermally freeze upon CO_2 desorption, requiring no steam or cooling water.
- Improved performance in the presence of flue gas contaminants due to physisorption separation mechanism (as opposed to a chemisorption mechanism).
- Carbon dioxide liquefaction and pumping can be used instead of CO_2 compression.
- Sub-ambient heat exchange and CO_2 liquefaction are commercially demonstrated.

R&D challenges

- Scale up of MOFs.
- Integrating MOF into the fiber to maintain CO_2 capacity.
- Integration of phase-change material into MOF-loaded fibers to maintain near isothermal operation.

- Effective operation of tightly heat- and work-integrated system.
- Monitoring and management of sorbent lifetime over extended operating periods.

status

The project was completed on September 30, 2019. Two MOFs were manufactured in large quantities and subsequently converted into adsorbent-loaded fiber materials. These were shown to have more than order-of-magnitude reductions in flue gas pressure drop compared to traditional adsorbent structures. The MOF materials could be composited with glycol-loaded capsules that would freeze and melt during each sorption-desorption cycle, enabling nearly isothermal operation of the RCPSA. The sub-ambient RCPSA process was estimated to have competitive operating and capital costs via a preliminary TEA based on the experimental data and computational modeling at molecular and process levels.

available reports/technical papers/presentations

Lively, R., et al. "Novel Process That Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process," Presented at the Final Project Meeting, Pittsburgh, PA, September 2019. *https://www.netl.doe.gov/projects/files/Final%20project%20presentation%20(FE0026433).pdf*.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/K-Walton-GIT-10-MOL-per-KG-Swing-Capacity.pdf*.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/R-Lively-GIT-10-MOLKG-Sorbent-Swing-Capacity.pdf*.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/files/R-Lively-GeorgiaIT-Sub-ambient-Pressure-Swing-Adsorption.pdf*.

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," Presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/projects/files/FE0026433-Kickoff-Meeting.pdf*.

Park, J,. et al. "Establishing upper bounds on CO_2 swing capacity in sub-ambient pressure swing adsorption via molecular simulation of metal–organic frameworks" J. Mater. Chem. A, 2017, 5, 12258-12265 *http://pubs.rsc.org/-/content/articlehtml/2017/ta/c7ta02916k*.

Park, J., et al. "*How Reproducible Are Isotherm Measurements in Metal–Organic Frameworks?*" Chem. Mater., 2017, 29, 24, 10487–10495.

DeWitt, SJA, et al. "*Development of Phase-Change-Based Thermally Modulated Fiber Sorbents*" Ind. Eng. Chem. Res. 2019, 58, 155, 768-5776.

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Evaluation of Amine-Incorporated Porous Polymer Networks as Sorbents for Post-Combustion CO_2 Capture

primary project goals

Texas A&M University is developing amine-incorporated porous polymer networks (aPPNs) for use as sorbents for post-combustion carbon dioxide (CO_2) capture, including lab-scale, fixed-bed testing of sorbent performance and the scale-up of sorbent synthesis.

technical goals

- Complete initial CO_2 adsorption testing with multiple aPPN formulations.
- Identify synthesis conditions that result in optimal sorbent performance and cost.
- Produce approximately 200 grams of at least the two top-performing sorbent formulations.
- Determine CO_2 working capacity of top-performing sorbent formulation after 30 cycles in automated fixed-bed testing.
- Scale-up to synthesis of at least 1 kilogram (kg) of top-performing aPPN.
- Complete fixed-bed cycling tests with top-performing aPPN in simulated flue gas in the presence of moisture and sulfur dioxide (SO_2).
- Perform initial technical and economic feasibility study.

technical content

Porous polymer networks are crosslinked polymers with high surface area, low density, and high thermal and chemical stability. These properties can be advantageous for CO_2 capture sorbents. The incorporation of amine groups also provides the capability to fine-tune CO_2 selectivity. Texas A&M is developing novel aPPNs with high CO_2 uptake capacities and working capacities. Multiple aPPN formulations, specifically the PPN-150 and PPN-151 series sorbents, are being synthesized and tested. Sorbent synthesis parameters, including reaction time, reaction headspace, solvent systems, and amine loading times and conditions, are being optimized. The PPN-150 series molecule is shown in Figure 1. The optimal sorbent, PPN-151 modified with diethylenetriamine (DETA), identified as PPN-151-DETA, is being scaled-up and CO_2 capture performance is being tested in fixed-bed cycling tests. The chemistry of the PPN-151-DETA synthesis is shown in Figure 2.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Porous Polymer Networks

participant:

Texas A&M University

project number:

FE0026472

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Hong Cai “Joe” Zhou
Texas A&M
zhou@chem.tamu.edu

partners:

framergy™, Inc.

start date:

10.01.2015

percent complete:

100%

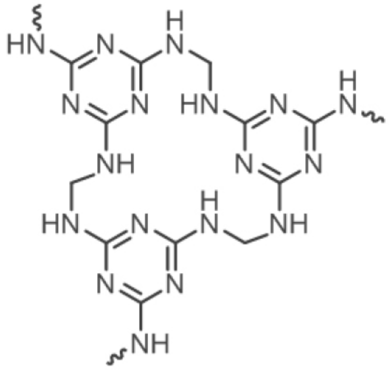
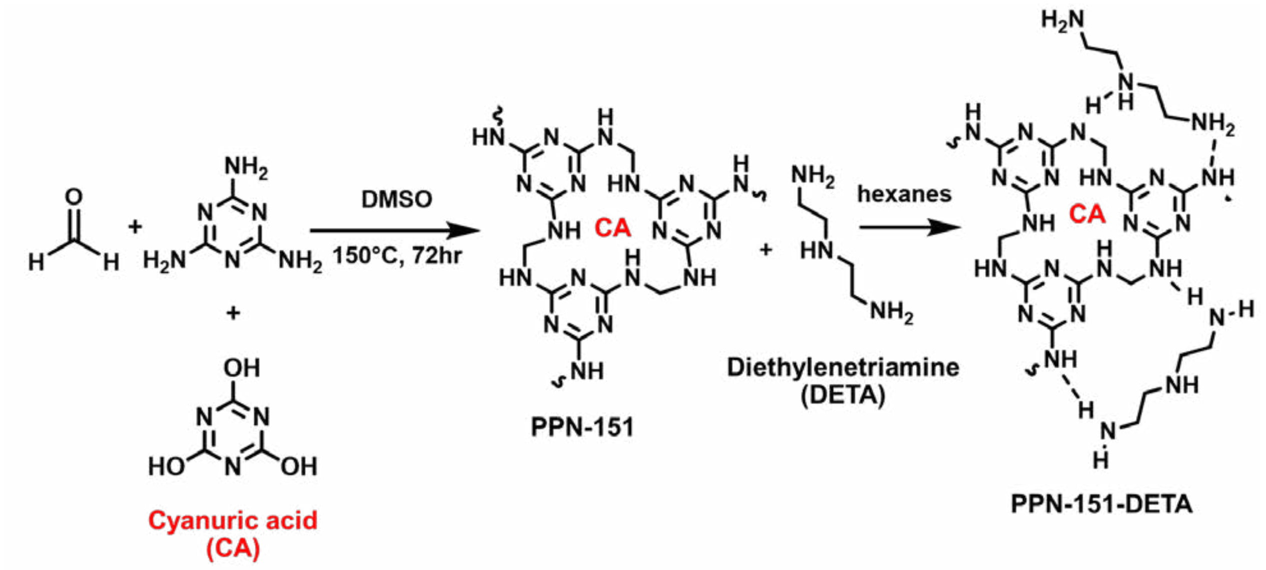


Figure 1: PPN-150 series.



Day, G. S., *et al. Advanced Sustainable Systems* **2019,** *3* (12), 1900051.

Figure 2: PPN-151-DETA synthesis chemistry.

technology advantages

- aPPNs have high surface area, extremely low density, and high thermal and chemical stability.
- aPPNs show large increases in CO_2 uptake capacities at low pressures and high CO_2/nitrogen (N_2) selectivity.

R&D challenges

- Reducing the cost of sorbent production.
- Scaling-up sorbent production while maintaining sorbent performance.

status

The project was completed on March 31, 2019. Texas A&M has synthesized and screened multiple aPPN candidates and demonstrated that their PPN-151-DETA aPPN sorbent can achieve up to 0.2 gram CO_2/gram sorbent (g/g) CO_2 loading at the laboratory scale. Sorbent synthesis parameters, including reaction time, reactor headspace, solvent systems, and amine loading times and conditions, have been optimized. Synthesis of PPN-151-DETA sorbent has been successfully scaled to a 1-kg batch size. Fixed-bed testing of the sorbent from the 1-kg batch showed greater than 0.12 g/g CO_2 loading. The material performed optimally in the presence of moisture, but SO_2 results in material degradation. An initial techno-economic assessment (TEA) shows a cost of CO_2 capture of $47/tonne, based on 3.5% loading from 1 part per million (ppm) SO_2 tests.

available reports/technical papers/presentations

Day, G. S.; Drake, H. F.; Joseph, E. A.; Bosch, M.; Tan, K.; Willman, J. A.; Carretier, V.; Perry, Z.; Burtner, W.; Banerjee, S.; Ozdemir, O. K.; Zhou, H. C., Improving Alkylamine Incorporation in Porous Polymer Networks through Dopant Incorporation. Advanced Sustainable Systems 2019, 3 (12), 1900051.

Zhou, H. “Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture,” presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/HC-Zhou-TAMU-Amine-Incorporated-Porous-Polymer-Networks.pdf*.

Zhou, H. “Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture,” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/H-C-J-Zhou-Texas-A-M-Porous-Polymer-Networks.pdf*.

Zhou, H. “Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture,” presented at the Budget Period 2 Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/FE0026472-BP2-Review-Presentation-08-15-17.pdf*.

Zhou, H. and Perry, Z. “Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/files/J-Zhou-TAMU-Amine-Incorporated-Porous-Polymer-Networks.pdf*.

Zhou, H. “Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture,” presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/projects/files/FE0026472-Kick-off-Presentation.pdf*.

Process for CO_2 Capture from Low-Concentration Sources

primary project goals

InnoSepra, LLC is developing a low-cost capture process using structured sorbents to remove carbon dioxide (CO_2) from low-concentration feed streams. This project is based on utilizing physical sorbents in structured form for concentrating CO_2 from low-concentration coal-based sources. The process utilizes a moisture-removal stage (if needed) and a CO_2-enrichment stage. The enriched CO_2 stream can then be combined with the feed stream of a post-combustion capture process, ultimately allowing cost-effective capture of 98 to 99% CO_2 from a coal-based power plant.

technical goals

- Fabricate adsorption test modules for CO_2 and moisture adsorption.
- Complete semi-bench-scale testing for moisture removal.
- Complete lab- and semi-bench-scale testing for CO_2 adsorption.
- Perform an engineering design for CO_2 enrichment of the residue stream for a 550-megawatt-electric (MWe) power plant.
- Prepare a techno-economic analysis (TEA) for a 1 million standard cubic feet per minute (scfm) feed plant.

technical content

InnoSepra developed a process, as shown in the schematic in Figure 1, using structured sorbents to capture CO_2 from low-concentration sources, which minimizes the pressure drop for the very high flows associated with the low-concentration sources. For a dry residue stream, a single-stage process is utilized to remove CO_2 with the structured sorbents. To treat a wet residue stream, a two-stage process is employed. Moisture is removed in the first stage in a rapid cycle adsorption process. The CO_2 adsorption occurs in the second stage, using the structured sorbents in an adsorption process. This stage produces a CO_2-enriched stream containing 10 to 15% CO_2 after regeneration, which can be fed to a new or an existing post-combustion CO_2 capture system. The structured sorbents used in this process have very high capacities at low-CO_2 concentrations and can be regenerated to produce the CO_2-enriched stream, achieving a CO_2 enrichment by a factor of five to 10.

Phase I focused on lab-scale evaluation of prototype adsorbents using low-CO_2 concentration simulated feed gas. Phase II included fabrication of test modules and evaluation of the structured sorbents for moisture removal and CO_2 adsorption capacity. Test unit modules were evaluated in two different configurations: a rotating-bed configuration and a fixed-bed configuration. Testing results inform parameters needed for an engineering design of a full-scale plant and for a TEA.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Structured Sorbent-Based Process for Low-Concentration Sources

participant:

InnoSepra, LLC

project number:

SC0015114

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Ravi Jain
InnoSepra, LLC
ravi.jain@innosepra.com

partners:

N/A

start date:

02.22.2016

percent complete:

100%

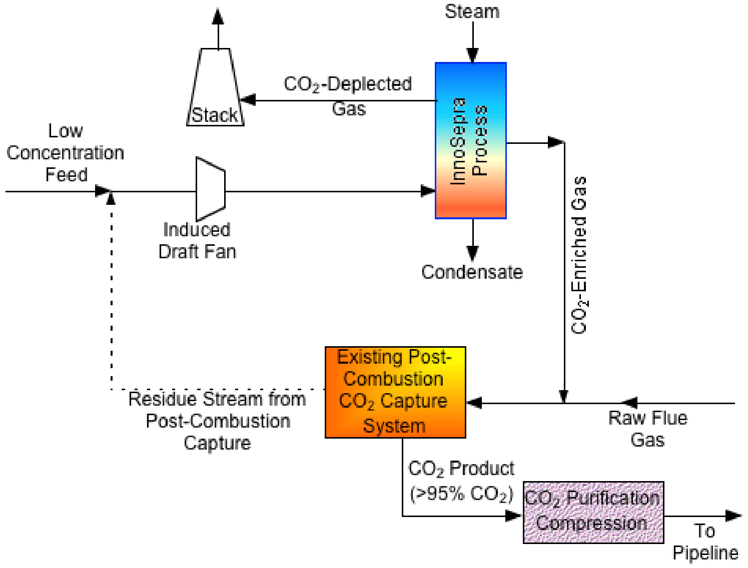


Figure 1: InnoSepra capture process.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,500	1,500
Bulk Density	kg/m^3	500	500
Average Particle Diameter	mm	N/A	N/A
Particle Void Fraction	m^3/m^3	0.45-0.50	0.45-0.50
Packing Density	m^2/m^3	1.3 e8	1.3e8
Solid Heat Capacity @ STP	kJ/kg-K	0.90	0.90
Crush Strength	kg$_f$	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	8.0	6.0-8.0
Adsorption			
Pressure	bar	1.05	1.02-1.03
Temperature	°C	25-35	25-35
Equilibrium Loading	g mol CO_2/kg	2.5	2.5
Heat of Adsorption	kJ/mol CO_2	35	35
Desorption			
Pressure	bar	0.97	0.98
Temperature	°C	100	100
Equilibrium CO_2 Loading	g mol CO_2/kg	1.0	1.0
Heat of Desorption	kJ/mol CO_2	42	40
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 10-15% 1.0	
Adsorber Pressure Drop	bar	0.03	

Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	300

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Contaminant Resistance – Under normal operation, the sorbent is not irreversibly damaged by any contaminant in the flue gas. The residue gas is likely to have little or no contaminants.

Sorbent Attrition and Thermal/Hydrothermal Stability – In the structured form, the sorbent attrition is minimal. If moisture should break through onto the CO_2 sorbent, the sorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300°C.

Flue Gas Pretreatment Requirements – No special flue gas pretreatment is required. A conventional FGD and a direct contact cooler (DCC) are sufficient for normal process operation.

Sorbent Makeup Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between five and 10 years. An adsorbent life of five years has been assumed to estimate the makeup requirements.

Waste Streams Generated – N/A.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

Proposed Module Design – Except for the sorbents loaded with flue gas components, no other waste streams are generated in the process. These can be disposed of as per current power plant practices for materials loaded with sulfur oxide (SO_X) and mercury (Hg).

technology advantages

The structured sorbents have:

- A very high surface area-to-volume ratio and a lower heat requirement for regeneration compared to amine-based absorption using structured packing.
- Are not subject to fluidization constraints or attrition concerns.
- Very low pressure drops, typically 1/5 to 1/10th of particulate adsorbents.
- Very small effective particle size (less than 80 µm) that provides very short mass transfer zones.
- Ability to process significantly higher flows for a given bed volume compared to particulate adsorbents, which is particularly beneficial for low-concentration source CO_2 capture where flow rates can be much higher.
- Able to be fabricated using virtually any commercially available adsorbent.

R&D challenges

- Assuring sufficient moisture removal to enable significantly higher CO_2 capacity for the sorbent in the CO_2 adsorption stage.
- Validating the process model with test results.

status

This project was completed on April 9, 2019. InnoSepra completed sorption isotherms at low-CO_2 concentrations (0.5 to 2.0 wt% CO_2). Breakthrough capacities of 5.0 to 8.5 wt% at 25°C and 4.0 to 7.0 wt% at 35°C, along with cyclic CO_2 capacities of greater than 90% of the breakthrough capacities, were achieved. Carbon dioxide enrichment by a factor five to 10 was achieved depending on the feed CO_2 concentration, regeneration temperature, and cycle time. Moisture-removal testing was completed in both fixed-bed and rotating-bed test units, with better performance and more process flexibility noted in the fixed-bed units. The CO_2 enrichment cost depends on the moisture content of the residue stream. If the residue stream is moisture-saturated (such as that from an amine-based capture process), the enrichment cost is about \$55/ton. If the residue stream is nearly dry (such as that from InnoSepra's adsorption-based post-combustion CO_2 capture process), the enrichment cost is about \$37/ton. The original project milestones, both in terms of process performance and the CO_2 capture cost, were exceeded during the execution of this project. The current CO_2 enrichment costs of \$37 to \$55/ton are significantly better than a cost of \$350/ton for the amine-based process for low-concentration streams. If the enriched CO_2 stream is mixed with the feed to a post-combustion CO_2 capture process, cost-effective capture of 98 to 99% of CO_2 is possible.

available reports/technical papers/presentations

Jain, R. "Process for CO_2 Capture from Low Concentration Streams," Presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/R-Jain-InnoSepra-Low-Concentration-Capture.pdf*.

High-Efficiency Post Combustion Carbon Capture System

primary project goals

Precision Combustion, Inc. (PCI) is developing a compact, modular post-combustion carbon capture system using high-capacity metal organic framework (MOF) nanosorbents supported on a tailorable mesh substrate. This system enables low-pressure drop, high volumetric utilization, and high mass transfer rates, and is suitable for the rapid heat transfer and low temperature regeneration operating modes needed for cost-effective carbon capture

technical goals

- Optimize the sorbent to higher capacities with good selectivity towards carbon dioxide (CO_2), as well as resistance to humidity and contaminants.
- Optimize mesh geometry and coating process to achieve higher loadings without affecting sorbent structure at increased production capacity.
- Simulate a scaled-up plant design with steady and dynamic process and computational fluid dynamics (CFD) modeling of the system.
- Assemble small-scale module and test with actual coal-derived flue gas to show the efficacy of the system and further refine the operating conditions.
- Integrate with U.S. Department of Energy (DOE) Carbon Capture Simulation Initiative (CCSI) software.
- Perform full-scale techno-economic modelling of CO_2 capture with sensitivity analysis.

technical content

PCI is developing a post-combustion carbon capture system using high-capacity MOF nanosorbents coated on PCI's patented Microlith® mesh sorbent substrate.

MOF materials are crystalline organic-inorganic compounds formed by coordination of metal clusters or ions with organic linkers – usually bivalent or trivalent aromatic carboxylic acids or nitrogen-containing aromatics. They have extremely high surface area, high pore volume, uniform size pores, and high metal content, making them excellent candidates for selective CO_2 capture. The modular cartridge form factor enables low-cost retrofit to existing systems. For the high space velocity sorbent structure, PCI has developed and patented a short contact time mesh-based substrate, trademarked Microlith® coated with the densified nanostructured sorbent. The combination enables higher surface area per unit volume and decreased bed volume with equivalent effectiveness to other types of monolithic or loose packing, without pressure drop penalty. Additionally, up to 20 times higher mass and heat transfer coefficients are obtainable as compared to other sorbent systems such as monoliths and pellets, due primarily to boundary

technology maturity

Bench-Scale, Actual Flue Gas

project focus:

Metal Organic Framework Nanosorbent

participant:

Precision Combustion, Inc.

project number:

SC0017221

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Codruta Loebick
Precision Combustion, Inc.
cloebick@precision-combustion.com

partners:

Boston University, BASF

start date:

02.21.2017

percent complete:

70%

layer minimization and break-up, boosting CO_2 removal rates with greater sorbent bed utilization and less bypass inherent to packed beds or monoliths. This sorbent manufacturing technology allows for adherent and durable MOF coatings (as well as alternative future high surface area sorbents) on the Microlith® substrate. Sorbent coated on Microlith® mesh is shown in Figure 1.

The process as shown in Figure 2 includes a modular capture system containing the MOF nanosorbents coated on Microlith®, with adsorption at 30°C and desorption at 80°C. This capture system configuration enables low-pressure drop, high volumetric utilization, and high mass transfer, and also has a low energy of regeneration.

During Phase II PCI:

- Selected the currently best capacity commercial large-scale intent MOF and further tested it under realistic conditions and developed means for improving its stability.
- Developed means for deploying the MOF at large scale by coating it on PCI's low-pressure drop Microlith® support and matured the operational map of the post-combustion carbon capture system unit in thermal swing adsorption (at 30ºC) and desorption (at 80ºC) to bring energy expense to 255 kWh/tonne of CO_2 recovered at the end of the Phase and utilization of materials with lower heat capacity. In comparison, a monoethanolamine (MEA) system requires more than 1,100 kWh/tonne due to steam injection.
- Developed a techno-economic analysis (TEA) showing that the system can achieve the $30/tonne of CO_2 captured target (including compression), with $35.8/tonne projected at Phase II performance and further cost savings expected from reduction of balance of plant components and increased efficiency to under the $30/tonne target (Phase II A target – $26/tonne – including compression).
- Developed CFD models of pilot-scale units – to be integrated with CFD package of the CCSI software.
- Assembled a small-scale MOF – Microlith® unit to be deployed at the National Carbon Capture Center (NCCC) for initial testing with live flue gas for model and economics validation.

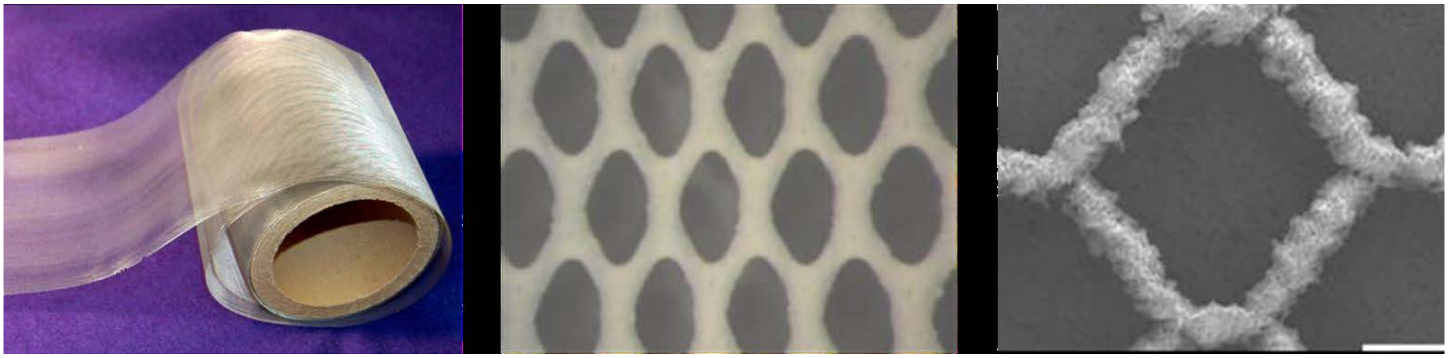


Figure 1: Microlith® mesh coated with sorbent.

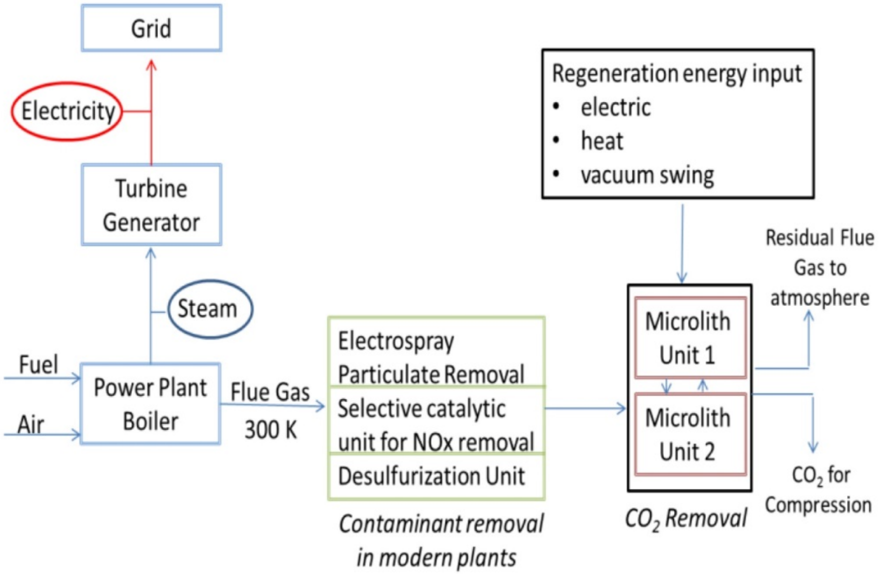


Figure 2: Process block diagram.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physical Sorption with selectivity for CO_2 over 95%.

Sorbent Contaminant Resistance – 200-hour test with 200 parts per million (ppm) sulfur dioxide (SO_2) showed no major effects

Sorbent Attrition and Thermal/Hydrothermal Stability – Excellent attrition resistance because the sorbent is immobilized on mesh, good thermal resistance up to 200 to250°C, tolerant to some humidity (still under development).

Flue Gas Pretreatment Requirements – Condensation of some of the water with heat recovery.

Sorbent Makeup Requirements – None. Cartridge replacement of the mesh coated with sorbent to be performed at sorbent lifetime end.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, if not included above – see above.

Proposed Module Design – Sorbent bed consists of coiled layers of Microlith® meshes coated with sorbents; ability to coat different sections of mesh with different sorbents for one-step removal of CO_2 and other contaminants.

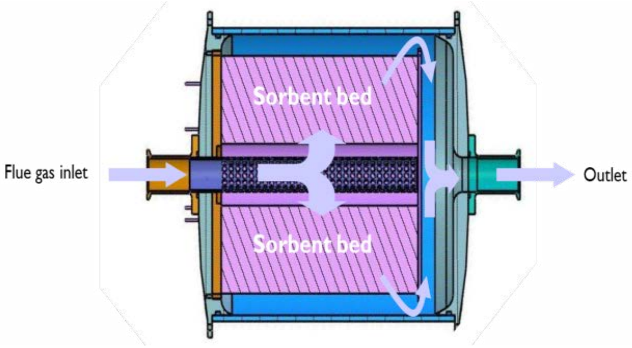


Figure 3: Sorbent bed.

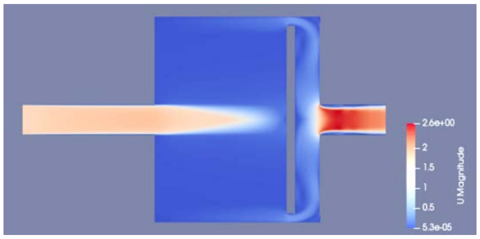


Figure 4: CFD model of post-combustion carbon capture system unit (Microlith® media), GHSV – 160,000 h^{-1}.

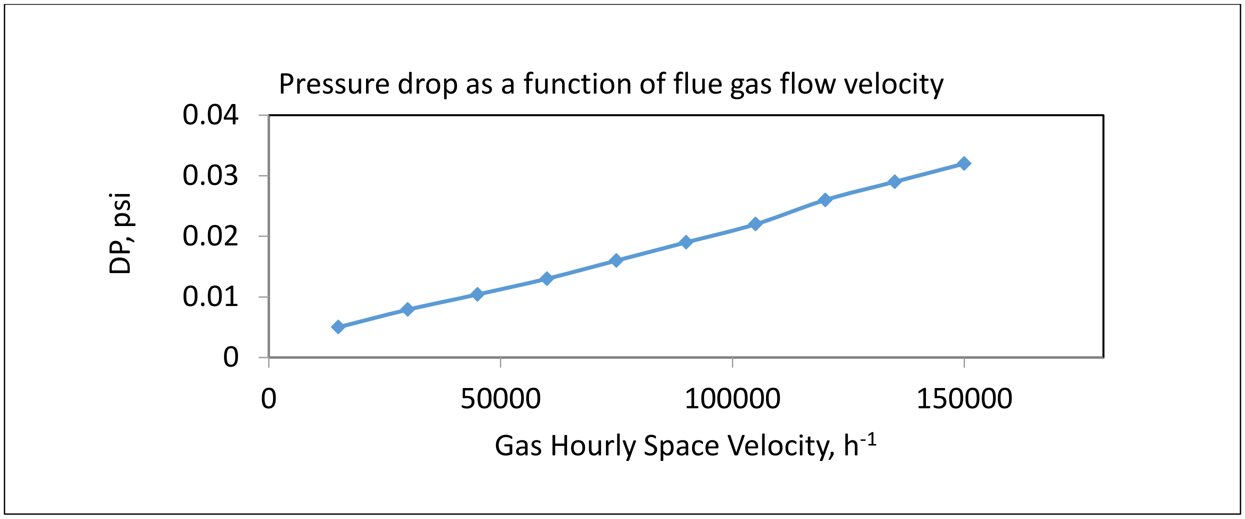


Figure 5: Pressure drop versus gas flow velocity.

technology advantages

- The MOF materials have a lower regeneration energy and a lower degradation rate due to their physical adsorption capture mechanism as opposed to chemical reaction.
    - Greatly reduces boundary layer formation, with reduced pressure drop for similarly performing post-combustion carbon capture systems (pellets or monoliths based), resulting in process intensification with corresponding reduction in post-combustion carbon capture system volume.
    - Increased mass and heat transfer coefficients and enhanced diffusion of gas in the sorbent.
    - Immobilizing the sorbent increases its lifetime by reducing attrition.
    - Modular design flexibility (e.g., planar, radial); easily scalable.
- PCI's Microlith® mesh substrate supporting the MOF material has higher surface area per unit volume and much higher mass and heat transfer coefficients, as well as low-pressure drop compared to other monolith substrates or pellets, resulting in increased CO_2 capture rate and reduced regeneration energy.

R&D challenges

- Maintaining higher CO_2 loadings without affecting sorbent structure at increased production capacity.
- Identifying optimal sorbent to maximize capacity and selectivity.
- Achieving acceptable sorbent cost at large-scale production.
- Optimizing the material for long-term (thousands of cycles) operation in flue gas environment.

status

In Phase II, PCI demonstrated the Microlith®-based approach to carbon capture via adsorption on MOF materials. The sorbent was stable over multiple thermal cycles and showed stability to contaminants and some humidity, as well as high selectivity for CO_2 over other components of the flue gas. The system was demonstrated to have energy-saving performance due to enhanced sorption properties, heat and mass transfer and low-pressure drop. A TEA shows potential for achieving the DOE goal of $30/tonne of CO_2 captured.

available reports/technical papers/presentations

Loebick, C., et al., "High-Efficiency Post Combustion Carbon Capture System," Presented at the Phase II Project Review Meeting, Pittsburgh, PA, November 2018. *https://www.netl.doe.gov/projects/files/High-Efficiency%20Post%20Combustion%20Carbon%20Capture%20System%20Nov%202018.pdf*.

Loebick, C. and Weisman, J., "High-Efficiency Post Combustion Carbon Capture System," Presented at the Phase I Project Review Meeting, Pittsburgh, PA, December 2017. *https://www.netl.doe.gov/projects/files/High-Efficiency%20Post%20Combustion%20Carbon%20Capture%20System%20Dec%202017.pdf*.

Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture

primary project goals

Lawrence Berkeley National Laboratory (LBNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative, is developing amine-appended metal-organic framework (MOF) sorbents having step-change adsorption isotherms with larger sorbent working capacities with minor temperature swings for low-energy post-combustion carbon dioxide (CO_2) capture.

technical goals

- Identify, synthesize, and characterize amine-MOF pairs using existing and new computationally designed MOF and amine structures.
- Test the synthesized sorbent materials using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to impurities, and cycling performance.
- Identify the most promising sorbents with realistic potential for implementation in carbon capture.
- Field test the MOF sorbent using actual coal-derived flue gas.

technical content

LBNL is combining computational and experimental programs to synthesize and characterize amine-appended MOF sorbents for energy-efficient carbon capture. An example of the structure of an MOF with appended amines is shown in Figure 1. These MOF materials show switch-like CO_2 adsorption behavior and can be tuned to optimize working capacities under mild regeneration conditions. They exhibit step-change isotherms enabled by a cooperative CO_2 adsorption mechanism, as shown in Figure 2. This step-change isotherm allows for larger sorbent working capacities with minor temperature swings, as opposed to the large temperature swings required by traditional amine-based sorbents. The step-change isotherm shows very little hysteresis upon desorption of CO_2, and the step shifts rapidly to higher pressure with increasing temperature. Balancing CO_2 capture performance and cost is done through vigorous optimization efforts of the amine molecules and pore geometries, combining computational modeling, characterization of molecules, and experiments to evaluate CO_2 capture performance.

Diamine-appended MOFs are being identified and synthesized, targeting materials showing step-change or switch-like reversible CO_2 adsorption isotherms. Computational modeling is used to identify promising amine-MOF pairs. The computational analysis and measurements of CO_2 adsorption behavior provide insight to identify second-generation materials with desired properties. The research team will identify, synthesize, and characterize amine-MOF pairs

technology maturity

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Amine-Appended Metal-Organic Framework Sorbent

participant:

Lawrence Berkeley National Laboratory

project number:

FWP-FP00006194

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Jeffrey Neaton
LBNL
jbneaton@lbl.gov

partners:

Mosaic Materials, Svante, Electricore

start date:

08.31.2017

percent complete:

55%

using existing and new computationally designed MOF and amine structures. The synthesized sorbent materials will be tested using simulated flue gas to determine CO_2 adsorption and desorption kinetics, tolerance to flue gas impurities, and cycling performance, as well as to identify the most promising sorbents with realistic potential for industrial implementation in carbon capture.

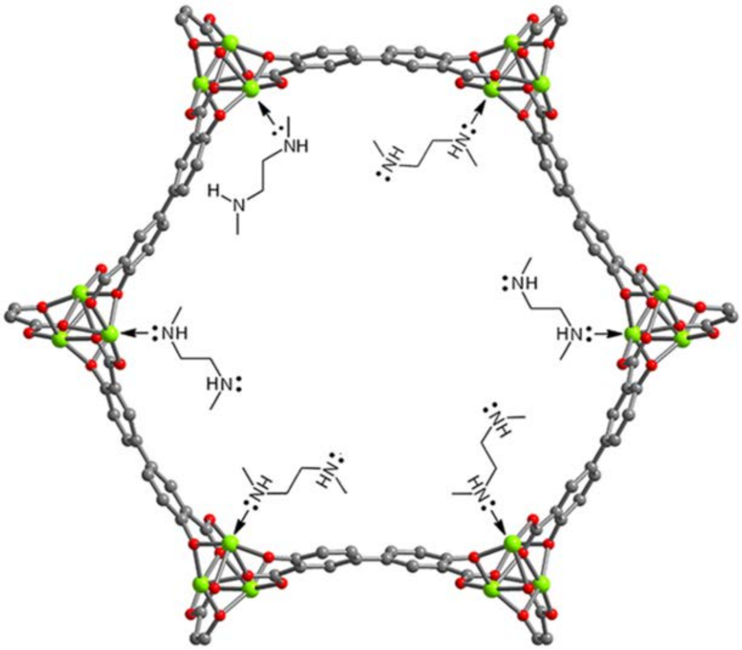


Figure 1: Example of an MOF with appended amines.

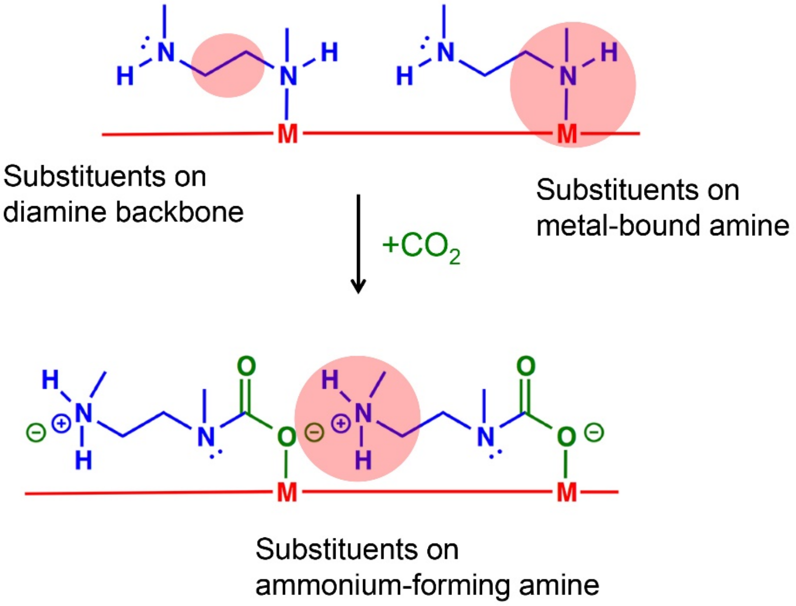


Figure 2: Cooperative CO_2 adsorption.

The project is part of DOCCSS, a partnership coupling unique skillsets of national laboratories, industry, and academic institutions to work collaboratively to facilitate discovery, synthesis, performance assessment, and functionalization of new carbon capture materials, and to accelerate the rate at which transformational processes for carbon capture are commercialized. This project includes a combined effort among several entities. LBNL is responsible for materials discovery, synthesis, and characterization. Mosaic Materials is developing materials production protocols and scale-up research and development. Sorbent production scale-up and optimization efforts include evaluating four distinct steps: synthesis of the MOF, purification of the MOF to remove impurities, amination where the purified MOF is impregnated with amines, and activation where the solvent is removed. Svante and Electricore are integrating the diamine-appended

MOFs in a cost-effective CO_2 capture system through system development efforts. Svante will perform testing of the sorbent in powder form and in a structured-bed form in their capture test units to confirm performance.

The overall effort will test first-generation (Gen1) materials, continue to develop and synthesize improved diamine-appended MOF (Gen2) materials, and evaluate long-term stability, impurity effects, and alternate regeneration strategies to recover greater CO_2 capacity, culminating in field testing using actual coal-derived flue gas.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,560	1,560
Bulk Density	kg/m^3	300	300
Average Particle Diameter	mm	N/A	N/A
Particle Void Fraction	m^3/m^3	N/A	N/A
Packing Density	m^2/m^3	N/A	N/A
Solid Heat Capacity @ STP	kJ/kg-K	1.46	1.46
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	4,586	3,033
Adsorption			
Pressure	bar	0.13	0.13
Temperature	°C	50	50
Equilibrium Loading	g mol CO_2/kg	2.5	2.5
Heat of Adsorption	kJ/mol CO_2	74	74
Desorption			
Pressure	bar	1	1
Temperature	°C	110	110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1	0.1
Heat of Desorption	kJ/mol CO_2	74	74
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	Fixed structured beds with rapid cycling	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 90 1	
Adsorber Pressure Drop	bar	0.08	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – See above.

Sorbent Contaminant Resistance – Flue gas pre-conditioning required in some applications to limit sulfur oxide (SO_X) and nitrogen oxide (NO_X) in contact with adsorbent material.

Sorbent Attrition and Thermal/Hydrothermal Stability – Thermal stability of the sorbent has been demonstrated for the operating temperature range of the process. Hydrothermal stability for the Gen1 material is insufficient due to water-amine-MOF interactions. Gen2 material development or a change in Gen1 material formulation are being evaluated to minimize the impact of steam on the composite material.

Flue Gas Pretreatment Requirements – To be determined. Initial pilot test on simulated flue gas without SO_X and NO_X supplemented by lab-scale tests and modeling of SO_X/NO_X interaction with the sorbent.

Sorbent Makeup Requirements – No makeup, structured sorbent modules do not allow for in-process addition of adsorbent material.

Waste Streams Generated – Condensate water from flue gas pre-conditioning unit with flue gas particulates, solid waste from discarded sorbent modules every two to five years. No makeup liquid amine solution to discard greatly reduces waste streams for solid sorbents compared to liquid amine sorbent technology.

Process Design Concept – Multi-bed structured solid sorbent assembled on rotary contactor for rapid adsorption-desorption cycle. Cycle times are between one to two minutes using rapid thermal swing.

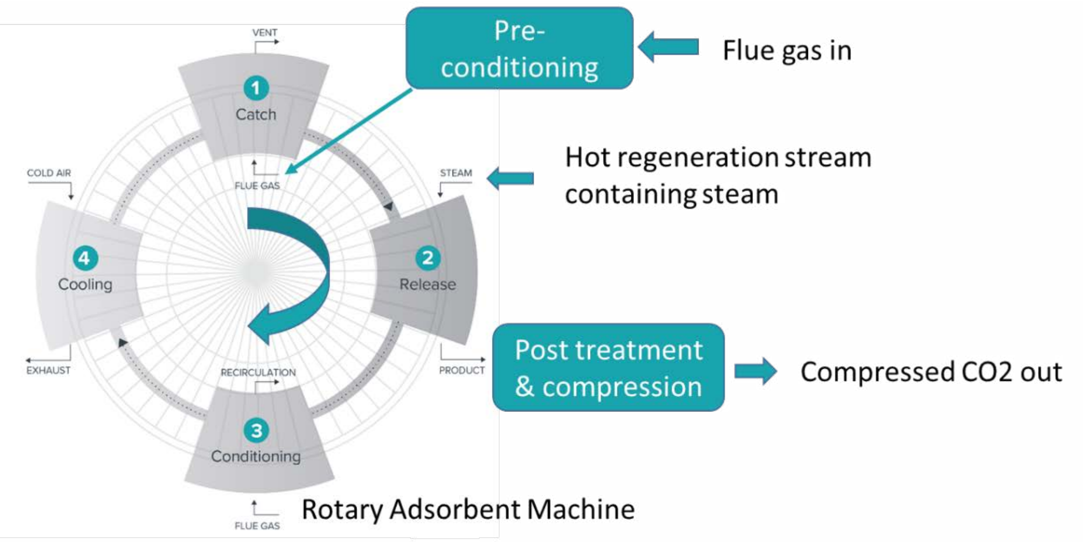


Figure 3: Rotary adsorbent machine.

Proposed Module Design – Modules are built to define parallel passageways, enabling large contact area between the solid and the gas while minimizing flow resistance and maximizing volumetric loading of adsorbing material. Modules are typically meter-scale in flow direction, with channels in the millimeter scale.

technology advantages

- Amine-appended framework materials are highly tunable.
- Sorbent has large working capacity due to step-shaped CO_2 adsorption.
- Sorbent has high CO_2 selectivity over nitrogen, oxygen, and water.

R&D challenges

- Large-scale and economic production of materials.
- Durability and chemical stability of these MOFs under actual flue gas.
- Reducing the regeneration cost in temperature swing.

status

LBNL has identified and synthesized a Gen1 material with a 2.4 mmol CO_2/gram working capacity with a 60°C temperature swing. Mosaic Materials successfully synthesized 1 kilogram of Gen1 material that met CO_2 performance metrics and was delivered for testing at the Svante test unit.

A screening database has been established to discover new MOFs with similar open metal site distance distributions to the Gen1 material, with three candidate materials of interest identified with potential for greater than 3.0 mmol/gram CO_2 uptake. One of these Gen2 materials showed a 3.6 mmol/gram working capacity with a 45°C temperature swing and an approximate regeneration energy of 2.2 MJ/kg CO_2. This Gen2 material was stable over 1,000 humid adsorption/desorption cycles under simulated coal flue gas conditions.

available reports/technical papers/presentations

Long, J., Neaton, J., and Haranczyk, M. "Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Long-LBNL-Amine-Appended-MOF.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at the Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/files/2019%20LBL%20DOCCSS%20Project%20Review%20Meeting_08-01-19.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/J-Long-LBNL-Amine-Appended-MOFs.pdf*.

Long, J., Neaton, J., and Haranczyk, M. “Amine-Appended Metal-Organic Frameworks as Switch-Like Adsorbents for Energy-Efficient Carbon Capture,” Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/J-Long-LBNL-Metal-Organic-Frameworks.pdf*.

A New Sorbent Process for Transformational Carbon Capture Process

primary project goals

TDA Research (TDA) is developing amine-functionalized resin sorbents to selectively remove carbon dioxide (CO_2) from flue gas using a vacuum swing adsorption (VSA) cycle. Activities include identification of polymers that can be formed with amine functionalities tuned for CO_2 uptake, scaling-up sorbent production, and testing performance at the bench-scale.

technical goals

- Optimize the sorbent formulations to achieve higher CO_2 capacity and uptake rates and evaluate use of co-polymers to increase the processability of the materials into structures easily integrated into modules.
- Screen polymers and structures in bench-scale testing and prepare test modules using the best identified polymers.
- Test the modules in the TDA test apparatus using the VSA cycle and optimize operating conditions and cycle sequence.
- Complete a minimum of 20,000 adsorption/desorption cycles in presence of flue gas contaminants.
- Design a CO_2 capture process around this new material.
- Assess the techno-economic viability of the process.

technical content

TDA is developing a sorbent based on amine-functionalized resin structures for the capture of CO_2 from coal-fired power plants. In Phase I, TDA modified commercial polymeric resins with amines and tuned them for CO_2 uptake. In-house polymers were also prepared with amine functionalities and showed higher CO_2 loading than the commercial resins, along with high selectivity and kinetics. The presence of moisture enhanced the CO_2 loading. Furthermore, the TDA resins provide the flexibility to be used as coatings on engineered structures, which can reduce pressure drop and allow for the treatment of high volumes of flue gas. The sorbent regeneration occurs using a VSA cycle, and the mild vacuum conditions required results in lower regeneration energy.

In Phase II, TDA is optimizing the sorbent formulations for improved CO_2 capacity and processability to form engineered structures capable of integration into modules. Polymer scale-up will occur in a 50-gallon reactor system. Polymers will be shaped into various forms, including pellets, extruded honeycomb structures, and polymer films via spin coating. Working with partner Membrane Technology and Research (MTR), polymer beads will be processed into thin sheets, which will then be made into spiral-wound and planar modules. Examples are shown in Figure 1.

Sorbent will be evaluated as loose granules and as modules in TDA's existing VSA prototype test system (shown in Figure 2), which can treat 5 standard cubic feet per minute (scfm) of flue gas and remove up to 2.5 kilogram (kg)/hour of CO_2. Testing includes optimization of the process and the VSA cycle sequence,

technology maturity

Bench-Scale, Simulated Flue Gas

project focus:

Amine-Functionalized Resin Sorbent

participant:

TDA Research, Inc.

project number:

SC0018682

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Gökhan Alptekin
TDA Research, Inc.
galptekin@tda.com

partners:

Membrane Technology and Research, Inc.

start date:

07.02.2018

percent complete:

30%

as well as long-term tests in the presence of contaminants. Testing results will inform the design of a CO_2 capture process around this new polymer-based adsorbent material.

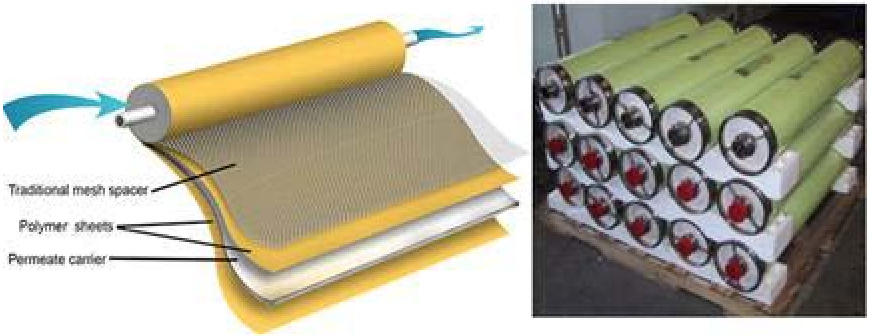


Figure 1: Example of preparation of spiral-wound modules (left) and of MTR's polymer membrane modules (right).

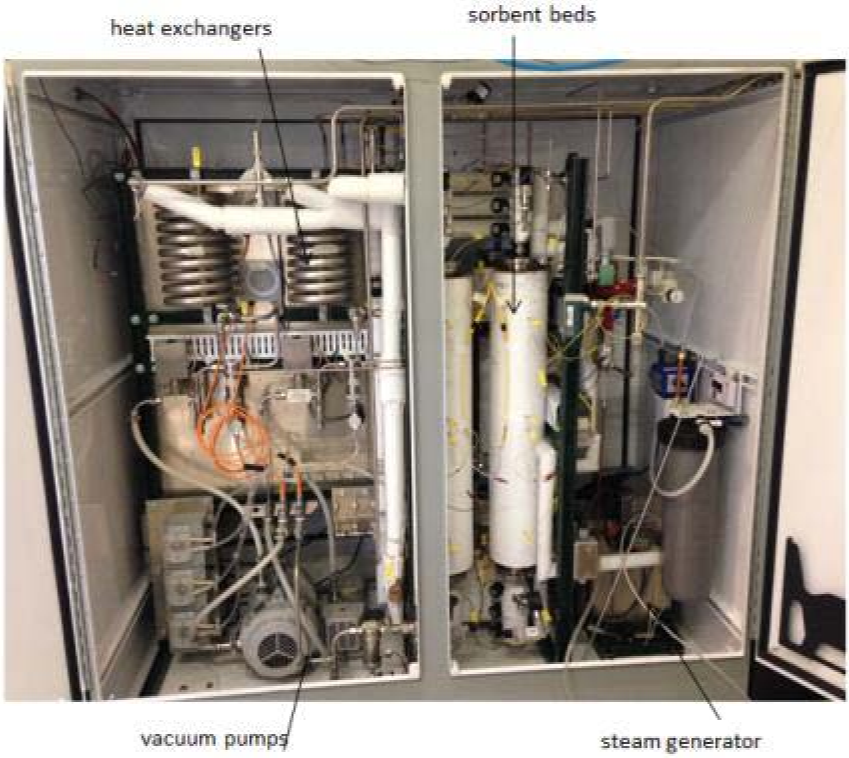


Figure 2: TDA's four-bed VSA system.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	600	600
Bulk Density	kg/m^3	300	300
Average Particle Diameter	mm	N/A	N/A
Particle Void Fraction	m^3/m^3	<0.1	<0.1
Packing Density	m^2/m^3	500	500
Solid Heat Capacity @ STP	kJ/kg-K	2.0	2.0
Crush Strength	kg$_f$	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	<20	<5

Adsorption				
Pressure	bar	1.1		1.1
Temperature	°C	60		60
Equilibrium Loading	g mol CO_2/kg	0.72		0.8
Heat of Adsorption	kJ/mol CO_2	<50		<50
Desorption				
Pressure	bar	0.2		0.2
Temperature	°C	60		60
Equilibrium CO_2 Loading	g mol CO_2/kg	0.04		0.04
Heat of Desorption	kJ/mol CO_2	<50		<50
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		Countercurrent	
Flue Gas Flowrate	kg/hr		TBD	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	150
Adsorber Pressure Drop	bar		0.15	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		TBD	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Amine-functionalized proprietary polymer.

Sorbent Contaminant Resistance – Sulfur oxide (SO_X) and nitrogen oxide (NO_X) tolerant up to 100 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – N/A.

Flue Gas Pretreatment Requirements – None.

Sorbent Makeup Requirements – Five-year replacements.

Waste Streams Generated – None.

Proposed Module Design – Plate and frame or spiral-wound.

technology advantages

- Structured sorbents have potential for high CO_2 uptake with low pressure drop while treating high volumes of gas.
- Use of sorbents in a structured form instead of pellets favors use of a modular design.
- Reduced regeneration energy through a regeneration process using mild vacuum.

R&D challenges

- Preparation of the functionalized resin sorbent in engineered structures.
- Life cycle of sorbents in operational conditions with flue gas contaminants.
- Economic viability in large power plant applications due to the volume of sorbent required and cost of ancillary equipment (ductwork distribution system, vacuum pumps, etc.).

status

In Phase I, TDA Research has identified new polymers that can be formed into desirable structures (monoliths or planar contactors) with amine functionalities tuned for high CO_2 uptake and selectivity. Carbon dioxide capture cost was estimated to be $29.7/tonne, excluding transportation, storage, and monitoring (T&SM).

available reports/technical papers/presentations

Alptekin, G. and Jayaraman, A., "A New Sorbent Process for Transformational Carbon Capture Process," Presented at the Phase I Final Briefing/Phase II Kickoff Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/files/Phase%20II_Project_Kickoff_DE-SC0018682_082119_NonConfidential.pdf*.

Alptekin, G, et al., "A New Sorbent Process for Transformational Carbon Capture Process," Presented at the Phase I Project Kickoff Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/A%20New%20Sorbent%20Process%20for%20Transformational%20Carbon%20Capture%20Process.pdf*.

Membrane-Sorbent Hybrid System for Post-Combustion Carbon Capture

primary project goals

TDA Research, Inc. (TDA) is designing and constructing a 1.0 megawatt-electric (MWe)-scale membrane-sorbent hybrid post-combustion carbon capture system and evaluating its operation in a long-duration field test using industrial flue gas that closely resembles coal-fired flue gas. Their hybrid process consists of a polymeric membrane and low-temperature physical adsorbent to remove carbon dioxide (CO_2) from flue gas.

technical goals

- Design the 1-MWe-scale test unit.
- Fabricate the test unit.
- Install the test unit at the Technology Centre Mongstad (TCM).
- Complete a 9- to 12-month-long field test campaign at TCM using actual flue gas.
- Complete an updated techno-economic analysis (TEA) based on the field test data.

technical content

TDA Research is designing, constructing, and operating a slipstream 1.0-MWe pilot-scale process for post-combustion CO_2 capture using actual flue gas. The hybrid process consists of a polymeric membrane and a low-temperature physical adsorbent. This technology is based on TDA's previously developed sorbent and a membrane developed by Membrane Technology and Research (MTR). TDA's sorbent uses a mesoporous carbon modified with surface functional groups to remove CO_2 via physical adsorption. Carbon dioxide-surface interaction is strong enough to allow low partial pressure operation and regeneration energy is low because the CO_2 is not bonded to the sorbent. The feasibility of the hybrid sorbent-membrane system was initially proven in a prior U.S. Department of Energy (DOE)-funded project (DE-SC0011885) using coal-derived flue gas at 4-kilowatt-electric (kWe) scale, showing greater than 90% CO_2 capture and high purity.

An overall schematic of TDA Research's system is shown in Figure 1, consisting of two primary components: (1) the membrane unit and (2) the CO_2 adsorption unit. The membrane operates at approximately 50°C under mild vacuum, removing approximately 50% of the CO_2 and nearly all of the water. The reduced vacuum pump requirements reduce power consumption and system cost. The sorbent removes the remaining CO_2 from the membrane effluent to ensure 90% carbon capture. Sorbent regeneration is facilitated using boiler feed air as a sweep gas and the CO_2-laden air after sorbent regeneration is fed to the boiler to generate a CO_2-rich flue gas stream to increase the driving force across the membrane. The overall energy intake of the CO_2 capture process is reduced by using a hybrid membrane-sorbent configuration, while the capture efficiency is not degraded.

technology maturity

Pilot-Scale, Actual Flue Gas Slipstream (1.0 MWe)

project focus:

Membrane-Sorbent Hybrid System

participant:

TDA Research, Inc.

project number:

FE0031603

predecessor projects:

SC0011885

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gokhan Alptekin
TDA Research, Inc.
galptekin@tda.com

partners:

Membrane Technology and Research, Technology Centre Mongstad, Gas Technology Institute, University of California Irvine

start date:

08.15.2018

percent complete:

40%

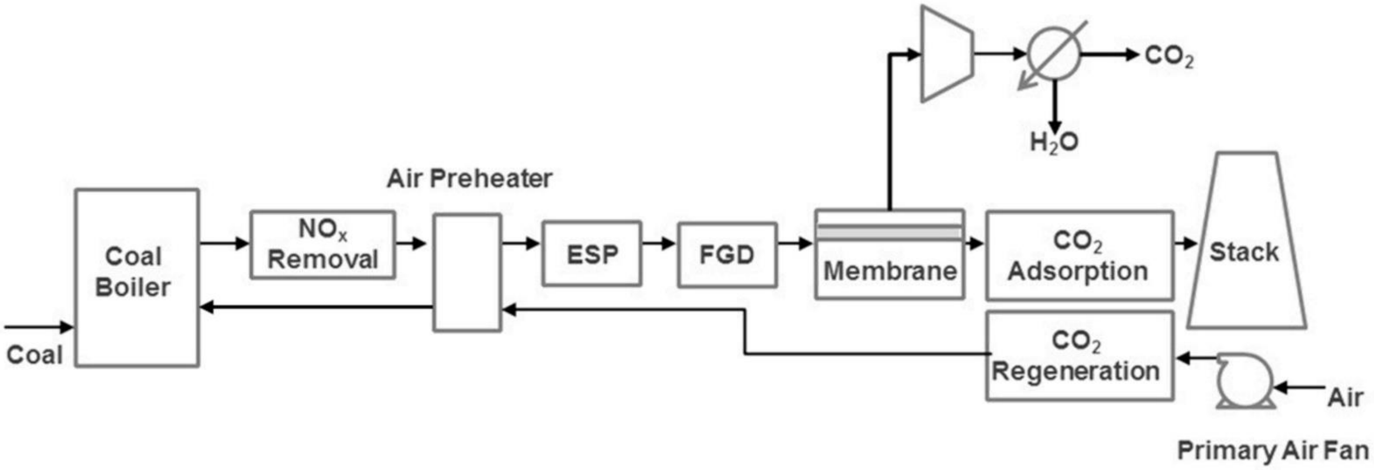


Figure 1: Flow diagram of the TDA Research hybrid membrane-sorbent CO_2 capture system.

TDA is developing its modular sorbent bed concept known as the radial outflow reactor, shown in Figure 2. Two modules would be used, one operating in adsorption and one in desorption, to provide continuous transfer of CO_2 into the boiler air. For the 1-MWe-scale tests at TCM, three modules are to be used, as shown in Figure 3, with two of the modules operating in series to show the modular design concept works.

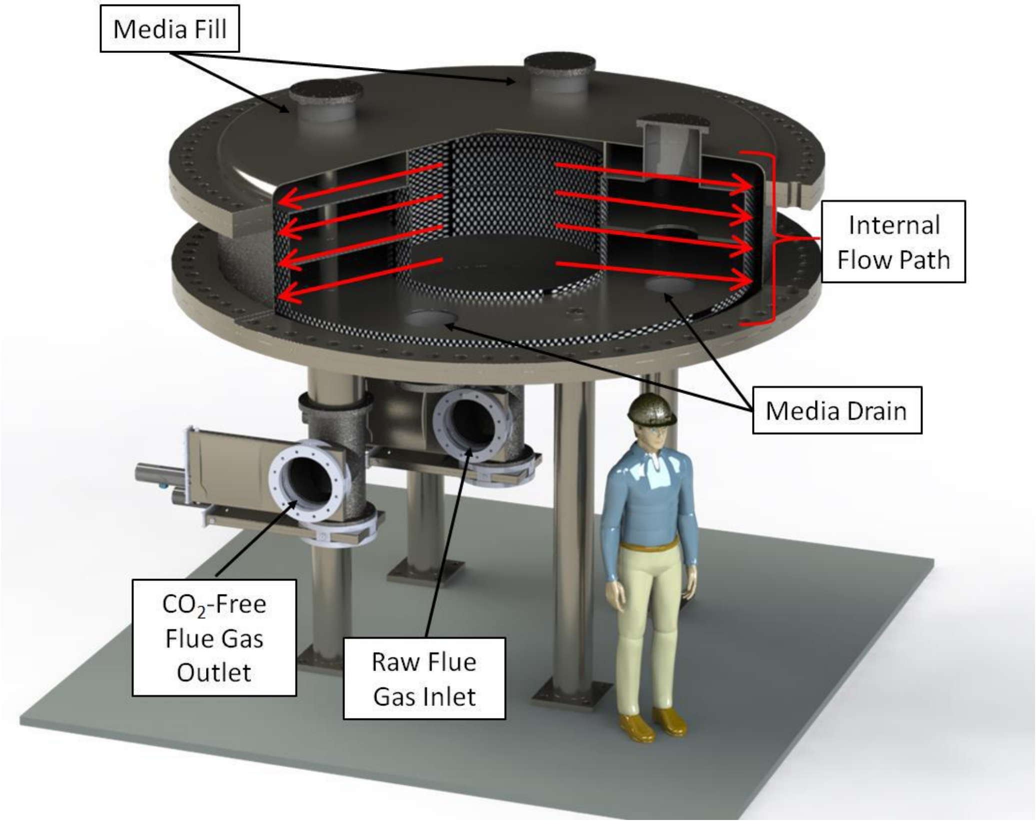


Figure 2: TDA Research's modular radial outflow reactor concept.

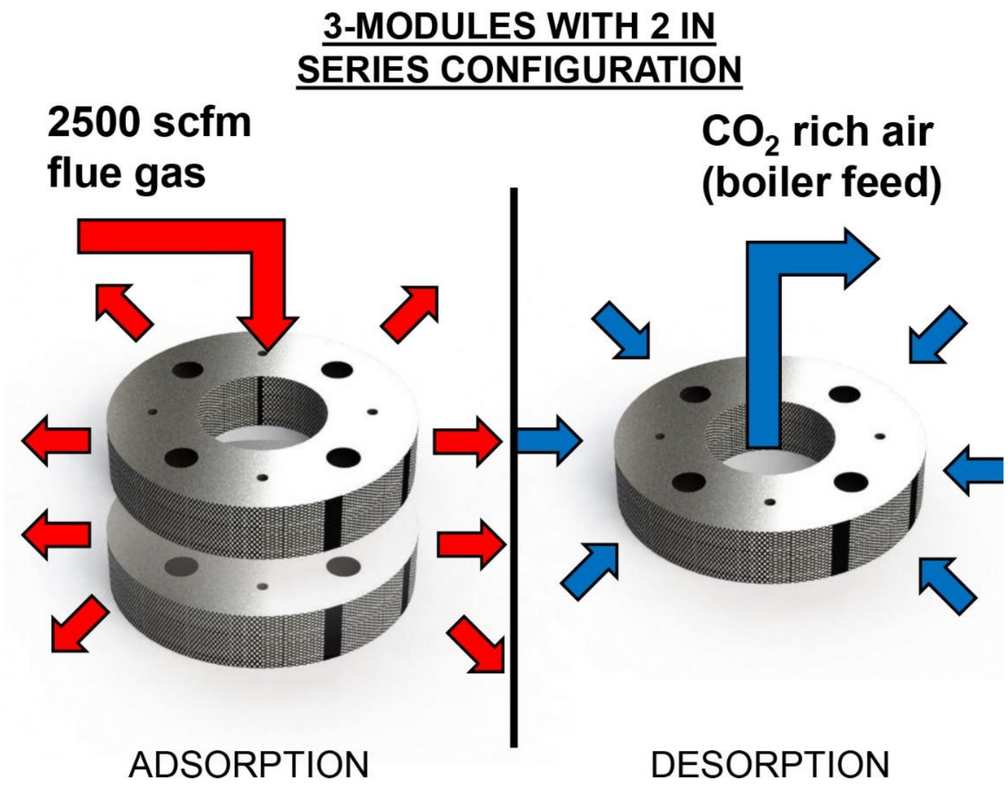


Figure 3: TDA Research 1-MWe modules.

The 1.0-MWe membrane-sorbent hybrid pilot test unit is being designed and built to be installed for testing at TCM in Norway. A 9- to 12-month test campaign using industrial flue gas that closely resembles coal-fired flue gas is planned to evaluate the operating performance of the capture system at various conditions and to complete at least 6,000 hours of continuous operation. This testing under both parametric and steady-state conditions provides data and recommended operating conditions to update the membrane performance data and the TEA and environment, health, and safety (EH&S) analysis. The project aims to demonstrate the novel hybrid system for reduction in carbon capture cost.

The sorbent and process parameters are provided in Table 1 and the membrane and process parameters are provided in Table 2.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1300	1300
Bulk Density	kg/m^3	589	589
Average Particle Diameter	mm	0.4-1.7	0.8-2.4[a]
Particle Void Fraction	m^3/m^3	0.37	0.37
Packing Density	m^2/m^3	240	240
Solid Heat Capacity @ STP	kJ/kg-K	0.93[b]	0.93[b]
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	3.75	3.75
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	30	30
Equilibrium Loading	g mol CO_2/kg	0.5	0.5
Heat of Adsorption	kJ/mol CO_2	20-30	20-30

Desorption				
Pressure	bar	1.0		1.0
Temperature	°C	30		30
Equilibrium CO_2 Loading	g mol CO_2/kg	0.05		0.05
Heat of Desorption	kJ/mol CO_2	20-30		20-30
Proposed Module Design		*(for equipment developers)*		
Flow Arrangement/Operation	—	Radial flow fixed beds		
Flue Gas Flowrate	kg/hr	TBD		
CO_2 Recovery, Purity, and Pressure+	% / % / bar	N/A	NA	N/A
Adsorber Pressure Drop	bar	<100 mbar		
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	TBD		

+ Sorbent subsystem does only recirculation of CO_2 and is the secondary separation system in the hybrid configuration.

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – U.S. Patent No. 9,120,079 B1.

Sorbent Contaminant Resistance – Sulfur oxide (SO_X) and nitrogen oxide (NO_X) tolerant up to 100 parts per million (ppm).

Sorbent Attrition and Thermal/Hydrothermal Stability – Less than 0.1% over one year.

Flue Gas Pretreatment Requirements – None.

Sorbent Makeup Requirements – Five-year replacements.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, included above.

Proposed Module Design – Radial flow fixed beds.

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary Polymer	
Materials of Fabrication for Support Layer	—	Proprietary Polymer	
Nominal Thickness of Selective Layer	μm	<1	<1
Membrane Geometry	—	Thin film composite	Thin film composite
Max Trans-Membrane Pressure	bar	1.0	1.0
Hours Tested without Significant Degradation	—	11,000	3 years
Manufacturing Cost for Membrane Material	$\$/m^2$	—	—
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000 to 3,000	3,000
CO_2/H_2O Selectivity	—	0.25	0.25
CO_2/N_2 Selectivity	—	25-30	30
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Partial countercurrent	
Packing Density	m^2/m^3	500 to 1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	TBD	
CO_2 Recovery, Purity, and Pressure$^+$	%/%/bar	90% 95% 150	
Pressure Drops Shell/Tube Side	bar	0.15	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	TBD	

$^+$ CO_2 recovery, purity, and pressure downstream of the cryogenic purification and pumping system.

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

***Flow Arrangement* –** Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

***Packing Density* –** Ratio of the active surface area of the membrane to the volume of the module.

***Shell-Side Fluid* –** Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

***Membrane Permeation Mechanism* –** proprietary polymeric membrane

***Contaminant Resistance* –** SO_x and NO_x tolerant up to 100 ppm.

***Flue Gas Pretreatment Requirements* –** None.

***Membrane Replacement Requirements* –** TBD.

***Waste Streams Generated* –** None.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

Proposed Module Design – Plate and frame module design for full-scale unit, spiral wound modules used in field test.

technology advantages

- Low pressure drop and high performance at the low CO_2 partial pressure in the adsorption stage.
- Efficient membrane operation due to high driving force and low cost due to mild vacuum requirements.
- Reduced capture cost while maintaining CO_2 capture performance due to the hybridization of the process.
- A preliminary TEA showed a substantial improvement in net plant efficiency (~3.5% increase on higher heating value [HHV] basis) compared with the state-of-the-art amine-based CO_2 capture system.

R&D challenges

- Scaling-up the hybrid system from bench-scale to the 1-MWe system size for testing in this project.
- Assuring high membrane selectivity to get to greater than 95% purity CO_2.
- Maintaining uniform flow distribution in sorbent reactor.

status

TDA Research has completed the design of the 1-MWe-scale test unit and completed their initial design review.

available reports/technical papers/presentations

Alptekin, G., et al. “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture,” Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Membrane-Sorbent-Hybrid.pdf*

Alptekin, G., et al. “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture,” Presented at the Project Kickoff Meeting, Pittsburgh, PA, October 2018. *https://www.netl.doe.gov/projects/files/Membrane-Sorbent%20Hybrid%20System%20for%20Post-Combustion%20CO2%20Capture%20Oct%202018.pdf*

Alptekin, G., et al. “Membrane-Sorbent Hybrid System for Post-Combustion CO_2 Capture,” Presented at 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/Membrane-Sorbent%20Hybrid%20System%20for%20Post-Combustion%20CO2%20Capture%20Aug%202018.pdf*

Advanced Structured Adsorbent Architectures for Transformational Carbon Dioxide Capture Performance

primary project goals

Electricore, Inc. is evaluating Svante Mark-II VeloxoTherm™ technology via development and optimization of novel bi-layer laminated structured sorbents for post-combustion carbon dioxide (CO_2) capture, including bench-scale testing on simulated coal-fired flue gas and on actual flue gas from a gas-fired boiler.

technical goals

- Select, synthesize, and characterize tailored solid adsorbents.
- Optimize the post-combustion CO_2 adsorption technology architecture, including the bi-layer, laminated adsorbent structure design, integrated rapid cycle temperature swing adsorption (RC-TSA) cycle, flow path architecture, and bi-layer adsorbent bed construction.
- Conduct bench-scale testing using an existing single-bed variable test station (VTS) and multi-bed process validation unit (PVU) with flue gas from a natural gas-fired boiler and simulated coal flue gas.
- Assess the techno-economic performance of the technology integrated into a 550-megawatt-electric (MWe) coal-fired power plant.

technical content

Electricore is developing a bi-layer structured sorbent-based process for post-combustion CO_2 capture and evaluating Svante's Mark II VeloxoTherm technology. The bi-layer configuration contains two separate sorbents, the layer A sorbent and the layer B sorbent, in a laminate structure form. An example of the bi-layer cycle design is shown in Figure 1. Layer A is steam-compatible with a high heat of adsorption (greater than 70 kilojoule [kJ]/mole). Water promotes CO_2 adsorption on this sorbent. Layer B has a low CO_2 heat of desorption (less than 40 kJ/mole), air-stable up to 120°C, and is stable to the feed moisture content. Both layer A and layer B sorbents have fast kinetics.

The bi-layer process cycle is approximately 60 seconds in duration and includes two different regenerative environments. Sorbent A uses steam-assisted desorption. Sorbent B has the lower heat of desorption and is regenerated using the heat generated during Sorbent A adsorption, eliminating the need for steam as a carrier gas in that step.

The process is optimized for thermal management in the thermal swing adsorption to allow synergistic design to reduce the amount of steam injected in the system. The combination of structured sorbents with a thermally conductive matrix enable a RC-TSA process that is faster than a conventional thermal swing process. Overall, this process has potential for increased sorbent CO_2 capacity with fast regeneration and reduced steam demands.

technology maturity

Bench-Scale, Simulated Coal-Fired Flue Gas and Actual Flue Gas from a Gas-Fired Boiler

project focus:

Advanced Structured Adsorbent Architectures

participant:

Electricore, Inc.

project number:

FE0031732

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Deborah Jelen
Electricore, Inc.
jelen@electricore.org

partners:

Svante Inc., Susteon, DNV GL USA, Inc.

start date:

05.01.2019

percent complete:

20%

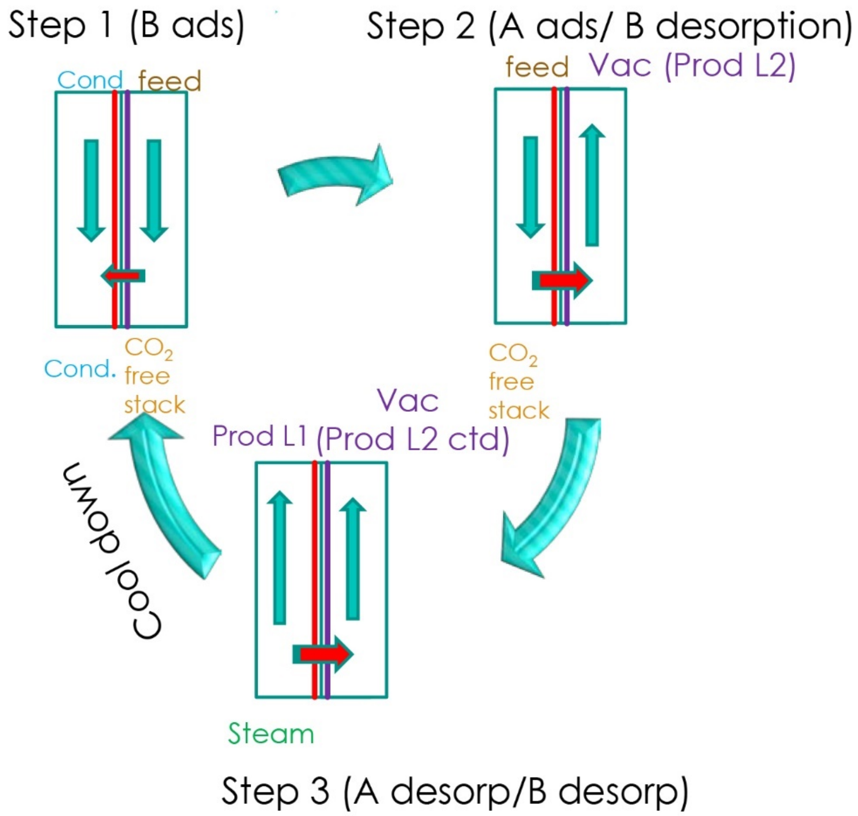


Figure 1: Typical example of the bi-layer cycle design.

Single-bed sorbent testing using simulated coal-fired flue gas is done in the Svante VTS shown in Figure 2, at a scale of approximately 1 to 10 kilograms (kg) of CO_2/day captured. The multi-bed process utilizes the Svante rotating adsorption machine in the PVU that is coupled with a natural gas-fired boiler for testing at a maximum of 10 kg of CO_2 captured/day scale.

Figure 2: The variable test station at Svante.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	N/A (laminate)	N/A
Bulk Density	kg/m^3	100-300 (structured)	100-300 (structured)
Average Particle Diameter	Mm	N/A (laminate)	N/A (laminate)
Particle Void Fraction	m^3/m^3	40-60%	40-60%
Packing Density	m^2/m^3	N/A	N/A
Solid Heat Capacity @ STP	kJ/kg-K	1.4-2.2	1.4-2.2
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	100-200	50-100
Adsorption			
Pressure	bar	1-1.1	1-1.1
Temperature	°C	40-50	40-50
Equilibrium Loading	g mol CO_2/kg	1.5-2.5	1.5-2.5
Heat of Adsorption	kJ/mol CO_2	35-100	35-100
Desorption			
Pressure	bar	0.9-1	0.9-1
Temperature	°C	100-120	100-120
Equilibrium CO_2 Loading	g mol CO_2/kg	0-0.3	0-0.3
Heat of Desorption	kJ/mol CO_2	35-100	35-100
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	Fixed structured bed	Rotary Adsorption Machine	
Flue Gas Flowrate kg/hr		Pilot scale	
CO_2 Recovery, Purity, and Pressure% / % / bar	80%, 80%, 0.9-1	90%, 90%, 0.9-1	
Adsorber Pressure Drop bar	0.1	0.1	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation ($/kg/hr)	N/A	TBD	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Using a combination of physisorption and chemisorption for CO_2 capture to have large difference in heat of CO_2 adsorption between the two adsorption sub-units.

Sorbent Contaminant Resistance – System requires sulfur oxide (SO_X) and nitrogen oxide (NO_X) abatement down to about 1 part per million (ppm) for sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) in order to maximize sorbent lifetime.

Sorbent Attrition and Thermal/Hydrothermal Stability **–** Sorbent developed for this rapid cycle system has excellent attrition resistance as it is embedded in sheets. Hydrothermal stability is also excellent, as the process used pure steam during regeneration steps.

Flue Gas Pretreatment Requirements – Removal of particulates, cooling of the flue gas to 40 to 50ºC, and condensate removal and control of NO_2 and SO_2 levels through the use of a solid sorbent guard bed.

Sorbent Makeup Requirements – N/A; solid sorbent in solid fix bed – estimated replacement frequency between two to five years.

Waste Streams Generated – Condensate water, SO_X and NO_X guard beds.

Process Design Concept – See above.

Proposed Module Design – Module of about 1 meter long; other dimensions scaled for flow. For pilot total adsorbent module of 0.6 to 1 liter.

technology advantages

- Using of the bi-layer made up of two sorbents working synergistically, has multiple advantages:
    - The second sorbent can have lower heat of desorption and use the heat generated by the first adsorbent, reducing the steam/energy requirement.
    - The second sorbent does not need to be steam resistant, therefore a metal-organic framework (MOF) can be used, for example.
    - MOFs can provide higher CO_2 capacity, highly tunable adsorption, and better oxygen resistance.

R&D challenges

- Tuning the two sorbents, materials and coatings, to work in synergy in the process.
- Designing sorbents for resistance to the water, oxygen, and contaminants in the feed.
- Maintaining defect-free barrier that is resistant to moisture with good transverse heat transfer.

status

Electricore has begun material down-selection and scale-up for candidate sorbent materials.

available reports/technical papers/presentations

Jelen, D. “Advanced Structured Adsorbent Architectures for Transformative CO_2 Capture Performance,” presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/D-Jelen-Electricore-Adsorbent-Architectures.pdf*.

Transformational Sorbent-Based Process for a Substantial Reduction in the Cost of CO_2 Capture

primary project goals

InnoSepra, LLC is developing a sorbent-based process using novel microporous materials to reduce the cost of carbon dioxide (CO_2) capture. The project includes identification of sorbent materials, process development, and lab-scale testing with simulated flue gas, culminating in bench-scale testing with actual flue gas at Technology Centre Mongstad (TCM).

technical goals

- Identify suitable materials through literature search and Monte Carlo simulations and produce/procure suitable materials for lab-scale testing.
- Complete lab-scale testing of multiple materials in simulated flue gas to determine CO_2 capture performance and down-select best materials.
- Simulate process to obtain heat and mass transfer parameters.
- Design and build the bench-scale test unit.
- Test the best identified materials on the bench-scale unit using actual flue gas at TCM.
- Perform engineering design and complete a techno-economic analysis (TEA) on the process for installation of the technology at a commercial 550-megawatt (MW) power plant to estimate CO_2 capture cost.

technical content

InnoSepra is developing a sorbent-based CO_2 capture process, utilizing physical sorbents based on microporous materials. These sorbents have low heats of adsorption (26 to 44 kJ/mole CO_2), high net CO_2 capacity (greater than 9 wt%), and high surface area-to-volume ratio (greater than 10×10^6 m^2/m^3). The combination of the process and sorbent materials provides capture performance similar to or better than amines, although needing much lower regeneration energy. The process schematic of the CO_2 capture process is shown in Figure 1. After the removal of moisture and sulfur oxides (SO_X) in a pretreatment system, the CO_2 is captured in an adsorber at 25 to 40°C. A high-purity CO_2 is produced during sorbent regeneration at 90 to 100°C. Some of the heat of adsorption is removed during the adsorption process; the remaining heat is removed during the cooling steps. Regeneration heat is supplied via low-pressure steam, as well as by utilizing other process waste heat in the system.

The first-generation of the InnoSepra process using the physical sorbents was developed and tested at the bench-scale in a previous U.S. Department of Energy (DOE)-funded project (DE-FE0007948). Testing occurred at NRG Energy's Indian

technology maturity:

Laboratory-Scale, Simulated Flue Gas; Bench-Scale, Actual Flue Gas

project focus:

Microporous Sorbent

participant:

InnoSepra, LLC

project number:

FE0031722

predecessor projects:

FE0007948
SC0010208

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Ravi Jain
InnoSepra, LLC
ravi.jain@innosepra.com

partners:

Main Line Engineering, Plant Process Equipment, Arizona State University

start date:

05.01.2019

percent complete:

15%

River Plant using actual flue gas, taken off the process after the dry flue gas desulfurization (FGD) unit, containing about 50 parts per million (ppm) sulfur dioxide (SO_2) and 10 to 12% CO_2, with 80 to 100 standard cubic feet per minute (scfm) flow rate. The adsorption test skid used at the testing at NRG is shown in Figure 2. Eight weeks of testing was completed showing 8 to 10.5 wt% net CO_2 capacity, greater than 94% CO_2 recovery, and greater than 98% purity.

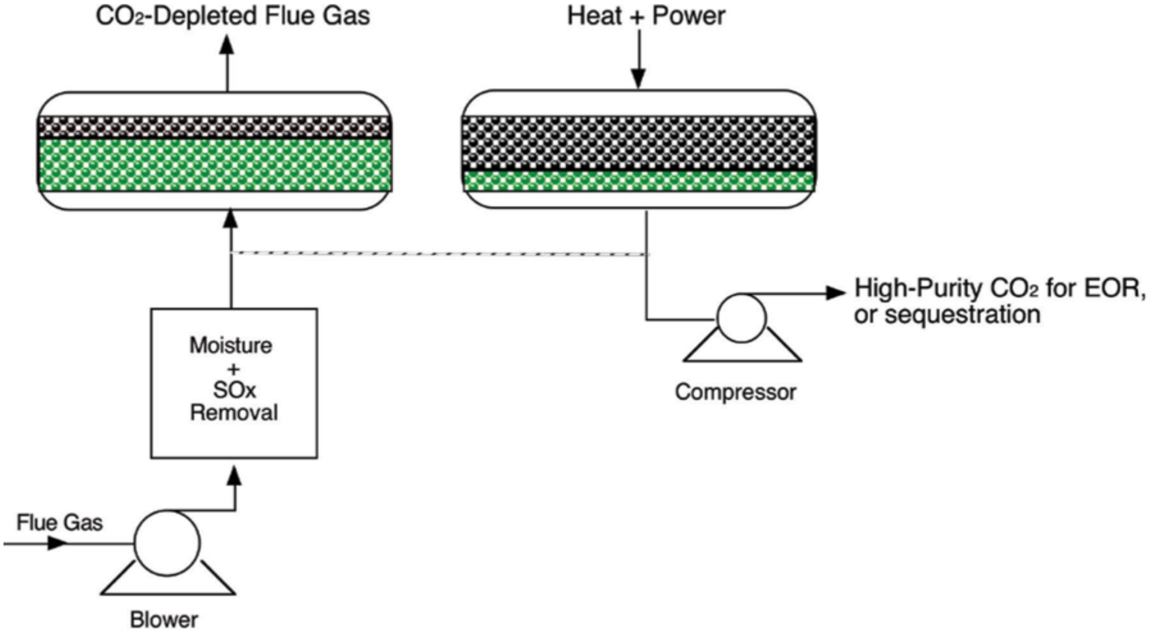


Figure 1: InnoSepra capture process schematic.

Figure 2: InnoSepra test skid used for testing at NRG Energy.

Projections based on detailed engineering evaluations show that at commercial scale, the first-generation process can reduce the power consumption for CO_2 capture by more than 40%, including CO_2 compression. There is about a 70% lower power loss due to steam extraction for the InnoSepra process compared to the amine process and approximately 48% reduction in capture cost compared to monoethanolamine (MEA).

In this current project, InnoSepra is developing the second-generation process, which is simpler, with capital savings, compared to the first-generation process. In testing of the second-generation process at the lab scale, an absolute energy requirement of 1.5 gigajoule (GJ)/metric ton (MT) of CO_2 was obtained, which is 57% lower than MEA, and lower than the 2.1 GJ/MT obtained for the first-generation process in field testing. The lower absolute amount of regeneration energy coupled with lower regeneration temperature leads to a 78% lower power loss due to steam extraction compared to MEA. The key feature of the second-generation process is a significant reduction in the heating requirement (from 1.3 GJ/MT to 0.7 GJ/MT) through a combination of the sorbent selection and regeneration method. The project team is demonstrating the effectiveness of the InnoSepra sorbent-based post-combustion capture technology to achieve at least 90% CO_2 removal with greater than 95% purity. Lab-scale testing and process simulation will support sorbent and regenerant identification and optimization of the process. The test unit will be designed, built, and installed for testing at TCM at greater than 100 scfm scale.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,990	1,990
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	1.5-3.0	0.5-1.5
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.79e8	1.79e8
Solid Heat Capacity @ STP	kJ/kg-K	0.96	0.96
Crush Strength	kg_f	2.9	2.9
Manufacturing Cost for Sorbent	$/kg	4.0	3.0-4.0
Adsorption			
Pressure	bar	1.15	1.1
Temperature	°C	25-32	25-32
Equilibrium Loading	g mol CO_2/kg	3.25	3.5-4.0
Heat of Adsorption	kJ/mol CO_2	38	38
Desorption			
Pressure	bar	0.3-1.0	0.3-1.0
Temperature	°C	100	90-110
Equilibrium CO_2 Loading	g mol CO_2/kg	1.5	1.5-2.0
Heat of Desorption	kJ/mol CO_2	38	38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed/cyclic	
Flue Gas Flowrate	kg/hr	2,320,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 99 1.0	
Adsorber Pressure Drop	bar	0.14	0.10
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	336	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Contaminant Resistance – Under normal operation, the sorbent is not irreversibly damaged by any contaminant in the flue gas. If substantial quantities of SO_2 are present in the feed to the CO_2 adsorption section, the sorbent may require higher than normal regeneration temperature to restore performance.

Sorbent Attrition and Thermal/Hydrothermal Stability – The process design protects the adsorbent from moisture and potential hydrothermal degradation. If moisture should break through onto the adsorbent, the adsorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300°C.

Flue Gas Pretreatment Requirements – No special flue gas pretreatment is required. A conventional FGD and a direct contact cooler (DCC) are sufficient for normal process operation.

Sorbent Makeup Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between five and 10 years. An adsorbent life of five years has been assumed to estimate the makeup requirements.

Waste Streams Generated – Except for the sorbents loaded with flue gas components, SO_X and mercury (Hg), no other waste streams are generated in the process. These can be disposed of as per current power plant practices for materials loaded with SO_X and Hg.

Process Design Concept – The commercial process configuration is shown in Figure 3. The adsorption equipment is modular in nature and five adsorption skids are needed for a 550-MW power plant. The rest of the process equipment, such as the feed blower, DCC, and the CO_2 compressor, is very similar to the amine process.

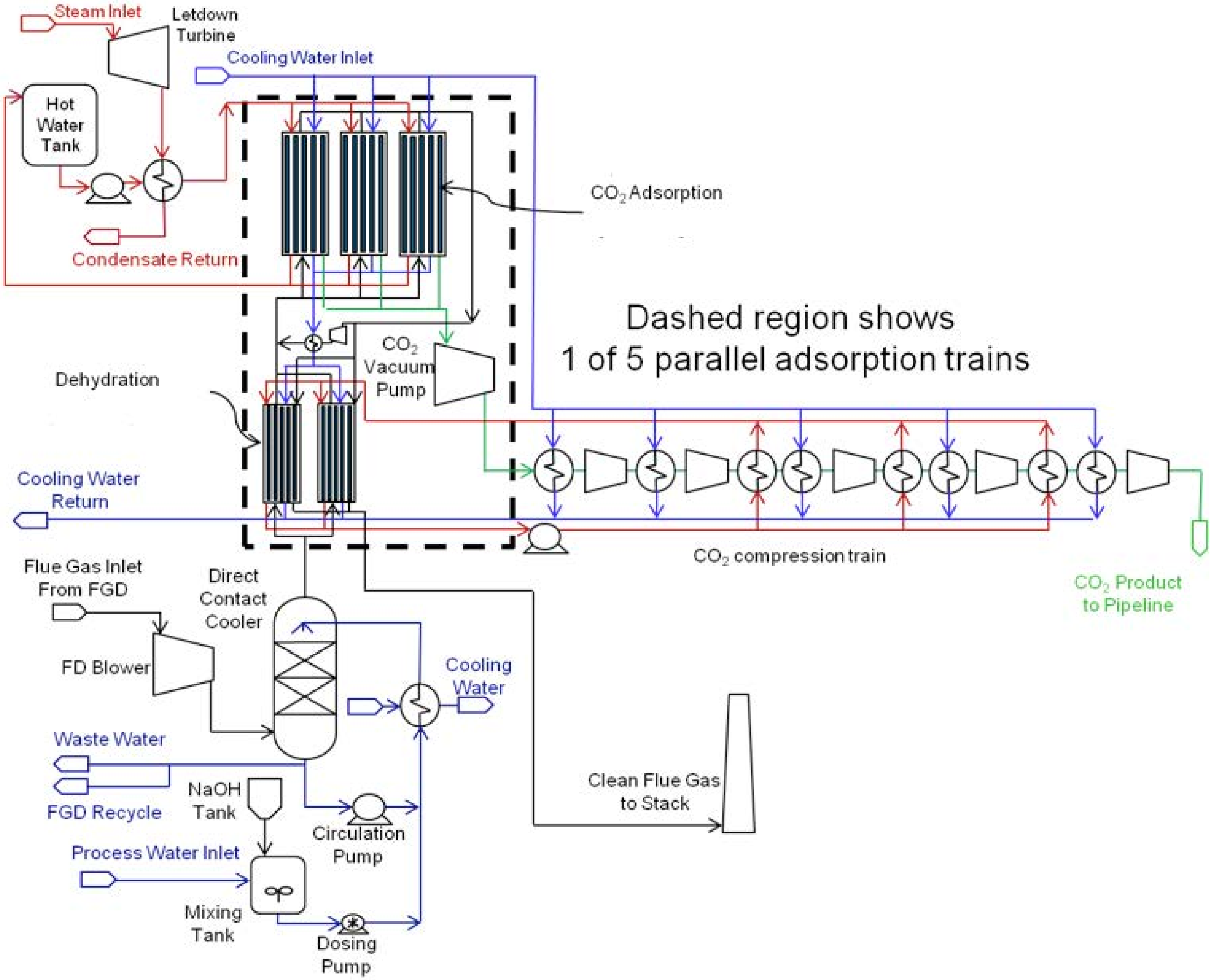


Figure 3: Commercial process configuration.

Proposed Module Design – The CO_2 capture modules will be designed to capture CO_2 from a 550-MW pulverized coal power plant. Multiple modules will be used to minimize field fabrication and maximize offsite fabrication. The separation skid will consist of a feed preparation section (flue gas compression and cooling), the CO_2 adsorption section (removal of impurities, CO_2 adsorption, and desorption), and the CO_2 compression section.

technology advantages

- The physical sorbents have a low heat of adsorption (approximately 0.8 GJ/MT).
- Combination of lower absolute amount of heat needed and lower steam extraction temperature leads to a 78% lower power loss compared to MEA.
- The process can produce high-purity CO_2 (greater than 98%) and recovery (greater than 90%).
- The estimated absolute energy required for the process, excluding compression, is 1.5 GJ/MT of CO_2, about 57% lower than for MEA.
- The process has a projected capture cost of \$31/MT CO_2, excluding transportation, storage, and monitoring (TS&M) costs.

R&D challenges

- Heat management during both adsorption and regeneration.
- Maintaining heat transfer rate upon scale-up.
- Assuring effective moisture and contaminant removal from the flue gas prior to adsorption to prevent decrease in sorbent performance.

status

The project has commenced.

available reports/technical papers/presentations

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the Project Kickoff Meeting, Pittsburgh, PA, September 2019. *https://www.netl.doe.gov/projects/files/FE0031722_InnoSepra%20Kickoff_09-30-19.pdf*.

Jain, R. "Transformational Sorbent-Based Processes for a Substantial Reduction in the Cost of CO_2 Capture," Presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/R-Jain-InnoSepra-Cost-Reduction-Capture.pdf*.

Transformational Sorbent System for Post-Combustion Carbon Capture

primary project goals

TDA Research, Inc. is developing a highly stable high-capacity metal-organic framework (MOF)-based physical adsorbent to remove carbon dioxide (CO_2) from the flue gas using a vacuum/concentration swing adsorption (VCSA) cycle scheme that will culminate in field testing in a prototype test unit using 3 to 5 cubic feet per minute (cfm) of actual coal-derived flue gas.

technical goals

- Optimize the sorbent formulation.
- Assess impact of flue gas contaminants (sulfur dioxide [SO_2], nitrogen oxide [NO_X], hydrogen chloride [HCl]).
- Scale-up sorbent production.
- Complete long-term sorbent cycling experiments at bench scale using simulated flue gas.
- Design and construct a prototype system with fixed-bed radial flow reactors.
- Design the VCSA cycle sequence.
- Perform field testing in a prototype test unit using actual flue gas for a minimum of 4,000 hours.
- Prepare a high-fidelity techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment.

technical content

TDA Research is developing a high-capacity sorbent for CO_2 capture in a system that uses a novel adsorption cycle scheme. TDA's MOF sorbent has very high CO_2 uptake, high CO_2 selectivity over nitrogen (N_2), and a relatively low energy requirement for regeneration. The process, shown in Figure 1, includes sorbent that operates at approximately 50°C during adsorption under mild vacuum (~0.2 to 0.3 atmosphere [atm]). The regeneration occurs in a two-step process, using vacuum to recover the CO_2 and a purge using the boiler intake air, which then feeds the CO_2-laden air back to the boiler. This approach generates a flue gas that is rich in CO_2, thereby benefiting the adsorption of the CO_2 on the sorbent while allowing use of a practical, single-stage vacuum pump with a low auxiliary load.

The project team is designing a fixed-bed radial flow reactor-based test unit for field testing at a project partner host site with actual coal-derived flue gas to show the performance of their CO_2 capture system. TDA's radial flow contactor increases the viability of using sorbents in fixed beds for post-combustion capture by reducing the pressure drop through the beds and allowing for rapid regeneration

technology maturity

Laboratory-Scale, Simulated Flue Gas; Bench-Scale, Actual Flue Gas (2-3 kWe)

project focus:

Metal-Organic Framework (MOF)-Based Sorbent

participant:

TDA Research, Inc.

project number:

FE0031734

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gökhan Alptekin
TDA Research, Inc.
galptekin@tda.com

partners:

University of California Irvine,
University of Alberta,
Wyoming Integrated Test Center

start date:

06.01.2019

percent complete:

15%

of the sorbent. The radial flow reactor configuration allows for use of multiple modular beds for ease of scale-up to large-scale processes.

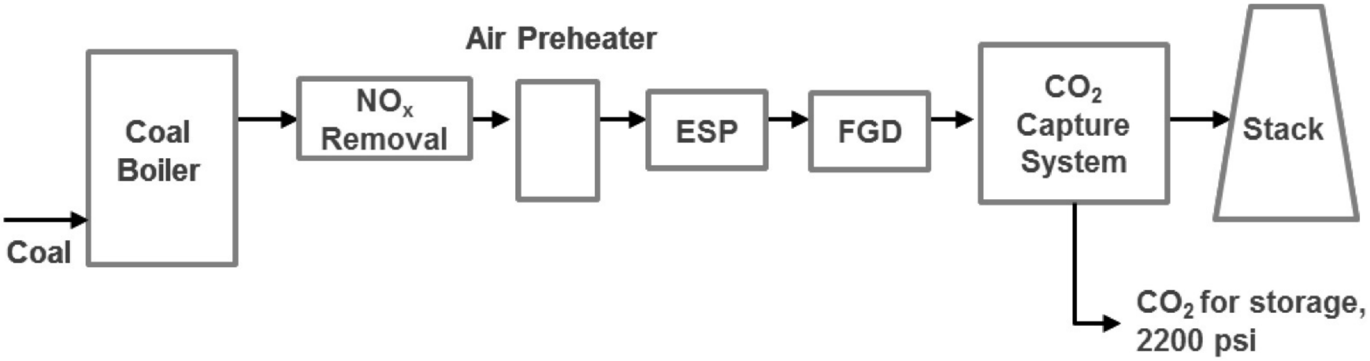


Figure 1: Schematic of TDA's CO_2 capture system.

TDA Research is optimizing sorbent performance through lab-scale experiments and using computational modeling to show the technical merit of both the sorbent and the capture process. The impacts of flue gas contaminants, including SO_2, NO_X, and HCl, on sorbent performance are being evaluated. The project team will also design and construct the prototype system, design the VCSA cycle, optimize the process design, and complete a detailed cost analysis to compare this process technology against amines. Evaluations using the prototype test unit will be completed first with simulated flue gas in the lab and then at the Wyoming Integrated Test Center (ITC) with actual coal-based flue gas, followed by optimization of the cycle design, finalization of the process design, and completion of an engineering analysis to fully assess the techno-economic viability of the process.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	650-1,000	650-1,000
Bulk Density	kg/m^3	540	550
Average Particle Diameter	mm	3	3
Particle Void Fraction	m^3/m^3	0.2-0.5	0.2-0.5
Packing Density	m^2/m^3	1.6x10^8	2.7x10^8
Solid Heat Capacity @ STP	kJ/kg-K	—	700
Crush Strength	kg$_f$	1.5-3	3
Manufacturing Cost for Sorbent	$/kg	—	30
Adsorption			
Pressure	bar	1.0	1.0
Temperature	°C	30	3.0
Equilibrium Loading	g mol CO_2/kg	2.3	2.3
Heat of Adsorption	kJ/mol CO_2	30-40	30-40
Desorption			
Pressure	bar	0.05	0.05
Temperature	°C	30	30
Equilibrium CO_2 Loading	g mol CO_2/kg	0.7	0.7
Heat of Desorption	kJ/mol CO_2	30-40	30-40

Proposed Module Design			(for equipment developers)	
Flow Arrangement/Operation	—		Radial flow fixed beds	
Flue Gas Flowrate	kg/hr		TBD	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%	95%	150
Adsorber Pressure Drop	bar		< 100 mbar	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		TBD	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physical adsorption

Sorbent Contaminant Resistance – TBD

Sorbent Attrition and Thermal/Hydrothermal Stability –TBD.

Flue Gas Pretreatment Requirements – TBD.

Sorbent Makeup Requirements – Five-year replacements.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagram, included above.

Proposed Module Design – Radial flow fixed beds.

technology advantages

- Very high CO_2 uptake (2 to 3 mmol/g) at 0.15 to 0.20 bar CO_2 partial pressure.
- High CO_2 selectivity over N_2.
- Relatively low energy input requirement for sorbent regeneration.

R&D challenges

- Minimizing the loss in adsorption capacity due to the sorbent pelletization process.
- Designing the sorbent to maintain stability and life in the presence of moisture.
- Maintaining the low vacuum and purge requirements for the process upon scale-up.

status

TDA Research has begun work to optimize the MOF sorbent formulations.

available reports/technical papers/presentations

Alptekin, G., et al. "Transformational Sorbent System for Post Combustion Carbon Capture," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/G-Alptekin-TDA-Next-Gen-Sorbent.pdf*.

Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture

primary project goals

Rensselaer Polytechnic Institute (RPI) is developing a transformational molecular layer deposition (MLD)-modified, size-sieving sorbent/pressure swing adsorption (PSA) process for post-combustion carbon dioxide (CO_2) capture from coal-fired and natural gas-fired power plant flue gas. The integrated technology provides step-change reductions in CO_2 capture cost and energy penalties.

technical goals

- Generate tailor-made, size-sieving sorbents by using MLD to coat sorbents.
- Identify promising sorbent materials through computational screening.
- Optimize MLD process to develop sorbents with high CO_2 adsorption capacity and stability in the presence of water vapor.
- Perform single-bed testing and simulation with the developed sorbents.
- Identify allowable contaminant levels for sorbents by further single-bed testing and simulation.
- Design PSA cycle schedule tailored to best MLD-modified sorbent.
- Design and construct MLD-modified sorbent/PSA skid system.
- Test skid system under simulated flue gas and actual flue gas conditions.
- Perform a techno-economic analysis (TEA) of process integrated with a 550-megawatt-electric (MWe) power plant.

technical content

RPI, in collaboration with the University of South Carolina (USC) and Gas Technology Institute (GTI), is developing a process that integrates transformational, tailor-made, MLD-modified sorbents with a novel PSA process concept to achieve U.S. Department of Energy (DOE) CO_2 capture performance and cost goals. RPI has developed sorbents with CO_2/nitrogen (N_2) selectivity as high as 130, much higher than state-of-the-art commercial sorbents, such as 13X zeolite, with similar CO_2 capacity under similar adsorption conditions, enabling achievement of 95% CO_2 purity in one stage of PSA for CO_2 capture from flue gas. The sorbents are coated with an inorganic material to achieve pore misalignment, which allows for fine-tuning the pore mouth size on the surface of sorbents (Figure 1). Using MLD, a vapor phase deposition technique utilizing self-limiting surface reactions, the external surface of the base sorbent is uniformly coated by ultrathin (less than 20 nanometers [nm]) microporous coatings. A wide range of porous materials (zeolites, activated carbon, and metal-organic frameworks) in different forms (powder or pellets) can be used directly as the base material for MLD coating, and the pore mouth size can be precisely designed by controlling the coating layer composition and thickness, as well as the thermal treatment conditions. The MLD-modified sorbents provide precise pore mouth size control in the range of 0.01 nm, which is crucial for achieving highly selective separation of

technology maturity

Bench-Scale, Actual Flue Gas Slipstream

project focus:

Size-Sieving Sorbent Integrated with Pressure Swing Adsorption

participant:

Rensselaer Polytechnic Institute

project number:

FE0031730

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Miao Yu
Rensselaer Polytechnic Institute
yum5@rpi.edu

partners:

University of South Carolina, Gas Technology Institute, Trimeric Corporation

start date:

10.01.2019

percent complete:

10%

CO_2 from N_2, as illustrated in Figure 2. MLD treatment results in minimal loss to the CO_2 adsorption capacity of the base sorbent.

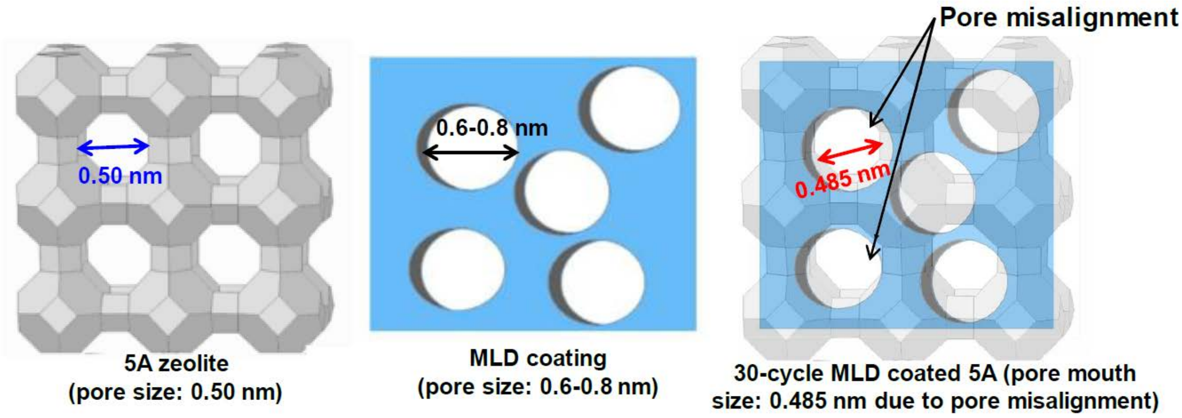


Figure 1: Schematic of pore misalignment for fine-tuning pore mouth size of sorbents.

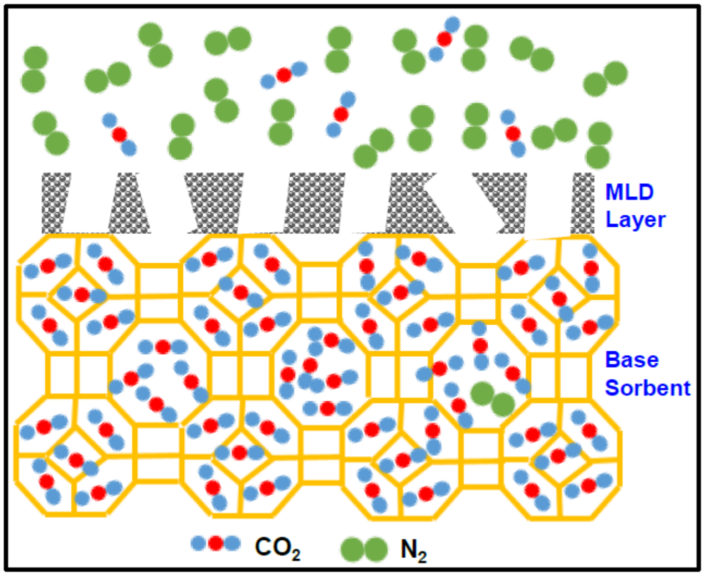


Figure 2: High CO_2/N_2 selectivity achieved by size-sieving for the MLD tailor-made sorbent.

Early studies on the pore misalignment concept show that 5A zeolite with and without MLD coatings have almost identical surface areas (343.5 ± 8.3 m^2/g) and micropore volume, suggesting that the coatings are only on the external surface and the internal cavity of the zeolite is maintained (Figure 3). Furthermore, the effective pore size of the treated 5A zeolite can be precisely controlled by the number of MLD cycles. Preliminary experiments on MLD-coated 13X zeolite show that almost no N_2 is adsorbed, suggesting a molecular sieving mechanism, and indicate a reduction in the heat of adsorption of CO_2. The sorbent and process parameters are provided in Table 1. In addition to 5A and 13X zeolites, other microporous sorbents have the potential to achieve high CO_2 adsorption capacity and CO_2/N_2 selectivity with MLD modification.

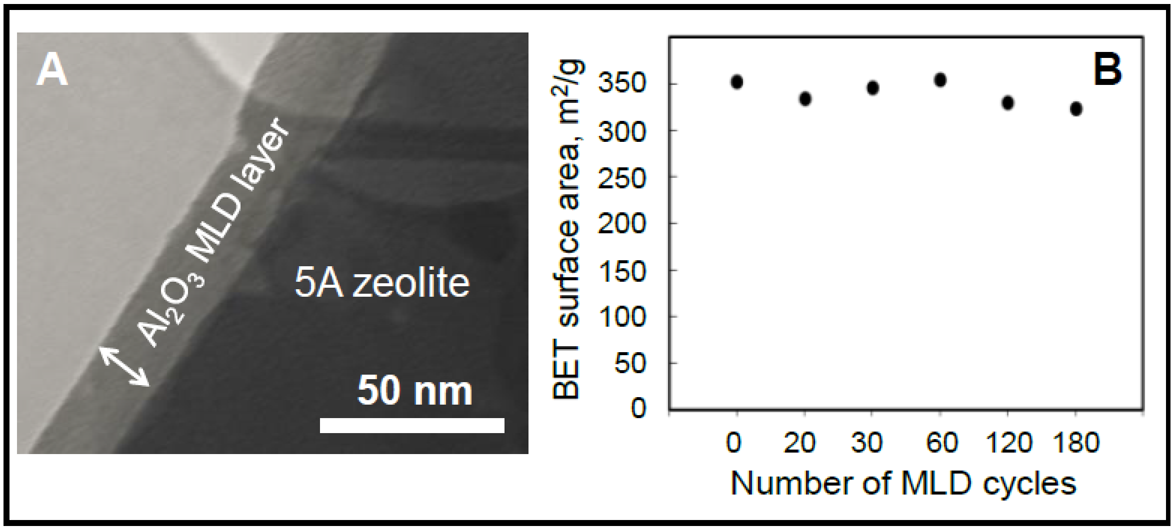


Figure 3: Characterization of MLD-modified 5A zeolite: (A) transmission electron microscopy (TEM) image of 5A zeolite with 60 cycles of aluminum oxide coating; (B) BET surface area of 5A zeolite with different cycles of MLD.

USC has recently developed a proprietary PSA cycle schedule concept for CO_2 capture from flue gas that involves the use of fewer number of beds than employed in their previously DOE-supported project DE-FE0007639, thereby reducing the CO_2 capture cost significantly. The number of required beds is reduced from 240 to 48 (i.e., six, eight-bed PSA systems operating in parallel) for the MLD-coated sorbent/PSA process integrated into a 550-MWe power plant. Figure 4 shows a diagram of the process, including identification of the numbered streams. The flow sheet incorporates desiccant wheels for water vapor removal upstream of the PSA process that are regenerated by a simple concentration swing with the light product from the PSA system and ambient air without the use of any heating. The dry light product (~2.4 mol% CO_2) produced by the PSA system is used to regenerate Dryer 2, and slightly compressed ambient air is used to regenerated Dryer 1. A reflux compressor produces a concentrated recycle stream containing ~83 mol% CO_2, facilitating the production of greater than 95 mol% CO_2 in the final CO_2 product. The system is uniquely designed with six adsorption beds being fed simultaneously, while two beds are being regenerated. This ensures low pressure drop during the feed step with a beaded adsorbent for large flow rate feed streams, allowing for the use of fewer number of adsorption beds in the PSA system since the adsorption bed height can be increased without a pressure drop penalty.

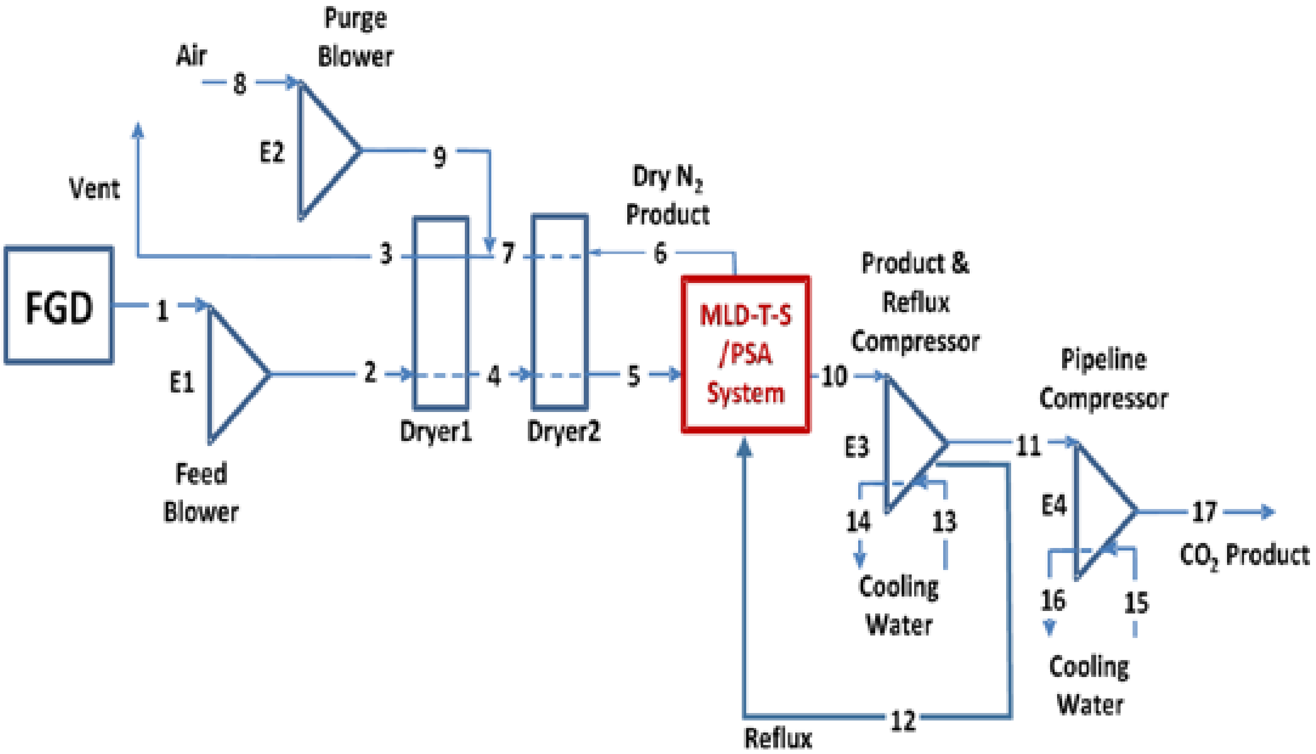


Figure 4: USC's PSA process flow diagram integrated with the MLD sorbent/PSA system.

USC's dynamic adsorption process simulator (DAPS) has been used to design a hypothetical MLD-treated sorbent/PSA system, showing a 6% reduction in separation energy when using MLD-coated 13X zeolite compared to commercial 13X. Preliminary TEA results compared to the DOE/National Energy Technology Laboratory (NETL) Base Case 9 (subcritical pulverized coal plant without CO_2 capture) and Base Case 10 (subcritical pulverized coal plant with amine scrubbing) are shown in Figure 5, indicating that the MLD-treated sorbent/PSA system can achieve 90% CO_2 capture rate with 95% CO_2 purity with a cost of \$28/tonne CO_2.

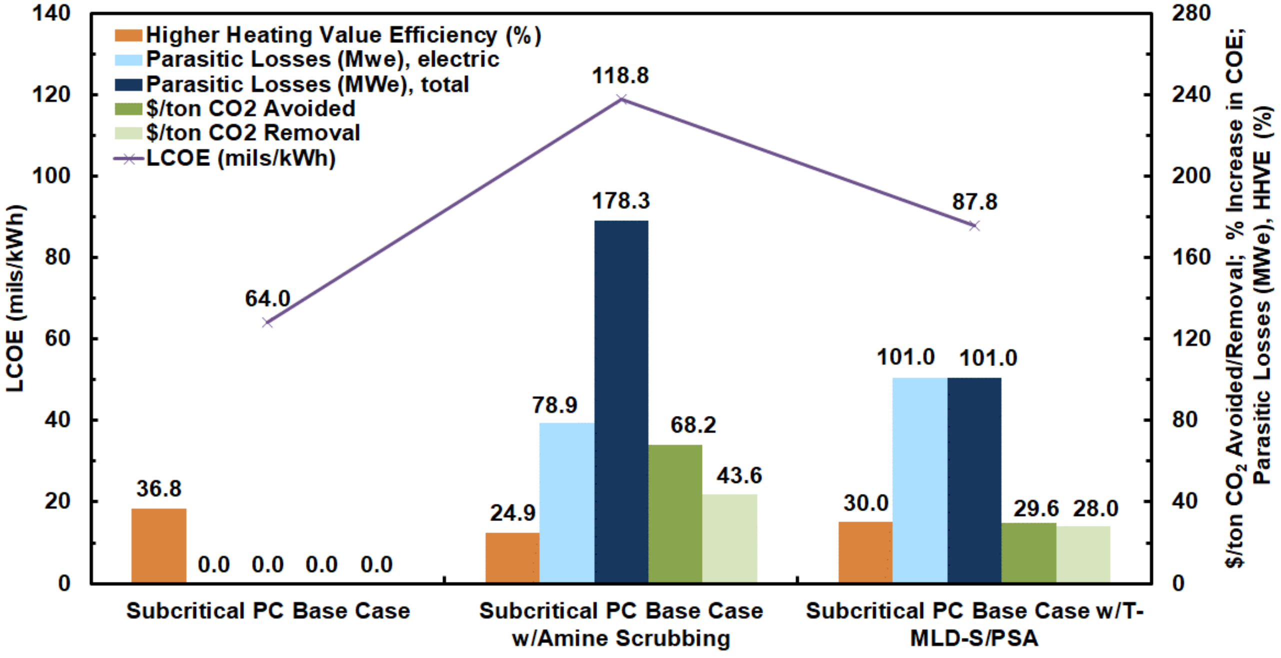


Figure 5: Comparison of the cost of CO_2 capture between DOE/NETL Base Case 9 (subcritical pulverized coal plant without CO_2 capture), Base Case 10 (subcritical pulverized coal plant with amine scrubbing), and the MLD-coated sorbent/PSA process.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,800	1,800
Bulk Density	kg/m^3	1,130	1,130
Average Particle Diameter	mm	0.003-0.005	0.003-0.005
Particle Void Fraction	m^3/m^3	0.374	>0.3
Packing Density*	m^2/m^3	$3.96x10^8–5.82x10^8$	$3.96x10^8–6.33x10^8$
Solid Heat Capacity @ STP	kJ/kg-K	0.96	<1
Crush Strength	kg_f	3.6	3.6
Attrition Index	-	<0.1	<0.1
Manufacturing Cost for Sorbent	$/kg	TBD	3.6
Adsorption			
Pressure	bar	0.15	0.15
Temperature	°C	20	20-60
Equilibrium Loading	g mol CO_2/kg	0.965-1.2	>1.5
Heat of Adsorption	kJ/gmol CO_2	43	<35
Desorption			
Pressure	bar	0.05	>0.05
Temperature	°C	20	40-80
Equilibrium CO_2 Loading	g mol CO_2/kg	0.32	<0.3
Heat of Desorption	kJ/gmol CO_2	32	<35

Proposed Module Design			(for equipment developers)	
Flow Arrangement/Operation	—		TBD	
Flue Gas Flowrate	kg/hr		1.5	
CO_2 Recovery, Purity, and Pressure$^+$	% / % / bar	90%	95%	TBD
Adsorber Pressure Drop	bar		0.07	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		TBD	

*Sorbent BET surface area used for packing density (m^2/m^3) calculation.

Definitions:

BET surface area – Surface area calculated using the Brunauer-Emmett-Teller (BET) equation, relating to the total surface area (reactive surface) based on gas adsorption.

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated bulk manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – See Figure 1 and Figure 2

Sorbent Contaminant Resistance – TBD

Sorbent Attrition and Thermal/Hydrothermal Stability – TBD

Flue Gas Pretreatment Requirements – TBD

Sorbent Makeup Requirements – TBD

Waste Streams Generated – TBD

Process Design Concept – See Figure 4.

Proposed Module Design – TBD

technology advantages

- High CO_2/N_2 selectivity (greater than 130), enabling a 95 vol% CO_2 purity to be achieved in a single stage for a typical coal flue gas containing 12 to 15 vol% CO_2.
- Uses low-cost commercial sorbents as base material.
- Metal and organic precursors required to form the coating materials are low cost.
- MLD is comparable to commercially available atomic layer deposition technology and suitable for roll-to-roll manufacturing.
- MLD tailor-made sorbent technology allows for reduced vacuum level and reduced light reflux flow during regeneration, thereby reducing the size and energy required by the product and reflux vacuum pump.
- Advanced sorbent fabrication procedure reduces manufacturing cost.
- Low pressure drop during feed step leads to use of fewer adsorption beds in PSA cycle, reducing capital costs.
- Compact, stand-alone, and modularized system design, reducing upfront installation costs and footprint.
- Serves as a platform for CO_2 capture from both coal-fired and natural gas-fired power plants.

R&D challenges

- Design of PSA process to achieve greater than 95% CO_2 purity.
- Improve manufacturing process to lower MLD sorbent costs.
- Sorbent performance in presence of flue gas contaminants.

status

The project team is using MLD to apply microporous coatings of less than 30 nm thickness on base sorbent material. Computational screening of various sorbent materials is underway to identify three promising sorbents for further development. The DAPS is being used to design the PSA system based on commercial 13X zeolite to establish baseline performance.

available reports/technical papers/presentations

Yu, M., et al. "Transformational Molecular Layer Deposition Tailor-Made Size-Sieving Sorbents for Post-Combustion CO_2 Capture," presented at the 2019 NETL Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/M-Yu-RPI-Tailor-Made-Sorbents.pdf*.

Ritter, J., et.al. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://netl.doe.gov/sites/default/files/event-proceedings/2015/co2captureproceedings/J-Ritter-USCarolina-Rapid-PSA.pdf*.

Ritter, J., et.al. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://netl.doe.gov/sites/default/files/event-proceedings/2014/2014%20NETL%20CO2%20Capture/J-Ritter-USCarolina-Rapid-Pressure-Swing-Adsorption.pdf*.

Ritter, J., et.al. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *https://netl.doe.gov/sites/default/files/event-proceedings/2013/co2%20capture/J-Ritter-USC-Rapid-Pressure-Swing-Adsorption.pdf*.

Ritter, J., "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://netl.doe.gov/sites/default/files/event-proceedings/2012/co2%20capture%20meeting/J-Ritter-USC-RPSA.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION MEMBRANE TECHNOLOGIES

Bench-Scale Testing of Next-Generation Hollow-Fiber Membrane Modules

primary project goals

Air Liquide is developing a novel polyimide-based membrane material, PI-2, for application in their hybrid process that combines cold membrane operation with cryogenic separation to reduce the overall cost of capturing carbon dioxide (CO_2) from flue gas. The focus of the project is to advance the high CO_2 permeance PI-2 material to commercial-scale, 6-inch bundles for testing with actual flue gas in a 0.3-megawatt-electric (MWe) test unit at the National Carbon Capture Center (NCCC).

technical goals

- Design and manufacture 4-inch PI-2 bundles reaching greater than 90 normal meters cubed per hour (Nm^3/hr) feed at 90% CO_2 recovery and greater than 58% CO_2 purity.
- Identify other hybrid processes with possibility of economic feasibility.
- Design and manufacture 6-inch PI-2 bundles reaching greater than 400 Nm^3/hr feed at 90% CO_2 recovery and greater than 58% CO_2 purity.
- Field-test 6-inch bundles at 0.3-MWe scale with real flue gas at NCCC.
- Complete a techno-economic analysis (TEA) to evaluate potential to meet greater than 90% carbon capture at a cost of electricity (COE) of 30% less than U.S. Department of Energy (DOE) baseline.

technical content

Air Liquide is developing a next-generation membrane material, PI-2, for application with their novel, sub-ambient temperature, membrane-based CO_2 capture technology. The process combines the use of commercial polyimide (PI) hollow-fiber membrane bundles with cryogenic operation to selectively remove the CO_2 from flue gas.

Figure 1 presents a simplified block diagram of the cold membrane process. A highly selective membrane provides pre-concentration of CO_2 prior to CO_2 partial condensation in a liquefaction unit. The membrane is operated at sub-ambient temperature, approximately -30°C, for enhanced CO_2/nitrogen (N_2) selectivity. The cryogenic heat exchanger system provides energy integration between the membrane and the CO_2 liquefaction system.

technology maturity:

Bench-Scale, Simulated Flue Gas (0.1 MWe) and Actual Flue Gas (0.3 MWe)

project focus:

Sub-Ambient Temperature Membrane

participant:

American Air Liquide, Inc.

project number:

FE0026422

predecessor projects:

FE0013163
FE0004278

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Shilu Fu
American Air Liquide
shilu.fu@airliquide.com

partners:

Air Liquide Engineering, Air Liquide – ALAS, Parsons Corporation

start date:

10.01.2015

percent complete:

98%

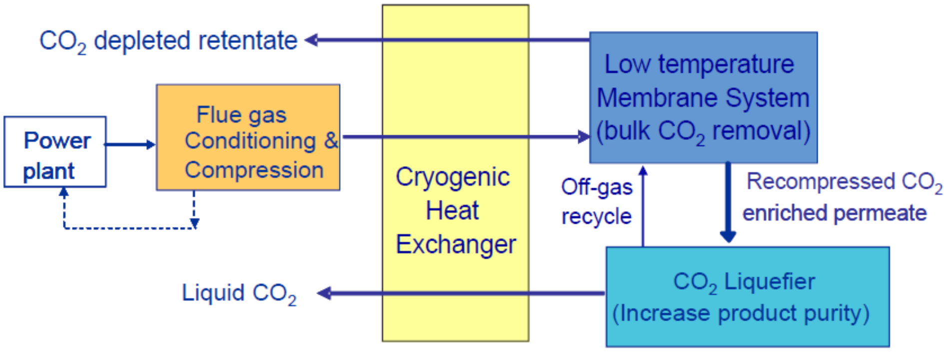

Figure 1: Block diagram of the cold membrane process.

Figure 2 shows a schematic diagram of the hybrid cold membrane process. The process lines in Figure 2 are color-coded (black for ambient temperature, dark blue for approximately -30°C, and light blue for approximately -50°C). The pre-treated flue gas is compressed to approximately 230 pounds per square inch (psi; 16 bar). The heat of compression is captured in boiler feed water, raising its temperature to approximately 147°C. The compressed flue gas is then dried in a dehydration unit to prevent water condensation when the stream is cooled in the brazed aluminum heat exchanger to approximately -40°C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with approximately 1.8% CO_2 at approximately 215 psi (15 bar) and a permeate stream with 60 to 70% CO_2 at approximately 17 psi (1.1 bar). After the residue is sent through the heat exchanger, further cooling and energy recovery is done via a series of turbo-expanders with the resulting stream at -57°C. The cold stream is again sent through the heat exchanger to provide cold for the overall process. Finally, the excess pressure energy remaining in the warmed residue is partly recovered in a warm turbo-expander before venting. A fraction of the vent gas is used to regenerate the drier. The permeate stream is recompressed, cooled in the heat exchanger, and undergoes phase separation in the cryo-phase separator. Liquid CO_2 is pumped from the separator to provide a storage-ready product CO_2 at approximately 870 psi (60 bar), or greater, and 20°C. The overhead from the cryo-phase separator is warmed through the heat exchanger and then undergoes energy recovery in a turbo-expander. This stream is mixed with the incoming dried flue gas, which raises the mixed feed concentration entering the membrane to 18% CO_2. The higher CO_2 content improves system recovery and efficiency of the membrane separation.

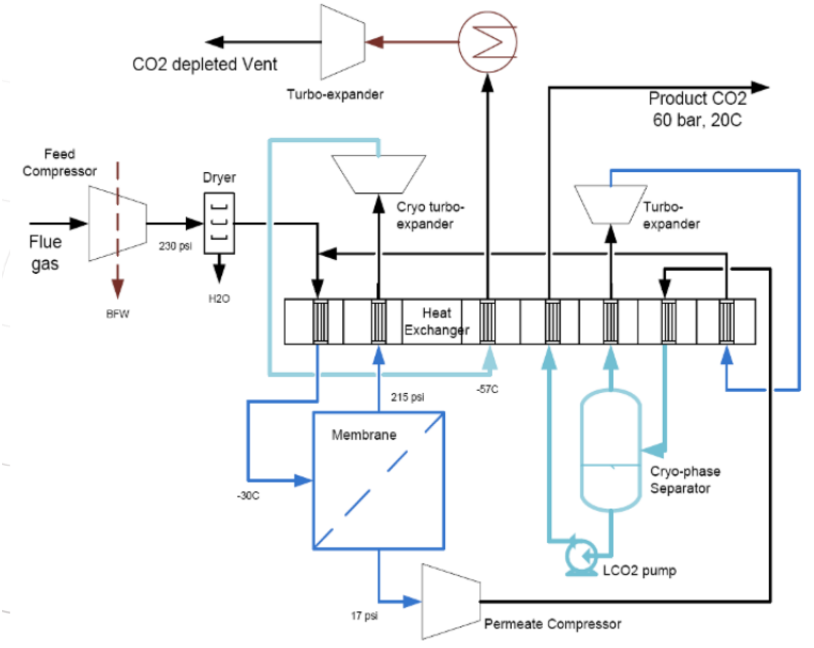

Figure 2: Schematic diagram of cold membrane process.

For most membrane materials, permeability decreases and selectivity increases with a decrease in operating temperature. However, laboratory measurements of Air Liquide's commercial PI hollow-fiber membranes operated at temperatures below -20°C show two- to four-times higher CO_2/N_2 selectivity with minimal loss of CO_2 permeance compared to ambient temperature values. Closed-loop, bench-scale (0.1 MWe) testing of Air Liquide's existing low-cost commercial membranes (PI-1) was conducted at sub-ambient temperatures in project FE0004278 using synthetic flue gas (CO_2 and N_2). The 6-inch bundles exhibited stable performance over eight months of operation and 12-inch bundles showed excellent mechanical integrity for two months. Preliminary data indicated that 12-inch bundle performance was lower compared to the 6-inch bundles due to non-ideal flow conditions. By modifying bundle fabrication methods and incorporating a membrane sweep stream in the process, productivity of the 12-inch bundles was improved by approximately 30%. A novel membrane material (PI-2) has shown the potential to have similar high selectivity and greater than five times the fiber permeance of PI-1 in initial laboratory testing with simulated flue gas. PI-2 has the potential for a significant reduction in membrane system cost. Productivity increases as the membrane is scaled to 4-inch and 6-inch bundles. Testing of the PI-2 membranes at 0.1- to 0.3-MWe scale with actual flue gas allows for a direct comparison with the PI-1 material based on identical test equipment and conditions.

Fabrication and installation of the 0.3-MWe field-test unit (Figure 3) at the NCCC allows for parametric testing and long-term continuous runs on the optimized PI-1 membrane modules, as well as the advanced high-permeance PI-2 membrane modules. Dynamic tests to quantify the performance of the carbon capture system provide data for a final TEA for a 550-MWe power plant with optimized membrane bundles to assess the system's ability to reach the targets of greater than 90% CO_2 capture and greater than 95% purity at a capture cost approaching $40/tonne.

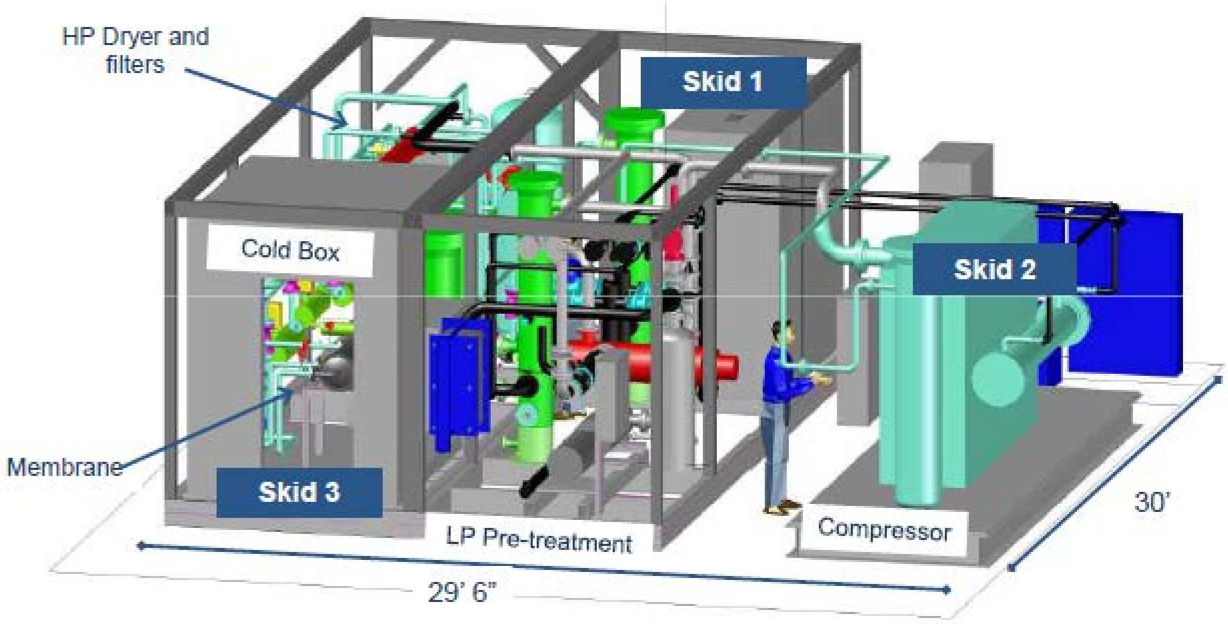

Figure 3: 0.3-MWe test unit at the NCCC, Pilot Bay 3.

Hybrid process configurations, such as membrane/absorption or membrane/sorbent processes, have also been proposed incorporating PI-2 membrane material to reduce the compression energy penalty.

The membrane and process parameters identified to date are provided in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polyimide	polyimide
Materials of Fabrication for Support Layer	—	polyimide	polyimide
Nominal Thickness of Selective Layer	µm	<0.1 µm	<0.1 µm
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	20
Hours Tested without Significant Degradation	—	PI-2: 4-inch bundle 340 hrs (synthetic flue gas) PI-2: 6-inch bundle 3,800+ hrs (actual flue gas)	500+ hours (actual flue gas)
Manufacturing Cost for Membrane Material	\$/m^2	-	-
Membrane Performance			
Temperature	°C	-30°C to -45°C	-30°C to -45°C
CO_2 Pressure Normalized Flux	GPU or equivalent	PI-2 6-inch bundle: 657 Nm^3/hr of bundle productivity	400 Nm^3/h
CO_2/H_2O Selectivity	—	<0.2 (dry gas)	<0.2 (dry gas)
CO_2/N_2 Selectivity	—	>50	>70
CO_2/SO_2 Selectivity	—	0.3	0.3
Type of Measurement	—	6" bundle parametric and long-term testing with actual flue gas	6" bundle parametric and long-term testing with actual flue gas
Proposed Module Design		(for equipment developers)	
Flow Arrangement	—	hollow fiber	
Packing Density	m^2/m^3	approximately 1,500 m^2/m^3	
Shell-Side Fluid	—	CO_2-rich permeate	
Flue Gas Flowrate	kg/hr	>400 Nm^3/hr / 6-inch bundle	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80-90%, >95% purity in hybrid process (>58% CO_2 purity from membrane), 16 bar	
Pressure Drops Shell/Tube Side	bar	0.1 bar shell side/1 bar tube side	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	100	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units). Bundle productivity in terms of feed flow rate in Nm^3/hr is reported.

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Nominally based on solution-diffusion.

Contaminant Resistance – Expected to be resistant to acidic components based on experience to date.

Flue Gas Pretreatment Requirements – Particulate removal and acid component removal to meet compressor specifications, dehydration to meet cold box specifications, Hg removal to meet heat exchanger specification.

Membrane Replacement Requirements – Membrane productivity decline was too small to be quantified in bench-scale test with synthetic gases.

Waste Streams Generated – Acidic water.

Process Design Concept – See Figure 2.

technology advantages

- Novel high flux PI-2 material enables a significant reduction in membrane area and corresponding capital cost.
- Sub-ambient operation improves membrane performance.
- Process design provides partial recovery of the flue gas compression energy.
- Process design provides an economic method of cooling the flue gas feed to the required sub-ambient temperature for optimal membrane operation without external refrigeration.
- The process design can be combined with a novel scheme for contaminant (sulfur dioxide [SO_2], nitrogen oxide [NO_X]) removal.

R&D challenges

- Sub-ambient membrane operation requires development of suitable membrane module materials with adequate permeance and selectivity in a commercial membrane module.
- Long-term membrane module performance stability.
- Integration of sub-ambient membrane process, including energy integration with the CPU, as well as energy integration with the power plant, such as compression and turbo-expansion schemes, heat economizers, and energy conservation.

- Flue gas contaminant-specific challenges, including acid gas (SO_2, NO_X) separation, compressor materials of construction, particulate removal, Hg removal, and water management.
- Novel PI-2 material development must achieve tolerance to operating pressure/temperature, effective epoxy seals, long-term stability, and manufacturing reproducibility.

status

The 1-inch PI-2 permeators and PI-1 commercial-scale bundles completed more than 500 hours of steady-state testing on the 0.3-MWe test unit at the NCCC showing stable performance. Multiple 4-inch prototype PI-2 membrane modules have achieved greater than 90 Nm^3/hr productivity at 90% capture and greater than 58% CO_2 purity through testing on the 0.1-MWe bench-scale skid with synthetic flue gas. Multiple 6-inch PI-2 bundles have achieved greater than 400 Nm^3/hr productivity at 90% capture and 58% CO_2 purity through testing on the 0.3-MWe field-test unit with real flue gas. The 6-inch PI-2 bundle long-term stability test was concluded successfully, showing 500-hour stable performance that exceeds the target. Air Liquide cold membrane process design and cost estimation have been validated by third-party Parsons Government Service.

available reports/technical papers/presentations

Fu, Shilu, "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/S-Fu-Air%20Liquide-Next-Gen-Hollow-Fiber.pdf*.

Augustine, A., "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/A-Augustine-AAL-Next-Generation-Hollow-Fiber-Modules.pdf*.

Augustine, A., "Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules (FE0026422)/CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas (FE0013163)," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/A-Augustine-Air-Liquide-Hollow-Fiber-Modules.pdf*.

Augustine, A., "Project Review: Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/A-Augustine-AirLiquide-Hollow-Fiber-Membrane-Modules.pdf*.

Chaubey, T., "CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/T-Chaubey-AirLiquide-Cold-Membrane-Operation.pdf*.

Augustine, A., "Project Kick-off: Bench Scale Testing of Next Generation Hollow Fiber Membrane Modules," Project kickoff meeting presentation, November 2015. *https://www.netl.doe.gov/projects/files/FE0026422-Next-Gen-Polyimide-Kick-off.pdf*.

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Chaubey, T., "CO_2 Capture by Cold Membrane Operation with Actual Power Plant Flue Gas," Project Continuation Request Meeting, March 2015.

Hasse, D., et al., "CO_2 Capture by Cold Membrane Operation," presented at the International Conference on Greenhouse Gas Technologies, October 2014.

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"CO_2 Capture by Cold Membrane Operation," GHGT-12, Energy Procedia, 2013.

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Kulkarni, S., "CO_2 Capture by Sub-Ambient Membrane Operation," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2012/co2%20capture%20meeting/S-Kulkarni-AAL-Sub-ambient-Membrane.pdf*.

Sanders, E., "CO_2 Capture by Sub-Ambient Membrane Operation," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

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Novel Carbon Dioxide-Selective Membranes for CO_2 Capture from Less than 1% CO_2 Sources

primary project goals

Ohio State University (OSU) is developing a cost-effective design and manufacturing process for new membranes and membrane modules that capture carbon dioxide (CO_2) from sources with less than 1% CO_2. Synthesis of novel CO_2-selective membranes using a nanoporous polyethersulfone (PES) polymer support and coating a top layer of thin, highly selective, yet permeable amine-containing polymer membrane will be performed. Pilot-size membranes will be used to fabricate at least three membrane modules for testing with the simulated gas mixture.

technical goals

- Synthesize and characterize membranes to obtain a CO_2 permeance of 1,800 gas permeation units (GPU) and a CO_2/nitrogen (N_2) selectivity of greater than 140.
- Fabricate a membrane prototype at least 14 inches in width and greater than 50 feet in length using the continuous membrane fabrication machine at OSU.
- Use prototype to fabricate at least three membrane modules and conduct pilot testing using a simulated gas mixture containing less than 1% CO_2.
- Perform an economic feasibility study.

technical content

OSU is continuing their work on developing novel CO_2-selective membranes that capture CO_2 from less than 1% CO_2 concentration sources. The membrane is inexpensive, consisting of a cost-effective nanoporous polymer support and a top layer coating of thin, highly selective, yet permeable amine-containing polymer membrane, as shown in Figure 1. The membrane modules are incorporated in a two-stage membrane process that would be implemented after the primary CO_2 capture system in a power plant, which has already captured greater than 90% CO_2 from flue gas. In the first membrane module, CO_2 is removed from the feed gas by using vacuum and the permeate stream is used as the feed for the second membrane module, where additional CO_2 is removed by vacuum such that the 90% capture and 95% purity targets are met.

technology maturity:

Pilot-Scale, Simulated Flue Gas

project focus:

Selective Membranes for <1% CO_2 Sources

participant:

Ohio State University

project number:

FE0026919

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

W.S. Winston Ho
Ohio State University
ho.192@osu.edu

partners:

TriSep Corporation;
American Electric Power

start date:

03.01.2016

percent complete:

100%

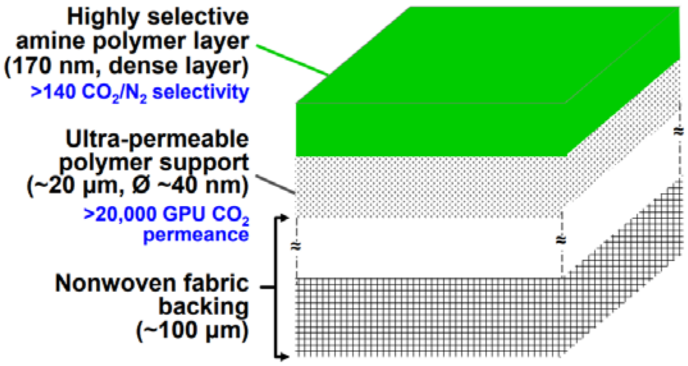

Figure 1: Selective amine polymer layer/polymer support.

Carbon dioxide permeates through the membrane via a facilitated transport mechanism where CO_2 reacts with amines reversibly to facilitate CO_2 transport, whereas N_2 cannot react with amines, resulting in very high CO_2/N_2 selectivity. The amine polymer layer contains mobile carriers that react with CO_2 to facilitate transport (Figure 2). The CO_2 flux increases as pressure increases until it reaches a saturation point in which CO_2 reacts with all carriers in the membrane. At low pressure (or low CO_2 concentration), more free carriers are available; therefore, the CO_2 permeance is higher due to greater CO_2 facilitation. Since sulfur dioxide (SO_2) permeates through the membrane, OSU proposes to add an SO_2 polishing step before the membrane process to remove SO_2 to less than 1 to 3 parts per million (ppm). A CO_2 permeance of 1,800 GPU and a CO_2/N_2 selectivity of greater than 140 using a simulated gas mixture containing less than 1% CO_2 are the target performance criteria for these membranes. New and improved membranes are synthesized, in which the polyamine layer is modified to achieve a higher CO_2 permeance and a hydrophilic agent is incorporated into the polymer support to improve its porosity, permeance, and adhesion. Membranes containing unhindered polyamine but with a thinner selective layer yielded a high CO_2 permeance of 2,299 GPU with a CO_2/N_2 selectivity of 179 at 67°C with 1% CO_2, which was the most permeable membrane developed during the project.

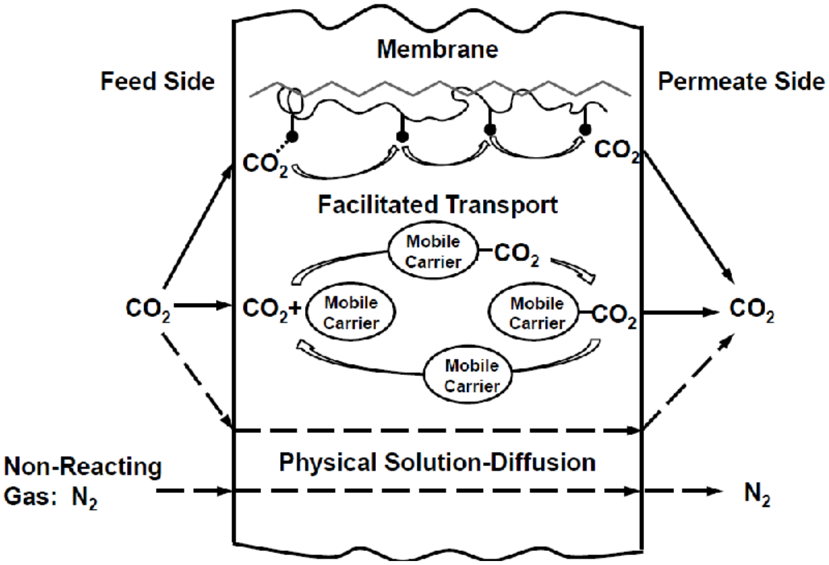

Figure 2: Facilitated transport on amine polymer layer.

The fabrication of the representative spiral-wound membrane modules for the performance testing at OSU was performed by using a multiple-leaf configuration for the membrane element (Figure 3). The number of membrane leaves was increased from six to seven pieces, while the length of each leaf was increased from 30 to 36 inches. Hence, the total membrane area was raised from 2 m^2 to 2.94 m^2. The spiral-wound membrane element was loaded in the stainless-steel housing to become the stainless-steel membrane module as shown in Figure 4.

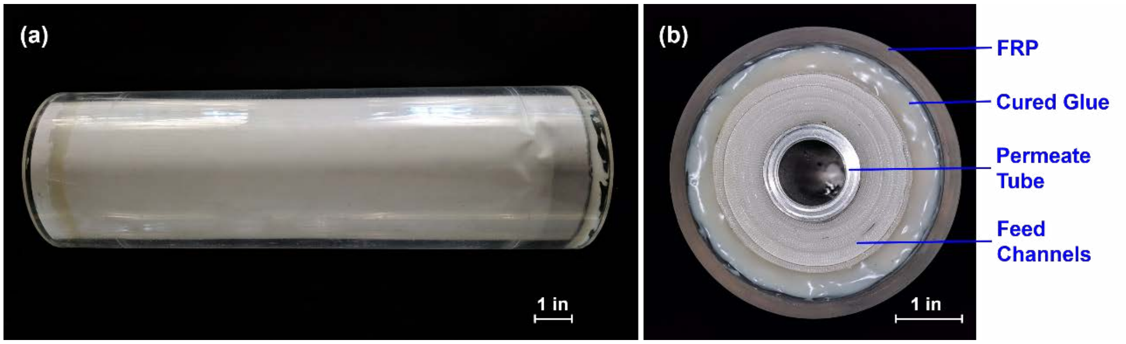

Figure 3: Images of a spiral-wound membrane element from (a) the side and (b) the end of the element.

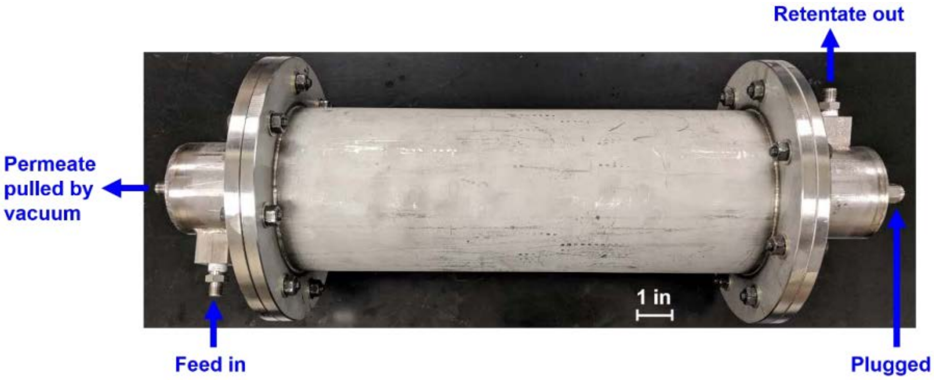

Figure 4: Image of an assembled stainless-steel spiral-wound membrane module.

A pneumatic unwinder was integrated into the existing module rolling machine. The new unwinder delivered the stack of membrane leaves to the central tube with better tension control. A schematic of the modified rolling machine is shown in Figure 5. Compared to the manual tension control, the modified machine ensured an even and steady rolling. This improved the membrane packing density and uniformity and minimized any feed gas channeling. In addition, the modified machine is capable of fabricating full-size commercial spiral-wound modules (8-inch diameter by 40-inch length).

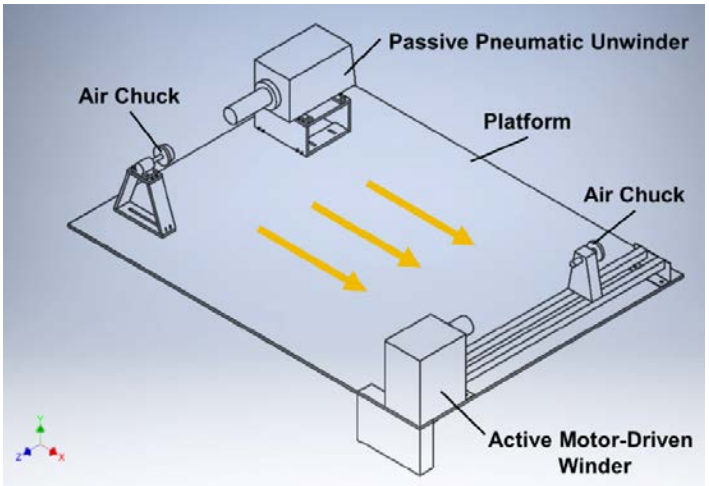

Figure 5: Schematic of spiral-wound membrane element rolling machine with tension control.

The two-stage membrane process is shown in Figure 6. The feed gas, containing less than 1% CO_2, is pressurized by Blower 1 to 4 atmosphere (atm) and passed to Membrane Stage 1. This stage produces a CO_2-depeleted retentate, with 90% CO_2 from the feed removed, and a CO_2-rich permeate, containing 15 to 20% CO_2 on dry basis. A vacuum of 0.2 to 0.3 atm is pulled on the permeate side of this stage to increase the transmembrane driving force. The permeate is re-compressed by Blower 2 to 4 atm and passed to Membrane Stage 2. This stage further enriches the CO_2 to greater than 95% purity in the permeate; the remaining CO_2 in the retentate is recycled back to the feed of Membrane Stage 1. A vacuum of 0.2 to 0.3 atm is also pulled on the permeate side. The vacuum discharge is eventually compressed to 150 atm for transport and storage.

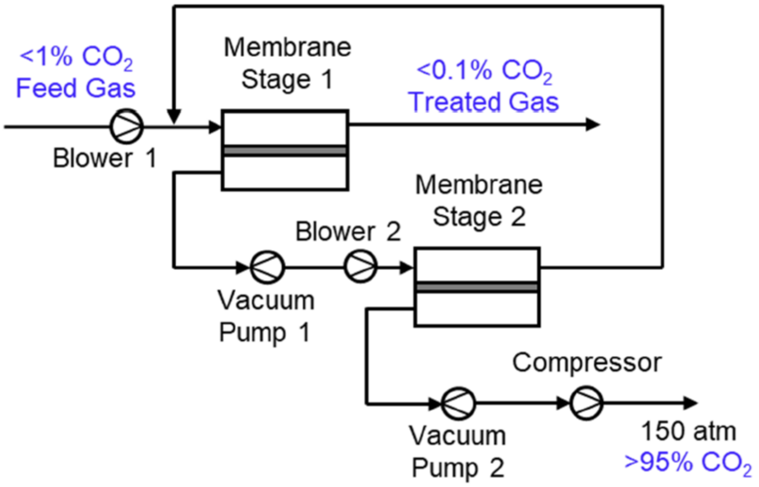

Figure 6: Schematic of the two-stage membrane process.

The techno-economic analysis (TEA) was updated. The membrane synthesized recently resulted in an estimated capture cost of $246/tonne (which takes into consideration the varying CO_2 permeance), and a cost of electricity (COE) increase of 17.9%.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Fixed and mobile amine carriers as the membrane matrix	
Materials of Fabrication for Support Layer	—	Nanoporous polyethersulfone	
Nominal Thickness of Selective Layer	nm	100–200	100–170
Membrane Geometry	—	Flat sheet	Flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	1,900	1,200
Manufacturing Cost for Membrane Material	$/m^2	10	<10
Membrane Performance			
Temperature	°C	57–67	57–87
CO_2 Pressure Normalized Flux	GPU or equivalent	2,299	2,200
CO_2/H_2O Selectivity	—	About 1	About 1
CO_2/N_2 Selectivity	—	140–200	150–225
CO_2/SO_2 Selectivity	—	About 1	About 1
CO_2/H_2 Selectivity	—	About 100	About 100
Type of Measurement	—	Simulated gas mixture	Simulated gas mixture
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Countercurrent spiral wound	
Packing Density	m^2/m^3	1,800	
Shell-Side Fluid	—	Permeate containing CO_2 (vacuum is used on the permeate side)	
Flue Gas Flowrate	kg/hr	4.346	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >95%, 152 bar	
Pressure Drops Shell/Tube Side	bar	0 bar/m permeate/0.07 bar/m feed	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	$500/(kg/hr), $32/m^2 or $246/tonne CO_2 capture cost	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.35×10^{-10} mol/(m^2-s-Pa) (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (hydrogen [H_2]-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD; wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	0.99	17.25	78.62	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport using chemical reaction to enhance separation.

Contaminant Resistance – 3 ppm SO_2 and 3 to 7% oxygen (O_2).

Flue Gas Pretreatment Requirements – SO_2 polishing step (with 5% sodium hydroxide [NaOH]) to have 1 to 3 ppm SO_2.

Membrane Replacement Requirements – About once every four years.

Waste Streams Generated – No additional waste streams generated.

technology advantages

- Energy-efficient technology.
- Low-cost membrane (less than \$2.00/ft^2).
- High CO_2/N_2 selectivity due to amine polymer layer.
- Facilitated transport mechanism allows for increase in CO_2 permeance at low CO_2 concentrations.
- Membrane stability.
- Hydrophilic additives in polymer support improve membrane performance.

R&D challenges

- Achieving very high membrane performance (CO_2 permeance of 1,800 GPU and CO_2/N_2 selectivity of greater than 140).
- Membrane stability in presence of contaminants.
- Requires two membrane stages.

status

Spiral-wound prototype membrane module with an active membrane area of 2.94 m^2 was tested with a simulated residual flue gas at 4 atm and 67°C. The membrane module showed a CO_2 permeance of 1,921 GPU and a CO_2/N_2 selectivity of 209 with 1% CO_2. The module showed good stability with 3 ppm SO_2. The TEA showed a CO_2 capture cost of $246/tonne, which is a 17.9% increase in COE. The project has concluded.

available reports/technical papers/presentations

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Final project review meeting presentation, Pittsburgh, PA, October 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=17279&filename=DE-FE0026919_Project%20Final%20Review%20Meeting%2010-28-19.pdf*.

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2019 NETL CCUS Integrated Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=17322&filename=FE0026919_OSU_2019%20NETL%20CCUS%20project%20review%20meeting.pdf*.

Ho, W., Han, Y., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2018 NETL CO2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13108&filename=Y-Han-OSU-Membrane-Capture-from-less-than-1--CO2-Sources.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2018 NETL continuation application status meeting, Pittsburgh, PA, February 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13105&filename=FE0026919-Mtg-021918.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/W-Ho-OSU-Capture-from-less-than-1--CO2-Sources.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Continuation Application Status Meeting, Pittsburgh, PA, February 2017. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13107&filename=DE-FE0026919-Continuation-Application-Status-Mtg-2-27-17.pdf*.

Ho, W. "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13109&filename=W-Ho-OSU-CO2-Selective-Membranes.pdf*.

Ho, W., "Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources," Project Kickoff Meeting presentation, April 2016. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13106&filename=DE-FE0026919-Project-Kick-off-Meeting.pdf*.

Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes

primary project goals

Luna Innovations will take a systems-level approach to demonstrating dual phase carbon dioxide (CO_2) separation membrane solid support technology. Luna will evaluate yttria-stabilized zirconia (YSZ) and its derivatives as standalone solid phase supports and in the presence of a single molten carbonate electrolyte. Through modification of current YSZ supports, development of structure-property relationships, and prototype modeling of scaled-up technology form factors, Luna's solid phase supports will have the unique potential to provide the performance and scalability to separate CO_2 from flue gas in the heat recovery steam generators (HRSGs). Successful demonstration of this dual phase carbon capture and storage (CCS) technology will pave the way for retrofit in high-temperature exhausts found in power plant HRSGs.

technical goals

- Establish performance and design requirements for the dual phase membrane technology, including the system, safety, and operating parameters for HRSG integration. Expand multitube module test capabilities.
- Design and fabricate a scalable CO_2 separation module prototype.
- Perform relevant testing on single and multitube membrane assemblies. Evaluate performance under relevant conditions in long-term (~months) tests to establish membrane durability and stability.
- Conduct a systems-level analysis and evaluate techno-economic viability.
- Evaluate membrane module performance results and create a module design for pilot-scale testing. Develop Phase III plan.

technical content

Luna Innovations, in partnership with the Lawrence Livermore National Laboratory (LLNL), the University of Illinois, Chicago (UIC), and Nooter/Eriksen, is leading the scale-up and demonstration of a new type of dual phase membrane technology. The dual phase membrane consists of a thin wall of nanoporous ceramic solid phase that retains a non-volatile molten phase within the pores with capillary action. The molten liquid phase selectively sorbs CO_2 with high concentrations and transport rates. This results in superior separation performance with an unrivaled combination of CO_2 permeability and selectivity of CO_2 over nitrogen (N_2). This Small Business Innovation Research (SBIR) program is focusing on developing YSZ nanoporous solid phase materials to achieve the mechanical performance and form factors required for integration and operation inside an HRSG or boiler for operation at 250 to 500°C.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Membrane Support Materials

participant:

Luna Innovations

project number:

SC0017124

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Matthew Merrill
Luna Innovations
merrillm@lunainc.com

partners:

Lawrence Livermore National Laboratory, Nooter/Eriksen, University of Illinois at Chicago

start date:

02.21.2017

percent complete:

85%

Currently, there is an unmet need for commercialized membrane systems that can efficiently separate CO_2 from power plant flue gas exhausts at thermally favorable conditions with reduced costs. The proposed solution is to develop a membrane that uses the difference in water vapor concentration between low-pressure steam and the flue gas to drive CO_2 separation through the membrane. This approach has a theoretical minimum separation energy 10 to 15 times smaller (0.2 gigajoules [GJ]/ton CO_2 at 300°C) than the conventional amine solvents. These high-temperature membranes have greater potential for large-scale, energy-efficient separation by being directly integrated within power plant HRSGs, as shown in Figure 1. Luna's dual phase membrane technology shows potential for meeting the power generation industry's needs by separating CO_2 from power plant flue gas under operational conditions (250 to 500°C) and with drastically reduced costs.

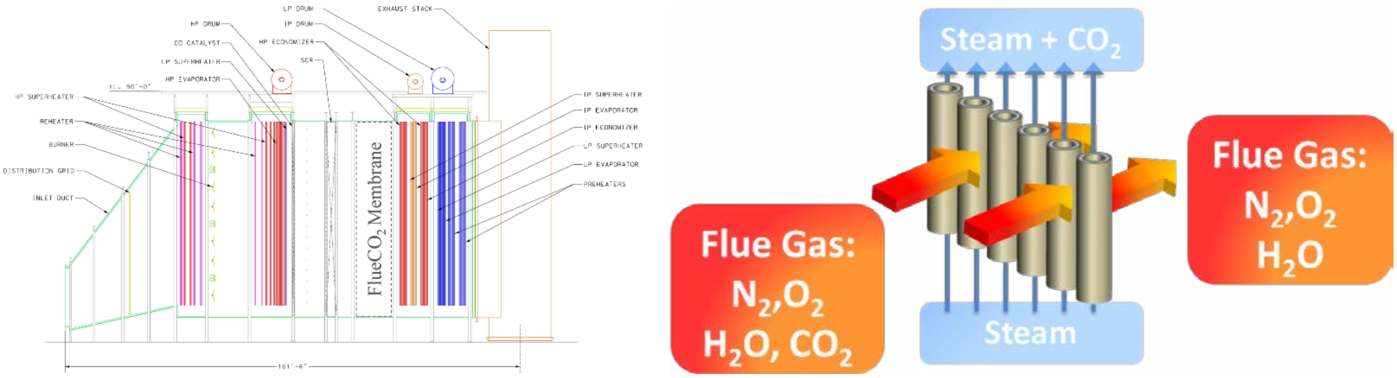

Figure 1: Luna's dual phase membrane technology introduces a unique ability to implement carbon capture technologies into power plant HRSGs (250 to 500°C).

In the dual phase membrane technology, a porous, solid material supports a non-volatile liquid electrolyte. Carbon dioxide actively absorbs into the molten electrolyte at the flue gas side, diffuses through the membrane as the carbonate ion (CO_3^{2-}) from high to low concentration, and desorbs from the membrane into a steam sweep gas (Figure 2). The steam sweep serves to both chemically desorb CO_2 and minimizes the concentration of permeated CO_2.

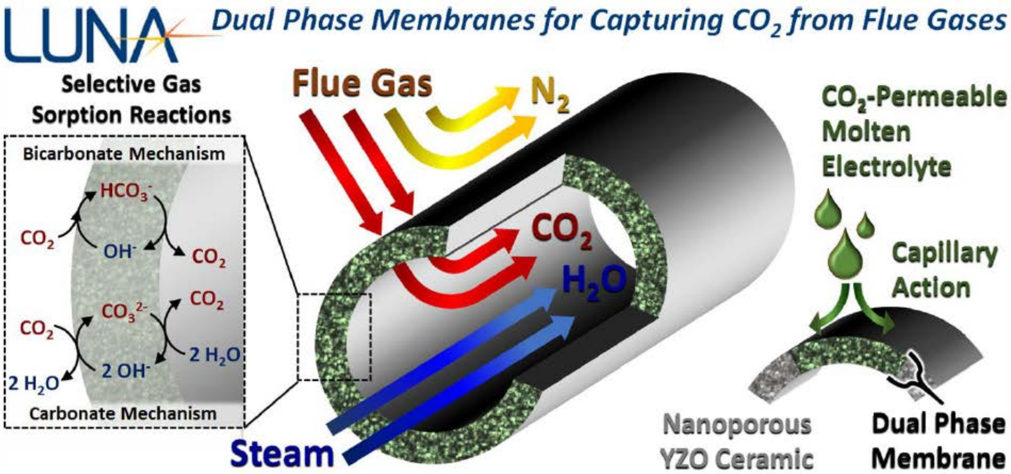

Figure 2: Luna's dual phase membrane technology for highly efficient and scalable CCS.

The unique operational conditions and performance capabilities of Luna's membrane enables a new opportunity to achieve more energy-efficient and less-expensive carbon capture. This membrane is not limited by the same physics governing Robeson's upper bound as conventional, polymer-based membranes and enables unrivaled combinations of permeability and selectivity (Figure 3). Such a novel system has never before been scaled-up to demonstrate the technical feasibility at the membrane module scale.

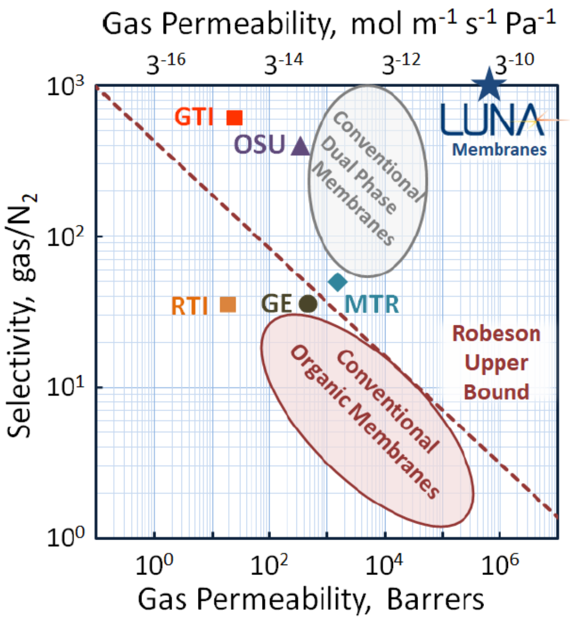

Figure 3: In a Robeson plot comparison, the Luna team's membrane (star) outperforms other CO_2 separation membrane technologies funded by the National Energy Technology Laboratory (NETL).

In Phase I of this project, the Luna Innovations team targeted solid phase support materials with high strength, increased CO_2 separation capabilities, and stability in the presence of the new molten electrolyte formulations. It was critical that these materials were evaluated in context of the HRSG operational conditions to demonstrate their mechanical, thermal, and chemical stability, as well as their scale-up to larger membrane systems. Luna developed the capability to manufacture membranes using nanoporous YSZ tubes procured from CoorsTek Ceramics. The nanoporous (~100 nm) ceramic materials from CoorsTek are 4 mol% YSZ tubes with 1/4-inch outside diameter (OD) and 3/16-inch inside diameter (ID). These tubes are initially extruded to 120 centimeters (cm) and then cut into smaller segments for this stage of testing by Luna. The mechanical properties of this high-strength ceramic material were characterized and determined to be scalable for the operational conditions expected for the membrane. The solid phase materials, fabrication methods, and design features were successfully developed in Phase I to manufacture and test multitube membrane modules in Phase II.

Luna has extensive experience operating the thermochemical membrane test setup constructed in the early stages of this Phase II project, which is now being referred to as the Scale I membrane reactor. Modifications to the Scale I reactor include: (1) automating the application of sequential steps of gas composition and flow rates; (2) complimenting the gas chromatograph (10-minute resolution) with nondispersive infrared (NDIR) CO_2 sensors (one-second resolution) to better evaluate permeation in real time; (3) modifying membrane holder design; and (4) upgrading to more robust heating tapes. This Scale 1 reactor presently enables testing of flue gas simulants based on 0 to 500 standard cubic centimeters per minute (SCCM) of N_2, CO_2, and oxygen (O_2) gases, as well as steam sweep simulants of argon (Ar), water (H_2O; up to 30 mol%), and CO_2. The concentration of H_2O in the steam simulant is limited in the Scale 1 reactor because of the technical challenges of generating steam with analytical control over flow rate and pressure for scales less than 500 SCCM. A Scale II membrane reactor is presently under construction that represents a 20-times scale-up for large membrane modules. The Scale II reactor will be used to test larger CO_2 separation membrane modules with advanced features, such as analytically controlled steam generation for greater than 500 SCCM at 1 to 6 atmospheres (atm).

While Luna has focused on developing low-temperature electrolyte formulations, parametric testing in conditions relevant to operation, and module scale-up and integration efforts, Luna's partner, UIC, has transitioned to focusing on complimentary membrane testing efforts on their smaller test setup. Upon completing the construction of UIC's two-path test setup, one path will be dedicated to achieving 1,000 hours of continuous membrane testing. The previous record of 400 hours of continuous membrane testing ended prematurely due to a tube furnace programming error. The other path will be modified to evaluate the effects, if any, of nitric oxide (NO) and/or nitrogen dioxide (NO_2) on membrane performance and stability.

Luna has reviewed the options for designing the CO_2 separation membrane module. Tube-based form factor designs remain the most reliable option for further developing and scaling-up the membrane technology primarily based upon the maturity of possible ceramic material manufacturing methods, as well as the supporting technical capabilities required to develop a complete, functional membrane module. The current tube module design is based upon a Swagelok flange and custom interface to multiple short tube samples (Figure 4). This design minimizes module development costs by using commercially available off-the-shelf (COTS) parts whenever possible, while also supporting flexibility and adaptability. The goal is to develop and demonstrate the construction and operation of a small module of five short (8 cm) single tubes. Once the basic design and construction approach is established, it is expected to be relatively easy to scale-up by using larger numbers of longer tubes. Larger Swagelok flange sizes will enable scale-up to 19 single-channel tubes or eight of the multichannel tubes. CoorsTek tube lengths can be extended to 120 cm. The initial multitube module has been manufactured and demonstrated to enable scaled-up test and evaluation.

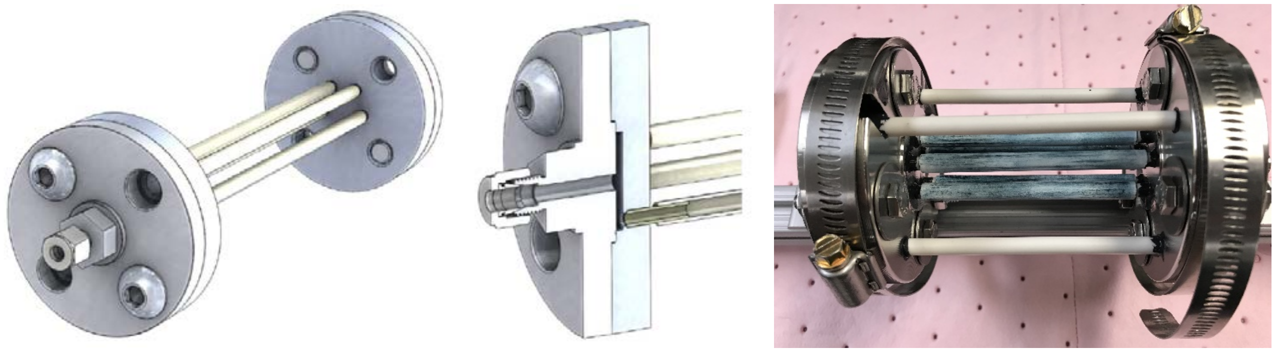

Figure 4: The multitube membrane module with five tubes has been revised to reduce the manufacturing time and costs, while also enabling easier and more flexible modifications for evolution and scale-up.

Luna has continued to achieve both faster CO_2 permeation rates and lower operational temperatures (Figure 5). The transition to lower operational temperatures is important to enable installation of the membrane system into the HRSG after the selective catalyst reduction (SCR), where the flue gas has reached temperatures below 400°C. Capturing the CO_2 at lower temperatures lowers separation energy costs and avoids the use of higher-temperature steam, which has a higher value use by generating electricity by the steam turbine. The present low-temperature electrolyte was selected for high CO_2 permeation rates, as well as a relatively wide operational temperature range of 300 to 450°C. The low-temperature limit of the membrane is generally governed by the freezing of the molten electrolyte phase. Additional molten phase development efforts may be able to extend the operational temperature down to 250°C; however, the present operational range is sufficient to demonstrate technical feasibility and the team will move forward to addressing other critical efforts of the Phase II program.

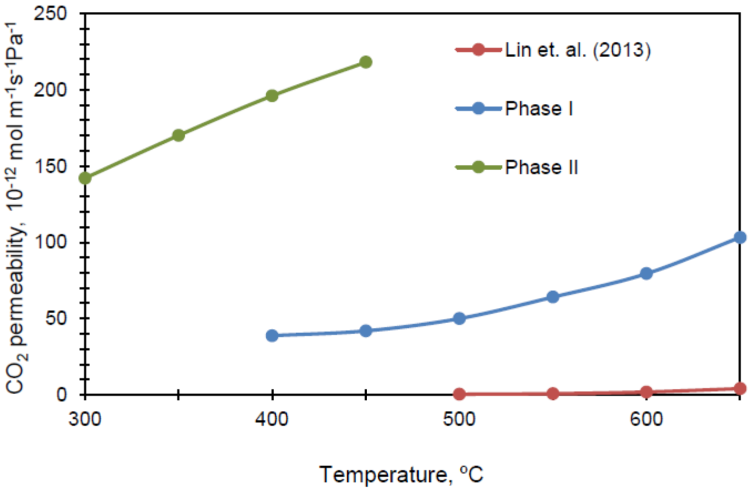

Figure 5: Progress in both improving the CO_2 permeability and decreasing the membrane operational temperatures for more efficient integration into new and retrofitted HRSGs of NGCC power plants.

UIC is presently preparing their two-line test setup for long-term stability testing, as well as stability with regards to NO and NO_2 exposure. The NO and NO_2 at 250 parts per million (ppm) will be included in the flue gas simulant, along with 10 mol% O_2, which is also present in significant concentrations in flue gases. In combination with oxidation by O_2, the NO and NO_2 gases could be incorporated into the molten electrolyte as nitrates. While a thermodynamic evaluation indicates that only a small concentration of nitrate could form in the molten phase, it is not yet clear whether the nitrogen oxide (NO_X) gases would become captured along with the CO_2 by permeation through the membrane or just reach a small, saturation concentration that would have little effect beyond slightly lowering the electrolyte melting temperature.

Nooter/Eriksen has begun modeling the integration of the CO_2 capture membranes into a 370-megawatt (MW) HRSG. If the target membrane performance metrics are achieved, there is enough space already available in the HRSG to incorporate the membrane system. The membranes could therefore be incorporated into new HRSGs with relatively little design modification or retrofit existing HRSGs for carbon capture. Retrofits of HRSGs of existing natural gas combined cycle (NGCC) power plants is expected to be the largest and most valuable market to target for commercialization. The membranes would be positioned downstream of the SCR, where flue gas temperature has decreased to about 350°C and has lower-value heat.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Molten hydroxide dual phase	
Materials of Fabrication for Support Layer	—	Metal oxide	
Nominal Thickness of Selective Layer	µm	950	<100
Membrane Geometry	—	tubes	tubes
Max Trans-Membrane Pressure	bar	30	30
Hours Tested without Significant Degradation	—	400	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	300	50
Membrane Performance			
Temperature	°C	300	300
CO_2 Pressure Normalized Flux	GPU or equivalent	800	>6,000
CO_2/H_2O Selectivity	—	undetermined	0.3
CO_2/N_2 Selectivity	—	999	999
CO_2/SO_2 Selectivity	—	undetermined	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	200	
Shell-Side Fluid	—	steam	
Flue Gas Flowrate	kg/hr	2,200	
CO_2 Recovery, Purity, and Pressure	%/%/bar	99%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: 1/sweep: 0.3	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the membrane occurs by the high concentration of H_2O in the steam sweep, selective gas sorption reactions (bicarbonate and carbonate mechanisms).

Contaminant Resistance – Significant quantities of ash in coal power plants represents a contaminant hazard for the membranes. NGCC power plants have therefore been identified as the target application.

Flue Gas Pretreatment Requirements – The temperature must be less than 450°C.

Membrane Replacement Requirements – The membrane lifetime is currently unknown.

Waste Streams Generated – The membrane process will generate a zirconia-based composite that may be recyclable.

technology advantages

- High thermal, mechanical, and chemical stability.
- Rapidly separates CO_2 from flue gas in a temperature range of 250 to 500°C, resulting in improved overall energy efficiency.
- Uses inexpensive materials.
- The combination of high selectivity and permeability exceeds those of competitive technologies.
- Modular design allows for easy integration with existing power plants.

R&D challenges

- Performance of materials under operational conditions.
- Possibility of degradation due to contaminants.
- Integration with HRSG systems.
- Design and modification of YSZ solid phase supports to prevent material degradation.

status

Multitube module testing is underway.

Nooter/Eriksen is focusing on further developing the systems-level analysis of how the membrane technology can be integrated into the HRSG and the resulting impact on HRGS performance.

available reports/technical papers/presentations

Ceron, M., Lai, L., Amiri, A., Monte, M., Katta, S., Kelly, J., Worsley, M., Merrill, M., Kim, S., Campbell, P. "Surpassing the conventional limitations of CO_2 separation membranes with hydroxide/ceramic dual-phase membranes," Journal of Membrane Science, 2018, Issue 567, pages 191-198. *https://www.sciencedirect.com/science/article/pii/S0376738818318209*.

Merrill, M. "Passive CO_2 Separation Membranes for Hot Flue Gases," presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-Separation-Membranes_Aug%202018.pdf*.

Merrill, M. "Solid Phase Supports for Flue Gas CO_2 Separation with Molten Electrolytes," Phase I Final Review Meeting, Pittsburgh, PA, November 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/DE-SC0017142%20Solid%20Membrane%20Materials%20Final%20Review%20NETL%2020171129.pdf*.

Merrill, M. "Passive CO_2 Separation Membranes for Hot Flue Gases," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/sites/default/files/2018-12/M-Merrill-Luna-Passive-CO2Separation_Aug%202017.pdf*.

Large Pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process

primary project goals

The overall goal of this project is to bring Membrane Technology and Research, Inc.'s (MTR) innovative membrane-based post-combustion carbon dioxide (CO_2) capture process to the final pre-commercial stage of development. The recipient's plan in this three-phase project is to design, build, and operate a 140 tonne-per-day (TPD) large pilot capture system at the host site for the project, the Wyoming Integrated Test Center (WITC) in Gillette, Wyoming. The membrane large pilot will be designed to achieve ~70% CO_2 capture from a 10 megawatt electricity (MWe) equivalent slipstream of flue gas. This range of partial capture using membranes offers the lowest cost of capture (\$/tonne CO_2). Completion of all phases of this project will signify that the MTR membrane capture process is ready to proceed to the demonstration scale.

technical goals

- Phase I (completed in year 1) included selection of the host power plant, securing financial commitments, conducting an environmental review, updating design and budget, and finalizing team commitments and organization for subsequent phases.
- Phase II (year 2) focuses on the detailed design portion of the program, including a complete front-end engineering and design (FEED) study, National Environmental Policy Act (NEPA) review, and finalized project cost projections.
- Phase III (years 3 to 6 if chosen from down-select) includes construction, installation, and operation of the large pilot system.

technical content

MTR has developed a new class of membranes, called Polaris™, that have 10 times the CO_2 permeance of conventional gas separation membranes. A tenfold increase in permeance leads to a tenfold decrease in the required membrane area, which substantially reduces the capital cost and footprint of the capture system. These membranes, along with innovative process modifications, address challenges for post-combustion carbon capture.

Over the past decade, MTR has worked with the U.S. Department of Energy (DOE) to develop these innovations into a cost-effective CO_2 capture process. As a result of these successes, the technology was scaled-up to a 20-TPD (1-MWe) small pilot system that was operated in slipstream tests at the National Carbon Capture Center (NCCC). These activities have brought the MTR technology to the point where it is ready for large pilot evaluation. The large pilot system to be built in this project will be based on the fully validated Gen-1 Polaris™ membranes. This membrane has been scaled-up to commercial production quantities. In addition

technology maturity:

Large Pilot-Scale, Actual Flue Gas (140 TPD)

project focus:

Large Pilot Polymer Membrane System

participant:

Membrane Technology and Research, Inc.

project number:

FE0031587

predecessor projects:

FE0005795
FE0026414
FE0007553

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigators:

Richard Baker/Brice Freeman
Membrane Technology and Research, Inc.
richard.baker@mtrinc.com
brice.freeman@mtrinc.com

partners:

The Wyoming Integrated Test Center, Sargent & Lundy, Trimeric Corporation, Electric Power Research Institute

start date:

04.01.2018

percent complete:

55%

to successful use for CO_2 capture in field tests at NCCC and Babcock & Wilcox Enterprises Inc. (B&W), the Polaris™ Gen-1 membrane has been used in commercial natural gas and refinery membrane applications.

A simplified version of the process to be used in the pilot plant is shown in the block diagram in Figure 1.

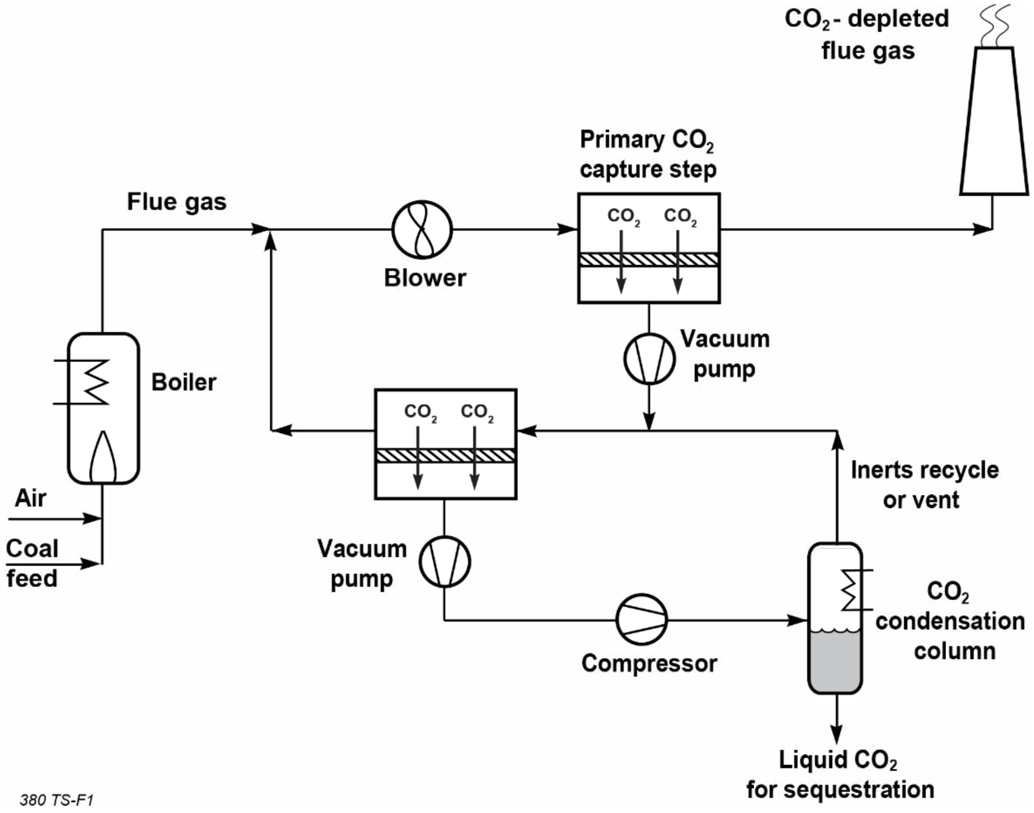

Figure 1: Simplified block diagram of the MTR large pilot CO_2 capture plant to be built.

The large pilot unit will capture ~70% of the CO_2 content (140 TPD) from a 10-MWe slipstream of flue gas provided by WITC. The flue gas to be delivered to the unit is at 85°C and contains 12.7% CO_2 and 18% water on average. A blower is used to increase the flue gas pressure to 1.2 bar absolute. The flue gas is then cooled in a direct contact cooler (DCC). A dedicated evaporative cooling tower will produce the cooling water required for the DCC and the various vacuum and compression intercoolers and aftercoolers. The DCC reduces the water content of the gas to 1.5% and increases the CO_2 content to ~15%.

The gas leaving the DCC then enters the first-stage membrane modules. The membranes partition the gas into a CO_2-enriched permeate (~50% CO_2) and a CO_2-depleted vent gas (~4% CO_2). The CO_2-depleted flue gas is vented to the atmosphere via a dedicated stack.

The driving force for CO_2 permeation is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. From the discharge of the vacuum pump, the CO_2-enriched permeate is compressed to about 1.1 bar and sent to a second-stage membrane, which further enriches the gas to ~85% CO_2. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

The twice-enriched permeate gas from the second membrane stage is compressed to 25 bar. Some of the water in the gas is removed in the inter-stage cooler of the compressor. Most of the water that remains is removed from the compressed gas by cooling to 5°C. A molecular sieve drier is then used to produce bone dry gas. The dry gas is passed to a low-temperature distillation unit to provide high-purity CO_2. The liquid CO_2 is then pumped to 153 bar as required for enhanced oil recovery (EOR) or storage.

A model of the 140-TPD large pilot membrane skid is shown in Figure 2. The membranes are housed in low-pressure-drop modules, which reduce cost and increase packing density. There are eight modules per stack and six stacks per container skid. The skids are stacked two high. This will be the final form factor for this membrane CO_2 capture technology. The membrane portion of the capture plant has a compact footprint, processing 10 MWe of flue gas in an area of approximately 100 by 100 feet, with a maximum height of 30 feet.

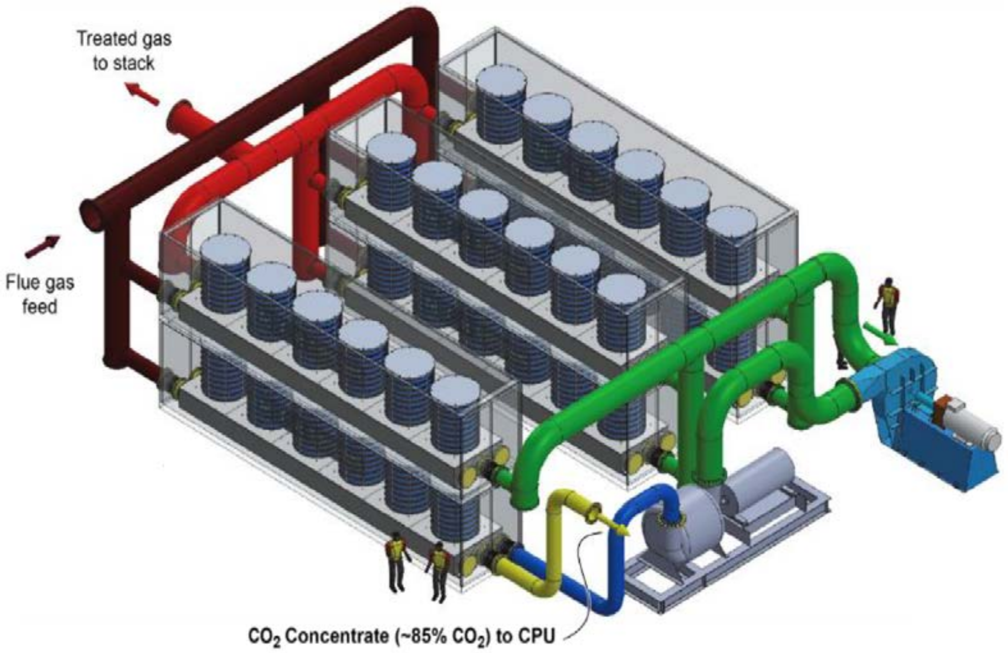

Figure 2: Preliminary general arrangement drawing of the 140-TPD large pilot system to be installed at WITC.

WITC will provide the test site and a significant cost-share contribution for the Phase II and Phase III programs. WITC is located in Gillette, Wyoming, adjacent to the Basin Electric Dry Fork 420-MWe coal power plant. Basin Electric will supply the project with the equivalent of 10 MWe of flue gas. Duct work and fans to deliver flue gas to the test site are in place. Power and water necessary for the project have also been installed. The membrane unit will recover ~70% of the CO_2 content of this gas, or ~140 TPD. At full-scale, a 70% reduction in CO_2 emissions would bring the remaining CO_2 emissions of a coal power plant to below that of an equivalent-sized natural gas power plant.

All of the objectives of the Phase I feasibility study were met. Preliminary engineering drawings for the 140-TPD plant have been prepared. Budget estimates have been obtained for the major equipment items and initial cost estimates for the Phase III construction and operation work have been prepared. A preliminary cost analysis indicates that at the end of the Phase III program, the technology will be ready for scale-up to large demonstrations and CO_2 capture costs in the \$40/tonne CO_2 range will be possible.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	11,000 h	11,000 h
Manufacturing Cost for Membrane Material (Module and Skid)	$/m^2	50-100	50-100

Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,000	2,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	flue gas	flue gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	tons/hr	70.31	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-75%, 99%, 153 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.05/sweep: 0.025	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation occurs by a passive, solution-diffusion process. Permeation driving force through the first-stage membrane module is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, etc., is unknown.

Flue Gas Pretreatment Requirements – Testing at NCCC showed no additional pretreatment was required downstream of a wet flue gas desulfurization (FGD).

Membrane Replacement Requirements – Greater than three-year membrane lifetime.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

technology advantages

- The process does not use any hazardous chemicals. No new emission streams are produced.
- The membranes developed are 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The system is compact and modular.
- The two-stage membrane design allows for high-purity CO_2 combined with high capture rates.
- The low-pressure-drop modules reduce parasitic energy.
- The system is very efficient at partial capture (50 to ~70%).

R&D challenges

- There is a risk that the membranes may be less stable at large scale than anticipated.

status

The overall design of the 140-TPD large pilot plant was finalized. Preliminary layout drawings for the system at the WITC site were prepared. Based on the final design, a table listing the expected cost of all the major equipment items was prepared. This information formed the basis of a preliminary estimate of the Phase III schedule and budget. The Phase II project team was assembled and a division of responsibilities for the Phase II and Phase III programs was completed. Finally, WorleyParsons finalized the preliminary environmental information volume (EIV) for the pilot system at WITC.

available reports/technical papers/presentations

Baker, R.W., et al. "Large pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process," Phase II kickoff meeting presentation, Pittsburgh, PA, October 2019. *https://www.netl.doe.gov/projects/plp-download.aspx?id=17214&filename=MTR%20Ph2%20DOE%20Kickoff%20Mtg%20100119.pdf*.

Baker, R.W., et al. "Large pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13129&filename=R-Baker-MTR-Membrane-Large-Pilot-Testing.pdf*.

Baker, R.W., et al. "Large pilot Testing of the MTR Membrane Post-Combustion CO_2 Capture Process," Phase I kickoff meeting presentation, Pittsburgh, PA, May 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13128&filename=MTR-Kickoff-Presentation-Public-FE0031587-FOA1788.pdf*.

Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station Using Membrane-Based Technology

technology maturity:

Commercial-Scale Design

project focus:

Polymeric Membrane-Based Process Retrofit

participant:

Electric Power Research Institute, Inc.

project number:

FE0031589

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Desmond Dillon
EPRI
ddillon@epri.com

partners:

Membrane Technology and Research, Inc., Duke Energy, Nexant Inc., Bechtel Inc., Trimeric Corporation

start date:

04.06.2018

percent complete:

80%

primary project goals

The Electric Power Research Institute, Inc. (EPRI) will produce an initial engineering design and cost estimate of a first-of-a-kind, full-scale, membrane-based post-combustion carbon dioxide (CO_2) capture system retrofit to an existing U.S. coal power plant. The capture technology is provided by Membrane Technology and Research (MTR), and the power plant is Duke Energy's East Bend Station (EBS) located on the Ohio River in Kentucky. The primary objective is to develop a design that will minimize the impact on the power plant by disrupting as little of the existing facilities as possible, minimizing the cost of each tonne of captured CO_2 while also maintaining the net 600 megawatt (MW) output of EBS. This will be done by optimizing the percentage of CO_2 captured from the coal-fired power plant (expected to be somewhere between 45 and 75% of the total CO_2 in the flue gas). The initial phase will also examine options for integrating waste heat from the new combustion turbine (CT) with the existing coal plant in order to improve the thermal efficiency of the coal-fired unit. Once an optimal configuration is selected, an engineering design, sufficient in detail to support a +/-30% capital cost estimate, will be generated, along with a techno-economic analysis (TEA).

technical goals

- Develop, review, and approve a design basis document for EBS.
- Develop a steam cycle model of an existing power plant and benchmark existing performance.
- Optimize the configuration of the membrane CO_2 capture system, including a decision on the level (percentage) of capture for the design that offers the lowest cost on a \$/tonne of CO_2 captured basis.
- Evaluate options for supplying auxiliary power to the CO_2 capture system.
- Develop a complete process design package of the membrane-based CO_2 capture system.
- Define retrofit modifications required to integrate the membrane-based process into EBS and conduct a hazard and operability (HAZOP)/constructability review of a retrofitted capture facility.
- Complete a TEA for the retrofitted power plant.

technical content

For this retrofit design project, second-generation Polaris™ membranes from MTR and an optimized level of CO_2 capture will be used to reduce capture costs, toward a goal of \$30/tonne CO_2. These second-generation Polaris™ membranes have double the CO_2 removal capacity of the original membrane and will be packaged in low-pressure-drop modules optimized for high-volume flue gas treatment. Prototypes of these modules have been validated in prior field trials that confirm large energy and cost savings. Targeting a lower degree of capture for this proposed project will obtain a post-combustion CO_2 capture system that provides the lowest cost on a \$/tonne CO_2 captured basis. Membrane-based post-combustion CO_2 capture systems achieve an optimal cost in the range of 45 to 75% capture.

Duke Energy's EBS will be the host site for the retrofit study (Figure 1). EBS is a 600-MW-net coal-fired power plant located on a 1,600-acre site along the Ohio River in Boone County, Kentucky. Duke originally envisioned having multiple 600 megawatt-electric (MWe) units at this site, but only one unit was built. As a result, there is an abundance of space around the existing facility, which will facilitate the addition of the CO_2 capture plant.

Figure 1: Duke Energy's East Bend Station 600-MWe coal-fired power plant.

The preliminary design case for the EBS post-combustion CO_2 capture system is shown in Figure 2. It will be a two-stage membrane system that aims for 45 to 75% CO_2 capture with no boiler recycle.

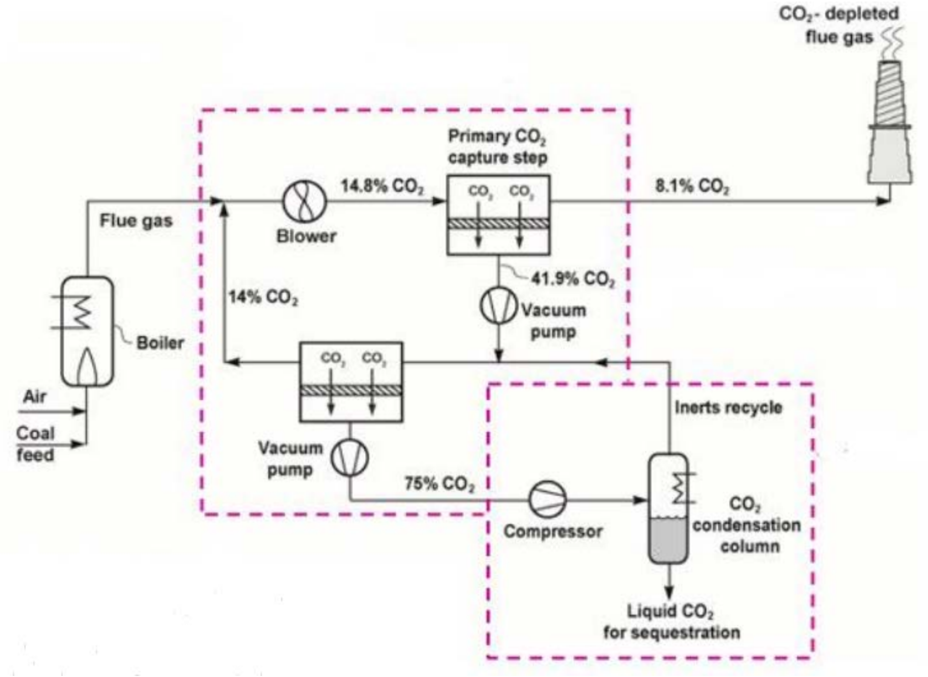

Figure 2: Preliminary design case for the East Bend unit.

Unlike solvent post-combustion CO_2 capture systems, there is no steam requirement for the membrane system. However, power is required to drive the membrane system's fans, blowers, vacuum compressors, pumps, and CO_2 compression. To make up for the increased auxiliary load imposed by the post-combustion CO_2 capture system, and to minimize the disruption to the existing power plant, the addition of a natural gas-fired CT power plant to the EBS site was investigated.

Four integration options were considered to provide power to the optimized membrane system retrofit:

1. New natural gas-fired simple cycle (maintain original net output).
2. New combined cycle (maintain original net output).
3. New simple cycle with additional waste heat recovery unit sized to supplying steam to power plant feedwater heaters.
4. Auxiliary power supplied from existing station (decrease net output).

Option 1 with the MTR post-combustion CO_2 capture plant supported by a single gas turbine simple cycle (GTSC) power island was determined to be the best arrangement for this project. It was found to provide:

- The lowest upfront cost of all the external power options considered.
- A phased implementation of feedwater pre-heat if required later (phase in Option 3 if required).
- Enough temperature and heat available for future EBS high-pressure feedwater preheating, if desired.
- Potential for future retrofit with full-size heat recovery steam generator (HRSG) for additional power export if New Source Review (NSR) regulations are relaxed.
- A well-established commercial operation history.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	11,000 (coal)	11,000 (coal)
Manufacturing Cost for Membrane Material	$/m²	50-100	50-100
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,600	1,600
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Actual flue gas	Actual flue gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	plate-and-frame	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	2,661,428	
CO_2 Recovery, Purity, and Pressure	%/%/bar	50-70%, >99%, 153 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.025	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation occurs by a passive, solution-diffusion process. Permeation driving force through the first-stage membrane module is provided by a vacuum pump, which pulls to about 0.1 bar absolute pressure on the permeate-side of the membrane. The second-stage membrane unit is much smaller than the first one, and also uses a vacuum pump to provide driving force.

Contaminant Resistance – Very fine particulates flow through the membrane channels and are discharged to the stack. Nitrogen oxides (NO_X) will not harm the membranes. The sulfur oxides (SO_X) that reach the membrane will not harm it. Some trace elements may reach the membrane. Their effect on the post-combustion CO_2 capture system is unknown.

Flue Gas Pretreatment Requirements –The flue gas desulfurization (FGD) system at EBS will remove SO_X, hydrogen chloride, soluble salts, and particulate matter (PM). EBS is also equipped with an electrostatic precipitator that will remove PM.

Membrane Replacement Requirements – Membrane modules will nominally be replaced every three years.

Waste Streams Generated – The post-combustion CO_2 capture system will generate liquid waste streams in the form of water condensate streams. Experience from test campaigns show that these streams are acidic and will either need to be pH-corrected prior to discharge or be combined and managed with other liquid waste streams present at the host power plant. Disposition and possible re-use of the condensates at EBS (e.g., as FGD makeup water) will be investigated as part of this design study. The current industry practice for membrane plants is to landfill the spent membrane elements. As part of the environment, health, and safety (EH&S) evaluation, the project team will review federal and state regulations regarding solid waste steams to determine if any flue gas contaminates entrained in the spent modules may require special handling or disposal. MTR's current understanding is that no special disposal measures are needed.

technology advantages

- The process does not use any hazardous chemicals. No new emission streams are produced.
- Reduces coal plant CO_2 emissions to those of a natural gas-fired plant.
- Utilizes MTR's second-generation Polaris™ membranes with CO_2 permeance two times that of their first-generation membrane technology.
- No modifications to existing plant steam cycle; potential to avoid NSR.
- Simple passive operation; no degradation caused by flue gas SO_X and NO_X.
- Compact modular system design.

R&D challenges

- Minimizing the cost of each tonne of CO_2 captured while maintaining current net output of the 600-MWe station.
- Efficiently supplying auxiliary power to the capture system at low cost.

status

The general arrangement of the membrane capture process has now been established, with the number and position of membranes, flow streams, membrane areas, expected utility requirement, and capture rate all calculated. Various sensitivities, such as the impact of air in-leakage and ambient temperature effects on the membrane system, have also now been examined and quantified. An option for auxiliary power has been chosen. The final overall design for the post-combustion CO_2 capture system retrofit is complete with major equipment specified and capital cost being finalized.

available reports/technical papers/presentations

Dillon, D.," Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station Using Membrane-Based Technology," presented at the 2019 NETL Carbon Capture, Utilization, Storage and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/D-Dillon-EPRI-East-Bend-Membrane.pdf*.

Bhown, A., "Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station using Membrane-Based Technology," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13091&filename=A-Bhown-EPRI-Duke-Energys-East-Bend-Station.pdf*.

Dillon, D., "Initial Engineering Design of a Post-Combustion CO_2 Capture System for Duke Energy's East Bend Station using Membrane-Based Technology," Kick-off meeting presentation, Pittsburgh, PA, June 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13090&filename=EPRI-KickOff-Meeting-FE0031589-FOA1791.pdf*.

Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost-Effective Carbon Capture

primary project goals

Membrane Technology and Research, Inc. (MTR) is developing composite membranes with superior carbon capture performance using a novel transformational approach. Two membrane targets have been identified: (1) carbon dioxide (CO_2) permeance of 4,000 gas permeation units (GPU) with mixed-gas CO_2/nitrogen (N_2) selectivity of 25, and (2) CO_2 permeance of 3,000 GPU with mixed-gas selectivity of 50. The first type will be used in the CO_2 removal step and the second type will be used in the CO_2 sweep step, both of which are parts of MTR's innovative post-combustion CO_2 capture process.

technical goals

- Develop methods to produce isoporous supports, first manufacturing single-layer supports (14 inches wide) using the laboratory's continuous casting system and then manufacturing dual-layer supports (40 inches wide) using MTR's commercial-scale casting equipment.
- Synthesize and characterize polymers containing high ether-oxygen content for CO_2/N_2 separation, and down-select polymers with most promising CO_2/N_2 separation properties for scale-up and production of composite membranes.
- Prepare composite membranes by coating selective layers onto isoporous support, first using a laboratory-scale coating machine (12 inches wide) and then using MTR's commercial-scale coater (40 inches wide).
- Fabricate and test laboratory-scale spiral-wound and plate-and-frame modules, optimize the design to minimize pressure drop, and produce prototype modules of both types for testing at the National Carbon Capture Center (NCCC).
- Design a bench-scale test skid for testing prototype membrane modules.
- Install and operate a test skid at NCCC for at least three months with actual coal-fired flue gas.
- Perform a techno-economic analysis (TEA) and sensitivity analysis of the process.

technical content

MTR will develop composite membranes with superior CO_2 capture performance using a novel transformational approach. Composite membranes consist of a selective polymer layer coated on a support that, ideally, does not hinder transport in the selective layer. MTR has conclusively demonstrated that this objective is not met for current supports when coated with very thin selective layers, leading to a reduction in permeance by a factor of two or larger. The proposed three-year project consists of two parallel technology developments that address the support issue, as well as the development of more selective materials.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Polymeric Membranes

participant:

Membrane Technology and Research, Inc.

project number:

FE0031596

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Hans Wijmans
Membrane Technology and Research, Inc.
hans.wijmans@mtrinc.com

partners:

State University of New York at Buffalo, University of Texas at Austin

start date:

06.01.2018

percent complete:

33%

The first development is to replace the conventional porous supports used to fabricate composite membranes with novel isoporous supports. The remarkable pore structure of isoporous supports is created through self-assembly of block copolymers and is the ideal surface to support the nonporous layers that perform the separation in composite membranes. Work at MTR has shown that the surface pore structure of conventional supports restricts diffusion in the adjacent selective layers, and this geometrical effect significantly reduces the permeance of layers thinner than 1 micron. The high surface porosity and uniformity in pore size and pore location of the isoporous supports (Figure 1) eliminates this restriction and allows fabrication of Polaris™ composite membranes with significantly increased CO_2 permeances as high as 4,000 GPU. Building on extensive work on isoporous membranes reported in the open literature, the isoporous support preparation methods will be adapted to MTR's commercial membrane casting equipment.

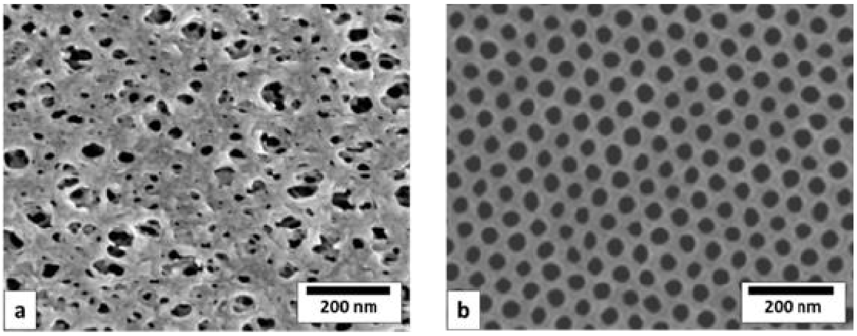

Figure 1: Surface pore structure of (a) a conventional porous support, and (b) an isoporous support.

The probability of successfully producing isoporous supports at commercial scale is high. The method to be used is very similar to existing methods for the manufacture of conventional supports. Moreover, the isoporous support, while of great importance, does not perform the actual separation, which means the occasional pore defects or misalignments are able to be tolerated. This is unlike the ultrafiltration and nanofiltration applications that are the traditional focus of isoporous membrane development.

The project team has prepared many support membranes using the Polystyrene-b-Poly-4-vinylpyridine (BCP1) polymer and has used scanning electron microscopes (SEMs) to evaluate the structures obtained. It is not easy to create the very perfect isoporous surfaces that are reported in the literature for these block copolymers. These surfaces likely represent a few out of many attempts, with the unsuccessful attempts not being reported. However, in the current work, perfect isoporous surfaces are not required; only surfaces that are an improvement over the conventional support membranes are needed. Figure 2 shows the top surface of a BCP1 support that by no means is perfectly isoporous, but is expected to be a better support membrane than the conventional support made by MTR, of which a surface SEM is shown in the inset.

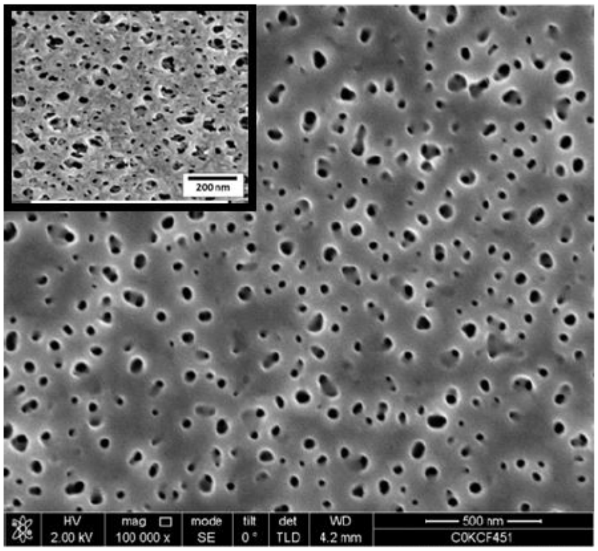

Figure 2: Top surface of a BCP1 support membrane. The inset is a conventional polyethylenimine (PEI) support.

The second development within this project is to build on materials research carried out at the University of New York at Buffalo (NYUB), where materials have been identified that, in the form of films, have shown the potential to double the mixed-gas selectivity of the Polaris™ membrane, albeit at the expense of permeability. Variations of the materials will be synthesized at NYUB, and MTR will produce and test composite membranes using both conventional porous supports and the novel isoporous supports. It is expected that by using the isoporous supports, composite membranes can be produced that are significantly more selective than the current Polaris™ membrane without increasing the membrane area required.

Recently, the research group at NYUB has developed a new series of copolymers based on poly(1,3 dioxolane), which has the highest ether-oxygen (O)/carbon (C) ratio of any known chemical structure and significantly higher than polyethylene oxide (PEO) (O/C ratio of 0.67 versus 0.5 for PEO). Initial work has confirmed that the higher ether-oxygen content leads to superior CO_2/N_2 separation properties. In the proposed project, a series of PDXLA-co-PDXLEA materials will be thoroughly evaluated with simulated flue gas at various temperatures, pressures, and compositions.

Some of the new materials developed at NYUB are 25 to 50% less permeable than the Polaris™ polymer, but have shown mixed-gas selectivities for CO_2 over N_2 as high as 50 at temperatures between 50 and 60°C. This mixture selectivity is nearly double what Polaris™ would give at this temperature. Figure 3 compares the predicted performance of these materials coated directly on an isoporous support with Polaris™ performance. The data point on the PPDXLA curves represents the target performance for the new Polaris™ high selectivity (HS). This type of performance is well-suited for the sweep step in MTR's patented process design.

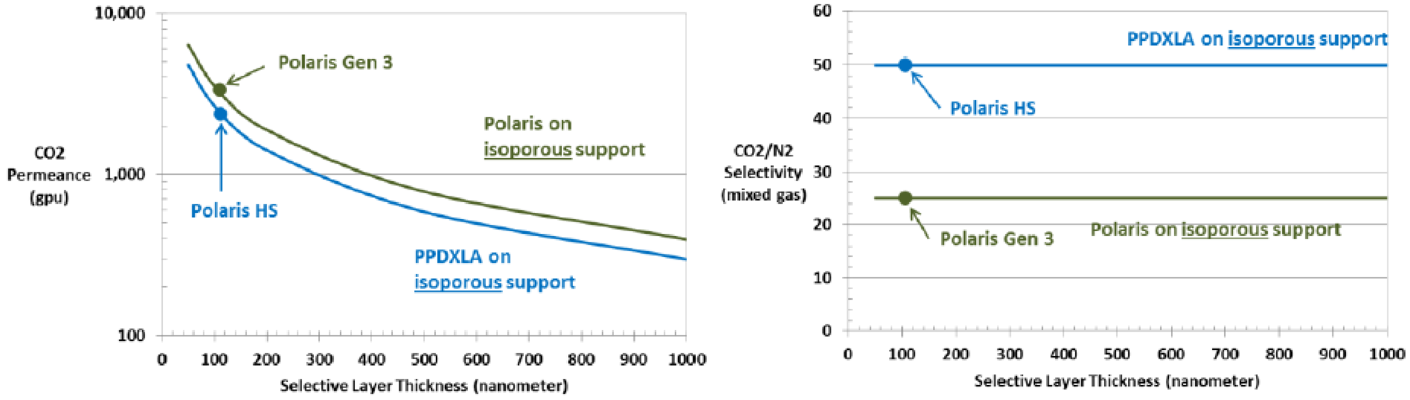

Figure 3: (a) Mixed-gas CO_2 permeance and (b) CO_2/N_2 selectivity as a function of selective layer thickness for Polaris™ and PPDXLA on an isoporous support.

The research group at NYUB will focus on the synthesis of polymers containing high ether-oxygen content for CO_2/N_2 separation. The production of polymers will be optimized and scaled-up gradually. The polymers with the most promising properties will be delivered to MTR for the production of thin-film composite membranes and then bench-scale membrane modules.

Composite membranes will be prepared by coating selective layers onto the isoporous support produced. The selective materials used will be (1) MTR's Polaris™ formulation and (2) the selective materials to be developed by NYUB. Composite membranes will be characterized first in pure-gas permeation experiments with CO_2 and N_2. Promising membranes will be tested more extensively, including pure-gas permeation at different pressures and temperatures, and experiments with $CO_2/N_2/O_2$ mixtures representative of coal-derived flue gas. It is expected that the coating step with Polaris™ will be straightforward, as MTR has considerable experience with this material. More development and optimization work will be required for the newly developed materials.

The very high permeance membranes under development will require a redesign of the feed and permeate channels in the MTR planar membrane module. A few options to reduce pressure-drop in those channels are starting to be developed.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	planar	planar
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	10,000+ hrs (coal)	10,000+ hrs (coal)
Manufacturing Cost for Membrane Material	$/m^2	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	Type 1: 4,000 Type 2: 3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	60	Type 1: 25 Type 2: 50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

***Flow Arrangement* –** Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

***Packing Density* –** Ratio of the active surface area of the membrane to the volume of the module.

***Shell-Side Fluid* –** Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

***Membrane Permeation Mechanism* –** Permeation of individual components through the Polaris™ membrane is driven by partial pressure differences across the membrane generated by a permeate vacuum.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is unknown.

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown.

Membrane Replacement Requirements – Membrane lifetime is estimated at three years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid.

technology advantages

- The novel isoporous supports increases the CO_2 permeance (up to 4,000 GPU).
- The novel membrane selective layer material nearly doubles the CO_2/N_2 selectivity compared to membranes that use Polaris™ selective material.
- The two-stage capture process allows for high CO_2 capture rates and a high-purity product.
- The selective recycle of CO_2 to the boiler using the air sweep stream increases the CO_2 concentration in flue gas, reducing capital and operating expenditures.

R&D challenges

- Producing dual-layer isoporous supports.
- Scale-up of polymer synthesis of improved selective layer materials.
- Coating of novel selective layer on isoporous support.

status

MTR continued to vary casting formulations and conditions to identify promising support membrane structures. Although a truly isoporous surface structure has not been produced yet, some of the support membranes exhibit promising surface porosity that may be superior to conventional supports used commercially. Membranes prepared from new selective layer materials synthesized by NYUB show pure-gas CO_2/N_2 selectivity up to 89, which is considerably higher than conventional Polaris™ membranes (CO_2/N_2 selectivity = 50) and demonstrates the potential of this approach.

available reports/technical papers/presentations

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," Kickoff meeting presentation, Pittsburgh, PA, September 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12056&filename=Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture%20Sept%202018.pdf*.

Wijmans, H., et al. "Development of Self-Assembly Isoporous Supports Enabling Transformational Membrane Performance for Cost Effective Carbon Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12057&filename=Development%20of%20Self-Assembly%20Isoporous%20Supports%20Enabling%20Transformational%20Membrane%20Performance%20for%20Cost%20Effective%20Carbon%20Capture%20Aug%202018.pdf*.

Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture

primary project goals

Gas Technology Institute (GTI) is developing a transformational graphene oxide (GO)-based membrane process that can be installed in a new or retrofitted into an existing pulverized coal or natural gas power plant for carbon dioxide (CO_2) capture ready for demonstration by 2030. The expected product from this project will be a compact, GO-based membrane prototype system capable of achieving at least 70% CO_2 removal with a single-stage process and 90% CO_2 removal with a two-stage process. The system will be tested over an extended duration on actual flue gas at GTI and the National Carbon Capture Center (NCCC).

technical goals

- Scale-up the GO-based membranes to 50 to 100 cm^2 area and demonstrate that the scaled membranes show CO_2/nitrogen (N_2) selectivity ≥200 and CO_2 permeance ≥1,000 gas permeation units (GPU) for the high-selectivity membranes (designated as GO-1 membranes), and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the high-flux membranes (designated as GO-2 membranes).
- Perform 100 hours of stability testing to demonstrate the CO_2 permeance and CO_2/N_2 selectivity decrease by less than 10% in the presence of flue gas contaminants (oxygen [O_2], sulfur oxide [SO_X], nitrogen oxide [NO_X]).
- Scale-up the GO-based membranes to 500 to 1,000 cm^2 area and demonstrate that the scaled membranes show CO_2/N_2 selectivity ≥200 and CO_2 permeance ≥1,000 GPU for the GO-1, and CO_2/N_2 selectivity ≥20 and CO_2 permeance ≥2,500 GPU for the GO-2.
- Achieve 95% CO_2 purity by integrating the GO-1 and GO-2 membranes in a skid (designated as GO^2) for both natural gas and coal-derived flue gases.
- Perform a techno-economic analysis (TEA) to validate that the cost of electricity (COE) is 30% less than the U.S. Department of Energy (DOE) baseline CO_2 capture approach.

technical content

GTI is developing GO-based membranes for CO_2 capture from flue gases. The high-selectivity membranes (GO-1) show CO_2 permeances as high as 1,020 GPU with a CO_2/N_2 selectivity of 680, which is much higher than state-of-the-art membranes. In addition, GTI is also developing high-flux membranes (GO-2) with

technology maturity:
Bench-Scale, Actual Flue Gas

project focus:
Graphene Oxide Membranes

participant:
Gas Technology Institute

project number:
FE0031598

predecessor project:
FE0026383

NETL project manager:
Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:
Shiguang Li
Gas Technology Institute
shiguang.li@gastechnology.org

partners:
Rensselaer Polytechnic Institute, The Ohio State University, Trimeric Corporation

start date:
06.01.2018

percent complete:
30%

CO_2 permeance as high as 2,500 GPU using GO quantum dots (GOQD) as a membrane building block. The proposed transformational GO-based membrane process integrates the GO-1 and GO-2 membranes (GO^2), offering a new opportunity to explore further reductions in the cost of CO_2 capture.

Graphene-based materials, such as graphene and GO (Figure 1), have been considered as next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux. The feasibility of using a vacuum filtration process to fabricate ultrathin GO membranes (thickness of ~1.8 nm) has been demonstrated. It was observed that the molecular-sized pores of structural defects on GO flakes could serve as a transport pathway for selective gas separations.

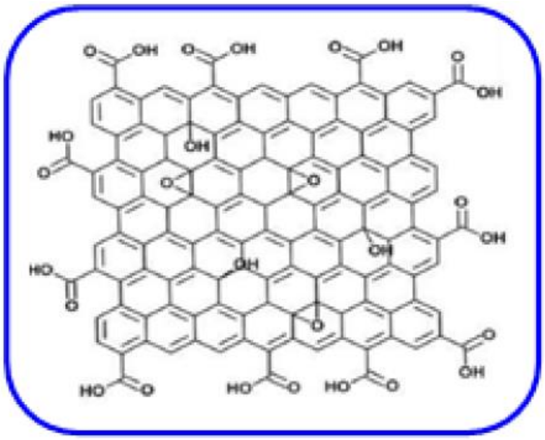

Figure 1: Chemical structural model of GO.

Because of the different morphologies of GO and GOQDs, ultrathin membranes (less than 20 nm) composed of these two different building blocks are expected to have different nanostructures. Figure 2 shows different membrane nanostructures of GO-1 and GO-2 membranes and the proposed transport pathways.

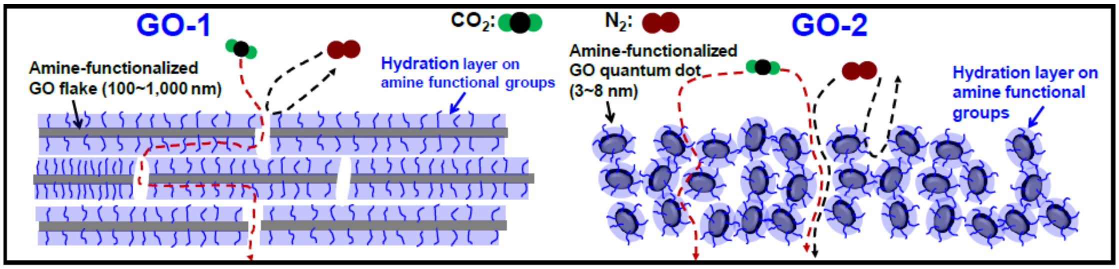

Figure 2: Membrane nanostructures of GO-1 and GO-2 membranes and proposed CO_2 separation mechanisms.

Large GO flakes (greater than 100 nm) with high aspect ratio of lateral size to the flake thickness typically lead to regular and uniform lamellar structure (GO-1, left in Figure 2) with a negligible quantity of defects after hydration of surface functional amine groups with water in the flue gas. As a result, CO_2 molecules can quickly transport through the membrane by a facilitated transport mechanism via reaction with amine ($CO_2 + R\text{-}NH_2 \leftrightarrow R\text{-}NH_3+ + HCO_3\text{-}$) and block the permeation of N_2 molecules. Therefore, GO-1 membranes have moderate CO_2 permeance but high CO_2/N_2 selectivity. In contrast, in GO-2 membranes, the small GOQDs may form a randomly packed nanostructure (right in Figure 2) containing defects that cannot be effectively sealed by the hydration layer. These defects greatly increase the CO_2 permeance, but also decrease the selectivity. Therefore, GO-2 membranes are expected to have high CO_2 permeance but lower CO_2/N_2 selectivity compared to the GO-1 membranes.

In addition to the hollow fiber GO-based membranes, the project team demonstrated for the first time an easy, fast, and scalable printing method with advanced computational controls to deposit ultrathin, high-quality GO-based membranes on a polymeric support for gas separation. A commercial ink cartridge was used to hold an appropriate GO dispersion for printing (Figure 3a). Using only GO "ink," ultrathin GO membranes for highly effective water nanofiltration have been printed. To promote membrane separation performance for a CO_2/N_2 mixture, an extra cartridge was added that holds various amine solutions, such as ethylene diamine (EDA), diethylenetriamine (DETA), triethylenetetramine (TETA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA), to increase both CO_2 permeance and CO_2/N_2 selectivity (Figure 3b). Uniform GO coatings with well-controlled thickness and a membrane area as large as 225 cm^2 have been printed (Figure 3c). Figure 3d shows a typical cross-sectional scanning electron microscopy (SEM) of the printed membrane. Figure 3e indicates the thicknesses of the printed membranes are between 6 and 60 nm and can be well-controlled by the GO concentration.

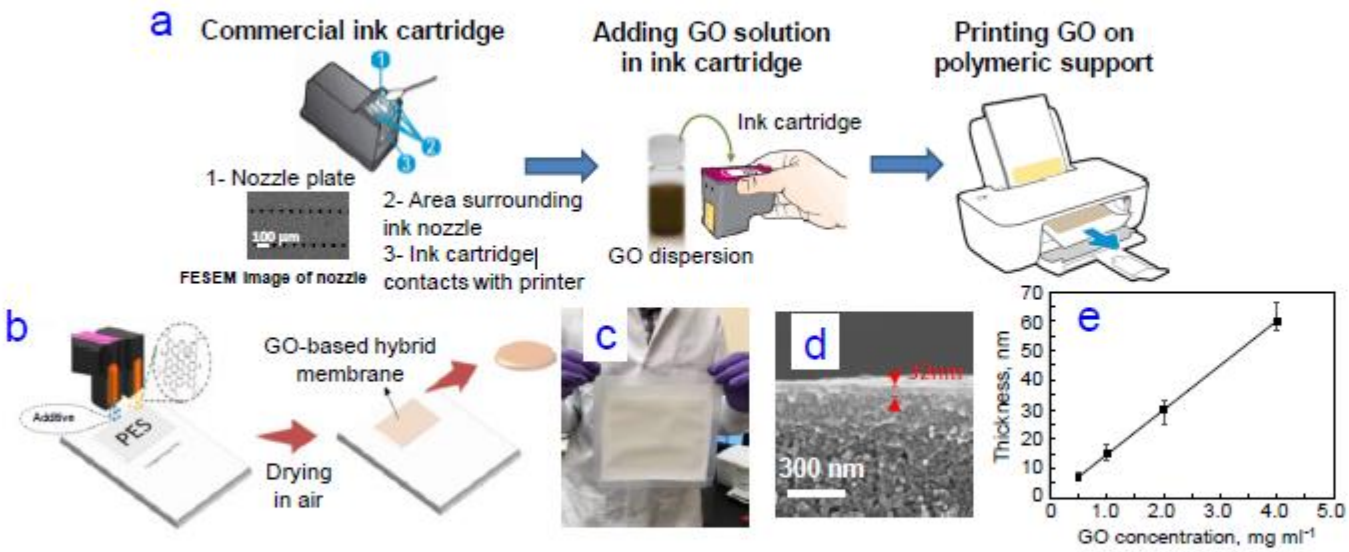

Figure 3: (a) Schematics of GO membrane fabrication by inkjet printing; (b) GO-based membrane preparation by printing from two cartridges containing GO ink and additives; (c) a picture of a printed GO membrane (15 cm × 15 cm); (d) cross-sectional SEM of the membrane; (e) dependence of membrane thickness on GO ink concentration.

The project team prepared GO-based flat-sheet membranes on a polyether sulfone (PES) substrate by printing. The resulting membrane was sealed in a plate-and-frame module for characterization and CO_2/N_2 separation testing.

The project team coated GO-based membranes on 50- to 100-cm^2 PES porous hollow-fiber modules by a vacuum filtration process. The sub-recipient systematically synthesized and optimized single-layered GO flakes via different GO synthesis methods. A variety of equipment was used to characterize the membrane morphology, thickness, composition, and structural defects density. The CO_2/N_2 separation properties were measured using an existing laboratory-scale testing system and simulated flue gas.

For coal-fired flue gas, the proposed GO^2 technology is designed to capture 90% CO_2 with greater than 95% CO_2 purity. The system will be installed downstream of flue gas desulfurization (FGD), as shown in Figure 4. It is a compact, stand-alone, membrane-based process, enabling easy integration into the power plant.

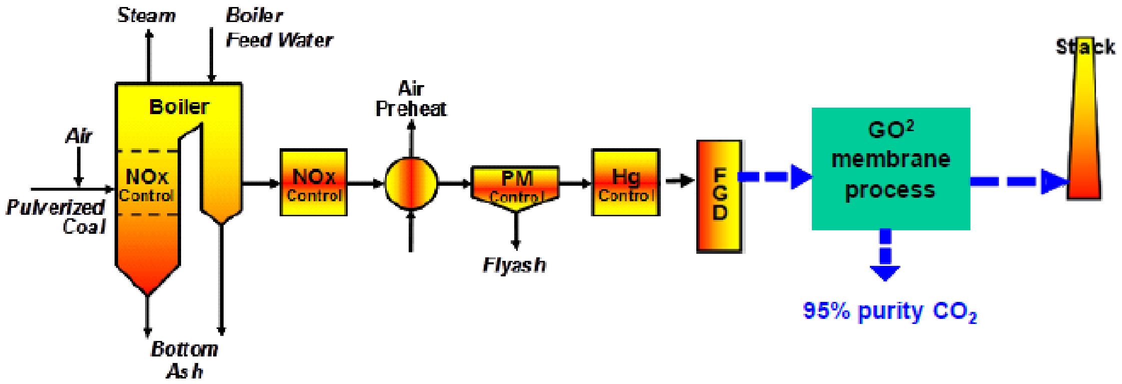

Figure 4: Process flow diagram for the proposed GO^2 process for CO_2 capture.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Graphene Oxide	
Materials of Fabrication for Support Layer	—	Polyether sulfone	
Nominal Thickness of Selective Layer	µm	0.002-0.05 for GO-1 0.005-0.1 for GO-2	0.002-0.02 for GO-1 0.005-0.05 for GO-2
Membrane Geometry	—	Hollow fiber and flat sheet	Hollow fiber and flat sheet
Max Trans-Membrane Pressure	bar	<5	1
Hours Tested without Significant Degradation	—	20	>200 (actual flue gas)
Manufacturing Cost for Membrane Material	$/m^2	TBD	TBD
Membrane Performance			
Temperature	°C	80 for GO-1 70 for GO-2	65
CO_2 Pressure Normalized Flux	GPU	1,020 for GO-1 2,500 for GO-2	1,000 for GO-1 2,500 for GO-2
CO_2/H_2O Selectivity	—	1/10 for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
CO_2/N_2 Selectivity	—	680 for GO-1 >30 for GO-2	>200 for GO-1 >20 for GO-2
CO_2/SO_2 Selectivity	—	N/A for GO-1 N/A for GO-2	<1/10 for GO-1 <1/10 for GO-2
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Crossflow	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	CO_2-rich permeate	
Flue Gas Flowrate	kg/hr	TBD	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70-90%, >95%, TBD	
Pressure Drops Shell/Tube Side	psi/m	Feed and permeate: <1.5	

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – A vacuum pump is used on the permeate side to provide a vacuum of 2.9 pounds per square inch absolute (psia; 0.2 bar). Because the GO-based membranes are highly water-permeable, the water vapor in the flue gas permeates through the membrane and lowers the partial pressure of CO_2 in the permeate side. Thus, the applied vacuum provides enough driving force for CO_2 permeation. The CO_2-depleted residue leaving the GO-1 unit is sent to a second membrane unit, GO-2, which also uses a vacuum on the permeate side to create the driving force for separation.

Contaminant Resistance – GO is typically prepared under strong acid and oxidation conditions in an aqueous solution, so it is expected to be very stable under these harsh conditions. Additionally, GO is hydrothermally stable at 150°C and has good chemical stability and mechanical strength. Therefore, GO is expected to be stable under flue gas conditions and with flue gas contaminants, such as nitrogen dioxide (NO_2), SO_X, etc.

Flue Gas Pretreatment Requirements – The proposed GO^2 system will be installed downstream of FGD.

Membrane Replacement Requirements – TBD

Waste Streams Generated – No waste streams are generated. The GO-based membranes are selective for water (H_2O) over CO_2, and the proposed GO^2 technology can recover the water vapor from the permeate streams. The recovered, mineral-free, high-purity water can be reused by the power plant.

technology advantages

- The technology achieves high CO_2 capture rates (≥70%) with 95% CO_2 purity.
- The water-permeable feature of the GO membrane overcomes the process pressure limitation issue, enhancing mass transfer.
- GO membranes have high thermal/chemical stability and mechanical strength.
- Graphene-based materials such as GO have been considered next-generation membrane materials. They are only sub-nanometer thick and thus may form ultrathin separation membranes to minimize transport resistance and maximize flux.
- GTI's printing method for GO membrane formation has several advantages, including:
    - Low-cost, fast, and scalable deposition of ultrathin GO-based membranes.
    - Capability of controlling coating properties by controlling printing parameters.
    - High utilization efficiency of GO material without waste.
    - Flexibility of forming GO-hybrid coatings by introducing desired additives.

R&D challenges

- When scaling-up GO-based membranes, the CO_2 permeance and/or CO_2/N_2 selectivity may not scale with size.
- There is risk that membrane sealing issues will be encountered in the development process.

- The commercial PES substrate quality is not sufficiently high for scale-up of GO-based membranes yet.

status

The preparation conditions of GO- and GOQD-based membranes on both hollow-fiber support and flat sheet support have been optimized.

A nitrogen-doped, GO-based membrane showed a CO_2 permeance as high as 2,800 GPU with a CO_2/N_2 selectivity of 150 at 90°C, 100% feed humidity, and 0.3 bara pressure on the permeate side. This type of membrane can be employed as the GO-1 membrane in the GO^2 process.

Carbon dioxide separation performance was investigated by using different amines mixed with GO. For a GO-based membrane prepared by printing, CO_2 permeance of greater than 2,500 GPU with CO_2/N_2 selectivity of greater than 30 was achieved. This type of membrane can be employed as the GO-2 membrane in the GO^2 process.

available reports/technical papers/presentations

Li, Shiguang, et al. "Bench-Scale Development of a Transformational Graphene Oxide-Based Membrane Process for Post-Combustion CO_2 Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/Bench-Scale%20Development%20of%20a%20Transformational%20Graphene%20Oxide-Based%20Membrane%20Process%20for%20Post-Combustion%20CO2%20Capture%20Aug%202018.pdf*.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/S-Li-GTI-Energy-Efficient-GO-PEEK-Hybrid-Membrane-Process.pdf*.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/FE0026383-March-22-2017-BP1-Review.pdf*.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture," presented at the BP1 Review Meeting, Pittsburgh, PA, March 2017. *https://www.netl.doe.gov/projects/files/FE0026383-March-22-2017-BP1-Review.pdf*.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture," presented at the presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/files/S-Li-GTI-Go-Peek-Hybrid-Membrane-Process.pdf*.

Li, Shiguang, et al. "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion CO_2 Capture," presented at the project kickoff meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/projects/files/FE0026383-Kickoff-Presentation.pdf*.

Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology

primary project goals

Membrane Technology and Research, Inc. (MTR) will design, build, and operate an advanced Polaris™ membrane carbon dioxide (CO_2) capture system at the Technology Centre Mongstad (TCM) using actual flue gas from a refinery catalytic cracker, which simulates coal flue gas. This test system will validate recent membrane technology advancements and mitigate risk in future scale-up activities. The overall MTR membrane process will show the potential to meet the 2030 U.S. Department of Energy (DOE) target of $30/tonne CO_2 captured from coal-fired power plants. This project will demonstrate a cost-effective advanced membrane process to capture CO_2 from flue gas through slipstream tests at TCM using commercial-scale components. Results from this field test will provide performance data to allow a thorough technical and economic evaluation of the proposed membrane process. Successful completion of this project will signify readiness to proceed to the next step – testing a larger proof-of-concept advanced membrane system on the scale of 10 to 25 megawatts-electric (MWe).

technical goals

- Design the membrane test system and complete host site preparations.
- Fabricate commercial-scale membranes and low-pressure-drop membrane modules.
- Fabricate membrane test system skid, with membrane modules incorporated into skid, and install system at TCM.
- Conduct a minimum six-month field test, including three months of steady-state operation and parametric tests that focus on verifying system performance at partial capture rates that minimize capture costs.
- Evaluate optimal integration of advanced compression into the membrane capture process, including cost estimates.
- Complete a techno-economic analysis (TEA) and environmental, health, and safety (EH&S) assessment of the membrane capture technology.

technical content

In this project, no additional membrane development is required. A previously validated second-generation (Gen-2) membrane will be scaled-up to commercial manufacturing equipment. It is expected that this production scale-up process will produce cost savings through bulk materials usage and application of automated manufacturing equipment.

The goal of this project is to scale-up advanced Polaris Gen-2 membranes and modules to a final form optimized for commercial use, and to validate their

technology maturity:

Engineering-Scale, Actual Flue Gas (equivalent to 1 MWe)

project focus:

Polymeric Membranes

participant:

Membrane Technology and Research, Inc.

project number:

FE0031591

predecessor projects:

FE0005795
FE0026414

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Tim Merkel
Membrane Technology and Research, Inc.
tim.merkel@mtrinc.com

partners:

Technology Centre Mongstad, Dresser-Rand, Trimeric Corporation, WorleyParsons/Advisian

start date:

08.01.2018

percent complete:

39%

transformational potential in an engineering-scale field test at TCM. This program will expand on work conducted by MTR over the past decade with DOE support to develop efficient membrane CO_2 capture technology. This effort has produced the MTR Polaris class of membranes and a patented selective recycle process design that lowers the cost of capture.

Over the course of this development effort, key improvements made were higher-permeance membranes, low-pressure-drop modules, and a process design that optimizes the efficiency of capture.

The Gen-2 Polaris membranes have demonstrated double the CO_2 removal capacity of the original membrane in bench-scale tests at the National Carbon Capture Center (NCCC) (Figure 1). They will be packaged into new modules designed for low-pressure flue gas treatment. Prototypes of these modules have been validated in prior field trials that confirm large energy and cost savings. Assemblies of these modules will be fitted into a standard container that represents the final form factor for this technology, with future commercial systems simply utilizing large numbers of this modular repeat unit.

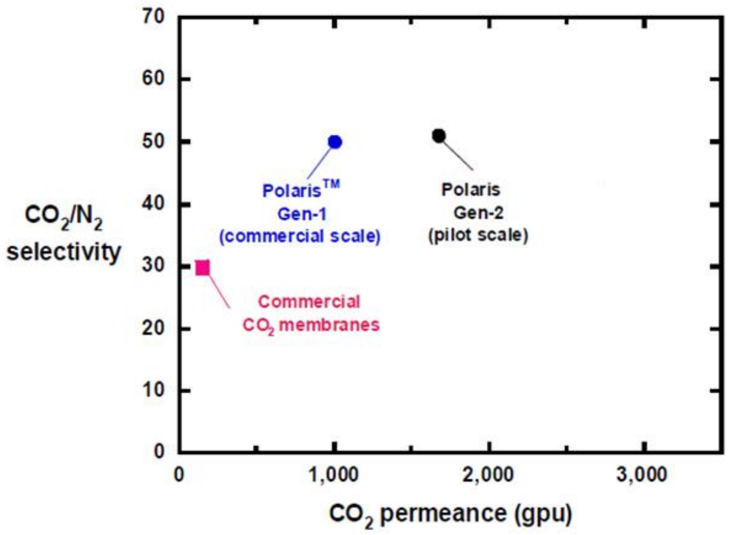

Figure 1: A CO_2/N_2 trade-off plot showing data for two generations of MTR Polaris membrane. Data are pure-gas values at room temperature.

These step-change material and device advances will be incorporated into a system design that takes advantage of the inherent efficiency of membranes for bulk separations. Capture costs can be minimized by operating at partial capture rates (50 to 75%), while still reducing coal plant CO_2 emissions to that of a gas-fired power plant or less. Finally, the pairing of Polaris Gen-2 membrane technology with advanced compression technology will be investigated. This technology combination was previously featured in the DOE Pathways Study as an attractive way to reach future cost targets.

In addition to an advanced membrane material, this project will also utilize a new type of low-pressure-drop module. This plate-and-frame module, in addition to its relatively compact size, had about four times lower pressure-drop at the same test conditions as the spiral modules during field testing at NCCC (Figure 2), resulting in large energy savings.

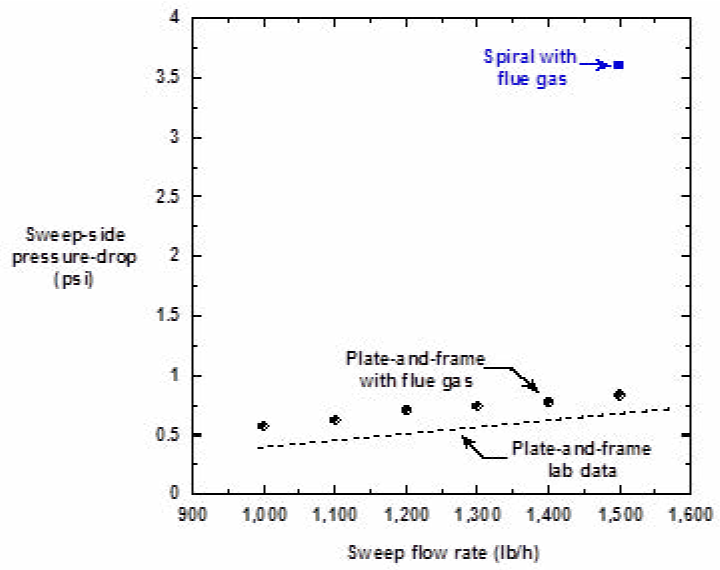

Figure 2: Difference in pressure-drop between spiral and plate-and-frame modules in NCCC field tests.

To reduce the cost of the membrane modules, MTR plans to fabricate them from structural plastics. During this project, a mold flow analysis was completed for the new module design. With this analysis, any issues with the mold design can be identified prior to actual fabrication of the mold and the molding company can determine how to operate their machinery with the MTR mold. Various process parameters were profiled and optimized, including temperature, pressure, number of gates, and gate locations.

Using the mold flow analysis, MTR, along with the domestic mold fabricator and custom plastics injection molding companies, finalized a mold design. A detailed drawing of the new planar stack containing eight membrane modules is shown in Figure 3.

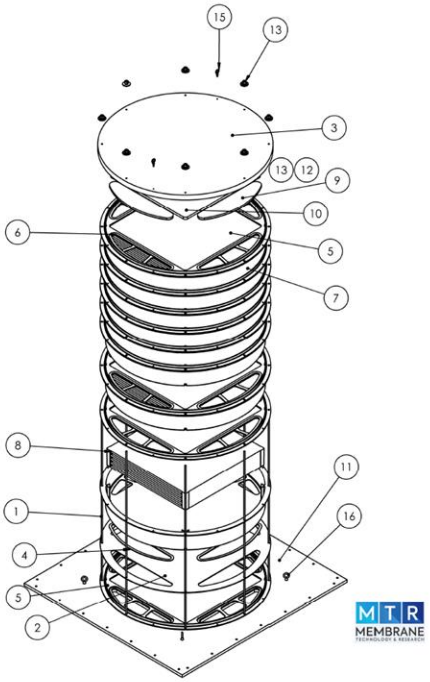

Figure 3: Detailed drawing of a membrane module stack containing eight membrane modules.

Figure 4 shows a simple process flow diagram for the MTR engineering-scale system to be installed at TCM. A slipstream of flue gas is sent to the membrane system (stream 1). After passing through a feed blower, the flue gas (stream 2) goes to the first membrane skid, where a vacuum on the permeate is used to remove CO_2. The membrane permeate (stream 4) is sent to a second-stage CO_2 purification unit (stream 5). Some of this purified CO_2 can be routed through a spillback line (stream 9) to the front of the membrane system to increase the concentration of CO_2 in the feed from 13 to ~20%. In this way, the feed to the membrane system will mimic the fully integrated case without having to recycle CO_2 to the boiler. With this spillback option, the 20% CO_2 membrane feed contains about 1 MWe worth of CO_2. The partially treated flue gas that leaves the first membrane step (stream 3) is then sent to the sweep membrane unit. Air (stream 6) flows on the permeate-side of these membranes and removes additional CO_2 from the flue gas. The CO_2-enriched air (stream 7) would be sent to the boiler in integrated operation, but here it is just vented after analysis. Finally, the cleaned flue gas (stream 5) flows to the stack.

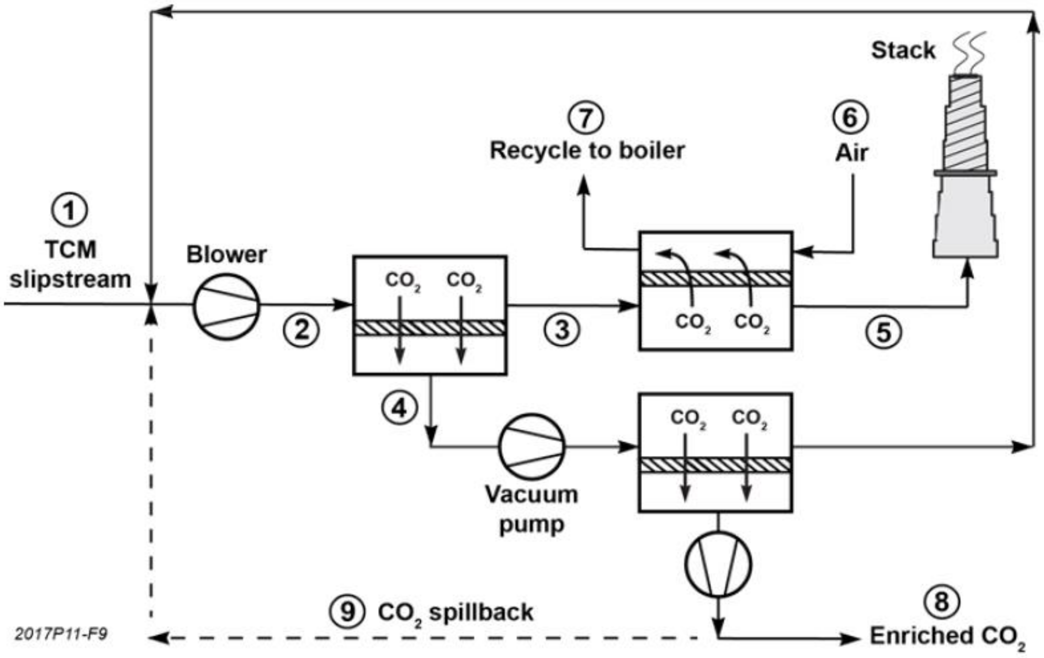

Figure 4: Simplified process flow diagram for the MTR skid operating at TCM.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	>11,000 (real coal)	>13,000 (real and simulated coal)
Manufacturing Cost for Membrane Material	$/m²	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	1,700
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed gas	mixed gas

Proposed Module Design		(for equipment developers)
Flow Arrangement	—	plate-and-frame (crossflow and countercurrent)
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flow rate	kg/hr	2,676
CO_2 Recovery, Purity, and Pressure	%/%/bar	75, >85, 1 (test system conditions)
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., is still under investigation. Polaris modules exposed to coal-fired fuel gas at NCCC for more than a year had no reduction in performance.

Flue Gas Pretreatment Requirements – When placed downstream of existing power plant flue gas emission treatment unit operations to remove particulates (nitrogen oxide [NO_X] and SO_2). The MTR Polaris post-combustion CO_2 capture membrane process design does not require additional pretreatment.

Membrane Replacement Requirements – MTR has installed hundreds of commercial membrane systems in the petrochemical, refinery, and natural gas industries over the past 30 years. The membrane module lifetime is estimated to be three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The MTR capture process will produce a dry, CO_2-depleted flue gas stream routed to the stack and a liquid stream containing much of the moisture in the flue gas (because the MTR membrane captures water as well as CO_2). Prior studies have determined that this water can be recycled to existing flue gas desulfurization (FGD) blowdown wastewater treatment.

technology advantages

- Gen-2 Polaris membranes have a CO_2 permeance approximately twice that of Gen-1 and about 20 times that of conventional membranes.
- There are no hazardous chemicals or emissions in the membrane process.
- The plate-and-frame membrane module minimizes pressure-drop.
- A single-stage system allows for low-cost partial capture, while a novel two-step design efficiently captures CO_2 at high removal rates and high purity.
- The CO_2 recycle increases feed concentration, reducing membrane area and energy requirements.
- High turndown, rapid response to dynamic conditions.
- The membrane module stack reduces module space and cost, which translates into additional cost savings in the system due to reduced ductwork and system complexity.

R&D challenges

- Optimizing CO_2 capture rate to minimize capture cost.
- Long-term stability of Gen-2 membranes.
- High-permeance membrane is required to lower capital cost.
- Pressure-drops must be minimized to reduce energy losses.
- Balance of plant equipment cost/efficiency, particularly for rotating equipment, are critical to system performance.
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves, and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-MWe plant.

status

A full hazard and operability (HAZOP) review of the MTR test system has been completed with MTR and TCM representatives. The results of the HAZOP were incorporated into the final system design; Progressive Recovery, Inc. of Dupo, Illinois, has been chosen as the fabricator for the MTR test system that will be installed at TCM.

available reports/technical papers/presentations

Merkel, T., et al. "Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology," presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/T-Merkel-MTR-Advanced-Polaris-Membrane-r1.pdf*

Merkel, T., et al. "Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology," Project Kickoff Presentation, Pittsburgh, PA, September 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12053&filename=Scale-Up%20and%20Testing%20of%20Advanced%20Polaris%20Membrane%20CO2%20Capture%20Technology%20Sept%202018.pdf*.

Merkel, T., et al. "Scale-Up and Testing of Advanced Polaris Membrane CO_2 Capture Technology," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/plp-download.aspx?id=12054&filename=Scale-Up%20and%20Testing%20of%20Advanced%20Polaris%20Membrane%20CO2%20Capture%20Technology%20Aug%202018.pdf*.

Rational Development of Novel Metal-Organic Polyhedra-Based Membranes for CO_2 Capture

primary project goals

The objective of this proposed program is to rationally develop solubility-selective mixed matrix membranes (MMMs) comprising highly polar rubbery polymers and soluble metal-organic polyhedra (MOPs) to achieve high carbon dioxide (CO_2) permeance (3,000 gas permeation units [GPU]), high CO_2/nitrogen (N_2) selectivity (75), and CO_2/oxygen (O_2) selectivity (30) at 60°C. Such membranes would outperform currently leading membranes by 50 to 100%, which can be implemented into Membrane Technology and Research Inc.'s (MTR's) membrane processes and may enable CO_2 capture at less than \$30/ton CO_2 from coal power plants.

technical goals

- Develop solubility-selective MMMs comprising polar rubbery polymers and MOPs.
- Develop thin-film composite (TFC) membranes achieving high CO_2 permeance (3,000 GPU) and high CO_2/N_2 selectivity (75) at 60°C.
- Demonstrate separation performance and stability with raw flue gas at the National Carbon Capture Center (NCCC).
- Perform techno-economic analysis (TEA) on the membrane processes.

technical content

The State University of New York (SUNY) at Buffalo is developing transformative solubility-selective MMMs containing MOPs and rubbery polar polymers. These transformative MMMs are built upon three key unique approaches. First, rubbery polymers with CO_2-philicity (and N_2-phobicity) will be designed, in contrast with most of the literature approach in pursuing glassy polymers with strong size-sieving ability. Second, MOPs with strong CO_2 affinity will be designed and added to increase the CO_2/gas solubility selectivity. In contrast to the commonly pursued insoluble metal-organic frameworks (MOFs), these MOPs are discrete nano-cages and soluble in organic solutions, making it easier to prepare TFC membranes with selective layers as thin as 100 nm. Third, the structure of polymers and MOPs can be independently designed with enormous possibilities, which can be accelerated using computational simulation.

A consortium of six organizations with complementary capabilities has been assembled to achieve these goals, including University at Buffalo (UB), Rensselaer Polytechnic Institute (RPI), California Institute of Technology (Caltech), MTR, NCCC, and Trimeric Corporation (Trimeric). The UB team will conduct fundamental and industrial membrane development and MOP synthesis and application to develop the novel materials, perform laboratory parametric tests, and scale-up the production. RPI will prepare functionalized polymers and scale-up the production. Caltech will simulate gas permeation to guide the design of the MMMs. MTR will prepare TFC membranes and bench-scale modules and

technology maturity:

Bench-Scale, Actual Flue Gas (5 kWe equivalent)

project focus:

Mixed Matrix Membranes

participant:

State University of New York (SUNY)–Buffalo

project number:

FE0031736

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Haiqing Lin
SUNY–Buffalo
haiqingl@buffalo.edu

partners:

Membrane Technology and Research Inc., National Carbon Capture Center, Rensselaer Polytechnic Institute, California Institute of Technology, Trimeric Corporation

start date:

7.01.2019

percent complete:

17%

perform field tests at NCCC. Trimeric will update the membrane process design and economic analysis based on MTR's patented processes. The endpoint of this project will be a field test of bench-scale membrane modules, and a TEA of the newly developed membranes elucidating their potential to meet U.S. Department of Energy's (DOE) goals for CO_2 capture.

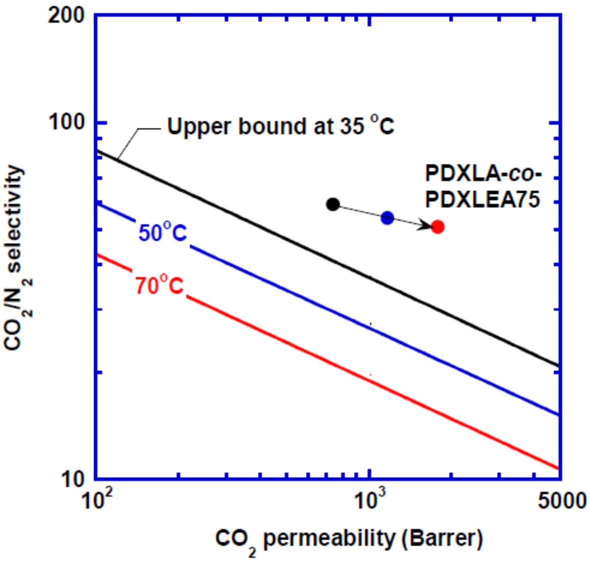

Figure 1: The "rubbery polymers": two macromonomers, poly(1,3-dioxolane) acrylate (PDXLA) and poly(1,3-dioxolane) ethyl ether acrylate (PDXLEA) are highly polar polymers that exhibit CO_2/N_2 separation properties above the upper bound in the Robeson's plot.

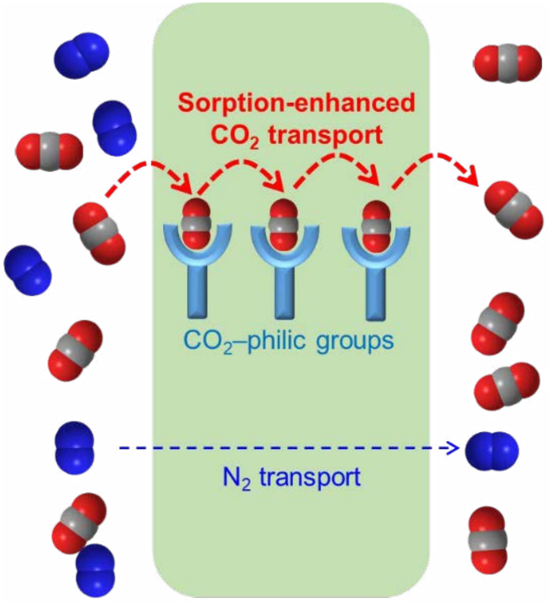

Figure 2: The highly branched amorphous polymers containing poly(1,3-dioxolane) (PDXL) in the branches interact favorably with CO_2, but not N_2, allowing for the design of solubility-selective membrane materials with superior performance for gas separations.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Mixed matrix materials of rubbery polymers and MOP	
Materials of Fabrication for Support Layer	—	Glassy polymers such as PAN, PSf	
Nominal Thickness of Selective Layer	nm	200–1,000	100–300
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	120	500
Membrane Performance			
Temperature	°C	60°C	60°C
CO_2 Pressure Normalized Flux	GPU	1,500–2,000	3,000
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	50	75
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	Mixed gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	300–600	
Shell-Side Fluid	—	feed	
Flue Gas Flowrate	ft^3/min	–	
CO_2 Recovery, Purity, and Pressure	%/%/bar	–	
Pressure Drops Feed/Permeate Side	psi/m	–	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	–	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} $cm^3/(cm^2 \cdot s \cdot cm$ mercury [Hg]) at 1 atmosphere (atm) and 0°C. For non-linear materials, the dimensional units reported shall be based on flux measured in $cm^3/(cm^2 \cdot s)$ (at 1 atm and 0°C) with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} $kgmol/(m^2 \cdot s \cdot kPa)$ (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities shall be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate stream.

technology advantages

- This membrane process builds upon innovative membrane process design using CO_2-selective membranes developed by MTR. If successfully developed, such membranes would outperform current leading membranes by at least 50%.

R&D challenges

- This approach of solubility-selective MMMs based on soluble MOPs directly addresses the two key challenges for membranes for CO_2 capture: (a) transport phenomena in new membrane materials, and (b) fabrication and use of the novel membrane systems in effective process designs.

status

Several batches of polymers, MOPs, and MMMs have been synthesized, and the characterization work has shown that increasing the MOPs loading in the MMMs increases pure-gas permeability. MMMs were thoroughly characterized, including density, glass transition temperature (Tg), and d-spacings. The morphology of the MMMs was characterized using scanning electron microscopy (SEM). The team will continue to optimize the polymer and MOPs structure, and the flat sheet membranes will be prepared.

available reports/technical papers/presentations

"Rational Development of Novel Metal Organic Polyhedra-based Membranes for CO_2 Capture," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/H-Lin-UB-SUNY-Metalorganic-Membrane.pdf*.

Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas

primary project goals

The Ohio State University (OSU), along with its partners Gas Technology Institute, the National Carbon Capture Center (NCCC), and American Electric Power, aims to develop a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture carbon dioxide (CO_2) from flue gas. The goal of this project is to achieve greater than 60 to 90% capture of the CO_2 with greater than 95% CO_2 purity ready for compression to 152 bar (2,200 pounds per square inch [psi]) for storage or enhanced oil recovery (EOR). For less than 90% capture, the goal is to achieve less than \$30/tonne CO_2 captured.

technical goals

- Optimize and characterize the transformational membrane (including morphology, transport properties, and stability).
- Synthesize an improved polymer support with a CO_2 permeance greater than 23,000 gas permeation units (GPU) for the membrane.
- Develop a polymeric composite membrane with CO_2 permeance greater than 3,300 GPU and CO_2/nitrogen (N_2) selectivity more than 140 at 77°C.
- Design and construct an integrated bench-scale testing system to be tested at OSU and NCCC.
- Complete a techno-economic analysis (TEA) of the project.

technical content

OSU and its partners will develop a cost-effective design and fabrication process for a novel transformational membrane and its membrane modules that capture CO_2 from flue gas. Based on density functional theory (DFT) calculations indicating a new carrier with high reactivity with CO_2, OSU will synthesize novel transformational polymer membranes with the new carrier, showing a very high CO_2 permeance of about 3,300 GPU (1 GPU = 10^{-6} cm^3[STP (Standard Temperature and Pressure])/(cm^2/s/cm mercury [Hg]) and a very high CO_2/N_2 selectivity of greater than 140. Optimization of the novel transformational membrane, scale-up of the membrane to a prototype size of about 14 inches wide in continuous roll-to-roll fabrication, and construction and testing of a bench skid for the integrated membrane process will be performed.

For the design of this membrane, OSU will use a cost-effective polyethersulfone (PES) support and coat a thin top layer of the membrane (Figure 1). This membrane design offers a low cost for the membrane element in commercial spiral-wound configuration (less than \$2.00/ft^2 or \$21/m^2). The prototype membrane will be used to fabricate at least six pilot-size membrane modules (each about 20-inch length and 35-m^2 membrane area) for testing with simulated flue gas at OSU and subsequently with actual flue gas at NCCC (Wilsonville, Alabama), using the skid to capture the CO_2 (at 60 to 90%) with at least 95% CO_2 purity (Figure 2). The prototype membrane modules will be in commercial spiral-wound configuration with a minimal pressure drop (less than 0.103 bar/meter or 1.5 psi/meter).

technology maturity:

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Polymeric Composite Membranes

participant:

The Ohio State University

project number:

FE00031731

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

W.S. Winston Ho
The Ohio State University
ho.192@osu.edu

partners:

Gas Technology Institute, National Carbon Capture Center (NCCC), American Electric Power

start date:

07.01.2019

percent complete:

9%

After the skid testing, OSU will determine the identity and concentration of any possible contaminates on the membrane via laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS), Fourier transform infrared spectroscopy (FTIR), X-ray photoemission spectrometry (XPS), and nuclear magnetic resonance spectroscopy (NMR).

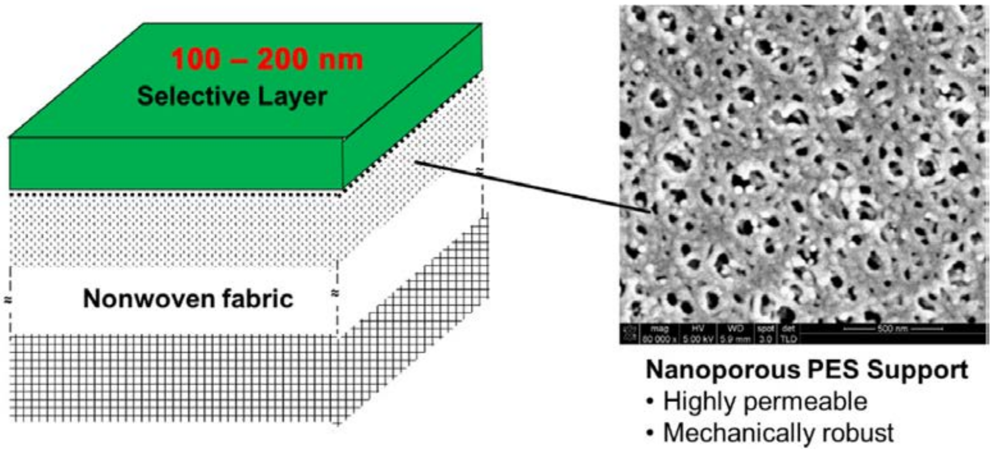

Figure 1: Schematic of thin-film composite membrane consisting of an amine-containing cover layer on a nanoporous PES support.

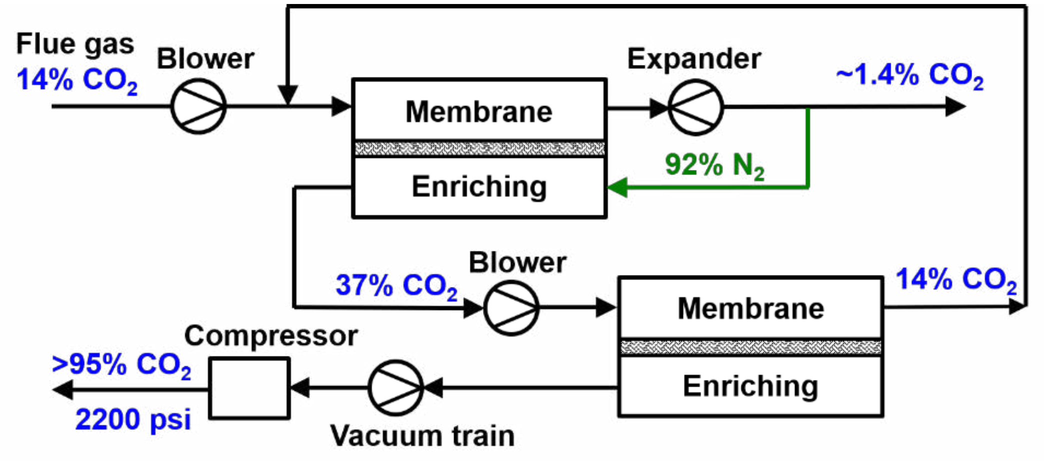

Figure 2: Process concept for two-stage membrane system.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	170	150–250
Membrane Geometry	—	flat sheet	flat sheet
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	1,600 hours	500 hours
Manufacturing Cost for Membrane Material	$/m^2	20	20
Membrane Performance			
Temperature	°C	57–77°C	57–77°C
CO_2 Pressure Normalized Flux	GPU	3,500 GPU	>3,300 GPU
CO_2/H_2O Selectivity	—	1	1
CO_2/N_2 Selectivity	—	170	>140

Proposed Module Design		*(for equipment developers)*
Flow Arrangement	—	Spiral-wound
Packing Density	m^2/m^3	about 2,000
Permeate-Side Fluid	—	vacuum or retentate recycle
Flue Gas Flowrate	ft^3/min	10.3
CO_2 Recovery, Purity, and Pressure	%/%/bar	>60%–90%, >95%, 1 bar
Pressure Drops Feed/Permeate Side	psi/m	1.5/1.5
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	40

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Permeate-Side Fluid – Either vacuum or a sweep gas.

Estimated Cost – Basis is m^2 membrane area.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport for amine-containing selective layer.

Contaminant Resistance – Resist up to 3 parts per million volume (ppmv) sulfur dioxide (SO_2).

Flue Gas Pretreatment Requirements – Removal of particulates and SO_2 polishing to 3 ppmv.

Membrane Replacement Requirements – Estimated approximately four years.

Waste Streams Generated – Nitrogen with water (H_2O), about 1% CO_2, and minor impurities.

Process Design Concept – See Figure 2.

technology advantages

This membrane consists of a thin selective polymer layer on a polymer support so that it can be made efficiently in continuous roll-to-roll manufacturing. The membrane offers high CO_2/N_2 selectivity at greater than 57°C, which does not require flue gas cooling or cryogenic distillation. The simplicity of this membrane design offers a low cost for the membrane element in commercial spiral-wound configurations. If successful, the proposed process can achieve less than $30/tonne CO_2 for 70% recovery.

R&D challenges

- Membrane stability in the presence of high-level contaminants, SO_2 and nitrogen oxide (NO_X).
- Design and fabrication of prototype spiral-wound membrane module with 8-inch diameter.
- Requires two membrane stages.

status

The project has commenced.

available reports/technical papers/presentations

Ho, W., Han, Y., “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas,” poster presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019.

Ho, W., Han, Y., “Novel Transformational Membranes and Process for CO_2 Capture from Flue Gas,” presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/Y-Han-OSU-Transformational-Membrane.pdf*.

Commercial-Scale Front-End Engineering Design Study for Membrane Technology and Research's Membrane Carbon Dioxide Capture Process

primary project goals

Membrane Technology and Research, Inc. (MTR) is conducting a front-end engineering design (FEED) study for an ~400-megawatt-electric (MWe) membrane carbon dioxide (CO_2) capture system installed at Basin Electric's Dry Fork Station in Gillette, Wyoming. The project builds on prior work in advancing MTR's membrane capture technology through small pilot testing and a pre-FEED study.

technical goals

- Complete FEED study of MTR capture process applied to the 400-MWe Dry Fork Station.
- Complete an environmental review of full-scale MTR membrane capture at Dry Fork Station.
- Provide a path to commercialization (detailed costs and construction plan) for a full-scale membrane capture plant based on actual equipment costs with a reliability of ±15%.

technical content

The project team is performing a FEED study of MTR's membrane CO_2 capture technology applied at commercial-scale as the next step in the development of the process, after the successful completion of small pilot testing and execution of a full-scale pre-FEED study. The study includes an estimate of the cost and performance of a first-of-its-kind commercial-scale membrane capture plant and a plan for its construction. The plant will be designed to capture approximately 5,600 tonnes per day (TPD) of CO_2 (approximately 2.0 million tonnes/year of CO_2), representing 70% of the Dry Fork Station power plant's CO_2 emissions. The system incorporates the innovative high-performance Polaris™ membrane, low-pressure-drop membrane modules, and a patented selective-recycle sweep module design. Earlier research has shown that the MTR process has the potential to capture CO_2 from coal-fired flue gas at the U.S. Department of Energy (DOE) capture cost target of less than \$40/tonne CO_2.

A preliminary process flow diagram of the membrane capture process to be examined in the FEED study is shown in Figure 1.

technology maturity:

Front-End Engineering Design (FEED)

project focus:

Polaris™ Polymeric Membrane-Based Process Retrofit

participant:

Membrane Technology and Research, Inc.

project number:

FE0031846

predecessor projects:

FE0026414
DE-NT0005312
FC26-07NT43085
FE0005795
FE0007553
FE0013118

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

Tim Merkel and Brice Freeman
Membrane Technology and Research, Inc.
tim.merkel@mtrinc.com
brice.freeman@mtrinc.com

partners:

Sargent & Lundy (S&L), Basin Electric, Trimeric Corporation, Electric Power Research Institute (EPRI), Efficient Fuel Additives (EFA)

start date:

10.01.2019

percent complete:

10%

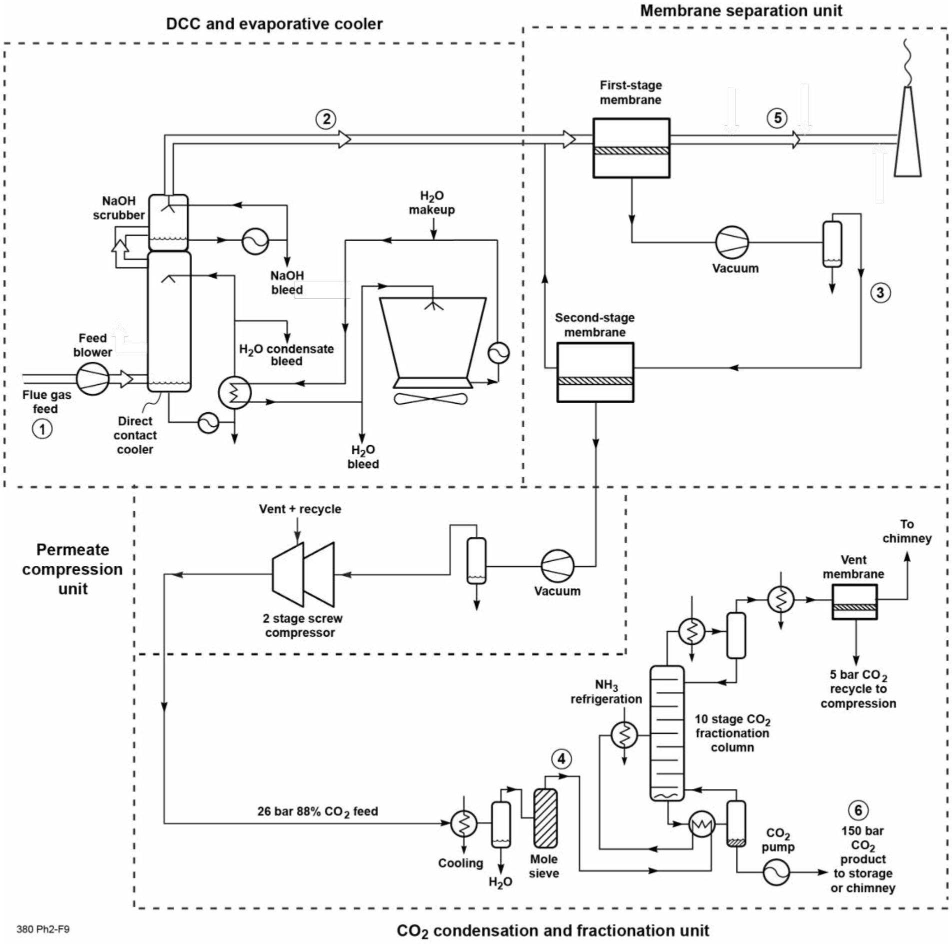

Figure 1: Preliminary design for full-scale membrane capture plant.

The main challenge of membrane technology for CO_2 capture is the low partial pressure of CO_2 in flue gas, resulting in a large membrane area being required due to the small driving force for separation. MTR's process includes three innovations that address this problem:

- A new class of membranes called Polaris that exhibit 10 times the CO_2 permeance of conventional gas separation membranes, leading to a large decrease in required membrane area and reduced capital cost.
- A membrane selective-recycle process that uses combustion air as a sweep stream to generate a driving force for transmembrane CO_2 transport. Separated CO_2 is recycled to the boiler, increasing the concentration of CO_2 in the flue gas, which reduces the energy and capital required for subsequent capture.
- A low-pressure-drop, low-cost membrane module design. The pressure differentials, and therefore the energy required, to circulate gas through the module is a fraction of that measured in conventional modules.

Single-stage membrane designs are unable to produce high-purity CO_2 combined with high CO_2 capture rates because the system performance is limited by the small pressure ratio across the membrane. MTR's multi-stage membrane process design (Figure 2) addresses the pressure ratio constraint to efficiently capture 50 to 75% of the CO_2 in flue gas. First, the combustion flue gas enters a primary capture module, which produces a permeate containing ~55 to 60% CO_2. This gas is then treated by a second membrane stage to further enrich the CO_2 stream to greater than 85% CO_2. The CO_2-rich permeate from the second-stage module is dehydrated and compressed. An optional selective-recycle membrane step can boost the CO_2 capture rate to 90% with the retentate from the primary capture module being fed into a countercurrent sweep module, from which the permeate is recycled back to the boiler via an air sweep. This increases the CO_2 concentration of the flue gas entering the initial module.

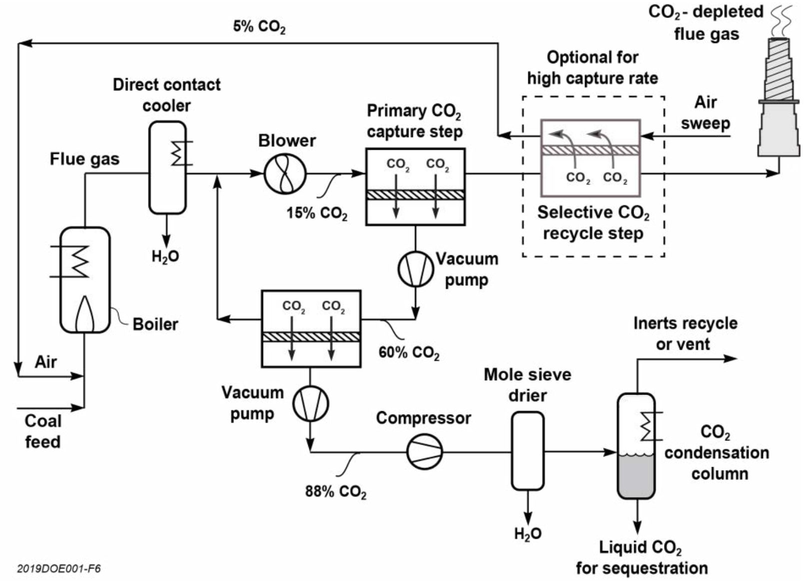

Figure 2: MTR CO_2 capture process.

MTR's Polaris membranes, developed in a previous DOE-funded project, DE-NT43085, exhibit high CO_2 permeance and high CO_2/nitrogen (N_2) selectivity for post-combustion flue gas applications. The thin-film composite membrane utilizes hydrophilic polymers. Commercial Polaris membranes offer a step-change improvement over typical commercial CO_2-selective membranes used for natural gas treatment, with an average CO_2 permeance of 1,000 gas permeation units (GPU) and a CO_2/N_2 selectivity of 50. Recent studies have improved membrane performance, demonstrating a CO_2 permeance of 3,000 GPU at lab-scale. The combination of these membranes with a novel sweep module design that utilizes incoming combustion air to generate a separation driving force greatly reduces the projected cost of CO_2 capture.

Membranes packed into spiral-wound modules is the most commonly used module design for commercial membrane installations today. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 3 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, which allow the flue gas and separated CO_2 to flow through the device. Each module contains 20 to 50 m^2 of membrane, meeting high packing-density performance targets. A total membrane area of about 0.5 to 1 million m^2 is required to achieve 90% CO_2 capture for a 550-MWe plant. Figure 4 shows a proposed design for efficient module packing in a full-scale membrane system that consists of seven tubes nested in a single pressure vessel. Each set of modules is stacked on a skid and connected together to form a single "mega-module." About 130 mega-module skids are required for a 550-MWe power plant. The process parameters for the Polaris membranes in a spiral-wound module configuration are shown in Table 1.

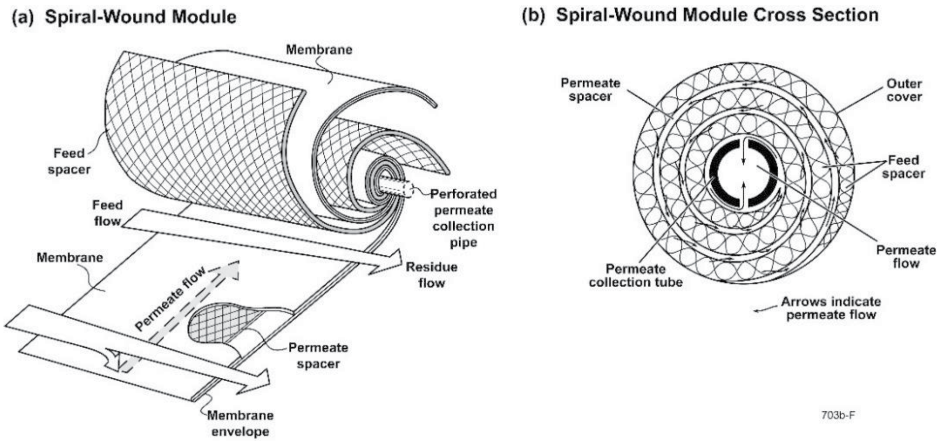

Figure 3: Schematic diagram of a spiral-wound membrane module.

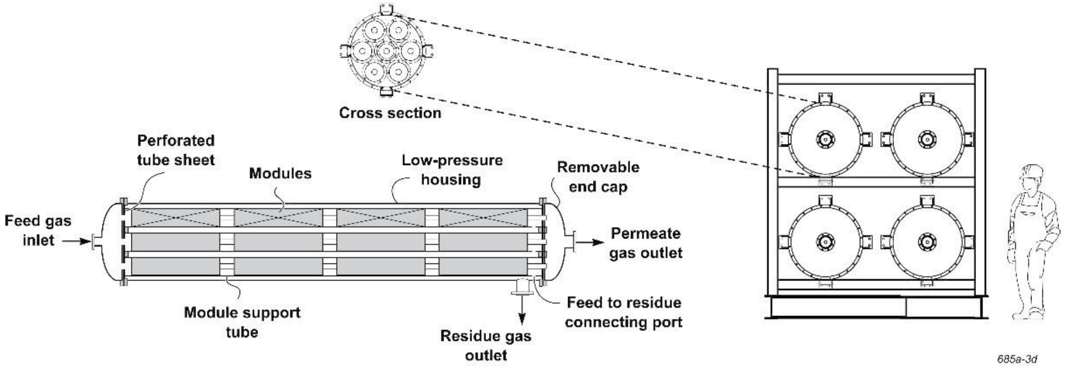

Figure 4: Full-scale membrane system design using spiral-wound modules.

TABLE 1: MEMBRANE PROCESS PARAMETERS IN SPIRAL-WOUND MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	spiral
Max Trans-Membrane Pressure	bar	70
Hours Tested without Significant Degradation	—	11,000
Manufacturing Cost for Membrane Material	$\$/m^2$	10
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,000
CO_2/H_2O Selectivity	—	0.3
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow and countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flow rate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >96% / 140
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Under a previous DOE-funded project, DE-FE0005795, a membrane skid designed to capture 1 tonne of CO_2 per day from a 7,000-standard-m^3/day (250,000 standard cubic feet per day [scfd]) flue gas slipstream was installed and tested at the National Carbon Capture Center (NCCC; Figure 5). The skid held up to eight (four crossflow and four countercurrent sweep), 8-inch-diameter Polaris membrane modules. The system accumulated more than 11,000 hours of operation with flue gas testing spiral-wound modules in both steps of the MTR process: a capture step operating with permeate vacuum and a selective-recycle step that uses air sweep to provide driving force for CO_2 removal. The test demonstrated membrane operation in commercial-scale modules and determined typical membrane lifetimes under coal combustion flue gas operating conditions.

Figure 5: Membrane skid used for 1-TPD bench-scale slipstream testing at NCCC.

Scale-up of the Polaris capture system from the 1-TPD bench-scale unit to a 20-TPD small pilot system using commercial-scale membrane components was also completed in FE0005795. The 20-TPD system is a two-level design, with membrane modules located on the upper level, and all rotating and associated equipment on the lower level. Like the 1-TPD unit, the 20-TPD unit was designed for slipstream operation at NCCC and is shown in Figure 6.

Figure 6: 20-TPD small pilot system installed at NCCC.

Pilot-scale operation of the existing 1-MWe (20-TPD) membrane CO_2 capture system, integrated with a Babcock & Wilcox (B&W) 0.6-MWe coal-fired research boiler, was performed in the DOE-funded project DE-FE0026414 to determine how various membrane parameters impact the performance of a boiler system. Operation of the integrated membrane-boiler system involves the recycling of CO_2-laden air back to B&W's boiler via a countercurrent sweep membrane. A modest reduction in boiler efficiency due to recycled CO_2 was measured (1.8%) at 90% capture, showing that the selective-recycle process is feasible and the impact on boiler performance is relatively small.

While previous tests have shown that recycle to the boiler is feasible, operation at ~70% capture without recycle is of most interest, because it offers lower capture costs and still reduces coal plant emissions to less than that of a natural gas power plant. Therefore, the FEED study focuses on a two-stage membrane system that captures 70% of the CO_2 in the flue gas without selective recycle and concentrates the gas to about 85% CO_2. A CO_2 purification unit is then used to produce greater than 99% CO_2 at 150 bar. For the full-scale capture plant, container-sized skids will be used as the basic modular building block. An evaluation of the most efficient arrangement of the membrane capture skids is being conducted in the FEED study.

MTR applied an alternative approach to membrane packing to develop plate-and-frame modules optimized for low-pressure operation. Testing of the small pilot-scale 20-TPD system at NCCC and B&W incorporated this novel large-area membrane module designed by MTR in project DE-FE0007553. A single 100-m^2 membrane module element has the equivalent membrane area of five 8-inch spiral-wound membrane modules. Figure 7 shows the plate-and-frame module design and Figure 8 shows a full-scale mega-module, which consists of a pressure vessel with five module elements, reducing the footprint of the plant. The simple, straight flow path of the new module design results in a pressure-drop that is almost four times lower than that measured for the spiral-wound module, as shown in Figure 9, resulting in energy and cost savings. At full-scale, this reduced pressure-drop represents about a 10-MWe savings in fan power. The plate-and-frame module skids are projected to cost $30/$m^2$ of membrane at full commercialization stage. Process parameters for the Polaris membranes in a plate-and-frame module configuration are shown in Table 2.

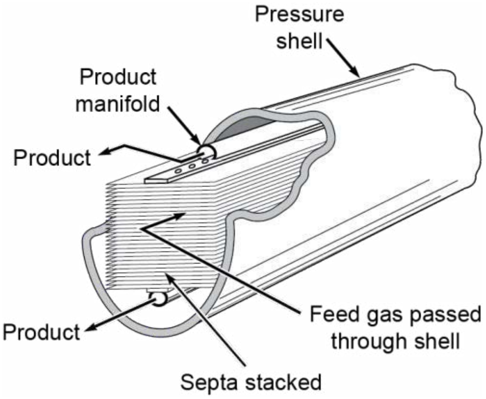

Figure 7: Plate-and-frame module.

Figure 8: Prototype plate-and-frame module during testing at NCCC.

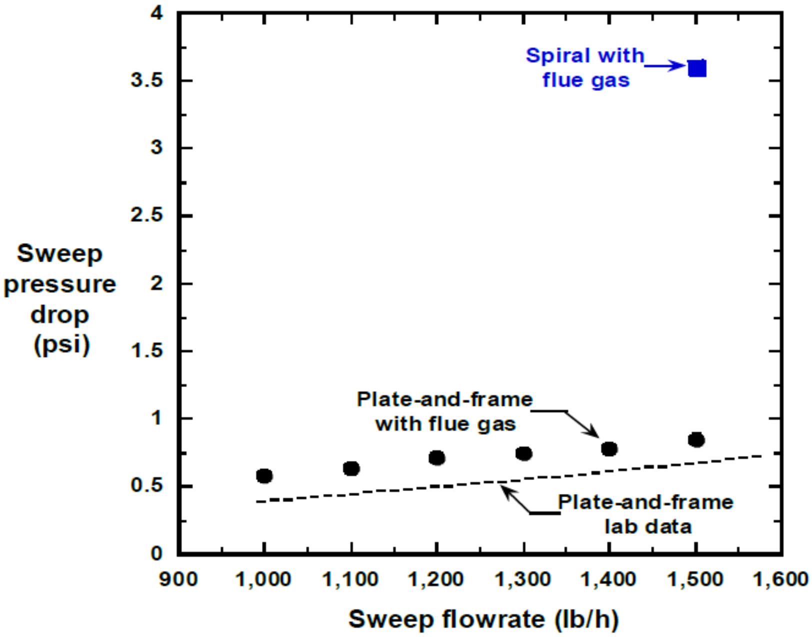

Figure 9: Measured pressure-drop in plate-and-frame module, compared to spiral-wound module.

TABLE 2: MEMBRANE PROCESS PARAMETERS IN PLATE-AND-FRAME MODULE CONFIGURATION

Materials Properties	Units	Design Value
Materials of Fabrication for Selective Layer	—	proprietary polymer
Materials of Fabrication for Support Layer	—	proprietary polymer
Nominal Thickness of Selective Layer	µm	<1
Membrane Geometry	—	plate-and-frame
Max Trans-Membrane Pressure	bar	2
Hours Tested without Significant Degradation	—	1,500
Manufacturing Cost for Membrane Material	$/m^2	30
Membrane Performance		
Temperature	°C	30
CO_2 Pressure Normalized Flux	gpu or equivalent	1,700
CO_2/H_2O Selectivity	—	0.5
CO_2/N_2 Selectivity	—	30
CO_2/SO_2 Selectivity	—	0.5
Type of Measurement	—	Mixed gas
Module Design		
Flow Arrangement	—	crossflow, partial countercurrent
Packing Density	m^2/m^3	1,000
Shell-Side Fluid	—	N/A
Flue Gas Flow rate	kg/hr	
CO_2 Recovery, Purity, and Pressure	%/%/bar	70% / >96% / 150
Pressure-Drops Shell/Tube Side	bar	0.1
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	50

Further improvements to the membrane module design to reduce fabrication costs resulted in a 3D-printed module prototype based on injection-molded, fiber-reinforced thermoplastics. The modules are designed to fit one on top of another to create a module stack, which is placed on a container-sized skid, as shown in Figure 10. The large membrane capture system will consist of multiple container-sized membrane module skids that will be prefabricated using advanced, high-volume manufacturing and shipped to the plant site. This approach minimizes expensive site assembly and installation work and enhances fabrication quality. The FEED study will evaluate and quantify savings based on the modular construction approach.

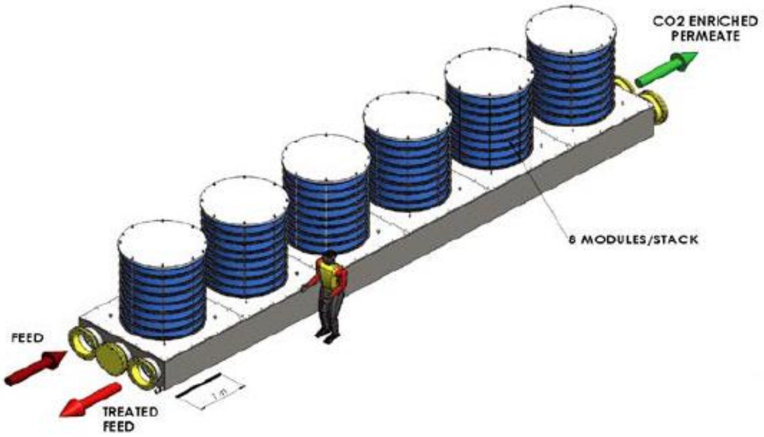

Figure 10: Drawing of container-sized skid housing six module stacks. Eight individual modules are connected together to form each stack.

MTR also previously evaluated a hybrid membrane-absorption process system combining Polaris membranes and an amine solvent-based capture system under DOE-funded project DE-FE0013118. The integrated system combines MTR's plate-and-frame sweep module with a CO_2 capture system developed by the University of Texas at Austin (UT-Austin) that uses a piperazine (PZ) solvent and advanced high-temperature/high-pressure regeneration. This hybrid design requires significantly less membrane area for a two-step CO_2 capture process, compared to MTR's all-membrane process. In the hybrid design, MTR's Polaris membrane recycle stage enriches flue gas from ~13 to ~20% CO_2 and a 5 molal PZ advanced flash stripper with cold-rich bypass is optimized to take advantage of the higher CO_2 concentration. Both series and parallel configurations were considered with the hybrid design, as shown in Figure 11. Process modeling of MTR's plate-and-frame skid integrated with UT-Austin's Separations Research Program (SRP) 0.1-MWe pilot plant showed that a hybrid-parallel configuration offers a lower cost of capture than the series configuration. However, the benefits of a hybrid system do not outweigh the costs.

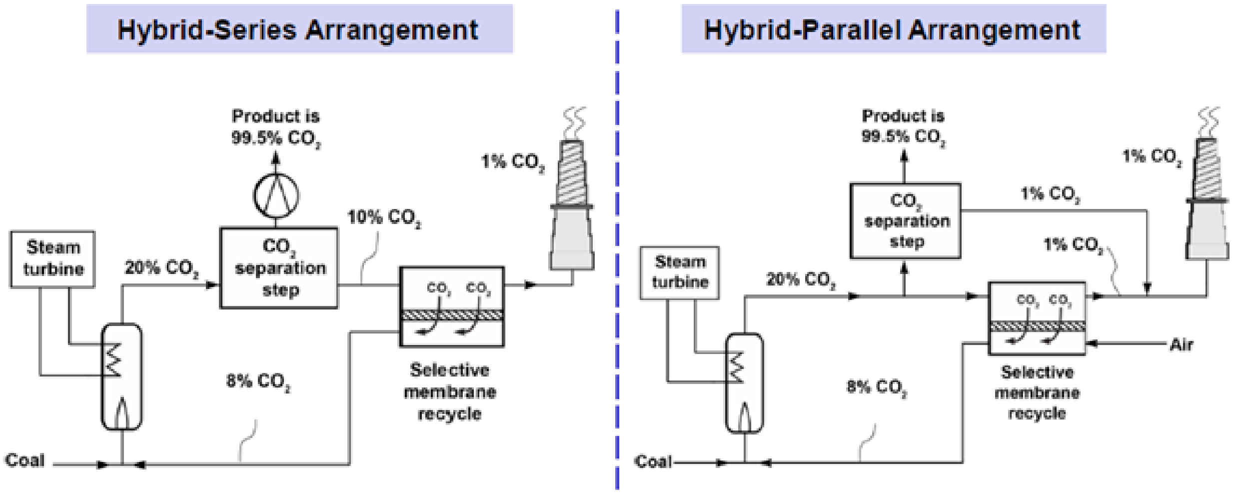

Figure 11: Two hybrid configurations for membrane-absorption CO_2 capture process.

MTR is also currently working on three additional DOE-sponsored projects related to this study. DE-FE0031587 is a three-phase project for the design, construction, and operation of a large-scale pilot system to treat 10 MWe of flue gas at Wyoming's Integrated Test Center, with support from Basin Electric's Dry Fork Station power plant. The Phase I feasibility program is completed and the project is now in Phase II. The National Environmental Policy Act (NEPA) review and Environmental Information Volume (EIV) that were completed in Phase I can be leveraged in this FEED project. The second project currently underway (DE-FE0031589) is a pre-FEED study led by the Electric Power Research Institute (EPRI), in collaboration with MTR, Nexant, and Bechtel, to evaluate a full-scale (640-MWe) membrane capture technology applied to Duke Energy's East Bend Station. The general configuration from the pre-FEED capture plant design is being used as the starting point for the Dry Fork Station FEED study. In project DE-FE0031591, MTR and its partners are scaling-up the next-generation Polaris membranes and modules to a final form optimized for commercial use, and validating their performance in an engineering-scale field test at Technology Centre Mongstad.

The Dry Fork Station power plant is an ideal location for installation of a membrane CO_2 capture system due to:

- High CO_2 content (~15% on dry basis) in the flue gas increases efficiency of membrane capture system.
- Cool, dry climate allows cooling water operation at ~25°C, resulting in an energy savings of 25 MWe/tonne of CO_2 captured.
- Dry Fork Station generates electricity at a low cost, which is important for a capture process powered only by electricity.
- CO_2 utilization opportunities with nearby oil fields and CO_2 pipeline.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow-fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed- or pure-gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as Hg, arsenic, etc., was examined in the field tests at NCCC and no major issues were found.

Flue Gas Pretreatment Requirements – The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. The field tests at NCCC treated post-FGD flue gas, and in extended testing (more than 13,000 hours), fouling was not a significant issue.

Membrane Replacement Requirements – The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

Waste Streams Generated – The membrane process will recover greater than 95% of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

Process Design Concept – See Figure 1.

technology advantages

- The Polaris membranes developed are more than 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The membrane material has a high tolerance to wet acid gases and is inert to O_2.
- The membrane system has a compact footprint and low energy cost.
- The membrane capture system can recover water from flue gas.
- The use of an existing air stream to generate a CO_2 partial-pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO_2 from the air sweep to the boiler increases the CO_2 partial-pressure driving force for separation in the initial CO_2 separation step (either membrane or absorption/stripper unit), reducing total system cost.

R&D challenges

- Uncertainty in vacuum pumps and compression equipment efficiency and stability treating flue gas.
- Potential performance problems with the CO_2 purification equipment.
- Scale-up of advanced Polaris membranes that exhibit a CO_2 permeance of 3,000 GPU to reduce the capital cost of the membrane system.

status

MTR is reviewing the preliminary heat and mass balances and process flow diagrams that were previously prepared, and then will decide on the design basis for the full-scale capture plant. Based on the design basis, the team will prepare a preliminary process design for the full-scale capture plant, focusing on design of the capture plant equipment (direct contact cooler columns, evaporative coolers, number and layout of the membrane skids, compression equipment, and the design and size of the CO_2 purification unit and refrigeration equipment, etc.).

available reports/technical papers/presentations

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION NOVEL CONCEPTS

Advanced Manufacturing to Enable Enhanced Processess and New Solvents for Carbon Capture

primary project goals

Lawrence Livermore National Laboratory (LLNL), Harvard University, and Carnegie Mellon University (CMU) teamed up to develop processes that enhance and enable the use of new solvents to capture carbon dioxide (CO_2). Primarily, the project aimed to develop and evaluate the concept of Micro-Encapsulated CO_2 Sorbents (MECS) and to develop new concepts for absorber packings for solvent-based CO_2 capture (advanced packings). The technology uses advanced manufacturing techniques to reduce the cost of carbon capture for coal-fired power plants and supports the U.S. Department of Energy's (DOE) Carbon Capture Program's goal of advancing the technical, economic, and environmental performance of second-generation and transformational systems and technologies for future deployment.

technical goals

- Develop processes to enhance and enable the use of thermodynamically favorable solvents to capture CO_2 using advanced manufacturing techniques to encapsulate the solvents in a permeable membrane.
- Identify and assess improvements to the design of industrial CO_2 absorbers made possible by advanced manufacturing.
- Identify the best process configuration for encapsulated solvents.
- Measure the properties of potential solvents using LLNL's microfluidic technique for rapid characterization of solvent properties.

technical content

LLNL, Harvard University, and CMU formed a team to develop processes that enhance and enable the use of advanced solvents to capture CO_2 from coal-fired power plants using advanced manufacturing techniques. New solvents for the capture of CO_2 pose challenges for conventional equipment due to slow kinetics, high viscosity, phase changes, corrosivity, or other issues. The team formed to develop processes to enhance and enable the use of these otherwise thermodynamically favorable solvents to capture CO_2 using advanced manufacturing techniques to encapsulate the solvents in a permeable membrane to overcome these challenges.

One of the key goals of the project was to take the micro-encapsulation concept, which had previously been demonstrated with sodium and potassium carbonate, and apply it to new solvents, especially water-lean solvents. Compatibility among the solvent, shell material, and production methods turned out to be a critical

technology maturity:

Laboratory-Scale

project focus:

Encapsulation of Solvents in Permeable Membrane for CO_2 Capture

participant:

Lawrence Livermore National Laboratory

project number:

FWP-FEW0194

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
Isaac.aurelio@netl.doe.gov

principal investigator:

Joshuah Stolaroff
Lawrence Livermore National Laboratory
Stolaroff1@llnl.gov

partners:

Harvard University,
Carnegie Mellon University

start date:

03.01.2015

percent complete:

100%

challenge, and extensive efforts to solve this challenge ran the course of the project.

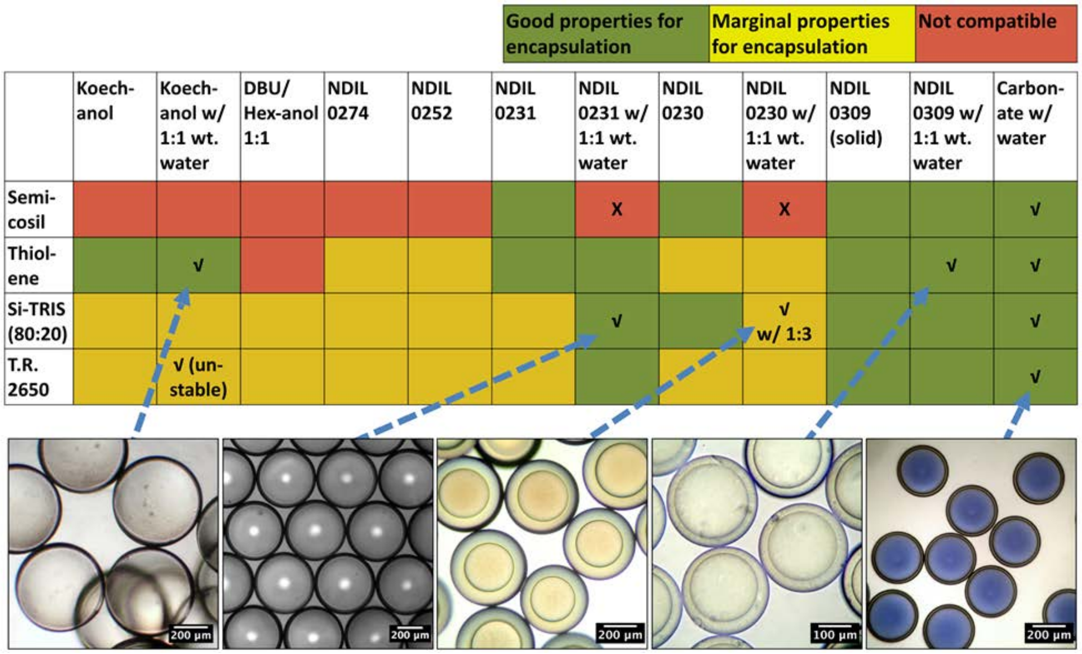
The primary selection criterion for a MECS shell material is high permeability to CO_2. Further criteria include heat stability at the regeneration temperature of the solvent (typically 80 to 120°C), mechanical robustness in the chosen process conditions (e.g., fluidized bed), and chemical compatibility with the solvents (CO_2-binding organic liquid [CO_2BOL], nanoparticle-organic hybrid material [NOHM], ionic liquid [IL], carbonates). For microfluidic production, ultraviolet (UV)-curable polymers with precursors that are liquid at room temperature are particularly suitable. Silicones have among the highest CO_2 permeabilities of common polymer classes, with typical values on the order of 3,000 barrer. After extensive screening and through past and concurrent work on encapsulation, two commercial silicones were identified as promising shell materials (Semicosil 949 and Tego-Rad 2650). Two new, in-house polymer classes, identified as Thiolene and SiTRIS, were developed for capsule screening. During the project, variations of Thiolene have been formulated by slightly changing the compositions for more robust capsule production and better suitability with scale-up production.

The shell materials tested in this project are summarized in Table 1, showing some of their relevant properties.

TABLE 1: SUMMARY OF SHELL MATERIAL CANDIDATES WITH BASIC PROPERTIES

Name	Manufacturer	Material	Permeability (barrer)	Amine Compatibility	Mechanical Properties	Curing Time
Semicosil 949	Wacker	Silicone	3100	No	Elastic, strong, tacky	30 mins
Thiol-ene	LLNL	Silicone	2700	Yes	Elastic, strong, tacky	30 secs
SiTRIS (80:20)	LLNL	Acrylic	400	After curing	Stiff, strong, untacky	10 secs
Tego Rad 2650	Evonik	Silicone	3200	After curing	Elastic, friable, untacky	10 secs

Several core solvents (Koechanol, 1,8-diazabicyclo[5.4.0]-undec-7-ene [DBU]/hexanol, five ILs, and an NOHM) were tested for compatibility with shell material candidates. The screening process involved three main tasks: (1) a solubility test, to determine whether the solvent would dissolve solid shell material; (2) a test of interfacial stability, to determine if the solvent and shell material precursor maintain distinct liquid phases; and (3) a curing test to determine if the shell material cures by UV in the presence of the solvent. Results of the screening are summarized in Figure 1.



🟩	🟨	🟥
Good properties for encapsulation	Marginal properties for encapsulation	Not compatible

	Koech-anol	Koech-anol w/ 1:1 wt. water	DBU/ Hex-anol 1:1	NDIL 0274	NDIL 0252	NDIL 0231	NDIL 0231 w/ 1:1 wt. water	NDIL 0230	NDIL 0230 w/ 1:1 wt. water	NDIL 0309 (solid)	NDIL 0309 w/ 1:1 wt. water	Carbon-ate w/ water
Semi-cosil	🟥	🟥	🟥	🟥	🟥	🟩	🟥 X	🟩	🟥 X	🟩	🟩	🟩 √
Thiol-ene	🟩	🟩 √	🟥	🟨	🟨	🟩	🟩	🟨	🟨	🟩	🟩 √	🟩 √
Si-TRIS (80:20)	🟨	🟨	🟨	🟨	🟨	🟨	🟩 √	🟩	🟩 √ w/ 1:3	🟩	🟩	🟩 √
T.R. 2650	🟨	🟨 √ (un-stable)	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟩	🟩	🟩 √

Figure 1: Summary of IL/shell material compatibility screening tests. "X"s mark unsuccessful capsule production; checks mark successful capsule production.

Multiple options to synthesize larger quantities (~1 kg) of encapsulated ILs were explored. Of those, the most successful was a new process developed specifically for the project. Figure 2 shows the In-Air Drop Encapsulation Apparatus (IDEA) built at LLNL. The system pumps fluids out of a coaxial nozzle to form a core-shell fluid jet in air. The jet of fluid is broken into drops with the use of an external device (a contact speaker in this case), which causes the nozzle to vibrate. When a sinusoidal wave with a certain frequency (related to fluid properties, flow rate, and nozzle size) is applied, monodisperse drops are formed. Capsules are produced when the drops are exposed to sufficient UV to crosslink the polymer shell. This method does not require a carrier fluid and potentially provides better control and reproducibility than the parallel microfluidic approach. IDEA was the leading option for scale-up of carbonate and IL capsules, with a maximum rate up to 400 g/hr per nozzle.

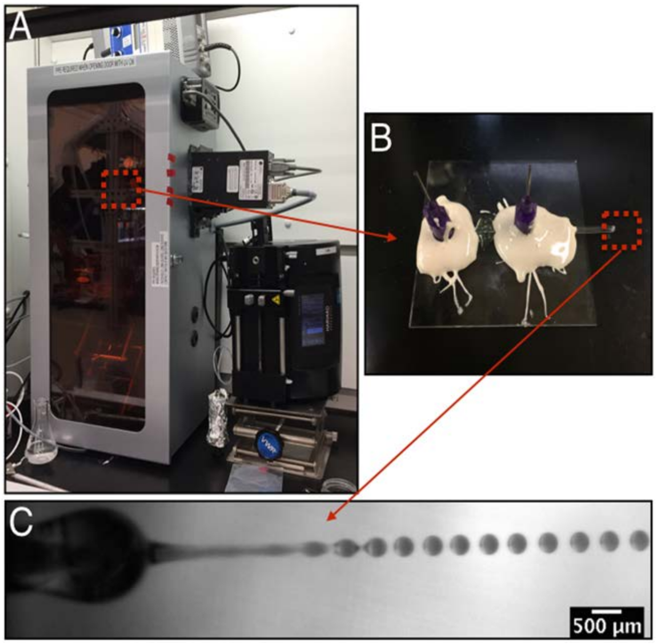


Figure 2: (A) Overview of in-air drop generator box; (B) a device example that was used to produce core-shell droplets; (C) production of carbonate SiTRIS droplets.

After developing formulations for the previously discussed solvents, six candidate MECS were selected for inter-comparison. The solvents were sodium carbonate (Na_2CO_3) solution, uncatalyzed and with two different promoters; two IL solvents; and one CO_2BOL. It was found that 17 wt% Na_2CO_3 capsules containing cyclen as a promoter outperformed Na_2CO_3 capsules with no promoter or with sarcosine as a promoter in terms of absorption rate. It was also discovered that the CO_2BOL liquid permeated or broke the capsule shell, and thus these MECS were not cycled. Both of the IL MECS outperformed the Na_2CO_3 capsules, having roughly twice the capacity and higher absorption rates. However, production of the IL MECS proved much more difficult to scaleup while maintaining multicycle performance.

One of the key innovations in this project is the development of printed composite sorbents, a variation of the capsule-based MECS that originated the research. The composites combine the same or similar silicone shell materials used for capsules with Na_2CO_3 or other solvents; however, rather than making core-shell spherical capsules, filaments or meshes of homogeneous material were produced.

The composite sorbents are similar to MECS in that the final material is composed of aqueous Na_2CO_3 solutions surrounded by CO_2 permeable silicone. Both materials use fine feature sizes (less than 500 µm) to enable high mass transfer rates into the carbonate solutions. However, the composite sorbents have the benefit of being 3D-printable, which enables geometric control of the material that can be optimized for parameters, such as pressure drop, though the system. The impact of geometry on CO_2 absorption rate was investigated. The smallest filament sizes were able to achieve slightly better rates than core-shell MECS.

These initial investigations of composites applied 3D printing. However, in follow-on projects, production was generalized to use either a simple extrusion of random mats or waffle patterns cast to make thin sheets. Thus, composites can achieve similar surface areas and mass transfer rates as spherical MECS and similar or better loading, but their production is more scalable. For this reason, composite MECS are the focus of several follow-on commercialization efforts.

One of the key goals of the fourth project year was to develop an integrated, automated, bench-scale packed-bed apparatus for testing extended cycles of absorption-desorption and for testing realistic regeneration conditions with steam. This apparatus was built and successfully tested. It contains twin jacked reactor columns (see Figure 3), which can be operated simultaneously to cycle between absorption and regeneration. The design enables the use of steam to directly or indirectly heat up sorbents.

Figure 3: Detail of the automated sorbent testing system.

A process diagram is shown in Figure 4. A gas line can also be used to purge a column depending on cycling requirements.

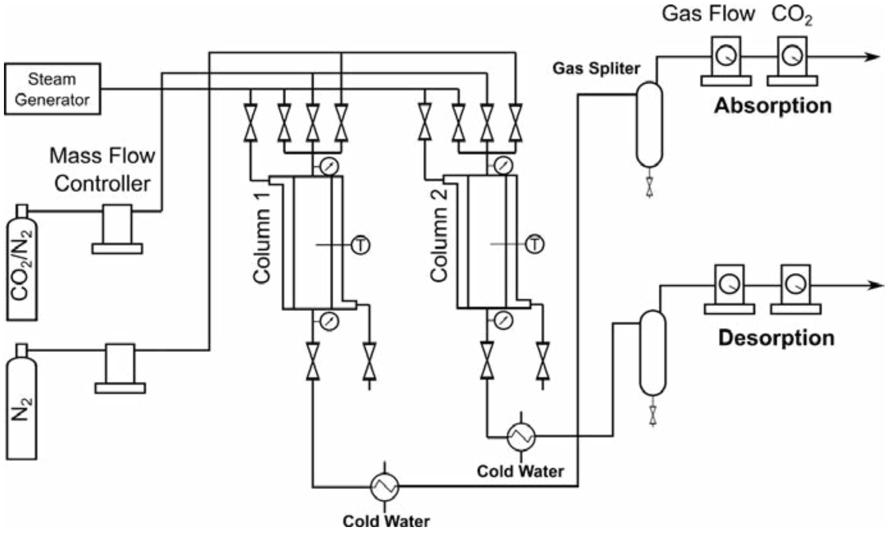


Figure 4: Process diagram of the automated sorbent testing system.

Steam, nitrogen (N_2), and/or a 10% N_2/CO_2 mixture can flow through the main columns. Steam can also flow through the jacketed portion of the column to indirectly heat the microcapsules. After passing through the column, the gas stream passes through a heat exchanger to condense any water and steam. The gas/condensed water mixture then passes through a gas splitter to separate the two phases. Lastly, the gas stream is passed through a flow meter and CO_2 meter.

After constructing the sorbent testing system, absorption-desorption tests on Na_2CO_3 MECS were conducted, focusing on direct steam regeneration. The gram-scale and smaller column experiments of prior test apparatuses could not be configured for these tests.

The CO_2 breakthrough curves for eight sequential cycles and the resulting integrated absorbed CO_2 amounts are shown in Figure 5. In the first cycle, just after loading the capsules into the column, breakthrough was nearly instantaneous, though there was a long tail to reach the final outlet concentration, suggesting slow absorption kinetics. In following cycles, breakthrough and equilibrium were both obtained more quickly. The result of this is that the amount of CO_2 that was able to be absorbed decreased over time.

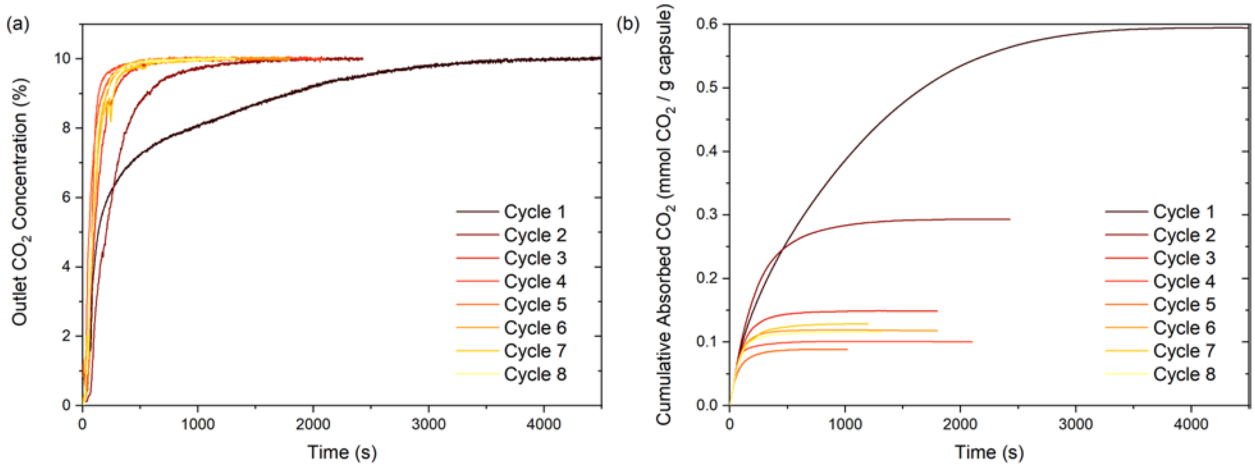


Figure 5: (a) CO_2 breakthrough curves for 10% CO_2/N_2 at ~500 sccm through the MECS column, followed by desorption in steam. (b) Cumulative absorbed CO_2 as a function of time.

Despite the initial setbacks with the material, the system can perform cyclic absorption and steam desorption. In future work, consistent performance should be demonstrated, such as that observed in the previously mentioned gram-scale experiments, using a different MECS formulation.

In the second half of the project, much of the focus for MECS was on process design and measurements to enable techno-economic analysis (TEA). From the beginning, fluidized-bed, fixed-bed, and moving-bed configurations had been considered. It remained difficult to down-select among these options. In an absorber sizing study and a separate process design and TEA, it was found that capsule MECS-based fixed beds or fluidized beds were generally larger than solvent towers with monoethanolamine (MEA) for carbon capture from a coal power plant. The TEA also found that the MECS system had higher overall costs than an MEA system. Because of this, and even allowing that better process configurations for MECS may be achievable, it is still unlikely that MECS will outperform second-generation solvents for carbon capture at power plants. Solids handling and heat integration with solids is a major challenge for MECS and for any sorbent system to outperform commercial solvents.

However, Na_2CO_3-based MECS have some special properties that may make them commercially attractive in niche applications. Chief among these is bio-compatibility (low toxicity). Also, as a sorbent, MECS downscale to small capture applications much better than solvents and, unlike most sorbents, are water-tolerant. MECS are also inexpensive compared to many other chemisorbents, like metal-organic frameworks (MOFs). Leveraging these advantages, MECS commercialization efforts are ongoing.

TABLE 2: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	980–1,050	—
Bulk Density	kg/m^3	~650	—
Average Particle Diameter	mm	0.5	0.3
Particle Void Fraction	m^3/m^3	0	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg$_f$	—	—
Manufacturing Cost for Sorbent	$/kg	100–1,000	5—10
Adsorption			
Pressure	bar	0.05–10	—
Temperature	°C	20–60	—
Equilibrium Loading	mol CO$_2$/kg	0.8–2	2–3
Heat of Adsorption	kJ/mol CO$_2$	~44–90	—
Desorption			
Pressure	bar	1	1–80
Temperature	°C	80–100	80–160
Equilibrium CO$_2$ Loading	g mol CO$_2$/kg	—	—
Heat of Desorption	kJ/mol CO$_2$	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	packed bed or fluidized bed	
Flue Gas Flowrate	kg/hr	—	
CO$_2$ Recovery, Purity, and Pressure	% / % / bar	90	95 1--140
Adsorber Pressure Drop	bar	<0.5	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO$_2$-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical.

Sorbent Contaminant Resistance –Water tolerant.

Sorbent Attrition and Thermal/Hydrothermal Stability – Lowered CO_2 capture capacity is seen with cyclic absorption and steam desorption in the bench-scale system. In future work, the team would most likely be able to demonstrate more consistent performance, such as that observed in the gram-scale experiments, using a different MECS formulation.

Process Design Concept – See above

technology advantages

- Microcapsules are high surface area, permeable microreactors that enable advanced solvents to achieve transformational carbon capture.
- MECS may overcome all or many of the characteristics inherent in some new CO_2 capture sorbents, which include slow kinetics, high viscosity, phase changes, corrosivity, or other issues.
- Overcomes mass transfer limitations of advanced solvents, reducing size and capital cost of absorber.

R&D challenges

- Selection of suitable shell materials.
- Testing packing methods.
- Developing capsule production scale-up.
- Capsule curing.
- Determining thermodynamic properties of micro-scale solvents.

status

This project has concluded.

available reports/technical papers/presentations

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Stolaroff, J., “Advanced Manufacturing to Enable New Solvents and Processes for Carbon Capture,” presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/projects/plp-download.aspx?id=13078&filename=J-Stolaroff-LLNL-Advanced-Manufacturing-for-New-Solvents.pdf*.

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Vericella, J. J.; Duoss, E. B.; Stolaroff, J. K.; Baker, S. E.; Hardin, J. O.; Lewicki, J.; Glogowski, E.; Floyd, W. C.; Valdez, C. A.;

Smith, W. L.; Jr., J. H. S.; Bourcier, W. L.; Spadaccini, C. M.; Lewis, J. A. & Aines, R. D. "Encapsulated liquid sorbents for carbon dioxide capture." *Nature Communications,* 2015, 6, 1-7.

Stolaroff, J.K., Bourcier, W.L., "Thermodynamic assessment of microencapsulated sodium carbonate slurry for carbon capture." *Energy Procedia* 63 (2014) 2331 – 2335.

Process Intensification for Carbon Capture

primary project goals

Altex Technologies Corporation, in partnership with Pennsylvania State University (PSU), have previously developed the integrated temperature and pressure swing (ITAPS) carbon capture system. The ITAPS system utilizes advanced molecular basket sorbents (MBSs) on microchannel heat exchangers, which can be quickly cycled between carbon dioxide (CO_2) sorption from coal-derived syngas and desorption into low-pressure steam exhausted from steam turbines in an integrated gasification combined cycle (IGCC) power system. This would replace the typical three-stage Selexol system (for acid gas removal and pre-combustion carbon capture in the context of IGCC) with smaller and energy-efficient desorption and sorption units.

The project is currently in Phase IIB, with the goal of developing the Compact Rapid Cycling CO_2 Capture (CRC3) system that would extend the concept of using the MBSs on microchannel heat exchangers to post-combustion applications. Also, work is continuing to reduce the size (and therefore costs) of the Altex CO_2 capture system by coating both sides of the heat exchanger with a sorbent with rapid sorption-desorption kinetics. Current objectives are to design a prototype-scale system for CRC3 to improve the MBSs for higher heat- and mass-transfer rates, to fabricate and test a prototype-scale CRC3 sorbing unit on actual flue gas, and to perform techno-economic analysis (TEA) of the CRC3 system integrated into a large-scale power plant.

technical goals

- Improve sorbent capacity and sorption/desorption rates.
- Demonstrate heat integration of sorption and desorption processes.
- Conduct prototype-scale testing of a post-combustion capture-geared prototype unit on actual flue gas at 10 to 50 standard liters per minute (slpm), equivalent to 0.2 to 1.0 kilowatt-electric (kWe).

technical content

The Altex team previously developed the ITAPS process with a view to produce a low-cost CO_2 capture technology that leverages process intensification principles (i.e., process capital and energy costs of the capture systems are shared with other unit operations of the power plant). In ITAPS, Altex-developed microchannel heat exchangers were wash-coated with PSU's advanced MBSs. By wash-coating the MBS on the microchannel heat exchanger, high heat- and mass-transfer rates were obtained. These high rates allow for quick cycling between CO_2 sorption and desorption. This should allow smaller sorption units with a lower capital cost than a typical three-stage Selexol system. Operating costs are also lower than a three-stage Selexol system because the system can operate at lower pressures and does not require circulation of a liquid amine sorbent. The system can also be integrated

technology maturity:

Prototype-Scale, Actual Flue Gas (equivalent to 0.2-1.0 kWe)

project focus:

Molecular Basket Sorbents on Microchannel Heat Exchangers

participant:

Altex Technologies Corporation

project number:

SC0013823

predecessor projects:

N/A

NETL project manager:

Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:

Kenneth Lux
Altex Technologies Corporation
ken@altextech.com

partners:

Pennsylvania State University, NCCC

start date:

06.08.2015

percent complete:

75% (combined Phases I, II, & IIB)

with the power plant steam loop to improve energy efficiency; the heat of sorption can be used to preheat the boiler feedwater, while the heat of desorption can be used to condense about 50% of the steam turbine exhaust. In terms of process integration, Figure 1 depicts the ITAPS units' process with boiler feed water flows and steam turbine flows (for sorption and desorption modes, respectively), which would be encountered in integrating an ITAPS system within the context of an IGCC cycle or a traditional power plant.

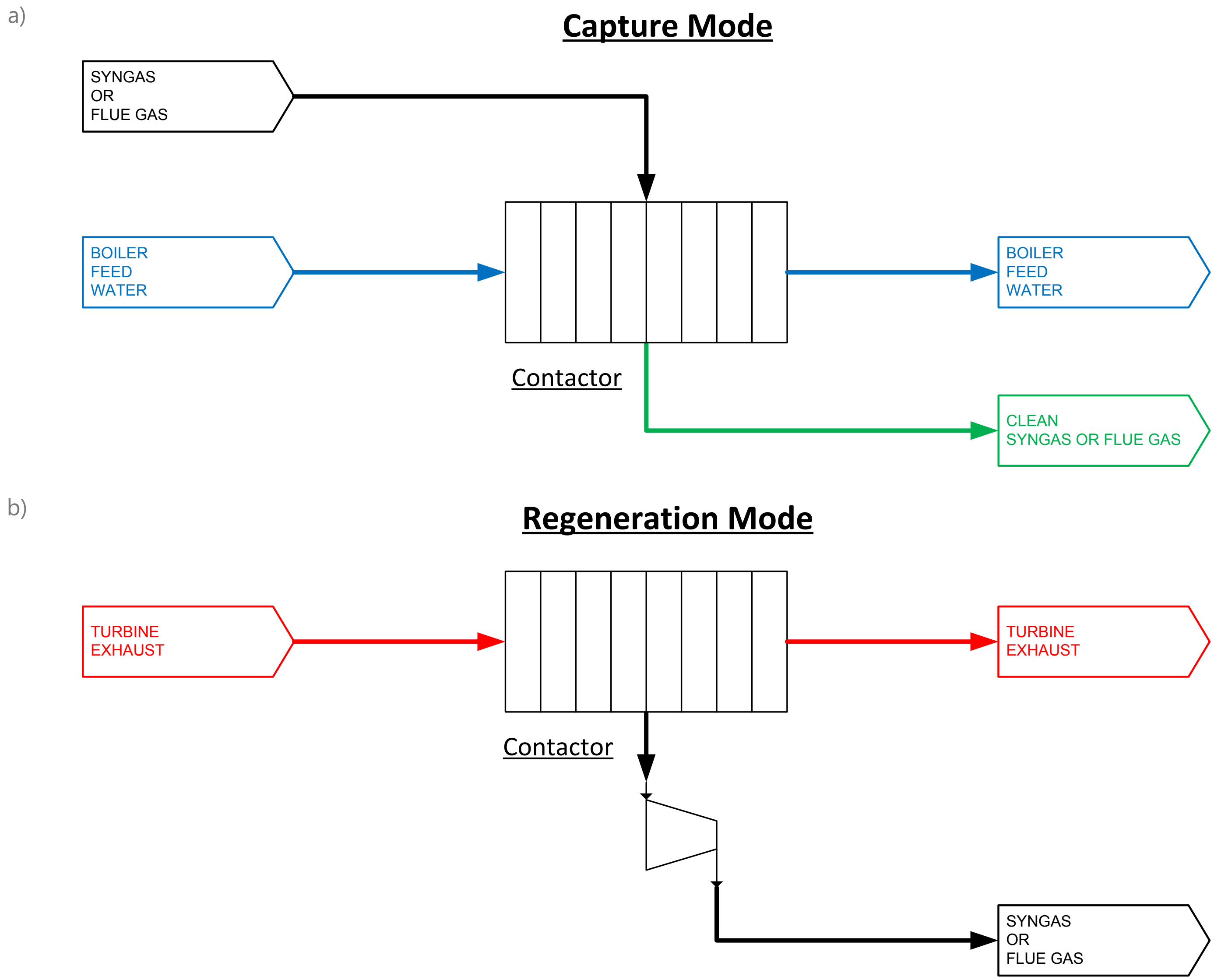


Figure 1: Simplified process flow diagram for Altex's integrated temperature and pressure swing carbon capture process. a) Capture mode – cooling provided by boiler feed water; b) Regeneration mode – heating provided by turbine exhaust.

PSU has been responsible for development of the sorbents they term as MBSs. The idea is to load CO_2-philic polymers such as polyethyleneimine (PEI) onto high-surface-area nano-porous inorganic materials such as MCM-41 and SBA-15, thereby increasing the accessible sorption sites per weight/volume of sorbent and improving the mass-transfer rate in sorption/desorption processes by increasing the gas-PEI interface. These sorbents can selectively adsorb large quantities of CO_2 compared to typical sorbents such as zeolites or activated carbons. The sorbents also pack CO_2 in a condensed form in the mesoporous molecular sieve basket and hence show a high CO_2 capacity and selectivity. The basic idea for preparation of MBS is illustrated in Figure 2.

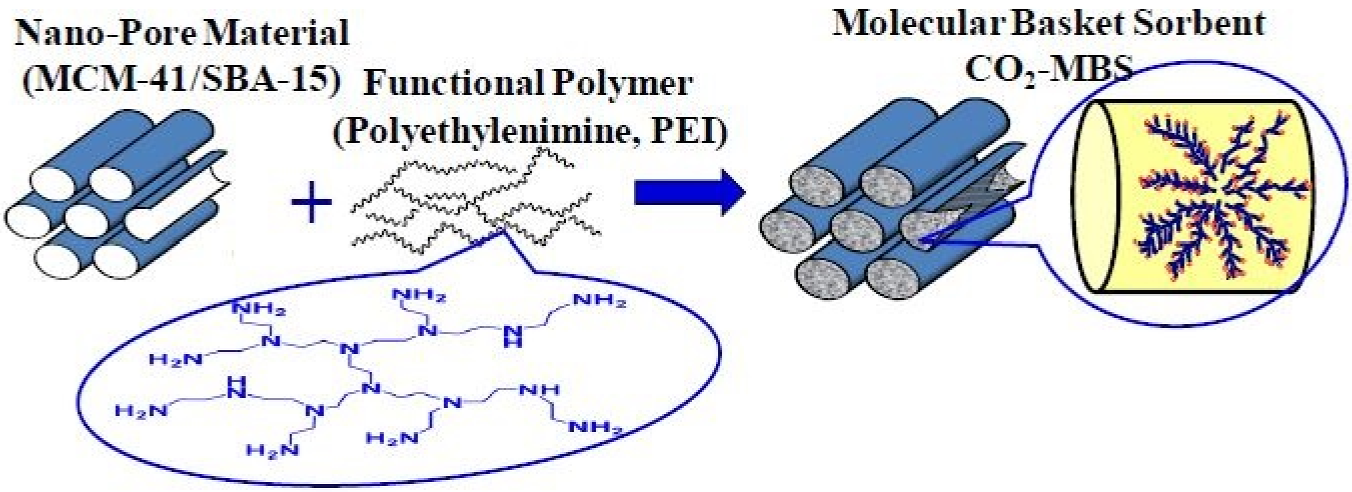
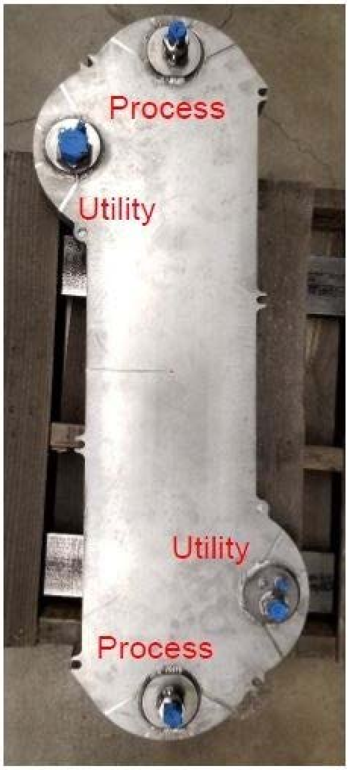


Figure 2: Principle for preparation of “molecular basket” sorbent (MBS).

The sorbents are applied by wash-coating the surfaces of microchannel heat exchangers. Altex is leveraging their expertise in design of these heat exchangers, which have been deployed in a wide range of sizes (fractions of kW to multiple megawatt [MW] capacities); materials (aluminum, copper, stainless steel, high-temperature alloys, corrosion-resistant alloys); counter-flow and cross-flow configurations; for various types of fluid flows; and in many fields, including oil and gas platform processes, separators, liquefied natural gas (LNG) processing, chillers, heat pumps, fuels reforming, waste heat power systems, and electronics cooling applications. For ITAPS, Altex developed the bench-scale prototype depicted in Figure 3. Note that finned inserts within the unit provide ample surface area onto which MBS can be wash-coated. In the pre-combustion capture case, the process stream of syngas containing CO_2 passes through the channels, and on the utility side, cooling water provides withdrawal of heat; in regeneration, steam would be passed through the channels to purge out the captured CO_2. Extensive surface area facilitates efficient heat transfer needed to accomplish the sorption and desorption steps for capture of CO_2.



Altex Highly Efficient Low Cost (HELC) heat exchanger

Figure 3: Illustration of ITAPS microchannel heat exchanger units/reactors.

In earlier project phases, PSU advanced the MBS material to improve the CO_2 capacity, and Altex demonstrated and established the feasibility of wash-coating this sorbent onto the microchannel heat exchanger. Advancements were made in both improving the mechanism of loading of the polymer into the solid matrix of the sorbent (low-cost fumed silica has been used in place of high-cost mesoporous silica, and sorbent performance improved by incorporating 3-aminopropyl triethoxysilane [APTES] along with PEI in the polymer formulation) and in improving the process for wash-coating the reactor (a single-step wash-coating method incorporating fumed silica, APTES, and PEI was devised, eliminating a separate impregnation step).

The bench-scale system prototype was tested for multiple cycles of CO_2 sorption/desorption, validating the feasibility of cycling and heat recovery. Data from these tests were used to determine the required wash-coat thickness needed to meet the target cost of electricity (COE) and ensure that this thickness can maintain a high effectiveness. From findings of the testing, analysis showed that the ITAPS process could significantly reduce cost of capture and COE.

Currently, the project is extending application of this technology into the area of post-combustion CO_2 capture. Figure 4 depicts the process concept for the CRC3 system, which deploys the Altex technology to capture of CO_2 from post-combustion flue gas.

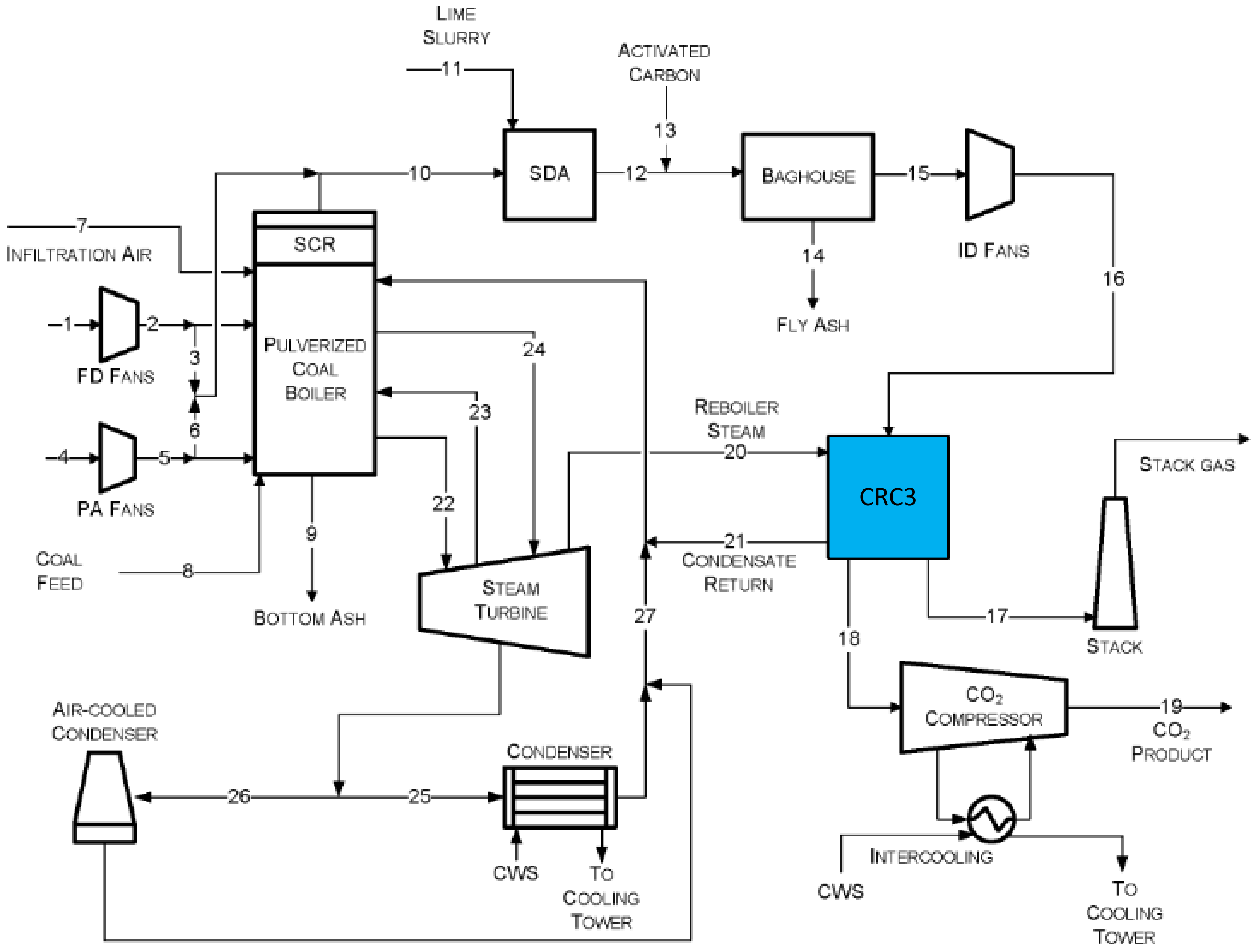


Figure 4: Process concept for the Compact and Rapid Cycling CO$_2$ Capture (CRC3) system.

Within this post-combustion capture context, current work is targeting better process approaches to integrate heat of sorption with the heat of desorption and to further improve sorbent performance, all of which are intended to reduce capture costs and enable the commercial potential of this technology.

technology advantages

- The CRC3 approach of applying sorbent to the high surface area, wash-coated minichannel reactor walls enables indirect heating and cooling of the sorbent.
- The sorbent on the minichannel reactor walls remains fixed in place and is not subject to particle attrition resulting from particle-particle contact, as would occur in a fluidized bed.
- The dispersion of sorbent over the high surface area of the walls of the minichannel reactor enables high mass-transfer rate of CO$_2$ to the sorbent.
- The pressure drop through the minichannel reactor can be reduced relative to a packed-bed absorber, much in the same way that monolith-supported catalysts reduce the pressure drop in selective catalytic reactors (SCRs) and, more commonly, in automobile catalytic converters. This will enable ITAPS to handle high gas-flow rates.

- The CO_2 MBSs developed by PSU exhibit high capacity and operate at low-desorption temperatures and with lower heat of sorption, requiring less parasitic energy draw and thereby boosting plant net efficiency.
- The MBSs are engineered with specific chemical surface functionality, which allows for high CO_2 sorption capacities in high-humidity conditions.
- Sorbent performance and the CRC3 approach enable lower round-trip energy costs for a complete sorption-desorption cycle.
- Enabling the production of CRC3 reactors at low cost and integrating a carbon capture system with existing unit operations should result in lower capital and operating costs for CO_2 capture from coal-fired power plants.

R&D challenges

- Operation at lower CO_2 partial pressures in flue gas as compared to syngas used in Phase I and Phase II.
- Implementing sorbent on both sides of the contactor and coordinating heat transfer between them.
- Operating on real flue gas.

status

Project Phase I and Phase II have been previously completed, in which ITAPS technology was developed and feasibility demonstrated for pre-combustion capture. Phase IIB is underway, in which the MBSs integrated in microchannel heat exchangers are to be improved, evaluated, and tested for post-combustion capture from flue gas.

available reports/technical papers/presentations

"Process Intensification for Carbon Capture," Altex Technologies Corporation and Pennsylvania State University, DE-SC0013823 (Phase IIB) Kickoff Meeting presentation (proprietary), September 5, 2019.

"*Process Intensification for Carbon Capture*," Phase II Final Report, Kenneth Lux, Tahmina Imam and Mehdi Namazian of Altex Technologies Corporation, Xiaoxing Wang and Chunshan Song of Pennsylvania State University, Submitted to the U.S. Department of Energy Office of Science (SBIR) / Office of Fossil Energy under Assistance Agreement Number DE-SC0013823, November 12, 2018.

Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System, and Process Integration

primary project goals

Liquid Ion Solutions LLC, with Penn State University and Carbon Capture Scientific (CCS), LLC, will develop and validate a transformational hybrid membrane/solvent system for post-combustion carbon dioxide (CO_2) capture from flue gas. The hybrid technology is a two-stage CO_2 capture system combining a membrane separation process and an absorption/stripping process with heat integration between the absorption column and stripping column through a heat pump cycle. Process air is used to sweep the stripper, resulting in much lower regeneration temperatures and enabling heat integration to the point that no process steam is required. To reduce capital cost, a next-generation membrane technology with higher permeance will be developed. The interfacially controlled envelope (ICE) membrane will make use of a transport zone neglected in conventional mixed matrix membranes (MMMs). By carefully controlling the interface between the polymer and inorganic particles within the MMM, CO_2 transport will be encouraged and nitrogen transport diminished in the gap between the two phases. Since permeance is directly tied to membrane area and capital cost, the development of the ICE membranes will reduce the capital cost of the hybrid process below that of the baseline technologies. The research team will combine computer simulation with lab-scale experimentation using simulated flue gas to develop, optimize, and test ICE membranes; test the absorption column and air stripper; and provide data to complete a techno-economic analysis (TEA) of the hybrid technology.

technical goals

- Conduct computer simulations to better understand the various unit operations in the hybrid process and set experimental conditions for project testing. Integrate the simulations and optimize the hybrid system.
- Conduct initial testing of the Generation 0 ICE (neat polymer) membrane formulations. Develop and optimize polymers, select and modify necessary filler particles, examine and validate fabrication techniques, and construct an isochoric test unit.
- Modify and install an existing lab-scale, packed-bed absorption column, and then use it to investigate the absorption column performance at a reduced operating temperature.
- Prepare and characterize the Generation 1 ICE membranes using the isochoric membrane testing unit.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Solvent-Membrane Hybrid Capture System

participant:

Liquid Ion Solutions

project number:

FE0026464

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Hunaid Nulwala
Liquid Ion Solutions
nulwala@liq-ion.com

partners:

Carbon Capture Scientific, LLC, Pennsylvania State University

start date:

10.01.2015

percent complete:

100%

- Modify the absorption column based on computer simulation results, then install and test.
- Fabricate the two optimal Generation 1 ICE membrane compositions for simulated flue gas testing in the isobaric membrane test system.
- Conduct an initial technical and economic feasibility study.

technical content

The objective of the project was to achieve lab-scale demonstration of a transformational hybrid membrane/solvent system for the capture of CO_2 from flue gas. A novel process integration scheme was proposed to overcome the low partial pressure of CO_2 present in flue gas. This scheme took advantage of the potential synergies inherent in the membrane and solvent capture systems. The proposed hybrid technology replaced the second-stage membrane with a methyl diethanolamine (MDEA) solvent capture process. The combustion air was used as a sweeping gas in the solvent stripper. This overall configuration had the major advantages of requiring much less air and eliminating the problems associated with oxygen slip in the membrane-based systems. Even more importantly, because of the presence of the air sweep in the stripper, much lower temperatures were required for solvent regeneration, which enabled heat integration to the point that no process steam was required.

Twenty-two poly(phosphazenes) were synthesized and fully characterized to identify the most optimal candidate matrix poly(phosphazene) polymer for ICE membrane development. The team performed detailed chemical analysis, solvent solubility studies, film formability, adhesion studies, membrane casting procedures, and thermal characterization studies on the 22 candidate polymers.

The base polymer material, called MM16, was not a film former, and it lacked the needed mechanical properties. To overcome these challenges, a cross-linker chemistry was developed and introduced in MM16 (CO_2/nitrogen [N_2] selectivity of 90 and permeability of 900 was observed for the MM16 polymer). The crosslinked material was termed MM19, which achieved a CO_2/N_2 selectivity of 50 and a CO_2 permeability of 500 barrer. MM19 had good film forming, as well as mechanical properties needed to cast membranes, and was selected as the base polymer for developing the ICE-1 membranes incorporating surface modified nanoparticles.

A variety of nanoparticles were evaluated, including surface-modified Quantum dots (QD). However, it was clear during the project that surface-modified silica nanoparticles are optimal for making ICE membranes. A synthesis methodology was developed to place a variety of functional groups on the surface of nanoparticles. Overall, there were three different functional groups placed on 10- to 15-nm silica particles. The functional groups used were cyclohexyl, octadecyl, and ethylene glycol. It was found that MM19 and the cyclohexyl surface-modified silica particles were compatible with each other. These colloidal nanoparticles were obtained from Nissan chemicals and are available in large quantities. The surface modification reaction is scalable. Figure 1 illustrates the general synthesis scheme.

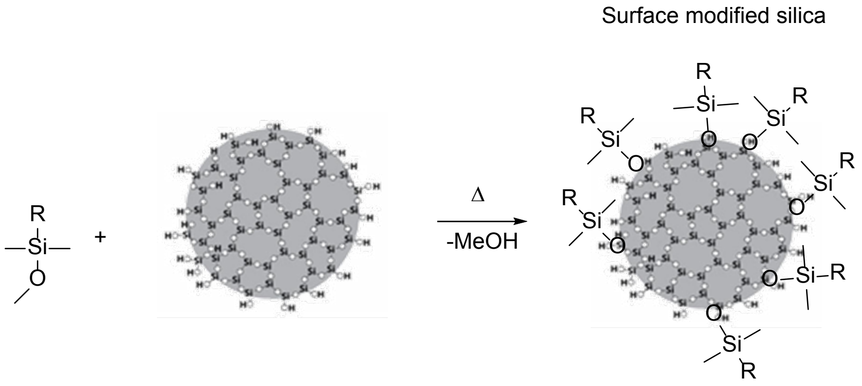


Figure 1: General synthesis scheme of surface modification for silica-nano material.

Additional membrane improvements were carried out by the team to optimize the mechanical and film casting properties. This included identifying the best support and lift-off procedures, as well as figuring out the additional types of crosslinker in the polymeric film. The team studied the impact of the support and determined which support would be ideal for this class of material. The team further improved the mechanical properties of the MM19 polymer by introducing a secondary crosslinking moiety. The addition of this crosslinking moiety resulted in interpenetrating networks (IPN) and improved membrane performance. The IPN approach is illustrated in Figure 2 with the chosen crosslinker. The team also developed an ultraviolet (UV)-initiator to cure the membranes extremely fast. Upon forming the IPN, the membranes obtained were mechanically robust. The implications of the vastly improved mechanical stability cannot be overstated, and lead to far more robust films. Synthesis of MM19 was routinely carried out at 20- to 40-gram scale.

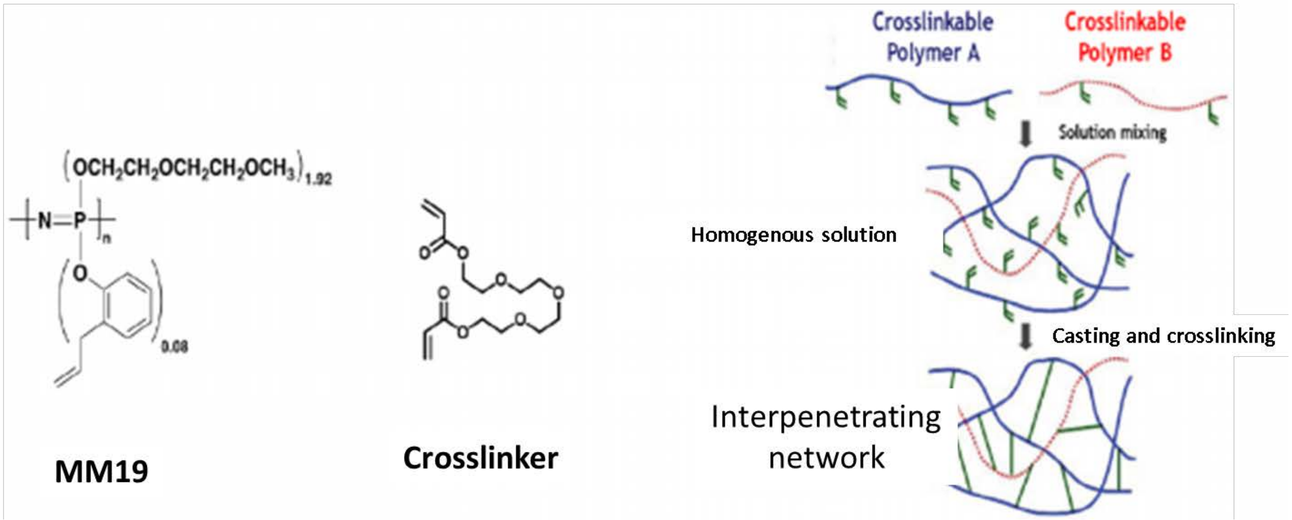


Figure 2: Accessing robust films using interpenetrating approach.

The membrane testing had many interdependent variables, and understanding them was important to developing an optimal membrane material. The team performed detailed design of experiment studies and built a test matrix to yield statistically relevant data. This matrix evaluated 30 different membrane compositions and was used to determine the most optimal composition for these membranes. These results are summarized in Figure 3. The membrane compositions number 1, 4, 9, 20, and 25 showed promise for the application. These materials show permeability of over 1,200 barrer and CO_2/N_2 selectivity over 35. The team was able to achieve 5X higher permeability that the current state-of-the-art materials.

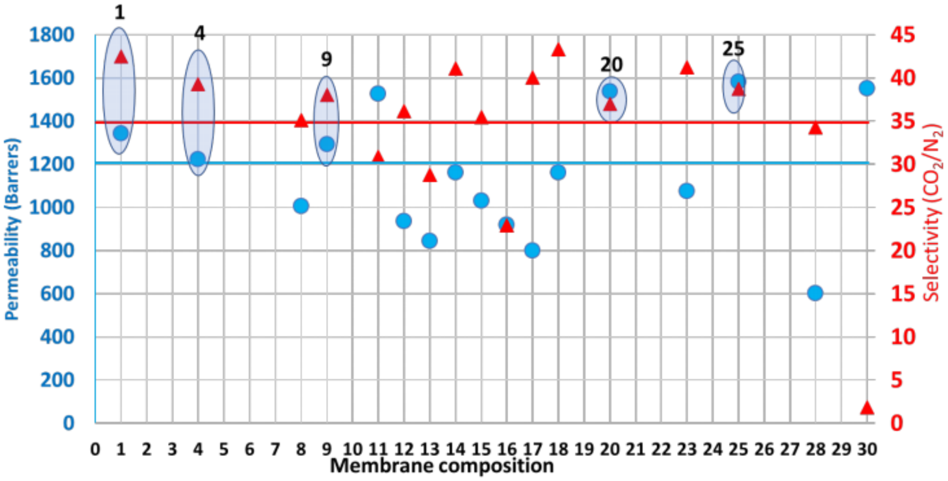


Figure 3: Testing results obtained from the isobaric unit. The blue line is the cutoff for the permeability (1,200 barrers), and the red line is the cutoff for selectivity (35 CO_2/N_2). Five compositions have permeability over 1,200 and selectivity over 35.

The initial simulation work for the membrane system, absorption/air stripping system, heat pump cycle, and optimization of the hybrid process was conducted by CCS LLC. On the membrane side, the team determined that it was economical to choose a one-stage compression unit over two-stage compression and refrigeration steps due to lack of additional performance and increased cost. On the solvent side, it was determined that an operating temperature of 25°C was the most economical temperature for the absorption process. The initial simulation provided the guidelines to perform the CO_2 absorption experiments.

Absorption and air stripping simulations were conducted using the ProTreat software package. Industrial operating conditions were used in the simulations to study the effect of several parameters on packing height, including operating temperature, gas-to-liquid (G/L) ratio, and air flow rates for CO_2 stripping in the desorption step. A simulation program that integrated an absorber and a stripper into the heat pump cycle was created, and further optimization work was carried out to reduce the energy consumption of the heat pump cycle. Preliminary optimization work revealed that the moisture contained in the stripping air would impact the performance of the heat pump cycle.

An existing lab-scale, packed-bed absorption column was modified and installed to investigate the absorption column performance at a reduced operating temperature. The installed absorption column can be seen in Figure 4. Parametric tests were performed to investigate the influence of G/L ratio and operating temperature on the CO_2 removal rate. Tests were run at three operating temperatures (15, 25, and 35°C). For each operating temperature, three G/L ratios were studied. For the hybrid process to work successfully, the absorption process needed to achieve at least 85% CO_2 removal. The parametric test results were in reasonable agreement with the computer simulations, showing that 85% CO_2 removal was achievable.

Figure 4: Installed absorption column.

On the membrane side of the simulation, an internally developed program was used to simulate the membrane separation step. Simulation work confirmed that major improvements in membrane performance were needed to produce CO_2 with 95% purity via one-stage membrane separation. Adding a simple compression and refrigeration step after the membrane separation allowed CO_2 with 95% purity to be produced in a more practical way.

The absorption column previously used was modified by CCS LLC based on computer simulation results to form the air stripper column. The modified air stripping column was installed and tested. This stripper column was then used to perform parametric testing. Preliminary parametric tests were carried out by the CCS LLC team. The variables to be investigated include stripping operating temperature, stripping air flow rate, and G/L ratio. For each test condition, data was collected once the operation reached steady-state. The parametric tests were mainly performed to investigate the influence of G/L ratio and operating temperature on CO_2 desorption. The tests were conducted at different operating temperatures (45 to 65°C) with different G/L ratios (80 to 160 L air/L solvent).

Several successful absorption/desorption cycles were identified: they were cycles with absorption temperature/desorption temperature of 15/55°C, 25/55°C, and 35/65°C. By combining the experiments and computer simulation results in the hybrid process, the following optimal processing conditions were obtained:

- Absorption temperature: 30°C.
- Desorption temperature: 60°C.
- Lean loading: 6.0 wt%.
- G/L ratio: 92 L air/L solvent.
- Number of inter-stage heating: 2.

The systematic parametric tests and computer simulations revealed that an absorption/stripping cycle between 30/60°C was optimal for the hybrid process. A heat pump cycle with a temperature lift of 40°C was enough for the absorption/stripping cycle when 80% of the combustion air was used in the stripping column, fulfilling the success criteria. In addition, the column heights of both the absorber and stripper were reasonable, at 25 meters or less for the Case B12B-scale power plant.

A considerable effort was spent on figuring out how the MM19 could be scaled-up. The synthesis of MM19 included multiple purification steps that were never a problem at smaller scales. However, the team's attempts at synthesizing polymers over 40 grams ran into difficulty. The general synthesis scheme is provided in Figure 5. It is also important to note that the chloropolymer is extremely reactive to air. The formation of the sodium salts are separate synthesis steps.

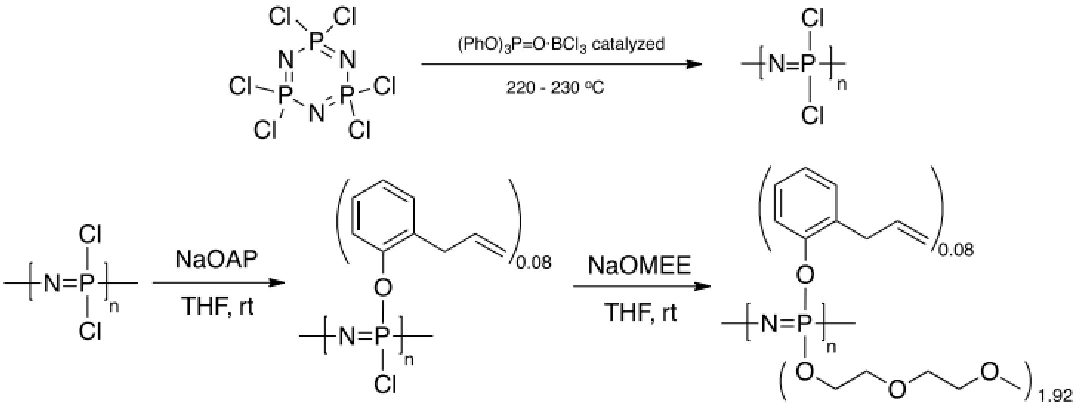


Figure 5: General scheme for the synthesis of MM19 polymer.

There were other problems that also started to show up, such as batch-to-batch variation from the chemical suppliers. The chloro-precursor for poly(phosphazene) quality became an issue as well. A significant effort was spent on the scale-up of these polymers and benchmarking them against the originally obtained polymers. However, the team was unable to benchmark the large-scale material with small-scale synthesized results.

The team evaluated the impact of contaminants on the membrane performance. It was found that upon introduction of contaminants, the permeability and selectivity is lowered. However, the membranes recovered upon removal of the contaminants.

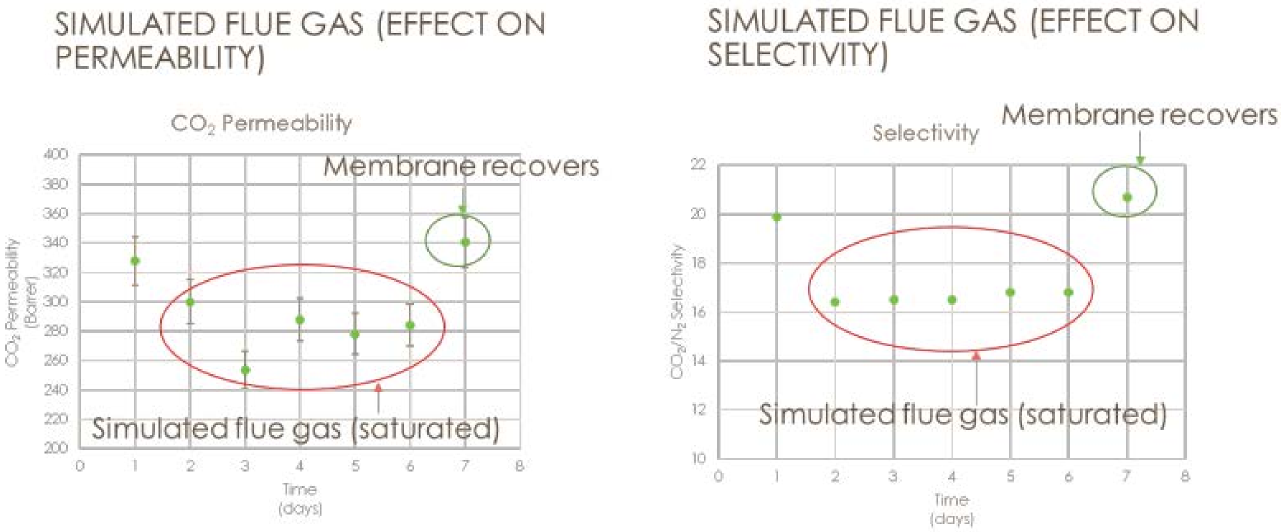


Figure 6: Simulated flue gas studies on ICE-1 membranes.

Figure 6 illustrated that despite the problems with synthesis, the overall ICE membrane concept holds true. The ICE membranes were not affected by the addition of contaminants to the simulated flue gas (50 parts per million [ppm] sulfur dioxide [SO_2] and 70 ppm nitrogen dioxide [NO_2] with 7.8 g of water [H_2O]/kg of air [16% relative humidity]), and upon removal, they recover.

The performances of the power plant equipped with the hybrid process and Baseline Case B12B were compared. Results showed that the power plant equipped with the hybrid CO_2 capture process had a thermal efficiency of 33.4%. This was better than the Baseline Case B12B, which was 32.5%. However, the cost of electricity (COE) for the hybrid process was \$146.3/megawatt-hour (MWh), which was higher than the \$142.8/MWh for Case B12B. It is important to note that these analyses were performed based on building a new power plant. For a retrofitting case, since the hybrid CO_2 capture technology would not require steam from an existing power plant, no modifications of the existing power plant would be needed. In the case of a retrofit, the capital cost of the hybrid CO_2 capture process could be lower and potentially a better fit for a CO_2 capture case.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	109.255	N/A
Normal Boiling Point	°C	N/A	N/A
Normal Freezing Point	°C	-	N/A
Vapor Pressure @ 15°C	bar	《1Pa	N/A
Manufacturing Cost for Solvent	$/kg	《3	N/A
Working Solution			
Concentration	kg/kg	1/1	N/A
Specific Gravity (15°C/15°C)	-	1.09	N/A
Specific Heat Capacity @ STP	kJ/kg-K	2.978	N/A
Viscosity @ 15°C	cP	10.2	N/A
Absorption			
Pressure	bar	1	1
Temperature	°C	30	30
Equilibrium CO_2 Loading	mol/mol	0.494	0.348
Heat of Absorption	kJ/mol CO_2	55.99	55.99
Solution Viscosity	cP	10.2	10.2

Desorption			
Pressure	bar	1	1
Temperature	°C	60	60
Equilibrium CO_2 Loading	mol/mol	0.347	0.347
Heat of Desorption	kJ/mol CO_2	55.99	55.99
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 ~20	
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	plate-and-frame	plate-and-frame
Max Trans-Membrane Pressure	bar	1.1	1.1
Hours Tested without Significant Degradation	—	- (simulated coal)	- (simulated coal)
Manufacturing Cost for Membrane Material	\$/m²	-	-
Membrane Performance			
Temperature	°C	40	40
CO_2 Pressure Normalized Flux	GPU or equivalent	5,000	5,000
CO_2/H_2O Selectivity	—	2	2
CO_2/N_2 Selectivity	—	44	44
CO_2/SO_2 Selectivity	—	-	-
Type of Measurement	—	simulated coal	simulated coal
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	-	
Shell-Side Fluid	—	-	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	%/%/bar	50, 95,140	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.05	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Foaming Tendency – For a flue gas environment, no foaming should be expected.

Flue Gas Pretreatment Requirements –SO_2 removal is required.

Solvent Makeup Requirements – Without water wash at the tops of both absorber and stripper, the makeup rate is about 10kg/hr MDEA and 20kg/hr piperazine (PZ).

Waste Streams Generated – A waste stream will be created only if a solvent reclamation process is installed.

Process Design Concept –

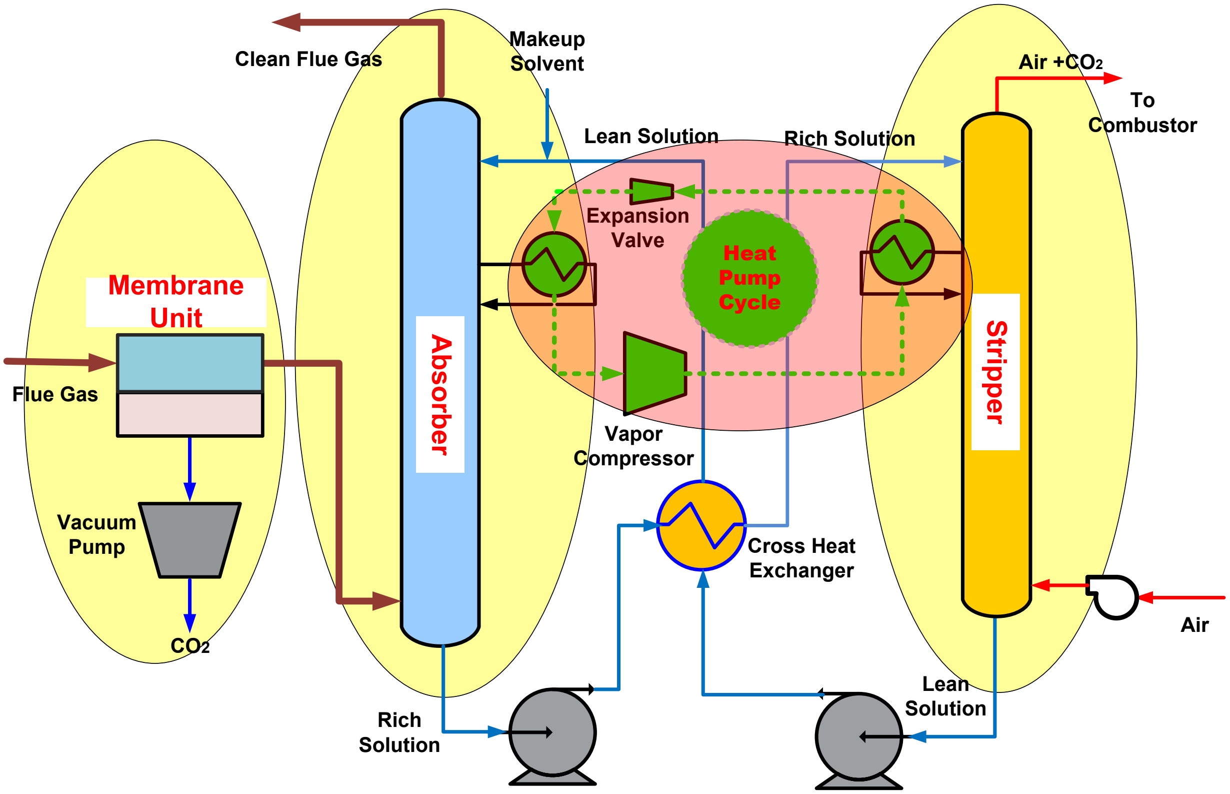


Figure 7: Overall membrane/solvent integrated process.

Membrane Permeation Mechanism – The membranes developed under this project are polar, rubbery/elastic with very low glass transition temperatures allowing higher permeabilities. The overall separation occurs mainly due to the solubility of CO_2 in the polymer, which is further facilitated by interfaces of the surface modified nano particles resulting in improved permeabilities.

Contaminant Resistance – The surface-modified nanoparticles are not affected by the addition of simulated flue gas and the addition of contaminants (50 ppm SO_2 and 70 ppm NO_2 with 7.8g of H_2O/kg of air [16% relative humidity]).

Membrane Replacement Requirements – Outside project scope.

technology advantages

- Polyphosphazenes have excellent chemical and thermal stability.
- Steam extraction is not required.
- Stripper operating pressure is flexible (depending on low-quality heat).
- The high-permeance membrane reduces capital costs.
- The heat pump cycle and use of air sweep for stripping eliminate the need for steam extraction, reducing parasitic power and operating expenditures.

R&D challenges

- Polyphosphazene performance is uncertain.
- Scale-up is a problem.
- The heat pump has high energy consumption.
- The long-term durability of the membrane in actual flue gas and variable conditions has not been determined.

status

This project has concluded.

available reports/technical papers/presentations

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Nulwala, H. "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System and Process Integration," Project Kickoff Meeting, Pittsburgh, PA, October 2015. *https://www.netl.doe.gov/sites/default/files/2017-12/FE0026464-Kickoff-Presentation.pdf*.

Advanced Carbon Dioxide Compression with Supersonic Technology

primary project goals

Dresser-Rand, a Siemens Business, is developing a unique compressor technology based upon flight-based supersonic/shockwave compression principles for use as a carbon dioxide (CO_2) compressor. Advancing supersonic compressor technology will help meet overall goals of lower capital costs, smaller footprints, and improved energy efficiencies of carbon capture systems.

technical goals

- Increase the performance of CO_2 supersonic compression from a previously demonstrated single-stage pressure ratio of 11.5:1 to the goal of efficient 100:1 total pressure ratio CO_2 compression across two stages.
- Operate at a compressor CO_2 flow rate of 100 pounds per second, suitable for carbon capture applications in 125-megawatt-electric (MWe) coal-fired power plants and be scalable to higher flowrates.
- Validate compressor performance of pilot-scale compressors, testing on gas representative of a CO_2 capture system.
- Perform techno-economic analysis (TEA) of the integration of supersonic CO_2 compression in a 550-MWe power plant to quantify economic benefits of the technology for scenarios of large-scale power generation with carbon capture.

technical content

Dresser-Rand (which acquired the assets of Ramgen Power Systems in 2014) is developing supersonic shockwave compression technology, similar in concept to an aircraft supersonic engine inlet, for use in a stationary compressor. This compressor design features a rapidly rotating enclosed disk that generates supersonic speeds at its rim, generating shockwaves, and thereby compressing gases introduced into a channel surrounding the rim. Compared to conventional compressor technologies, supersonic compression offers several potential advantages: high compression efficiency, high single-stage compression ratios, opportunity for waste heat recovery, and low capital cost. For example, Dresser-Rand's shock compression has the potential to develop compression ratios from 2.0 to 12.0 per stage. For CO_2 compression applications, a nominal two-stage 100:1 compression ratio is envisioned, featuring a pair of 10:1 compression stages with an intercooler located between the stages.

Figure 1 provides a cross-sectional view of an early concept for a single-stage supersonic compressor, which gives some idea of the engineering embodied in a compressor of this type.

technology maturity

Pilot-Scale, 1.5 MTPA (million tons per annum) of CO_2

project focus:

Supersonic Compression

participant:

Dresser-Rand, A Siemens Business

project number:

FE0026727

predecessor projects:

FE0000493
FC26-06NT42651

NETL project manager:

Robin Ames
robin.ames@netl.doe.gov

principal investigator:

Kirk Lupkes
Dresser-Rand
Kirk.Lupkes@Siemens.com

partners:

N/A

start date:

03.10.2016

percent complete:

100%

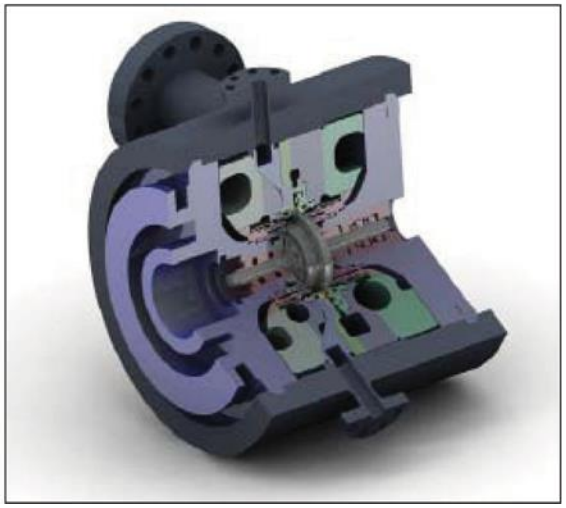

Figure 1: Cross-sectional model of a single-stage supersonic compressor.

When shockwaves pass through a gas, they cause a localized compression. Figure 2 shows that the rotating rotor rim has small, shallow angles that, when rotating at supersonic speed, will produce a series of oblique shocks terminating in a final normal shock. These shockwaves can be seen in the 3D Euler computational fluid dynamics (CFD) image shown in Figure 2.

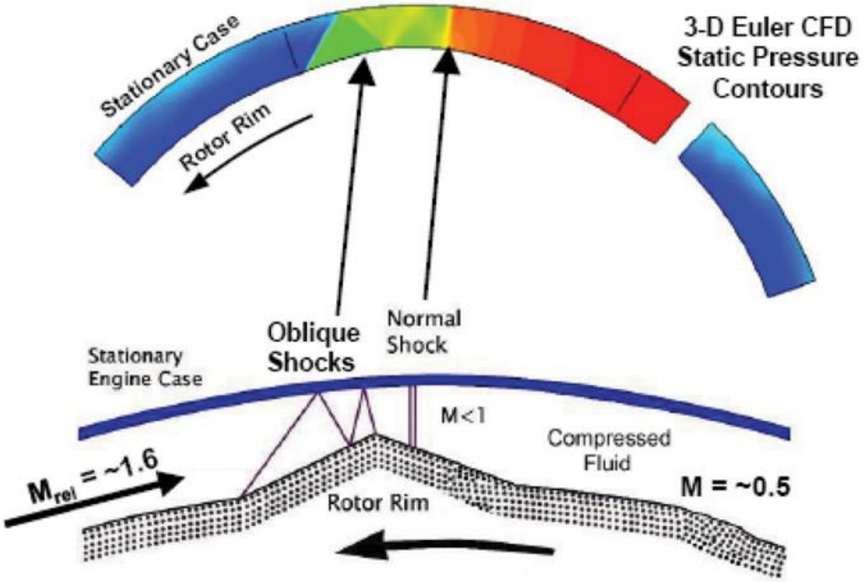

Figure 2: Schematic of rotor rim and engine case and 3D Euler CFD image depicting shockwave behavior.

Additionally, strakes (ridges) are incorporated into the design of the rotor to form sidewalls. The strakes are utilized to segregate individual shock compression ducts, as well as to separate high-pressure discharge gas from low-pressure suction. The combination of shocks and strakes result in a compressed fluid delivered from a stationary discharge duct with compression efficiencies comparable to conventional industrial turbo-compressors, but with much higher single-stage pressure ratios. The heat generated during this single stage of shockwave compression is higher than that generated during conventional compression, yielding gas discharge temperatures exceeding 290°C (550°F). This is a relatively high-quality source of waste heat that can be recovered and utilized gainfully in optimizing overall system thermal efficiency. The high mechanical efficiency and waste heat recovery opportunity combine to deliver significant installed and operational cost savings versus existing turbo-compressors.

The project includes testing of the high-pressure compressor in a CO_2 test loop and the design, build, and testing of a high-flow coefficient low-pressure stage to complete the 100:1 total pressure ratio testing, along with the completion of a TEA for the integration of the supersonic compressor technology and heat integration into a 550-MWe power plant. The 10-MW high-pressure compressor on the close-loop CO_2 test stand is shown in Figure 3.

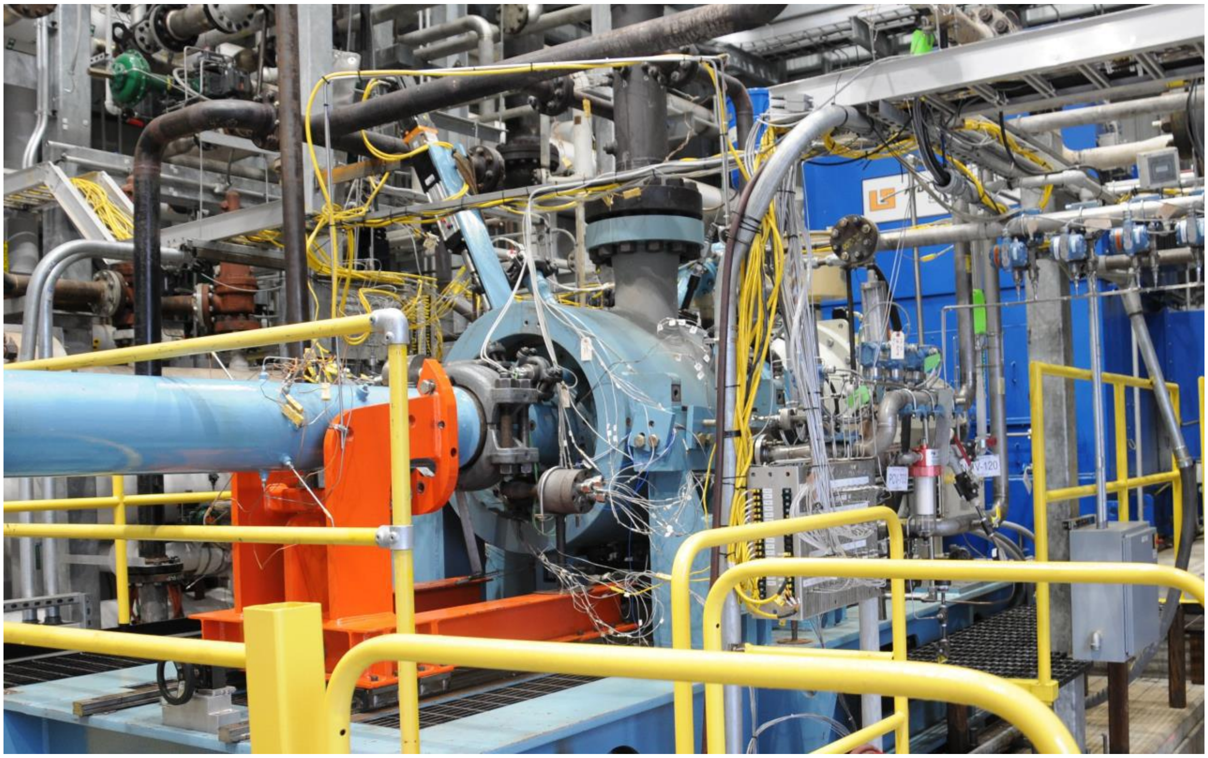

Figure 3: High-pressure CO_2 compressor on test stand.

technology advantages

- Competitive operating efficiency and reduced installed capital cost (approximately 50%) over multistage bladed turbo-compressors.
- Lowered footprint of the CO_2 compression island in the plant, less piping and fewer intercoolers.
- High-stage discharge temperature enables cost-effective recovery of heat of compression:
  - Improves carbon capture system efficiency.
  - Reduces power plant de-rate.

R&D challenges

- Complicated shockwave aerodynamics in the gas flow path require intensive computing capabilities and model development.
- High rotational speeds and the resulting loads and stresses.
- High-speed rotordynamic stability that meets industry standards.
- High-pressure ratio compressors yield high rotor thrust loads on bearings and structure.

status

Testing for the high-pressure CO_2 compressor was concluded with the final test phase achieving a 11.5:1 compression ratio, better than the required 10:1 ratio. Testing of a high-flow, low-pressure compressor was completed at a 12.0:1 pressure ratio. A TEA was completed, including integration of waste heat showing benefits for carbon capture applications, with a 28% reduction in cost of electricity (COE) for the cost of compression duty and 21,000-gallon reduction in cooling water.

available reports/technical papers/presentations

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Cryogenic Carbon Capture Development

primary project goals

The objective of this project is to increase the reliability, efficiency, and scalability of the Cryogenic Carbon Capture™ (CCC) process to prepare for a pilot-scale (up to 5 megawatt-electric [MWe], or 100 tonnes/day [tpd] of carbon dioxide [CO_2] captured) demonstration.

technical goals

- Improve key areas of the process through iterative design and experimentation, culminating with recommendations for improvements to be integrated into the existing skid-scale CCC External Cooling Loop (CCC-ECL™) system developed under previous funding.
- Integrate the recommended improvements into the CCC-ECL system and confirm their contributions through experimental process testing.
- Perform modeling and estimation analyses to improve the techno-economic analyses (TEAs).

technical content

Sustainable Energy Solutions (SES), in partnership with PacifiCorp, Brigham Young University, Electric Power Research Institute, Inc., and Tri-State Generation & Transmission Association, Inc., has implemented process improvements to the ECL version of their CCC technology, further advancing it. SES developed the CCC-ECL technology under previous research funded by the Advanced Research Projects Agency-Energy (ARPA-E) project "Cryogenic Carbon Capture" (DE-AR0000101), the state of Wyoming, and others. Previous analyses and field tests of skid-scale (1-tpd) versions of the CCC process have shown that the technology reduces CO_2 emissions by more than 95% and has a parasitic load of less than 15% for coal-fired power plants. This project addressed issues discovered during the previous field tests at power plants, cement kilns, and heating plants, resulting in the implementation of various process improvements.

The foundation of the CCC process relies on refrigeration to cryogenic temperatures, rather than a chemical reaction, to separate CO_2 from flue gas from a power plant or industrial source. Typically, refrigeration cycles consume large amounts of energy, but this is only true if the final products are at lower temperature than the incoming streams (e.g., air conditioning). While the CCC process relies on refrigeration process principles, the products are at nominally the same temperature as the incoming flue gas, and thus the energy efficiency is much higher than for typical refrigeration processes. The CCC technology, shown in Figure 1, separates CO_2 and other pollutants from coal-derived flue gas by cooling the flue gas to approximately -130°C, at which temperature CO_2 forms a solid (desublimates). The CCC process utilizes a large amount of recuperative heat exchange through commercially available heat exchangers to cool the flue gas to

technology maturity:

Skid-Scale, Actual Flue Gas

project focus:

Cryogenic Carbon Capture Process

participant:

Sustainable Energy Solutions

project number:

FE0028697

predecessor project:

DE-AR0000101 (ARPA-E)

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Larry Baxter
Sustainable Energy Solutions
l.baxter@sesinnovation.com

partners:

PacifiCorp, Brigham Young University, Electric Power Research Institute, Inc., Tri-State Generation & Transmission Association, Inc., Press Technology and Manufacturing, Sargent & Lundy

start date:

10.01.2016

percent complete:

100%

the verge of CO_2 desublimation before it enters a proprietary desublimating heat exchanger that desublimates, or freezes, the CO_2 out of the carrier gas stream. In the CCC-ECL system, an external refrigeration loop is used to provide cooling to the desublimator (Figure 2). The process separates the solid CO_2 from the carrier gas and recovers heat as the solids warm and melt under pressure. The process delivers a high-pressure (150 bar), high-purity (99+%) liquid. The process compresses liquid CO_2 rather than a gas, so the energy input for CO_2 compression is minimal. The cold, light gasses (nitrogen [N_2], oxygen [O_2], and others) do not condense, but they do return through the recuperator for energy recovery, which, in turn, minimizes the cooling load on the desublimator. The CCC process is minimally invasive and represents a bolt-on carbon capture retrofit technology, allowing it to be easily retrofitted to existing plants. Additionally, the process recovers water from flue gas and robustly handles impurities in the flue gas stream. It also requires 50% less energy and costs about 50% less than an amine absorption process (Figure 3). Additional energy and cost savings ($14/tonne CO_2 avoided) can be achieved through integration with steam cycle and control methods for sulfur oxides (SO_X), nitrogen oxides (NO_X), and mercury (Hg).

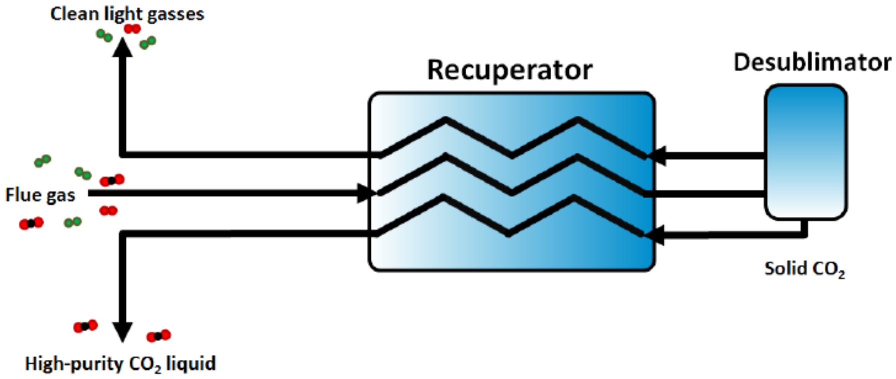

Figure 1: CCC process.

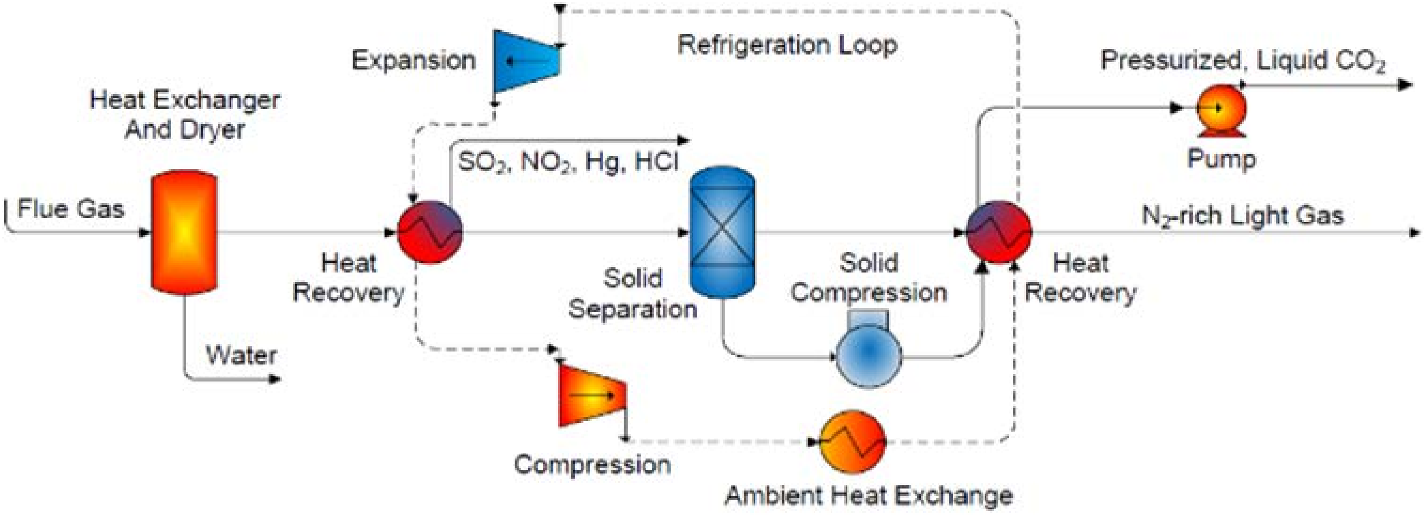

Figure 2: CCC process implemented using an ECL system.

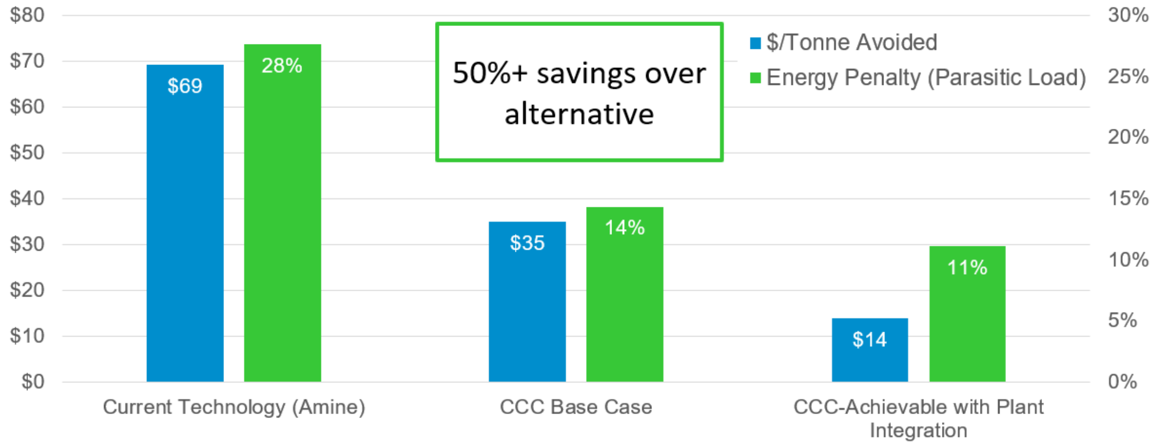

Figure 3: CO_2 capture costs for CCC process compared to amine absorption process (NETL 2013 amine costs).

In this project, the team used existing CCC equipment and analytical tools to optimize the CCC unit operations and improve technical performance through iterative design and experiment. The project explored issues affecting process reliability, efficiency, and scalability, culminating in recommended improvements that will enhance the performance of commercial CCC systems. The investigation of unit operation improvements to the CCC-ECL system included: (1) state-of-the-art adsorption and phase-change drying processes, as well as alternative drying techniques, to decrease the energy consumption and CO_2 absorption in the flue gas drying stages of CCC; (2) options to mitigate potential heat exchanger fouling to eliminate the accumulation of dissolved CO_2, solid CO_2, and other possible impurities in the CCC process; (3) alternative solid-liquid separation operations to improve the reliability and performance and to decrease the energy consumption of the separation process; (4) three alternative heat exchanger designs for commercial-scale implementation of CCC; (5) skid modifications to implement measurements and controls that can extend the skid testing time; (6) several options for managing the light gas stream produced by the CCC process; and (7) models that describe CCC capture of pollutants other than CO_2, validated with experimental data. The project integrated the recommended alternatives into the existing skid-scale CCC-ECL system and operated the modified skid at PacifiCorp's Hunter Power Plant using a slipstream of flue gas for approximately 600 cumulative hours during a series of tests over several months. Photos of the CCC-ECL skid are shown in Figure 4. Test results and process modeling informed an updated TEA of the CCC technology. The primary figures of merit for improving unit operations are as follows:

- **Reliability**: The ability of the unit to operate without maintenance or performance degradation for a period of 18 to 24 months (average time between scheduled power plant maintenance).
- **Efficiency**: The energy or other resource consumption of the unit operation and its effect on overall process energy efficiency.
- **Scalability**: The performance or existence of the unit operation at scales up to 1 gigawatt-electric (GWe) equivalent and the impact of such scalability on cost, efficiency, and reliability.
- **Techno-Economic Performance**: Energy demand and ancillary pollutant capture efficiency as a function of CO_2 capture fraction and cost estimates for retrofit and greenfield installations as measured by the increase in cost of electricity (COE) and cost per unit mass of CO_2 avoided.

Figure 4: CCC-ECL process test skid.

technology advantages

- The CCC process retrofits existing plants or provides a greenfield solution to any continuous CO_2 source (coal-based power, natural gas, cement, integrated gasification combined cycle, refineries, etc.).
- The CCC process captures 90 to 99+% of the CO_2, and most pollutants (e.g., SO_X, NO_X, Hg), at half the cost and energy of alternative carbon capture technologies and recovers more water from flue gas than it requires for operation (reduces overall water demand).
- The CCC process integrates with renewables through grid-scale energy storage, which can result in further reductions in cost and substantial value added for renewables.
- An increase in the process reliability, efficiency, and scalability represents significant progress toward the U.S. Department of Energy's (DOE) goal of $40/tonne of CO_2 captured by 2025.

R&D challenges

- Innovative desublimating heat exchangers can be further optimized.
- Solids handling and other process equipment must avoid fouling, plugging, and level upsets.
- Innovative, scalable flue gas dryer requires demonstration.
- Effectiveness of solid-liquid separation is critical for pilot-scale implementation.

status

SES refined the CCC process in several areas, including flue gas drying, mitigating heat exchanger fouling, managing light gas dispersal, and developing predictive capability for the capture of pollutants other than CO_2. The individual unit improvements were implemented, and the modified skid was operated at Hunter Power Plant for more than 600 cumulative hours, consistently capturing more than 90% CO_2 and reaching 1 tpd CO_2 capture capacity during short-term tests.

available reports/technical papers/presentations

"Cryogenic Carbon Capture – Development Project DE-FE0028697," Final Briefing – Public, September 2019. *https://www.netl.doe.gov/projects/files/CCC-Dev%20Final%20Briefing%20-%20Public.pdf*.

Baxter, L., “Cryogenic Carbon Capture Development Progress and Field Test Data,” presented at the 2019 NETL CCUS Integrated Project Review meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/files/Cryogenic%20Carbon%20Capture%20Development%20(FE0028697).pdf*.

Baxter, L, et al., “Cryogenic Carbon Capture Development,” presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, August 2018. *https://www.netl.doe.gov/projects/files/L-Baxter-SES-BYU-Cryogenic-Capture-Development.pdf*.

Baxter, L. and Stitt, K., “Cryogenic Carbon Capture Development,” presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/projects/files/L-Baxter-SES-Cryogenic-Carbon-Capture.pdf*.

Sayre, A., Frankman, D., Baxter, A., Stitt, K., and Baxter, L., “Field Testing of Cryogenic Carbon Capture,” Carbon Management Technology Conference, Houston, Texas, July 17-20, 2017. *https://www.osti.gov/servlets/purl/1412681*.

Baxter, L. and Stitt, K., “Cryogenic Carbon Capture Development,” Project Kickoff Meeting, December 2016. *https://www.netl.doe.gov/projects/files/SES-FE0028697-kick-off.pdf*.

Jensen, M. J., C. S. Russell, D. Bergeson, C. D. Hoeger, D. J. Frankman, C. S. Bence and L. L. Baxter (2015). "Prediction and validation of external cooling loop cryogenic carbon capture (CCC-ECL) for full-scale coal-fired power plant retrofit." International Journal of Greenhouse Gas Control, Vol. 42: 200-212.

Additively Manufactured Intensified Device for Enhanced Carbon Capture

primary project goals

Oak Ridge National Laboratory (ORNL) is developing intensified devices combining multiple thermodynamic operations for improved efficiency for solvent-based carbon dioxide (CO_2) capture. These additive-manufactured packing structures combine heat and mass transfer, simultaneously increasing the reactive surface area and enhancing heat exchange efficiency.

technical goals

- Utilize a computational fluid dynamics (CFD) model to realize a design and perform a parametric study on key design and operational parameters.
- Demonstrate the manufacturability of an equivalent geometry of a widely used packing structure (Mellapak 250) and intensified device design with additive manufacturing techniques.
- Validate the core-scale metrics of the additively manufactured device to compare to its commercial counterpart.
- Design and print a device-scale prototype.
- Test the device-scale prototype with a commercially available solvent and simulated flue gas to evaluate overall capture performance.

technical content

ORNL is developing intensified CO_2 capture devices, which can combine multiple thermodynamic operations into one unit. Improvements in solvent-based CO_2 capture devices are targeted through analysis of monoethanolamine (MEA) absorption and desorption of CO_2. The multi-functionality of these intensified devices is envisioned to be achieved through graded packing structures with built-in heat exchanging channels made by additive manufacturing technologies, namely 3D printing.

Conventional carbon capture systems are configured with multiple unit operations that use sequentially coupled stages for mass and heat transfer. Since solvent- and sorbent-based capture intrinsically couples mass and heat transfer at the fundamental length scales, multiple stages of single-purpose unit operations would result in larger equipment size, higher equipment costs, and potentially less than optimal operating conditional for the equipment. This project aims to use additive manufacturing technologies to develop a graded packing structure to allow for the integration of heat exchange, reaction, and potentially mass exchange in one multi-functional structure, and then to optimize the geometry to maximize the capture performance. By combining these operations in the single unit, this device would lead to intensification of the capture process.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Additively Manufactured Intensified Device for Solvent-Based CO_2 Capture

participant:

Oak Ridge National Laboratory

project number:

FWP-FEAA130

predecessor projects:

N/A

NETL project manager:

David Lang
David.Lang@netl.doe.gov

principal investigator:

Xin Sun
Oak Ridge National Laboratory
sunx1@ornl.gov

partners:

N/A

start date:

07.01.2017

percent complete:

100%

To execute this project, ONRL applied capabilities in CFD, additive manufacturing, and absorber-scale demonstration/validation experiments. The team utilized a Carbon Capture Simulation for Industry Impact (CCSI^2)-developed CFD model to enable optimization of an additive-manufactured intensified carbon capture device. This computational tool was used for design realization and for a parametric study on key design and operational parameters. The target structured packing control was the commercial Mellapak 250 (shown in Figure 1). ORNL fabricated 3D-printed devices with different cell densities (Figure 2). The test packing was 8 inches in diameter and 5.57 inches tall. Cell sizes of 25.4 millimeter (mm), 12.7 mm, and 6.3 mm were printed.

Figure 1: Mellapak (commercial) structured packing.

Figure 2: Packing with different cell densities, 3D-printed at ORNL.

ORNL fabricated a second-generation intensified device (Figure 3) for use in heat and mass transfer studies. The solvent-based reactive test system, shown in Figure 4, included the 3D-printed intensified device within a column containing commercial packing elements.

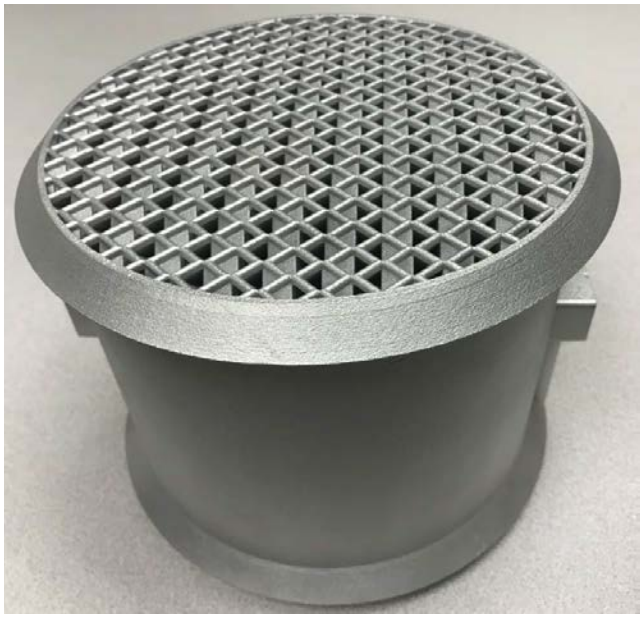

Figure 3: Second-generation intensified device.

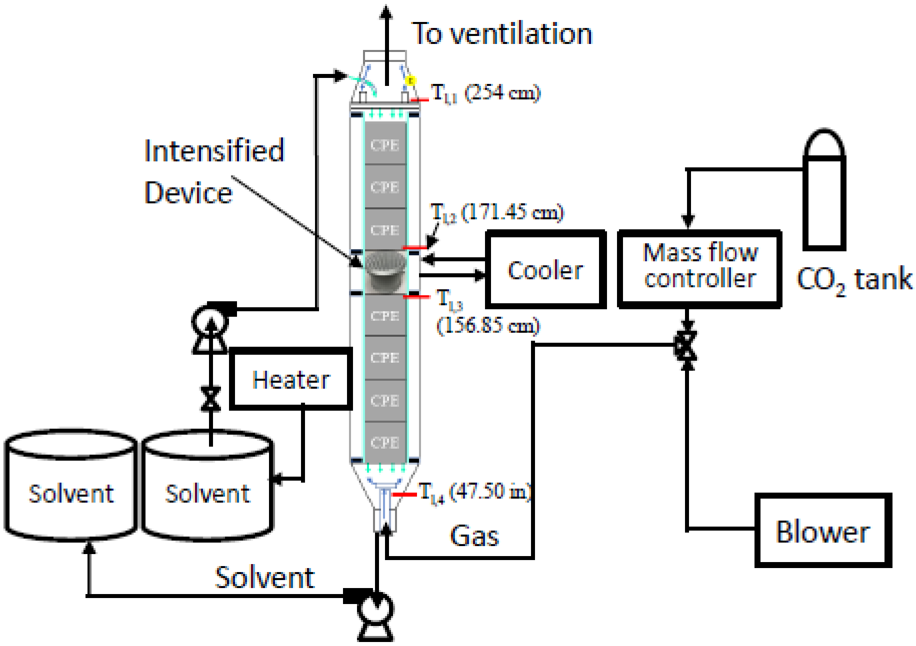

Figure 4: Reactive system test facility.

technology advantages

- Improvement of CO_2 capture efficiency by simultaneously increasing reactive surface area and enhancing heat exchange efficiency in order to maintain the forward absorption reaction in the absorber column.

R&D challenges

- Fabrication of a benchmark geometry for a conventional packing structure, interpreting the computationally derived intensified device requirements, and demonstrating the manufacturability of the intensified device design additive manufacturing techniques.

status

ORNL has successfully designed, printed, characterized, and tested a 3D-printed intensified packing device. The intensified device had hydrodynamic behavior that was not much different than that of the commercial-structured packing elements. The intensified device was capable of substantially reducing the amine solvent temperature *in situ*. Experiments showed enhanced CO_2 capture rates using the intensified device.

available reports/technical papers/presentations

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at Final Project Review Meeting, Pittsburgh, PA, November 2019. *https://www.netl.doe.gov/projects/files/ORNL%20FWP-FEAA130%20final%20project%20review_110819.pdf*.

Bolton, S., Kasturi, A., Palko, S., Lai, C., Love, L., Parks, J., Sun, X., and Tsouris, C., “3D Printed Structures for Optimized Carbon Capture Technology in Packed Bed Columns,” Separation Science and Technology, 54, 2047-2058 (2019).

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at the 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/X-Sun-ORNL-Additively-Manufactured-Device.pdf*.

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at the 2018 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/X-Sun-ORNL-Additive-Manufacturing-Utilization.pdf*.

Sun, X., et al. “Additively Manufactured Intensified Device for Enhanced Carbon Capture,” Presented at Project Kickoff Meeting, Pittsburgh, PA, October 2017. *https://www.netl.doe.gov/projects/files/FWP-FEAA130-Kickoff-101917.pdf*.

High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing

primary project goals

Lawrence Livermore National Laboratory (LLNL), as part of the Discovery of Carbon Capture Substances and Systems (DOCCSS) initiative, is designing and fabricating high-efficiency reactors supporting advanced sorbents, solvents, or membranes for transformational carbon capture. An integrated design process coupling computational design optimization with additive manufacturing (AM) is creating novel reactor geometries customized for new carbon dioxide (CO_2) capture materials.

technical goals

- Assess new reactor geometries and identify design principles.
- Assess AM for each reactor type.
- Identify the most promising reactor class (sorbent, solvent, or membrane) for the next phase of development.
- Design and test the first-generation bench-scale reactor.
- Evaluate a small-scale integrated prototype of the first-generation reactor design with simulated flue gas.
- Design and test a second-generation bench-scale reactor.
- Design an integrated prototype of the second-generation reactor concept.

technical content

LLNL is designing high-efficiency reactors to support advanced sorbents, solvents, or membranes for CO_2 capture. An integrated design process utilizing computational design optimization combined with AM is utilized to create new reactor geometries designed for advanced carbon capture materials resulting in efficient, low-cost carbon capture. The reactors can offer a range of improvements for CO_2 capture, including absorbers and fixed beds with integrated heat exchange, enabled by the unique structure of the triply periodic minimal surfaces (TPMS). They can also enable membrane-based separators with minimal pressure drop and strippers capable of extreme high pressure. The bases of these novel reactors are hierarchical networks and TPMS, shown in Figure 1. These new geometries will be fabricated using AM techniques at LLNL. An example of a TPMS structure fabricated using AM at LLNL is shown in Figure 2. The TPMS geometries can be made into packing for columns. These printed plastic packings allow TPMS geometries with integrated heat exchange. LLNL has demonstrated printed packing in multiple different plastics, including acrylonitrile butadiene styrene

technology maturity

Bench-Scale, Simulated Flue Gas

project focus:

Additively Manufactured High-Efficiency Reactors for Sorbents, Solvents, and Membranes

participant:

Lawrence Livermore National Laboratory

project number:

FWP-FEW0225

predecessor projects:

N/A

NETL project manager:

Andy Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Joshuah Stolaroff
LLNL
stolaroff1@llnl.gov

partners:

N/A

start date:

08.01.2017

percent complete:

60%

(ABS), high-density polyethylene, and polycarbonate. The ABS-based packing with TPMS showing the same geometry as conventional stainless-steel packing is shown in Figure 3.

LLNL will evaluate novel geometries and identify the design principles for these new reactor types. AM techniques will be assessed. The most promising reactor class, either sorbent, solvent, or membrane, will be identified to move forward with in the development process. A first-generation reactor will be designed, fabricated with the AM techniques, and tested on simulated flue gas at the bench-scale. Based on the test results, the team will design a more advanced second-generation reactor. Integrated prototype testing for both will include adsorption and desorption with continuous operation.

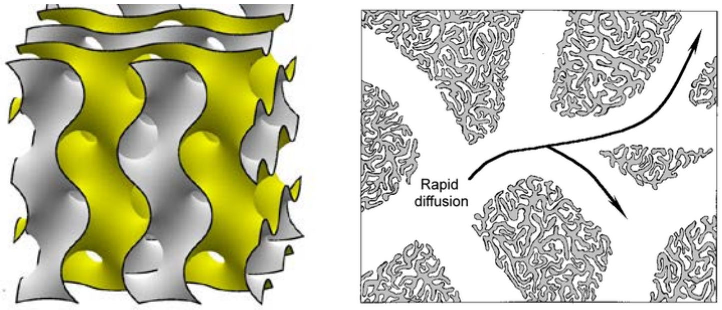

Figure 1: Design features focused on at LLNL: triply periodic minimal surface (l), hierarchical flow channels (r).

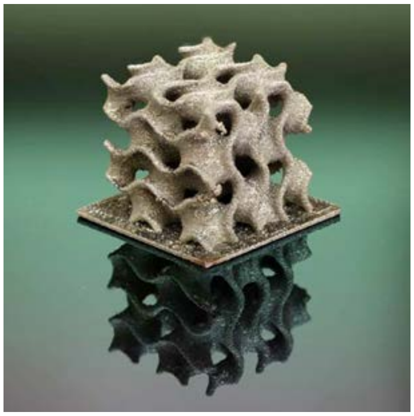

Figure 2: TPMS structure printed using AM at LLNL.

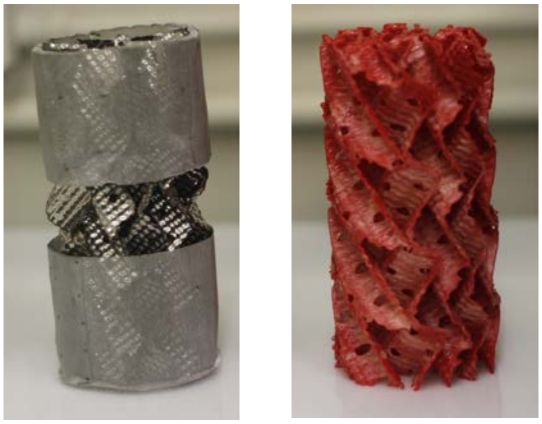

Figure 3: Conventional stainless-steel packing (l) and ABS-printed packing (r).

technology advantages

- Novel reactor geometries enable absorbers and fixed beds with integrated heat exchange, membrane separators with minimal pressure drop, and extremely high-pressure-capable strippers.
- TPMS geometries enhance fluid mixing.
- Lower cost of plastic printed packings compared to stainless steel.

R&D challenges

- Optimizing geometry of TPMS for best performance.
- Identifying new material or fabrication strategy for TPMS membrane reactors.
- Part-scale fabrication using AM.

status

LLNL has concluded that for single-phase flow, smaller feature sizes are better, to the limits of fabrication. Printed plastic packings using multiple materials were demonstrated. Hydrophobic surfaces in the stripper are promising for polarity-swing solvents.

available reports/technical papers/presentations

Stolaroff, J., "High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing," Presented at 2019 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Stolaroff-LLNL-Additive-Manufacturing.pdf*.

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Stolaroff, J., "High-Efficiency, Integrated Reactors for Sorbents, Solvents, and Membranes Using Additive Manufacturing," Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/1J-Stolaroff1-LLNL-High-Efficiency--Integrated-Reactors.pdf*.

Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing

primary project goals

ION Clean Energy, Inc. (ION) is developing advanced gas-liquid contacting devices that enable more efficient capture of carbon dioxide (CO_2) with reduced process footprints. The Modular Adaptive Packing (MAP) design incorporates a mathematically driven model for creating a contacting device built for integrated mass transfer and heat transfer based on computational fluid dynamics (CFD). The overall objective of this project is to design, fabricate, and evaluate packing internals in a packing characterization rig.

technical goals

- Design MAP modules for testing at ION's pilot facility.
- Use 3D-printing techniques to fabricate MAP modules in plastic for design verification, including but not limited to fit, performance, and stress testing.
- Use 3D-printing techniques to fabricate metal MAP module prototypes for packing characterization.
- Modify ION's capture rig to a packing characterization rig for suitable evaluation of packings regarding pressure drop, active surface area, and liquid hold-up measurements.
- Perform baseline testing in the modified rig using a commercially available packing.
- Install the 3D-printed metal MAP modules into the packing characterization rig and perform systematic testing to verify packing design performance.
- Incorporate experimental test results into process models and perform simulations on new structured packings.
- Implement simplified packing models that are descriptive of the MAP with monoethanolamine (MEA) in the acid-gas software modeler, ProTreat®, for further data analysis and concept evaluation.

technical content

Standard CO_2 absorption technologies create heat (i.e., exothermic) upon reacting CO_2 with a liquid absorbent. When optimizing for process efficiency, the greatest amount of heat released occurs towards the top of the absorber in close proximity to the clean flue gas exit and as such carries the risk of solvent loss through evaporation at an elevated temperature. Therefore, the program described herein addresses the challenges of internal gas-liquid contactors and novel methods for controlling evaporative solvent loss risks.

The internals of process columns (e.g., distributors, packing, and collectors), heat exchangers, and emissions control measures are among the highest capital costs

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture

participant:

ION Clean Energy, Inc.

project number:

FE0031530

predecessor project:

SC0012056

NETL project manager:

Katharina Daniels
katharina.daniels@netl.doe.gov

principal investigator:

Erik Meuleman
ION Clean Energy, Inc.
erik.meuleman@ioncleanenergy.com

partners:

3D Systems, ANSYS, Optimized Gas Treating, Inc., Sulzer Chemtech USA

start date:

01.19.2018

percent complete:

85%

in CO_2 capture plants. ION's MAP technology provides a way to lower the cost of column internals in CO_2 capture systems, while simultaneously reducing degradation rates and emissions of typical amine-based capture solvents, thereby allowing for more economically sustainable capture plant operations. The use of 3D printing to fabricate packing internals reduces the costs, which allows for the total freedom of design of the gas-liquid interaction area and the complete integration of intra-column cooling. 3D printing is an "additive" fabrication technique that offers unprecedented advantages in accelerating the design cycles of gas-liquid contacting devices, minimizing manufacturing costs, and expediting the deployment timeline for CO_2 capture commercially.

Through the use of 3D printing, ION can maximize the surface area to void volume of the contactor surface through complete geometric freedom. The flow domain consists of a cylindrical tube that encapsulates a hollow structure. The hollow structure forms a network of channels filled with cooling water, where CO_2-containing air and liquid absorbent can chemically react in the space outside the cooling water channels for heat transfer. The design essentially combines the absorber gas-liquid contactor with an in-situ heat exchanger.

This project is a continuation of a previous U.S. Department of Energy (DOE)-funded Small Business Innovation Research (SBIR) project, DE-SC0012056. Phase I results of the SBIR project showed that the mass transfer increases with increasing surface area to volume ratios in the packing. In Phase II, ION developed a dual-function mass and heat transfer packing medium to incorporate heat transfer into the design. The design team first 3D-printed plastic prototypes to test for overall fit, check for design flaws, and evaluate the potential for commercialization. ION engineers landed with a final design using metal and then tested in ION's 0.001-megawatt-electric (MWe) lab pilot (Figure 1) CO_2 capture unit using a common benchmark solvent of 30 wt% MEA and synthetic flue gas. The results were compared to commercially available and optimized structure packing (Sulzer Mellapak 350X) tested in the same unit under the same process conditions. The results of the testing showed more than a 10°C reduction in absorber maximum temperature compared to baseline structured packing, which leads to significantly reduced emissions. Additionally, the mass transfer was comparable and within 5% of the benchmark results. As expected, the MAP was shown to have inferior pressure drop properties, mainly due to the addition of cooling channels. Other contributing factors to the increased pressure drop were the internal support structures within the additive packing, which were necessitated by the metal printing process and had to be added to the design prior to printing. However, when cooling was implemented, the pressure drop was lower (~15%) compared to the uncooled version. At a larger scale, important for commercial viability, the pressure drop will decrease since a much lower volume fraction will be occupied by the cooling channel and its wall thicknesses. During Phase II, ION also designed a CFD model to simulate the CO_2 capture process. The model predicted the flow and energy dynamics of coolant water, the gas flow, and the distribution of liquid solvent in the domain, as well as the CO_2 absorption for a various geometries and operating conditions. CFD lends itself to parameterization—wherein geometry, flow rates, and other tunable variables, such as the reaction mechanism and rate, can be changed to understand the entire design space available and optimize the model before the fabrication of prototypes. Figure 2 shows a computer model and the resulting plastic and metal printed prototypes. Overall, the SBIR project successfully demonstrated the commercial viability of customizable and modular packing devices that incorporate both heat and mass transfer for CO_2 capture and other applications where exothermic reactions are involved.

Figure 1: ION's lab-pilot (0.001 MWe) CO_2 capture test unit.

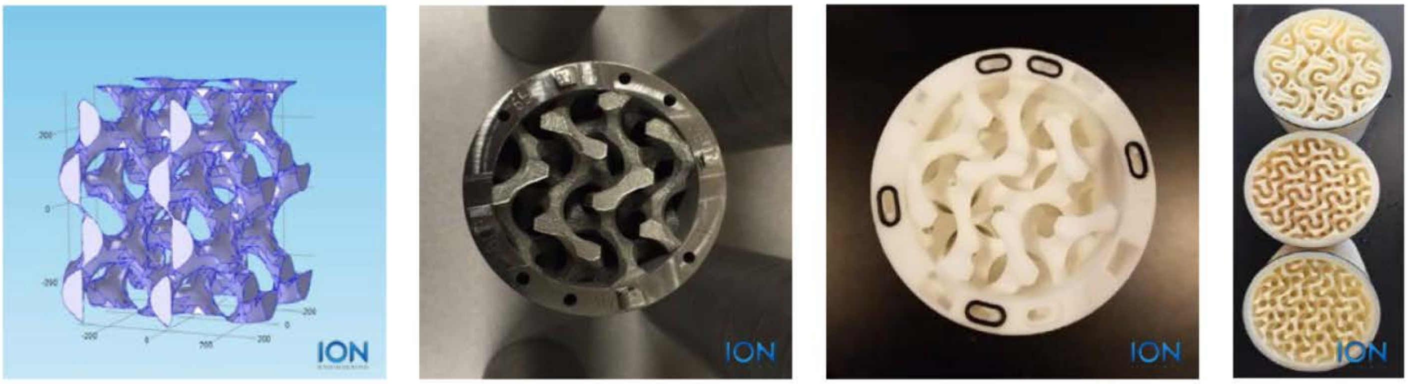


Figure 2: Design model, metal prototype, and plastic prototypes from SC0012056.

This Phase III project consists of advanced manufacturing efforts that will result in a 3D-printed commercial prototype of a gas-liquid contacting device that is modular and adaptable to both small- and large-scale applications. Further enhancements are being made to the heat exchange, which will allow for further improved mass transfer and a significant decrease in pressure drop. ION is utilizing the design work from the previous SBIR project and incorporating expertise from commercial experts such as ANSYS and 3D Systems to produce an optimized MAP prototype design. Parameters that are being evaluated include the shape of inner walls and structures to promote primary and secondary mixing, liquid-gas mass transfer contact area, liquid-liquid heat exchange area, wall thickness and integrity, material choice, and the ratio of area for gas and liquid flow versus coolant flow. These design parameters are being evaluated across a range of process parameters, such as pressure drop, mass and heat transfer between gas and liquid phases, heat transfer between cooling or heating medium and liquid-gas channel, heat transport within a module and within a range of modules, connectivity, safeguards in event of leakage, wall-effects, entrainment, and flooding.

Prototypes were printed in plastic using a stereolithographic apparatus for design and structural verification and metal prototypes were printed based on the final design. Successfully printed metal MAP modules are being tested at ION's packing characterization rig that has been modified to accommodate the MAP modules, as well as a standard column that incorporates a commercial structure packing. The characterization aims to empirically determine packing characteristics, including pressure drop over the height of the packing as a function of gas- and liquid-load and viscosity; packed-bed liquid hold-up over a broad range of column gas and liquid loads; and effective surface area of the packings as a function of gas and liquid load. Development strategies focus on optimal designs for the MAP from three angles by computational analyses:

- Optimized heat transfer by liquid flow design (using CFD), inlet and outlet positioning, material choice, and vanes.
- Optimized specific area by vanes and printing surface roughness.
- Optimized pressure drop on the gas side.
    - Incorporate aerodynamic principles and circumvent channeling.
    - Incorporate considerations on gas volumetric flow changes throughout packing (temperature, CO_2 removal).

Figure 3: 3D-printed columns in plastic and metal.

TABLE 1: SOLVENT PROCESS PARAMETERS

Proposed Module Design			(for equipment developers)	
Flue Gas Flowrate	kg/hr		> 600	
CO_2 Recovery, Purity, and Pressure	% / % / bar	95%	99%	1.0
Absorber Pressure Drop	bar		< 0.020	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		TBD	

Definitions:

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Lower cost of column internals, including distributors, packing, and collectors.
- Reduces degradation rates and emissions of typical amine-based capture solvents.
- Modular and scalable, which allows for customization of temperature profiles, mass transfer, and pressure drop.
- The use of 3D printing allows for the use of lower-cost materials and minimizes manufacturing costs.
- It allows for control of absorber profile temperatures, which leads to reduced emissions-related issues and lower energy consumption. This allows for significant capital savings in the water wash by reducing packing height requirements and results in lower operating expenses due to reduced solvent makeup.
- The rapid and flexible feedback loop between design, fabrication, and testing provided through 3D printing advances the performance and lowers the costs of gas-liquid contacting devices for CO_2 capture.

R&D challenges

- Module leakage.
- Blockage of the intercooling tubes.
- Structural integrity of 3D-printed modules.

status

CFD modeling efforts have resulted in an advanced 3D design model incorporating mass transfer, reaction, heat transfer, and pressure drop calculations for CO_2 capture. ION has completed a redesign of the module internals to reduce the calculated printing time from 100 days to the design limit of the machine, which is under 10 days. Full-size 3D prototypes have been printed in plastic by 3D Systems for design and structural verification. After the final design was selected, two modules were printed in metal for quality assurance testing and then were put together for fitting and leak testing. The remaining metal modules have been printed by 3D Systems and shipped to the ION facility for testing. ION has coordinated with a third-party fabrication shop to assemble the in-house packing characterization rig.

available reports/technical papers/presentations

Meuleman, E., Panaccione, C., et al., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," presented at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/E-Meuleman-ION-Novel-Contacting-Devices.pdf*.

Meuleman, E., Atcheson, J., and Panaccione, C., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," presented at the 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://netl.doe.gov/sites/default/files/netl-file/E-Meuleman-ION-Rapid-Design-and-Testing-of-Contacting-Devices.pdf*.

Meuleman, E., Atcheson, J., and Panaccione, C., "Rapid Design and Testing of Novel Gas-Liquid Contacting Devices for Post-Combustion CO_2 Capture via 3D Printing: Modular Adaptive Packing (MAP)," Project Kickoff Meeting. July 2018.

A Process with Decoupled Absorber Kinetics and Solvent Regeneration Through Membrane Dewatering and In-Column Heat Transfer

primary project goals

The University of Kentucky Center for Applied Energy Research (UK CAER) has teamed with Media and Process Technology Inc. and Lawrence Livermore National Laboratory (LLNL) through support project FWP-FEW0242 to develop an intensified, innovative carbon dioxide (CO_2) capture process. The project goals are to increase system efficiency and enable significant reductions in capital and operating costs of solvent-based post-combustion capture through: (1) the use of 3D-printed, two-channel structured packing material to control absorber temperature profile and increase the CO_2 absorption rate, thereby allowing decreases in absorber size; (2) implementation of a zeolite membrane dewatering unit capable of substantial dewatering of carbon-rich solvent to decouple solvent concentrations that are optimum for CO_2 absorption and desorption; and (3) utilization of a two-phase flow heat exchanger prior to the stripper, providing a secondary point of vapor generation for CO_2 stripping resulting in significant energy savings.

Project scope is to design and fabricate advanced structured packing and a dewatering membrane module, and retrofit and test the intensified process on UK CAER's small and large (0.1-megawatt-thermal [MWth]) bench-scale post-combustion CO_2 capture facilities with simulated and coal-derived flue gas. Results will underpin a process techno-economic analysis (TEA), an environmental, health, and safety (EH&S) risk assessment, and a technology gap analysis to advance the technology toward further scale-up and commercialization.

technical goals

- Enable reduction of absorber size (compared to baseline conventional absorber) by up to 50% through application of the in-situ heat removal structured packing material.
- Attain at least 15% dewatering of the carbon-rich solvent in the process loop.
- Attain 30% energy savings in the solvent reboiler-specific energy consumption.
- Demonstrate the process at 0.1 MWth bench-scale on coal-derived flue gas.
- Collect data to perform the detailed TEA of CO_2 capture process integration to a full-scale coal-fired power plant.
- Advance this technology to meet U.S. Department of Energy (DOE) capture goals of 95% CO_2 purity at a cost of approximately $30 per tonne of CO_2 captured.

technology maturity:

Large Bench-Scale (0.1 MWth), Actual Flue Gas

project focus:

Integrated Advanced Solvent Process

participant:

University of Kentucky Center for Applied Energy Research (UK CAER)

project number:

FE0031604
(support project FWP-FEW0242)

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Kunlei Liu
University of Kentucky
kunlei.liu@uky.edu

partners:

Media and Process Technology Inc., Lawrence Livermore National Laboratory (LLNL)

start date:

05.01.2018

percent complete:

55%

technical content

UK CAER's starting point for development of this technology was consideration of the drivers for capital and operating costs of aqueous post-combustion capture process systems. While still utilizing the general process arrangement of CO_2 absorption-desorption by contacting the flue gas with solvent (which might even be a commonly used aqueous solvent such as an amine) in the absorber and water vapor stripping the rich solvent in the regenerator, UK CAER has postulated that significant efficiency and cost savings could be obtained by deploying several design improvements in this process and innovations in certain units. The basic process arrangement and units involved are depicted in Figure 1.

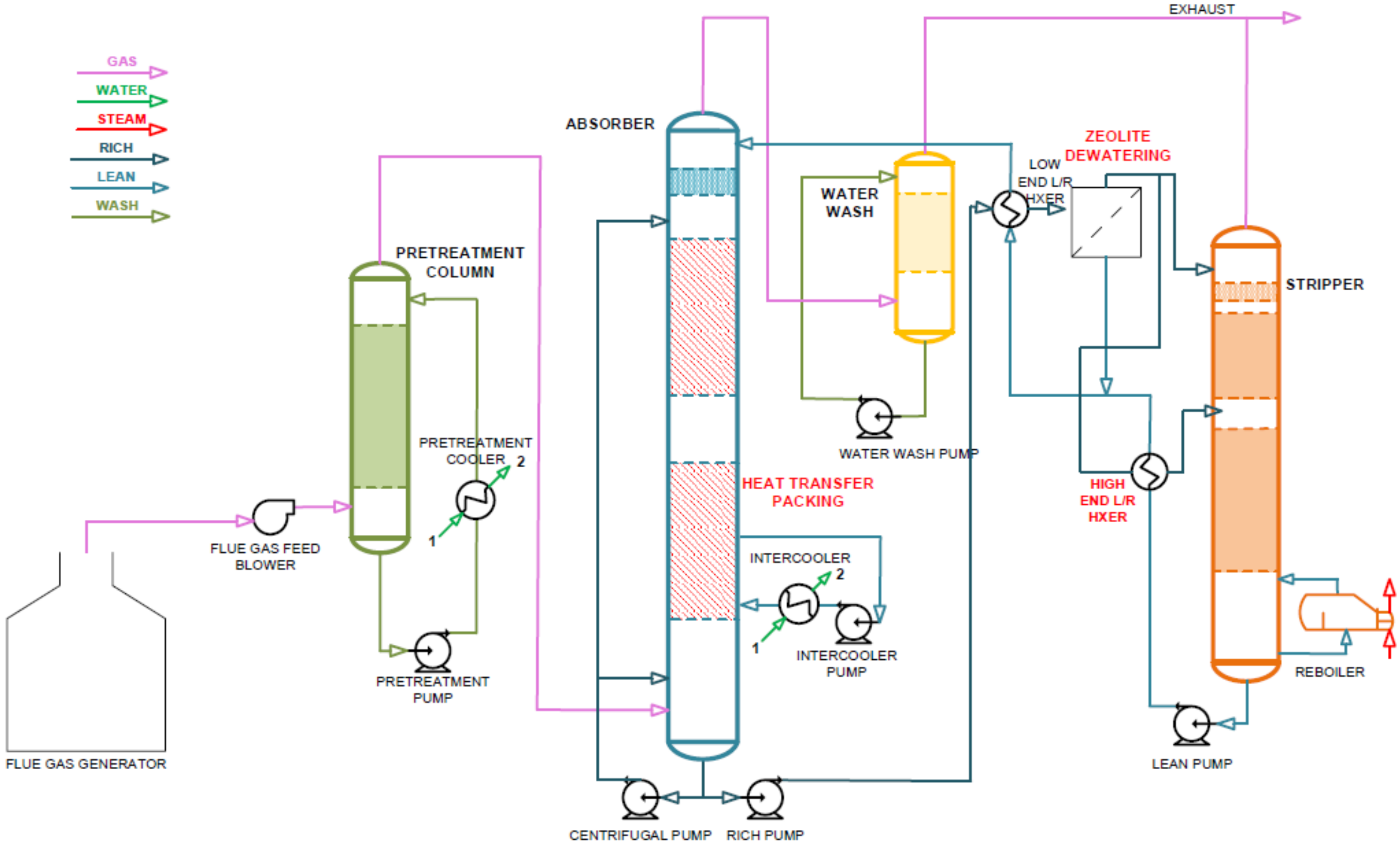


Figure 1: UK CAER CO_2 capture process.

Improvement of Temperature Profile in the Absorber—3D-Printed Packing

The absorber for contacting flue gas with solvent to remove the CO_2 from the flue gas is a packed column type containing either random or structured packing to increase mixing/contacting of the gas and liquid solvent. The diameter of the absorption column is determined by the flooding point at the liquid/gas (L/G) ratio; the diameter must be large enough to prevent flooding. The highest flooding potential for a fast-reacting solvent occurs at a characteristic temperature bulge, which typically occurs in the top packing section, 15 to 30% of packing height from the top. A measured temperature profile for UK CAER's 0.7-megawatt-electric (MWe) small pilot-scale absorber is shown in Figure 2 for contacting flue gas with amine solvent. With L/G ~3.2, a temperature rise of ~50°F is observed ~10 feet below the lean amine feed.

Because the driving force for CO_2 absorption is inhibited by high temperature, temperature excursions like this decrease performance, which means that larger internal column diameter and increased column height (translating directly into increased column cost) would be necessary to accomplish a given required amount of CO_2 capture. However, if internal temperatures in the column can be aggressively managed, column size can be substantially reduced.

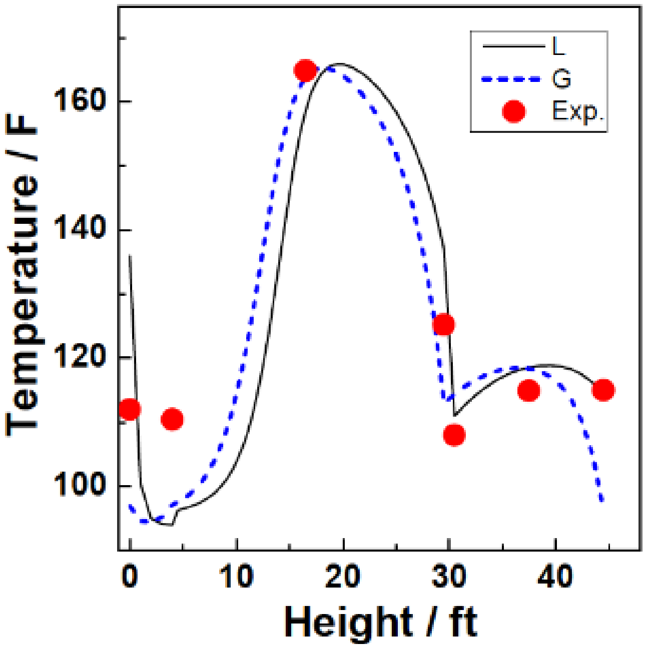


Figure 2: Absorber temperature profile (solid lines indicate model predictions for liquid and gas, experimental data in dots).

The UK CAER team's approach for temperature management in the absorber is to deploy innovative, 3D-printed structured packing that incorporates heat transfer channels in the packing. This would provide in-process substantial cooling at appropriate locations without the need for separate, multiple external inter-stage cooling sections (reducing column height). Use of 3D printing/additive manufacturing provides the capability to fabricate the packing with the complex dimensional patterns required at reasonable cost.

Polymeric materials, such as acrylonitrile butadiene styrene (ABS), polystyrene, and high-density polyethylene, were investigated for use. They are stable in the presence of loaded amine solvent at operating temperature, while they are readily amenable to 3D printing via methods such as fused deposition modeling and stereolithography. Figure 3 shows the design (left) and a fabricated unit printed in ABS via stereolithography (middle). Instances of leakage, structural integrity issues, and fouling have occurred with certain polymeric materials made by certain methods; recently, use of direct metal laser sintering to fabricate packing from 316 stainless steel (Figure 3, right) has delivered promising results.

Figure 3: 3D-printed packing.

Evaluation of the performance of the packing for improving the temperature profile in the absorber column has been ongoing using the bench-scale unit at UK CAER. Figure 4 shows results of putting the new packing material into the column. The solid line is the baseline without the heat transfer packing, and the dotted and dashed lines are with it in place. Thermocouples are located at regular intervals from position 1 at the top of the column (lean solvent inlet) to position 7 at the bottom (flue gas inlet). Note that the typical temperature increase at positions 2 and 3 in the baseline has been greatly improved when the heat transfer packing is deployed.

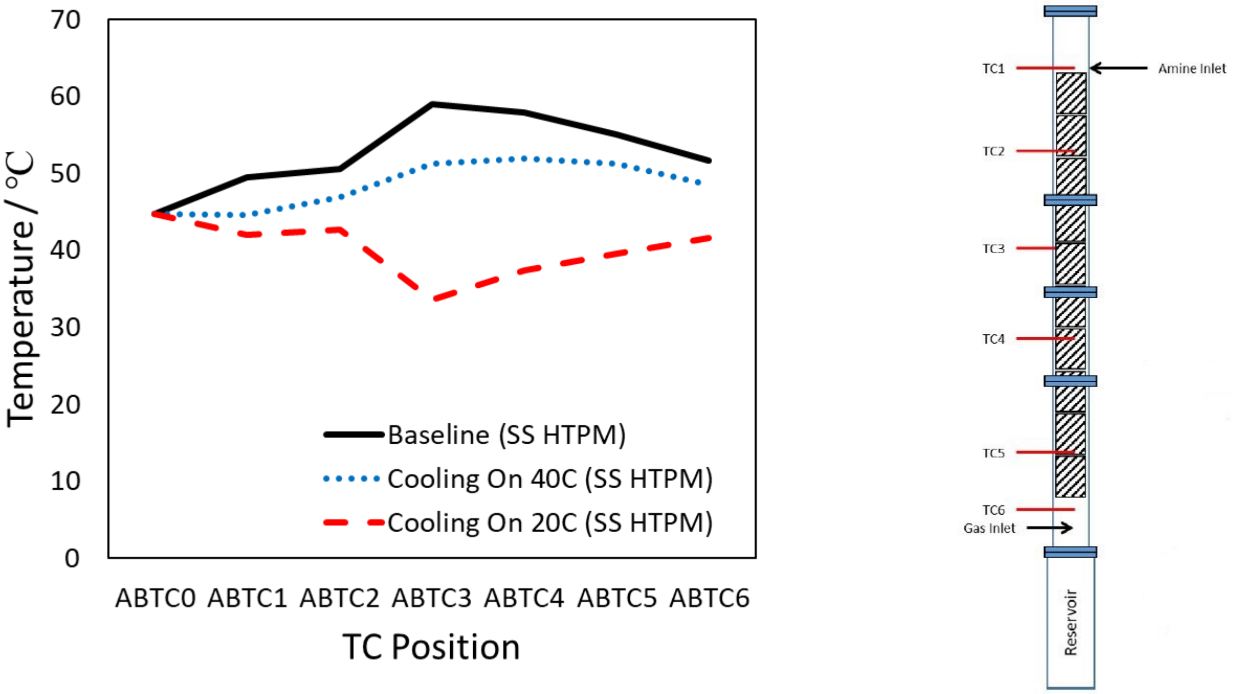


Figure 4: Heat transfer packing effect on absorber column temperature profile.

Dewatering Rich Solvent—Membrane-Based Dewatering Unit

Another element of this innovative process approach is tackling the conflicting requirements for solvent concentrations between the absorber and stripper. In terms of transport phenomena, it is well accepted that the stripper is equilibrium-controlled while the absorber is mass transfer/diffusion-controlled. For the equilibrium-controlled stripper, the carbon loading via CO_2 partial pressure will determine the size of the stripper as well as the energy associated with stripping gases, which typically accounts for approximately 40% of the overall energy required for solvent regeneration. Higher solvent concentrations typically produce higher carbon loadings per kilogram solution at a given temperature compared to a diluted solvent, so more concentrated solvents are preferable for stripper applications. However, higher solvent concentrations always correspond to higher viscosities. For a diffusion-controlled absorber using any advanced fast solvent, the mass transfer coefficient is dominated by the resistance from the chemical reaction of CO_2 and amine in the reaction film and diffusion of unreacted amine and carbamate between the reaction interface and bulk solvent. Unfortunately, the diffusivity between the reaction interface and the bulk solvent is governed by a mildly exponential relationship in which higher solvent viscosity increases the diffusion resistance, thereby reducing mass transfer.

To better attain desired solvent concentrations between the absorber and stripper, a dewatering unit using zeolite membranes is being developed and evaluated. The unit receives rich solvent from the absorber and permeates it through membranes, resulting in concentrated solvent retentate and a permeate stream of mostly water. The target is to accomplish at least 15% dewatering of the solvent coming from the absorber in this membrane-based dewatering unit. The permeate water is returned to the absorber, leaving a carbon- and solvent-concentrated solution to enter the stripper for regeneration. This has the dual desired result of lowering energy consumption in the stripper, while simultaneously maintaining more dilute solvent in the absorber so as not to negatively impact CO_2 absorption rates there. The dewatering step is indicated in Figure 1 as Zeolite Dewatering; note that the recovered water is mixed with the lean solvent from the stripper and the combined stream goes to the top of the absorber.

Design and fabrication of the zeolite membrane dewatering modules is an important aspect of technology development. The membranes themselves consist of a thin zeolite layer on a sublayer of dense alumina, all of which is supported on tubes of highly porous conventional alumina. The very dense alumina layer is needed to confine the molecular seed particles to the surface of the alumina, from which the zeolite layer is grown. Figure 5 shows a scanning electron microscopy (SEM) cross-section of a membrane showing the juxtaposition of these layers, with a fully formed 3.5 µm layer of zeolite on the outside. The membrane tubes are to be deployed in bundles in modules, per the design depicted in Figure 6 for the intended bench-scale testing. Membrane packing density can reach ~322 m^2/m^3 in these modules.

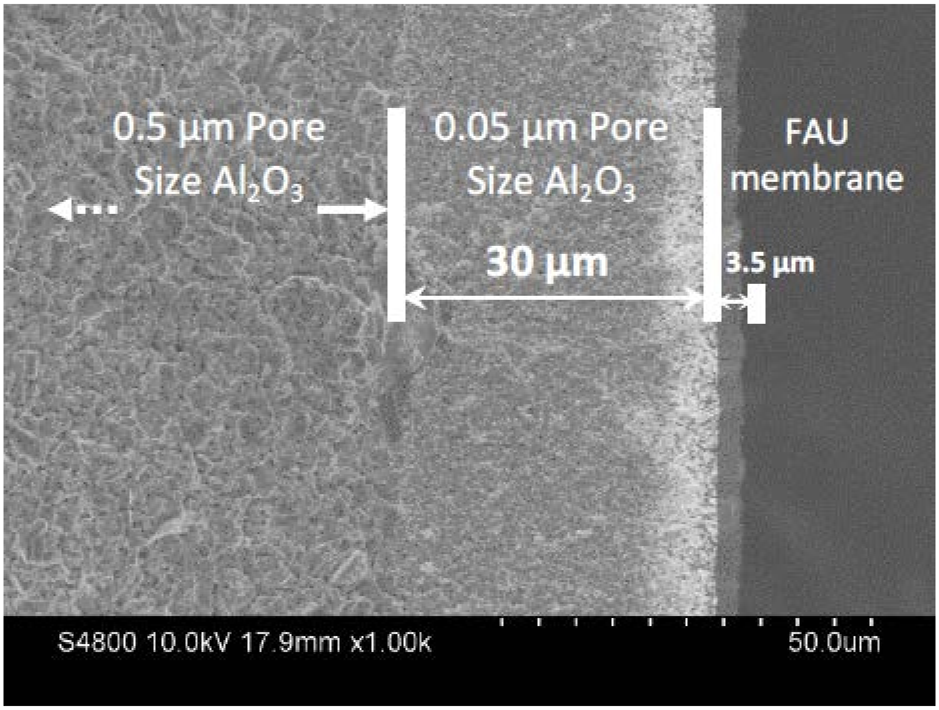
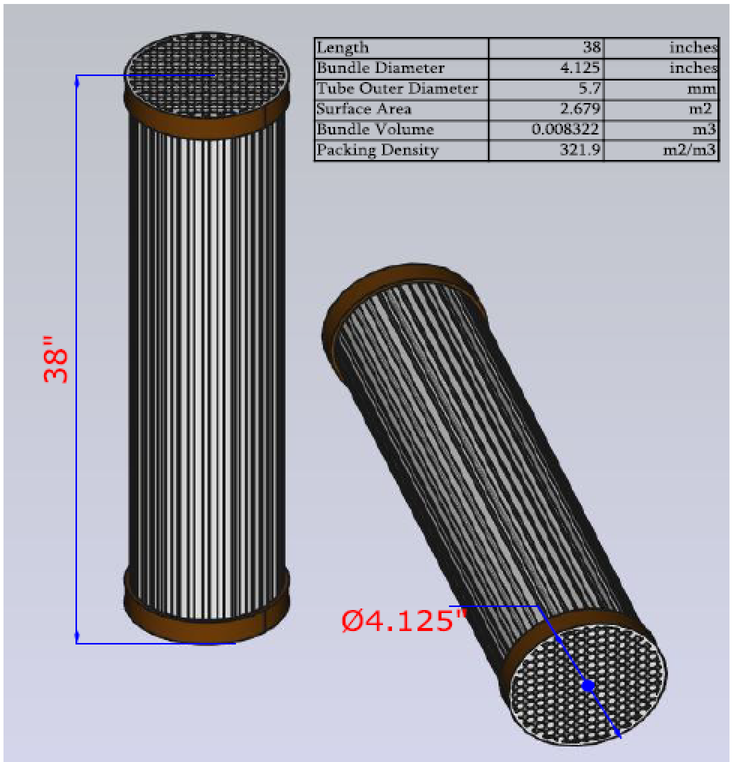


Figure 5: Dewatering membrane structure.



Length	38	inches
Bundle Diameter	4.125	inches
Tube Outer Diameter	5.7	mm
Surface Area	2.679	m2
Bundle Volume	0.008322	m3
Packing Density	321.9	m2/m3

Figure 6: Dewatering membrane module design.

Advanced Stripping and Secondary Vapor Generation Point

An additional improvement in this process approach targets reduction of steam consumption by considerations of phase transitions occurring in the stripper and optimization of heat exchange and points of solvent feed to the stripper. In a conventional stripping process, the stripper reboiler uses extracted steam to evaporate water in the solvent both as a carrier gas to strip CO_2 out of the solvent and as an energy carrier to heat the stripper to a desired temperatures profile as required by the solvent and stripper operating pressure. During this process, significant exergy is lost. Secondarily, high rich solvent temperature from the rich/lean heat exchanger entering the stripper prevents the gaseous phase from condensing at the top of the stripper, reducing heat recovery within the system as more water vapor is lost with the gaseous exhaust. Consequentially, the typical temperature profile (left) and CO_2 and water fluxes (right) as a function of height in the stripper have been observed on UK CAER's 0.7-MWe post-combustion capture facility and modeled as plotted in Figure 7. This clearly indicates that most of the CO_2 is liberated from the solvent in the bottom 14 feet or so of the 30-foot-long stripper (corresponding with the nearly flat plateau seen in the right-side panel).

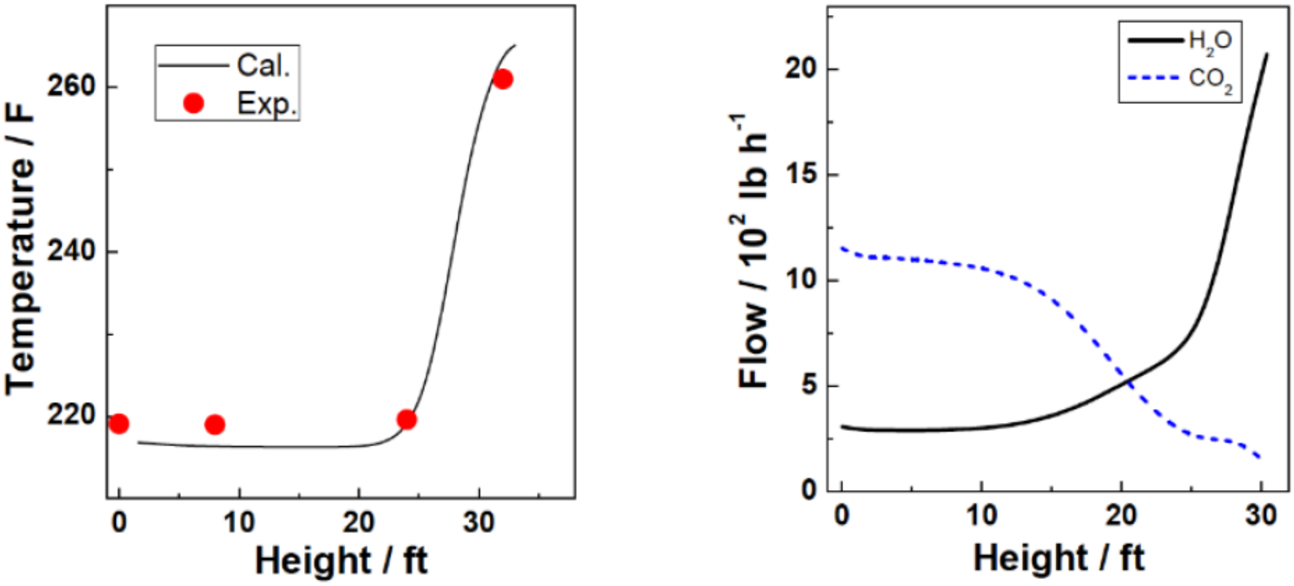


Figure 7: Temperatures and mass fluxes in solvent stripper.

To overcome these inefficiencies characteristic of the conventional stripper regenerator, UK CAER is evaluating a process design using a secondary entry point for rich solvent feed. The multi-point rich solvent feed is accomplished by dividing the traditional lean/rich (L/R) heat exchanger into two sections – a low-end L/R exchanger and a high-end L/R exchanger (which essentially creates a second source for vapor generation). The basic arrangement of these is diagrammed in Figure 1. The feed to the stripper from the dewatering unit is split into two streams: (1) after the low-end exchanger, about half of the total rich flow with a temperature (solvent and carbon loading dependent) is fed to the top of stripper packing as a heat sink to condense water vapor and subsequently reduce the water (H_2O)/CO_2 ratio; and (2) the remaining rich flow is heated through the high-end exchanger so that two-phase flow is achieved with 5 to 6% vapor entering the middle of the stripper packing. This vapor will act as a secondary source of carrier gas for CO_2 stripping. UK CAER modeling indicates the H_2O/CO_2 ratio in the stripper exhaust will be significantly reduced from 0.8 to 1.0 as experienced conventionally, to 0.3 to 0.4, allowing an ~26% reduction in steam consumption.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	Amine	Amine
Normal Boiling Point	°C	155-170	155-170
Normal Freezing Point	°C	-2	-2
Vapor Pressure @ 15°C	bar	0.0007	0.0007
Manufacturing Cost for Solvent	\$/kg	14.74	14.74
Working Solution			
Concentration	kg/kg	0.35-0.45	0.35-0.45
Specific Gravity (15°C/15°C)	-	~1.0	~1.0
Specific Heat Capacity @ STP	kJ/kg-K	2.7-3.3	2.7-3.3
Viscosity @ 15°C	cP	5-7	5-7
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5	0.45
Heat of Absorption	kJ/mol CO_2	~-65	~-70
Solution Viscosity	cP	3-5	3-5
Desorption			
Pressure	bar	3-5	3-5
Temperature	°C	110-130	110-130
Equilibrium CO_2 Loading	mol/mol	0.20	0.20
Heat of Desorption	kJ/mol CO_2	~85	~85
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	24	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 ~20	
Absorber Pressure Drop	bar	<20"WC	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	\$36K	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted otherwise, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The solvent is an aqueous solution of a hindered primary amine. A carbamate species is formed upon CO_2 absorption. In a CO_2 capture absorber, the absorption rate, **R**, as a function of temperature, **T**, and carbon loading, **C/N**, can be expressed as: $\mathbf{R(T, C/N) = k_G{\cdot}a{\cdot}(P_{CO2} - P^*_{CO2})}$ where $\mathbf{k_G}$ is mass transfer coefficient, **a** is effective wetted surface area, and $\mathbf{(P_{CO2} - P^*_{CO2})}$ is the driving force, the difference in the concentration of CO_2 in liquid from the gas. Significant increase in **R**, via $\mathbf{k_G}$ and **a**, and corresponding reduction of capital cost comes from the mass transfer enhancement of the proposed aqueous system compared to any second-generation technology because there is an order of magnitude greater effective wetted surface area n in the top of the absorber.

Solvent Contaminant Resistance – UK CAER analysis show the solvent is more resistant to degradation, 40 to 50% improvement than 30 wt% MEA. Accumulation of metals within the solvent is expected to be equivalent to that within 30 wt% MEA.

Solvent Foaming Tendency – The experimental data from a packed column (2-inch ID mini-scrubber) and large-bench (4-inch ID column) indicate the foaming tendency of proposed solvent is very low.

Flue Gas Pretreatment Requirements – The flue gas pretreatment requirement is sulfur dioxide (SO_2) removal to less than 5 parts per million (ppm) to minimize heat stable salt formation. This can be done with a standard counter-current pretreatment column with a circulating solution of either of soda ash (Na_2CO_3) or sodium hydroxide (NaOH). The solvent used is a hindered primary amine and does not form stable nitrosamine species; therefore, no additional nitrogen oxide (NO_X) removal is required. No additional moisture removal is required, as it is for ionic liquids.

Solvent Makeup Requirements – Two factors contributing to solvent makeup rate are degradation and emission. UK CAER analysis shows the solvent has degradation rates less than 30 wt% MEA, and when the UK CAER developed solvent recovery technology is applied, the solvent emission will be about 0.5 ppm. The anticipated solvent makeup rate is less than 0.5 kg/tonne CO_2 captured.

Waste Streams Generated – The waste streams of the post-combustion CO_2 capture process using the proposed compact absorber are the same as any other post-combustion CO_2 capture process. There will be a blowdown stream from the SO_2 pretreatment column and a reclaimer waste stream from the solvent loop.

Process Design Concept – See Figure 1.

technology advantages

- Reduction in absorber column size, reducing both capital and operating costs.
- Reduction in stripper column size and steam demand for solvent regeneration, reducing both capital and operating costs.

- Applicability to a variety of solvents in absorption-based capture process implementation.

R&D challenges

- Innovative absorber packing fabrication cost, structural/performance integrity, fouling.
- Dewatering membrane unit zeolite membrane fabrication, module integrity.
- Increased controls and control schemes, mainly because of more complicated process flows and heat exchange around the dewatering unit.

status

Absorber testing with deployment of 3D-printed packing material has resulted in 10°C temperature reductions, proving the concept for the structured packing enabling column size reductions. The zeolite membrane-based dewatering has been validated on amine solvent at 10 kg/m^2/hr, and modules with required membrane packing density have been established. Individual components in the UK CAER bench-scale unit have been evaluated, paving the way for the larger-scale testing in continued work.

available reports/technical papers/presentations

"*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," BP1 project review meeting presentation, October 2, 2019.

"*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," presentation by James Landon, University of Kentucky, 2019 NETL CCUS Integrated Project Review Meeting, Pittsburgh, PA, August 2019.

"*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," presented by James Landon, University of Kentucky, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA.

"*A Process with Decoupled Absorber Kinetics and Solvent Regeneration through Membrane Dewatering and In-Column Heat Transfer*," Project kickoff meeting presentation, May 18, 2018.

Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses

primary project goals

Linde Gas North America, LLC and their project partners will evaluate three flue gas aerosol pretreatment technologies that have the potential to significantly reduce high flue gas aerosol concentrations, which have been shown to contribute to amine losses in solvent based post-combustion carbon dioxide (CO_2) capture (PCC) processes. The options that will be evaluated are: (1) a novel high-velocity water spray concept previously tested at a Rheinisch-Westfälische Elektrizitätswerk (RWE) power plant in Niederaussem, Germany; (2) an innovative electrostatic precipitator (ESP) with optimized operating conditions; and (3) a non-regenerative sorbent-based sulfur oxide (SO_X) and nitrogen oxide (NO_X) removal technology with potential for aerosol particle reduction. The objectives of this project are to design, build, and independently test these technologies at a coal-fired power plant host site using a slipstream of flue gas containing high concentrations of aerosol particles (greater than 10^7 particles/cm^3). The results will be used to benchmark the performance and cost of these technologies against existing options for pretreatment of coal-based flue gas for aerosol mitigation. The impact of this reduction in aerosol concentrations could be leveraged across a variety of solvent-based PCC systems to minimize solvent losses.

technical goals

- Perform a literature study to identify mechanisms that contribute to aerosol particle nucleation and growth in flue gas streams.
- Develop a model to simulate the mechanisms and assess the impact of aerosols on amine losses based on particle size distribution and particle number concentration.
- Complete basic engineering and design and provide cost estimates for the three aerosol pretreatment technologies selected for testing at the Abbott Power Plant.
- Fabricate, install, and commission the high-velocity water spray-based system, ESP system, and sorbent technology system at the host site.
- Perform independent parametric testing of each aerosol pretreatment technology, evaluate test results, and identify the optimum operating and design conditions for maximum performance of each technology.
- Compare test results against predefined targets and standard capabilities of conventional aerosol treatment methods described in literature and complete a techno-economic evaluation for each system to compare system costs at scale.
- Dismantle and remove pilot equipment from the host site.

technical content

Aerosol mitigation methods to reduce aerosol-driven amine losses include: (1) baghouse installation in the flue gas upstream of the PCC plant; (2) amine wash sections and wash section operating conditions for the PCC plant absorber; (3) specific absorber operating temperature and pressure conditions that can also

technology maturity:

Pilot-Scale, Actual Flue Gas

project focus:

Flue Gas Aerosol
Pretreatment

participant:

Linde Gas North America, LLC

project number:

FE0031592

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Devin Bostick
Linde Gas North America, LLC
devin.bostick@linde.com

partners:

University of Illinois at Urbana-Champaign, Washington University in St. Louis, InnoSepra LLC, Affiliated Construction Services

start date:

06.01.2018

percent complete:

70%

negatively impact specific regeneration energy; and (4) flue gas aerosol pretreatment, which is the focus of the proposed technologies and testing.

Figure 1 shows the range of upstream flue gas aerosol particle number concentrations able to be managed by current methods used today to achieve less than 0.3 kg amine emitted per tonne of CO_2 captured for solvent-based PCC processes. For power plants without baghouses producing flue gas containing particle concentrations greater than 10^7 particles/cm^3, the only realistic option available to mitigate aerosol-driven amine losses from PCC plants is flue gas aerosol pretreatment. Flue gas aerosol pretreatment has traditionally been performed using simple ESPs and Brownian filters, but no systematic study has been performed yet to evaluate the performance of these systems over the complete range of possible operating conditions, aerosol particle number concentrations, and aerosol particle sizes. It is important to note that even with lower flue gas aerosol number concentrations (fewer than 10^7 particles/cm^3), there is still a sizeable benefit to using pretreatment systems to minimize amine losses for the entire range of solvent-based PCC operating conditions. Hence, this project focuses on evaluation of flue gas aerosol pretreatment solutions to determine an optimum technology that can minimize aerosol-driven amine losses for any power plant, including plants producing flue gas with the highest range of possible flue gas aerosol concentrations and size distributions. Based on previous 1.5-megawatt-electric (MWe) pilot-scale tests of the Linde-BASF PCC technology at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama, from 2015 to 2016, high aerosol concentrations in the size range of 70 to 200 nm contribute most significantly to amine losses. Hence, this technology development project targets high removal efficiency for particles in and around this size range. Additionally, previous aerosol number concentration measurements performed at the Abbott Power Plant host site, a power generating unit without a baghouse, show the presence of very high aerosol concentrations (greater than 10^7 particles/cm^3). The ability to apply pretreatment technologies on the wide range of aerosol concentrations measured at Abbott will enable demonstration of the performance of each technology as applied at most coal-fired power plants in the world based on aerosol measurement data collated from scientific literature.

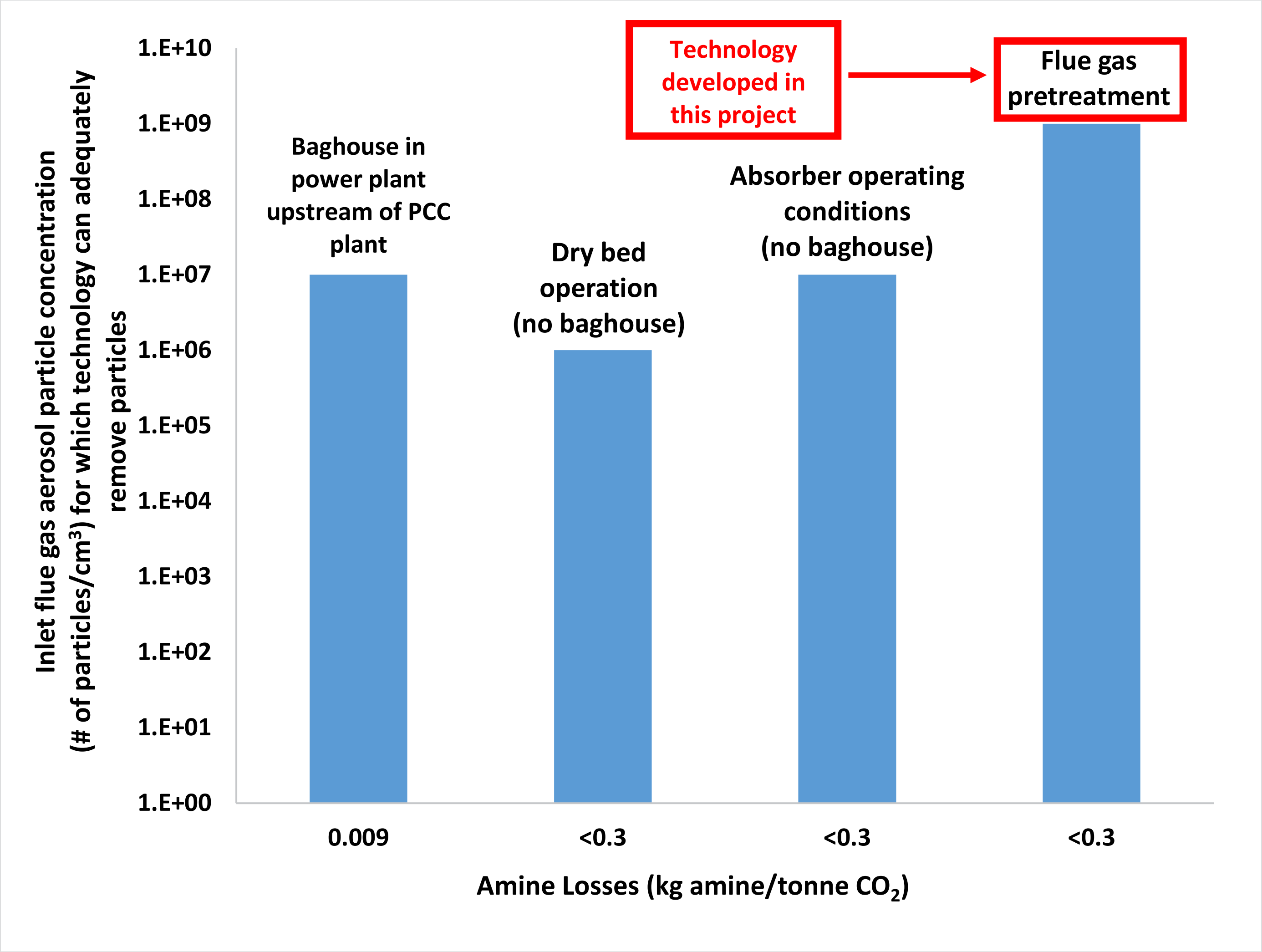


Figure 1: Flue gas aerosol particle number concentration ranges for which aerosol mitigation technologies are applicable and sufficient.

The first aerosol pretreatment technology tested in this work is a novel high-velocity water spray-based system originally developed by RWE and previously tested by RWE in Niederaussem, Germany. A process flow diagram of this system is shown in Figure 2. The high-velocity water spray provided by the specialized nozzle distributor design enables rapid growth and collection of aerosol particles in the liquid phase through water condensation before further removal by the demister at the top of the spray column. In addition, the perforated tray at the midsection of the column optimizes vapor-liquid distribution to enhance aerosol removal. Aerosol particles collected in the liquid-phase are discharged in the process condensate removed from the column, effectively removing the aerosols from the treated flue gas exiting the top of the vessel. The project team has designed, constructed, and tested the water spray-based system on up to 1,000 standard cubic feet per minute (scfm) of actual flue gas emitted from two coal-fired boilers at the Abbott Power Plant host site. Parametric tests have been performed to evaluate the impact of specific spray nozzle and perforated tray designs and operating conditions to determine the optimal system configuration and design conditions maximizing aerosol particle removal efficiency for very high flue gas particle concentrations (up to and greater than 10^7 particles/cm^3) for aerosol particles in the 70 to 200 nm diameter size range.

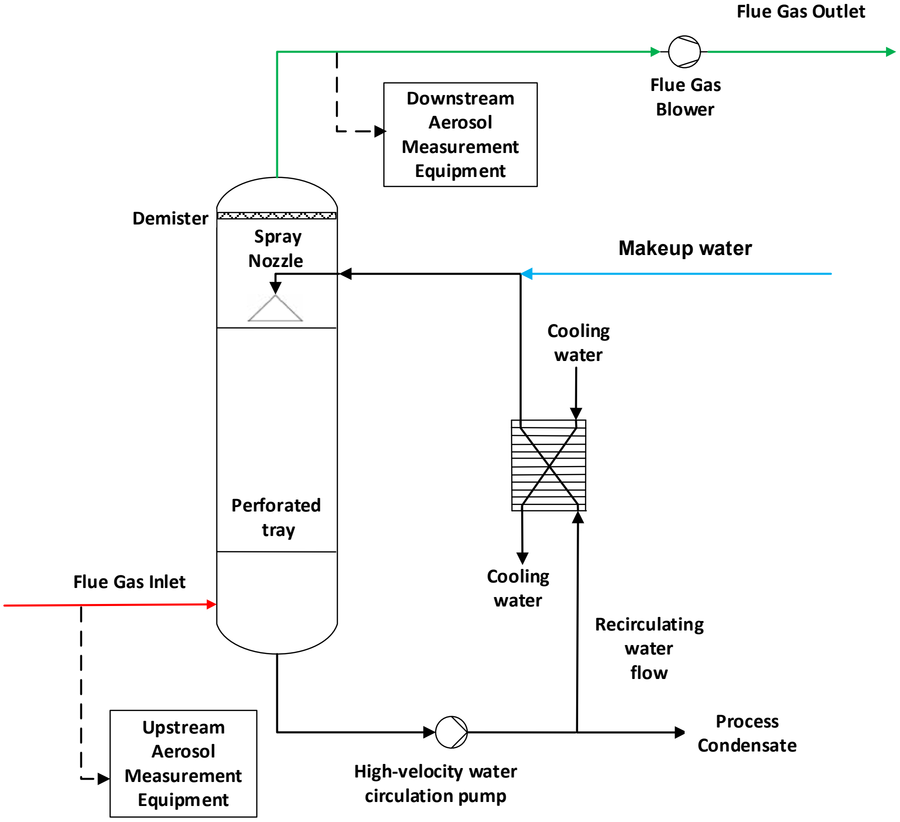


Figure 2: Process flow diagram of high-velocity water spray-based aerosol pretreatment system.

The second aerosol pretreatment technology tested in this project is an advanced ESP system developed by Washington University in St. Louis (WUSTL) that incorporates a patented photo-ionizer technology to enhance aerosol removal efficiency. The ESP functions by applying a high voltage between a plate and a wire. This voltage ionizes aerosol particles in the entering flue gas. Due to electrostatic force, ionized particles are diverted from the gas towards collecting plates, removing them from the gas. The specific collection area (SCA) of an ESP is the most important design parameter in terms of achieving required aerosol removal efficiency. A typical SCA for an ESP capable of obtaining 98 to 99% removal efficiency for 1,000 scfm gas flow is ~95 $m^2/(m^3/s)$; the area can be increased further to remove particles in the range of 10 to 500 nm at very high efficiencies. The pilot-scale ESP system will be tested to remove aerosol particles from flue gas at a capacity of 500 scfm. The photo-ionizer device is expected to greatly enhance the capture efficiency of nano-sized particles. In full-scale applications, the photo-ionizer developed by WUSTL can be retrofitted to existing ESPs at commercial power plants, reducing the capital costs of implementation.

A process flow diagram of the WUSTL ESP is shown in Figure 3. Specific ESP voltages may increase particle concentrations for certain particle sizes due to secondary aerosol generation inside the ESP from nucleation of water-sulfuric acid (H_2O-H_2SO_4) aerosols when sulfur dioxide (SO_2) present in the flue gas is oxidized. Hence, the ESP voltage needs to be carefully optimized during pilot tests. This project will determine the optimum design and operating conditions for the ESP system to treat flue gas with high aerosol concentrations. Through parametric testing, the performance of the advanced ESP will be compared against predefined aerosol removal efficiency targets. In addition, the costs to incorporate the ESP technology upstream of a PCC plant will be assessed.

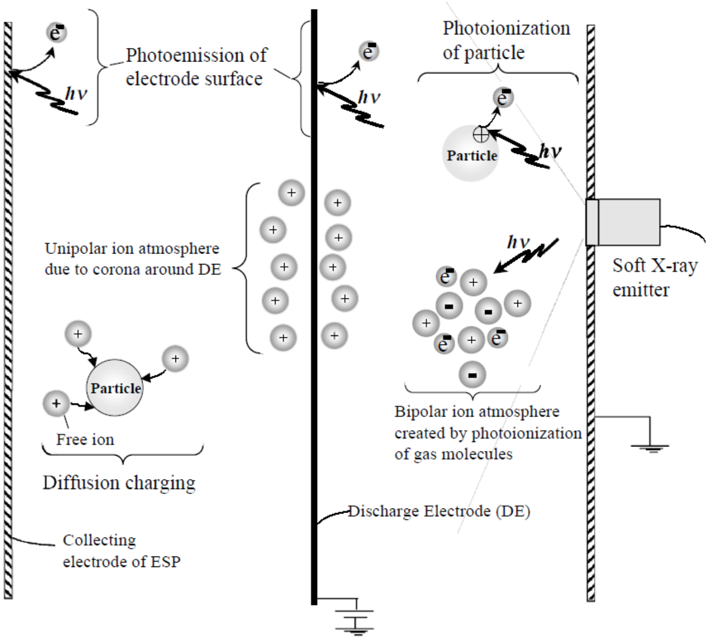


Figure 3: Conceptual flow diagram of the advanced ESP system developed by WUSTL.

The third technology tested in this project is a non-regenerative sorbent filter system developed by InnoSepra LLC. It has been proven to remove residual sulfur trioxide (SO_3), SO_2, nitrogen dioxide (NO_2), hydrogen chloride (HCl), and hydrogen fluoride (HF) from flue gas after the power plant flue gas desulfurization (FGD) unit to limit the detrimental impact of PCC solvent components reacting with flue gas contaminants. In addition to contaminant removal, the aerosol removal efficiency of the InnoSepra sorbent filter technology will be evaluated as a potential means to limit aerosol-driven amine losses as well. A process flow diagram of the InnoSepra sorbent-based filter technology is depicted in Figure 4.

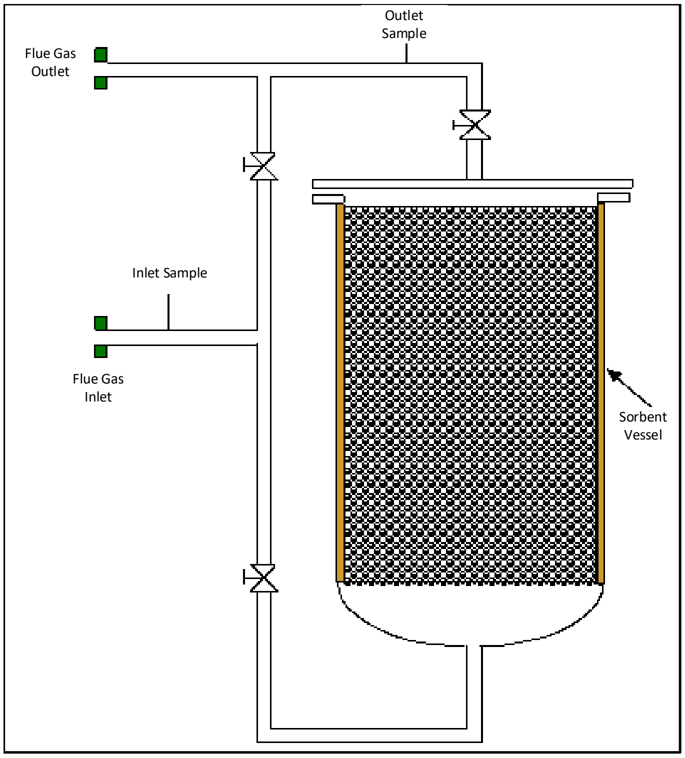


Figure 4: Process flow diagram of the InnoSepra sorbent-based filter technology.

The host site chosen for the testing is the University of Illinois' Abbott Power Plant located in Champaign, Illinois. As shown in Figure 5, Abbott's own ESPs and a wet jet bubbling FGD scrubber are used to remove some SO_2 and large particulate matter from the flue gas. The pilot testing will withdraw the flue gas from the outlet of the reheat burner at the flue gas stack and return downstream, as Figure 5 depicts. Abbott flue gas composition, temperature, and pressure at the inlet to the aerosol pretreatment units are listed in Table 1 (based on data collected when two out of three boilers are in operation). Each technology will be built in modules and installed at the Abbott site connected to common flue gas inlet and outlet piping.

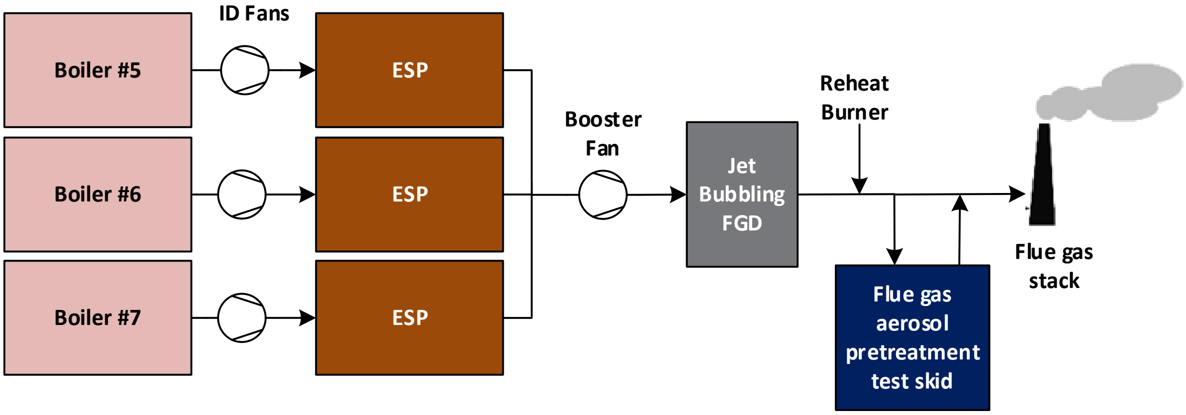


Figure 5: Abbott Power Plant layout and connection to flue gas aerosol pretreatment test skid.

TABLE 1: ABBOTT FLUE GAS PROPERTIES

Parameter	Unit	Value
Temperature	°F	200
Pressure	psig	0.75
Gas composition		
H_2O	vol%	19.2
CO_2	vol %, dry	9.2
O_2	vol%, dry	7.35
SO_2	ppmv, wet	177
NO_X	ppmv, wet	211

Preliminary performance targets for the three flue gas aerosol pretreatment systems are listed in Table 2. Cost competitiveness and environmental sustainability targets will be based on scaled-up commercial versions of each technology for performance comparison with the U.S. Department of Energy's (DOE) National Energy Technology (NETL) Case B12B reference excluding baghouse capital and operating costs. From an allotted test period of eight weeks, four consecutive weeks of parametric testing are planned for the water spray-based system, two consecutive weeks of testing are planned for the ESP system, and one to two weeks of testing are planned for the InnoSepra sorbent filter system. Each technology will undergo parametric testing to examine their impact on particle removal efficiency, overall capital and operating costs, and environmental sustainability performance.

TABLE 2: PRELIMINARY PERFORMANCE TARGETS FOR AEROSOL PRETREATMENT TECHNOLOGIES TESTED AT ABBOTT

Performance Parameter	Target for High-Velocity Water Spray Aerosol Pretreatment Technology	Target for ESP-Based Aerosol Pretreatment Technology	Target for InnoSepra Filter Aerosol Pretreatment Technology
Particle removal efficiency (%) for 500 to 1,000 scfm flue gas slipstream. *(# of particles/cm^3 before aerosol treatment - # of particles/cm^3 after aerosol treatment) / (# of particles/cm^3 before aerosol treatment)*	>98% for aerosol particles 70-200 nm in diameter		
Cost competitiveness when integrated with PCC technology for 550-MWe pulverized coal supercritical power plants without a baghouse (COE = cost of electricity).	COE < \$133.20/MWh and cost of CO_2 captured < \$58/tonne CO_2 when compared to DOE-NETL Case B12B without a baghouse		
Environmental sustainability when integrated with PCC technology for 550-MWe pulverized coal supercritical power plants without a baghouse.	Energy consumption < 14 MWe; process condensate adequately removed and treated	Energy consumption < 14 MWe; ESP solids adequately removed	Energy consumption < 14 MWe; sorbent material inventory safely managed

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD unit (wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%, wet					ppmv, wet	
		CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
15.45	200	7.4	19.2	66.6	5.9	0.80	200	211

Other Parameter Descriptions:

Flue Gas Pretreatment Requirements – The proposed work will provide as a test option effective flue gas SO_X and NO_X removal achieved using the already pilot-validated, low-cost, high-capacity, non-regenerative InnoSepra sorbent material installed in a packed bed upstream of the test skid. In addition to the physical effects of the sorbent bed on aerosol removal, the InnoSepra sorbent can improve aerosol reduction performance by reducing nucleation of H_2SO_4 aerosols in the flue gas by minimizing its SO_X content.

Waste Streams Generated – Acidic process condensate is generated by the high-velocity water spray-based system in a similar manner to how a direct contact cooler operates upstream of a solvent-based PCC plant. This condensate contains nitric acid (HNO_3) and H_2SO_4 from reaction of NO_X and SO_X in the flue gas with the circulating process water used in the spray column. This water is sent to Abbott's onsite water pretreatment facility where it is neutralized. The ESP plates collect a very small mass of solid particles during operation on coal-fired flue gas. The solids collected include metal oxides, dust, and other contaminants. These can be easily removed from the plates and discarded in the power plant's gypsum pile. The InnoSepra sorbent material must be removed after use and sent to the vendor's processing facility to either be specially processed for reuse or discarded in an approved manner compliant with all waste management regulations.

Process Design Concept – See above.

technology advantages

- Mitigates a wide range of flue gas aerosol concentrations and size distributions, including very high concentrations (up to and above 10^7 particles/cm^3) in the 70 to 200 nm particle size range.
- Reduced solvent makeup requirements lower operating expenditures for solvent-based PCC processes, enhance PCC performance in terms of energy consumption, reduce the need for solvent reclamation units, and improve solvent inventory logistics for full-scale operations.
- Reduced solvent emissions to the environment and aerosol contaminant exposure to personnel and environment.
- Smaller process footprint, more cost-effective, flexible operation, and higher aerosol removal efficiency compared to installing a baghouse at a coal-fired power plant.

R&D challenges

- Waste management.
- Effects of variability in flue gas composition, temperature, and pressure, as well as power plant load changes on aerosol measurements.
- Material compatibility with corrosive flue gas contaminants.

status

A comprehensive summary of the results from the aerosol-driven amine loss mechanisms study and modeling effort, as well as the environmental health and safety (EHS) analysis, have been completed. Basic and detailed engineering for the Linde spray-based system, ESP-based system, and InnoSepra filter system were completed by Affiliated Construction Services (ACS), WUSTL, and InnoSepra, respectively. All pilot equipment procurement and fabrication activities have been completed, and all pilot system components were delivered to the Abbott site and installed on a concrete pad. Pilot system commissioning and test-readiness checks were completed.

Since mid-January 2020, pilot tests of the spray-based system have been completed and testing of the InnoSepra filter and ESP systems are currently underway. The full parametric test campaign for all pilot systems is expected to be completed by late March 2020, followed by data analysis and evaluation of aerosol removal efficiency and cost performance for each technology

available reports/technical papers/presentations

Bostick, D. “Flue Gas Aerosol Pretreatment Technologies to Minimize Post-Combustion CO_2 Capture (PCC) Solvent Losses,” NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://www.netl.doe.gov/projects/files/Flue%20Gas%20Aerosol%20Pretreatment%20Technologies%20to%20Minimize%20PCC%20Solvent%20Losses%20(FE0031592).pdf*.

Bostick, D. “Flue Gas Aerosol Pretreatment Technologies to Minimize Post-Combustion CO_2 Capture (PCC) Solvent Losses,” Budget Period 1 Review Meeting, Pittsburgh, PA, January 2019. *https://www.netl.doe.gov/projects/files/FE0031592%20%e2%80%93%20Flue%20Gas%20Aerosol%20Pretreatment%20Technologies%20to%20Minimize%20Post-Combustion%20CO2%20Capture%20(PCC)%20Solvent%20Losses.pdf*.

Bostick, D. “Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses,” NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018. *https://www.netl.doe.gov/projects/files/Flue%20Gas%20Aerosol%20Pretreatment%20Technologies%20to%20Minimize%20PCC%20Solvent%20Losses%20Aug%202018.pdf*.

Bostick, D. “Flue Gas Aerosol Pretreatment Technologies to Minimize PCC Solvent Losses,” Project Kickoff Meeting, Pittsburgh, PA, July 2018. *https://www.netl.doe.gov/projects/files/Flue%20Gas%20Aerosol%20Pretreatment%20Technologies%20to%20Minimize%20PCC%20Solvent%20Losses%20July%202018.pdf*.

Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications

primary project goals

LumiShield Technologies is developing and demonstrating durable and inexpensive anti-corrosion coatings for application on carbon steel, which is used extensively in power plant boilers' and capture systems' vessels and piping. By reducing corrosion and allowing substitution of coated mild or carbon steel for expensive stainless steel, capital and maintenance costs of power plant systems could be significantly reduced, helping to enable cost-effective carbon dioxide (CO_2) capture for coal- and natural gas-fired power generation.

The multi-layer coating structure consists of a novel mixed metal oxide coat covered with an organic anti-corrosion coating. Project objectives are initially focusing on optimizing the metal oxide base layer for applying the organic coatings and proving the effectiveness of a prototype two-layer coating in preventing corrosion. Subsequently, the objectives are for optimization through identification of the organic coatings that give the best performance in combination with the optimized metal oxide base layer and showing the economic advantage of using the coatings through cost-benefit analysis.

technical goals

- Improve the corrosion resistance of organically coated steel (by at least 10% in terms of higher salt spray hours) by addition of the LumiShield metal oxide base coat underneath the conventional organic top coat.
- Perform lab-scale testing of LumiShield-coated carbon steel samples in simulated amine capture system conditions (CO_2 saturated 30% monoethanolamine [MEA] solution at 60°C) and realistic flue gas conditions (slipstream bench-scale testing at the National Carbon Capture Center [NCCC]).
- Optimize top-coating chemistry to maximize adhesion to LumiShield aluminum oxide coating under exposure to acids and amines, as evidenced by no change in appearance or adhesion, including blistering or swelling of organic coatings under realistic testing/exposure conditions.
- Provide a cost-benefit analysis for completed composites and compare with existing coatings and materials, making quantified estimates of: (1) how much stainless steel is replaceable by carbon steel with LumiShield coating in a baseline system, and (2) savings in capital and operating costs for the baseline system (with the quantitative target that at least one of the coatings should result in a decrease in cost per tonne of CO_2 by 1% or greater).

technology maturity:

Up to 100-Gallon Electroplating Bath Tank Sizes

project focus:

Corrosion-Resistant Coated Carbon Steel Components in CO_2 Capture Processes

participant:

LumiShield Technologies Inc.

project number:

FE0031659

predecessor projects:

N/A

NETL project manager:

Sai Gollakota
sai.gollakota@netl.doe.gov

principal investigator:

John Watkins
LumiShield Technologies Inc.
watkins@lumishieldtech.com

partners:

AECOM, Southern Company—NCCC

start date:

10.01.2018

percent complete:

75%

technical content

In fabrication of piping and vessels in power plants, carbon steel is the preferred material of construction given its relatively high strength and relatively low cost. However, in applications for corrosive environments (e.g., acid gas-containing flue gas streams, amine solutions in capture systems, and wet CO_2 captured by amine systems), carbon steel may not provide suitable corrosion resistance. Stainless steel provides high corrosion resistance, but it is expensive. Conventional organic-coated steel initially confers corrosion resistance but tends to develop defects though which diffusion of water and gas species can occur, leading to corrosion of the substrate and delamination of the coating (as illustrated in Figure 1). Therefore, better anti-corrosion coatings are needed in applications such as corrosive solvent-containing carbon capture systems.

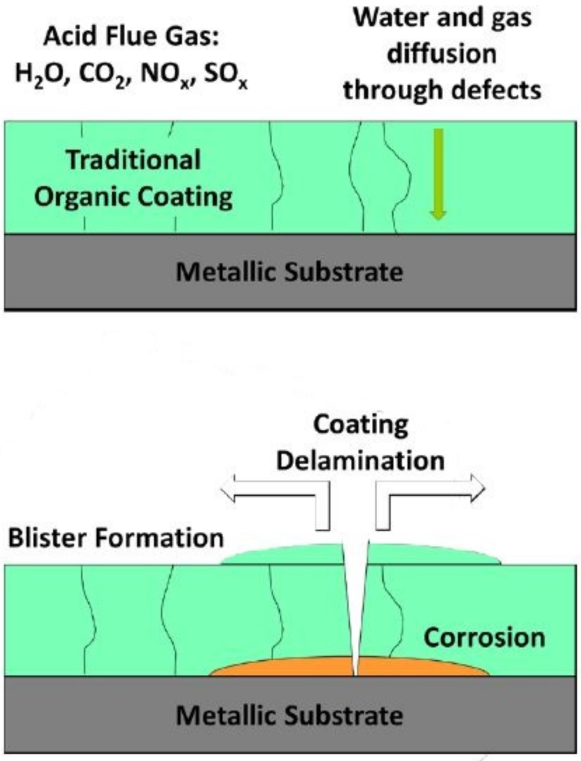


Figure 1: Mechanism for corrosion of coated metallic substrates.

The approach to this problem involves utilization of previously developed LumiShield metal oxide coating technology to establish a base metal oxide layer on carbon steel, on which organic coatings tailored for resistance to amine solutions could be applied. The basic geometry of the dual coating concept is depicted in Figure 2. The presence of the LumiShield coating improves the adhesion of the organic coating, preventing the coating from being undermined and considerably increasing the overall coating performance. The LumiShield coating was initially developed as a stand-alone anti-corrosion coating to replace toxic metal coatings like chromium and cadmium. However, realization occurred that the metal oxide surface would allow excellent adherence of organic coating molecules and that the resulting composite coating could make use of a thinner organic layer with fewer defects, improving corrosion resistance performance and reducing cost. The metal oxide layer itself may be applied in a single step using equipment and expertise well-known to the industry. These characteristics allow competitive or even lower costs than conventional primed steel coatings, which sometimes require multiple layers at increased cost.

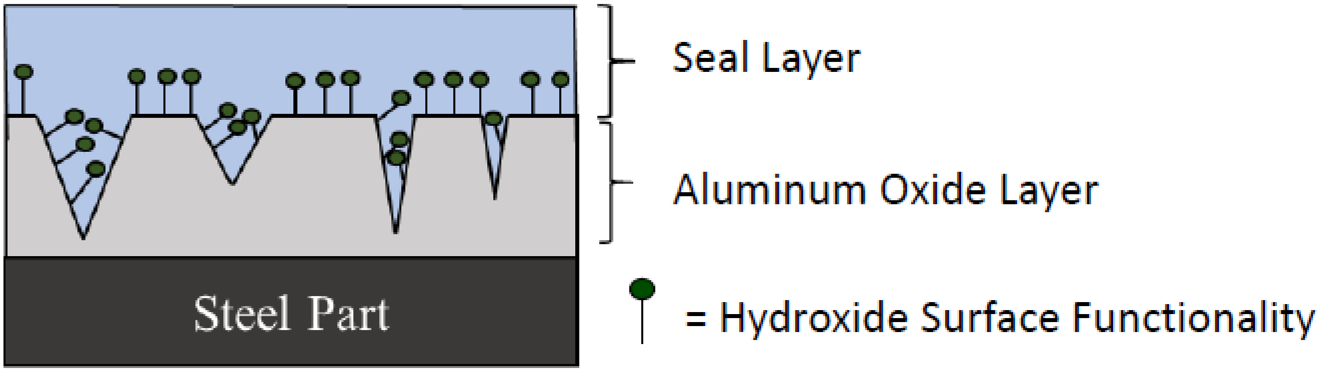


Figure 2: Coating structure.

Metal Oxide Base Layer

The metal oxide layer consists mainly of aluminum oxide applied via electroplating, utilizing water-stable aluminum complexes (with proprietary additions) in the electroplating bath, which form a coherent and highly adherent aluminum oxide layer on steel via a proprietary cathodic electroplating process. It has been observed that the aluminum oxide layer formation allows for some degree of metal-to-metal bonding between aluminum centers and the steel substrate, giving the coating excellent adhesion. The LumiShield alumina electrodeposition process takes place in an aqueous system, offering significant cost advantages over non-aqueous methods of alumina deposition that require processes to be free of atmospheric water and oxygen. The process is analogous to the electroplating of common metals like zinc and can be applied using standard equipment present in every electroplating facility.

The LumiShield approach makes use of pulse-plating methods (in which electrical field strength is varied to improve control over electroplating processes). By adopting a pulsed-plating procedure (example illustrated in Figure 3), the LumiShield coating is further improved in adhesion and density. Also, the nature of the coating process allows a large degree of control of the morphology of the coating. By adjusting the electroplating conditions of pulse, pH, temperature, and solution composition and concentrations, it is possible to create morphologies ranging from plate-like growth with a so-called cracked glass appearance under magnification (Figure 4, left side) to granular growth structures (Figure 4, right side). The cracked glass morphology is valuable because its high surface area will improve the adhesion of organic layers deposited on top of it.

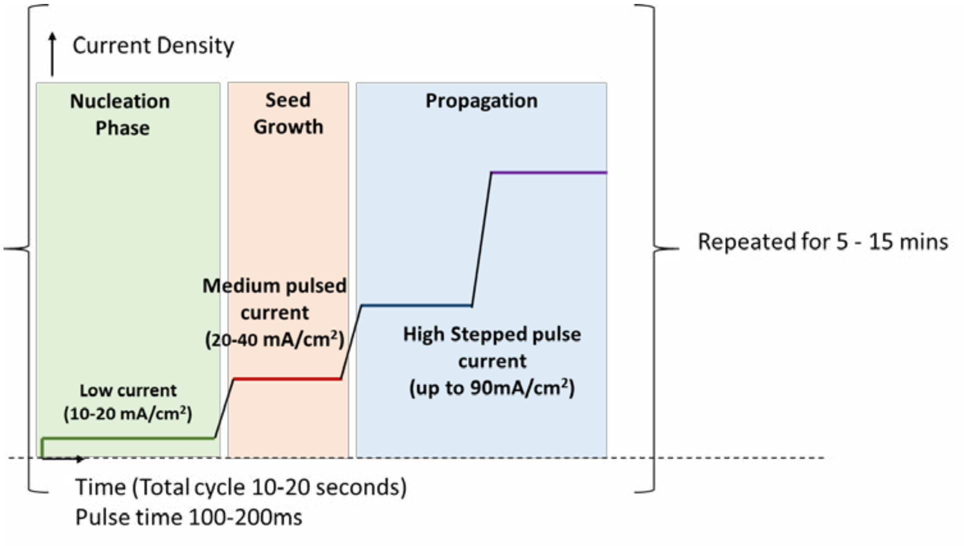


Figure 3: Complex electroplating pulse scheme.

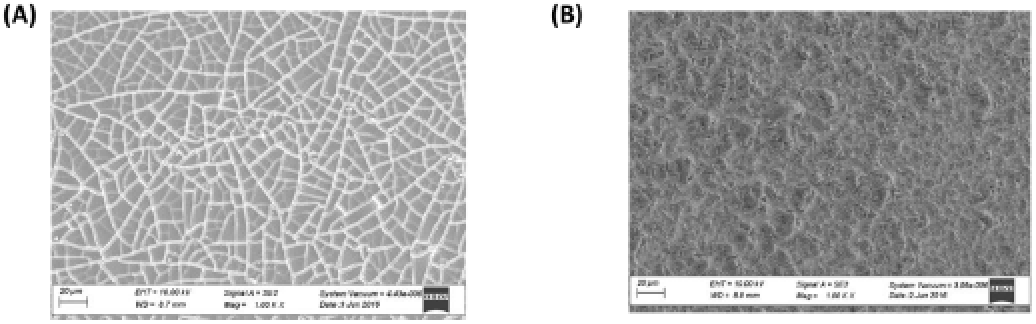


Figure 4: Variation in metal oxide coating morphology.

A major focus at the start of the project was optimization of the LumiShield metal oxide base layer. This was accomplished by varying process and electroplating solution conditions in forming the metal oxide coatings, which were then characterized for morphology and adhesion through physical and optical methods. Polarization testing to determine corrosion rates, electrochemical impedance spectroscopy to determine corrosion mechanisms, and salt spray exposure testing were conducted. LumiShield has identified plating solution parameters (temperature, pH, concentrations), as well as electrochemical process variables (pulse scheme, current density, timing), which result in thin, rough, adherent metal oxide coatings that will promote organic top-layer adhesion.

Organic Top Layer

For the essential organic top layer, LumiShield has surveyed existing/available organic anti-corrosion coating materials and identified epoxy resins, phenolic resins, and fluoropolymer resins as the three types for consideration for applications involving amine solutions, flue gas, and wet CO_2, given their formulation flexibility, robustness at elevated temperatures (as high as 180 to 250°C for epoxy coatings and 120 to 200°C for phenolic coatings), chemical resistance, and physical characteristics. Project work has involved testing of these three types with and without the LumiShield base coat to establish baselines for each polymer class for corrosion resistance, adhesion and scribe creep, and measure improvement of corrosion resistance in salt spray tests. Testing has shown significant improvement in corrosion performance with both epoxy and phenolic coatings, both of which likely have enhanced adhesion on the LumiShield metal oxide base layer that is improving corrosion protection. Specifically, epoxy coatings appear to be the best candidate for modification and further work to improve performance as the project progresses. On the other hand, it has been concluded that fluoropolymer coatings (which show poor adhesion to many materials) will probably not meet performance goals. Figure 5 shows interim results on these evaluations for the more promising epoxy and phenolic coating choices.

	Scribe creep at 1000 Hours of Salt Spray				
	Industry Standard		Aluminum Oxide Coated Steel		
	Average creep / mm	max creep / mm	Average creep / mm	max creep / mm	Improvement
Epoxy	1.08	1.6	0.77	1.1	**29%**
Phenolic	1.12	1.8	0.89	1.3	**21%**

	Salt Spray Hours Initial Testing to Failure		
	Industry Standard	Aluminum Oxide Coated Steel	Improvement
Epoxy	500	1500	**300%**
Phenolic	500	1000	**200%**

Figure 5: Comparisons of performance of epoxy and phenolic top coats with and without LumiShield metal oxide base coat.

To facilitate the attachment of top layer to the aluminum oxide base coating, several organic treatments have been considered based on silane treatment (silane is an inorganic compound with the chemical formula SiR_4). Silanes are used in a large variety of high-performance coatings as a binding agent between organic resins and inorganic substrates. The aim is to bind silanes to the pendant hydroxide functionality of the aluminum oxide layer (refer to Figure 2 depicting this idea) to create a synthetic handle for incorporation of the silane into the polymer top layer. To this end, several silane candidates will be investigated.

Non-Capture Applications

Although LumiShield's project focus has been application of the coatings for carbon capture systems, it has two customers that are interested in piloting LumiShield technology with specific modifications to their specific paints:

- An automotive company interested in high-temperature paint adhesion for heat shields.
- Expansion of an oil and gas program towards other markets and corrosion sites using heavy brine solutions.

There is also interest in corrosion resistance to other corrosive amines to serve the needs of the broader chemical industry.

Cost-Benefit Analysis

The LumiShield team includes AECOM, who have performed a preliminary cost-benefit analysis of LumiShield's coating technology. An initial objective was to determine the highest value targets in the carbon capture system for materials replacement with the developed aluminum oxide coating over incumbent construction methods. Initial analysis has found that stainless steel currently used for fabrication of both the absorber and stripper could be replaced by LumiShield-coated mild steel with powder-coating at a capital cost saving of 13% and 17%, respectively. They also note that the replacement of stainless steel parts with mild steel may have additional nonquantifiable benefits (e.g., improved materials of construction may allow a wider range of operating conditions or allow use of amine species previously ruled out due to their effects on the stainless steel construction materials). Furthermore, cost savings might be improved significantly based on increasing part lifetime by using a new coating system.

technology advantages

- Coated mild steel can cost-effectively replace stainless steel constructions.
- Coatings can be made acid- and amine-resistant with suitable topcoats.
- Coatings can be readily fabricated using straightforwardly implemented aqueous electroplating methods.
- Coatings of the type being developed are non-toxic and can replace heavy metal-based processes.
- May be used to avoid chloride stress cracking of stainless steel in some services.

R&D challenges

- Achieving a dense base metal oxide coating layer with high roughness suitable for securely attaching the upper coating layer, and the general difficulties of controlling results in utilization of electroplating methods.
- Achieving chemical and physical compatibility between the metal oxide base layer and upper organic layer.
- Attaining substantially improved performance of prototype organic coatings on the metal oxide base layer.
- Larger electroplating bath tank sizes are needed for coating of large steel equipment items.
- Developing surface repair technique for coatings when damaged during shipping or installation.

status

Optimization of the parameters for fabrication of dense metal oxide base coatings with high surface roughness, characterization of prototype organic coatings, and a preliminary cost-benefit analysis have been completed.

available reports/technical papers/presentations

"*Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications*," presented by John Watkins, LumiShield Technologies Incorporated, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, October 2019.

LumiShield Technologies, "Inexpensive and Sustainable Anti-Corrosion Coating for Power Generation Applications," kickoff meeting presentation, January 2019.

"Electrochemical Deposition of Aluminum-Based Coatings from Aqueous Systems," presented by John Watkins, LumiShield Technologies Incorporated, SSPC Coatings+ 2020, Long Beach, CA, February 2020. Also submitted as a proceeding of the same title.

Advancing Post-Combustion CO_2 Capture Through Increased Mass Transfer and Lower Degradation

primary project goals

The University of Kentucky Center for Applied Energy Research's (UK CAER) project will develop three techniques to enable aqueous post-combustion carbon dioxide (CO_2) capture technologies to meet the U.S. Department of Energy (DOE) performance and cost targets of 90% CO_2 capture, 95% purity, at a cost of less than $30/tonne CO_2 captured. To reduce the cost of CO_2 capture, critical elements need to be addressed, including how to increase CO_2 mass transfer (reduce capital cost), how to reduce solvent makeup (lower the operational cost) resulting from degradation, and how to address the potential environmental issues (permitting hurdles) from nitrosamine formation. The specific objectives of this project are to develop a 3D-printed dynamic polarity packing material with increased turbulent liquid flow and controlled gas-liquid bubble formation to increase CO_2 mass transfer into amine solvents; investigate the impact of additives on the physical properties of solvents and their relationship to bubble formation to boost mass transfer while reducing aerosol formation; and destruct nitrosamines derived from amine solvents through development of an electrochemical treatment process. The project team will develop and fabricate customized dynamic packing using advanced manufacturing techniques, install the packing into UK CAER's bench-scale (less than 0.1-megawatt-thermal [MWth]) CO_2 capture unit, and conduct parametric and long-term testing with additive-modified solvents. Additionally, an electrochemical cell with stationary carbon electrodes will be designed and evaluated for the adsorption and decomposition of nitrosamines from wash water solutions collected from UK CAER's 0.7-megawatt-electric (MWe) small pilot CO_2 capture system located at Kentucky Utilities' E.W. Brown Generating Station.

technical goals

- Develop a library of structure/property relationships that can be used as a guideline for choosing effective additives for a given solvent or blend.
- Design and fabricate dynamic polarity packing based on a range of solvent property parameters for a given liquid-gas ratio.
- Evaluate selected solvents in UK CAER's bench-scale CO_2 capture unit with conventional structured packing to serve as a baseline.
- Replace the conventional packing in the bench-scale unit with 3D-printed dynamic packing and test the selected solvents under the same operating conditions to determine mass transfer enhancement.
- Test selected solvent additives in the bench-scale unit to evaluate mass transfer enhancement and reduced energy demand.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Solvent Enabling Techniques

participant:

University of Kentucky

project number:

FE0031661

predecessor projects:

N/A

NETL project manager:

Naomi O'Neil
naomi.oneil@netl.doe.gov

principal investigator:

Jesse Thompson
University of Kentucky
jesse.thompson@uky.edu

partners:

Lawrence Livermore
National Laboratory

start date:

10.01.2018

percent complete:

50%

- Evaluate the electrochemical cell using wash water collected at UK CAER's 0.7-MWe small pilot CO_2 capture system to measure the ability to maintain nitrosamine levels below 0.5 parts per million (ppm).
- Conduct parametric testing of the combined dynamic packing solvent/additive system and identify optimum operating conditions to achieve an increase in mass transfer.
- Perform a long-term testing campaign under optimized operating conditions to evaluate the stability of dynamic packing and electrochemical cell and examine aerosol formation, corrosion, and solvent degradation.
- Perform a high-level techno-economic analysis (TEA) based on the collected bench-scale test data.

technical content

This UK CAER and Lawrence Livermore National Laboratory (LLNL) project will involve the development and fabrication of customized 3D-printed dynamic packing to increase CO_2 mass transfer in the absorber column. UK CAER will design, fabricate, and test an electrochemical cell to adsorb and decompose nitrosamines from the water wash. After both systems have been constructed, they will be tested on UK CAER's bench-scale CO_2 capture unit. The specific activities is this proposal include: (1) quantifying the CO_2 mass transfer improvement from the customized 3D-printed dynamic polarity packing in the absorber by utilizing UK CAER's existing less-than-0.1-MWth 3-inch ID CO_2 capture column; (2) quantifying the energy consumption saving associated with mass transfer enhancement from the dynamic polarity packing; (3) conducting detailed studies to understand how solvent physical property can be utilized to form controllable gas bubbles to boost the mass transfer area and impact wettability, degradation, and aerosol formation; (4) quantity the benefits of UK CAER's electrochemical cell to decompose nitrosamines; and (5) collect the necessary information/data to conduct a high-level TEA of the proposed technologies.

A systematic approach was taken to develop understanding of the structure/function relationships for additives in a rational series of amine solvents in terms of bubble formation, the stability of gas-liquid interface film, and solvent polarity. First, physical properties such as surface tension, viscosity, elasticity, and contact angle were measured in aqueous amine solvents with different pKa, polarity, and functional groups (i.e., –OH, -N, -R). Commercially available amines, including primary, secondary, and tertiary amines, as well as amines with different functional groups, were prepared and examined at various concentrations (e.g., 3 to 5 M) and at lean (~0.2 carbon/nitrogen ratio) and rich CO_2 loading (~0.4 carbon/nitrogen ratio). Water-soluble chemical additives were then selected with different functionality and chemical structures (surfactants, inorganic metal corrosion inhibitors, organic oxidation inhibitors, and metal-ligand CO_2 hydrolysis catalyst) and added to the amine solvents. The physical properties of the amine solvents with the additives were then measured at lean and rich CO_2 loading to assess how the additives changed the solvent physical properties. The main physical property modification came from addition of a surfactant, which resulted in a decrease in the surface tension of the solvent and a reduction in the contact angle relative to a hydrophobic surface, such as a polymeric material. The decrease in contact angle implied better wetting (coating) on the packing by the solvent, leading to better gas-liquid contact. This result has implications when considering the use of plastic 3D-printed packing material as a substitute for steel structure packing in the absorber column.

One important factor when exploring the use of polymer packing is the stability of the polymer when exposed to the caustic CO_2-loaded amine solution at elevated temperatures. The stability of the polymeric packing material after exposure to CO_2-loaded amine solvent at absorber temperature (60°C) was examined through an estimated 5,000 hours. Changes to mass, thickness, and contact angle (°) versus water and the amine solvent were monitored every 1,000 hours. The results are shown in Figure 1. The three polymer materials examined showed minimal changes in mass, thickness and contact angles versus both water and the CO_2-loaded amine solvent. Based on the amine stability studies, acrylonitrile butadiene styrene (ABS), Nylon, and high-density (impact) polystyrene (HDPS) were shown to be stable upon exposure to CO_2-loaded amine solvent at anticipated absorber temperatures.

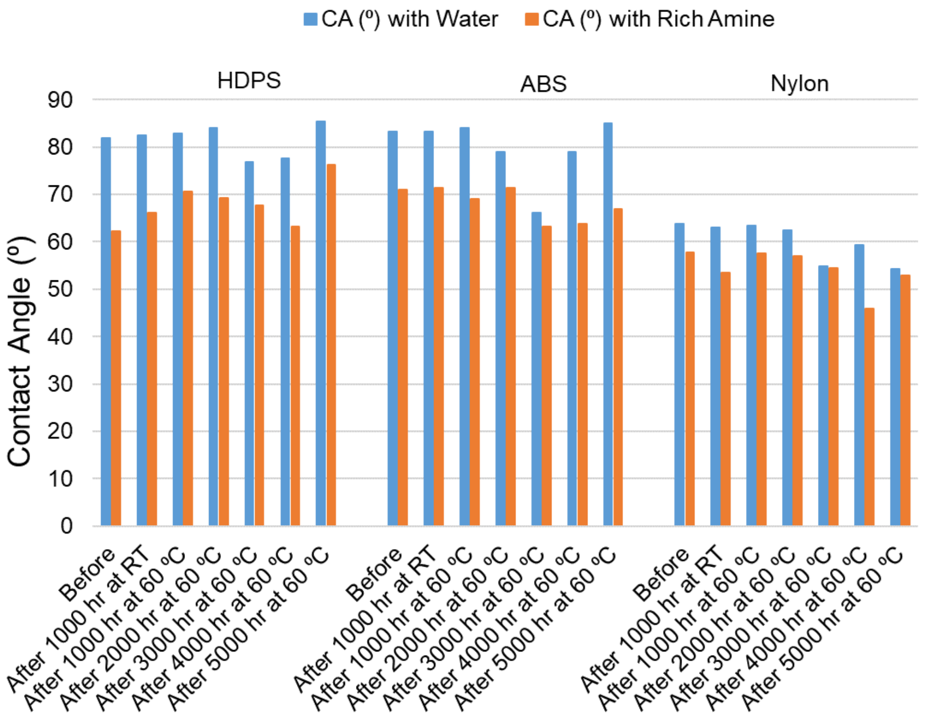


Figure 1: Contact angle (°) changes of polymeric materials after long-term exposure to CO_2-loaded amine solvent.

To compare the wettability of the polymer packing, polished coupons of the HDPS, ABS, Nylon, and stainless steel (SS) were collected, and contact angles were measured with water and an amine solution (Figure 2). The contact angle (wettability) versus water of HDPS and ABS are similar, while Nylon and SS are lower and closer to each other. All the packing materials showed a lower contact angle with the amine solvent compared to water. The contact angle of Nylon was the closest to SS, with both ABS and HDPS having two to three times larger contact angles.

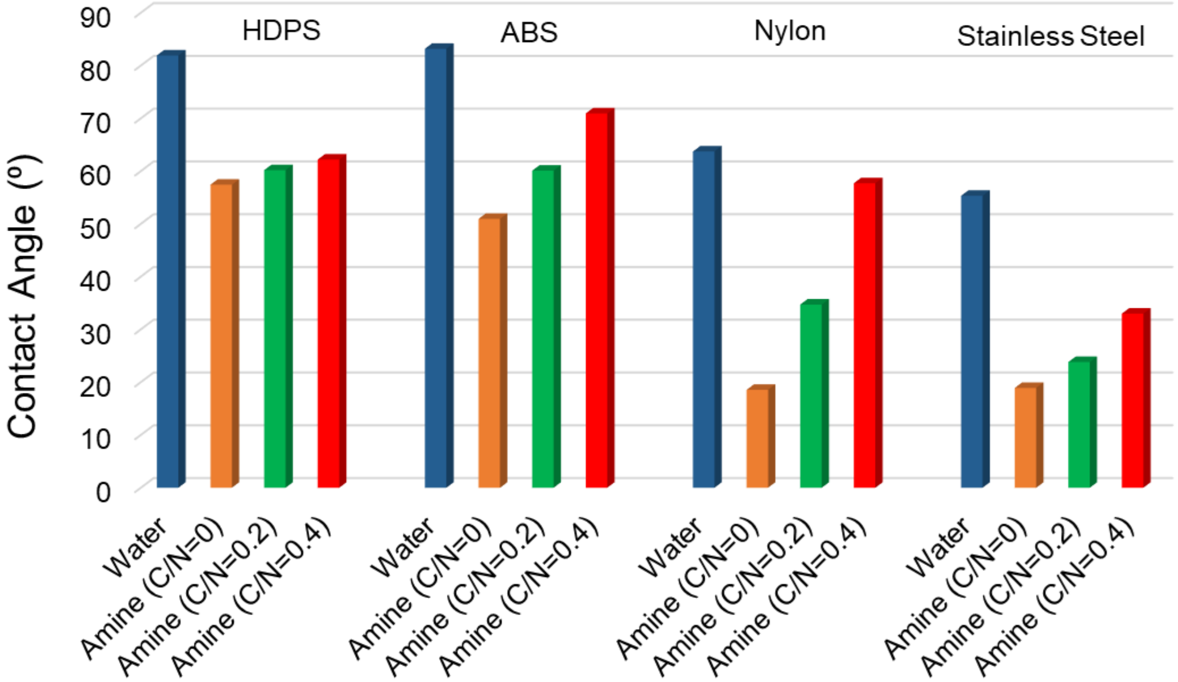


Figure 2: Contact angle of water and aqueous amines (at different CO_2 loadings) on different packing material surfaces.

Next, the contact angles of an amine solvent with the surfactant additive (0.1 wt.%) at different CO_2 loadings were also measured on all the packing material surfaces (Figure 3). The addition of the surfactant in the amine solvent lowered the contact angle of the solutions versus the HDPS, Nylon, and ABS surfaces. This observation indicated that the wettability of the aqueous amine solvent on these polymeric packing could be enhanced by adding a surfactant.

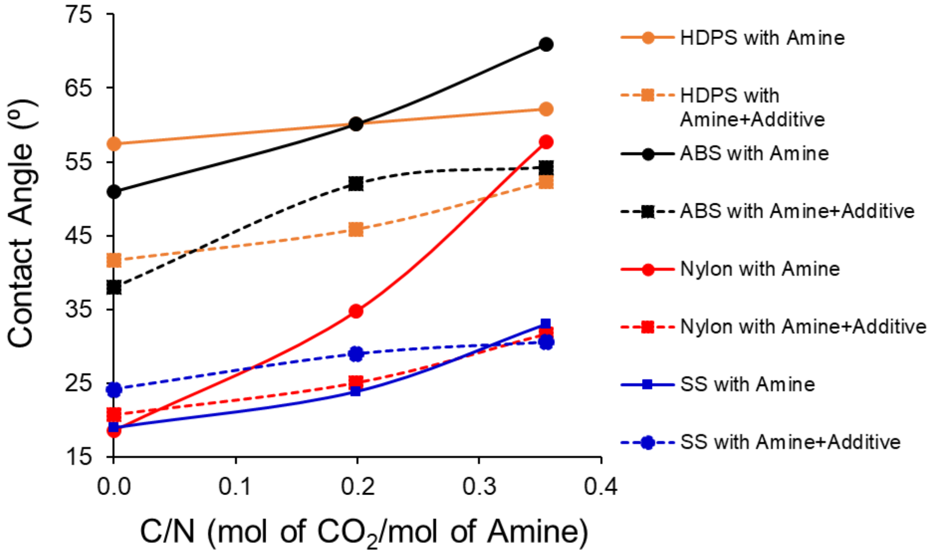


Figure 3: Contact angle of amine solvent with Tween 20 additive at variable CO_2-loading on different packing materials surfaces.

To address the potential environmental concerns associated with nitrosamine formation in CO_2 capture systems, an electrochemical treatment cell is being developed to destruct nitrosamines from the absorber water wash. The electrochemical cell is being evaluated using wash water solutions collected at UK CAER's 0.7-MWe small pilot CO_2 capture system. The liquid under investigation represents the actual composition of wash water from an operating pilot CO_2 capture system that treats coal flue gas. A preliminary design of a flow-through electrochemical cell with carbon xerogel (CX) electrodes was generated (Figure 4) and fabrication has been completed. Recent testing demonstrated the ability to continuously reduce at least 85% of the nitrosamines present in the water wash with an efficiency above 15%, well above the original target values.

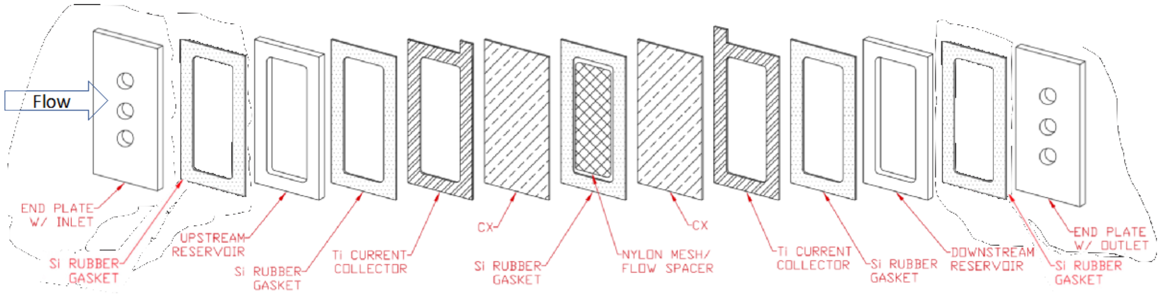


Figure 4: Flow-through electrochemical cell schematic with CX electrodes.

technology advantages

- Increased CO_2 mass transfer and lower solvent regeneration energy.
- Enhanced CO_2 absorption rate reduces absorber size, lowering capital and operating costs.
- Use of solvent additives increases solvent wetting on packing.
- Electrochemical treatment process addresses environmental concerns at high selectivity with very low operational cost.
- Technology can extend over a broad spectrum of CO_2 capture systems, including many solvent-based systems.

R&D challenges

- Compatibility of packing material with actual flue gas and solvent impurity.
- Foaming with additives in long-term operation.

status

Experiments are being performed to gather data on solvent physical properties, dynamic packing development, and performance of the nitrosamine decomposition electrochemical cell.

available reports/technical papers/presentations

Thompson, J. and Liu, K., "Advancing Post-Combustion CO_2 Capture through Increased Mass Transfer and Lower Degradation," presented at the 2019 NETL Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/J-Thompson-UKY-CAER-Increased-Mass-Transfer.pdf*.

Thompson, J. "Advancing Post-Combustion CO_2 Capture through Increased Mass Transfer and Lower Degradation," Project Kickoff Meeting, Pittsburgh, PA, November 2018. *https://www.netl.doe.gov/projects/files/31661%20Kickoff%20Nov%202018_Public.pdf*.

CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION SORBENT TECHNOLOGIES

Pilot Testing of a Highly Effective Pre-Combustion Sorbent-Based Carbon Capture System

primary project goals

TDA Research, Inc., is continuing development of a new sorbent-based pre-combustion carbon capture technology for integrated gasification combined cycle (IGCC) power plants. The process uses an advanced physical adsorbent that selectively removes carbon dioxide (CO_2) from coal-derived synthesis gas (syngas) above the dew point of the gas. The project aims to prove the viability of the new technology by using data collected from the pilot plant tests to complete high-fidelity engineering and cost analyses to calculate the impact of the carbon capture system on the cost of electricity generation at a coal-fired IGCC power plant and the potential of the technology to meet the U.S. Department of Energy (DOE) goals of 90% CO_2 capture and 95% purity at a cost of less than $40/tonne CO_2 captured.

Having shown promise under a previously-funded DOE project (FE0000469), this sorbent is being evaluated at a larger scale, for longer durations, and under conditions that are more representative of a coal gasification-based application. Current research objectives are to collect performance data for this advanced sorbent, including: two 0.1-megawatt-electric (MWe) tests with a fully equipped prototype unit using actual syngas to prove the viability of the new technology; long-term sorbent life evaluation in a bench-scale setup; the fabrication of a pilot-scale testing unit that will contain eight sorbent reactors; and the design of a CO_2 purification subsystem.

technical goals

- Enable pre-combustion CO_2 capture from syngas at 200 to 250°C and pressures up to 60 bar, with greater than 90% recovery and CO_2 purity of at least 95% using a functionalized carbon sorbent in a pressure swing adsorption (PSA)-based cycle.
- Improve adsorber reactor design, including the optimized reactor internals and bed geometry through computational fluid dynamics (CFD) analysis and PSA cycle optimization with adsorption modeling.
- Complete pilot-scale field tests on syngas slipstreams at 0.1 MWe equivalent, at design conditions and for extended durations (e.g. greater than 3,000 hours), to demonstrate capability to meet all performance objectives (e.g., CO_2 removal efficiency, hydrogen [H_2] recovery, sorbent life, and performance).
- Validate long-term performance and lifetime of the sorbent through 60,000 cycles with no more than 2% decrease in adsorption capacity over fresh sorbent (enabling projected lifetime of five years for the sorbent).

technology maturity:

Pilot-Scale, Actual Syngas Slipstream (equivalent to 0.1 MWe)

project focus:

High-Capacity Regenerable Sorbent

participant:

TDA Research, Inc.

project number:

FE0013105

predecessor projects:

FE0000469

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gökhan Alptekin
TDA Research, Inc.
galptekin@tda.com

partners:

Gas Technology Institute, CDM Smith, Inc., University of California at Irvine (UCI), University of Alberta, Sinopec

start date:

10.01.2013

percent complete:

80%

- Enable improved IGCC plant efficiency (3 to 4 percentage points) over IGCC plants using conventional CO_2 removal technology, thereby improving cost of electricity in coal-based power production.

technical content

TDA Research, Inc. is designing, constructing, and operating a slipstream 0.1-MWe pilot-scale process for pre-combustion CO_2 capture to assess their novel adsorbent for the selective removal of CO_2 from syngas. The adsorbent consists of a mesoporous carbon grafted with surface functional groups that remove CO_2 via an acid-base interaction. The novel process is based on TDA's high-temperature PSA technology, using the new adsorbent to selectively remove CO_2 from syngas in an IGCC power plant. The integration of the CO_2 separation unit into the IGCC plant is shown in Figure 1.

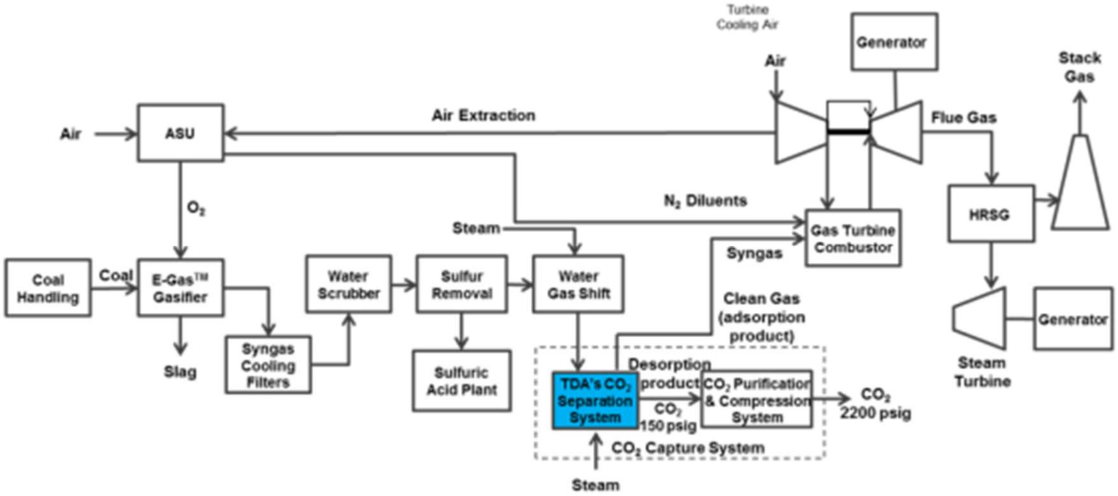


Figure 1: TDA's CO_2 capture system integration in an IGCC power plant.

The CO_2 capture system uses multiple sorbent beds that switch operating modes between adsorption and regeneration. In adsorption mode, which is operated isothermally (temperature of about 240 to 250°C) and at syngas pressure of about 500 pounds per square inch absolute (psia), the sorbent removes CO_2 via strong physical adsorption. The CO_2 surface interaction is strong enough to allow operation at these elevated temperatures.

In regeneration mode, also operated isothermally (temperature of about 240 to 250°C), CO_2 is recovered via combined pressure and concentration swing by contacting the sorbent with a steam purge stream. The operating pressure ranges from 150 to 158 psia and partial pressure of CO_2 ranges from 0 to 75 psi. Because the CO_2 is recovered at ~150 psia, energy requirement for CO_2 compression for storage is reduced. Also, the isothermal operation eliminates heat/cool transitions, and rapid cycling reduces cycle times and increases sorbent utilization. Because the CO_2 is not bonded via a covalent bond, the energy input to the regeneration is low—only 4.9 kcal/mole of CO_2 removed (comparable to Selexol™). This energy requirement is much lower than that of the chemical absorbents (e.g., sodium carbonate [Na_2CO_3] requires 29.9 kcal/mol) and amine solvents (≈14 kcal/mol). The energy output loss of the IGCC plant is expected to be similar to that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO_2 capture.

The pilot plant design includes a gas conditioning unit and a high-temperature PSA-based CO_2 separation unit, as shown in Figure 2. The gas conditioning unit allows for adjustment of the concentration and purity of the syngas. The CO_2 separation unit consists of eight high-temperature sorbent beds. The design of the CO_2 capture skid for the 0.1-MW pilot unit is shown in Figure 3.

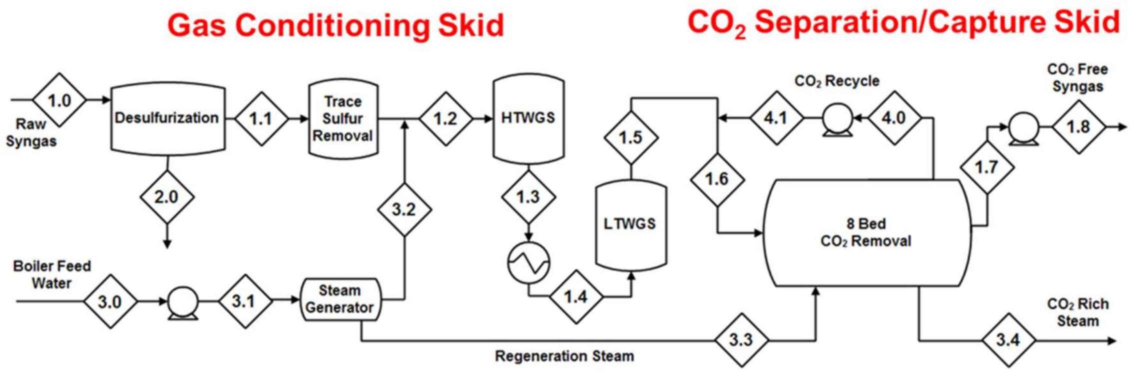


Figure 2: Flow diagram for TDA's pilot test unit.

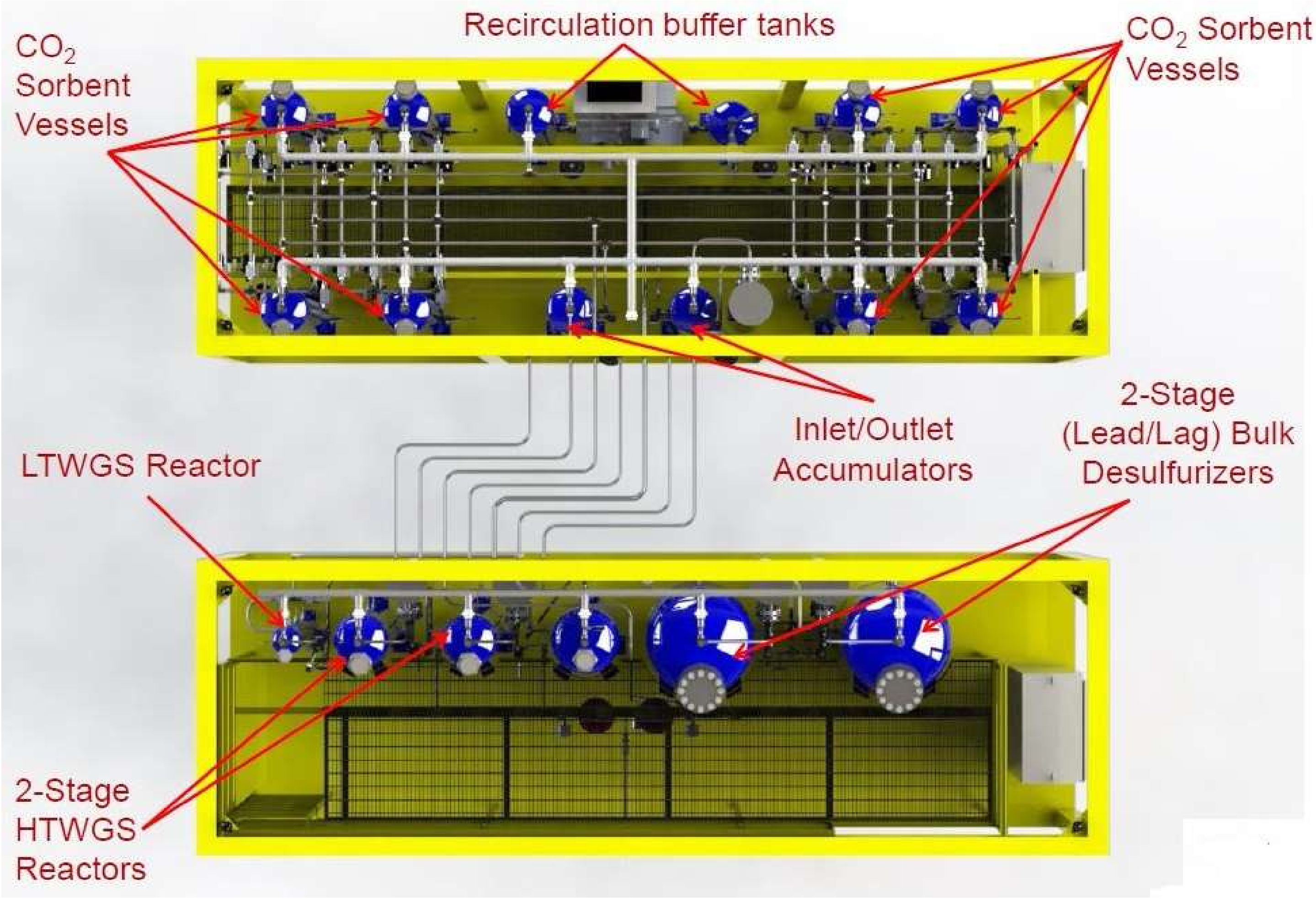
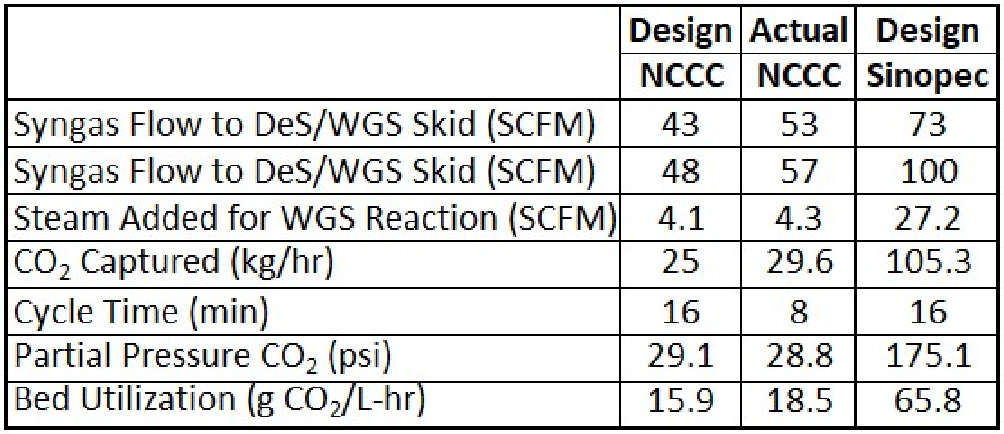


Figure 3: Overhead view of carbon capture skid.

In 2017, TDA's 0.1-MWe pilot-scale eight-bed PSA unit was installed at the National Carbon Capture Center (NCCC; Figure 4) and tested in real coal-derived syngas. The pilot unit ran for 707 hours of continuous operation at up to 97.3% carbon capture at 53 standard cubic feet per minute (SCFM) of syngas flow, exceeding design specifications. The summary results are given in Figure 5. This table also shows the upcoming design performance parameters for the Sinopec oxygen-based gasifier testing at considerably increased throughput.

Figure 4: TDA's 0.1-MWe pilot unit installed in the test pad at the NCCC (Wilsonville, AL).



	Design NCCC	Actual NCCC	Design Sinopec
Syngas Flow to DeS/WGS Skid (SCFM)	43	53	73
Syngas Flow to DeS/WGS Skid (SCFM)	48	57	100
Steam Added for WGS Reaction (SCFM)	4.1	4.3	27.2
CO_2 Captured (kg/hr)	25	29.6	105.3
Cycle Time (min)	16	8	16
Partial Pressure CO_2 (psi)	29.1	28.8	175.1
Bed Utilization (g CO_2/L-hr)	15.9	18.5	65.8

Figure 5: Summary performance results of pilot-scale testing.

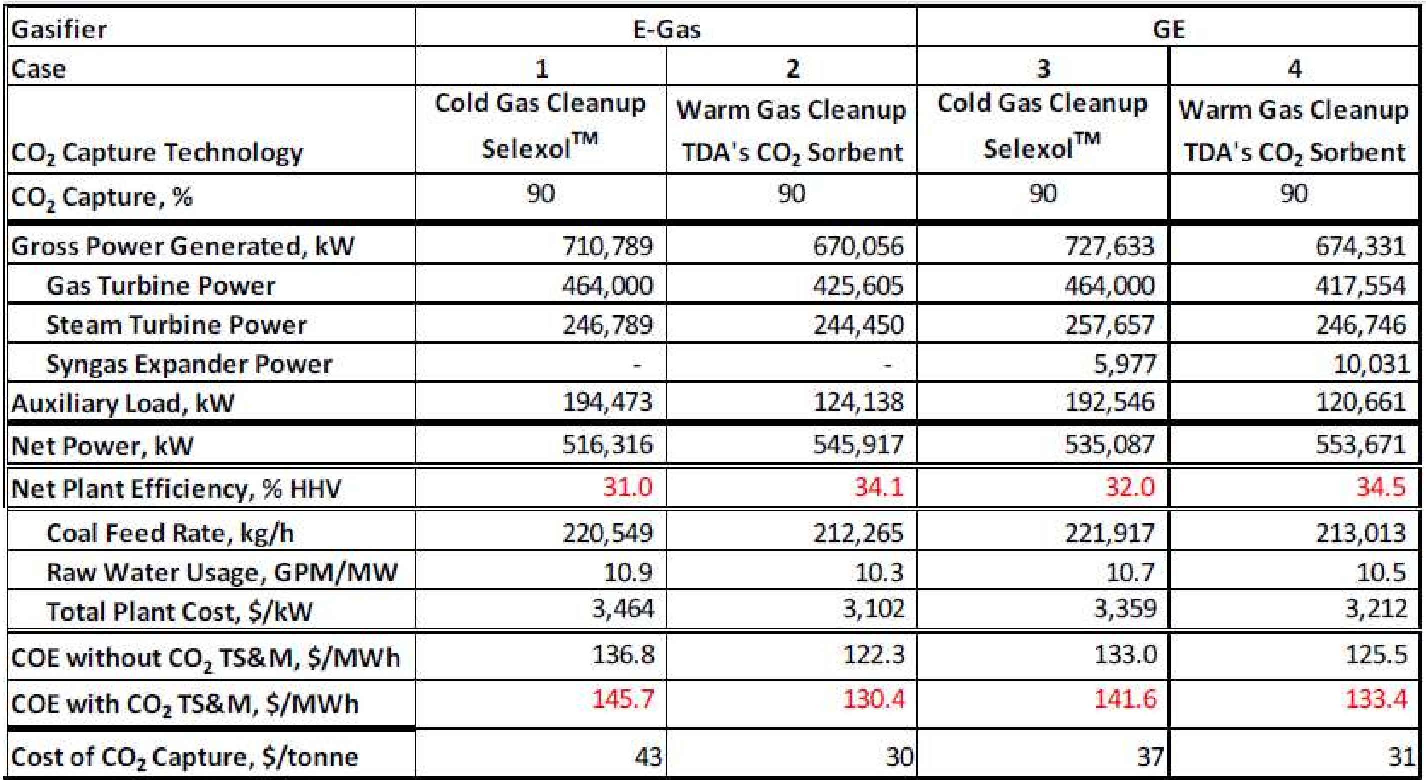
In 2018 and 2019, TDA shipped, installed, and performed shakedown testing on field units at Sinopec (see Figure 6), which allow oxygen-based gasifier testing at considerably increased throughput.

Figure 6: Field test units at Sinopec, China.

Very early testing results at 88 SCFM syngas flow have resulted in ~85% CO_2 removal efficiency at a rate of ~110 kg/hr CO_2.

TDA has also performed preliminary techno-economic analyses (TEAs) of cases assuming application of TDA's sorbent-based CO_2 capture system in IGCC plant cycles, based upon performance data available to date from recent testing. The comparisons involve a baseline of conventional cold-gas cleanup and Selexol™ acid gas removal, compared to TDA's assumption of warm-gas cleanup combined with the sorbent units for CO_2 capture. Results are shown in Figure 7. Overall, the findings are as follows:

- TDA system achieves higher efficiencies (34.5% and 34.1%) than IGCC with Selexol™ (32.0% and 31.0%) for E-Gas™ and GE gasifier-based plants.
- Cost of CO_2 capture is calculated as $31 and $30/tonne for GE and E-Gas™ gasifier-based plants, respectively (16 to 30% reduction against Selexol™).
- Cost of CO_2 capture is calculated as $40 and $28/tonne for Shell and TRIG gasifier-based plants, respectively (15 to 28% reduction against Selexol™).



Gasifier	E-Gas		GE	
Case	1	2	3	4
CO_2 Capture Technology	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent	Cold Gas Cleanup Selexol™	Warm Gas Cleanup TDA's CO_2 Sorbent
CO_2 Capture, %	90	90	90	90
Gross Power Generated, kW	710,789	670,056	727,633	674,331
Gas Turbine Power	464,000	425,605	464,000	417,554
Steam Turbine Power	246,789	244,450	257,657	246,746
Syngas Expander Power	-	-	5,977	10,031
Auxiliary Load, kW	194,473	124,138	192,546	120,661
Net Power, kW	516,316	545,917	535,087	553,671
Net Plant Efficiency, % HHV	31.0	34.1	32.0	34.5
Coal Feed Rate, kg/h	220,549	212,265	221,917	213,013
Raw Water Usage, GPM/MW	10.9	10.3	10.7	10.5
Total Plant Cost, $/kW	3,464	3,102	3,359	3,212
COE without CO_2 TS&M, $/MWh	136.8	122.3	133.0	125.5
COE with CO_2 TS&M, $/MWh	145.7	130.4	141.6	133.4
Cost of CO_2 Capture, $/tonne	43	30	37	31

Figure 7: Preliminary Techno-economic comparisons.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg$_f$	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10
Temperature	°C	195.5	195.5
Equilibrium CO_2 Loading	g mol CO_2/kg	0.005	0.005
	g mol CO_2/m^3	3.22	3.22
Heat of Desorption	kJ/mol CO_2	28.5	28.5

Proposed Module Design			(for equipment developers)	
Flow Arrangement/Operation	—		radial-flow fixed bed/cyclic	
Syngas Flowrate	kg/hr		668,083	
CO_2 Recovery, Purity, and Pressure$^+$	%/%/bar	90.0%	96.0%	10
Adsorber Pressure Drop	bar		1.41	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		212.8	

$^+$ CO_2 is recovered at 10 bar from TDA's CO_2 capture system, which is further purified and compressed to 152.7 bar with a final CO_2 purity of 99.96%.

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the syngas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3) and trace metals such as mercury (Hg), arsenic (As), etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of the 707-hour-long testing with coal-derived syngas with the 0.1-MWe pilot unit at the NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in syngas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900°C and in steam stable up to 400°C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 hours of operation.

Syngas Pretreatment Requirements – Syngas needs to be shifted to convert carbon monoxide (CO) present into CO_2 and H_2 via water-gas shift (WGS) reaction and sulfur content needs to be reduced to less than 100 parts per million (ppm) before CO_2 removal.

Sorbent Makeup Requirements – The expected life of the sorbent is five years. The annualized sorbent makeup requirement is expected to be 261.5 tonnes on the 550-MWe process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 1.

Proposed Module Integration – TDA's CO_2 separation, purification, and compression system is located downstream of the warm-gas sulfur removal and the WGS processes as shown in Figure 1.

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
497.5	388.4	30.28	0.73	2.04	0.45	39.11	26.59	<10

technology advantages

- Warm-gas CO_2 capture above dew point of syngas leads to more steam in the hydrogen-rich gas entering the turbine.
  - Improved efficiency.
  - Higher mass throughput to gas turbine.
  - Lower-gas turbine temperature, which lowers the need for high-pressure nitrogen (N_2) dilution and lowers nitrogen oxide (NO_X) formation.
- High steam content feed more suited for next-generation hydrogen turbines under development.
- High working capacity and cycle life of sorbent.
- Carbon dioxide recovered at pressure reduces compression costs for storage.
- A weak CO_2 surface interaction allows fast regenerations at lower temperature with minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight, corresponding to reduced adsorber vessel size and costs.

R&D challenges

- Assuring consistency in sorbent material and minimizing batch-to-batch variation for large-scale manufacture.
- Reducing the use of purge gas during regeneration.
- Confirming resistance to syngas contaminants.

status

Pilot-scale testing at the NCCC was completed in mid-2017, with successful attainment of 90%+ carbon capture at greater than design flows of syngas. Testing of the sorbent over 60,000 cycles has successfully demonstrated that the sorbent maintains stability and retains high CO_2 capacities over long-term cycling.

A CFD model to support reactor design was developed and tuned/optimized using the data from 1-kilowatt (kW) and 0.1-MW systems evaluated at Wabash River IGCC Plant and NCCC field tests.

TDA completed installation of field test units at Sinopec in mid-2019 and very early testing has subsequently begun, which is expected to run six to 12 months from late-2019.

Preliminary TEAs of cases assuming application of TDA's sorbent-based CO_2 capture system in IGCC plant cycles have been completed.

available reports/technical papers/presentations

"*Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System*," presented by Gökhan Alptekin of TDA Research, Inc. at the 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting – Capture and Utilization Sessions, Pittsburgh, Pennsylvania, August 2019.

"*PSA Based CO_2 Capture Above the Dew Point of Synthesis Gas for IGCC Power Plants*," presented at the 2017 AIChE Annual Meeting, Minneapolis, MN, November 2017.

"*Highly Efficient Warm Gas Carbon Capture System for IGCC Power Plants*," presented at the 2016 AIChE Annual Meeting, Minneapolis, MN, November 2016.

"*Pilot Testing of a Highly Efficient Pre-combustion Sorbent-based Carbon Capture System*," presented by Gökhan Alptekin, TDA Research, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System,*" presented by Gökhan Alptekin, TDA Research Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," presented by Gökhan Alptekin, TDA Research Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

Alptekin, G., et. al. "*A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture*," Final Report, September 30, 2012.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," presented by Gökhan Alptekin, TDA Research Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," Project Kick-Off Meeting, January 2013.

Alptekin, G., Jayaraman, A., Dietz, S., Bonnema, M., Rao, A., *"Low Cost, High Capacity Regenerable Sorbent for Precombustion CO_2 Capture*," Final Report, September 2012.

Alptekin, G., "A Low Cost, High Capacity Regenerable Sorbent for CO_2 Capture," presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, CA, February 2012.

Alptekin, G., Jayaraman, A., Dietz, S., and Schaefer, M., "High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture," presented at the 28th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, PA, September 2011.

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CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION MEMBRANE TECHNOLOGIES

Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

primary project goals

Arizona State University's (ASU) project objectives are to develop tools and methods for scaling-up zeolite membrane fabrication and water-gas shift (WGS) zeolite membrane reactors (ZMRs), and to construct bench-scale zeolite membrane modules and test their performance for WGS with carbon dioxide (CO_2) capture on coal-derived syngas.

This will be the first effort to study ZMRs for high-temperature chemical reaction and gas separation at this scale. The process design and techno-economic analysis (TEA), with the input of the experimental findings, will validate the effectiveness of the ZMR for WGS reaction and CO_2/hydrogen (H_2) separation. The results of this project will provide a foundation and guide for further scaling-up of the membrane reactor technology for pre-combustion CO_2 capture at pilot-scale.

technical goals

- Identify structure and operation conditions for a bench-scale membrane reactor through modeling and experimental study of the WGS reaction in a single-tube ZMR.
- Fabricate chemically and thermally stable alumina tubule supports and zeolite membranes of suitable quantity in consistent quality.
- Design and fabricate multiple-tube zeolite membrane modules with adequate seals for H_2 separation and WGS reaction at high temperature and pressures.
- Assemble and test the bench-scale zeolite membrane modules with desired catalyst for WGS reaction.
- Demonstrate effective production of H_2 and CO_2 capture by the bench-scale ZMR from coal gasification syngas at temperatures of 400 to 550°C and pressures of 20 to 30 atmosphere (atm), to produce 2 kg H_2/day (equivalent to 2 kilowatt-thermal [kW_{th}] integrated gasification combined cycle [IGCC] power plant).
- Perform process design and techno-economic and environmental, health, and safety (EH&S) risk analyses to evaluate performance and cost-effectiveness of the ZMR integrated in a 550-megawatt-electric (MW_e) IGCC plant with CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates zeolite-based H_2 separation membranes. Within the zeolite membrane WGS reactor, H_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are

technology maturity:

Bench-Scale, Actual Syngas (2 kg per day equivalent to 2 kWth)

project focus:

Zeolite Membrane Reactor

participant:

Arizona State University

project number:

FE0026435

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Jerry Lin
Arizona State University
jerry.lin@asu.edu

partners:

Media and Processes Technology Inc., University of Cincinnati, Nexant Inc.

start date:

10.01.2015

percent complete:

95%

replaced by a single, elegantly performing reactor. This process concept, with the ZMR replacing the conventional WGS process stages and amine absorption unit, is depicted in Figure 1.

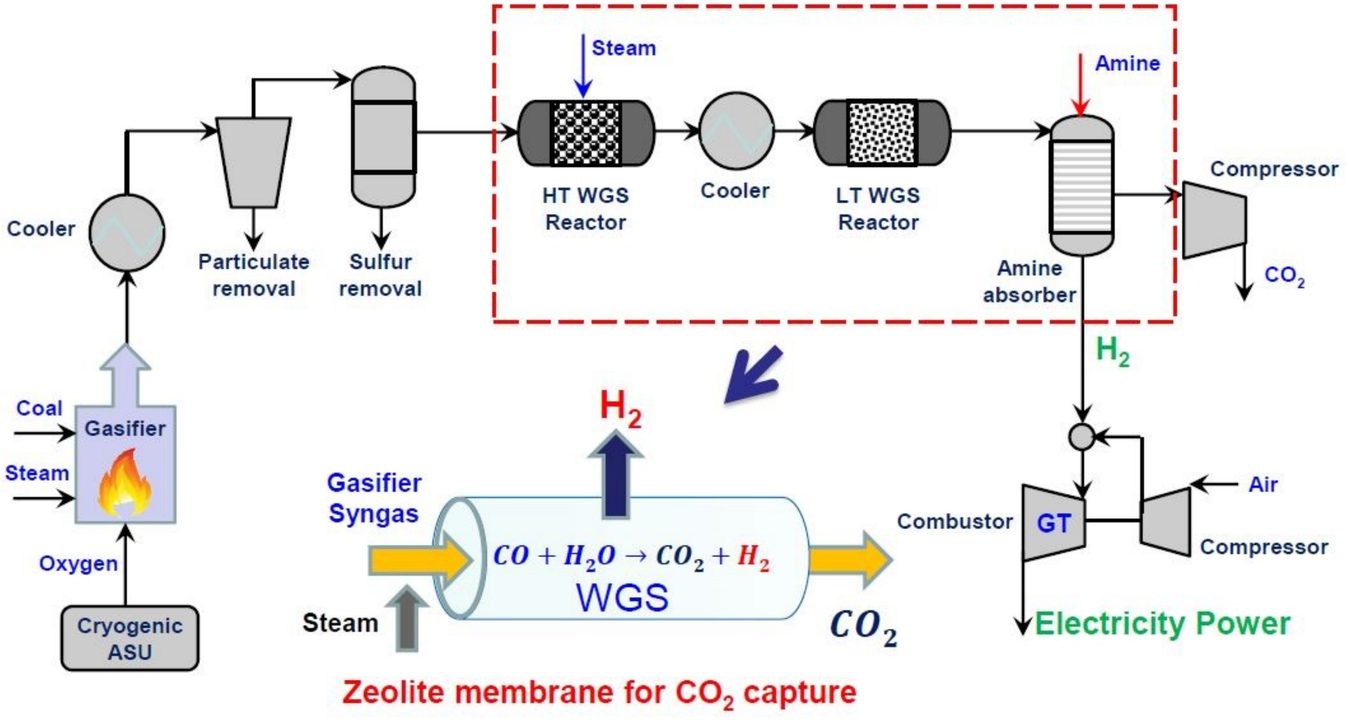

Figure 1: Zeolite membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

However, the operating environment in the reactor is challenging. Past findings have suggested that zeolite membranes, which are inorganic and can be tailored or selected for specific gas-separation applications, can meet the functional requirements and operational conditions as follows:

- Operation at 350 to 550°C.
- Chemically stable in hydrogen sulfide (H_2S), thermally stable at ≈400°C.
- Hydrogen permeance = 2×10^{-7} mol/m^2.s.Pa (600 GPU).
- Hydrogen/CO_2 selectivity = 20 to 40.

In ASU's previous work, Mobil-type 5 (MFI) zeolite (an aluminosilicate zeolite belonging to the pentasil family of zeolites) was used in a laboratory-scale zeolite membrane WGS reactor and continues as the basis in current work. See Figure 2 for the zeolite structure and a highly magnified view of the zeolite layer deposited on an alumina substrate. Although this zeolite has been traditionally used as a catalyst for hydrocarbon isomerization and the alkylation of hydrocarbons, it serves in the current work as an H_2-permeable membrane layer suitable for deposition on alumina, which can be formed into the desired tubes for fitting into WGS reactor modules.

The MFI zeolite pores have an effective diameter of ~0.56 nm, which is large enough for the small gas molecules involved in the WGS reaction to permeate through by gaseous diffusion mechanism. Therefore, pristine MFI-type zeolite membranes offer high H_2 permeance but with limited H_2/CO_2 selectivity defined by the Knudsen factor (~4.75) at high temperatures where the permeating gases become non-adsorbing to the zeolite. The MFI-type zeolite membranes can be modified by in situ deposition of mono silica species to the internal pore wall that narrows down the effective zeolite pore diameter from ~0.56 nm to less than 0.36 nm. Such a reduced pore size enables the highly selective size-exclusion effect between the small H_2 molecule (kinetic diameter d_k = 0.289 nm) and other slightly larger molecules like CO_2 (d_k = 0.330 nm), carbon monoxide (CO) (d_k = 0.376 nm), and methane (CH_4) (d_k = 0.380 nm).

ASU and the University of Cincinnati have developed an on-stream catalytic cracking deposition (CCD) method for modification of the MFI-type zeolite membrane that effectively controls the silica deposition within a small portion of the zeolitic channels near the membrane surface. This well-controlled modification avoids excessive loss in H_2 permeance while achieving substantially improved H_2 selectivity over CO_2, CO, and water (H_2O).

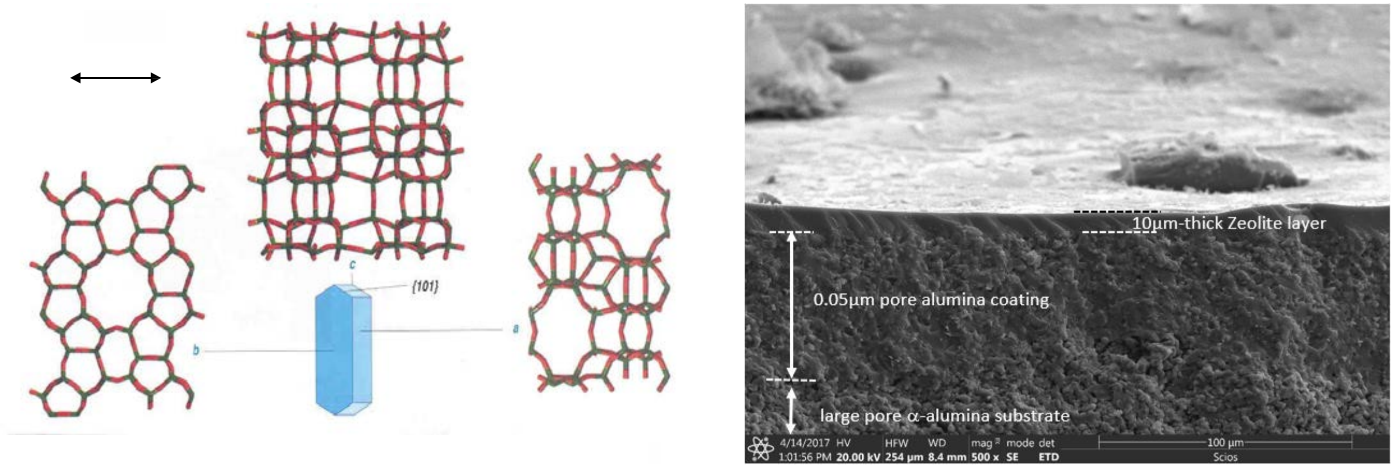

Figure 2: MFI-type zeolite (ZSM-5 or silicalite) (on left); magnified view of zeolite membrane (on right).

Figure 3 depicts the laboratory-scale tubular membrane reactor for testing separation performance and WGS reaction of a zeolite membrane tube containing a WGS catalyst. Feed gas is passed to the bore side of the tube, and as the gas passes over the catalyst, increasing amounts of H_2 are generated. The zeolite allows H_2 to readily pass through the membrane tube, while keeping the larger CO, H_2O, and CO_2 molecules inside. Retentate is enriched in CO_2 after the WGS reaction.

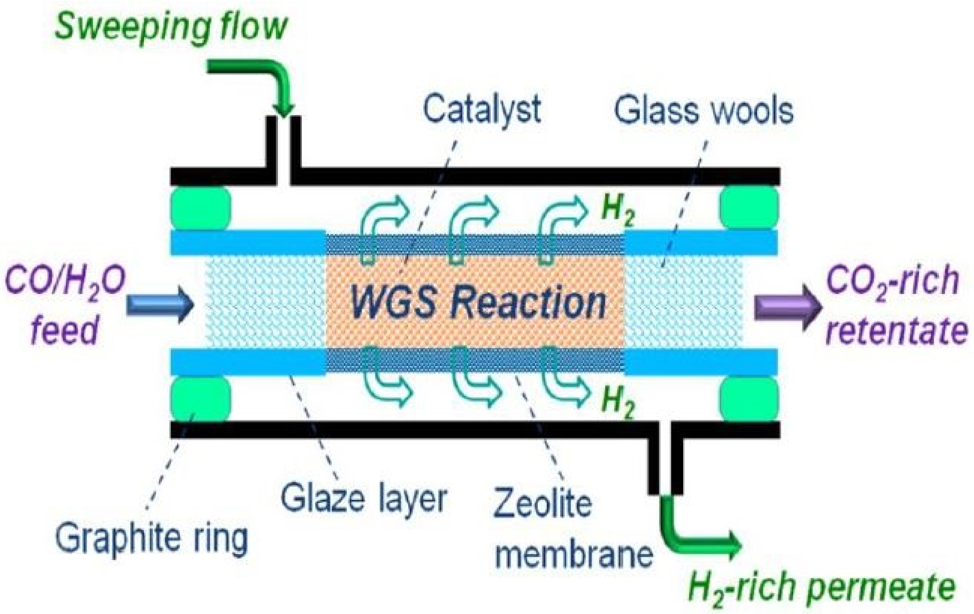

Figure 3: Zeolite membrane tubular WGS reactor.

Previously, CCD-modified MFI zeolite membranes showed long-term stability in WGS reaction at 400 to 550°C with a high H_2S content of ~400 parts per million (ppm) in feed. Modified MFI zeolite membranes with an H_2/CO_2 selectivity higher than 10 showed the ability to achieve CO-conversion well exceeding the equilibrium conversion in WGS reaction.

In this project, ASU reported the first experimental demonstration of near-complete CO conversion (~99.9%) in a single high-temperature and high-pressure WGS-ZMR that uses a CCD-modified MFI zeolite membrane supported on a commercially available low-cost small diameter alumina tube (outer diameter: 5.7 mm, provided by Media and Processes Technology Inc.).

This basic arrangement persists in the multi-tube reactors for bench-scale testing (these modules are depicted in Figure 4). The housing accommodates a full-length, 21-tube bundle, and the main feed port can be completely removed to permit catalyst packing/removal.

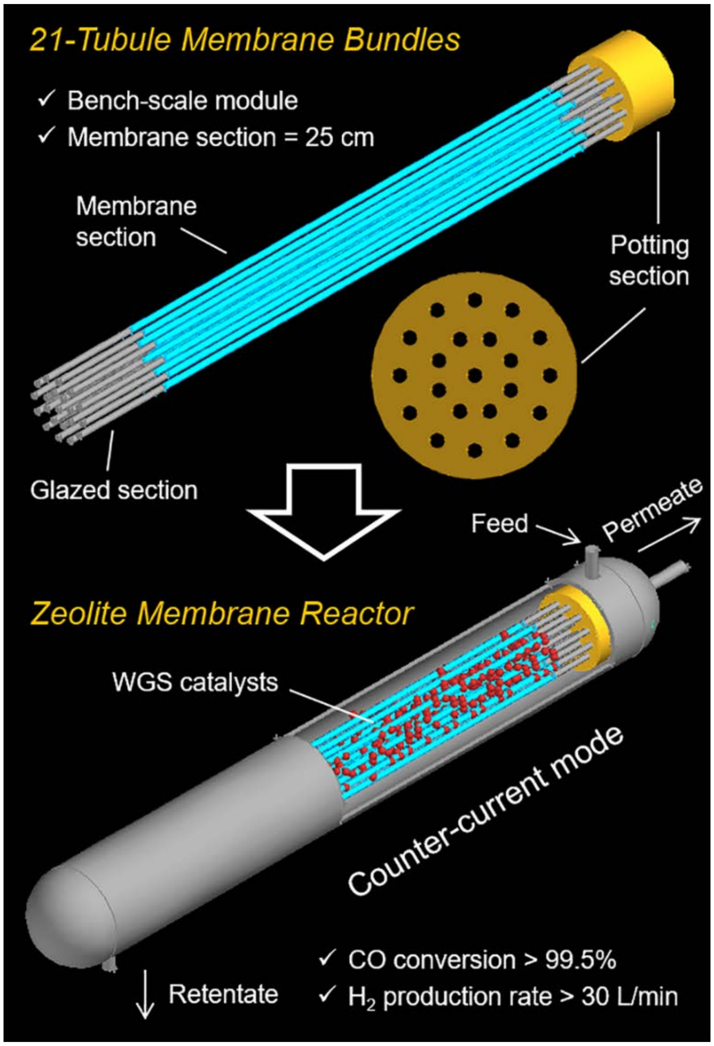

Figure 4: Zeolite membrane bundles and modules.

ASU performed a 425-hour challenge test on the 21-tube ZMR bundle and seals to evaluate performance and durability. Testing conditions were at temperatures from 400 to 450°C, pressure from 100 to 400 pounds per square inch (psi), and steam content from 60 to 100%. No deterioration was noted throughout the duration of the testing, as depicted in Figure 5.

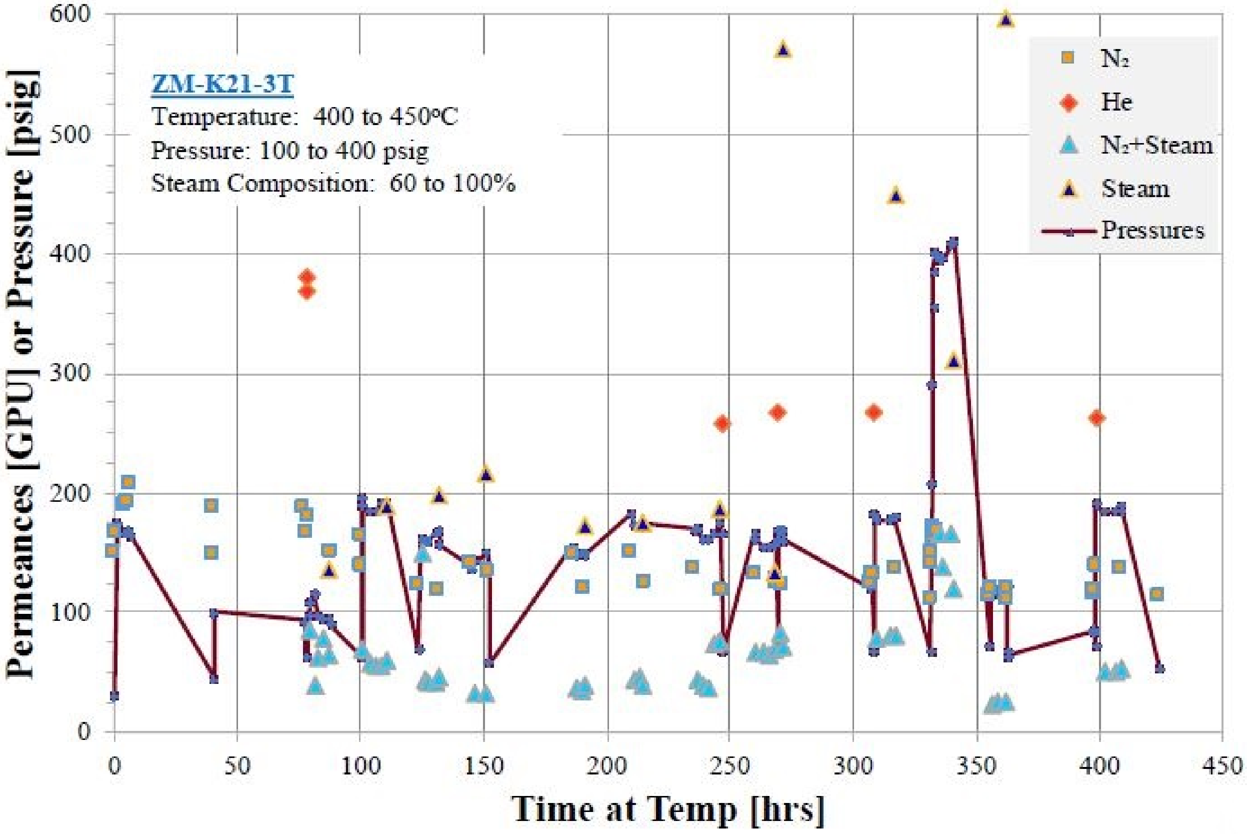

Figure 5: Challenge testing on zeolite tube bundles.

ASU completed fabrication and installation of the bench-scale reactor test skid at the University of Kentucky facility, and testing is underway.

Preliminary performance results of the WGS-ZMR have been used in process modeling and a TEA of a ZMR-based IGCC plant scenario; the results were compared to a National Energy Technology Laboratory (NETL) baseline case (conventional WGS and Selexol acid gas removal [AGR]) and the Nexant IGCC case. Compared to the NETL baseline, which has a cost of electricity (COE) of 141.5 mills/kilowatt-hour (kWh), including CO_2 transportation, storage, and monitoring (TS&M), the ZMR COE was higher at 147.3 mills/kWh. Notwithstanding somewhat lower capital costs, auxiliary power consumption is higher in the ZMR case, chiefly causing the higher COE.

TABLE 1: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="3">Current R&D Value *</th><th colspan="3">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="3">modified MFI zeolite</td><td colspan="3">modified MFI zeolite</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="3">α-alumina</td><td colspan="3">α-alumina</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="3">~10</td><td colspan="3">~5</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="3">discs</td><td colspan="3">tubes</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="3">~20</td><td colspan="3">~30</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>—</td><td colspan="3">~100</td><td colspan="3">>200</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m^2</td><td colspan="3">~800</td><td colspan="3">~600</td></tr>
<tr><th>Membrane Performance</th><th></th><th colspan="3"></th><th colspan="3"></th></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">400-500</td><td colspan="3">400-500</td></tr>
<tr><td>H_2 Pressure Normalized Flux</td><td>GPU or equivalent</td><td colspan="3">~300</td><td colspan="3">300-600</td></tr>
<tr><td>H_2/H_2O Selectivity</td><td>—</td><td colspan="3">>100</td><td colspan="3">>100</td></tr>
<tr><td>H_2/CO_2 Selectivity</td><td>—</td><td colspan="3">10–30</td><td colspan="3">20-45</td></tr>
<tr><td>H_2/H_2S Selectivity</td><td>—</td><td colspan="3">>60</td><td colspan="3">>60</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="3">1,000</td><td colspan="3">10,000</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="3">mixed-gas</td><td colspan="3">mixed-gas</td></tr>
<tr><th>Proposed Module Design</th><th></th><th colspan="6"></th></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="6">Counter-current</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="6">50-200</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="6">Retentate, CO_2-rich flow</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="6">5-20</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">90</td><td colspan="2">95 **</td><td colspan="2">~30</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">92</td><td colspan="2">95</td><td colspan="2">~20</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="6">10-30</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{\text{kg/hr}}$</td><td colspan="6">~1,000</td></tr>
</table>

* For the Current R&D Value, the calculation is based on lab-scale zeolite membranes reported in literature. Palladium-based membranes have high hydrogen selectivity but low sulfur tolerance, which is not presented here.

** Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 400°C, the separation of H_2 and CO_2 through modified zeolite membranes is governed by translational gas diffusion in micropores.

Contaminant Resistance – Zeolite membranes and catalysts have excellent resistance to syngas contaminants.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle will be applied in the ZMR continuously over 200 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensed water at the outlet of retentate side is recycled back as makeup water for the WGS reaction.

Process Design Concept – As presented in Figure 1. A skid for bench-scale ZMRs consisting primarily of a flow control system and a high-temperature oven is connected into a coal-to-liquids facility by replacing the WGS unit.

Proposed Module Integration – The proposed bench-scale study of ZMRs will be conducted at the University of Kentucky, Center for Applied Energy Research. The multiple-tube membrane bundle will be located downstream of a Coal/Biomass-to-Liquids (CBTL) pilot facility that produces syngas with a rated feed capacity of 1 ton/day. The pressure and temperature of syngas entering the membrane module are 435 pounds per square inch absolute (psia) and 845°F, respectively. The composition of the gas mixture is assumed:

		Composition						
Pressure	**Temperature**	vol%						ppmv
psia	°F	**CO_2**	**CO**	**CH_4**	**N_2**	**H_2**	**H_2O**	**H_2S**
435	845	32.3	34.1	0	2.8	25.7	3.4	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- Modified MFI zeolite membranes have remarkable resistance to sulfur species in the syngas feed and good thermal and hydrothermal stability and show superior hydrogen permeance and high H_2/CO_2 selectivity.
- These tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.
- The ZMR-based process will create a high-pressure CO_2 stream, capturing greater than 90% of CO_2 in post-shift syngas.

R&D challenges

- Low reproducibility of laboratory fabrication of long-tube zeolite membranes in large quantity with H_2 separation performance the same as a single, short-tube membrane.
- High-temperature hydrothermal stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- WGS catalysts' thermal stability, poison resistance, and product selectivity maintained at high pressures (greater than 15 atm) and temperatures (up to 550°C).
- Removal of particulate matter from the syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

Zeolite membranes have been fabricated on cost-effective industrial tubular alumina substrates, and high-pressure and high-temperature intermediate-scale zeolite membrane modules have been built and tested. WGS on ZMR was studied by experiments and modeling. Also, a process concept for ZMR integration into an IGCC power plant system has been identified and will serve as the basis for eventual cost and performance estimates for this technology.

available reports/technical papers/presentations

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Jerry Lin, Arizona State University, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," MPT Site Visit, February 2019.

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

A. Arvanitis, X. Sun, S. Yang, D. Damma, P. Smirniotis, J. Dong, "*Approaching complete CO conversion and total H_2 recovery for water gas shift reaction in a high-temperature and high-pressure zeolite membrane reactor*," Journal of Membrane Science, 549 (2018) 575–580.

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Jerry Lin, Arizona State University, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," presented by Jerry Lin, Arizona State University, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and Carbon Dioxide Capture

primary project goals

The overall objective is to combine crosslinked polymers having molecular size-sieving ability, and palladium (Pd)-based nanomaterials with very high hydrogen (H_2)/carbon dioxide (CO_2) solubility selectivity, to achieve membranes with superior gas-separation performance relative to stand-alone polymeric membranes. This project may lead to a new generation of membrane materials that combine robust performance with good processability to significantly decrease the cost of CO_2 capture, utilization, and storage (CCUS), enabling environmentally responsible energy production from abundant domestic coal.

technical goals

- Identify mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 at 150 to 200°C with simulated syngas.
- Prepare thin-film mixed matrix composite membranes with H_2 permeance of 500 gas permeation units (GPU) and H_2/CO_2 selectivity of 30 at 150 to 200°C and perform parametric testing of these membranes using simulated syngas in the laboratory.
- Conduct a 20-day field test of membrane stamps with real syngas from a gasifier, providing duration testing as well as assessing effects of exposure to syngas contaminants.

technical content

The State University of New York (SUNY) at Buffalo is developing a membrane-based process to capture CO_2 from coal-derived syngas. The key advancement of this technology is a series of novel sorption-enhanced mixed matrix membranes (MMMs) with high H_2 permeance (500 GPU) and high H_2/CO_2 selectivity (30) at temperatures up to 200°C. The approach combines highly crosslinked polymers with strong molecular size-sieving ability and Pd-based nanomaterials with high H_2/CO_2 selectivity to achieve membranes with performance superior to stand-alone polymeric membranes.

The working hypothesis explored in this technology development is that Pd nanoparticles exhibit extraordinary H_2 sorption, and therefore would confer favorable H_2/CO_2 solubility selectivity to thin-film composite (TFC) membranes into which they are incorporated (allowing H_2 to “hop” along the particle array). Such membranes, consisting of metallic Pd particles dispersed in a polymer matrix, are termed MMMs. Figure 1 depicts this approach, in which an MMM should improve both permeance and selectivity for H_2 separation above those typical of base polymer membranes.

technology maturity:

Bench-Scale, Actual Syngas (10 lb/hour equivalent to 0.007 MWe)

project focus:

Mixed Matrix Membranes

participant:

State University of New York (SUNY)–Buffalo

project number:

FE0026463

predecessor projects:

N/A

NETL project manager:

Andy Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Haiqing Lin
State University of New York (SUNY)–Buffalo
haiqingl@buffalo.edu

partners:

Membrane Technology and Research Inc.

start date:

10.01.2015

percent complete:

95%

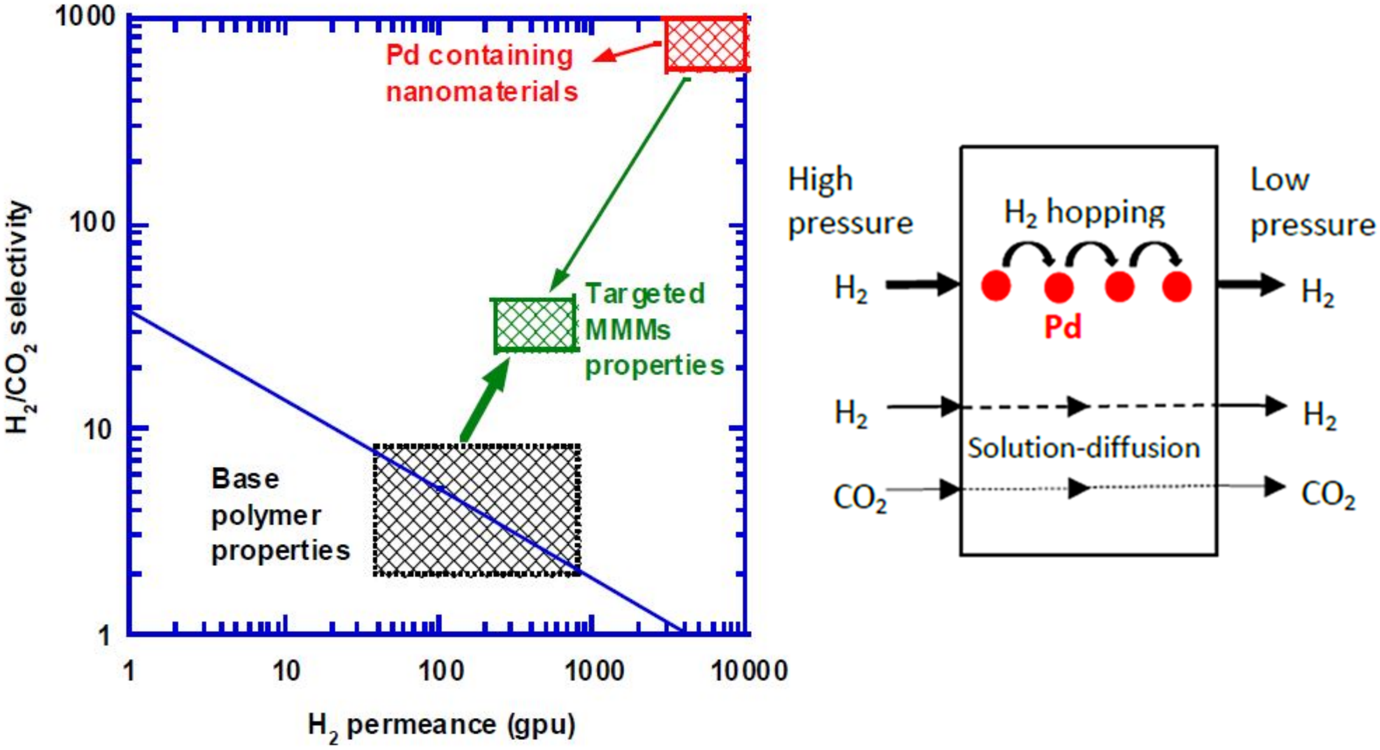

Figure 1: Mixed matrix materials approach.

One of the most suitable choices of polymeric material for membranes intended for H_2 separation from hot syngas is poly[2,2'-(m-phenylene)-5,5'-bisbenzimidazole] (m-PBI), which has been widely investigated for elevated temperature H_2/CO_2 separation. One of the strategies to enhance the size-sieving ability in m-PBI is to crosslink the polymer chains to increase chain rigidity and/or decrease free volume, and in this work, the m-PBI is crosslinked using terephthaloyl chloride. SUNY also discovered that by doping with phosphoric acid (H_3PO_4), the PBI is favorably modified toward greater H_2/CO_2 selectivity while decreasing H_2 permeability. The H_3PO_4 tightens the polymer structure and increases size-sieving ability while exhibiting stability up to 200°C. The improvement in PBI polymer properties thus demonstrated is depicted in Figure 2.

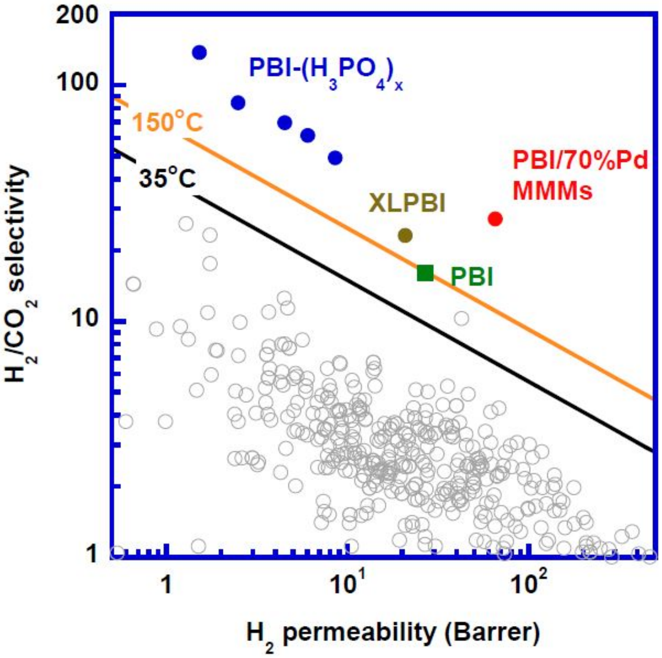

Figure 2: Polymer development and scale-up.

An important aspect of development of this technology is synthesis of the Pd nanoparticles for incorporation in the MMMs. Both solution-phase (colloidal) synthesis and gas-phase (aerosol) synthesis using a high-temperature reducing jet (HTRJ) reactor developed by SUNY were investigated. This reactor is depicted in Figure 3. The solution-phase synthesis directly provides nanoparticles that are dispersible in common organic solvents, including those from which the polymer membranes are cast. However, the HTRJ process can more readily produce alloy nanoparticles and is likely to be a more scalable and cost-effective process at larger scale. Pd-copper (Cu) (60/40) alloy nanoparticles with typical size of 4 to 8 nm were successfully prepared using the HTRJ reactor; when tested, these evidenced extremely high H_2/CO_2 solubility selectivity (≈840), and H_2 chemisorption independent of gas pressure.

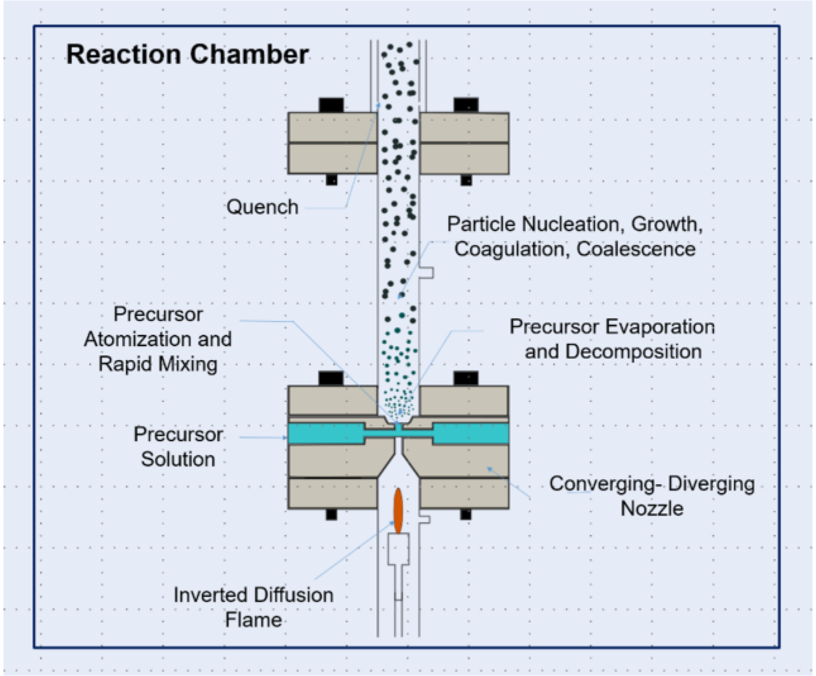

Figure 3: HTRJ reactor.

Particles prepared in the gas phase are collected as dry powders. For incorporation into polymer membranes, these nanoparticles must be stably dispersed in solvents that are also capable of dissolving the polymers of interest. The Pd alloy nanoparticles are suspended in toluene solvent and mixed with 5.0 wt% PBI in dimethylacetamide (DMAc) solvent. The combined dual solvent system incorporating both the dissolved PBI and nanoparticles is sonicated, then placed on a plate or support and allowed to dry at elevated temperature and under vacuum. Currently, the mixed matrix PBI/Pd layer is created directly on a support structure of polydimethylsiloxane (PDMS) silicone on pure PBI support, all of which is underlain by stainless steel mesh. In Figure 4, a very thin mixed matrix layer only 900 nm thick with embedded nanoparticles is visible on the silicone gutter layer, with porous PBI support underneath. In this image, the mixed matrix layer is 58 wt% or 13 vol% of Pd nanoparticles (designated PBI-Pd-58/13). Syntheses have increased Pd nanoparticle content up to 70 wt%; the point depicted in red in Figure 2 shows early performance properties of the 70 wt% Pd/PBI MMM.

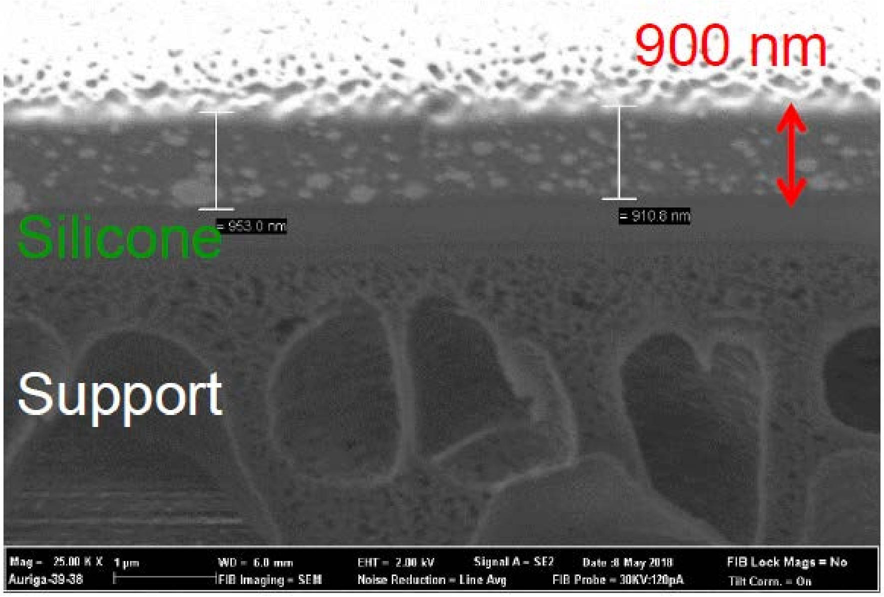

Figure 4: Cross-sectional scanning electron microscopy (SEM) of membranes.

Figure 5 shows the final laboratory-scale testing results for MMM permeability and selectivity for H_2/CO_2 separation. Behavior of optimized membranes at temperatures ranging from 150 to 225°C is show for three loadings of nanoparticles (22%, 46%, and 58% nanoparticles by weight). Note that the target performance region has been attained with the PBI-PD-58/13 MMM.

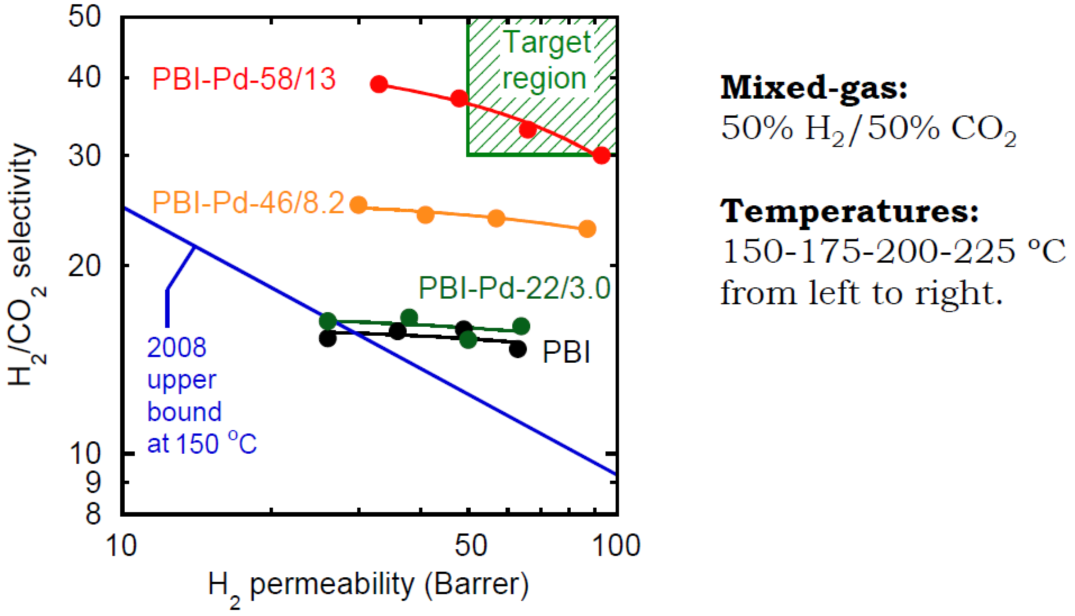

Figure 5: Effect of increasing Pd nanoparticle content on H_2/CO_2 separation in MMMs.

Also, stability of the MMMs in the presence of hydrogen sulfide (H_2S) and water (H_2O) was experimentally evaluated by measuring any changes of membrane permeability and selectivity with and without these species added to the simulated syngas mixtures. Satisfactory stability was observed in long-term laboratory-scale testing.

An important performance target of H_2 permeance of 500 GPU or greater at 150 to 200°C (with selectivity at least 30) had been set for this technology. Figure 6 shows the laboratory-scale permeances attained in this project (red) for a 70-nm thin-film MMM and various other competing H_2 separation membranes' permeance performance for comparison. Note that a thin-film MMM at 230°C would have more than adequate selectivity; however, with permeance of 400 GPU, it does not attain the target field.

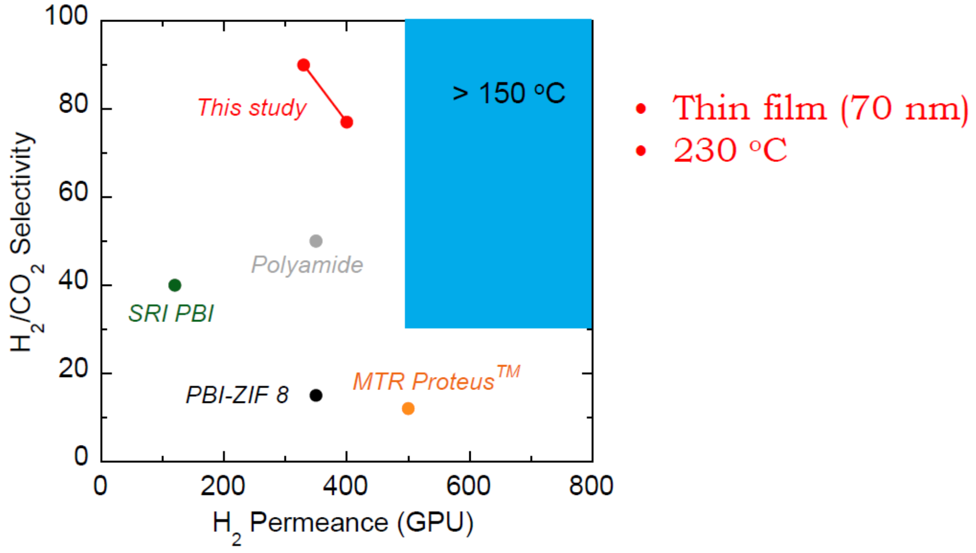

Figure 6: Hydrogen permeance target performance.

Final project work involves testing of field stamps of MMMs using real syngas. Testing is to be conducted at the University of Kentucky's Center for Applied Energy Research (CAER), using syngas from the opposed multi-burner entrained flow coal gasifier at CAER.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymers	
Materials of Fabrication for Support Layer	—	polysulfone, polyethersulphone, etc.	
Nominal Thickness of Selective Layer	µm	0.1–0.2	0.1
Membrane Geometry	—	Flat sheet or hollow fiber	Flat sheet
Maximum Trans-Membrane Pressure	bar	50	50
Hours Tested without Significant Degradation	—	1 month	3 weeks
Manufacturing Cost for Membrane Material	$\$/m^2$	10-50	20-50
Membrane Performance			
Temperature	°C	100-300	250
H_2 Pressure Normalized Flux	GPU	200	500
H_2/H_2O Selectivity	—	0.1-0.5	—
H_2/CO_2 Selectivity	—	20	30
H_2/H_2S Selectivity	—	10-20	20
Sulfur Tolerance	ppm	50	10
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	spiral-wound modules	
Packing Density	m^2/m^3	1,000-5,000	
Shell-Side Fluid	—	syngas	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
H_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Barrer – Gas permeability unit of membrane selective materials, 10^{-10} cm^3 (STP)/(cm^2 s cm Hg)

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Resistant to water, high-pressure CO_2. However, the effects of sulfur and carbon monoxide (CO) on gas separation properties are to be determined.

Syngas Pretreatment Requirements – Sulfur removal and temperature adjustment.

Membrane Replacement Requirements – Not determined.

Waste Streams Generated – None identified.

Process Design Concept – Not determined.

Proposed Module Integration – The membrane system is after the low-temperature shift reactor.

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
750	480-750	35-45	1-2	1-2	1-2	50-60	2-5	5-100

technology advantages

- Synergism created by incorporating Pd in a polymer membrane, taking advantage of the well-understood properties and performance of PBI in membrane gas separations with the extremely high H_2 selectivity and permeability of Pd.
- Cost savings over pure Pd membranes, using relatively little expensive Pd metal, but still taking advantage of its H_2 sorption properties and stability against sulfur compounds.
- Good processability derived from polymer-based materials for the fabrication of the industrial thin-film composite membranes.

R&D challenges

- Membrane stability at operating conditions (elevated pressure and temperature).
- Fabrication of thin-film composite membranes consistently to specification and without defects.
- Scaled-up production of high-purity Pd nanoparticles and improving process yield.
- Attaining target region of selectivity vs. permeability in MMMs.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

Mixed matrix materials with superior H_2/CO_2 separation properties, and polymers and nanomaterials with promising H_2/CO_2 separation properties, were identified and prepared. Laboratory-scale testing of MMM-based membranes has been completed, from which adequate H_2/CO_2 selectivity, targeted gas permeability, and stability in the presence of simulated syngas has been confirmed. Current work is on readying the field test unit to perform testing on membrane samples in actual coal syngas.

available reports/technical papers/presentations

"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019.

"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," presented by Haiqing Lin, State University of New York (SUNY) - Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

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"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," project kickoff meeting presentation, Pittsburgh, PA, October 5, 2015.

L. Zhu, M. Swihart and H. Lin, Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane H_2/CO_2 separation, *Energy & Environmental Science*, 2018, DOI: 10.1039/c7ee02865b

L. Zhu, M. Swihart and H. Lin, Tightening nanostructure of PBI for membrane H_2/CO_2 separation, *Journal of Materials Chemistry A*, 5, 19914-19923, 2017, DOI: 10.1039/C7TA03874G

Lingxiang Zhu, Maryam Omidvar and Haiqing Lin. "Manipulating Polyimide Nanostructures via Crosslinking for Membrane Gas Separation," Chapter 6 in *Membranes for Gas Separation*, pp. 243-270, World Scientific, Aug 11, 2017.

H. Lin, "Molecularly Engineering Membrane Materials for Separations through Enhanced Interactions: A Road Less Traveled," Department of Chemical and Materials Engineering and Center of Membrane Science, University of Kentucky, Lexington, KY, March 1, 2017.

Adams and Chen, *Materials Today*, **14** (2011) 282-289.

H. Lin et al., *J. Membr. Sci.* **457**, 149-161 (2014).

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Integrated Multichannel Water-Gas Shift Catalytic Membrane Reactor for Pre-Combustion Carbon Capture

primary project goals

The Bettergy Corporation team is developing an integrated catalytic membrane reactor (CMR) system that combines, in a one-stage process, a high-temperature water-gas shift (WGS) reaction with a hydrogen (H_2) separation membrane to produce H_2 while simultaneously delivering carbon dioxide (CO_2) at high pressure, minimizing the cost of CO_2 compression. The core of the novel process is built upon a robust modularized membrane supported on catalytic substrates, which is based on Bettergy's patented nanopore engineering membrane (NEM) platform technology. Previously, a lab-scale WGS-CMR system was successfully tested, achieving high WGS conversion, high-purity H_2 through membrane separation, and enriched CO_2 in the retentate stream. Currently, the main project goals are to optimize the process, develop and test a multichannel prototype system, and generate a commercialization plan.

technical goals

- Optimize the formulation for the catalytic membrane substrate.
- Develop and optimize the fabrication processes for making both tubular and multichannel membrane substrates.
- Optimize membrane synthesis procedures on the substrates.
- Optimize CMR performance to attain carbon monoxide (CO) conversion exceeding the thermodynamic limit at high temperature (up to 500°C) and pressure of 450 pounds per square inch (psi).
- Investigate the effect of impurities (e.g., hydrogen sulfide [H_2S]) on membrane performance, and achieve stability of at least 500 hours without appreciable degradation.
- Demonstrate prototype performance at syngas (simulated) flow rate of 5 kg/day.
- Enable improvement of energy efficiency of a CMS reactor system integrated in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant with CO_2 capture by 25 to 30%, relative to a multistage WGS reaction with amine-based carbon capture and pressure swing adsorption (PSA) H_2 purification.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification or steam reforming plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit (for

technology maturity:

Laboratory-Scale, Simulated Syngas (5 kg/day)

project focus:

Water-Gas Shift Catalytic Membrane Reactor

participant:

Bettergy Corporation

project number:

SC0018853

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Zhong Tang
Bettergy Corporation
ztang@bettergy.com

partners:

University of Cincinnati, Dawnbreaker, Inc.

start date:

07.02.2018

percent complete:

50%

capturing the CO_2 from the shifted syngas) could be replaced in whole by a one-stage WGS-CMR process unit. In this one-stage process, the WGS reaction occurs in the CMR, which incorporates H_2 separation membranes that permit pure H_2 to be drawn off, efficiently increasing the driving force for the equilibrium WGS reaction to go to completion. Carbon dioxide exiting the WGS-CMR remains at relatively high pressure, reducing subsequent CO_2 compression costs. As a result, the multiple stages of the conventional WGS unit would be replaced by a single-stage reactor (or banks of reactors in parallel as syngas throughput requires). The process concept is depicted in Figure 1 (for a natural gas reforming scenario).

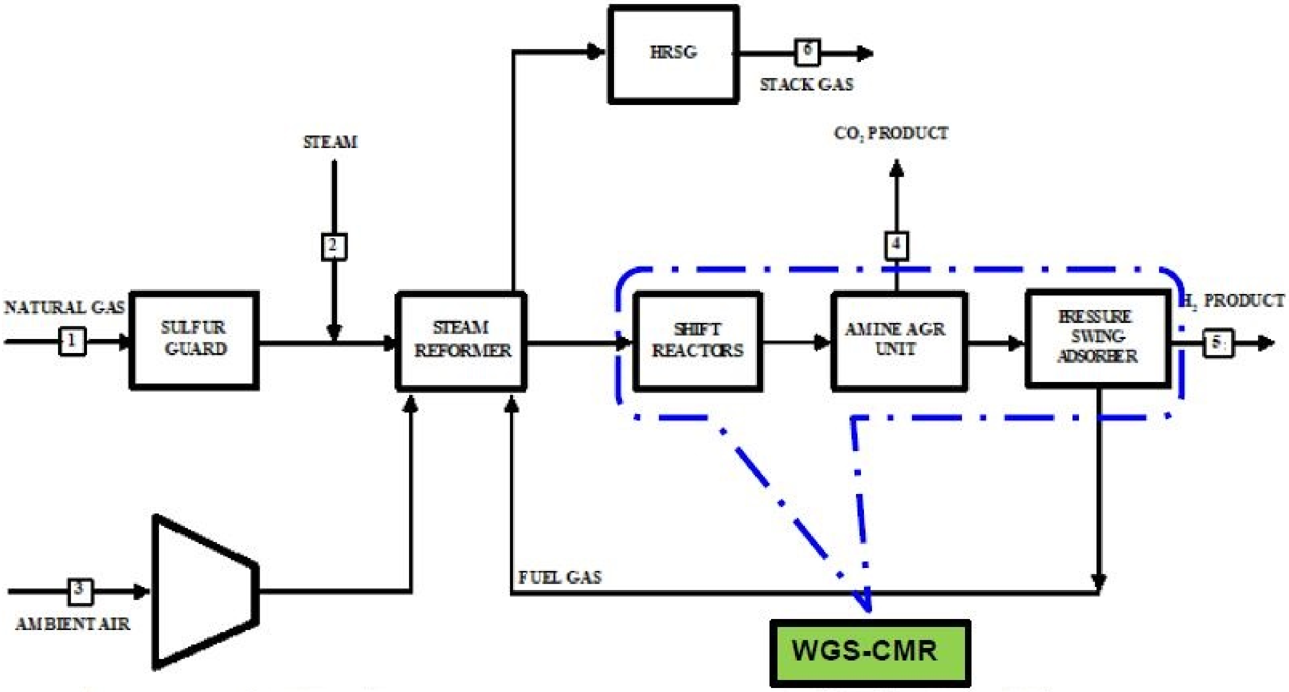


Figure 1: WGS-CMR (in green shadow) replacing two-stage shift, amine CO_2 capture, and PSA systems (in blue envelope) in natural gas steam reforming H_2 production process.

The basic structure of the WGS-CMR will consist of tubular channels having a configuration of the sort illustrated in Figure 2. Each reactor gas channel consists of a porous tubular support on which two different active layers are applied. The internal tube layer is made of WGS catalyst, while the outer layer is an H_2-selective zeolite. Pressurized syngas flows through the bores of the tubes, where it contacts the WGS catalyst layer inducing increased H_2 production. The H_2 permeates through the support and can exit through the outside selective layer. Other syngas species do not readily permeate through the outside zeolite layer and remain at pressure inside the tubes. Given suitable WGS kinetics and gas flow rates, high levels of syngas conversion can be obtained, and a large fraction of H_2 can be recovered on the permeate side of the reactor. Retentate from the reactor can be made to contain most of the carbon in the incoming syngas in the form of CO_2. An alternate WGS-CMR configuration is similar but dispenses with the WGS layer and has only an H_2-selective layer on a porous substrate of WGS catalyst. In this case, the WGS catalyst might be in monolith form with many channels, and the H_2-selective zeolite layer will be on the outside surface of the monolith.

The dimensions of the gas channels may be made very small, and as such the WGS-CMR is a type of microchannel membrane reactor. Microchannel reactors offer multiple benefits, including better control over temperature profiles, minimal catalyst loading for given levels of gas throughput, moderate pressure drop, and favorable trade-off between capital cost and performance.

This novel WGS-CMR does pose developmental challenges, including optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate), preparing the H_2-selective composite zeolite thin layer membrane on the support/substrate, and development and optimization of WGS-CMR assemblies.

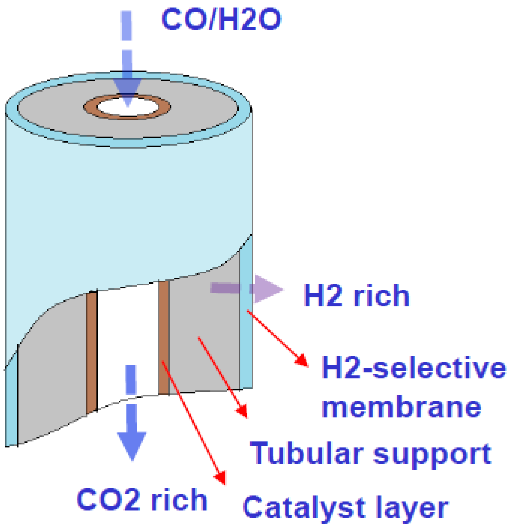


Figure 2: WGS-CMR tubular configuration.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	composite	composite
Materials of Fabrication for Support Layer	—	WGS catalyst	WGS catalyst
Nominal Thickness of Selective Layer	µm	10-20	10-20
Membrane Geometry	—	tubular	multichannel
Max Trans-Membrane Pressure	bar	10	30
Hours Tested without Significant Degradation	—	500	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	1,200	355-657
Membrane Performance			
Temperature	°C	350-550	400-500
H_2 Pressure Normalized Flux	GPU or equivalent	150	50-250
H_2/H_2O Selectivity	—	N/A	N/A
H_2/CO_2 Selectivity (Dense layer thickness)	—	>75	>75
H_2/H_2S Selectivity (Dense layer thickness)	—	N/A	N/A
Sulfur Tolerance	ppm	200	500
Type of Measurement	—	mixed	mixed
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	counter flow	
Packing Density	m^2/m^3	n/a	
Shell-Side Fluid	—	retentate	
Syngas Flowrate	kg/hr	0.21	
CO_2 Recovery, Purity, and Pressure	%/%/bar	80%, 80%, 20 bar	
H_2 Recovery, Purity, and Pressure	%/%/bar	80%, >95%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	1/1.5	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	TBD	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, monolith, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – TBD.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – Hydrogen sulfide would remain in the retentate and must be separated. This may result in a waste stream containing H_2S.

Process Design Concept – See Figure 1.

Proposed Module Integration – TBD.

The composition of the gas entering the module:

Pressure	Temperature	Composition (Dry)						
		vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435.1	842	15.95	49.75	0.12	1.15	32.55	0.46	0.02

technology advantages

- The novel pre-combustion CO_2 capture technology can be used in current gasification plants or future IGCC plants for industrial H_2 production while simultaneously capturing CO_2.
- Bettergy's CMR system offers substantial simplification of the CO_2 capture process, reduction in the cost of CO_2 capture, and increased energy efficiency, providing economic and environmental benefits for the general public.
- Microchannel reactors facilitate favorable operating temperature profiles in the reactor.
- Microchannel reactors minimize catalyst loading and limit pressure drop.
- Microchannel reactors provide optimized balance between capital cost and performance.

R&D challenges

- Optimizing the formulation of the high-temperature WGS catalyst (as either a layer on an inert porous support, or itself as the catalytically active porous substrate).
- Preparation of the H_2-selective composite zeolite thin layer membrane on the support/substrate.
- Development and optimization of WGS-CMR assemblies.

status

Proof-of-Concept has been successfully accomplished. Tubular and multichannel modules are being developed.

available reports/technical papers/presentations

"*Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-Combustion Carbon Capture*," Phase I final briefing/Phase II kickoff meeting, August 2019.

"*Integrated Multichannel WGS Catalytic Membrane Reactor for Pre-combustion Carbon Capture*," Phase I kickoff meeting presentation, July 2018.

Bench-Scale Development of a Transformative Membrane Process For Pre-Combustion CO_2 Capture

primary project goals

Membrane Technology and Research, Inc. (MTR) and partners Susteon and the Energy and Environmental Research Center (EERC) are maturing technology based on a novel, hydrogen (H_2)-selective, multi-layer composite polymer membrane called Proteus™ for use in the separation of H_2 from post-shifted syngas. The current project focuses on the scale-up of a second-generation Proteus™ membrane, including fabrication of high-temperature prototype modules using Gen-2 membranes and validating module performance in laboratory tests. A prototype module test system will be designed, built, and installed at EERC for parametric and lifetime testing of the modules with actual coal-derived syngas. The process will be optimized, and a techno-economic analysis (TEA) will be updated based upon the results of testing.

technical goals

- Optimize the Gen-2 Proteus™ membrane and develop modules capable of operation up to 200°C.
- Demonstrate membrane module performance while processing coal-derived syngas during a field test at EERC by demonstrating an H_2/carbon dioxide (CO_2) selectivity = 30 and recovering 2.5 lb/h H_2 at 75% purity at a syngas flow rate of 20 lb/h.
- Advance the Gen-2 Proteus™ membrane pre-combustion membrane capture technology from Technology Readiness Level (TRL) 4 to TRL 5.
- Optimize processes for integrating membrane modules into the integrated gasification combined cycle (IGCC) process with carbon capture (including evaluating sulfur treatment options), showing the potential via a TEA to reduce the cost of capture by more than 30% compared to Selexol.

technical content

MTR is developing composite membranes for application in pre-combustion carbon capture where essential membrane characteristics include high H_2/CO_2 selectivity and high H_2 permeance rates. The MTR composite membrane for H_2 separation is called Proteus™. Figure 1 illustrates the membrane structure and some characteristic composite membrane layers. Note that the key to competitive industrial performance is a very thin selective layer, which is required to allow high gas fluxes (or permeances) for given membrane surface areas.

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 0.015 MWe)

project focus:

Polymeric Membranes

participant:

Membrane Technology and Research, Inc.

project number:

FE0031632

predecessor projects:

FE0001124

NETL project manager:

Andy Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Jay Kniep
Membrane Technology and Research, Inc.
jay.kniep@mtrinc.com

partners:

Susteon Inc., Energy and Environmental Research Center

start date:

10.01.2018

percent complete:

40%

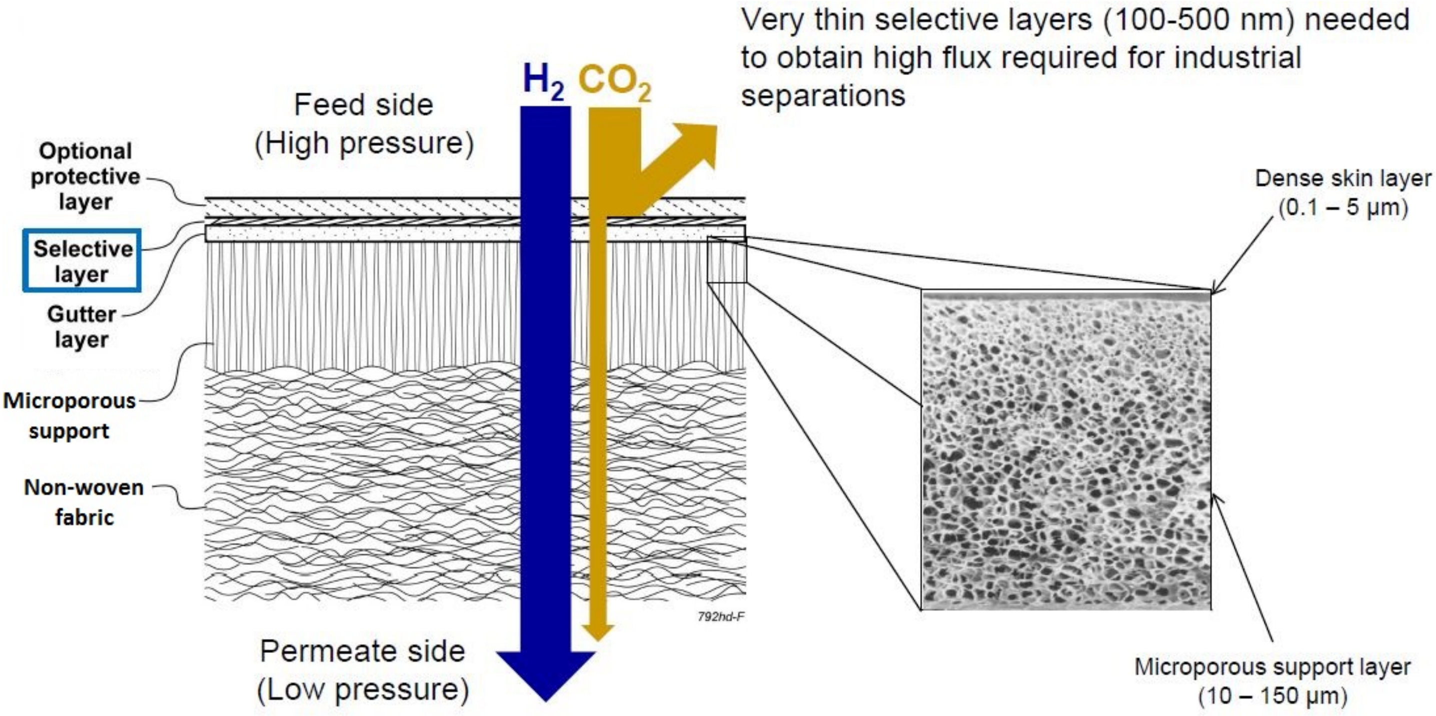


Figure 1: Proteus™ membrane multi-layer composite structure.

The H_2-selective Proteus™ membranes were first developed by MTR in work funded by the U.S. Department of Energy (DOE; DE-FE0001124). The first-generation membrane (Gen-1 Proteus™) had an upper temperature limit of 150°C. Semi-commercial modules made from this membrane demonstrated stable operation for extended periods in the presence of sulfur and other contaminants in slipstream tests of actual coal-derived syngas from an air-blown gasifier at the National Carbon Capture Center (NCCC). By the end of testing in 2017, Gen-1 Proteus™ was evaluated in more than 15 different gasification campaigns accumulating 5,500 hours of run time for membrane stamps or lab-scale modules and 3,625 hours for semi-commercial modules at NCCC.

The recently developed Gen-2 Proteus™ has a higher temperature limit compared to the Gen-1 membrane (200°C versus 150°C), which allows for better heat integration into pre-combustion processes. The Gen-2 membrane also has improved H_2/CO_2 selectivity compared to the Gen-1 membrane, with an average value of 32 measured in membrane stamp testing at NCCC (compared to 15 to 20 for Gen 1 in the same tests). In ongoing work, a new membrane treatment technique has been developed that improves the membrane H_2/CO_2 selectivity to 50, which significant exceeds the project success criteria of 30. This improved selectivity will reduce energy use and the required purification equipment size, thereby lowering operating and capital expenses.

To highlight the improved permeation performance of the Gen-2 Proteus™ membrane, Figure 2 compares the selectivity and permeance of this membrane with other polymers on a Robeson tradeoff plot.

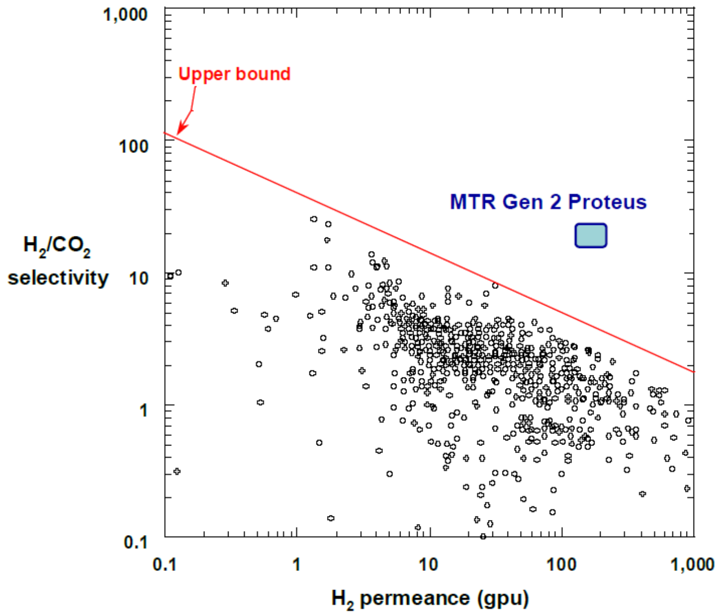


Figure 2: Robeson plot with Gen-2 Proteus™ membrane performance.

Process Scenarios

A simplified process flow diagram for carbon capture with membranes in an IGCC power cycle is depicted in Figure 3. Coal is converted by oxygen-based pressurized gasification resulting in a raw syngas. This syngas is shifted via the water-gas shift (WGS) reaction to produce syngas consisting mostly of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane capture unit. The high-partial pressure driving force, combined with a nitrogen (N_2) sweep on the lower-pressure permeate side of the membrane, causes selective H_2 permeation into the N_2 sweep, which serves as fuel gas in a combustion turbine. The high-pressure membrane retentate is enriched in CO_2 that can then be further purified, compressed, and sent to storage.

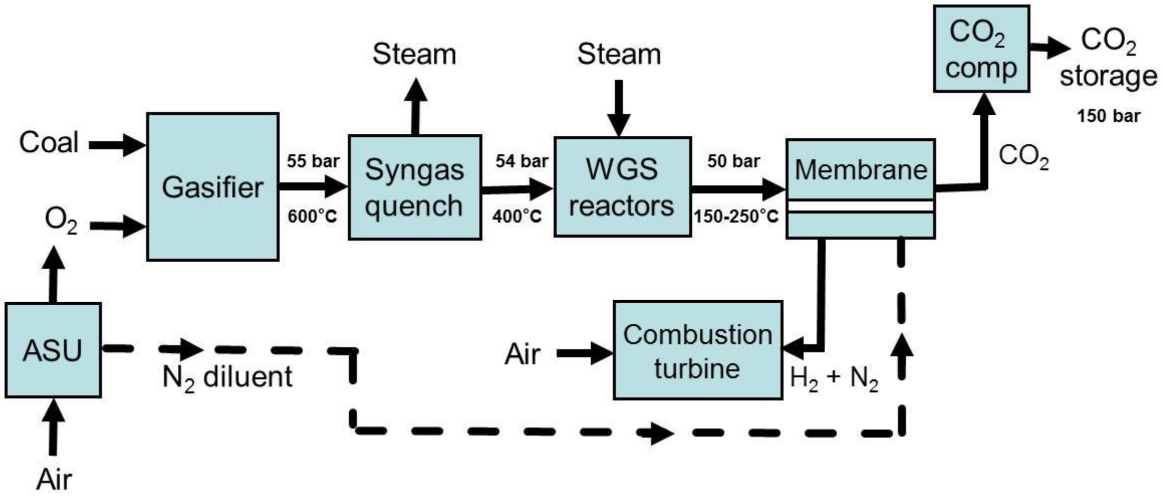


Figure 3: Overall process design for the pre-combustion capture membrane system.

Figure 4 shows additional process details for the MTR pre-combustion CO_2 capture process. After using the Proteus™ membrane to recover H_2, a series of steps are used to purify CO_2. These steps include (1) sulfur removal, (2) gas drying, (3) refrigeration to produce liquid CO_2, (4) additional CO_2 recovery with the MTR Polaris™ membrane, and (5) pumping liquid CO_2 to storage pressure. The CO_2 purity can be readily increased to greater than 99% in this process. In comparison to a baseline case (GE Gasifier with two-stage Selexol [i.e., Case 2 of DOE Bituminous Baselines Study]), prior studies showed that the MTR membrane process provides a 27-megawatt-electric (MWe) net power improvement and a 7.4% lower cost of energy (COE) using Gen-1 Proteus™ membrane properties. Both the warm (H_2 membrane) and cold (CO_2 membrane) portions of the MTR process have been validated in independent skid field tests at NCCC.

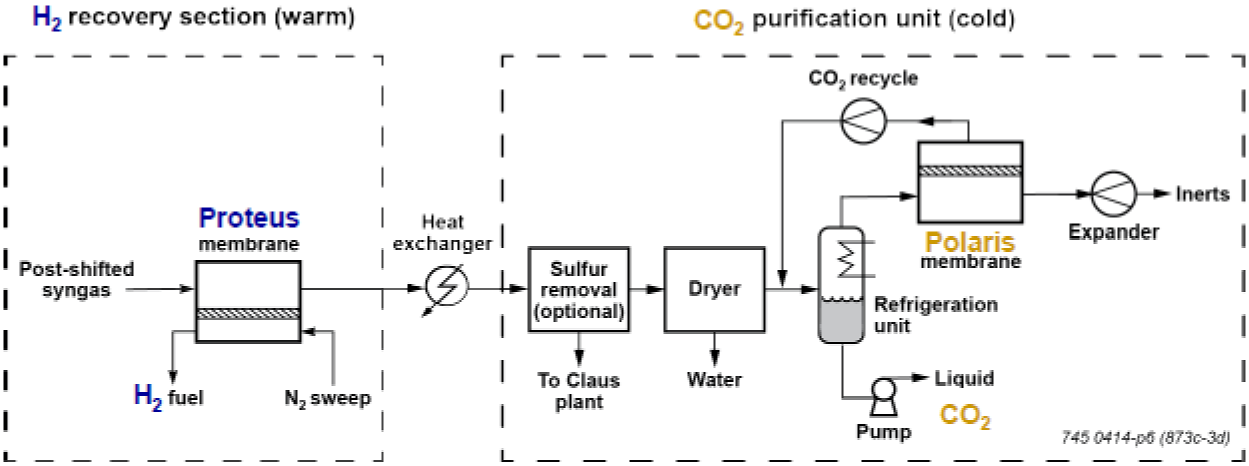


Figure 4: MTR dual-membrane process for H_2 recovery and CO_2 capture in IGCC power generation.

For industrial applications, Proteus™ membranes will be packed into spiral-wound membrane modules, a commonly used module design for commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 70% of the membrane market for CO_2 removal from natural gas. Figure 5 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, allowing separated H_2 to be swept by N_2 on the permeate side and CO_2 retained on the feed site to flow through the device. In bench-scale work, modules have membrane area of 1 to 4 m^2, and accommodate gas flow of about 50 lb/h. Commercial modules have membrane area of 20 to 50 m^2, and accommodate gas flow of about 500 lb/h.

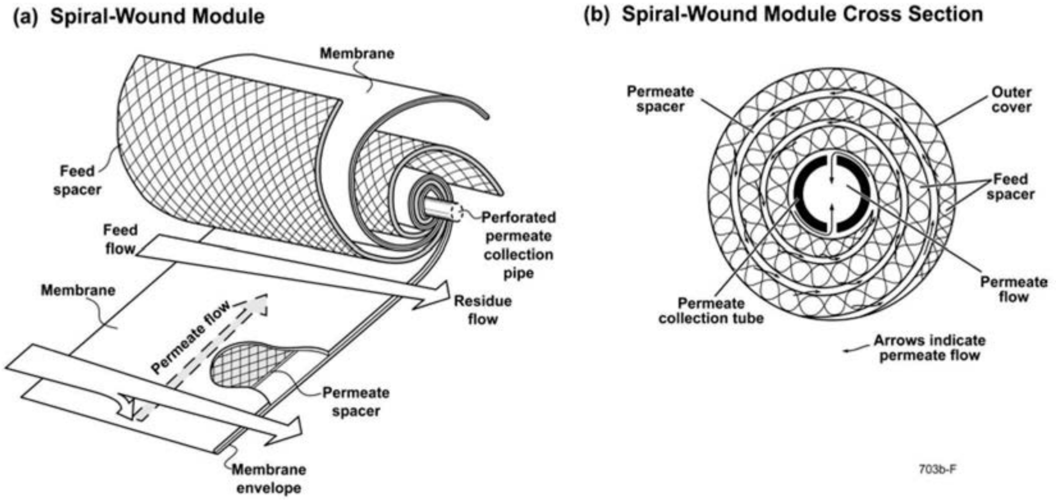


Figure 5: Schematic diagram of a spiral-wound membrane module.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Proprietary polymers	
Materials of Fabrication for Support Layer	—	Proprietary polymers	
Nominal Thickness of Selective Layer	µm	< 1 micron	< 1 micron
Membrane Geometry	—	Flat sheet	Flat sheet
Maximum Trans-Membrane Pressure	bar	75	75
Hours Tested without Significant Degradation	—	1 month	3 months
Manufacturing Cost for Membrane Material	$/m^2	500	250
Membrane Performance			
Temperature	°C	200	200
H_2 Pressure Normalized Flux	GPU	225	200
H_2/H_2O Selectivity	—	0.4	0.4
H_2/CO_2 Selectivity	—	50	30
H_2/H_2S Selectivity	—	>50	50
Sulfur Tolerance	ppm	Inert to Sulfur	Inert to Sulfur
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	Spiral-wound modules	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	Syngas	
Syngas Gas Flowrate	kg/hr	717,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 99.5 152.7	
H_2 Recovery, Purity, and Pressure	%/%/bar	99.4 44 % in N_2 as fuel 30	
Pressure Drops Shell/Tube Side	bar	feed: 1 /sweep: 1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	15	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Estimated Cost – – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

***Membrane Permeation Mechanism* –** Permeation through the Proteus™ membrane occurs by the passive solution-diffusion mechanism.

***Contaminant Resistance* –** The MTR membranes and membrane module components are compatible with the species found in coal-derived syngas. This is one of the major findings from syngas field tests conducted at NCCC between 2009 and 2017 for both the Polaris™ (5,200 cumulative hours online) and Proteus™ (9,125 cumulative hours online) membranes.

***Syngas Pretreatment Requirements* –** The MTR pre-combustion CO_2 capture membrane process design does not require syngas pretreatment.

***Membrane Replacement Requirements* –** The target membrane module lifetime is three years, which is at the conservative end of the typical industrial gas separation module lifetime of three to five years.

***Waste Streams Generated* –** No additional waste streams are generated when adding the MTR pre-combustion CO_2 capture system to an IGCC process. Similar to the stand-alone IGCC process, water removed from the MTR process can be recycled to process demand and the removed sulfur species can be sent to a Claus plant for processing. The high-purity CO_2 product can be used for enhanced oil recovery or other industrial applications.

technology advantages

- The Proteus™ membrane allows separation of H_2 from syngas at elevated temperatures. This ability to operate warm/hot reduces the need for heat exchange (e.g., membrane modules operate at a higher temperature than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and water condensation).
- A membrane system does not contain moving parts or involve chemical reactions, making it simple to operate and maintain.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- The membrane capture system permeates water in syngas (increase mass to turbine and reduces CO_2 dehydration costs).
- Membrane modules downstream from pressurized WGS maintain CO_2 effluent at pressure; therefore, less compression of CO_2 product is required compared to conventional acid gas removal processes.
- The proposed N_2 sweep on the H_2 permeate side increases the partial-pressure driving force for separation and decreases the required membrane area.

R&D challenges

- Countercurrent sweep module design could result in several potential inefficiencies, including sweep-side pressure drop, concentration polarization, poor utilization of the membrane area due to module geometry, and non-countercurrent flow patterns.
- Feed and permeate side pressure drops could lead to excessive energy losses if modules are not designed properly.
- Membrane module cost reductions will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-MWe plant.

status

A second-generation Proteus™ membrane has been made with performance that exceeds H_2/CO_2 selectivity targets, and robust membrane module components have been identified for use in syngas environments at high temperatures. Development work underway includes mixed-gas module testing at MTR and fabrication of a field test skid for prototype commercial-scale module testing on oxygen-blown, gasifier-produced syngas at EERC.

available reports/technical papers/presentations

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," presented by Jay Kniep, Membrane Technology and Research, Inc., 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019.

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," presented by Jay Kniep, Membrane Technology and Research, Inc., 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

"*Bench-Scale Development of a Transformative Membrane Process for Pre-Combustion CO_2 Capture*," Project kick-off meeting presentation, December 2018.

"*Novel Polymer Membrane Process for Pre-combustion CO_2 Capture from Coal-fired Syngas*," Final Report for DE-FE0001124, Membrane Technology and Research, Inc., December 2011.

Development and Testing of a High-Temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 50 kWth)

project focus:

PBI Polymer Membrane

participant:

SRI International

project number:

FE0031633

predecessor projects:

FC26-07NT43090; FE0012965

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Indira Jayaweera
SRI International
indira.jayaweera@sri.com

partners:

Enerfex, Inc., PBI Performance Products, University of Kentucky Research Foundation

start date:

10.01.2018

percent complete:

40%

primary project goals

SRI's overall goal is to develop a technically and economically viable carbon dioxide (CO_2) capture system based on a high-temperature polybenzimidazole (PBI) polymer hollow-fiber membrane separation technology. This is intended for deployment at elevated temperatures to separate hydrogen (H_2) and CO_2 in shifted syngas, enabling pre-combustion carbon capture in integrated gasification combined cycle (IGCC) power plants. Current project goals are to extend previous work on PBI hollow-fiber membranes and bench-scale test skids with second-generation (Gen-2) fibers having improved selectivity. These are to be deployed in bench-scale testing on actual coal-derived syngas from an oxygen-blown gasifier. Results are to demonstrate if Gen-2 PBI-based hollow-fiber membranes provide a pathway to achieving the U.S. Department of Energy's (DOE) pre-combustion capture targets.

technical goals

- Produce at least 100 kilometers of Gen-2 fibers that provide an H_2/CO_2 selectivity of about 40 and H_2 permeance of 80 to 120 gas permeation units (GPU) at greater than 150°C at a 150 pounds per square inch (psi) pressure differential.
- Modify the existing 50-killowatt-thermal (kWth) bench-scale test skid (fabricated and used in FE0012965) with Gen-2 hollow-fiber modules of 4- to 6-inch diameter, and complete bench-skid acceptance testing for 50 hours achieving H_2/CO_2 selectivity greater than 35.
- Perform bench-scale testing at temperatures ≈225°C and up to a pressure of 30 bar under various operating conditions, including long-term steady-state conditions using actual coal-derived syngas (throughput equivalent to 50 kWth) from the entrained flow oxygen-fed gasifier at the University of Kentucky's Center for Applied Energy Research (CAER).
- Prepare techno-economic analysis (TEA) based on latest Gen-2 bench-scale testing results to re-evaluate technology performance to achieve DOE's pre-combustion capture targets.

technical content

SRI's PBI membrane-based technology is being developed for high-temperature pre-combustion separation of H_2 from shifted syngas, leaving a high-concentration, high-pressure CO_2-rich stream in the retentate and yielding a high

H_2-content permeate stream. SRI's membranes are asymmetric hollow-fiber PBI (molecular structure of the polymer shown in Figure 1), which is chemically and thermally stable at temperatures up to 300°C and pressures up to 55 atmospheres (atm; 800 pounds per square inch gauge [psig]). PBI membranes are also sulfur tolerant. These characteristics permit the use of the PBI membrane for CO_2 capture downstream of a sour water-gas shift (WGS) reactor without requiring further gas cooling before the PBI membrane, significantly increasing plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.

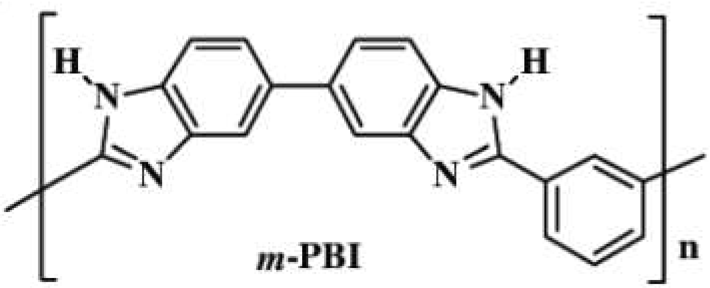


Figure 1: m-polybenzimidazole molecular structure.

Single-bore PBI-based hollow fibers have been shown to be highly durable, with near-constant levels of permeability and selectivity over the course of 330 days while in the presence of H_2, carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250°C. Therefore, PBI fiber modules can be successfully used in pre-combustion CO_2 capture applications.

PBI-based hollow fibers, as seen in various magnified views in Figure 2, offer a considerable advantage over coated stainless-steel tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1 to 0.5 micrometer separation layer (the dense layer). Ease of large-scale manufacturability, high packing density, and the cost are notable advantages of hollow-fiber membrane systems.

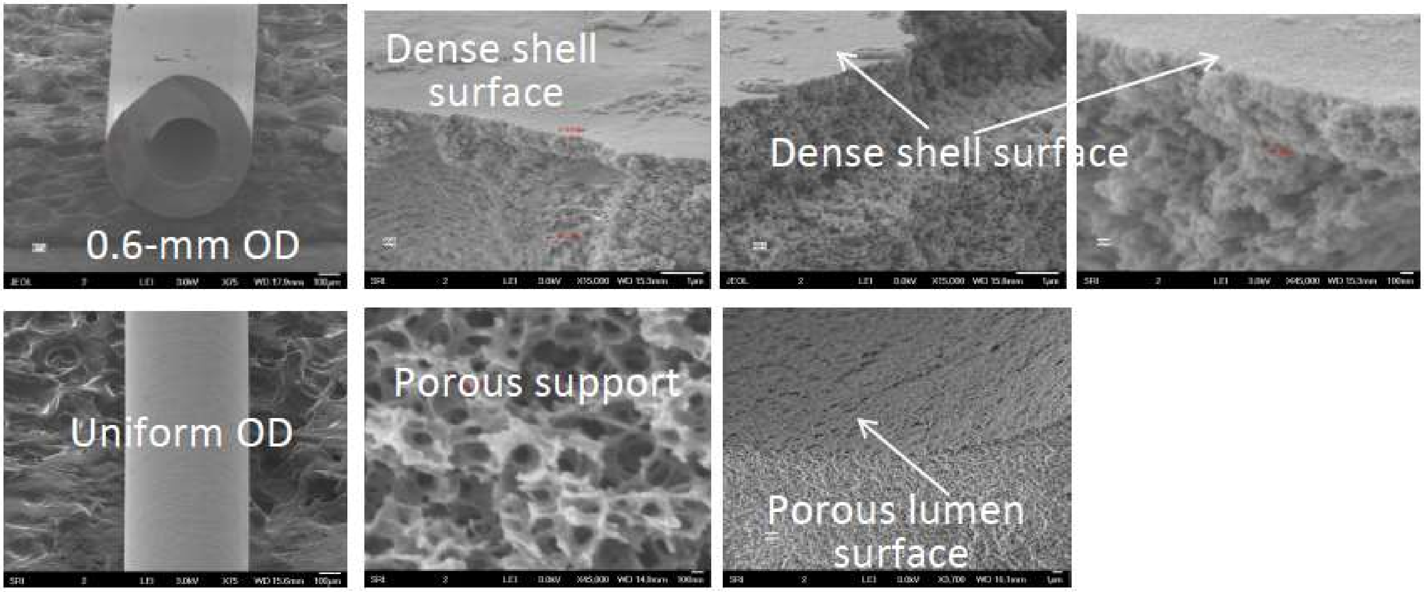


Figure 2: PBI hollow-fiber membranes and details of physical structure.

Fiber Fabrication and Modules

Hollow-fiber membrane fabrication is accomplished in a spinning line as depicted in Figure 3. An important part of technology maturation involves improvements in fiber spinning technology enabling an improved and robust spinning process that can be transferred to industry. Improvements in the spinning line have enabled use of multiple coagulation solvents, increased productivity (one-gallon reservoir size), process monitoring and data collection, precise flow controls and draw ratios, optimization of fiber diameter, and optimization of the fiber dense-layer thickness.

SRI has been improving its developed protocols to enable spinning <0.3-µm dense layer hollow-fiber membranes with membrane OD 450 to 650 µm. Figure 2 includes photographs of a hollow-fiber membrane well within this range, with ~0.1-µm dense layer fibers having ~600-µm OD. Optimization of OD and dense layer has been supported through testing of more than 100 fiber bundles (1-inch). Fabrication of the Gen-1 hollow-fiber membrane with a very thin, dense layer (<0.3 µm) in kilometer lengths has been accomplished with very good reproducibility. In previous work, more than 100 kilometers of Gen-1 fibers have been spun for both Generon and SRI modules (4-inch diameter size fiber modules). In latest work, more than 10 kilometers of the improved performance Gen-2 fibers have been produced so far for deployment in the new modules to be used in upcoming testing at the University of Kentucky's CAER.

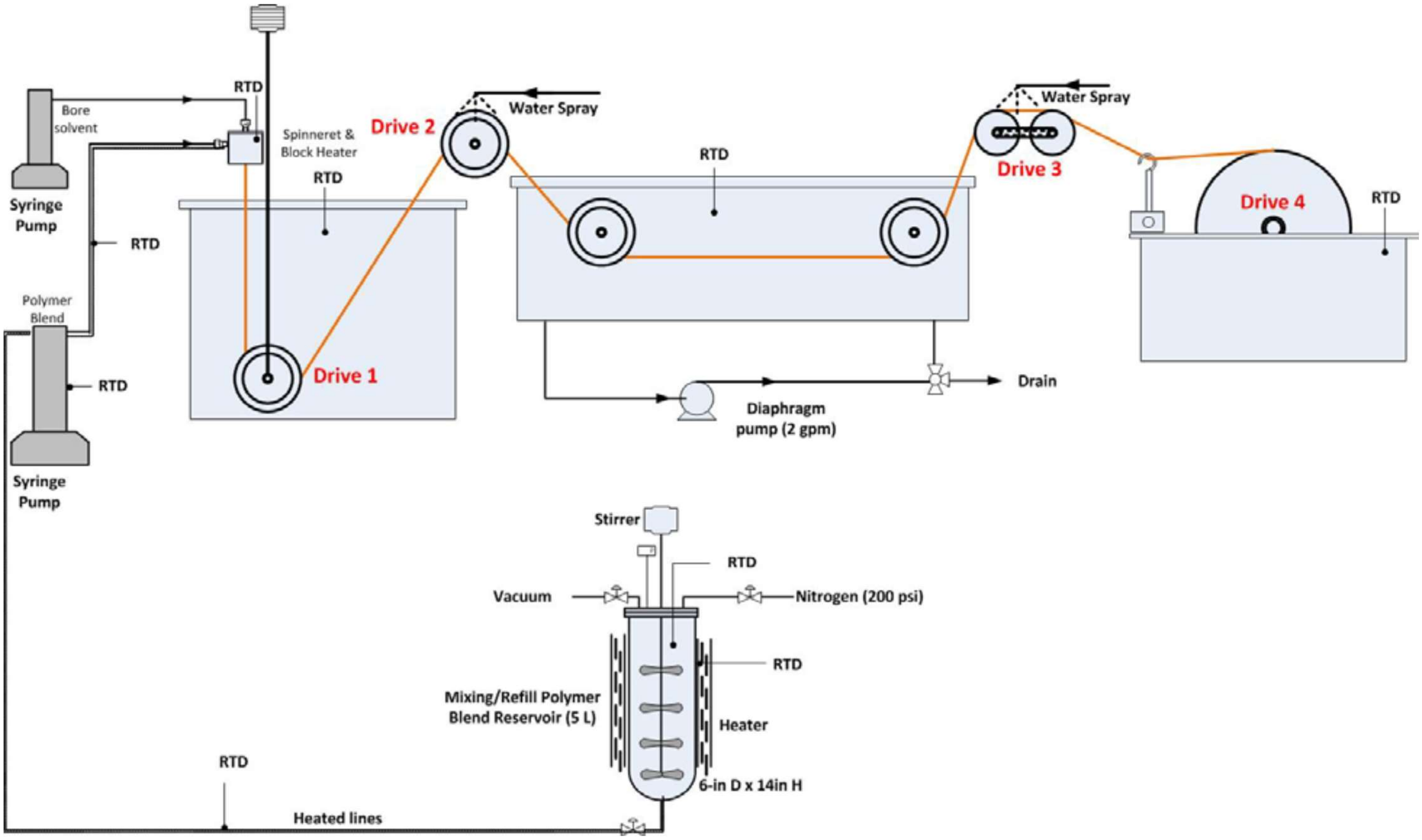


Figure 3: SRI hollow-fiber membrane spinning line.

Large bundles of hollow fibers are potted in tube sheet modules (currently in 4- or 6-inch diameters), which can then be assembled into larger-scale gas separation units/skid for process implementation. Figure 4 shows the cross-section of an actual 4-inch fiber module as fabricated at SRI (on the left); these are the type that had been incorporated in the bench-scale skid, which was deployed in past testing at the National Carbon Capture Center (NCCC) on a syngas slip stream. SRI fiber modules are designed for easy fabrication, easy handling, and easy drop-in replacement. A new tube sheet module design is being deployed (images on right side of Figure 4). These will enable faster module swapping and reduced gas bypass characteristics.

Figure 4: Potted module cross-section (left-most); new tube sheet module design (right).

Testing Results

Results of testing PBI modules at NCCC on air-blown gasifier syngas have established performance characteristics of both the Gen-1 and Gen-2 PBI modules. Specifically, membrane element TS-1 (consisting of SRI Gen-1 fibers having GPU ~150, H_2/CO_2 selectivity ~25 at 150°C) was tested for about 500 hours. Membrane element TS-2 (consisting of SRI Gen-2 fibers having GPU ~100, H_2/CO_2 selectivity ~40 at 200°C, and at 200 psi) was tested for 48 hours. Figure 5 plots selectivity results of various testing runs for both Gen-1 and Gen-2 testing campaigns. Selectivity of Gen-2 shows definite improvement with potential for superior performance at target operating temperatures of ~200°C. Taken with gas permeance measurements (Figure 6), the Gen-2 modules evidence significant performance advantages over Gen-1.

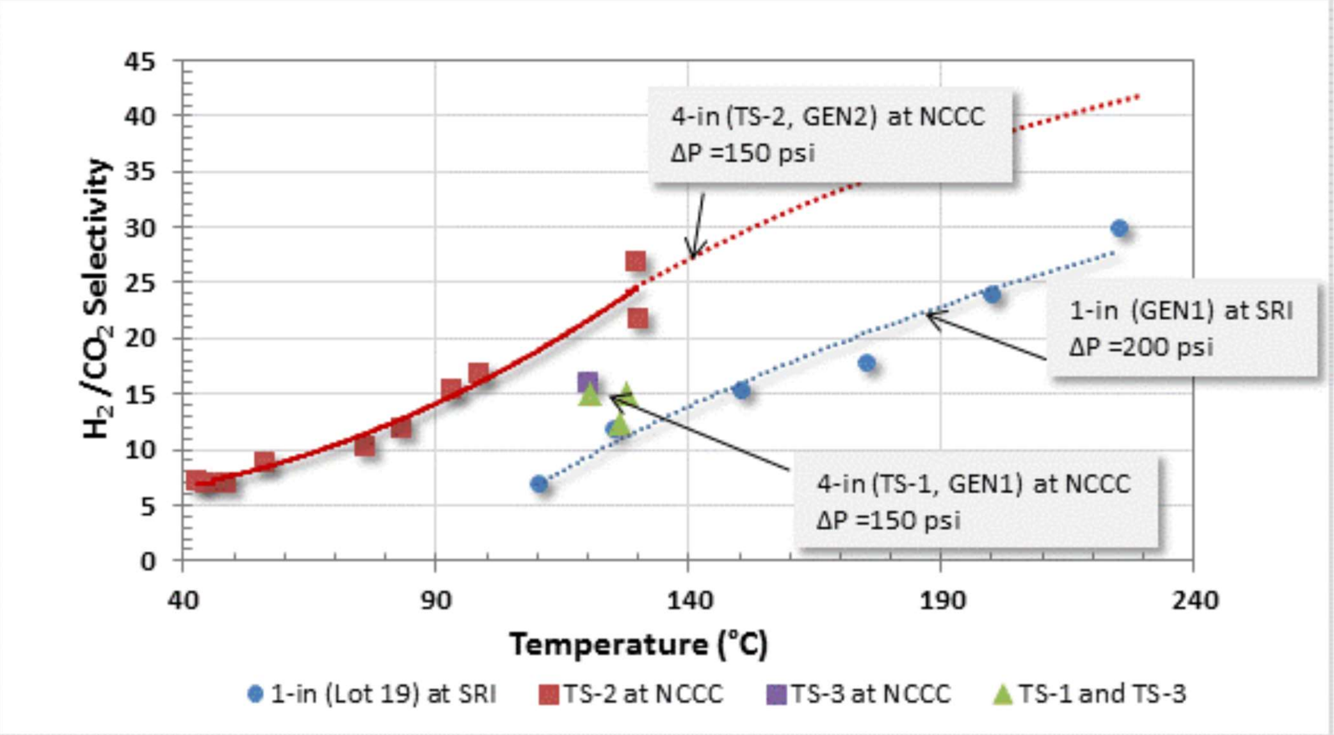


Figure 5: Comparison of measured H_2/CO_2 selectivity for Gen-1 and Gen-2 PBI modules.

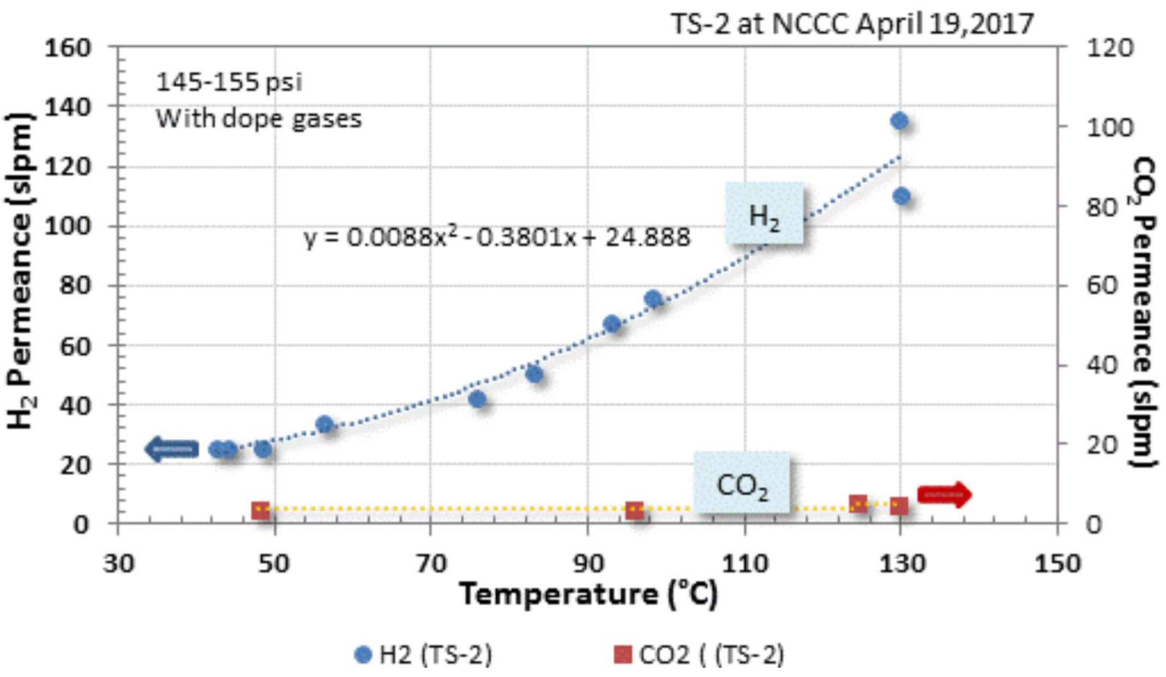


Figure 6: Measured H_2 and CO_2 permeances for the Gen-2 module at varying temperatures under a pressure differential of 145 to 155 psi.

Preliminary Techno-Economic Analysis Findings

SRI has previously made estimations of cost of electricity (COE) reductions that should be possible by application of the PBI membrane technology in process implementation in the context of an IGCC power plant cycle. From testing of Gen-1 and Gen-2 membranes, performance parameters have been quantified. Given expected Gen-1 and Gen-2 gas selectivities and different gas permeance assumptions, it is possible that the PBI membrane technology can meet National Energy Technology Laboratory (NETL) targets, assuming the membrane system has capital cost reductions that are expected to emerge in industrial-scale economies and savings associated with high levels of system optimization, which are anticipated as higher Technology Readiness Levels (TRLs) are attained.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer		PBI	PBI
Materials of Fabrication for Support Layer		PBI	PBI
Nominal Thickness of Selective Layer	µm	0.3–2	<0.5
Membrane Geometry		hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	≈14	>20
Hours Tested without Significant Degradation	hr.	1,000	1,000
Manufacturing Cost for Membrane Material	$/m^2	30–80	TBD
Membrane Performance			
Temperature	°C	200–250	225
H_2 Pressure Normalized Flux	GPU or equivalent	80–120	80–120
H_2/H_2O Selectivity	—	<1	<1
H_2/CO_2 Selectivity (Dense layer thickness)	—	40 (>1 µm) and 22 (<0.3 µm)	40 (<0.3 µm)
H_2/H_2S Selectivity (Dense layer thickness)	—	>200 (>1 µm)	>200 (<0.3 µm)
Sulfur Tolerance	ppm	300	300
Type of Measurement		pure and mixed	mixed gases
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement		countercurrent	
Packing Density	m^2/m^3	>3,000	
Shell-Side Fluid		retentate or permeate	
Syngas Flowrate	kg/hr	22	
CO_2 Recovery, Purity, and Pressure	%/%/bar	TBD	
H_2 Recovery, Purity, and Pressure	%/%/bar	>98%, >49%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	<0.007/0.03	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*A commercial 4-inch module design with 200 µm bore diameter and 28–48 bar feed pressure was assumed.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – PBI is resistant to acidic contaminants.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – Required frequency of membrane replacement to be determined.

Waste Streams Generated – Gaseous waste stream generated includes CO_2 and H_2S separated from the syngas. This stream will be further treated to remove H_2S.

Process Design Concept – Flowsheet/block flow diagram is shown in Figure 7. Note that the PBI hollow-fiber membrane is both a water and H_2 transporting membrane, so most water vapor/steam in the shifted syngas will segregate into the permeate stream along with the H_2.

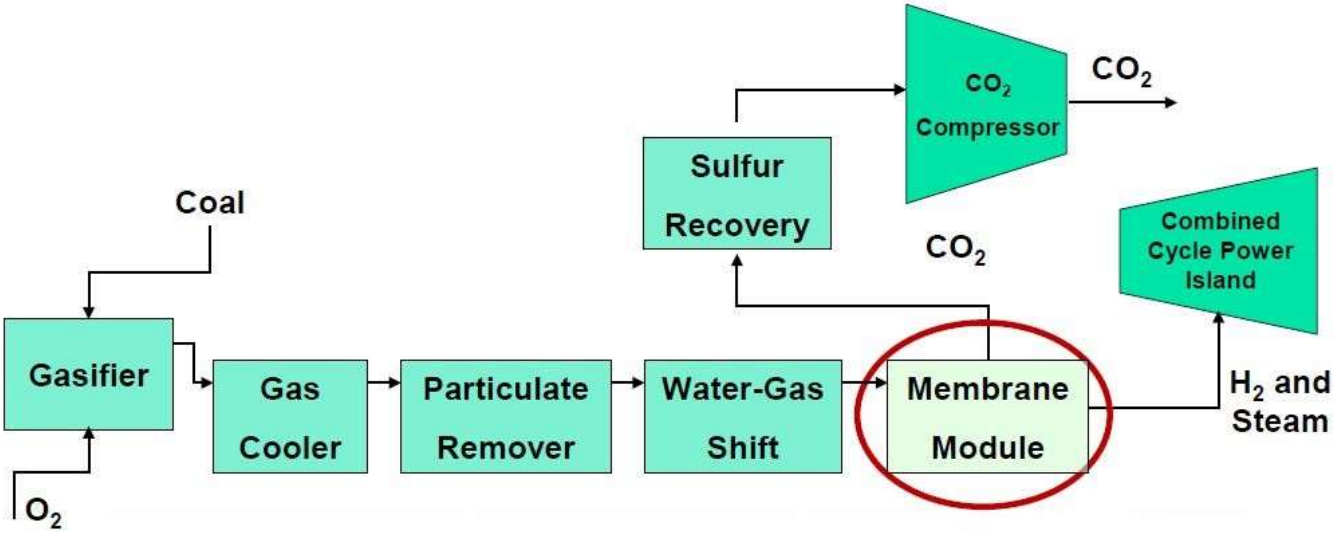
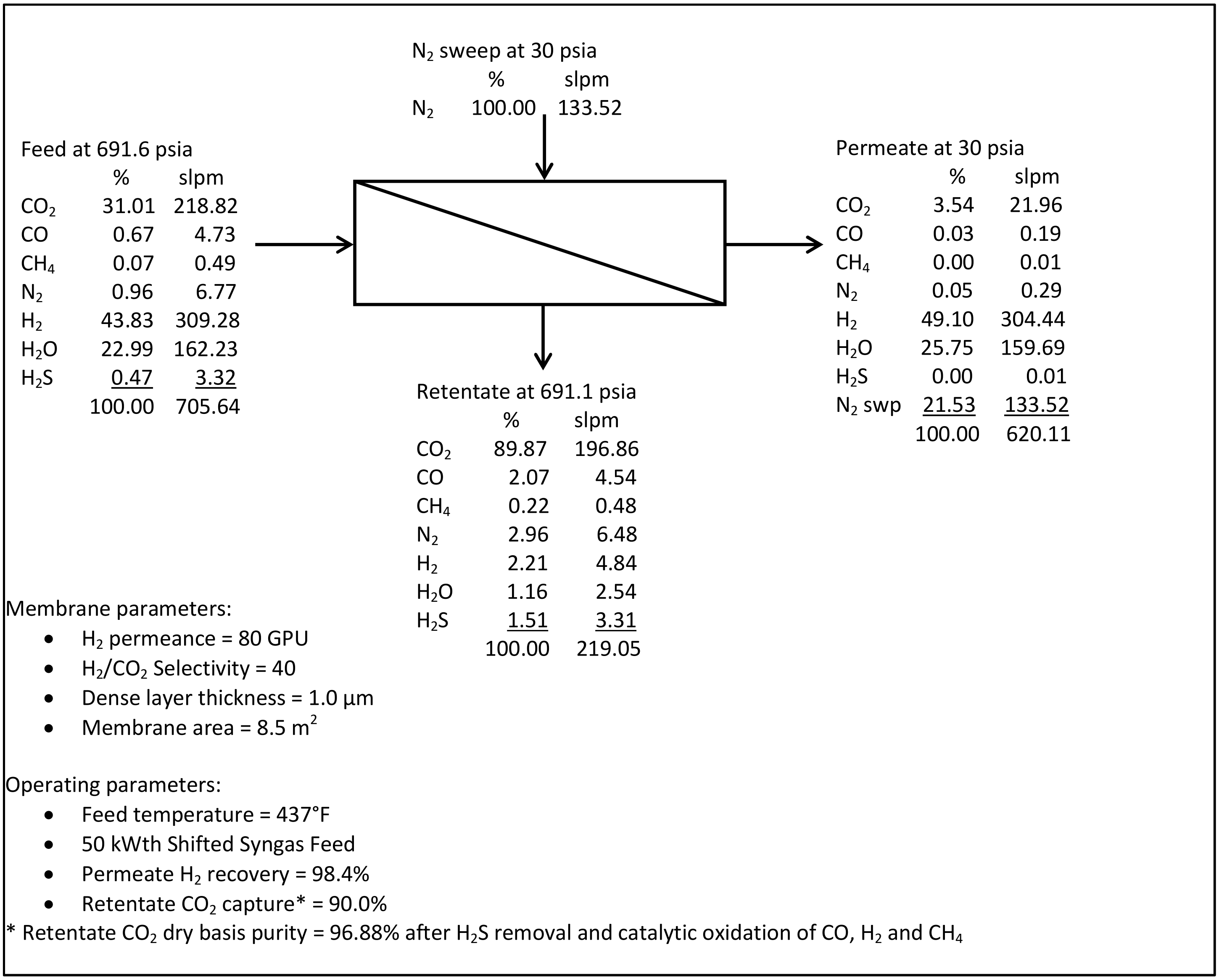


Figure 7: Flowsheet/block flow diagram showing PBI membrane module integration in the IGCC plant process.

Proposed Module Integration – Module design is tubular with 4-inch diameter and 36-inch length. Figure 8 shows the simulated module performance: the pressure, temperature, and composition of the gas entering the module, assuming H_2/CO_2 selectivity of 40. Note that the module feed gas is from an oxygen-blown gasifier with a shifted syngas feed to the membrane. In an oxygen-blown gasifier (assumed in TEA), the permeate recovers 98.4% of the feed H_2 and the retentate captures 90% of the feed CO_2. The retentate stream is further processed in a Claus plant to remove H_2S and a catalytic oxidizer to convert CO and CH_4 to CO_2 and H_2 to water (H_2O). The final retentate dry basis CO_2 purity is 96.88%.

The composition of the gas entering the module:

Pressure	Temperature	Composition						
		vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
691.1	437	31.01	0.67	0.07	0.96	43.83	22.99	0.47



N_2 sweep at 30 psia

	%	slpm
N_2	100.00	133.52

Feed at 691.6 psia

	%	slpm
CO_2	31.01	218.82
CO	0.67	4.73
CH_4	0.07	0.49
N_2	0.96	6.77
H_2	43.83	309.28
H_2O	22.99	162.23
H_2S	0.47	3.32
	100.00	705.64

Permeate at 30 psia

	%	slpm
CO_2	3.54	21.96
CO	0.03	0.19
CH_4	0.00	0.01
N_2	0.05	0.29
H_2	49.10	304.44
H_2O	25.75	159.69
H_2S	0.00	0.01
N_2 swp	21.53	133.52
	100.00	620.11

Retentate at 691.1 psia

	%	slpm
CO_2	89.87	196.86
CO	2.07	4.54
CH_4	0.22	0.48
N_2	2.96	6.48
H_2	2.21	4.84
H_2O	1.16	2.54
H_2S	1.51	3.31
	100.00	219.05

Membrane parameters:

- H_2 permeance = 80 GPU
- H_2/CO_2 Selectivity = 40
- Dense layer thickness = 1.0 µm
- Membrane area = 8.5 m^2

Operating parameters:

- Feed temperature = 437°F
- 50 kWth Shifted Syngas Feed
- Permeate H_2 recovery = 98.4%
- Retentate CO_2 capture* = 90.0%

* Retentate CO_2 dry basis purity = 96.88% after H_2S removal and catalytic oxidation of CO, H_2 and CH_4

Figure 8: Simulation of a PBI module performance with an oxygen-blown gasifier and a 50-kWth shifted syngas feed.

technology advantages

- PBI combines both useful throughput (permeability) and degree of separation (selectivity).
- PBI is thermally stable up to 300°C and is sulfur tolerant.
- PBI asymmetric hollow fibers can be fabricated at increasingly small diameters, allowing increased fiber packing densities in modules realistically consistent with 7,000 m^2 of membrane surface area per m^3 of module volume.
- Membrane gas separation systems have reduced costs for syngas cooling.
- Membrane gas separation systems should result in reduced CO_2 compression costs.
- Membrane gas separation systems are emissions-free (i.e., they use no solvents such as amines).
- Membrane gas separation systems may have decreased capital costs (assuming membrane costs are managed).
- Membrane gas separation systems have relatively low maintenance demands.
- Membrane gas separation systems are scalable and modular.

R&D challenges

- Maintaining fiber and module fabrication quality/performance (avoiding membrane pinholes, macrovoids; module seal integrity) in scale-up/transfer of technology to larger-scale manufacturing.
- Designing and synthesizing materials structure and configurations.
- Integration and optimization of membrane-based CO_2 separation systems in coal gasification-based plants.

status

SRI is currently refurbishing the bench-scale test skid for eventual deployment at CAER and a long-term test campaign of Gen-2 modules on oxygen-blown gasifier syngas. Large quantities of Gen-2 fibers are being spun for incorporation in the larger Gen-2 modules required. New module designs are being developed for improved module handling and performance.

available reports/technical papers/presentations

"*Development and Testing of a High-temperature PBI Hollow-fiber Membrane Technology for Pre-combustion CO_2 Capture*," presented by Elisabeth Perea, SRI International, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, Pittsburgh, PA, August 2019.

"*Development and Testing of a High-temperature PBI Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture*," presented by Indira Jayaweera, SRI International, Final Project Review (FE0012965) and Project Kickoff (FE0031633), January 2019.

"*Development and Testing of Polybenzimidazole (PBI) Hollow-Fiber Membrane Technology for Pre-Combustion CO_2 Capture (FE0031633)*," presented by Indira Jayaweera, SRI International, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

"*Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow Fiber Membranes*," presented by Indira S. Jayaweera, SRI International, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes (HFMs)*," presented by Indira S. Jayaweera, SRI International, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes*," presented by Indira S. Jayaweera, SRI International, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

"*Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane*," presented by Gopala Krishnan, SRI International, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane Fact Sheet*," July 2014.

"*Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes*," Project Kickoff Meeting Presentation, Pittsburgh, PA, June 9, 2014.

Krishnan, G.; Steele, D.; O'Brien, K.; Callahan, R.; Berchtold, K.; and Figueroa, J., "Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane," *Energy Procedia*, Volume 1, Issue 1, February 2009, pp. 4079-4088.

Gopala Krishnan; Indira Jayaweera; Angel Sanjurjo; Kevin O'Brien; Richard Callahan; Kathryn Berchtold; Daryl-Lynn Roberts; and Will Johnson," *Fabrication and Scale-up of Polybenzimidazole (PBI) Membrane Based System for Precombustion-Based Capture of Carbon Dioxide*," DOE Contract Number: FC26-07NT43090, 2012-March 31.

High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

primary project goals

Arizona State University (ASU), in collaboration with the University of South Carolina (USC), seeks to develop technology for a high-temperature, high-pressure, ceramic-carbonate dual-phase (CCDP) membrane reactor in this project. The reactor is intended to perform the water-gas shift (WGS) reaction on syngas (maximizing hydrogen [H_2] content of the syngas) while simultaneously separating a high-purity carbon dioxide (CO_2) stream from the reactor for capture. Project goals include designing and fabricating CCDP membranes with improved CO_2 permeance and mechanical strength for testing in a lab-scale reactor with simulated coal-derived syngas. The results will inform a mathematical model used to support process design and a techno-economic analysis (TEA) for a scenario of incorporation of a CCDP membrane reactor in a full-scale integrated gasification combined cycle (IGCC) plant.

technical goals

- Synthesize chemically and thermally stable CCDP membranes with CO_2 permeance greater than 2,000 gas permeation units (GPU) (6.5×10^{-7} mol/m^2·s·Pa), CO_2/H_2 selectivity greater than 500, and resistant to poisoning from hydrogen sulfide (H_2S) to the extent that CO_2 flux drops less than 5% after 24 hours of exposure to typical levels of H_2S.
- Fabricate tubular CCDP membrane modules suitable for lab-scale WGS reactor operation (i.e., functional and durable at temperatures in excess of 700°C) and at pressures in excess of 20 atmosphere (atm), and experimentally verify performance at simulated syngas flow rate of 0.25 kg per day equivalent to 0.007 kilowatt-thermal (kWth).
- Determine CCDP membrane WGS reactor process conditions/protocols enabling 99% carbon monoxide (CO) conversion for the WGS reaction, 90% CO_2 recovery, 99% purity of the CO_2 permeate stream, and 90% purity of the H_2 retentate stream.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification-based power plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced, in whole, by a novel WGS shift reactor that integrates CO_2-selective CCDP membranes and WGS catalyst. Within

technology maturity:

Laboratory-Scale, Simulated Syngas (0.25 kg per day equivalent to 0.007 kWth)

project focus:

Ceramic-Carbonate Dual-Phase Membrane Reactor

participant:

Arizona State University

project number:

FE0031634

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Jerry Lin
Arizona State University
jerry.lin@asu.edu

partners:

University of South Carolina

start date:

10.01.2018

percent complete:

40%

the CCDP membrane WGS reactor, CO_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor. This process concept, with the unified CCPD membrane reactor (depicted in callout) replacing the multistage conventional WGS process and amine absorption unit (both within red dotted line), is depicted in Figure 1.

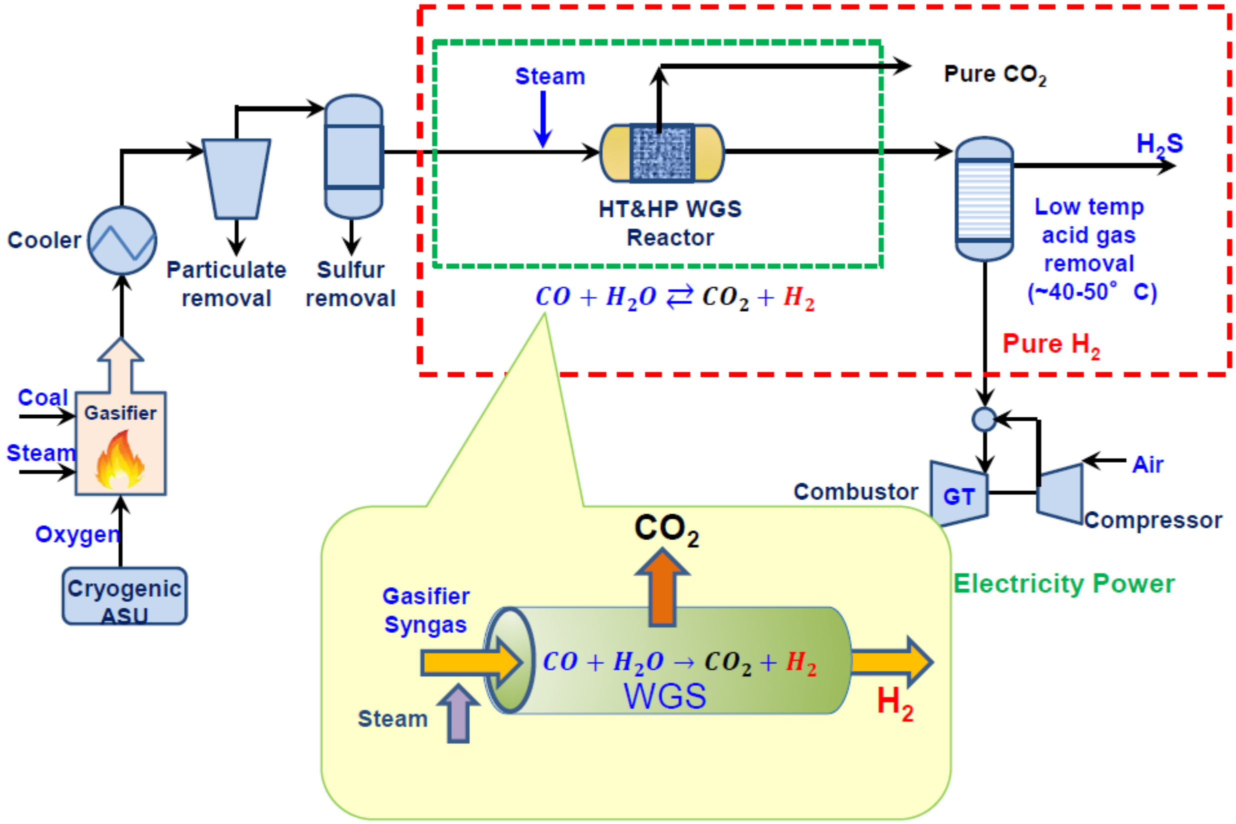


Figure 1: CCDP membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle.

CCDP membranes are composed of a porous ceramic phase as the structural support matrix, infiltrated with a molten carbonate phase, as illustrated in Figure 2. At working temperatures of 600 to 900°C, the CCDP membrane possesses extremely high CO_2 selectivity and high CO_2 permeance.

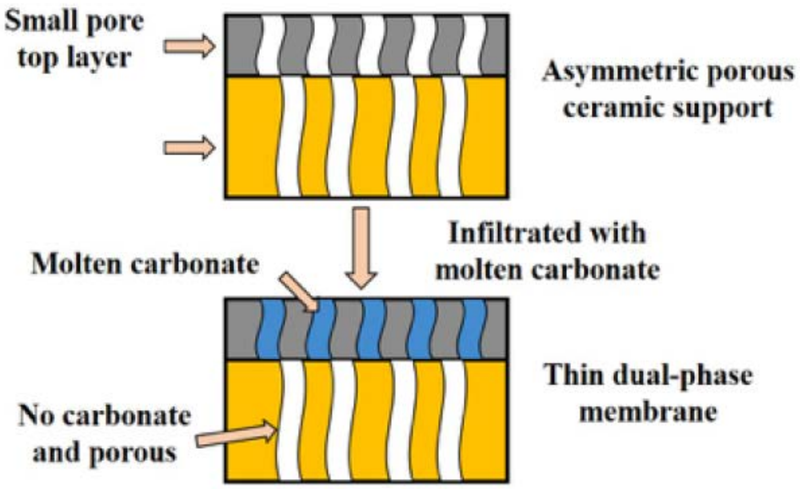


Figure 2: Physical structure of CCDP membrane.

Scanning electron microscopy (SEM) images of actual CCDP membranes are shown in Figure 3. Note that the bright areas in the SEM images are the ceramic phase, while dark zones consist of carbonate mixture. These illustrate the formation of a dense, highly gas-tight dual-phase membrane, which has been verified by pre- and post-infiltration gas permeation measurements.

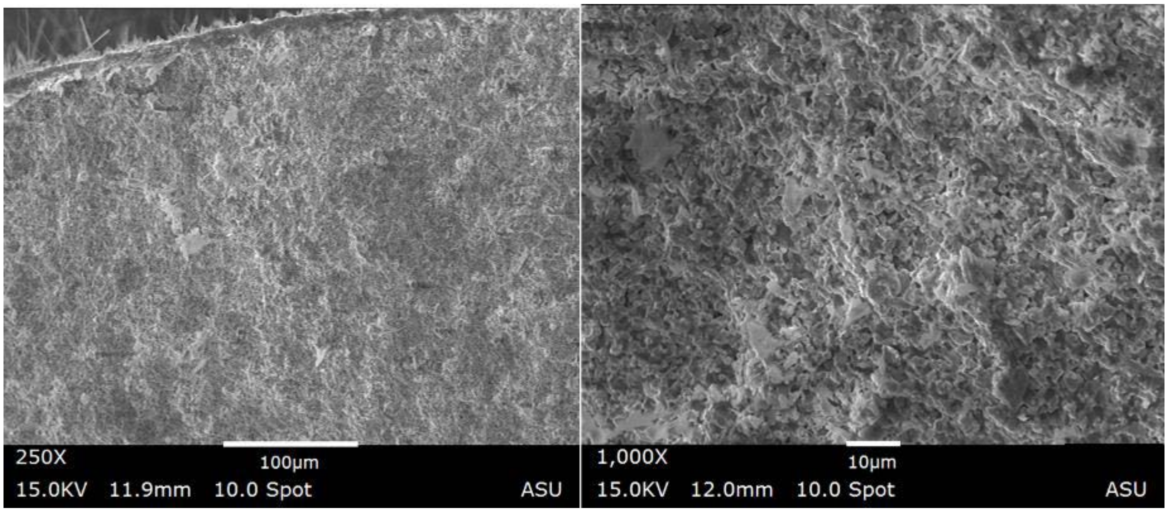


Figure 3: SEM images of CCDP membrane cross-section at 250x (left) and 1,000x (right).

The high selectivity and permeance for CO_2 in the CCDP membrane are a result of the electrochemical transport mechanism illustrated in Figure 4. At elevated process operating temperatures, CO_2 tends to form carbonate ions (CO_3^{2-}) by combining with oxygen ions (O^{2-}), the latter readily transporting through the ionically conducting ceramic phase in the membrane. At the same time, carbonate ions readily transport through the molten carbonate phase in the opposite direction. Syngas on the feed side is at high pressure, resulting in high partial CO_2 pressure on that side. The permeate side is at ambient pressure (and possibly swept), resulting in low partial CO_2 pressure. The CO_2 partial pressure differential provides the driving force for the ionic transport behavior in the membrane. High CO_2 permeance values are expected for the CCDP membrane if the functional layer is made of suitably thin (10 to 100 µm) ceramic with high oxygen ionic conductivity.

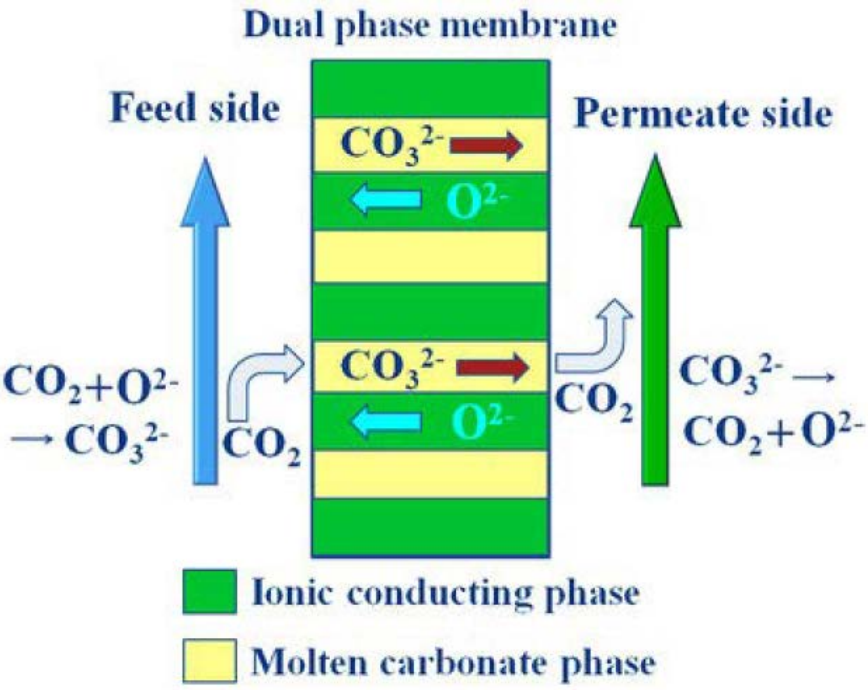


Figure 4: CO_2 separation mechanism in CCDP membrane.

The novel choice of ceramic-carbonate membrane in a WGS reactor overcomes various problems observed with possible alternatives. Theoretically, H_2 could be removed from the WGS reactor through H_2-selective membranes, which would also constitute removal of product of the WGS reaction to drive conversion forward to completion. Inorganic membranes with good H_2 perm-selectivity at high temperatures do exist, and include amorphous microporous carbon, amorphous silica, microporous crystalline zeolite, and dense perovskite-type proton-conducting ceramics. However, all of those choices are hampered by one or more serious issues, including insufficient H_2 permeance (particularly at the elevated temperatures involved in the WGS reactor), poor H_2 stability, poor hydrothermal stability, and membrane fabrication difficulty and high cost, which translate into high costs for a membrane WGS reactor solution. Finally, organic membranes of any type are simply incapable of application at the high operating temperatures involved. Considering these shortcomings, a CO_2-selective ceramic-carbonate membrane offers a favorable choice for this application.

An important aspect of technology development for the CCDP membrane concerns optimizing the choices of ceramic and carbonate materials deployed in the membrane, characterization of membrane morphologies and properties, and membrane fabrication. For the ceramic phase of the membrane, desired characteristics include high ionic conductivity, long-term chemical stability in presence of characteristic syngas species and contaminants (particularly H_2S), compatibility with molten carbonate, and controllability of pore size and porosity.

ASU has previously investigated several ceramics for application in the CCDP membrane. The ceramics are in the family of perovskite- or fluorite-structured metal oxides with oxygen vacancy defects:

- $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF)
- Yttria-stabilized zirconia (YSZ)
- $La_{0.85}Ce_{0.1}Ga_{0.3}Fe_{0.65}Al_{0.05}O_{3-\delta}$ (LCGFA)
- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (Samarium Doped Ceria-SDC). Note: Figure 3 SEM images are of an SDC-based membrane.
- $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ (BYS)

In ongoing developmental work, improved materials are being sought, mainly to deliver improved CO_2 permeances and improved stability to H_2S. ASU is currently evaluating Sc_2O_3-doped ZrO_2 (ScSZ) as the preferred material for the membrane's ceramic phase; it avoids the tendency to form compounds with sulfur that is characteristic of cerium (Ce)-containing ceramics. Fabrication methods are being optimized to deliver the desired microstructure. The ethylenediaminetetraacetic acid (EDTA)-citric acid method is effective; this involves dissolving Sc_2O_3 in nitric acid and mixing with $ZrO(NO_3)_2$, to which EDTA and citric acid are added to the stirred solution in sequence. The solution is pH adjusted and then heated until a clear, viscous gel is formed after water evaporation. The gel is dried and calcined, resulting in almost pure-phase ScSZ with good microstructure.

Tubular membranes for incorporation in modules are formed by establishing thin layers on suitable supports. The ScSZ-based CCDPs are established on BYS support tubes by dip coating them in ScSZ slurry, sintering, and infiltrating the molten carbonate (MC). Essential steps are diagrammed in Figure 5.

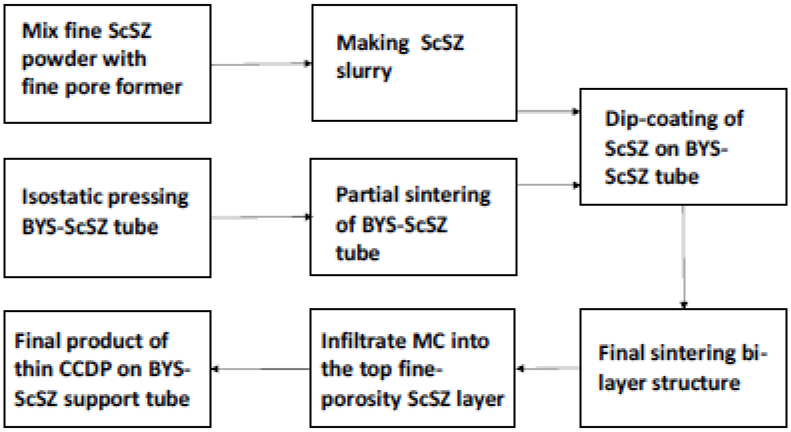


Figure 5: Tubular CCDP membrane fabrication

For the molten carbonate phase, mixtures of common alkali metal carbonates (i.e., $Li_2CO_3/Na_2CO_3/K_2CO_3$) have been found to be suitable. Varying ratios of the alkali metal carbonates have been evaluated (e.g., a Li/Na/K ratio of 43.5/31.5/25 offers both relatively low melting point [less than 400°C] and good carbonate ion conductivity [1.24 S/cm]). In current work, a binary eutectic mixture of 52% Li_2CO_3 and 48% Na_2CO_3 is being used with the ScSZ ceramic.

An apparatus for characterizing CCDP membrane performance has been developed and is operated in laboratory-scale work, as depicted in Figure 6. Synthetic syngas can be mixed up and flowed to the tubular reactor module enclosed in a high-temperature furnace, while resulting gas compositions of permeate and retentate can be measured in a gas chromatograph. The fabrication of the tubular membrane reactor module itself is a challenge (see enlarged view of the reactor in Figure 6), with a notable point of development concerning seals able to withstand the high-targeted operating pressures and temperatures.

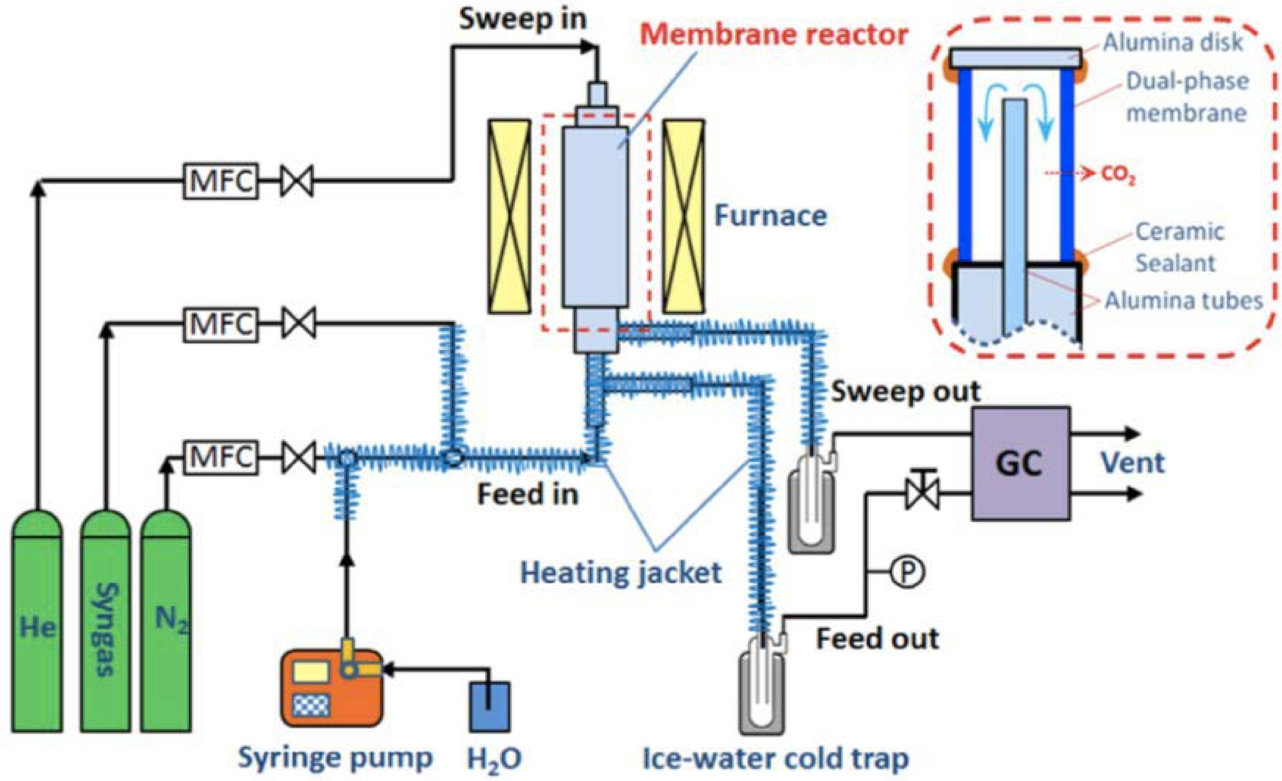


Figure 6: Laboratory-scale apparatus for CCDP membrane CO_2 permeation studies.

With this test bed, various experiments and evaluations are possible, which provide invaluable data for optimizing membrane and module materials and fabrication methods. For example, the reactor module with SDC ceramic infiltrated with $Li_2CO_3/Na_2CO_3/K_2CO_3$ carbonate mixture was evaluated under the following test conditions:

- Temperature: 800 to 900°C.
- Feed and sweep side pressure: 1 atm.
- Simulated syngas: 49.5% CO, 36% CO_2, 10% H_2, 4.5% N_2.
- Feed-side flow rate: syngas 10 to 30 mL/min and N_2 10 mL/min.
- Steam to CO molar ratio: 1.0-3.0.
- Sweep-side flow rate: He 60 $mL \cdot min^{-1}$.

Results of CO conversion as a function of temperature, syngas flow rate, and ratio of steam to CO are shown in Figure 7, along with behavior of CO conversion, CO_2 permeation, and flux over long-term steady-state operation.

Also, the test bed allows long-term testing to evaluate changes to morphology of CCDP that may occur. For example, Figure 8 shows surfaces on both sides of a tubular membrane after long-term testing.

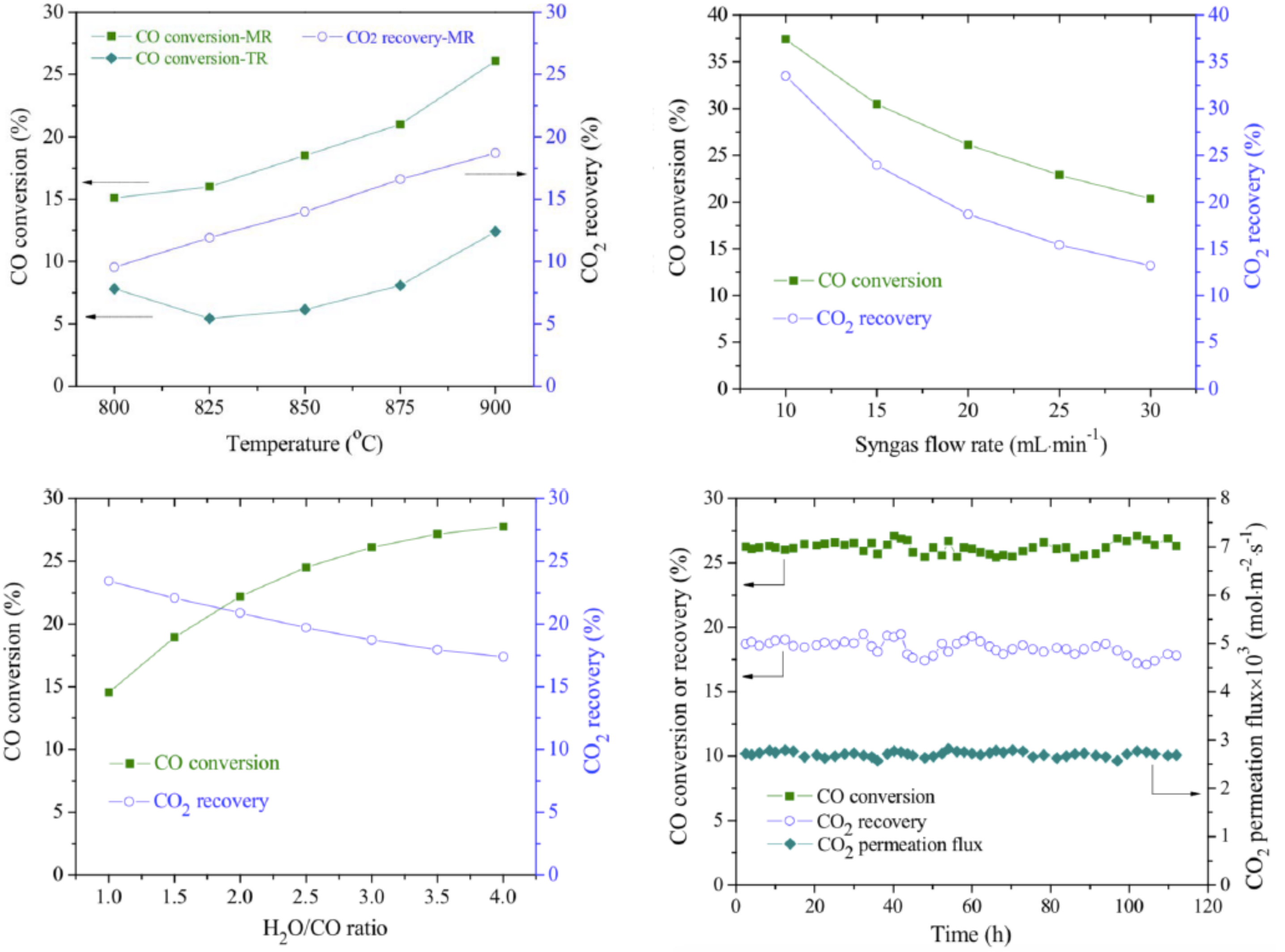


Figure 7: Measurements from tubular CCDP modules in high-temperature WGS testing.

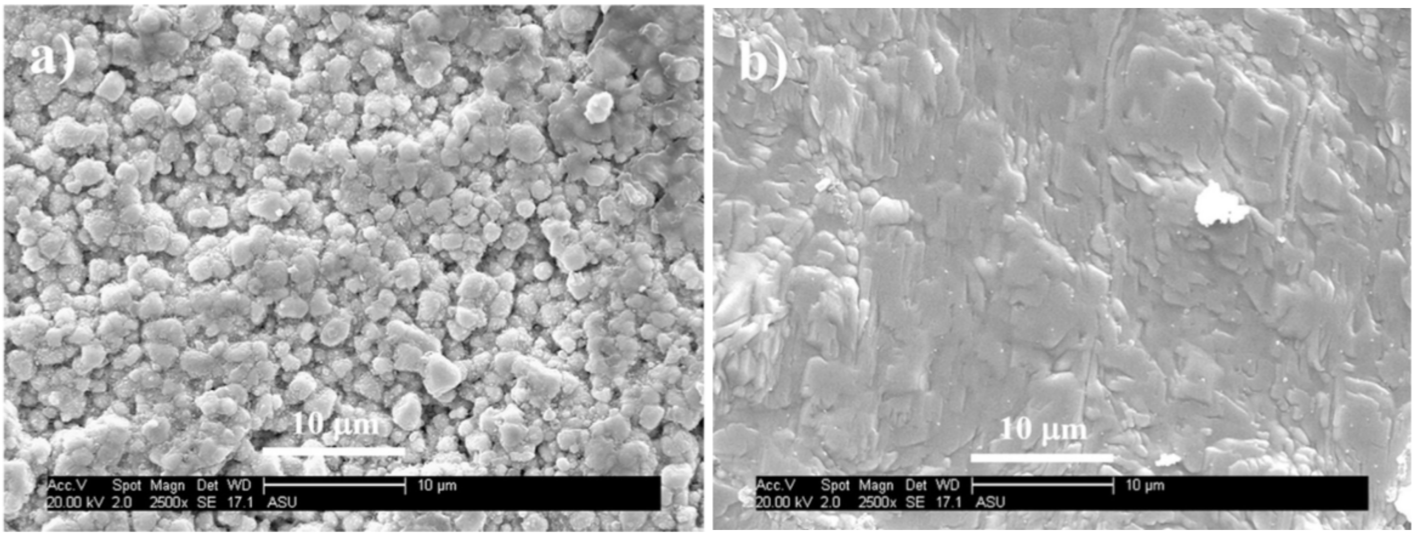


Figure 8: SEM images of CCDP surfaces after long-term WGS testing—sweep side (left); reaction side (right).

TABLE 1: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="3">Current R&D Value</th><th colspan="2">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="3">$Ce_{0.8}Sm_{0.2}O_{2-\delta}$(SDC)-(42.5/32.5/25 Li/Na/K)$_2$CO$_3$ (MC)</td><td colspan="2">Sc-doped ZrO_2 (ScSZ) (42.5/32.5/25 Li/Na/K)$_2$CO$_3$ (MC)</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="3">BYS</td><td colspan="2">BYS</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="3">1,500</td><td colspan="2">50-200</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="3">tubes</td><td colspan="2">tubes</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="3">1</td><td colspan="2">30</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>hour</td><td colspan="3">120</td><td colspan="2">>200</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m^2</td><td colspan="3">1,000</td><td colspan="2">500</td></tr>
<tr><th>Membrane Performance</th><th></th><th colspan="3"></th><th colspan="2"></th></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">700-900</td><td colspan="2">700-900</td></tr>
<tr><td>CO_2 Pressure Normalized Flux</td><td>GPU</td><td colspan="3">300-600</td><td colspan="2">>2,000</td></tr>
<tr><td>CO_2/H_2O Selectivity</td><td>—</td><td colspan="3">>500</td><td colspan="2">>500</td></tr>
<tr><td>CO_2/H_2 Selectivity</td><td>—</td><td colspan="3">>500</td><td colspan="2">>500</td></tr>
<tr><td>CO_2/H_2S Selectivity</td><td>—</td><td colspan="3">>500</td><td colspan="2">>500</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="3"><5 ppm</td><td colspan="2">>400 ppm</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="3">mixed-gas</td><td colspan="2">mixed-gas</td></tr>
<tr><th>Proposed Module Design</th><th></th><th colspan="3"></th><th colspan="2"></th></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="5">Counter-current</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="5">50-200</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="5">Retentate, H_2-rich flow</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>kg/hr</td><td colspan="5">0.005-0.01</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">90</td><td colspan="2">99</td><td>~1</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">99</td><td colspan="2">90*</td><td>~ 10</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>bar</td><td colspan="5">10-30</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="5">~1,000</td></tr>
</table>

* Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 600°C, the separation of H_2 and CO_2 through CCDP membranes is governed by ionic transport of carbonate ion in MC phase in meso/macropores and oxygen ion in the ceramic phase support.

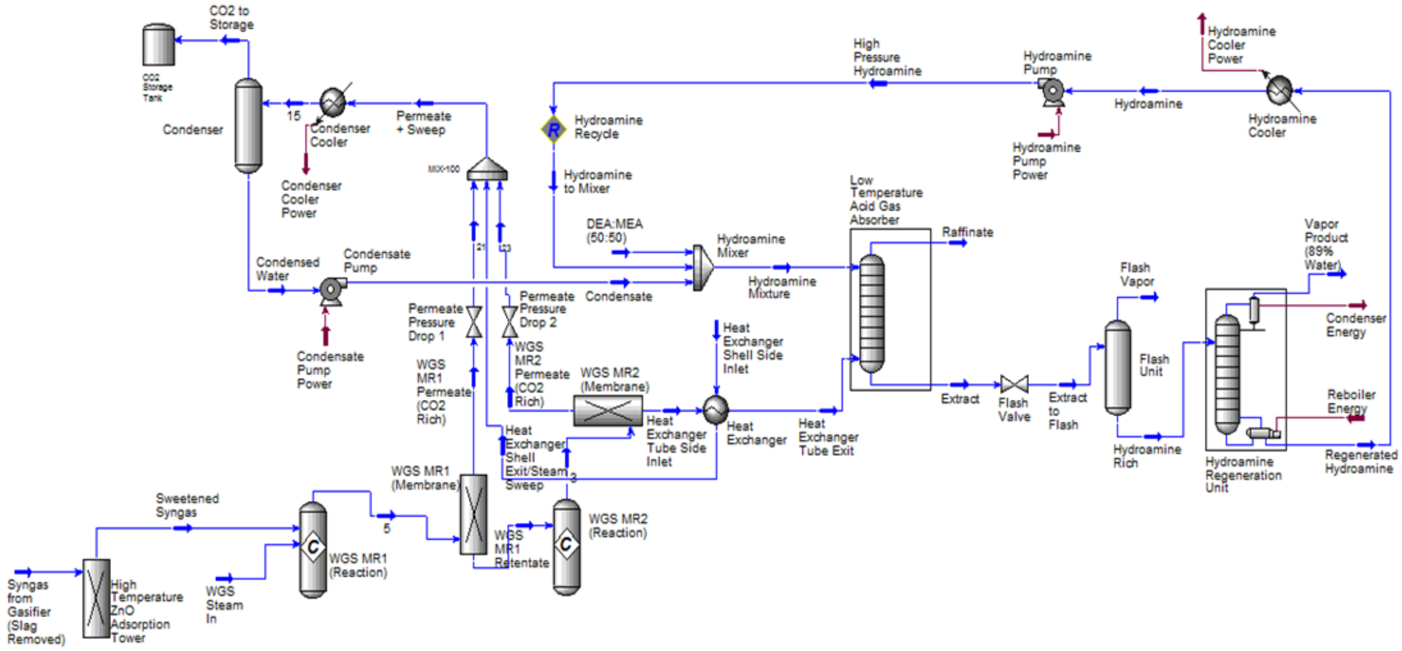
Contaminant Resistance – The developed CCDP membranes have resistance to syngas contaminants such as H_2S.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle is intended to operate in the membrane reactor continuously over 1,000 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere.

Process Design Concept –



Proposed Module Integration – The composition of the gas mixture is assumed:

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
435	1500	11.6	26.7	0.08	2.8	25.7	33.6	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- WGS reactors containing CO_2-selective membranes to recover CO_2 have potential to achieve higher H_2 delivery to the turbine in an IGCC cycle than if H_2 were being selectively recovered from the syngas stream.
- Carbon dioxide removal through a membrane process in a WGS reactor retains the H_2 at high pressure, maximizing the efficiency of the combustion turbine in an IGCC cycle.
- Tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.

R&D challenges

- Loss of carbonate from CCDP at high temperatures (especially loss of lighter Li_2CO_3).
- Gas leakage through membrane from unsealed pores (imperfect carbonate infiltration).
- High-temperature stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- CCDP thermal stability, poison resistance, and product selectivity maintained at high pressures (greater than 20 atm) and temperatures (700 to 900°C).
- Removal of particulate matter from the hot syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

A laboratory-scale module of the high-temperature and high-pressure CCDP-based WGS membrane reactor has been successfully fabricated, which involved development of new seals to avoid leakage. SDC tubular membranes have been fabricated at 11 cm length, and their CO_2 permeation fluxes were measured at high temperatures. The new ScSZ-based CCDP membrane disks were fabricated and tested, with CO_2 permeance at 650ºC measured at 1,200 GPU.

available reports/technical papers/presentations

"*High-Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Oscar Ovalle-Encinia, Arizona State University, 2019 NETL CO_2 Capture, Utilization, Storage, and Oil & Gas Technologies Integrated Review Meeting, Pittsburgh, PA, August 2019.

"*High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," Kick-off meeting presentation, November 2018.

"*High Temperature Ceramic-Carbonate Dual-Phase Membrane Reactor for Pre-combustion Carbon Dioxide Capture*," presented by Lie Meng, Arizona State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

M Anderson & YS Lin, Proc. ICIM 2006, pp. 678-681 (2006); J. Membr. Sci. 357, 122 (2010).

Transformational Membranes for Pre-Combustion Carbon Capture

primary project goals

Ohio State University (OSU) will develop cost-effective design and fabrication methods for a novel amine-containing membrane to capture carbon dioxide (CO_2) from coal gasification-derived syngas. The membrane is to be used in a single-stage membrane process utilizing modules in commercial spiral-wound configuration with a minimal pressure drop. Work towards optimization and scale-up of transformational membranes with high CO_2/hydrogen (H_2) selectivity and CO_2 permeance, along with testing of spiral-wound membrane modules using simulated syngas, will make progress towards CO_2 capture with improved performance to meet U.S. Department of Energy (DOE) targets for cost of electricity and efficiency in advanced power generation plants.

technical goals

- Synthesize and characterize membranes, scale-up the best performing membrane using a continuous roll-to-roll fabrication method, and fabricate at least nine prototype membrane modules, each with an approximate membrane area of 800 cm^2.
- Establish module stability by testing of the modules at 31.7 bar and 107°C for at least 200 hours on simulated syngas at 34 standard liter per minute (slpm) flowrate.
- Enable CO_2 capture at 95% CO_2 purity, with greater than 99% H_2 recovery from syngas.
- Optimize processes for integrating membrane modules into integrated gasification combined cycle (IGCC) with carbon capture, showing potential via techno-economic analysis (TEA) to reduce the cost of electricity by 30% relative to conventional/baseline approaches (Selexol).

technical content

Many common membranes for gas separations are based on simple rubbery polymers, which are simple to fabricate and low in cost. However, these membranes face considerable performance limitations, along with the inevitable trade-off between selectivity and permeability. Figure 1 illustrates this for polymer membrane separation of CO_2 and H_2. In order to exceed the upper bound, utilization of selective facilitated transport is essential.

OSU's technological approach for the membrane focuses on a CO_2-selective and permeable membrane layer on top of a polymer support, with amino groups added to facilitate CO_2 transport. The basic structure of the membrane is depicted in Figure 2. Because this membrane is to be deployed to remove CO_2 from coal-derived syngas, it is required to exhibit chemical stability to hydrogen sulfide (H_2S)

technology maturity:

Laboratory-Scale, Simulated Syngas (equivalent to 0.58 kWe)

project focus:

Amine-Containing Polymeric Membranes

participant:

Ohio State University

project number:

FE0031635

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

W. S. Winston Ho
Ohio State University
ho.192@osu.edu

partners:

American Electric Power
Microdyn-Nadir US Inc.

start date:

10.01.2018

percent complete:

40%

gas, which is always present in at least trace amounts in coal syngas. Also, it is preferred that it can function at elevated temperatures, such as are characteristic of warm syngas cleanup regimes. The top layer of the membrane is the selective layer containing amine in the form of amino groups, while the support layer is made of nanoporous polysulfone, which is both highly permeable to gases and is mechanically robust. Some details of composition of the selective polymer layer are proprietary.

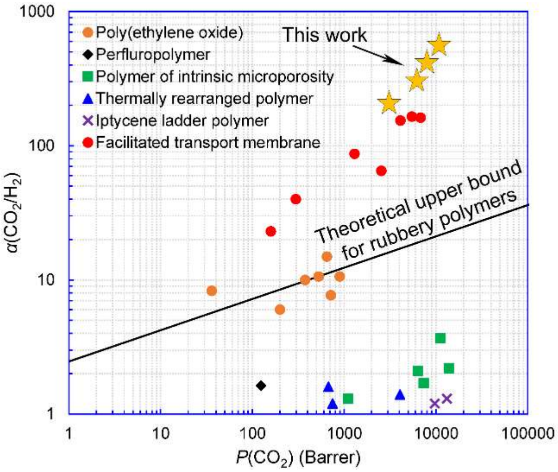


Figure 1: Typical performance of polymer membranes for CO_2/H_2 separations.

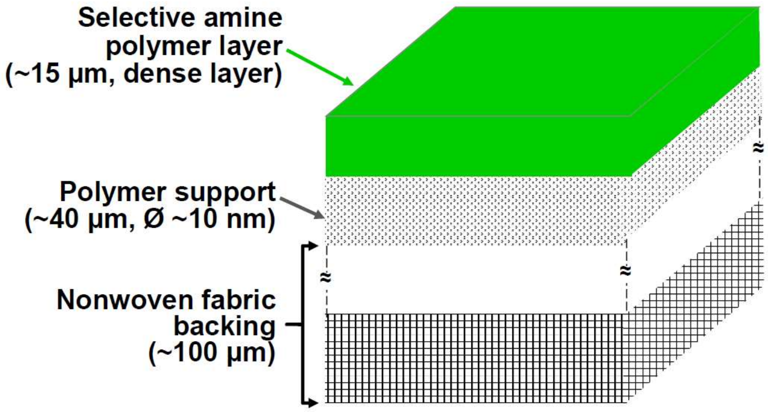


Figure 2: Membrane structure.

The facilitated transport mechanism involves enhancement of CO_2 transfer or flux through the membrane via chemical reaction with amino groups located in the selective layer. The reversible reaction of CO_2 with amino groups is as follows:

$$CO_2 + R\text{-}NH_2 + H_2O \rightarrow R\text{-}NH_3^+ + HCO_3^-$$

The facilitated transport mechanism is depicted in Figure 3. Other non-acid gases, including H_2, carbon monoxide (CO), methane (CH_4), and nitrogen (N_2), are non-reactive with the membrane, and can therefore only slowly permeate through the membrane by a physical solution-diffusion mechanism. This results in high selectivities for CO_2 relative to these non-reactive gases. In contrast, the acid gas H_2S has even higher rates of permeation through the membrane than CO_2. This means that high levels of sulfur removal from the syngas will be accomplished in a membrane separation module, with less than 10 parts per million (ppm) H_2S remaining in the syngas retentate on the feed side. The CO_2 permeate does require further treatment to remove the sulfur from the CO_2 before the latter could be stored or used.

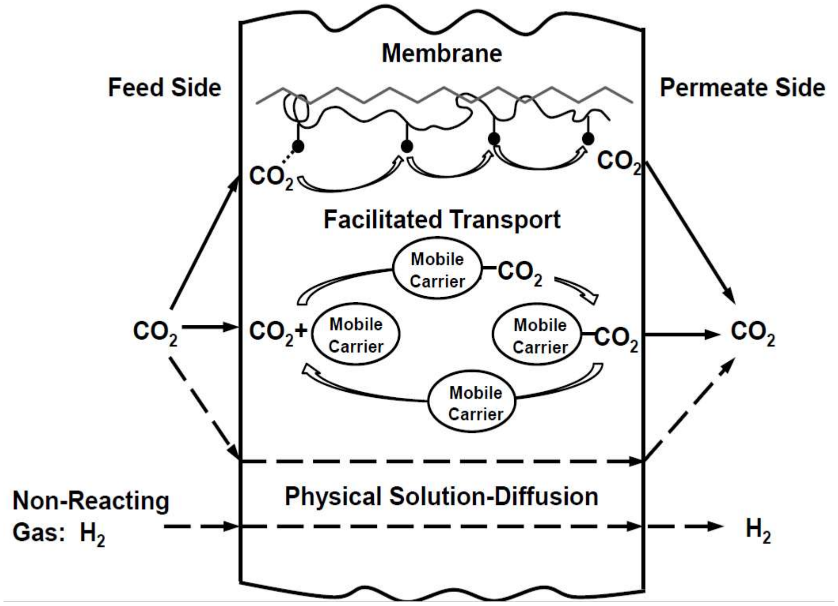


Figure 3: Mechanism of facilitated transport.

Process Scenario

One scenario for an overall plant process context is depicted in Figure 4. In order to enable greater than 90% carbon capture in coal gasification-based IGCC processes, the preferred method is oxygen-based pressurized gasification resulting in low nitrogen content raw syngas. Syngas is shifted via the water-gas shift (WGS) reaction in a WGS unit, resulting in syngas containing large fractions of H_2 and CO_2. This shifted syngas is introduced at the high-pressure feed side of the membrane unit. Carbon dioxide and H_2S permeate to the low-pressure permeate side of the membrane unit; H_2S can be subsequently separated from the permeate mixture in a single-stage Selexol unit, while the purified CO_2 is compressed and sent to storage. The high-pressure syngas retentate serves as fuel gas for a combustion turbine.

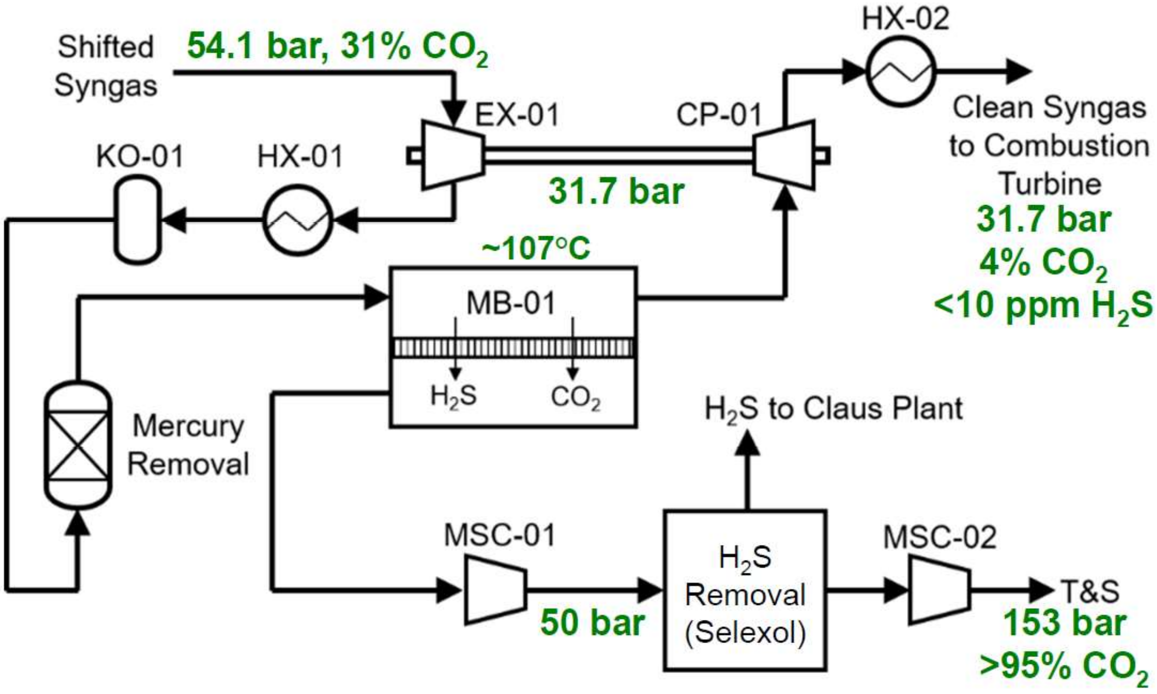


Figure 4: Process integration of membrane separation unit.

For industrial applications, it is intended that the polymeric membrane would be packed into spiral-wound membrane modules, a commonly used module design for current commercial membrane installations. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis (RO) desalination industry and more than 60% of the membrane market for CO_2 removal from natural gas. Figure 5 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers. In current testing, the laboratory-scale membranes are in the form of flat-sheet stamps with a membrane area of about 50 cm^2. In future project work, the membrane will be scaled-up to 14 inches in width by 20 feet in length in roll-to-roll manner, and then used for prototype spiral-wound membrane module fabrication. Each of the laboratory-scale modules has a membrane area of 0.08 m^2, and three modules in series in the process accommodate syngas flow of about 34 slpm. Each of commercial modules has a membrane area of 20 to 50 m^2, and three modules in series in the process accommodate syngas flow of about 8,500 to 21,250 slpm.

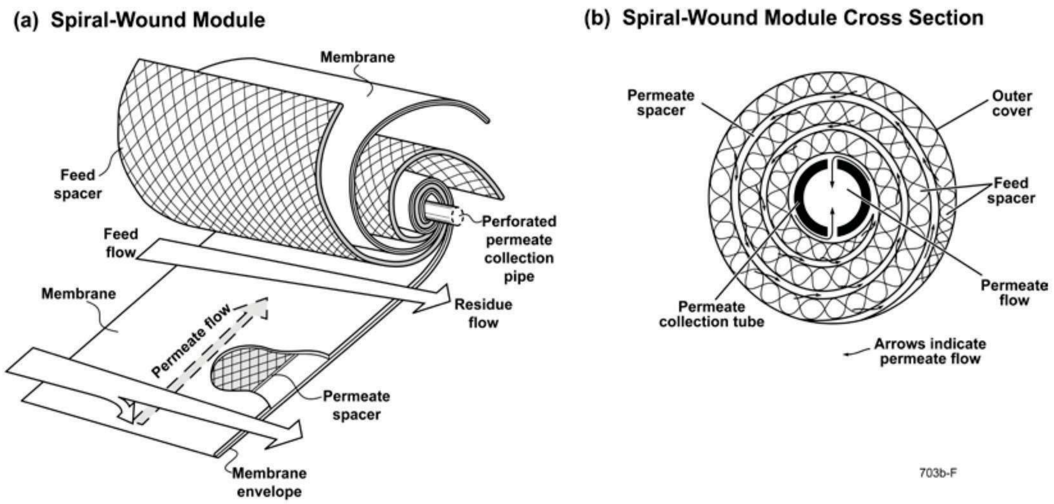


Figure 5. Schematic diagram of a spiral-wound membrane module [R. W. Baker, Membrane Technology and Applications, John Wiley & Sons, West Sussex, United Kingdom (2012)].

Current Work and Results

A major technology development focus has been in improving performance of the membrane, chiefly in terms of increasing CO_2 permeance (while maintaining CO_2/H_2 selectivity in the range of greater than 100). Approaches for improving permeance include the following:

- Using sterically hindered amines as CO_2 carriers: Comparing the mechanisms of reaction of CO_2 with both unhindered and hindered amines, the latter can double the CO_2 carrying capacity. In the latest work, a new alkanolamine has been identified as an effective carrier to enhance both the chemisorption and physisorption of CO_2 at working temperature of 107°C. Also, a series of aminosilanes containing various amino groups was used as coupling agents to graft amine onto the polymer matrix. An aminoacid salt with severe steric hindrance was synthesized to explore the possibility of effective H_2S/CO_2 separation by the membrane.
- Incorporating certain molecular substituents or side chains in the membranes' polymer molecular structure to improve facilitated transport: Specifically, (1) ethylene oxide moieties and (2) amine-containing hydroxyethyl moieties are being investigated in this respect.
- Tuning the composition of the membrane polymers: Different molecular weights of the polymers and different carrier structures in the membrane will have effects on performance. It is possible to optimize membrane polymer composition for different ranges of CO_2 partial pressures.
- Incorporation of nanofillers: Linkages between molecular chains are not rigid in the polymer membrane. This means that at working temperatures (e.g., 107°C), the crosslinked polymer network is rubbery and compressible. At high syngas pressure, induced hydrostatic compression reduces the polymer free volume, causing reduced gas diffusivity through the polymer. In order to mitigate the membrane compaction, nanofillers can be dispersed in the polymer network as reinforcement. In current work, nanofiller in the form of perforated carbon nanosheet has been economically synthesized in-house at OSU and is incorporated for this purpose.

Preliminary TEA of a single-stage membrane process based on the OSU-facilitated transport membrane in an IGCC plant context has been made, informed by current membrane performance data. For the process designed to achieve 90% CO_2 removal with 95% purity, estimations are that the cost of electricity increases 15.4% over the non-capture baseline, and that 99.4% of the H_2 in the input syngas can be recovered.

TABLE 1: MEMBRANE PROCESS PARAMETERS

<table>
<tr><th>Materials Properties</th><th>Units</th><th colspan="3">Current R&D Value *</th><th colspan="3">Target R&D Value</th></tr>
<tr><td>Materials of Fabrication for Selective Layer</td><td>—</td><td colspan="3">polymer with amino groups</td><td colspan="3">polymer with amino groups</td></tr>
<tr><td>Materials of Fabrication for Support Layer</td><td>—</td><td colspan="3">polysulfone</td><td colspan="3">polysulfone</td></tr>
<tr><td>Nominal Thickness of Selective Layer</td><td>µm</td><td colspan="3">~15 – 25</td><td colspan="3">15 – 25</td></tr>
<tr><td>Membrane Geometry</td><td>—</td><td colspan="3">spiral wound</td><td colspan="3">spiral wound</td></tr>
<tr><td>Maximum Trans-Membrane Pressure</td><td>bar</td><td colspan="3">34</td><td colspan="3">34</td></tr>
<tr><td>Hours Tested without Significant Degradation</td><td>—</td><td colspan="3">24</td><td colspan="3">≥200</td></tr>
<tr><td>Manufacturing Cost for Membrane Material</td><td>$/m^2</td><td colspan="3">~54</td><td colspan="3">≤54</td></tr>
<tr><th>Membrane Performance</th><th></th><th colspan="3"></th><th colspan="3"></th></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">107</td><td colspan="3">107</td></tr>
<tr><td>CO_2 Pressure Normalized Flux</td><td>GPU</td><td colspan="3">327</td><td colspan="3">275 – 350</td></tr>
<tr><td>CO_2/H_2O Selectivity</td><td>—</td><td colspan="3">1</td><td colspan="3">1</td></tr>
<tr><td>CO_2/H_2 Selectivity</td><td>—</td><td colspan="3">139</td><td colspan="3">120 – 140</td></tr>
<tr><td>H_2S/CO_2 Selectivity</td><td>—</td><td colspan="3">3</td><td colspan="3">3</td></tr>
<tr><td>Sulfur Tolerance</td><td>ppm</td><td colspan="3">>6,000</td><td colspan="3">>6,000</td></tr>
<tr><td>Type of Measurement</td><td>—</td><td colspan="3">mixed gas</td><td colspan="3">mixed gas</td></tr>
<tr><th>Proposed Module Design</th><th></th><th colspan="3"></th><th colspan="3"></th></tr>
<tr><td>Flow Arrangement</td><td>—</td><td colspan="6">Counter-current</td></tr>
<tr><td>Packing Density</td><td>m^2/m^3</td><td colspan="6">2000</td></tr>
<tr><td>Shell-Side Fluid</td><td>—</td><td colspan="6">Retentate, H_2-rich flow</td></tr>
<tr><td>Syngas Gas Flowrate</td><td>slpm</td><td colspan="6">34</td></tr>
<tr><td>CO_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">90</td><td colspan="2">95</td><td colspan="2">1.1</td></tr>
<tr><td>H_2 Recovery, Purity, and Pressure</td><td>%/%/bar</td><td colspan="2">99.4</td><td colspan="2">94</td><td colspan="2">31.7</td></tr>
<tr><td>Pressure Drops Shell/Tube Side</td><td>psi/m</td><td colspan="6">1.5</td></tr>
<tr><td>Estimated Module Cost of Manufacturing and Installation</td><td>$\frac{\$}{m^2}$</td><td colspan="6">97</td></tr>
</table>

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

***Membrane Permeation Mechanism* –** Facilitated transport mechanism.

***Contaminant Resistance* –** Membrane is tolerant to greater than 6,000 ppm H_2S.

***Syngas Pretreatment Requirements* –** Thermal expansion for mild syngas cooling, and filtration to remove any particulate matter.

***Membrane Replacement Requirements* –** Spiral-wound membrane elements are expected to be replaced every five years.

***Waste Streams Generated* –** Elemental sulfur recovered from the captured H_2S and CO_2 stream via the Claus process.

technology advantages

- The simplicity of the amine-polymer membrane structure lowers its manufacturing cost.
- Membrane modules do not contain moving parts or involve chemical reaction, simplifying operation and maintenance.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- The membrane capture system has a compact footprint and low energy cost.
- The membrane capture system can operate warm/hot to reduce the need for heat exchange (e.g., membrane modules operate at a higher temperature and pressure than conventional acid gas removal processes like Selexol, reducing the need for syngas cooling and lowering the energy and capital cost required to convert captured CO_2 to liquid).
- The membrane can remove H_2S simultaneously with CO_2, resulting in low-sulfur H_2 for combustion or chemical synthesis.

R&D challenges

- Increasing the CO_2 permeance of the membrane.
- Assuring polymer support performance and properties.
- Choice of spacer and glue for high-temperature membrane module fabrication.
- Scale-up and integration issues are possible given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

Efforts in syntheses of improved membranes, membrane characterization, and TEA are in progress.

available reports/technical papers/presentations

"Facilitated Transport Membranes with Tunable Amine-CO_2 Chemistry for Highly Selective CO_2/H_2 Separation," presentation by Yang Han and W.S. Winston Ho, 2019 AIChE (American Institute of Chemical Engineers) Annual Meeting. Orlando, FL, November 2019, Paper 750a.

"*Transformational Membranes for Pre-combustion Carbon Capture*," presentation by Winston Ho and Yang Han, The Ohio State University, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019.

"*Transformational Membranes for Pre-combustion Carbon Capture*," project kickoff meeting presentation, November 2018.

"*Transformational Membranes for Pre-combustion Carbon Capture*," Poster presentation by Yang Han, The Ohio State University, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties

primary project goals

The goal of this State University of New York (SUNY) – Buffalo project is to develop scalable membrane technology by engineering polymers to achieve superior hydrogen (H_2)/carbon dioxide (CO_2) separation properties in readily fabricated and easily deployed membranes. The application is for capture of CO_2 from coal-derived syngas. Specifically, the approach is to derive carbon molecular sieve (CMS) membranes from polybenzimidazole (PBI) doped with polyprotic acids, with the expectations that they will be chemically stable, be able to operate in temperatures up to 300°C, be easily scalable, and have high H_2 permeance and H_2/CO_2 selectivity. The scope of the work is to improve CMS hollow fiber membrane characteristics, fabricate small membrane modules, and perform testing with simulated syngas to establish module/membrane CO_2 separation performance and robustness. Data from testing is to inform techno-economic analysis (TEA) to determine process costs for large-scale carbon capture in an integrated gasification combined cycle (IGCC) plant scenario.

technical goals

- Develop CMS hollow fiber membranes having a H_2 permeance of 1,000 gas permeation units (GPU) and an H_2/CO_2 selectivity of 40 at 200 to 300°C.
- Demonstrate membrane durability via testing of a pencil membrane module under simulated syngas flow at 0.01 kilowatt-electric (kWe) equivalency for 120 hours.
- Characterize a CMS membrane-based system able to capture 90% CO_2 from coal-derived syngas with 95% CO_2 purity at a cost of electricity 30% less than baseline capture approaches (Selexol).

technical content

Conventional methods for pre-combustion carbon capture consist mainly of solvent-based processes such as Selexol and Rectisol. Although enabling high levels of capture at high gas purity, these processes have high capital and operating costs and result in severe energy penalties. Membrane-based carbon capture is of continued interest as an alternative, given its potential advantages in simplicity, lower costs, and potential for large savings in energy use. Among membranes for separation of CO_2 from syngas, inorganic membranes such as

technology maturity:

Laboratory-Scale, Simulated Syngas (equivalent to ~0.01 kWe)

project focus:

Carbon Molecular Sieve Hollow Fiber Membranes

participant:

State University of New York – Buffalo

project number:

FE0031636

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Haiqing Lin
SUNY–Buffalo
haiqingl@buffalo.edu

partners:

Los Alamos National Laboratory
Trimeric Corporation

start date:

10.01.2018

percent complete:

40%

palladium alloys, ceramics, metal-organic frameworks (MOFs), and graphene oxide have been evaluated, given their excellent H_2/CO_2 separation properties. However, they are faced with challenges in the cost and reliability, scale-up of membrane production, and module fabrication. In contrast, polymer-based membranes are much easier to implement than inorganic membranes, provided that the membrane materials demonstrate suitable separation properties. Production scale-up and module fabrication using polymeric membranes have been widely practiced, creating a substantial engineering knowledge base across the polymer membrane industry. Building on this foundation, the current work targets development of scalable membranes by engineering polymers to achieve superior H_2/CO_2 separation properties.

Most work in H_2/CO_2 gas separations by polymeric membrane materials relies solely on strong size-sieving derived from the rigid polymer chains. Polymers available commercially in this class include examples like poly(p-phenylene oxide) (PPO), Matrimid, poly(bisphenol-A sulfone) (PSF), and cellulose acetate (CA). However, the commercially available polymers have low H_2 diffusivity and permeability, are limited by the permeability/selectivity trade-off, and are well below the Robeson bound, as illustrated in Figure 1.

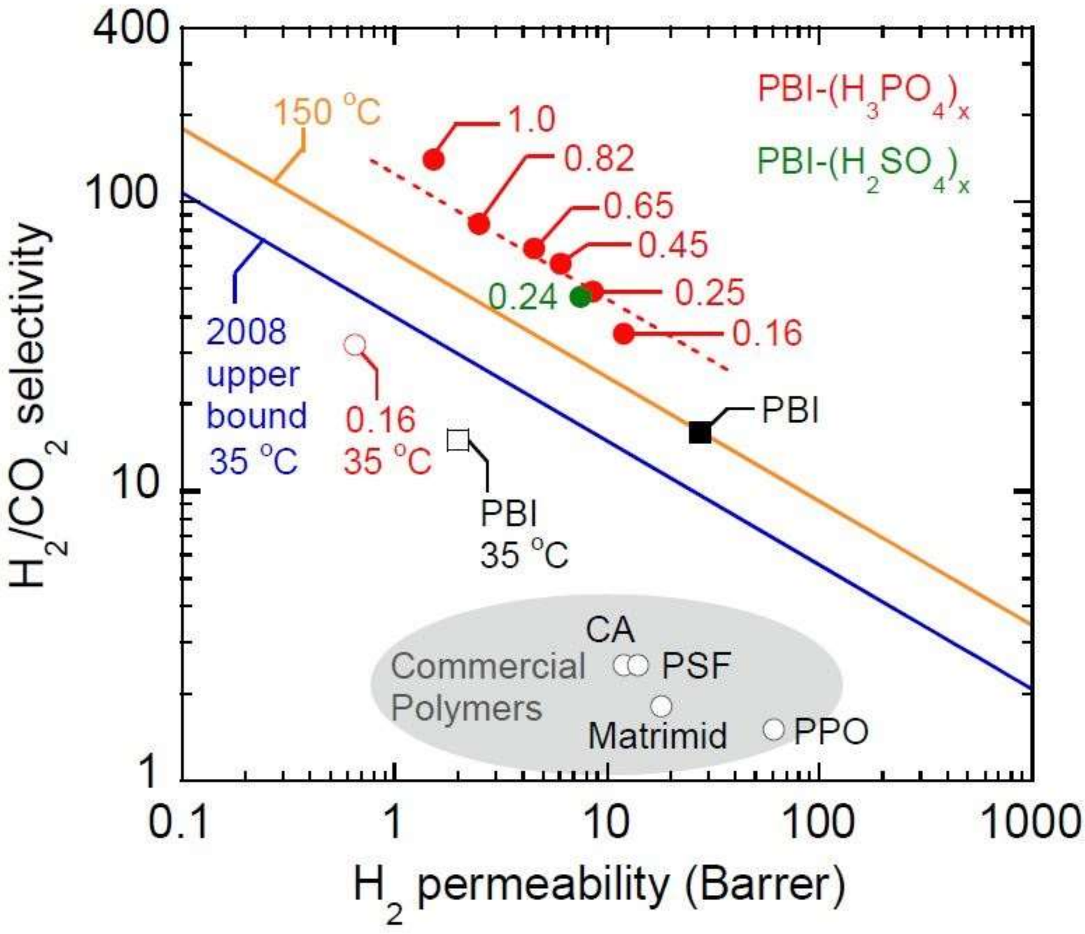


Figure 1: Pure-gas H_2/CO_2 separation performance of $PBI-(H_3PO_4)_x$ (x = 0.16-1.0) and $PBI-(H_2SO_4)_{0.24}$ at 150°C versus Robeson's upper bound at 35°C and 150°C.

The SUNY team has demonstrated considerable improvement in polymer membrane performance by doping the polymer PBI with polyprotic acids such as phosphoric acid (H_3PO_4) and sulfuric acid (H_2SO_4) to improve the size-sieving ability and H_2/CO_2 separation properties at 120 to 180°C. As shown in the upper part of Figure 1, increasing the H_3PO_4 doping level (defined as the molar ratio of H_3PO_4 to the PBI repeating units) decreases the pure-gas permeability and drastically increases the H_2/CO_2 selectivity at 150°C. For example, plain PBI shows an H_2/CO_2 selectivity of 16, while $PBI-(H_3PO_4)_{1.0}$ exhibits a remarkable selectivity of 140, which is much higher than that of any previously studied polymers. Phosphoric acid can strongly interact with multi-PBI chains via proton transfer from the acid to imidazole rings of PBI and hydrogen bonding, and thus it crosslinks the PBI. In comparison, a monoprotic acid such as hydrogen chloride (HCl) does not crosslink the PBI chains and has minimal effect on H_2/CO_2 separation properties.

In current developmental work, the approach is to start with the already strongly size-sieving polymers (i.e., PBI doped with polyprotic acids), and then carbonize them (by heating/pyrolysis at 500 to 800°C in inert nitrogen [N_2] for at least an hour) to increase both permeability and selectivity into a range suitable for commercial deployment. This approach is diagrammed in Figure 2. Carbonizing the acid-doped PBI results in CMS in which microcavities form, tending to increase gas permeability, and ultra-microporous necks increasing size-sieving ability.

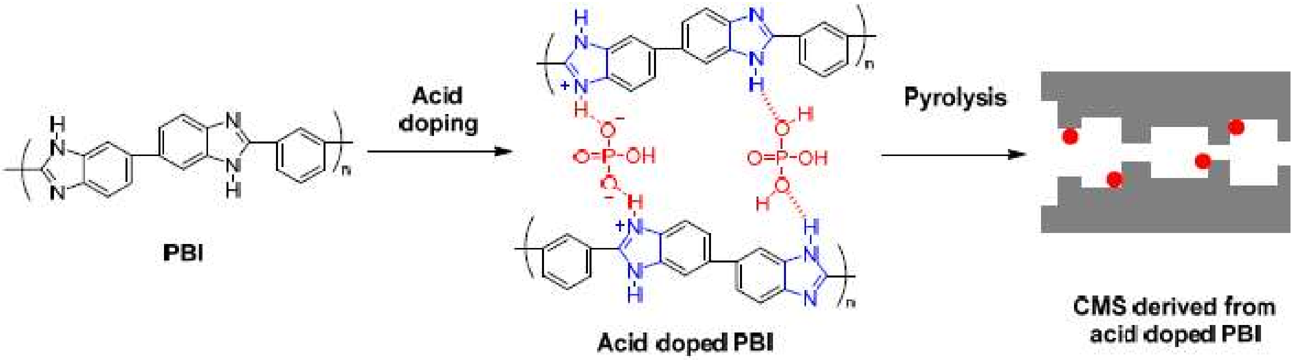


Figure 2: Steps to CMS membranes derived from PBI doped with polyprotic acids.

In past work, CMS membranes were made by carbonizing plain PBI. The pyrolysis increases the porosity and generates graphite-like structure. As shown in Figure 3 in blue, the carbonization of PBI substantially increases H_2 permeability while retaining or slightly increasing H_2/CO_2 selectivity at 100°C. All CMS samples have exhibited H_2/CO_2 separation properties above the upper bound. For example, pure PBI exhibits an H_2 permeability of 12 Barrers and an H_2/CO_2 selectivity of 14 at 100°C, while the CMS prepared by pyrolysis of PBI at 800°C shows an H_2 permeability of 670 Barrers (which is 50 times higher than pure PBI) and an H_2/CO_2 selectivity of 18 at 100°C.

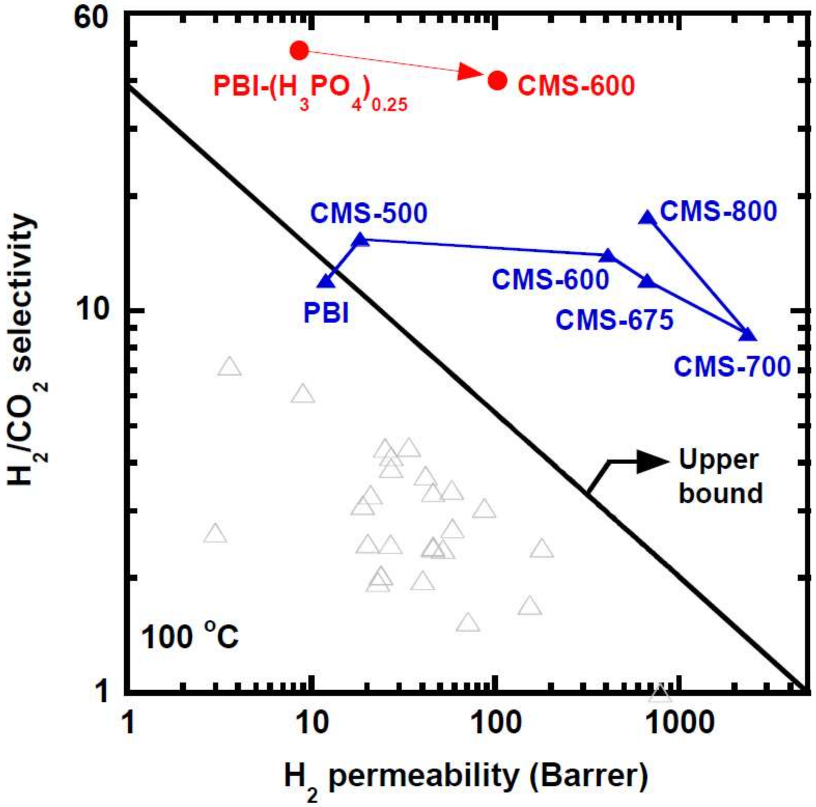


Figure 3: Improvement in membrane performance upon carbonization to CMS.

The SUNY team hypothesizes that the CMS membranes can meet targeted separation properties (H_2 permeance of 1,000 GPU and H_2/CO_2 selectivity of 40) if the starting polymers are PBI doped with polyprotic acids with strong size-sieving ability. For example, PBI-$(H_3PO_4)_{0.25}$ exhibits an H_2 permeability of 8.6 Barrers and an H_2/CO_2 selectivity of 48 at 150°C. The pyrolysis at 600°C increases the permeability to 100 Barrers while retaining an H_2/CO_2 selectivity of 40 at 100°C, as shown in red in Figure 3. During the pyrolysis, the H_3PO_4 gradually decomposes to polyphosphoric acid ($(HPO_3)_n$), retaining the rigid chains and strong molecular size-sieving ability. By optimization of the acid type, composition, and pyrolysis temperature, the CMS should be able to achieve H_2 permeability of 200 Barrers with an H_2/CO_2 selectivity of 40, which can be used to prepare hollow fiber membranes with a selective layer thickness of 0.2 µm exhibiting an H_2 permeance of 1,000 GPU and an H_2/CO_2 selectivity of 40. This is feasible because carbonization has been demonstrated to increase H_2 permeability by 50 times, and Los Alamos National Laboratory (LANL) has successfully fabricated nearly defect-free PBI hollow fiber membranes with a 0.2 µm selective layer.

Figure 4 shows images of (a) a base PBI hollow fiber membrane and (a′) carbonized hollow fiber. This illustrates that the carbonized fiber retains the porous support morphology of the starting fiber.

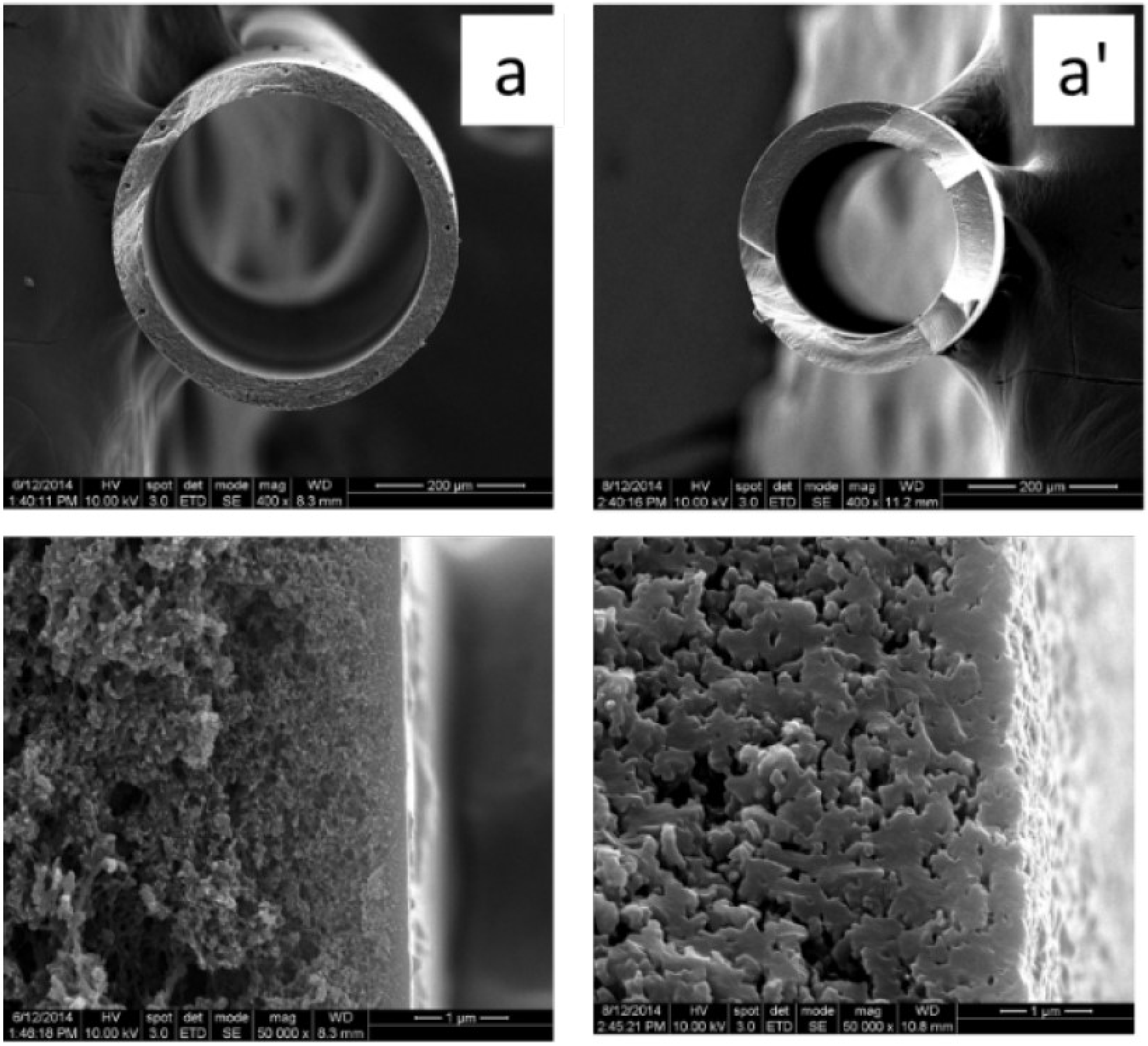


Figure 4: Scanning electron microscopy (SEM) images of PBI hollow fibers, before (left) and after (right) carbonization.

CMS membranes are intended for incorporation in hollow fiber modules for deployment in gas separation systems. LANL currently uses the hollow fiber spinning system depicted in Figure 5 to fabricate the hollow fibers. A custom micro-machined spinneret forms the fiber. The steps resulting in CMS carbon fibers are also diagrammed.

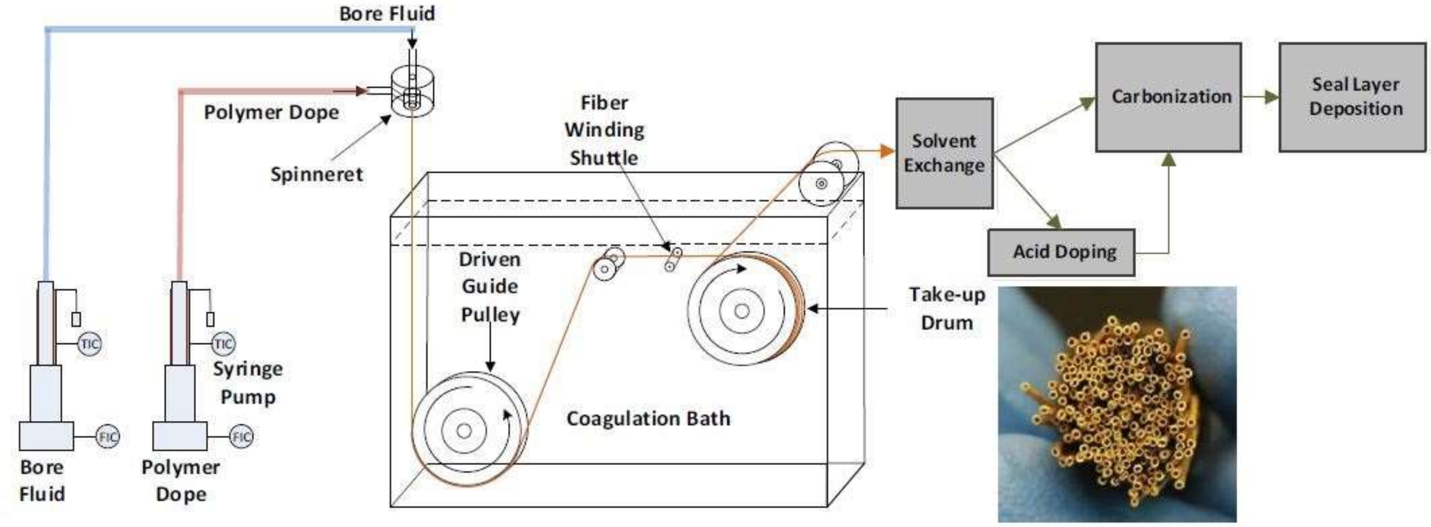


Figure 5: LANL lab-scale continuous hollow fiber spinning system.

Process implementation of CMS membrane modules would follow the basic flow diagram shown in Figure 6. Shifted syngas (1) containing mostly H_2 and CO_2 passes through membrane modules. Hydrogen selectively permeates and is swept away by N_2 (3), which is available in large quantities from the air separation unit producing oxygen for coal gasification (not shown on this figure). The H_2 and N_2 mixture comprises fuel gas (4) to be combusted in the power turbine. Retentate from the membrane modules is conditioned, dewatered, and compressed/pumped into liquid CO_2 for storage or use (2).

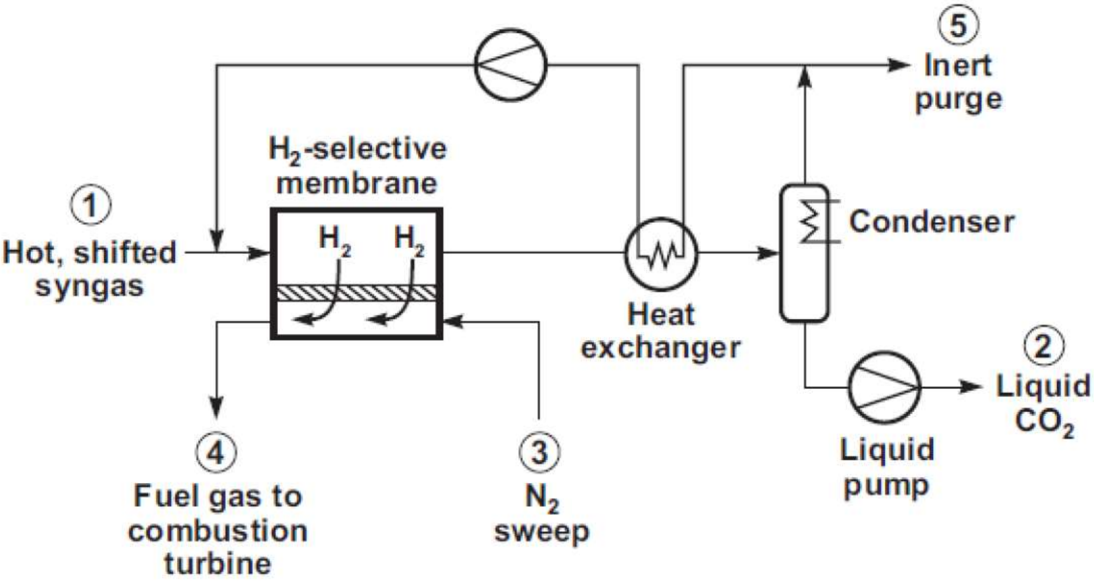


Figure 6: Membrane process integration in process cycle.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbonized acid-doped PBI	carbonized acid-doped PBI
Materials of Fabrication for Support Layer	—	carbonized acid-doped PBI	carbonized acid-doped PBI
Nominal Thickness of Selective Layer	μm	0.1	0.1
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	20
Hours Tested without Significant Degradation	h	120	120
Manufacturing Cost for Membrane Material	$/m^2	20	20
Membrane Performance			
Temperature	°C	150	200-300
CO_2 Pressure Normalized Flux	GPU or equivalent	200	1,000
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/H_2 Selectivity	—	0.025	0.025
CO_2/H_2S Selectivity	—	2	2
Sulfur Tolerance	ppm	20	20
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	Countercurrent	
Packing Density	m^2/m^3	~1,000	
Shell-Side Fluid	—	Permeate, CO_2-rich flow	
Syngas Gas Flowrate	kg/hr	0.02	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 95 20	
H_2 Recovery, Purity, and Pressure	%/%/bar	90 50 15	
Pressure Drops Shell/Tube Side	bar	0.2	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	~1,000	

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atmosphere [atm], 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in syngas.

***Flow Arrangement* –** Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either concurrent, countercurrent, crossflow arrangements, or some complex combination of these.

***Packing Density* –** Ratio of the active surface area of the membrane to the volume of the module.

***Shell-Side Fluid* –** Either the permeate (CO_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

***Membrane Permeation Mechanism* –** Physical solution-diffusion.

***Contaminant Resistance* –** Membranes are resistant to chemicals in the syngas.

***Syngas Pretreatment Requirements* –** Removal of particles.

***Membrane Replacement Requirements* –** Module lifetime is three to five years.

***Waste Streams Generated* –** Water vapor will permeate with H_2, and the water stream will be produced after the H_2 combustion.

technology advantages

- The capability of CMS membranes with high permeance and selectivity to operate at high temperature eliminates the need for syngas cooling and avoids water vapor loss, which improves energy and cost efficiency of the carbon capture process.
- The simplicity of the membrane structure lowers its manufacturing cost.
- A membrane system does not contain moving parts or involve chemical reactions, conferring some operation and maintenance (O&M) advantages.
- The membrane material has a high tolerance to acid gases and is inert to all primary syngas species.
- Membrane capture systems (particularly those based on hollow fiber membrane modules) have compact footprint.

R&D challenges

- Assuring polymer performance and properties.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Durability and gas integrity of membrane modules (gas seals, fouling).
- Scale-up and integration issues (and operational complications from multiple vacuum pumps and valves and complicated ductwork in multiple flow banks) likely given the large number of membranes needed to service a 550-megawatt-electric (MWe) plant.

status

Recently, PBI-$(H_3PO_4)_{0.11}$ carbonized at 700°C was demonstrated to have an H_2 permeability of 240 Barrer and an H_2/CO_2 selectivity of 54 at 225°C, which has met the target of an H_2 permeability of 200 Barrer and an H_2/CO_2 selectivity of 40. Work has just started in making the first generation of PBI-CMS hollow fiber modules needed for eventual parametric testing and evaluation.

available reports/technical papers/presentations

"*Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties*," presentation by Haiqing Lin, SUNY Buffalo, 2019 NETL CCUS Integrated Project Review Meeting. Pittsburgh, PA, August 2019.

"*Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties*," project kickoff meeting presentation, November 2018.

"*Development of Carbon Molecular Sieves Hollow Fiber Membranes Based on Polybenzimidazole Doped with Polyprotic Acids with Superior H_2/CO_2 Separation Properties*," presented by Haiqing Lin, State University of New York (SUNY) at Buffalo, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA. August 2018.

"*Unexpectedly Strong Size-Sieving Ability in Carbonized Polybenzimidazole for Membrane H_2/CO_2 Separation*," M. Omidvar, H. Nguyen, L. Huang, C.M. Doherty, A.J. Hill, C.M. Stafford, X. Feng, M.T. Swihart, and H. Lin, ACS Appl. Mater. & Interfaces, 11 (50), 47365-47372 (2019)

"*Ultraselective Carbon Molecular Sieve Membranes with Unprecedented Performance for H_2/CO_2 Separation for Pre-combustion CO_2 Capture*," presented by Hien Nguyen, State University of New York (SUNY) at Buffalo, 2019 Materials Research Society, Boston, MA. December 2019.

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CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION NOVEL CONCEPTS

Bench-Scale Testing of a High-Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture

primary project goals

The main objective is to scale-up and field-validate the technical feasibility of the University of Southern California's (USC) membrane- and adsorption-enhanced water-gas shift (WGS) process that employs a carbon molecular sieve (CMS) membrane reactor (MR), followed by an adsorption reactor (AR), for pre-combustion carbon dioxide (CO_2) capture. The project begins at Technology Readiness Level (TRL) 4, as the system prototype has already been validated in the laboratory on simulated syngas (under predecessor project FE0026423). The project aims to end at TRL 5, via scaling-up of the prototype system and its testing on actual syngas at the University of Kentucky (UKy). Project tasks include designing, constructing, assembling, and validating the bench-scale experimental MR-AR system; preparing suitable membranes, adsorbents, and catalysts needed for the bench-scale system; and deploying the unit at UKy and testing system performance using real syngas. Results are to be used to complete an updated process techno-economic analysis (TEA) and environmental, health, and safety (EH&S) risk assessment.

technical goals

- Demonstrate CO_2 capture from actual coal gasification syngas at a bench-scale syngas flow rate of 50.7 to 253 kg/day, at a temperature of 250°C, at a pressure of 25 atmosphere [atm], and for 500 hours of testing.
- Increase stability of membranes and adsorbents in the process system in terms of degradation by syngas constituents, with an interim target of less than 30% decline in performance over 500 hours of testing at typical syngas conditions.
- Hydrogen (H_2) permeance greater than 1 m^3/m^2.hr.bar for the H_2-selective membrane, with a target range for H_2/carbon monoxide (CO) selectivity exceeding 80.
- Sorbent working capacity greater than 2.5 weight % CO_2; sorbent attrition rate less than 0.2.
- Demonstrate progress (TRL 4 to TRL 5) toward enabling an MR-AR system in a 550-megawatt-electric (MWe) integrated gasification combined cycle (IGCC) plant, capable of CO_2 capture with greater than 95% purity, while reducing the cost of electricity (COE) by 30% over IGCC plants employing conventional methods of CO_2 capture.

technology maturity:

Bench-Scale, Actual Coal-Derived Syngas (50.7-253 kg per day equivalent to 3-14.9 kW)

project focus:

Combined CMS Membrane/WGS Reactor and Adsorption Reactor

participant:

University of Southern California

project number:

FE0031737

predecessor projects:

FE0026423

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Theodore Tsotsis
University of Southern California
tsotsis@usc.edu

partners:

Media and Process Technology Inc.,
University of California Los Angeles
University of Kentucky Research Foundation

start date:

06.01.2019

percent complete:

15%

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily H_2 and CO_2) and the downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced in whole by a unique membrane- and adsorption-enhanced WGS reactor system (previously developed for H_2 production via methane steam reforming) that allows for in situ preferential H_2 permeation and simultaneous CO_2 adsorption. The reactor system is depicted, in the context of a typical IGCC power plant cycle, within the blue border-surrounded process block in Figure 1.

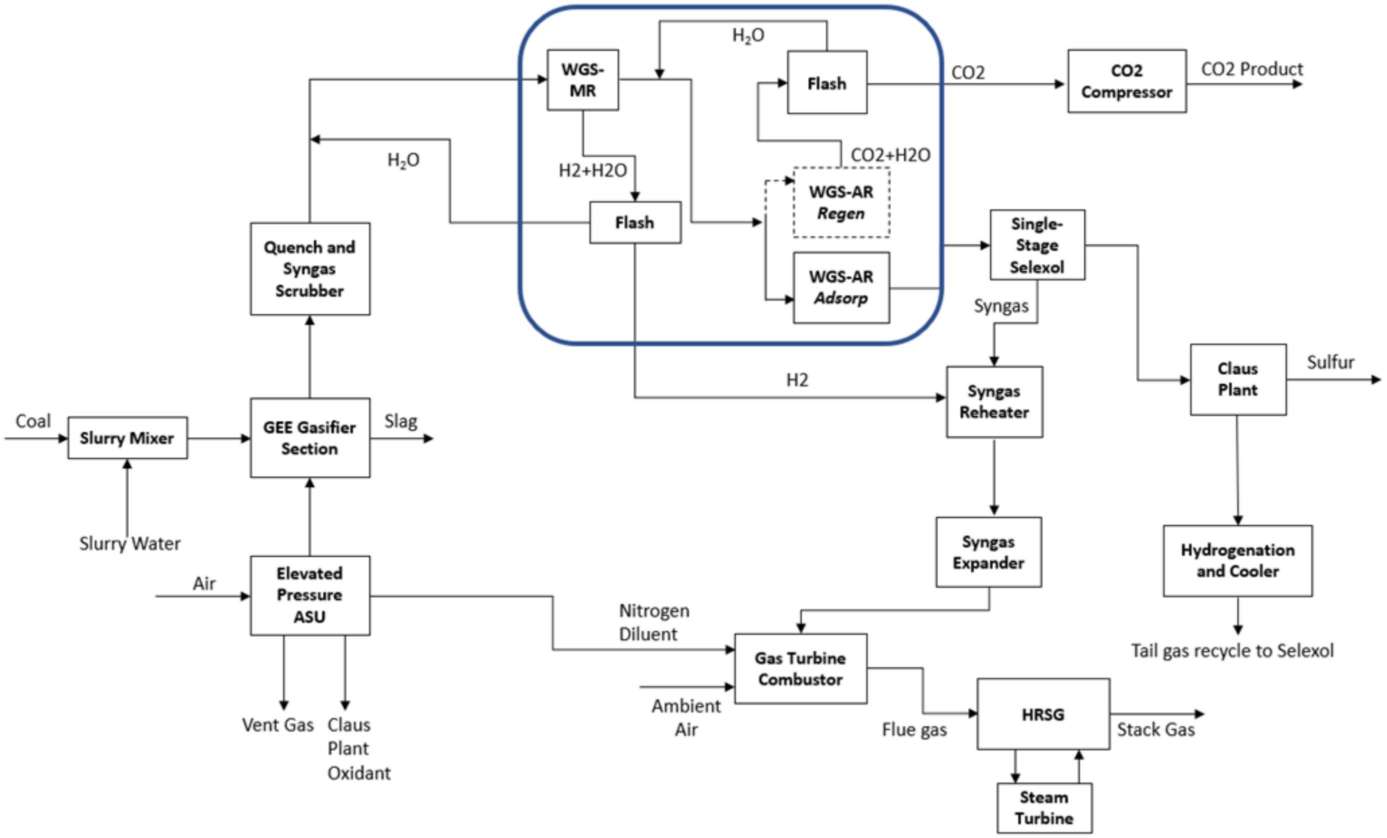

Figure 1: Proposed MR and AR system in the context of an IGCC plant process.

The system combines an MR and AR in tandem to continuously produce a pure H_2 product (while attaining greater than 99% CO conversion) until the adsorbent (in the AR unit) is saturated. The AR unit must then be taken off-stream and regenerated via steam-enhanced temperature swing adsorption (TSA). This unique reactor configuration can, therefore, be viewed as a hybrid MR-AR system with TSA cycling. Compared to conventional WGS followed by CO_2 capture using a conventional amine process, the MR-AR system is more efficient and compact. Furthermore, the use of a TSA rather than a pressure-swing CO_2 recovery step (as commonly practiced in AR systems) allows the recovery of CO_2 at higher pressures aiding system efficiency.

The combined MR-AR process is shown in more detail in Figure 2. Here, the syngas first passes into the MR vessel, consisting of WGS catalyst packed around an array of membrane tubes. The tubes are CMS-based membranes on ceramic support, which are highly selective to H_2. The MR permeate consists of high-purity H_2. As the H_2 is withdrawn from the MR vessel, the WGS reaction equilibrium is pushed toward further H_2 production. Retentate/rejected gases are passed to an array of ARs operating in a periodic manner, whereby at any given time some ARs are fed retentate gases and operate in reaction/adsorption mode, while the remaining ARs are fed steam and operate in a TSA regeneration mode. The ARs contain additional WGS catalyst, in addition to CO_2 sorbent. In this technology, hydrotalcite (HTC) is utilized as the CO_2 sorbent. This co-location of the WGS reaction and CO_2 separation functions in the AR allows traditional WGS reaction equilibrium limitations to be overcome, thus enabling enhanced shifting of the syngas to occur until most of the carbon as CO is converted into CO_2 and adsorbed. This results in a relatively pure H_2 gas exiting the AR at high pressure when the ARs operate in reaction/adsorption mode, while a high-pressure steam/CO_2 mixture exits the ARs when they operate in regeneration mode. In summary, the proposed process configuration combining the MR and AR in tandem provides significant process flexibility, efficient high-pressure and high-purity H_2 production, and CO_2 recovery.

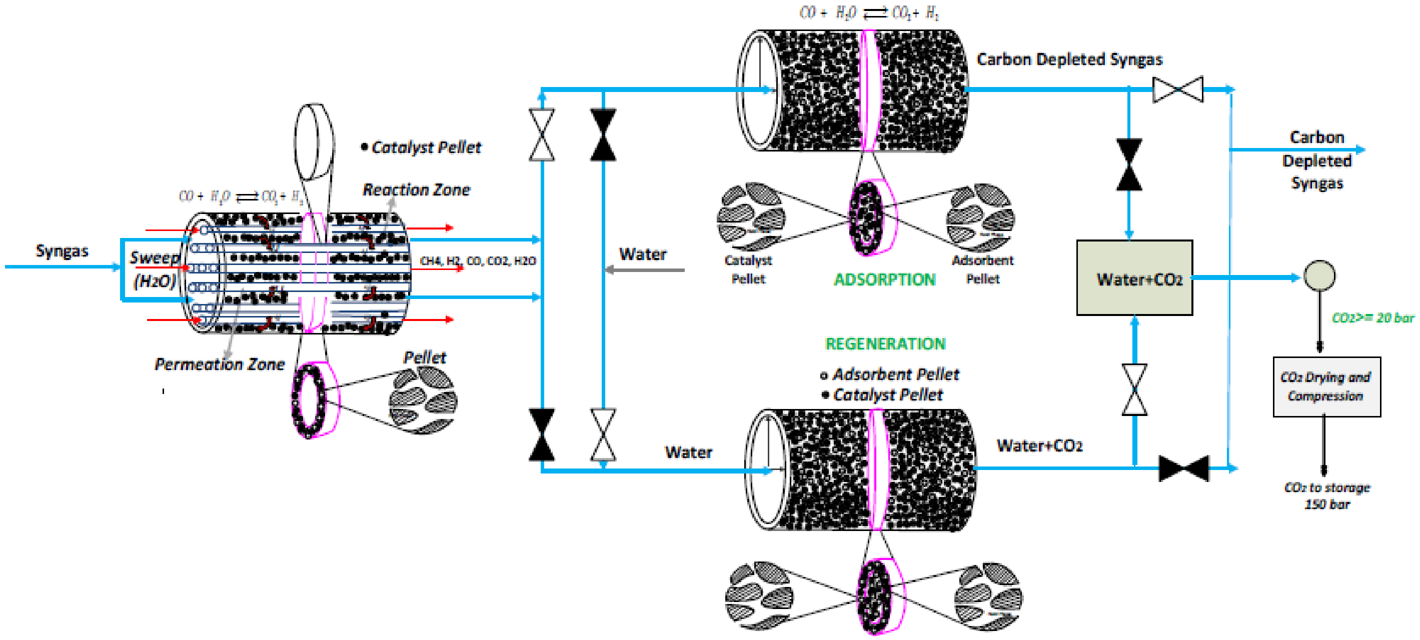

Figure 2: Proposed MR-AR process.

The HTC sorbent mentioned previously is an anionic clay magnesium (Mg)/aluminum (Al)-layered double hydroxide, as depicted in Figure 3. It has a relatively high CO_2 capacity over a wide range of temperatures and pressures; can be easily prepared by precipitation of Mg/Al from solution in sodium hydroxide; and is unaffected by hydrogen sulfide (H_2S) and simulated tars at anticipated operating temperature, thereby conferring process stability.

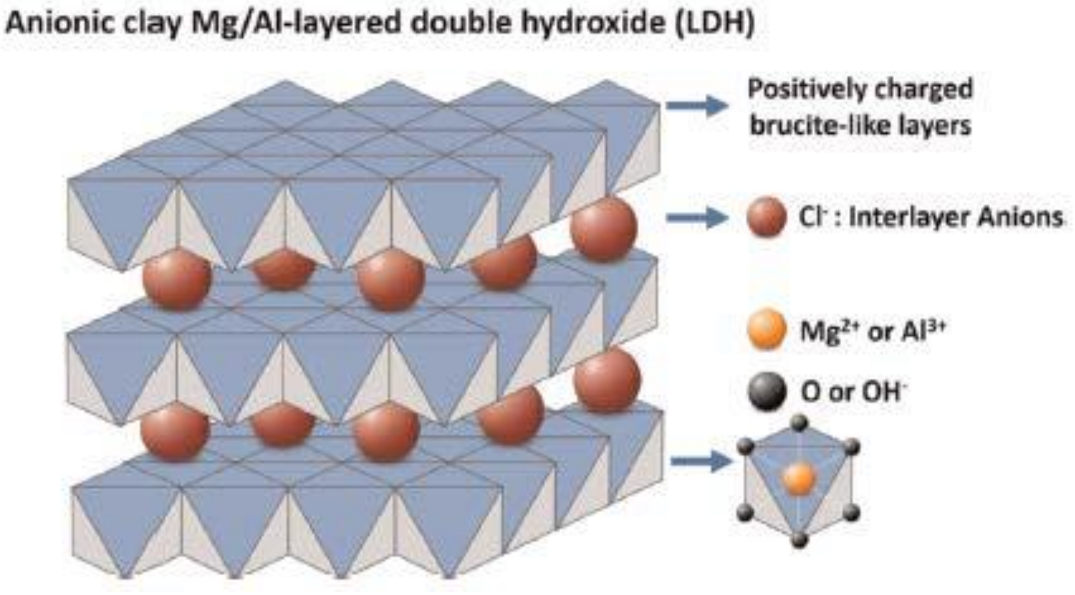

Figure 3: Hydrotalcite (HTC) adsorbent.

The main accomplishments and findings of the USC team's predecessor project included the following:

- CMS membranes were prepared and tested over the full range of expected operating temperatures (up to 300°C) and pressures (10 to 25 bar). Performance targets for H_2 permeance (350 to 550 gas permeation units [GPU]) and H_2/CO selectivity of greater than 80 were met.
- HTC sorbent was prepared, and adsorption/desorption kinetics and working capacity measured at expected operating conditions of 300 to 450°C and pressure up to 25 bar. A performance target for working capacity of greater than 3 weight % CO_2 was met.
- Kinetics of a commercially available sour-shift WGS catalyst were measured at expected operating conditions. This information is essential in modeling and in preparing a TEA of the MR-AR process.
- An MR-AR system operating run of greater than 500 hours was carried out on simulated syngas at a flow rate of less than 0.9 kg/day in a lab-scale integrated experimental apparatus. This effectively advanced the MR-AR technology to TRL 4. Also, the membranes, sorbents, and catalysts were shown to be robust at expected operating conditions.
- Preliminary TEA study results comparing an MR-AR integrated system to a baseline Selexol system (both in the IGCC context) show substantial reductions in required compression work and WGS catalyst requirements. The overall COE target of 30% lower cost than the baseline COE would be closely approached or met given known performance parameters and assumptions.

It should be noted that there are several major points of departure of the case of MR-AR within an IGCC power plant context from the baseline IGCC case. These become important in process performance and cost analysis:

1. The WGS reaction occurs in the MRs and ARs alongside H_2 removal (in the MRs) and CO_2 removal (in the ARs).
2. The amount of steam needed in the MR-AR case is higher because steam not only serves as a feed in the AR, but it is also used as a sweep stream to evacuate the WGS reaction products.
3. A single-stage Selexol unit is needed for H_2S removal, as opposed to a dual-stage Selexol unit for H_2S and CO_2 removal in the baseline case.
4. Steam is used as diluent in the combustion turbine, as opposed to nitrogen (N_2) in the baseline case.

Clearly, item 3 is beneficial from both cost and efficiency considerations, but items 2 and 4 are not beneficial because of the extra steam needed and its cost. If credit is taken for sale of N_2 in the MR-AR case, economics are obviously better than if N_2 cannot be sold. In any case, the added complication of N_2 marketing must be regarded as a negative aspect of MR-AR process technology.

Current project work focuses on design and construction of a bench-scale unit. Ultimately, this will be sited at UKy's Center for Applied Energy Research (CAER) to enable testing on actual coal-derived syngas from CAER's entrained-flow coal gasifier. The bench-scale unit will utilize 30-inch membrane tubes in 2-inch outer diameter modules for the MR. Test campaigns totaling 500 hours are planned, enabling determination of performance at this larger scale, affording an opportunity to evaluate membrane, catalyst, and sorbent stability over time. The performance data will allow improved TEA of the MR-AR system.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$/m²	<1,500	<750
Membrane Performance			
Temperature	°C	250–300	250–300
H_2 Pressure Normalized Flux	GPU or equivalent	500	900
H_2/H_2O Selectivity	—	2–4	>3
H_2/CO_2 Selectivity	—	.200	>200
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>10,000	>10,000
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	co/counter-current or cross-flow	
Packing Density	m²/m³	>450	
Shell-Side Fluid	—	Permeate	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 95 >60	
H_2 Recovery, Purity, and Pressure	%/%/bar	>80 >90 Up to 20	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	1,500	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane’s permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm³ (1 atm, 0°C)/cm²/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0°C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m²-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving.

Contaminant Resistance – Resists all chemical contaminants in gasifier off-gas including H_2S, ammonia (NH_3), heavy metals, organic vapors, tars, etc., based on bench-scale testing conducted at the National Carbon Capture Center (NCCC).

Syngas Pretreatment Requirements – Particulate removal should be practiced.

Membrane Replacement Requirements – Not known presently, but assumed to be five to 10 years. More than 16,000 hours of laboratory thermal stability testing has been demonstrated with no failure. More than 1,000 hours of live syngas testing at NCCC has been conducted with no failure.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

Proposed Module Integration – See below.

Entering Module	Pressure psia.	Temperature °F	Composition						
			vol%						ppmv
			CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
MR	800	440-540	0.1089	0.2823	0.0010	0.0055	0.2689	0.3190	5700
AR	800**	440-540*	0.2480	0.1466	0.0009	0.0055	0.2590	0.3253	5700

* Species compositions shown for inlet temperature of 440°F; **To match the exit gasifier conditions.

TABLE 2: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	2,849–3,066	2,849–3066
Bulk Density	kg/m^3	1,322–1,423	1,322–1,423
Average Particle Diameter	mm	0.6–0.8	2–3
Particle Void Fraction	m^3/m^3	0.536	0.536
Packing Density	m^3/m^3	0.406	0.406
Solid Heat Capacity @ STP	kJ/kg-K	0.5–0.65	0.5–0.65
Crush Strength	kg_f	N/A	10-15
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	25	>25
Temperature	°C	250–300	250–300
Equilibrium Loading	g mol CO_2/kg	~3	~3
Heat of Adsorption	kJ/mol CO_2	~10 kJ/mol	~10 kJ/mol
Desorption			
Pressure	bar	25	>25
Temperature	°C	400–450	<400
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1-0.2	<0.1
Heat of Desorption	kJ/mol CO_2	—	—

Proposed Module Design			(for equipment developers)	
Flow Arrangement/Operation	—		See Figure 2	
Flue Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90	95	25
Adsorber Pressure Drop	bar		—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

STP – Standard temperature and pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent volume to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figures 1 and 2.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

technology advantages

- Hybrid concept process allows the simultaneous removal from the reacting phase and recovery of both H_2 and CO_2, resulting in significant reaction rate enhancement over the conventional WGS system.
- Significantly reduced catalyst weight usage requirements: reaction rate enhancement (over conventional WGS) permits operation at lower weight of catalyst/inlet molar flow rate of CO (W/F_{CO}), thus resulting in significant catalyst savings.
- No syngas pretreatment required given use of sour-shift catalyst and use of CMS membranes, which have demonstrated stability to all gaseous contaminants present in coal-derived syngas.
- Efficient H_2 production and superior CO_2 recovery and purity: the synergy of the MR and AR units satisfies the CO_2 recovery/purity, carbon utilization (CO conversion), and H_2 recovery/purity goals.

R&D challenges

- Heat management in reactors.
- Process integration with IGCC.
- Particulate matter needs to be controlled to reduce its potential impact on the reactor units.
- Scale-up and integration issues, given the large number of reactor modules needed to service a 550-MWe plant.

status

Design and construction of the bench-scale unit for testing at UK CAER is underway.

available reports/technical papers/presentations

"*A High Efficiency, Ultra-compact Process for Pre-combustion CO2 Capture*," presentation by Theo Tsotsis, University of Southern California, 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting - Capture and Utilization Sessions, August 2019.

"*Bench-Scale Testing of a High Efficiency, Ultra-Compact Process for Pre-Combustion CO2 Capture*," project kickoff meeting presentation, May 2019.

"*A High Efficiency, Ultra-compact Process for Pre-combustion CO2 Capture*," Final Report submitted to the U.S. Department of Energy, National Energy Technology Laboratory. DOE Award Number DE-FE0026423, University of Southern California, April 2019.

Karagöz, S., Tsotsis, T.T., and Manousiouthakis, V.I., "Multi-scale Modeling and Simulation of a Novel Membrane Reactor (MR)/Adsorptive Reactor (AR) Process," In Press, *Chemical Engineering & Processing: Process Intensification,* 137, 146, 2019.

Karagöz, S., Tsotsis, T.T., and Manousiouthakis, V.I., "Energy Intensification of H_2 Generation and CO_2 Capture/Utilization by Carrying-out the Water Gas Shift Reaction in an Adsorptive Reactor: Multiscale Dynamic Modeling and Simulation," *AIChE J.,* 2019.doi: 10.1002/aic.16608.

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Chen, H., Garshasbi, A., Karagöz**,** S**.,** Cao, M., Pichardo, P., Ciora, R., Liu, P.K.T, Manousiouthakis, V., and Tsotsis, T.T., "Carbon Molecular Sieve-Based Reactive Separations for Power Generation Applications," Presentation at the 15th International Conference on Inorganic Membranes, June 18-22, 2018, Dresden, Germany

Tsotsis, T., Manousiouthakis, V., Ciora, R., "A High Efficiency, Ultra-Compact Process for Pre-combustion CO_2 Capture (FE0026423)," Presented at the CO_2 Capture Technology Meeting, August 13-17, 2018, Pittsburgh, PA.

Karagoz S., Tsotsis, T., Manousiouthakis, V.I., "Process Intensification of Hydrogen Production Systems," Session 185ag Interactive Session: Systems and Process Design, presented at AIChE Annual Meeting, Pittsburgh, PA, 10-29-2018.

Karagoz S., Tsotsis, T., Manousiouthakis, V.I., "Effectiveness Factor Phenomena for the Transition between PBR and MR via Coupled Heat and Mass Transfer," Session 360g Process Intensification by Enhanced Heat and Mass Transfer, presented at AIChE Annual Meeting, Pittsburgh, PA, 10-30-2018.

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Karagoz S., Tsotsis, T., Manousiouthakis, V., “A Parametric Study of the Adsorption/Desorption Steps for an Adsorptive Reactor (AR) Intensifying the Water Gas Shift (WGS) Reaction,” Presentation at 2017 AIChE Conference, October 29-November 3, Minneapolis, MN.

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Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems

primary project goals

Southern Research Institute (SR) is developing a combined magnesium oxide (MgO)-based carbon dioxide (CO_2) sorbent/water-gas shift (WGS) reactor that offers high levels of durability, simplicity, flexibility, and heat management ability. The primary project goal is to develop a combined CO_2 sorbent/WGS reactor-based process with advanced integrated heat management to capture 90% of the CO_2 from the Transport Reactor Integrated Gasifier (TRIG™) syngas for integrated gasification combined cycle (IGCC) applications.

technical goals

- Identify sorbent and operation conditions for a combined CO_2 sorbent/WGS reactor through modeling and experimental study of the WGS reaction at bench scale.
- WGS reaction conversion extent of 90 to 95% of equilibrium carbon monoxide (CO) conversion.
- Carbon dioxide capture from coal gasification syngas at a temperature of 350°C and pressure of 40 atmosphere (atm), with syngas throughput at space velocity of 500 to 2,000 standard cubic centimeter (scc)/g/hr (for sorbent), 1,000 to 4,000 scc/cc/hr (for catalyst).
- Carbon dioxide capacity of sorbent 3 to 5 mol/kg, and regenerability and durability of more than 500 cycles.
- Progress toward enabling combined MgO-based CO_2 sorbent/WGS reactor technology in a 550-megawatt-electric (MWe) IGCC plant, capable of 90% capture of CO_2 at over 95% purity, while reducing the cost of electricity (COE) by 30% over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily hydrogen [H_2] and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas could be replaced in whole by a combined MgO-based CO_2 sorbent/WGS reactor unit. Within the WGS reactor, CO_2 would be withdrawn directly by the sorbent, efficiently increasing the driving force for the equilibrium WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor (or banks of reactors in parallel as syngas throughput requires).

technology maturity:

Laboratory-Scale, Simulated Syngas

project focus:

Combined CO_2 Sorbent/Water-Gas Shift Reactor

participant:

Southern Research Institute

project number:

FE0026388

predecessor projects:

N/A

NETL project manager:

Andy Aurelio
isaac.aurelio@netl.doe.gov

principal investigator/ responsible person:

Santosh Gangwal/
Amit Goyal
Southern Research Institute
agoyal@southernresearch.org

partners:

IntraMicron Inc., Nexant Inc.

start date:

10.01.2015

percent complete:

100%

The CO_2 sorbent is stabilized meso-porous high-surface area MgO promoted by alkali salts. Magnesium oxide captures CO_2 according to reactions 1 through 3. Carbon dioxide is present in the syngas from the original gasification reactions, and is additionally formed as a product of the WGS reaction (reaction 4):

$$MgO(s) + CO_2(g) \leftrightarrow MgCO_3(s);\ \Delta H = -100.7\ KJ/mol \qquad (1)$$

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s);\ \Delta H = -81.1\ KJ/mol \qquad (2)$$

$$Mg(OH)_2(s) + CO_2(g) \leftrightarrow MgCO_3(s) + H_2O(g);\ \Delta H = -19.5\ KJ/mol \qquad (3)$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g);\ \Delta H = -41.2\ KJ/mol \qquad (4)$$

The MgO sorbent gradually transforms to carbonate in the forward reactions and must be regenerated to MgO in the reverse reactions to enable ongoing operation. Accordingly, the reactor must be operated in cyclic mode, with combined WGS reaction/CO_2 capture interval followed by a regeneration interval, with multiple reactors needed to maintain continual process operation. The regeneration is accomplished by reverse gas flow through the reactor at decreased pressure (atmospheric). Therefore, this can be regarded as a pressure swing adsorption system for CO_2 capture.

This technology takes advantage of IntraMicron's technology of Microfibrous Entrapped Catalysts (MFECs). These are based on microfibrous media (MFM), a highly porous structure (≈94%) that consists of randomly oriented microfibers. The random orientation of the microfibers provides a uniform flow profile throughout the bed, which minimizes channeling, assists with mixing, and generally allows improved fluid flow to facilitate mass transport at catalytic reaction sites. MFECs are prepared using a proprietary method that locks small catalyst particles (0 to 35 vol. %, and with size 40 to 300 microns) within the microfibrous media, as depicted in Figure 1(a). The microfibrous structure can be formed from a variety of materials, including metals (copper [Cu], nickel [Ni], etc.), alloys (stainless steel, brass), polymers, and glass, allowing the support structure to be tailored to a given reaction system. Metals are typically used when enhanced heat transfer is needed, because high-conductivity metal MFM enable rapid heat transfer to or from the embedded catalyst particles. As such, this technology is helpful in intensifying catalytic processes where catalyst performance is otherwise limited by heat transfer limitations. Also, distributing catalyst particles on a highly porous structure allows gas flow more akin to a fluidized bed than a packed bed; this might be termed "frozen-fluidized bed" to distinguish it from the conventional alternatives.

Conventional WGS reactors have the catalyst in traditional packed beds, and it is believed that significant advantages can be realized by performing the WGS reaction using MFECs in the frozen-fluidized bed configuration (Figure 1(c), which would reduce or eliminate intra-particle heat and mass transfer limitations experienced conventionally. For example, Figure 1(b) shows the better heat transfer in MFM as compared to a conventional packed bed of alumina.

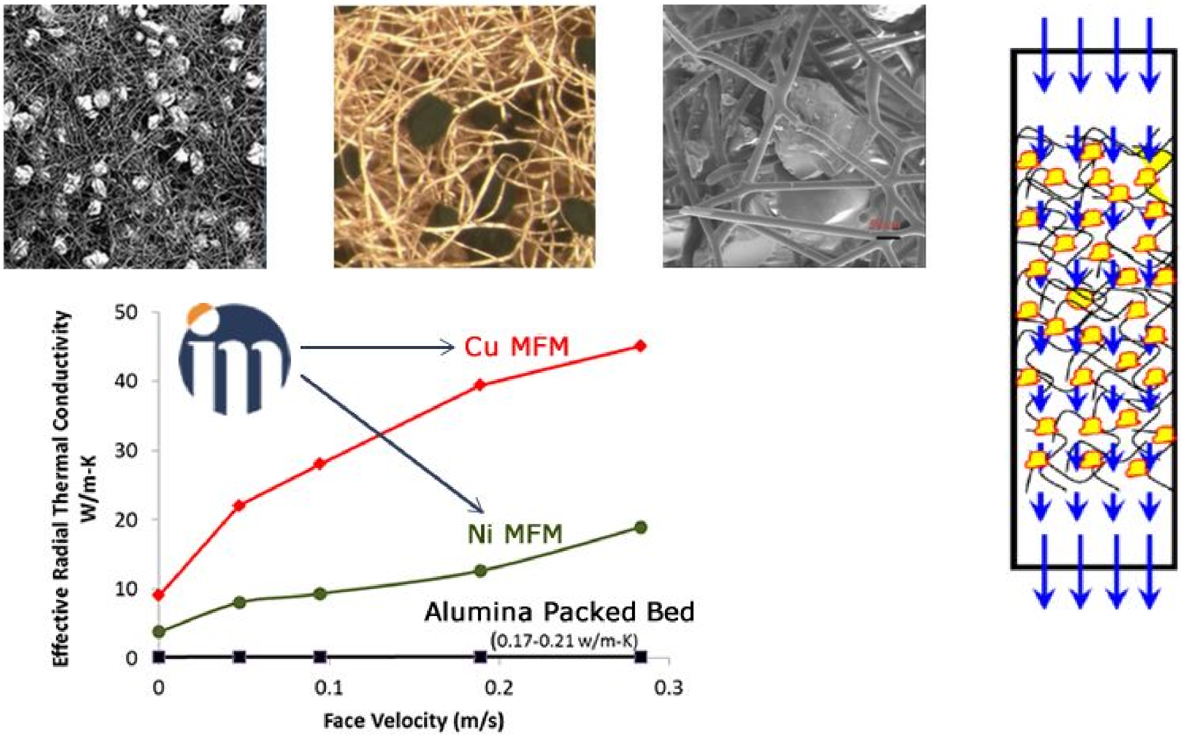


Figure 1: (a) Images of catalyst and sorbent particles entrapped in sintered microfibrous media (top left); (b) comparison of thermal conductivities of metal MFEC with alumina packed bed (bottom left); (c) improved gas flow through frozen fluidized bed configuration of MFECs (on right).

In the SR application, commercial WGS catalyst is used as the source material for the catalyst particles in the MFECs. Promoted MgO sorbent particles are also introduced into the MFM. The result consists of finely divided sorbent and catalyst particles in close proximity, which allows good heat transfer characteristics and gas flow through the mesh holding them.

Although combining the WGS reaction and CO_2 capture in the same media provides intrinsic process intensification, it does create challenges in terms of the inevitable regeneration cycle demanded by the sorbent. The WGS catalyst is present in the reactor as the sorbent undergoes regeneration; the WGS catalyst obviously experiences no benefit from the regeneration cycle and could experience degradation due to some conditions applied for regeneration.

Figure 2 depicts the laboratory-scale apparatus that SR has employed to determine performance characteristics of the combined WGS/MgO sorbent media in a small MFEC reactor, operated on simulated syngas compositions resulting from an air-blown TRIG™ gasifier and an oxygen-blown GE gasifier.

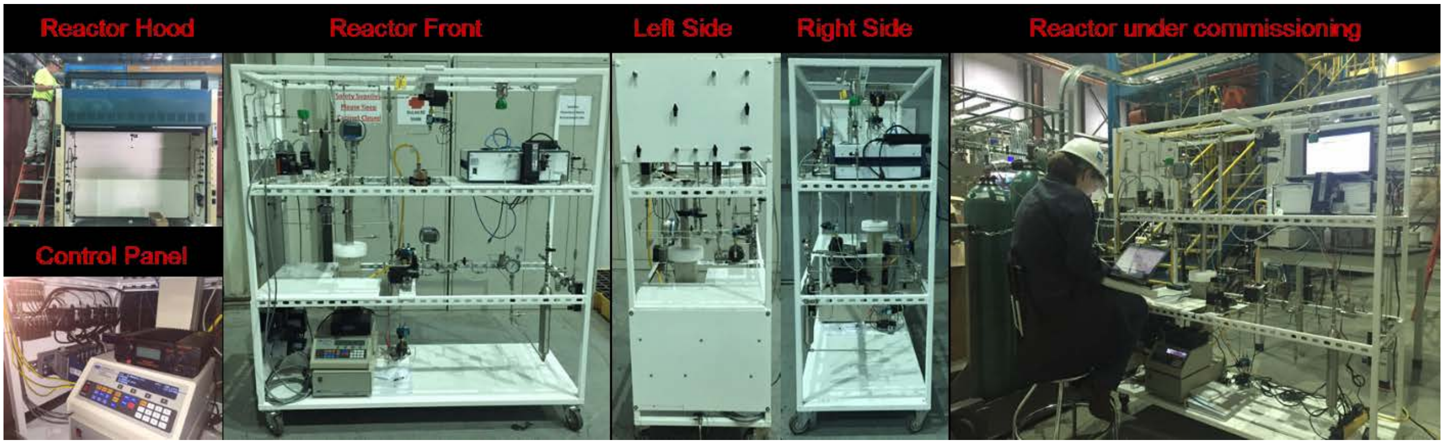


Figure 2: SR's bench-scale CO_2 reactor system.

In experimental evaluation of the bench-scale MFEC reactor, SR discovered desulfidation of WGS catalyst resulting in reduced CO conversion activity and observed structural changes in copper metal MFEC. The sulfidation caused reduction of thermal conductivity and creation of hot spots. Desulfidation with steam caused degradation of fibrous structure. These problems were addressed by modifications of the reactor system to prevent regeneration steam from affecting the catalyst bed by changing MFEC materials from copper to stainless steel and further optimizing reaction conditions.

Under optimized conditions, the sorbents achieved up to 8 mmol/g of CO_2 working capacity and remained stable over 500 cycles of adsorption and regeneration. The selected WGS process achieved 96% CO per pass conversion and remained isothermal during the test duration that lasted more than 500 cycles.

Figure 3 shows the concept for integration of this technology in the context of a representative IGCC process cycle, indicating the primary process flows and their temperatures for both absorption and regeneration of the WGS-MgO reactors. Based on this general process arrangement for inclusion of the SR technology in an IGCC cycle with carbon capture, techno-economic analyses (TEAs) have been prepared comparing this to U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) baselines of a GE gasifier-based IGCC cycle with capture and a subcritical pulverized coal plant with capture. Results are reported in Figure 4. Overall, given known performance parameters and assumptions for costs, the SR MFEC-based WGS/CO_2 capture process has lower overall investment costs than the comparative IGCC baseline, but suffers from lower gross power output and therefore yields approximately the same COE as the baseline IGCC case.

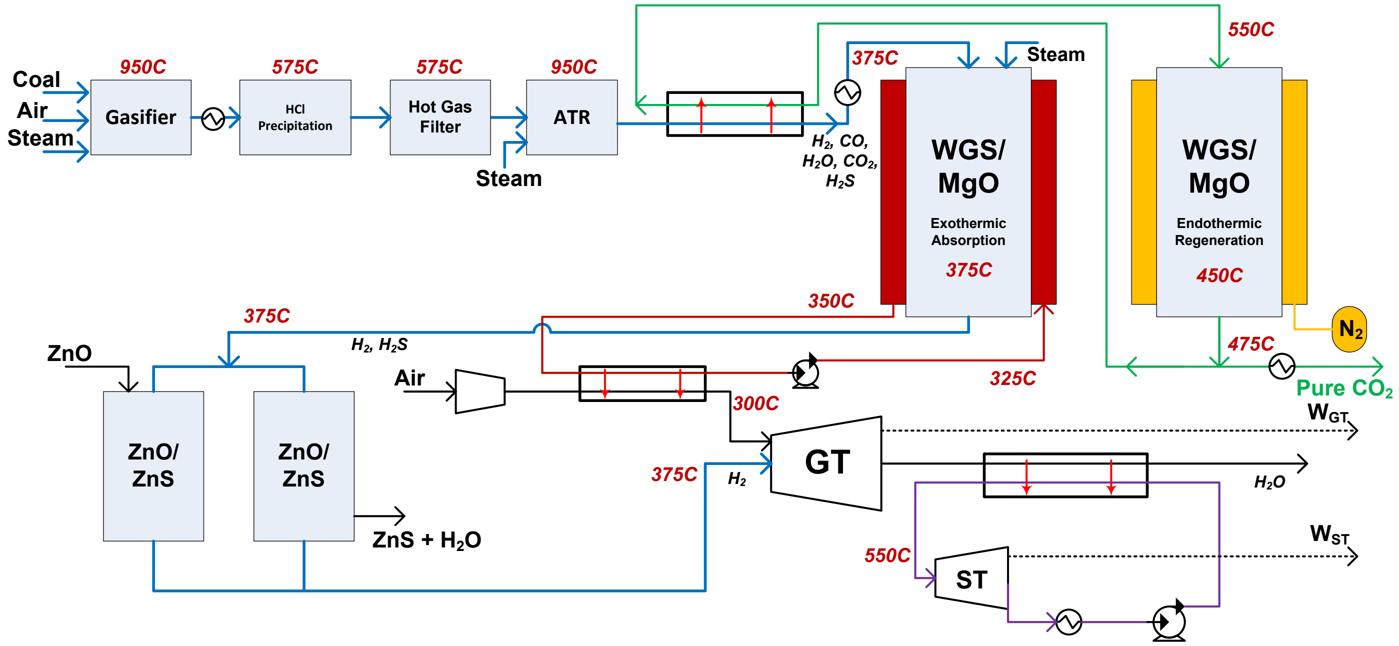


Figure 3: Integration of the combined sorbent/WGS-based CO_2 capture process in context of an IGCC plant cycle.

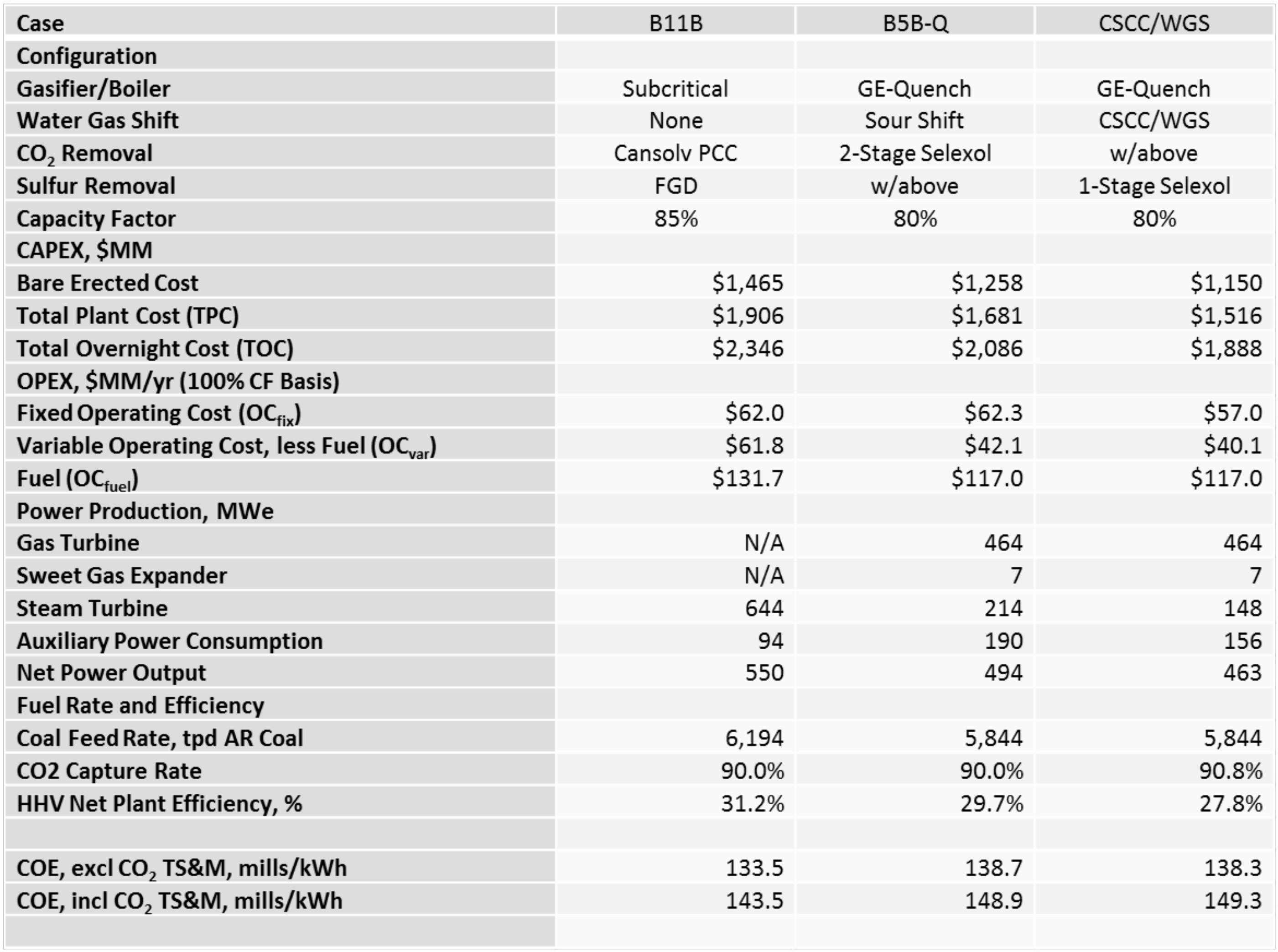
At the end of technology and process development efforts, SR concludes that the combined WGS/CO_2 capture process has technical feasibility to replace conventional two- to three-stage WGS reactor systems with intercooling plus a separate CO_2 capture unit with a single WGS reactor unit, with potential for energy efficiency increase and equipment cost savings.

Notwithstanding the above finding, SR concluded that a single WGS reactor coupled to multiple CO_2 sorbent beds would be a preferred commercial approach compared to several mixed-adsorption/WGS reactors, after considering the comparative implications of these process arrangements. It turns out that high-CO conversions approaching 96% can be achieved in the WGS reactor containing only the WGS catalyst supported on MECS and thereby made to be isothermal. In this case, sorbent-only reactors would be located downstream for CO_2 capture. This configuration would meet capture performance requirements but be less complicated in terms of sorbent regeneration (obviously, because regenerating a dedicated sorbent-only reactor with steam is not problematic, which regenerating one containing combined WGS catalyst and sorbent would deleteriously expose the WGS catalyst to steam).

In all cases, heat management using MFECs was demonstrated to enable thermodynamically favorable reaction temperatures for both exothermic CO_2 capture/WGS and endothermic regeneration.

The current state-of-the-art CO_2 capture process involves scrubbing the gas stream at low temperature. SR's elevated-temperature CO_2 capture technique eliminates the need to cool the gas stream coming from WGS reactor, resulting in thermodynamic advantage.

SR's high-capacity CO_2 sorbent provides fast adsorption/desorption kinetics, but regeneration with steam causes slow degradation that needs further investigation.



Case	B11B	B5B-Q	CSCC/WGS
Configuration			
Gasifier/Boiler	Subcritical	GE-Quench	GE-Quench
Water Gas Shift	None	Sour Shift	CSCC/WGS
CO_2 Removal	Cansolv PCC	2-Stage Selexol	w/above
Sulfur Removal	FGD	w/above	1-Stage Selexol
Capacity Factor	85%	80%	80%
CAPEX, $MM			
Bare Erected Cost	$1,465	$1,258	$1,150
Total Plant Cost (TPC)	$1,906	$1,681	$1,516
Total Overnight Cost (TOC)	$2,346	$2,086	$1,888
OPEX, $MM/yr (100% CF Basis)			
Fixed Operating Cost (OC_{fix})	$62.0	$62.3	$57.0
Variable Operating Cost, less Fuel (OC_{var})	$61.8	$42.1	$40.1
Fuel (OC_{fuel})	$131.7	$117.0	$117.0
Power Production, MWe			
Gas Turbine	N/A	464	464
Sweet Gas Expander	N/A	7	7
Steam Turbine	644	214	148
Auxiliary Power Consumption	94	190	156
Net Power Output	550	494	463
Fuel Rate and Efficiency			
Coal Feed Rate, tpd AR Coal	6,194	5,844	5,844
CO2 Capture Rate	90.0%	90.0%	90.8%
HHV Net Plant Efficiency, %	31.2%	29.7%	27.8%
COE, excl CO_2 TS&M, mills/kWh	133.5	138.7	138.3
COE, incl CO_2 TS&M, mills/kWh	143.5	148.9	149.3

Figure 4: TEA case comparisons.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
Pellet Density	kg/m^3	1,700	1,600
Bulk Density	kg/m^3	1,100	1,050
Average Particle Diameter	µm	150	150
Packing Density	kg/m^3	750	730
Sorbent Heat Capacity	kJ/kg-K	0.93	0.93
Manufacturing Cost for Sorbent	$/kg	0.47	TBD
Adsorption			
Total pressure	bar	40	40
Temperature	°C	350	350
Equilibrium Loading	g mol CO_2/kg	7.2	5.6
Heat of Adsorption	kJ/mol CO_2	-130	-130
Desorption			
Total pressure	bar	1	1
Temperature	°C	390	350
Heat of Desorption	kJ/mol CO_2	130	130

Definitions:

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Packing Density – Ratio of the active sorbent mass to the total adsorber volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figure 3 above.

Syngas Conditions – Pressure, temperature and composition of the gas entering the reactor, TRIG™ (air-blown) case:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	8.5	17.5	2.6	50.5	11.7	9.2	500

Pressure, temperature, and composition of the gas entering the reactor, GE (oxygen-blown) case:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	13.7	35.8	0.12	0.8	34.2	15.4	500

technology advantages

- Could replace conventional two-stage WGS reactor system with intercooling plus a separate CO_2 capture unit with a single WGS reactor unit, with potential for energy efficiency increase and equipment cost savings.
- Carbon dioxide capture drives equilibrium-limited WGS toward CO_2 and H_2.
- Integrated heat management maintains thermodynamically favorable reaction temperatures for both exothermic CO_2 capture/WGS and endothermic regeneration.
- The current state-of-the-art CO_2 capture process involves scrubbing the gas stream at low temperature. SR's elevated-temperature CO_2 capture technique eliminates the need to cool the gas stream coming from WGS reactor
- SR's high-capacity and highly regenerable CO_2 sorbent provides fast adsorption/desorption kinetics, which can be applied in a pressure swing process under minimum temperature swing condition.

R&D challenges

- High levels of CO and CO_2 in syngas.
- Effect of contaminants in coal syngas on MFECs, MFECs' thermal stability, and product selectivity maintained at high pressures and temperatures.
- Sorbent capacity, kinetics, and durability.
- WGS catalyst degradation during cycling.
- Heat management in reactor.
- Process integration with IGCC.
- Scale-up and integration given the large number of reactor modules needed to service a 550-MWe plant.

status

The project is complete. The hybrid CO_2 capture/WGS reactor has been run for hundreds of cycles at bench scale and testing has shown the sorbent to meet both CO_2 capture capacity and durability targets. WGS performance was close to target. Reactor modeling and techno-economic evaluation have been completed, and a 1,000-cycle test has been completed to gauge durability at optimum process conditions.

available reports/technical papers/presentations

Zhao S, McCabe K. and Gangwal, S. "*Combined Sorbent/WGS-based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," Final Scientific/Technical Report, April 2019.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Santosh Gangwal, Southern Research Institute, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2018.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Combined Magnesium Oxide/Water Gas Shift-Based CO_2 Capture Process,*" poster presentation at CO_2 Summit II: Technologies and Opportunities Conference, Santa Ana Pueblo, New Mexico, April 2016.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," project kickoff meeting presentation, October 2015.

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CARBON CAPTURE TECHNOLOGY SHEETS

R&D COLLABORATIONS

National Carbon Capture Center

primary project goals

The U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) and Southern Company operate the National Carbon Capture Center (NCCC), a neutral research facility working to advance technologies to reduce greenhouse gas emissions from natural gas- and coal-based power plants. Located in Wilsonville, Alabama, the center offers a unique test bed for third-party technology evaluations of cost-effective carbon dioxide (CO_2) capture technologies—bridging the gap between laboratory research and large-scale demonstrations.

The NCCC offers exceptional benefits to technology developers by providing them with testing opportunities in the real-world operating conditions of a power plant, thereby accelerating the commercialization of low-cost, carbon capture processes. The center has surpassed 110,000 hours of technology testing for carbon capture innovators from the United States and six other countries. Through the testing of more than 60 technologies, the center has directly participated in the reduction of the projected cost of carbon capture by one-third.

The NCCC will continue to meet its objective of evaluating advanced technologies, both domestic and international, to identify and resolve environmental, health and safety, operational, component, and system development issues, as well as to achieve scale-up and process enhancements in collaboration with technology developers. Evaluations of DOE-sponsored projects, as well as projects from industry, universities, and other collaborative institutions, will provide a full spectrum of technologies for testing at the center.

technical content

The DOE Office of Fossil Energy's NETL, in cooperation with Southern Company, established the NCCC in 2009 to provide an independent, flexible, and cost-efficient carbon capture technology testing facility with industrial operating conditions. In undertaking its mission, the center and its staff have been involved in a range of activities to develop the most promising carbon capture technologies for future commercial deployment.

The NCCC provides numerous test bays for simultaneous bench- and pilot-scale operation of advanced carbon capture technologies at commercially relevant process conditions. These include two fully integrated processes for solvent evaluations—a pilot-scale test unit (PSTU) and a bench-scale slipstream solvent test unit (SSTU)—as well as seven pilot- and bench-scale test bays. In addition to the flexible test site, the facility provides support for design, procurement, construction, installation, operation, data collection and analysis, and reporting in compliance with environmental and government regulations.

The types of technologies tested at the NCCC include advanced enzymes, membranes, sorbents, solvents, hybrids, and associated systems for carbon capture. Testing with the PSTU and SSTU is conducted to provide extensive data on physical properties of solvents and perform solvent emission and degradation studies.

technology maturity:

Laboratory-Scale/Bench-Scale/Pilot-Scale, Actual Flue Gas

project focus:

Carbon Capture Testing Center

participant:

Southern Company

project number:

FE0022596

predecessor projects:

NT0000749

NETL Project Manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

John Northington
Southern Company
jnorthin@southernco.com

partners:

American Electric Power, ClearPath Foundation, Electric Power Research Institute, ExxonMobil, NRECA, Peabody Energy, Inc., Tennessee Valley Authority, Total, Wyoming Infrastructure Authority

start date:

06.06.2014

percent complete:

90%

Since its inception, researchers at the NCCC have conducted numerous tests for the advancement of post-combustion carbon capture for pulverized coal or natural gas power plants, as well as gasification technologies and pre-combustion carbon capture. In mid-2017, after completing more than 30 projects in the gasification and pre-combustion carbon capture areas, the center concluded that scope of work. The gasification and pre-combustion carbon capture equipment is currently being decommissioned and dismantled.

While the demand for post-combustion carbon capture options grows, new projects are planned as the NCCC continues to bring advanced post-combustion carbon capture technologies closer to the marketplace. Significant infrastructure expansion is underway to increase carbon capture testing with flue gas under natural gas-fired conditions—research that will support the nation's continued reliance on natural gas as a reliable and affordable power generation resource. In addition, future testing at the NCCC will also include CO_2 utilization technologies.

Figure 1: Post-combustion test facilities at the National Carbon Capture Center.

technology advantages

The ability of the center's facilities to support multiple technology developers and tests simultaneously at various scales, and to offer flexibility in capacity and process conditions, provides a wide range of data and information to accelerate the commercialization of carbon capture technologies and enable natural gas- and coal-based power plants to achieve near-zero emissions while reducing capture costs. The NCCC project is instrumental in supporting the DOE objective of CO_2 capture in advanced coal-fired power plants at a cost of less than $30/tonne by 2030.

R&D challenges

As the need to reduce carbon emissions from fossil-fueled power generation continues to grow, adding carbon capture to fossil fuel-based electricity generation using conventional technologies would significantly increase the cost of electricity. To utilize the nation's abundant fossil-fuel resources in a carbon-constrained future, power generation must be equipped with advanced, cost-effective carbon capture technology. To address this challenge, the NCCC provides a highly skilled team, along with the infrastructure, realistic operating conditions, and flexible testing needed for commercial application of carbon capture for natural gas- and coal-based power generation.

status

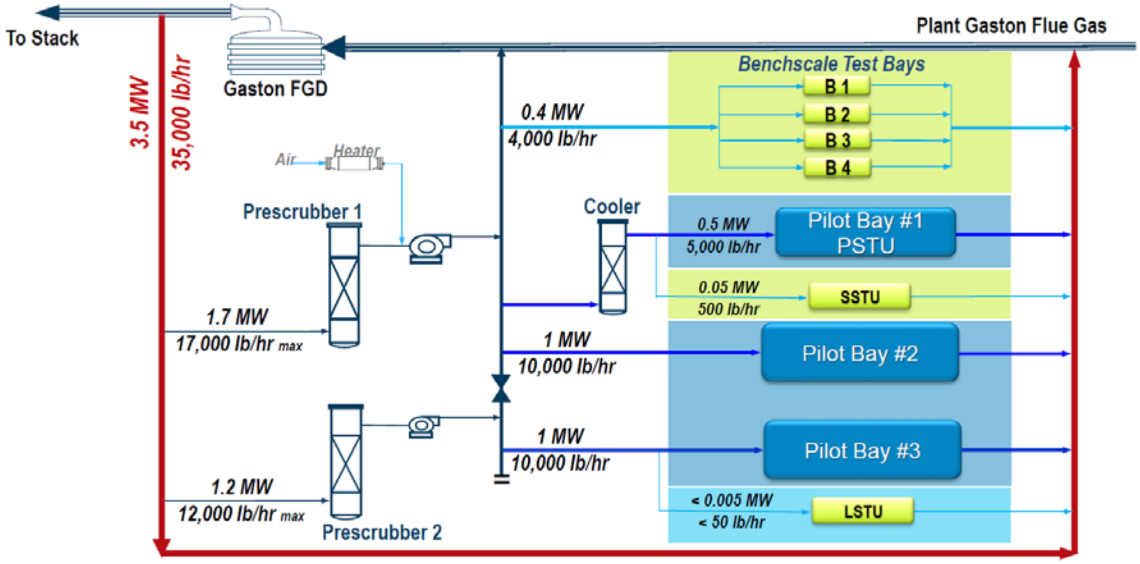

Figure 2: Diagram of post-combustion test facilities at the National Carbon Capture Center.

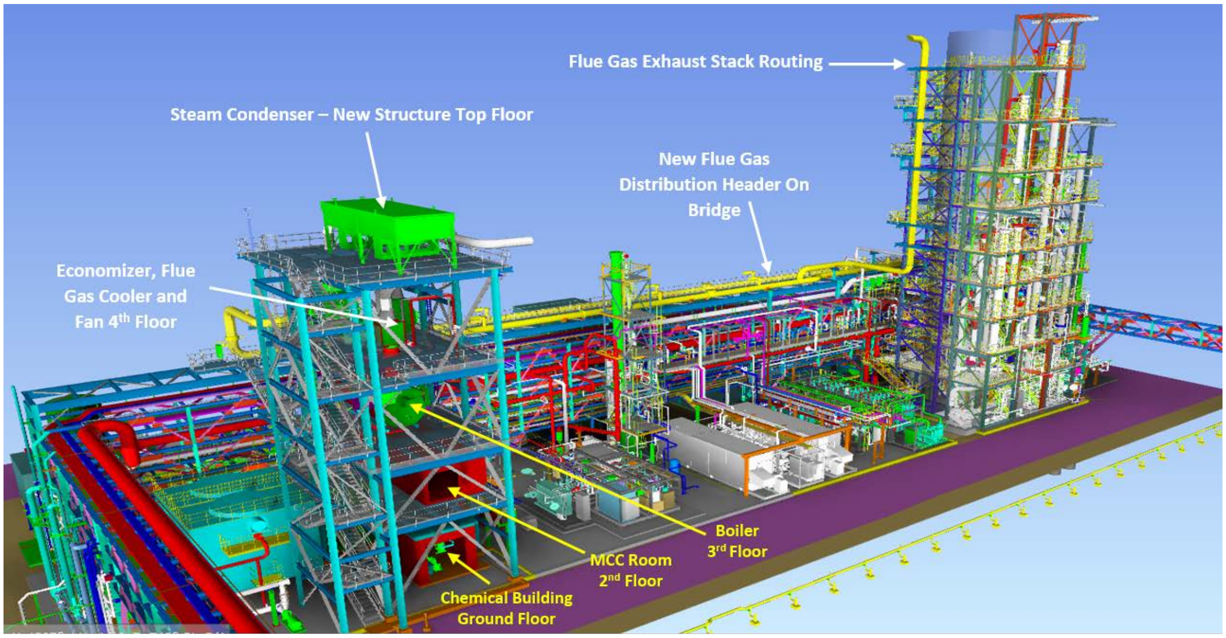

Figure 3: 3D model of natural gas testing system at the National Carbon Capture Center.

The center's post-combustion test facilities utilize a flue gas slipstream from Southern Company subsidiary Alabama Power's Plant Gaston Unit 5 (see Figure 2: Plant Gaston Flue Gas), a base-loaded, 880-megawatt (MW) supercritical pulverized coal boiler. The unit meets all environmental requirements utilizing state-of-the-art controls (see Figure 2: Flue Gas Desulfurization [FGD]); thus, the flue gas extracted for testing is fully representative of commercial conditions. As shown in Figure 2, the site houses up to four bench-scale and three pilot-scale technology developer units, the PSTU and SSTU for comprehensive solvent characterization, and the lab-scale test unit (LSTU) for bench-scale testing of mixed-matrix membranes and other technologies. An air dilution system is also available for carbon capture testing under simulated natural gas flue gas conditions.

Construction of a new system for generating natural gas-derived flue gas for carbon capture testing is progressing and expected to begin operation in 2020. This will create operational independence from the host coal unit, increase operational flexibility for the center, and provide a contaminant-free flue gas source to allow expanded testing of new technologies on both natural gas- and coal-derived flue gas.

Post-combustion operation has provided more than 60,000 hours of testing enzymes, membranes, sorbents, solvents, hybrids, and associated systems, and included 37 technologies from 25 developers, with eight technologies scaled-up (or ready) to be demonstrated at 10+ MW. More than 8,000 hours of testing has been conducted under simulated natural gas conditions. The PSTU has operated for more than 19,000 hours in support of commercial developers and DOE's Carbon Capture Simulation Initiative, with several solvents progressing to larger-scale testing at other facilities and commercial demonstration. Since its creation, the NCCC has more than doubled its plant capacity from 12,000 to 35,000 lb/hr flue gas and has added systems (SSTU, air dilution, etc.), along with enhanced instrumentation, sampling methods, and analysis systems. The new natural gas infrastructure currently being installed (see Figure 3: Natural Gas Testing System) will provide an equivalent capacity of natural gas-derived flue gas for carbon capture testing.

Prior to concluding the gasification and pre-combustion program, accomplishments in these areas included more than 50,000 hours of testing by technology developers. Scale-up and process intensification was achieved for several technologies. Gasification testing was conducted in both air- and oxygen-blown operation. Sensor testing involved tunable diode laser sensors, particulate monitors, thermowells, and coal feeder instrumentation. Water-gas shift (WGS) catalyst tests showed that steam-to-carbon monoxide ratios can be reduced, relative to traditional recommendations, which in turn increases the net power output of an integrated gasification combined-cycle plant and reduces the cost of electricity with carbon capture. A number of advanced CO_2-absorbing chemical and physical solvents, various hydrogen- and CO_2-selective membranes, WGS catalysts, high-temperature mercury capture sorbents, and solid oxide fuel cells were tested.

Performance data generated in post-combustion, gasification, and pre-combustion technology testing at the NCCC has been used to validate laboratory data allowing for engineering scale-up, in turn driving new breakthroughs in carbon capture solutions.

available reports/technical papers/presentations

Advanced Technology Testing at the National Carbon Capture Center, Presented by Michele Corser, Southern Company, 2019 NETL Carbon Capture, Utilization and Storage, and Oil and Gas Technologies Integrated Review Meeting, Pittsburgh, PA, Aug 2019.

Update on National Carbon Capture Center, Presented by Tony Wu, Southern Company, 2018 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, Aug 2018.

Advanced Technology Testing at the National Carbon Capture Center, Presented by John Carroll, Southern Company, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, Aug 2017.

2017 Update on Technology Testing at the National Carbon Capture Center, Presented by Barry Shirley, Southern Company, 42nd International Technical Conference on Clean Energy, Clearwater, FL, June 2017.

Advanced Technology Testing at the National Carbon Capture Center, Presented by Justin Anthony and John Carroll, Southern Company, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, Aug 2016.

Pre-Combustion Carbon Capture at the National Carbon Capture Center, Presented by John Socha, Southern Company, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

National Carbon Capture Center: Post-Combustion, Presented by Patrick Crossley, Southern Company, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

National Carbon Capture Center: Pre-Combustion CO_2 Capture, Presented by Tony Wu, Southern Company, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. (July 2014)

National Carbon Capture Center: Post-Combustion, Presented by John Wheeldon, National Carbon Capture Center, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Website: *https://www.nationalcarboncapturecenter.com/*.

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COMPENDIUM OF CARBON CAPTURE TECHNOLOGY

APPENDIX: Completed Projects

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: POST-COMBUSTION SOLVENT TECHNOLOGIES

Bench-Scale Process for Low-Cost Carbon Dioxide Capture Using a Phase-Changing Absorbent

primary project goals

GE Global Research is designing and optimizing a bench-scale process using a novel phase-changing aminosilicone-based carbon dioxide (CO_2)-capture solvent (absorbent) to establish scalability and technical and economic feasibility of using a phase-changing CO_2-capture absorbent for post-combustion capture, with the ultimate goal of achieving an overall reduction in CO_2 capture cost.

technical goals

- Design and build a bench-scale system for post-combustion CO_2 capture using a phase-changing aminosilicone-based solvent.
- Develop preliminary process and cost models.
- Conduct bench-scale testing on unit operations to evaluate performance and define parameters for scale-up.
- Evaluate materials of construction, manufacturability of solvent, assemble continuous bench-scale system, and update the process model.
- Perform testing on continuous system to optimize process parameters.
- Perform EH&S and techno-economic assessments and devise a scale-up strategy.

technical content

GE Global Research is designing and optimizing a new process for a phase-changing CO_2 capture solvent for use in post-combustion capture in coal-fired power plants. The process is based on the use of the silicone-based phase change solvent (GAP-0), which was developed at the lab-scale in a previous ARPA-E project (DE-AR0000084). The liquid solvent rapidly absorbs CO_2 at low temperatures (40–50 °C) with high loading (>17 percent weight gain) to form a solid carbamate salt. The carbamate salt readily decarboxylates at high temperatures. The innovative process is designed to make use of the unique phase-change properties of the aminosilicone solvent.

The process as originally designed, shown in Figure 1, starts in the absorber, where the liquid phase-changing solvent is sprayed in fine droplets into the flue gas, reacting with the CO_2 to form solid particles. The solids are conveyed in an extruder, moving from the low-temperature, low-pressure absorber to the high-temperature, high-pressure desorber. The unique design of the extruder permits heating and compression of the solids, allowing for continuous delivery of the solids into the pressurized desorber. The solids are heated in the desorber, leading to decarboxylation. CO_2 is separated from the liquid phase-changing solvent in the desorber, allowing for recovery of the CO_2 and recycle of the solvent.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Phase-Changing Absorbent

participant:

GE Global Research

project number:

FE0013687

predecessor projects:

ARPA-E project DE-AR0000084

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Tiffany Westendorf
GE Global Research
westendo@research.ge.com

partners:

Coperion Corporation

start date:

01.01.2014

percent complete:

100%

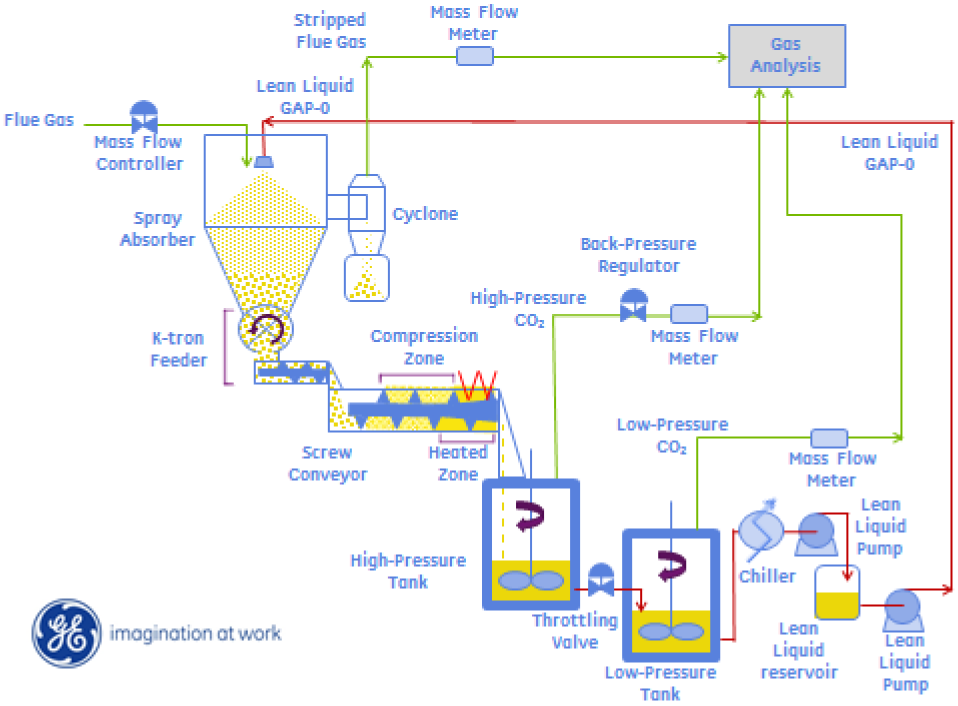

Figure 1: Phase-changing absorbent process

During the project, the process was modified based on understanding water effects on the carbamate and thermal stability of the carbamate. This revised process, as shown in Figure 2, produces a water-carbamate solids slurry in the spray absorber, which is transferred to the desorber inlet by a slurry pump. The single stage desorber operates at near-atmospheric pressure.

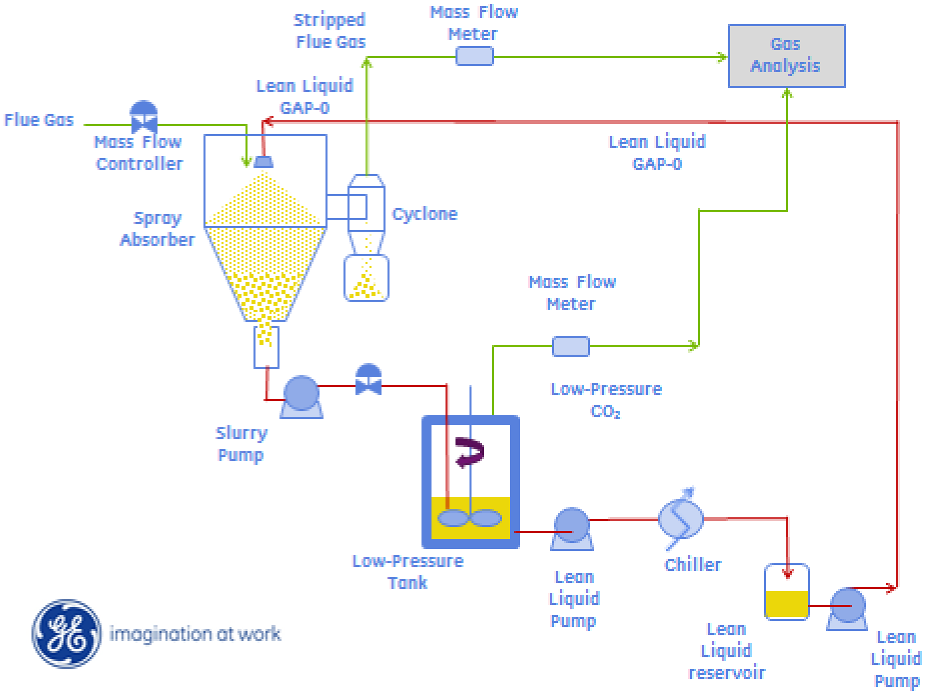

Figure 2: Updated process using a slurry rich phase

Testing of the bench-scale system provided data, including mass transfer parameters, kinetic parameters, heat transfer parameters, solvent stability, effects of flue gas contaminants, and recommended operating conditions, to perform a techno-economic assessment and develop a scale-up strategy. The project aimed to establish scalability and technical and economic feasibility of using a phase-changing CO_2-capture absorbent for post-combustion capture of CO_2 from coal-fired power plants.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	248.51	248.51
Normal Boiling Point	°C	258.7	258.7
Normal Freezing Point	°C	<0	<0
Vapor Pressure @ 15 °C	bar	1.8×10^{-5}	1.8×10^{-5}
Manufacturing Cost for Solvent	$/kg	TBD	TBD
Working Solution			
Concentration	kg/kg	1	0.9
Specific Gravity (15 °C/15 °C)	-	0.891	0.891 (GAP-0)/1.0 (water)
Specific Heat Capacity @ STP	kJ/kg-K	2.29	2.29 (GAP-0)/4.18 (water)
Viscosity @ STP	cP	4.4	12.3 (10% water, 90% GAP-0)
Absorption			
Pressure	bar	1	1
Temperature	°C	30	40-60
Equilibrium CO_2 Loading	mol/mol	0.9	0.65
Heat of Absorption	kJ/mol CO_2	-113.4	-113.4
Solution Viscosity	cP	N/A	N/A
Desorption			
Pressure	bar	7	1
Temperature	°C	160	130
Equilibrium CO_2 Loading	mol/mol	0.34	0.23
Heat of Desorption	kJ/mol CO_2	-113.4	-113.4
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,767,497	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 150	
Absorber Pressure Drop	bar	TBD	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA} in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption

Solvent Contaminant Resistance – Solvent absorbs sulfur dioxide (SO_2), forming heat-stable salts.

Solvent Foaming Tendency – Limited.

Flue Gas Pretreatment Requirements – Flue gas desulfurization, cooling to <40 °C.

Solvent Make-Up Requirements – TBD.

Waste Streams Generated – In the commercial scale process, a small slipstream of the phase-changing absorbent may be purged from the process to limit accumulation of sulfur compounds in the solvent.

Process Design Concept – See Figure 2 above.

technology advantages

- Non-aqueous, pure solvent.
- Superior properties compared to reference case (MEA) results in potential for cost reduction.
    - Lower heat capacity.
    - Low corrosivity.
    - Low vapor pressure.
- High CO_2 loading and intensified mass transfer requires smaller equipment.

R&D challenges

- Cost and availability of the solvent.

- Thermal degradation of solvent.
- Development of an advanced low-temperature desorber.
- Development of correlations between the primary system variables and unit operations performance to determine scale-up effects, particularly on heat transfer in the absorber and desorber.

status

GE and NETL mutually agreed to terminate the project prior to completion of the final task due to internal changes within GE. GE had designed, built, and tested a bench-scale system to evaluate their phase-changing solvent system. A techno-economic assessment based on bench-scale testing data indicated a first-year CO_2 capture cost of $52.1/tonne compared to $66.4/tonne for an aqueous amine process, with cost improvement primarily due to higher working capacity, lower corrosivity, lower vapor pressure, and lower heat capacity of the phase changing solvent. However, as much as $88/tonne could be added to the CO_2 capture cost for solvent make-up costs due to the thermal degradation of this solvent at the Continuous Stirred Tank Reactor (CSTR) desorber operating temperatures, confirming the need for development of a low-temperature desorber.

available reports/technical papers/presentations

"Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," Final Report, May 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/fe0013687-final-report.pdf*

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/T-Westendorf-GE-Phase-Changing-Absorbent.pdf*

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Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," Budget Period 1 Briefing Presentation, Pittsburgh, PA, February 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/2015-02-23-DE-FE0013687-BP1-briefing.pdf*

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Accelerating the Development of “Transformational” Solvents for CO_2 Separations

primary project goals

Pacific Northwest National Laboratory (PNNL) developed transformational carbon dioxide (CO_2) capture solvents based on their nonaqueous switchable organic solvents, known as CO_2-binding organic liquids (CO_2BOLs). The project focus used computation-aided molecular design to optimize, synthesize, and characterize CO_2BOLs with a CO_2-rich viscosity of less than 50 cP at a cost of less than $10/kg.

technical goals

- Develop a physical property model to predict the viscosity of CO_2BOL compounds.
- Develop a model to predict thermodynamic properties of CO_2BOL compounds.
- Design and synthesize promising CO_2BOL candidate compounds and compare solvent properties with predicted molecular simulations.
- Synthesize candidates meeting desired cost and viscosity targets for further evaluation to determine how molecular structure impacts solvent system viscosity.
- Update thermodynamic and process models using data from CO_2BOL testing to predict process performance and cost.

technical content

Solvent Platform

PNNL developed transformational CO_2 capture solvents based on their nonaqueous switchable organic solvents, known as CO_2BOLs. This project advanced the development efforts of the previously funded DOE project DE-FE0007466.

CO_2BOLs are a class of switchable ionic liquids (molecular liquids that become ionic in the presence of CO_2) that have lower specific heat and higher CO_2 working capacities compared to aqueous amines, resulting in potential savings in the sensible heat required to strip CO_2.

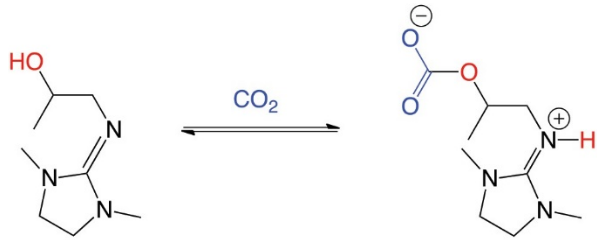

Figure 1: Uptake of CO_2 by Alkanolguanidine BOL (left), and formation of Zwitterionic CO_2BOL (right)

Like aqueous amines, CO_2BOLs are basic, but the base (e.g., guanidine, amidine) does not directly react with CO_2. Instead, the alcohol component reacts with CO_2, forming

technology maturity:
Laboratory Scale

project focus:
CO_2-Binding Organic Liquid (CO2BOL) Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-65872

predecessor projects:
FE0007466

NETL project manager:
Isaac Aurelio
Isaac.aurelio@netl.doe.gov

principal investigator:
David Heldebrant
Pacific Northwest National Laboratory
david.heldebrandt@pnnl.gov

partners:
N/A

start date:
04.01.2014

percent complete:
100%

alkyl carbonic acid, and subsequently transfers a proton to the base, forming liquid alkylcarbonate. Current CO_2BOL generation combines the base and the alcohol moieties in a single molecule, lowering volatility (Figure 1).

The addition of a non-polar solvent (anti-solvent) to CO_2BOLs and other switchable solvents during the solvent regeneration destabilizes bound CO_2, thus potentially lowering the temperature at which the stripper can be operated; (this is referred to as the polarity-swing-assisted regeneration [PSAR] process). Preliminary results indicate that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C. This allows novel possibilities for heat integration, such as transferring heat from the absorber to the stripper using heat pumps, thereby lowering steam demand for solvent regeneration. The anti-solvent can be separated out from the CO_2BOL by cooling and liquid-liquid phase separation. A schematic of the CO_2BOL-PSAR process is shown in Figure 2.

Previous generations of single-component CO_2BOLs were highly viscous before CO_2 absorption. The current generation of alkanolguanidine CO_2BOLs has lower viscosity before CO_2 absorption.

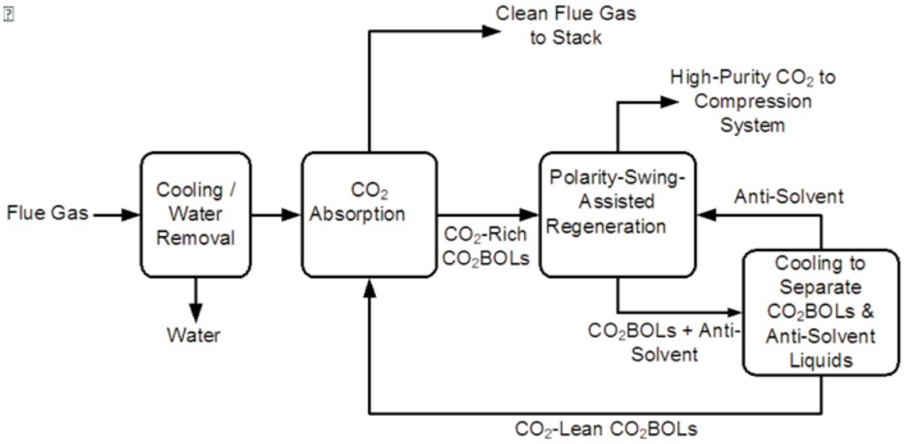

Figure 2: CO_2BOL absorption and PSAR process

The solvent and process parameters identified to date are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	171.14	171.14
Normal Boiling Point	°C	262 (decomposes >200)	262 (decomposes >200)
Normal Freezing Point	°C	<0	<0
Vapor Pressure @ 15 °C	bar	0.179 (37 °C) (DBU) 0.001 (100 °C)	0.001
Manufacturing Cost for Solvent	$/kg	$35	$10
Working Solution			
Concentration	kg/kg	1 (anhydrous) 0.91 (hydrated)	1 (anhydrous) 0.91 (hydrated)
Specific Gravity (15 °C/15 °C)	-	1.03	1.03
Specific Heat Capacity @ STP	kJ/kg-K	1.9	1.9
Viscosity @ STP	cP	1.9 (CO_2-free solvent) 50 (lean solvent)	1.9 (CO_2-free solvent) 11 (lean solvent)
Absorption			
Pressure	bar	1 (near atmospheric, 0.15 bar CO_2 partial pressure)	1 (near atmospheric, 0.15 bar CO_2 partial pressure)
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5 (at 0.15 bar CO_2 partial pressure)	0.5 (at 0.15 bar CO_2 partial pressure)
Heat of Absorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Solution Viscosity	cP	356	50
Desorption			
Pressure	bar	2	2
Temperature	°C	103.8	103.8
Equilibrium CO_2 Loading	mol/mol	0.25	0.25
Heat of Desorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Molecular Design and Optimization

The objective of this project was to expand DOE's Office of Fossil Energy's (FE) capabilities for molecular design and optimization of transformational solvent systems, starting with PNNL's CO_2BOLs solvent platform as a model for this activity. Key program metrics include identification of a viable candidate with a CO_2-loaded viscosity below 50 cP and at a cost no greater than $10/kg, and to learn why viscosity increases occur in water-lean solvents and how to minimize viscosity increases. To achieve this, PNNL has developed a novel physical property prediction model that can accurately reproduce laboratory-measured material properties. Previously synthesized and characterized CO_2BOL derivatives from PNNL's completed programs were used to establish the molecular model. A concurrent molecular design effort was started to produce libraries of new compounds with reduced viscosity by introducing design motifs based on organic chemistry principles. Once the molecular model was completed, molecules in the library were simulated to determine which compounds showed reduced viscosity, and, more importantly, why they were less viscous. Modeled compounds are compared against synthesized compounds for validation and refinement (Figure 3). Once design principles were discovered, these new structural motifs were introduced into subsequent molecular designs to achieve reductions in rich-solvent viscosity.

To date, the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The model has identified hydrogen bonding and electrostatic (specifically dipole-dipole between molecules) interactions as the most critical design elements for low-viscosity CO_2BOLs, and from this knowledge we have designed and simulated hundreds of molecules, with tens of candidate molecules that are projected to be less viscous than the previous derivative. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE's solvent portfolio.

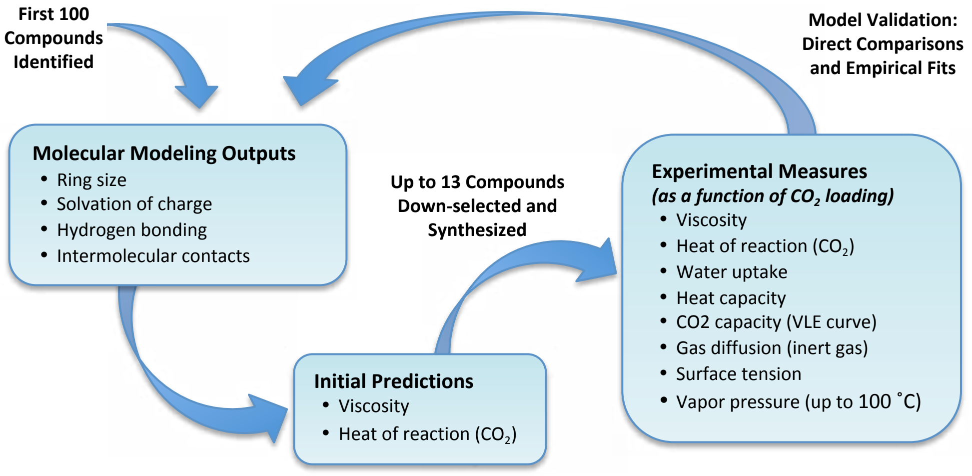

Figure 3: Molecular modeling prediction vs. experimental measures

Definitions:

***STP* –** Standard temperature and pressure (15 °C, 1 atm).

***Pure Solvent* –** Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

***Manufacturing Cost for Solvent* –** "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

***Working Solution* –** The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

***Absorption* –** The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

***Desorption* –** The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

***Pressure* –** The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

***Concentration* –** The mass fraction of pure solvent in working solution.

***Loading* –** The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism **–** The chemical reaction for the CO_2 capture process with a representative CO_2BOL is shown in Figure 1.

Solvent Contaminant Resistance **–** Tests of CO_2BOL reactivity with hydrogen chloride (HCl), sulfur oxide (SO_x) and nitrogen oxide (NO_x) will be conducted. In general, CO_2BOLs form heat-stable salts (HSS) with sulfur dioxide (SO_2), NO_x, and HCl. The solvent can be recovered from the HSS using caustic wash or with ion exchange resins. Levels of HSS formation are expected to be similar to that of MEA. Minimal adverse impacts due to arsenic and mercury in the flue gas are expected.

Solvent Foaming Tendency **–** Foaming tendency has not been observed in prior formulations during bench-scale testing. Foaming of future derivatives remains unknown.

Flue-Gas Pretreatment Requirements **–** Water management with any of the alkanolguanidine-based CO_2BOLs is different from that with MEA.CO_2BOL solvents are designed to minimize water uptake by the solvent, as the presence of water increases solution viscosity and increases the energy required to regenerate the CO_2BOL. As such, CO_2BOL formulations are favored energetically to run with a 5 wt% steady-state loading of water. To achieve this loading target, the process requires a small refrigeration unit upstream of the absorber to condense out water. Other flue-gas pretreatment requirements (for acid-gas contaminants) are expected to be similar to those with MEA.

Solvent Makeup Requirements **–** Until a formal lifetime analysis can be made, the estimated makeup rate of CO_2BOLs will depend on the anticipated thermal and chemical degradations. Currently, evaporative losses are projected to be 40 kg per annum.

Waste Streams Generated **–** CO_2BOLs have lower vapor pressure than MEA, and post-absorber CO_2BOL emissions would be at lower levels (estimated at 0.7 parts per billion [ppb]). Other major waste streams may include stripper wastes and reclaimer wastes.

Proposed Module Design **–** Unless noted, the following should be assumed for flue gas leaving the flue gas desulfurization (FGD) (wet basis): feed pressure 1.014 bar, temperature 57 °C, and composition as shown in the table below.

Pressure	Temperature	Composition						
		vol%					ppmv	
bara	°C	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1.014	57	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

Solvent Platform

- The lower solvent specific heat and water content leads to smaller parasitic load than current solvents (MEA).
- The lower solvent evaporative losses and thermal degradation may lead to lower cost of CO_2 capture.
- The rates of liquid-phase mass-transfer kinetics with CO_2BOLs are comparable to those of current solvents (MEA and piperazine), albeit at higher solution viscosity.
- PSAR may enable low-temperature CO_2BOL regeneration, reducing the pressure of low-pressure steam used for regeneration, thereby increasing net power production and reducing parasitic loads.
- Heat integration possibilities with PSAR and CO_2BOLs may have minimal impact on steam plant cycles, facilitating retrofits for existing plants.

Molecular Design and Optimization

- The current PNNL-developed reduced molecular model can predict solvent thermodynamic and kinetic behavior, providing projections of solution viscosity and heats of reaction. This model enables rapid screening of advanced water-lean solvent platforms for development, as compared to conventional computationally intensive molecular dynamics simulations.
- The PNNL model has identified hydrogen bonding and electronic stacking as the two most critical contributors to viscosity in water-lean solvent platforms such as CO_2BOLs, enabling rapid optimization of solvent chemistry.
- The PNNL model is translatable to other solvent platforms across DOE’s portfolio.

R&D challenges

Solvent Platform

- The estimated cost of manufacturing the current-generation CO_2BOL solvent is high, leading to high operation costs.
- Water absorption by the CO_2BOL requires the amount of water in the flue gas to be reduced significantly by refrigeration to avoid water buildup in the solvent recirculation loop. However, these nominal capital costs and auxiliary electric loads are recovered in the net power gains by the PSAR.

Molecular Design and Optimization

- The challenge is to make targets from molecular predictions at a cost of $10/kg.

status

The project was completed on September 30, 2017. PNNL results indicated that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C, allowing novel possibilities for heat integration thereby lowering steam demand for solvent regeneration. PNNL also determined that the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE's solvent portfolio.

available reports/technical papers/presentations

Heldebrant, D., "Accelerating the Development of 'Transformational' Solvents for CO2 Separations," 2017 NETL CO2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/2D-Heldebrant2-PNNL-Transformational-Solvents.pdf*

Heldebrant, D., "Accelerating the Development of Transformational Solvent Systems for CO2 Separations," June 20, 2017, Morgantown, WV. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/PNNL-FWP-65872-Project-Update-June-2017.pdf*

Heldebrant, D., Final Report, "CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," August 31, 2014. *http://www.osti.gov/scitech/servlets/purl/1151840*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2014 CO_2 Capture Technology Meeting, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/D-Heldebrant-PNNL-CO₂-Binding-Organic-Liquids.pdf*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2013 CO_2 Capture Technology Meeting, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/Events/2013/CO₂%20Capture/D-Heldebrant-Battelle--Organic-Liquids-with-PSA-Regen.pdf*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2012 CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/co2-binding-organic-liquids-gas-capture-july2012.pdf*.

Large Pilot-Scale Carbon Dioxide (CO_2) Capture Project Using Aminosilicone Solvent

primary project goals

GE Global Research developed a plan to define a 10-MW_e large pilot-scale project for post-combustion carbon dioxide (CO_2) capture using their novel aminosilicone-based solvent, minimizing and quantifying risks associated with technical success, cost, and schedule. The information from this Phase I project can be used to inform the experimental design, budget, and schedule for a Phase II pilot test project.

technical goals

- Evaluate and select a site for the 10-MW_e large pilot plant.
- Qualify a supplier for the aminosilicone solvent.
- Develop a technology gap analysis, a screening-level design and cost estimate.
- Prepare an environmental, health, and safety assessment.
- Complete a techno-economic analysis for the CO_2 capture system.

technical content

GE Global Research, in Phase I of this large-pilot project, developed a project plan for large-scale (10-MW_e) testing of their aminosilicone-based solvent CO_2 capture process. In prior project FE0013755, GE Global Research designed, constructed, and operated a 0.5-MW_e slipstream post-combustion CO_2 capture pilot-scale process using this solvent at the NCCC Pilot Solvent Test Unit (PSTU), as shown in Figure 1. The process is based on the use of the aminosilicone-based solvent which was developed on the bench-scale in previous US DOE funded projects (DE-FE0007502 and DE-NT0005310). Specifically, the solvent system is composed of a mixture of GAP-1m and triethylene glycol (TEG). The carbamate formed upon CO_2 absorption does not precipitate out in this solvent mixture. The solvent has a much lower volatility than monoethanolamine (MEA), which simplifies the desorption process and decreases the energy required for CO_2 desorption. The solvent can be regenerated at elevated pressures, resulting in lower compression costs. The solvent also shows higher CO_2 capacity, high thermal stability, and low corrosivity.

technology maturity:

Large Pilot-Scale (10-MW_e),
Actual Flue Gas

project focus:

Aminosilicone Solvent

participant:

GE Global Research

project number:

FE0026498

predecessor projects:

FE0013755
FE0007502
NT0005310

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

Philip DiPietro
GE Global Research
phil.dipietro@ge.com

partners:

N/A

start date:

10.01.2015

percent complete:

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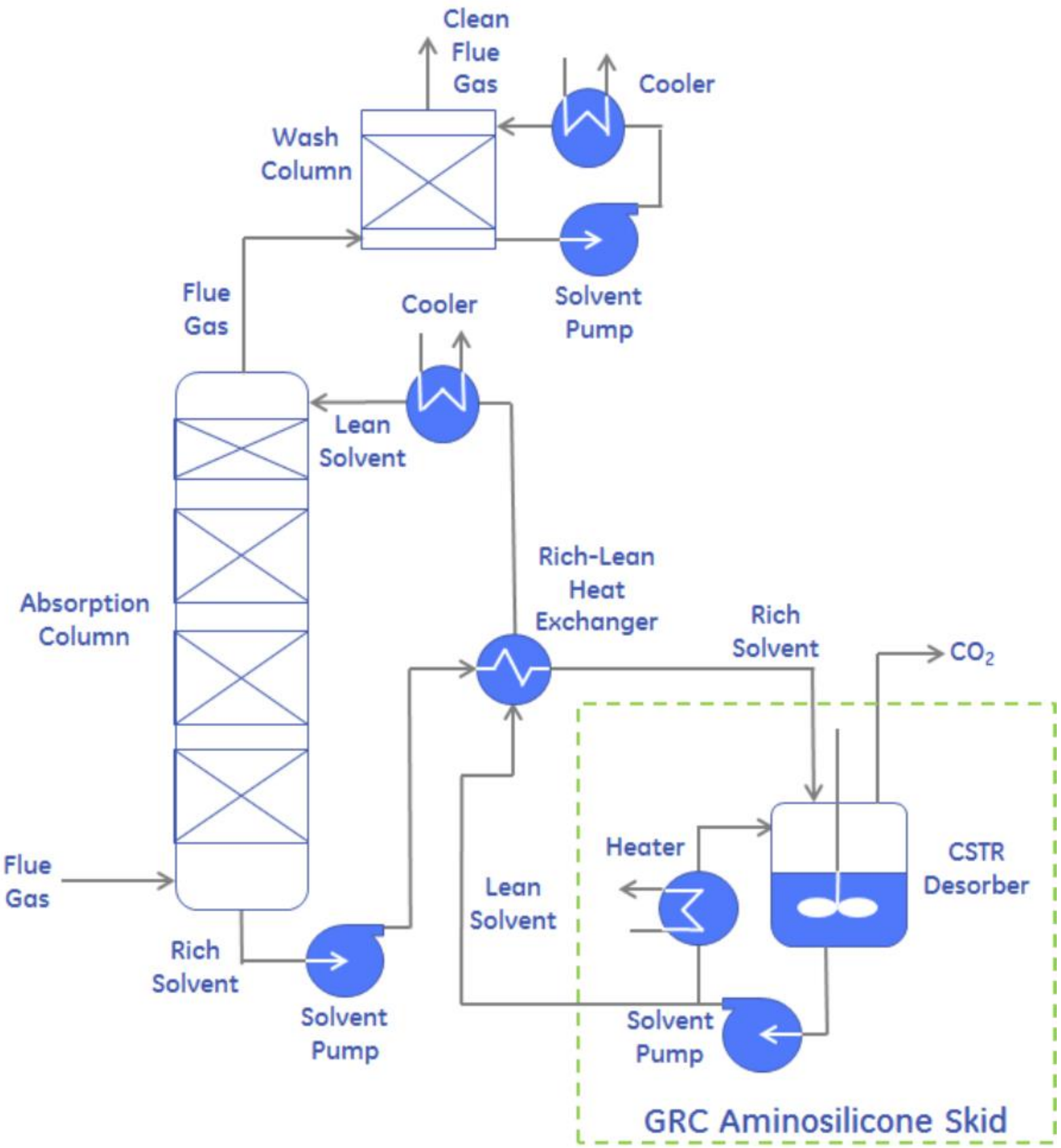

Figure 1: Pilot-scale system at NCCC

Testing on the 0.5-MW_e pilot-scale system using coal-fired flue gas provided data, including mass transfer parameters, kinetic parameters, heat transfer parameters, solvent stability, effects of flue gas contaminants, and recommended operating conditions, to update process models and to perform a techno-economic assessment and determine a scale-up strategy.

Two different desorption concepts were evaluated. The first, as shown above in Figure 1, used a continuous stirred tank reactor (CSTR) for desorption. The benefits of this concept include lower capital cost, simple operation, single stage desorption, and a small footprint. Adding water recycle can lower thermal degradation, decrease wastewater, and reduce solvent loss.

The other concept evaluated, shown in Figure 2, used a steam stripper column (SSC). This is a multistage desorption process resulting in a lower desorption temperature.

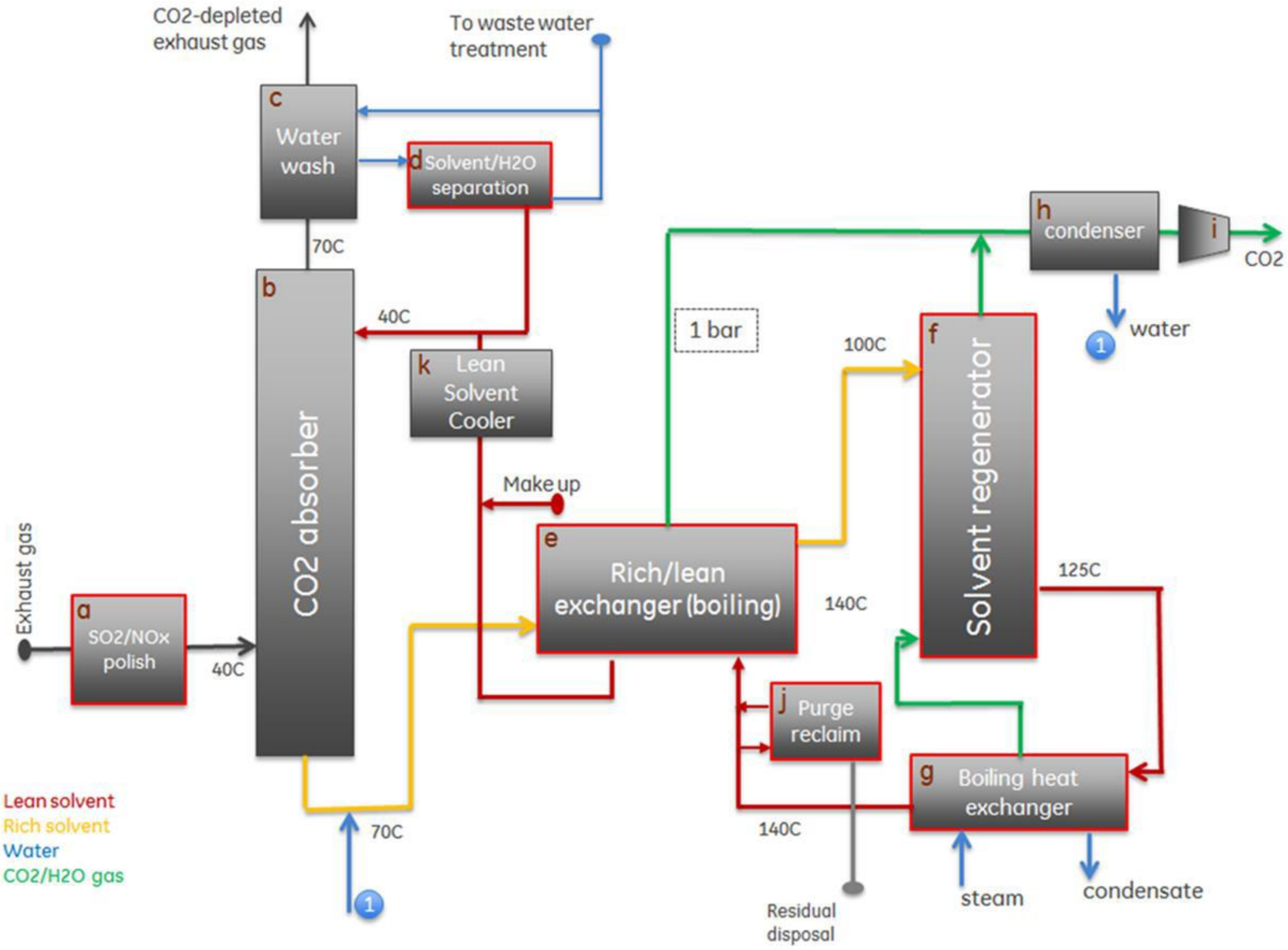

Figure 2: Process design with steam stripper

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	322.67 (GAP-1$_m$)/150.17 (TEG)	322.67 (GAP-1$_m$)/150.17 (TEG)
Normal Boiling Point	°C	310 (GAP-1$_m$)/287 (TEG)	310 (GAP-1$_m$)/287 (TEG)
Normal Freezing Point	°C	-85 (GAP-1$_m$)/-7 °C (TEG)	-85 (GAP-1$_m$)/-7 °C (TEG)
Vapor Pressure @ 15°C	bar	0.005 bar @ 140 °C (TEG) 0.037 bar @ 140 °C (GAP-1m)	0.005 bar @ 140 °C (TEG) 0.037 bar @ 140 °C (GAP-1m)
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	60/40 GAP-1$_m$/TEG	60/40 GAP-1$_m$/TEG
Specific Gravity (15°C/15°C)	-	0.913 (GAP-1$_m$)/1.124 (TEG)	0.913 (GAP-1$_m$)/1.124 (TEG)
Specific Heat Capacity @ STP	kJ/kg-K	2.319 (60/40 GAP-1$_m$/TEG)	2.319 (60/40 GAP-1$_m$/TEG)
Viscosity @ STP	cP	4.37 (GAP-1$_m$)/49 (TEG)	4.37 (GAP-1$_m$)/49 (TEG)
Absorption			
Pressure	bar	0 (gauge)	0 (gauge)
Temperature	°C	40-60 °C	40-60 °C
Equilibrium CO_2 Loading	mol/mol	0.78 (CO_2)/1 (GAP-1$_m$)	0.78 (CO_2)/1 (GAP-1$_m$)
Heat of Absorption	kJ/mol CO_2	99.7 (60/40 GAP-1$_m$ in TEG)	99.7 (60/40 GAP-1$_m$ in TEG)
Solution Viscosity	cP	431 (60/40 GAP-1$_m$ in TEG)	431 (60/40 GAP-1$_m$ in TEG)
Desorption			
Pressure	bar	2 (gauge)	2 (gauge)
Temperature	°C	140 °C	140 °C
Equilibrium CO_2 Loading	mol/mol	0.25 (CO_2)/1 (GAP-1)	0.25 (CO_2)/1 (GAP-1)
Heat of Desorption	kJ/mol CO_2	99.7 (60/40 GAP-1$_m$ in TEG)	99.7 (60/40 GAP-1$_m$ in TEG)
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	99.7 (60/40 GAP-1$_m$ in TEG)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 3	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure psia	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The reaction of the GAP class of aminosilicones with CO_2 is shown in Figure 2. The aminosilicone in this study is a mixture of GAP molecules where the average value of the subscript (x) shown in Figure 2 is one. This solvent is designated GAP-1. GAP-1 is combined with TEG in a 60/40 (by weight) mixture to inhibit the solidification that occurs when the neat solvent (GAP-1) reacts with CO_2.

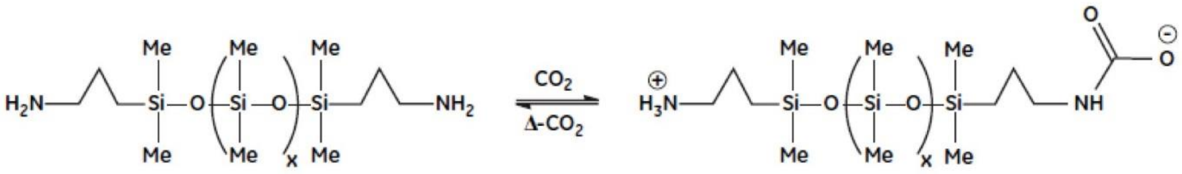

Figure 2: Reaction of GAP class of aminosilicones with CO_2 to form GAP carbamate

Solvent Contaminant Resistance – As with MEA, aminosilicones will react irreversibly with sulfur dioxide (SO_2) to form heat- stable salts (HSS). Solvent makeup will be required to replace aminosilicone lost to reaction with SO_2.

Solvent Foaming Tendency – None observed.

Flue Gas Pretreatment Requirements – In a full-scale system, the flue gas pretreatment requirements are identical to those of an MEA-based process, including a selective catalytic reduction reactor, particulate removal, and flue gas desulfurizer (FGD).

Solvent Make-Up Requirements – In addition to the solvent makeup required due to reaction of aminosilicone with SO_2, additional solvent makeup will be required due to thermal decomposition. However, it has been demonstrated that GAP-1 is significantly more thermally stable than MEA, as discussed below.

Waste Streams Generated – A waste stream of HSS from the reaction of SO_2 with aminosilicone will be generated.

Process Design Concept – The process flow diagram for the aminosilicone-based, bench-scale CO_2-capture system is shown in Figure 3.

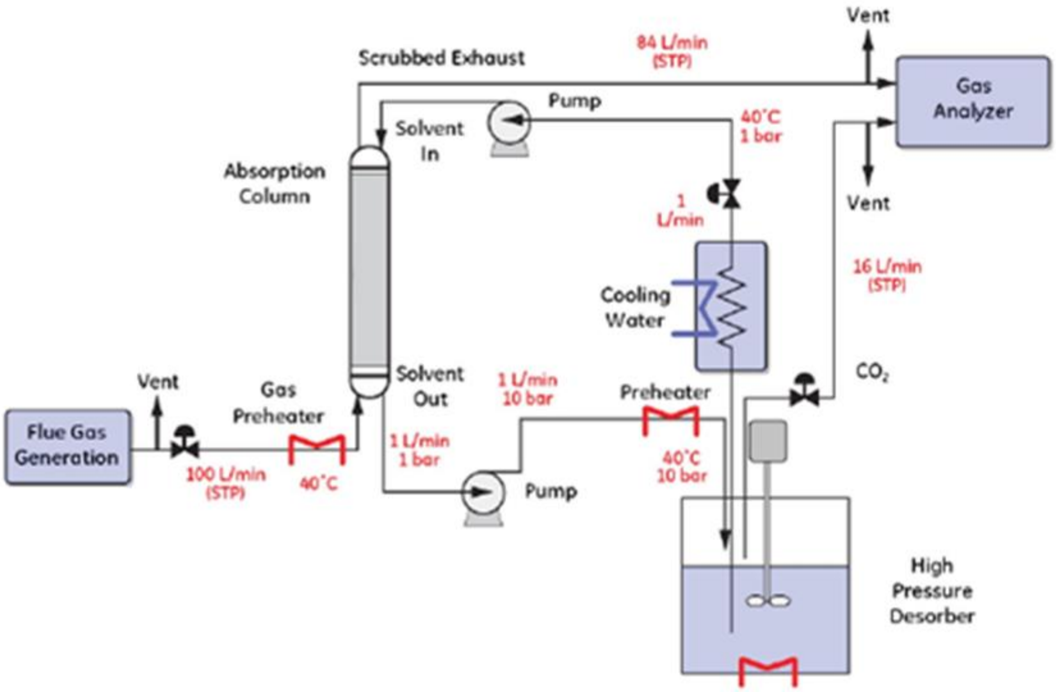

Figure 3: The process flow diagram for the bench-scale system

technology advantages

- Lower volatility.
    - Simplified separations.
    - Less energy wasted vaporizing solvent and/or water.
    - Lower airborne release rates.
- Lower heat capacity.
- Reduced corrosion.
- Potential for decreased issues with aerosol formation.

R&D challenges

- Completing design to integrate the process into the host site.

status

This project was completed. GE qualified a major chemical manufacturer as the GAP-1 solvent supplier. A 100-kg solvent sample was received and tested on the bench-scale, meeting purity and performance specifications. The phase I project effort identified Technology Centre Mongstad as a host site, and designed and estimated the cost for retrofit to accommodate the GE solvent at the TCM plant. The techno-economic analysis indicated a CO_2 removal cost using the steam stripper for desorption as \$42/tCO_2 (entitlement) and \$48/tCO_2 (with degradation, at ~15 percent/year solvent makeup). The CO_2 removal cost using the CSTR desorber was higher, with the cost dominated by the solvent make-up costs. Due to a schedule slip in the testing at NCCC (predecessor project FE0013755), GE decided not to submit a Phase II application.

available reports/technical papers/presentations

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Wood, B., “Pilot-Scale Silicone Process for Low-Cost CO_2 Capture,” 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *http://netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/B-Wood-GE-Pilot-Silicone-Process.pdf*

Wood, B., “Pilot-Scale Silicone Process for Low-Cost CO_2 Capture,” 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/B-Wood-GE-Pilot-Scale-Silicone-Process.pdf*.

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Wood, B., “Bench-Scale Silicone Process for Low-Cost CO_2 Capture,” 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/B-Wood-GE-Bench-Scale-Silicone-Process.pdf*.

Wood, B., “Bench-Scale Silicone Process for Low-Cost CO_2 Capture,” 2012 NETL CO_2 Capture Technology Meeting, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/bench-scale-silicone-process-low-cost-july2012.pdf*.

Wood, B., “Bench-Scale Silicone Process for Low-Cost CO_2 Capture,” Project Kick-Off Meeting Presentation, Pittsburgh, PA, November 22, 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/bench-scale-silicone-process-low-cost-kickoff-nov2011.pdf*.

Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas

primary project goals

Southern Company Services developed viable heat integration methods for the capture of carbon dioxide (CO_2) produced from pulverized coal (PC) combustion. The project quantified energy efficiency improvements to an existing amine-based CO_2 capture process by utilizing a waste heat recovery, high-efficiency system (HES) and evaluated the technical and economic feasibility of full-scale implementation of this technology.

technical goals

- Reduction of the amount of extraction steam required for sensible heat load in the solvent regeneration system by providing process stream heating through waste heat streams.
- Heating of boiler feed water through waste heat to reduce extraction steam demands on the low-pressure (LP) turbine.
- Increasing LP steam available for power generation or CO_2 regeneration.

technical content

Southern Company Services developed viable heat integration methods for the capture and sequestration of CO_2 produced from PC combustion. A waste heat recovery technology, HES, was integrated with an existing 25-megawatt electric (MW_e) amine-based CO_2 capture process, (MHI's Kansai Mitsubishi Carbon Dioxide Recovery (KM-CDR™) process), at Plant Barry to evaluate improvements in the energy efficiency of the CO_2 capture process. Pilot-scale testing also provided operational experience to determine the stability of the integrated HES/CO_2 capture process, particularly with use of a high-sulfur flue gas. An advanced level of heat integration between the power plant and the CO_2 capture facility is demonstrated by using waste heat to provide process heating to the CO_2 absorber process condensate and boiler feed-water, reducing the extraction steam requirements, making more low pressure steam available for CO_2 regeneration or power generation. The heat integration approach involves the incorporation of a CO_2 cooler within the carbon capture and storage (CCS) plant and a low temperature flue gas cooler (HES) installed downstream of the power plant's air-preheater. The CO_2 cooler is a standard heat exchanger that recovers waste heat from the outlet of the stripper in the CO_2 capture facility and the HES is a form of regenerative heat exchange that extracts waste heat from the flue gas exiting the plant's air-preheater. The HES technology provides other benefits to the host plant, including reduced water usage in the flue gas desulfurization (FGD) due to lower flue gas temperatures, better electrostatic precipitator (ESP) performance due to lower ash

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

Waste Heat Integration

participant:

Southern Company Services

project number:

FE0007525

predecessor projects:

N/A

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Nick Irvin
Southern Company Services
jairvin@southernco.com

partners:

Mitsubishi Heavy Industries, America, Inc., AECOM

start date:

10.01.2011

percent complete:

100%

resistivity, and enhanced removal of sulfur trioxide (SO_3) and trace metals from the flue gas in existing systems. These improvements have the added benefit of reducing both amine solvent loss and accumulation of metals, thereby reducing operating costs of the solvent capture process.

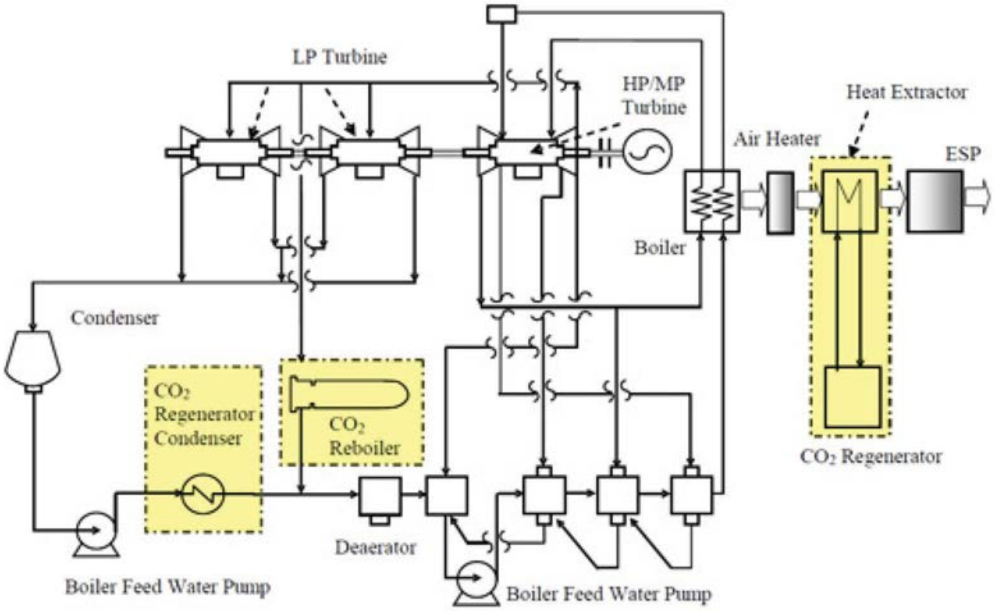

Figure 1: Heat integration of power plant and CCS, including HES

technology advantages

- Costs driven by flue gas compression. The HES provides the efficient use of traditionally wasted heat in coal-fired flue gas and captured CO_2.
- Water usage and parasitic energy loss in carbon capture and storage (CCS) is reduced by the technology.
- The HES accommodates more efficient removal of SO_3 and heavy metals in the ESP by reducing the flue gas temperature and resistivity of fly ash.
- This technology could prove to be a vital method of controlling water usage in FGD due to lower flue gas inlet temperature.
- Potential to simplify the boiler/steam turbine cycles and reduce the number of heat exchange systems in base plant, leading to reduced capital cost.

R&D challenges

- Developing and demonstrating control schemes that maintain proper heat balance in the steam cycle and carbon capture plant.
- Lowering flue gas temperature after the air-preheater can be problematic due to metal corrosion potential as a result of acid gas condensation; developing specific operating parameters and controls to manage the threat is a specific challenge.
- Uncertainty on the reliability of the system with higher sulfur fuels (>1 percent).

status

Operation and testing of the KM-CDR™ CO_2 capture process was completed at the host PC power plant, Plant Barry, with heat integration, confirming an improvement in energy efficiency and cost of electricity. Testing also showed removal of SO_3 to less than 0.05 ppm and removal of other trace metal impurities, confirming an improvement in ESP performance, as well as a reduction in water consumption. The HES was operated for 913 hours for the long-term durability test and showed no damage to tubes or soot blowers and no ash deposition on tube walls.

available reports/technical papers/presentations

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Wall. T., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/T-Wall-Southern-Waste-Heat-Integration-With-Solvent-Process.pdf*

Wall, T., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *https://www.netl.doe.gov/File%20Library/Events/2013/Co2%20Capture/T-Wall-SouthernCo-Waste-Heat-Integration.pdf*

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Advanced Solvent-Based Carbon Capture Technology Development

primary project goals

Southern Company Services evaluated the technical and economic feasibility of adding an integrated stripper/reboiler, particulate matter management, and a new solvent to the existing 25-megawatt electric (MW_e)-scale, amine-based Kansai Mitsubishi Carbon Dioxide Recovery Process (KM CDR Process™) at Southern Company's Plant Barry.

technical goals

- Perform preliminary techno-economic analysis, preliminary design, and technical gap analysis for a large-scale pilot plant project.
- Define a project plan to include baseline, parametric, and long-term testing.
- Evaluate technical and economic feasibility of full-scale installation of further improvements to the KM CDR Process™, including a built-in reboiler, particulate matter management, and a new solvent.

technical content

The KM CDR Process™ at Plant Barry (Figure 1) is a fully-integrated carbon capture and storage (CCS) plant and has achieved 90 percent CO_2 capture at a production rate of 500 metric tons per day. The large-scale pilot plant uses the proprietary KS-1™ solvent, which shows several benefits relative to monoethanolamine (MEA)-based processes. In this project, the key technical challenges of high-steam consumption, solvent performance degradation, and process equipment footprint were investigated by Southern Company Services by: (1) evaluating a built-in reboiler, (2) evaluating the reduced operating and capital costs associated with reduction or elimination of mechanical filtration of particulate matter, and (3) conducting a new solvent test plan (referred to as NSL) to demonstrate a new solvent (termed New Solvent A), which is expected to reduce regeneration steam as well as raw material costs. This Phase I of the project was to evaluate the technical and economic feasibility of full-scale installation of these improvements to the KM CDR Process™. Phase II, which was not awarded, would have covered the engineering, construction, and testing at the pilot plant.

The built-in reboiler would replace the regenerator reboiler and stripper with an integrated unit as shown in Figure 2. It would use a welded-plate heat exchanger, designed for high condensation or evaporation duty, installed in the column, reducing capital and operating cost and footprint.

Particulate matter management would determine if solvent purification can be eliminated. By turning off the solvent purification system to mimic removal of the flue gas filtering process, allowing particulate matter levels in the solvent to build, the maximum allowable particulate matter concentration at which the solvent performance degrades can be determined.

A new improved amine solvent, Advanced Solvent A developed by Mitsubishi Heavy Industries America (MHIA), was proposed to replace their KS-1™ amine solvent. This solvent offers reduced steam consumption compared to both the KS-1™ and MEA solvents.

technology maturity:

Large-Pilot, Actual Flue Gas (equivalent to 25 MW_e)

project focus:

Amine-Based Solvent and Process Improvements

participant:

Southern Company Services

project number:

FE0026590

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

John Carroll
Southern Company Services
johcarro@southernco.com

partners:

Mitsubishi Heavy Industries America; AECOM

start date:

10.01.2015

percent complete:

100%

Figure 1: KM CDR Process™ at Plant Barry

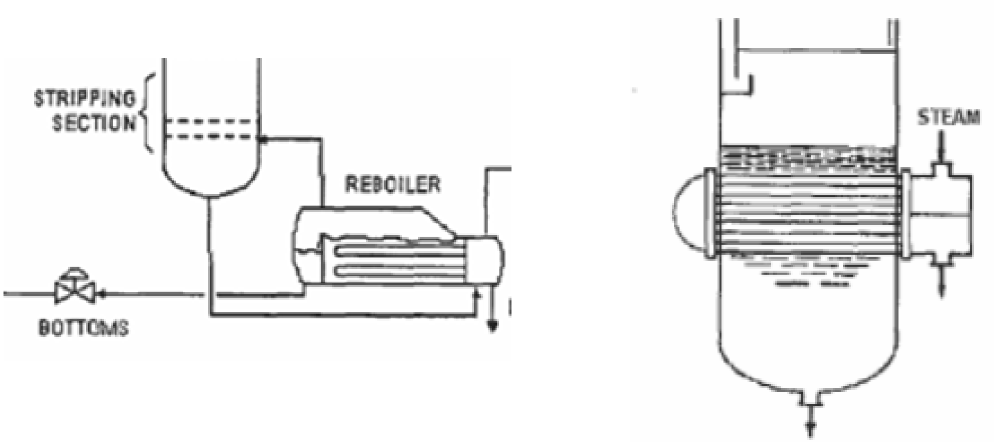


Figure 2: (L) Conventional reboiler and stripper; (R) proposed integrated built-in reboiler

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary data	proprietary data
Normal Boiling Point	°C	proprietary data	proprietary data
Normal Freezing Point	°C	proprietary data	proprietary data
Vapor Pressure @ 15 °C	Bar	proprietary data	proprietary data
Manufacturing Cost for Solvent	\$/kg	proprietary data	proprietary data
Working Solution			
Concentration	kg/kg	proprietary data	proprietary data
Specific Gravity (15 °C/15 °C)	-	proprietary data	proprietary data
Specific Heat Capacity @ STP	kJ/kg-K	proprietary data	proprietary data
Viscosity @ STP	cP	proprietary data	proprietary data
Absorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data
Heat of Absorption	kJ/mol CO_2	proprietary data	proprietary data
Solution Viscosity	cP	proprietary data	proprietary data
Desorption			
Pressure	Bar	proprietary data	proprietary data
Temperature	°C	proprietary data	proprietary data
Equilibrium CO_2 Loading	mol/mol	proprietary data	proprietary data
Heat of Desorption	kJ/mol CO_2	proprietary data	proprietary data
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	proprietary data	
CO_2 Recovery, Purity, and Pressure	% / % / bar	proprietary data	
Absorber Pressure Drop	Bar	proprietary data	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary data	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – CO_2 is captured by chemical absorption.

Solvent Contaminant Resistance – New Solvent A is highly resistant to contaminant compared to conventional solvent MEA.

Solvent Foaming Tendency – New Solvent A has low foaming tendency compared to conventional solvent MEA.

Flue Gas Pretreatment Requirements – Flue gas cooling and SO_x removal unit may be required depending on flue gas conditions.

Solvent Make-Up Requirements – Solvent makeup rate depends on the impurities level in the flue gas but is generally lower than conventional solvent MEA.

Waste Streams Generated – Solvent reclaiming waste is the main waste stream generated.

Process Design Concept – KM CDR Process™ is equipped with proprietary amine emission reduction system, energy-saving system, and amine purification system, which maximize the capture efficiency while minimizing the energy consumption and environmental impact.

Proposed Module Design –Not applied.

technology advantages

- New Solvent A has potential to reduce steam regeneration requirements by 5 percent from their KS-1™ amine solvent and by 37 percent from MEA.
- Reduced capital and operating cost and footprint for the built-in reboiler.

R&D challenges

- Determining maximum allowable particulate matter concentration at which solvent performance degrades.
- Matching or reducing heat transfer efficiency and steam consumption for the built-in reboiler compared to non-integrated reboiler.
- Minimizing corrosion, scaling, and impurity buildup from testing.
- Integration of process updates with operations at Plant Barry.

status

Phase I has been completed. A preliminary techno-economic analysis of the KM CDR Process™ indicated a cost of CO_2 capture of $58.8/tonne and cost of electricity (COE) of 133.7mils/kW. Adding the built-in reboiler, particulate matter management, and new solvent further improved costs to $56.0/tonne CO_2 captured and COE of 130.6 mils/kW. The project was not awarded a Phase II.

available reports/technical papers/presentations

Thomas, J., "Advanced Solvent-Based Carbon Capture Technology Development," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/J-Thomas-SouthernCo26590-Advanced-Solvent-Based-Capture.pdf*

Thomas, J., "Demonstration of Advanced CO_2 Capture Process Improvements for Coal-Fired Flue Gas," Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026590-Kickoff-Presentation.pdf*

Slipstream Pilot-Scale Demonstration of a Novel Amine Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas

primary project goals

Linde is refining a post-combustion carbon dioxide (CO_2) capture technology incorporating BASF's novel amine-based solvent, with the main technical goal of significantly reducing solvent regeneration energy requirements over conventional monoethanolamine (MEA)-based amine capture. Technology development has been fostered by designing, building, and operating a 1-megawatt electric (MW_e) equivalent slipstream pilot plant at the National Carbon Capture Center (NCCC) to evaluate and optimize performance.

technical goals

- Capture at least 90 percent of CO_2 from coal-derived flue gas while demonstrating significant progress toward achievement of the DOE target of less than 35 percent increase in levelized cost of electricity (LCOE) (<\$40/tonne CO_2).
- Produce a CO_2 product with a purity of at least 99.9 percent (dry basis) with low O_2 impurity levels that can meet the requirements for CO_2 utilization applications such as enhanced oil recovery (EOR).
- Successfully test the CO_2 capture technology at a capacity of >1.5 MW_e (>15,500 lb/hr flue gas).
- Validate amine emissions control methods.
- Successfully test regenerator at an operating pressure of 3.4 bar absolute (bara).
- Validate unique design features that lower overall capital and operating costs: (1) high-capacity packing, (2) gravity-driven interstage cooler, (3) blower positioned downstream of absorber, and (4) unique reboiler design providing low solvent holdup and fast dynamics.
- Reduce energy requirements ~27 percent relative to that of baseline MEA capture (2.65 GJ/tonne CO_2 vs. 3.61 GJ/tonne CO_2). Achieve specific regeneration energy of 2.65 GJ/tonne CO_2 (with additional heat integration concepts to further reduction to 2.3 GJ/tonne CO_2).
- Demonstrate solvent stability by showing a very low accumulation of heat stable salts (HSS) over the entire duration of parametric and long-term continuous testing (4,109 hours of testing with flue gas).
- Complete techno-economic assessment of a 550-MW_e power plant integrated with the Linde-BASF post-combustion capture plant incorporating BASF's OASE® blue aqueous amine-based solvent, and leveraging Linde's innovative process features to increase energy efficiency, improve emissions performance, and reduce plant footprint.

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 1 MW_e)

project focus:

Slipstream Novel Amine-Based Post-Combustion Process

participant:

Linde, LLC

project number:

FE0007453

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Krish Krishnamurthy
Linde
krish.krishnamurthy@linde.com

partners:

BASF, Linde Engineering Dresden GmbH, Selas Fluid Processing Corporation, EPRI

start date:

12.01.2011

percent complete:

100%

technical content

Linde's technology uses BASF's OASE® blue solvent, which has been developed to address the key drawbacks in the large-scale application of MEA for flue gas carbon capture, including: (1) high specific energy for rich solvent regeneration/CO_2 recovery, (2) lack of solvent stability toward thermal and oxidative degradation, (3) increased solvent corrosiveness with increased CO_2 loading, and (4) lack of solvent tolerance to impurities from coal combustion products. The specific proprietary solvent was selected by: (1) screening approximately 400 chemical substances using vapor-liquid equilibrium measurements to determine approximate cyclic capacities, (2) laboratory measurements of the key thermodynamic and kinetic properties of the 70 screened candidates and their mixtures to identify approximately 15 targets, (3) testing of the targets to determine optimum circulation rate and specific energy consumption in a laboratory-scale mini-plant to identify the leading candidates, and (4) pilot testing of three candidates with real power plant flue gas to identify the optimum solvent for the flue gas application. CO_2 recovery from the solvent is carried out by using low-pressure steam, typically from the power plant steam cycle. Testing using a 0.45-MW_e pilot plant utilizing lignite-fired power plant flue gas has shown that the OASE® blue solvent is stable and little degradation was observed over 5,000 hours, whereas the reference MEA solvent started to degrade appreciably under same conditions after 2,000 hours.

Linde's post-combustion CO_2 capture process using BASF OASE® blue solvent technology has several distinct characteristics. Firstly, the direct-contact cooler, CO_2 absorber, and water wash are integrated into a single column with high-performance structured packing for increased capacity (smaller absorber diameter) and an advanced material of construction to minimize capital costs. Secondly, the absorber also has an inter-stage solvent cooler operating on gravity flow, eliminating the capital and operating expenses of a solvent pump. The flue gas blower is located downstream of the absorber to minimize its size (due to the reduced volume of flue gas handled by the blower). Further, the stripping column can be operated at higher pressures (up to 3.4 bara) than that of a MEA stripper, lowering compression costs. Finally, optional process heat integration allows steam, which is raised by heat exchange with flue gas upstream of the flue gas desulfurization (FGD) unit, to be used at an intermediate point in the desorber, and the use of back-pressure steam turbines allows the recovery of part of the energy of the intermediate-pressure (IP), low-pressure (LP) crossover steam.

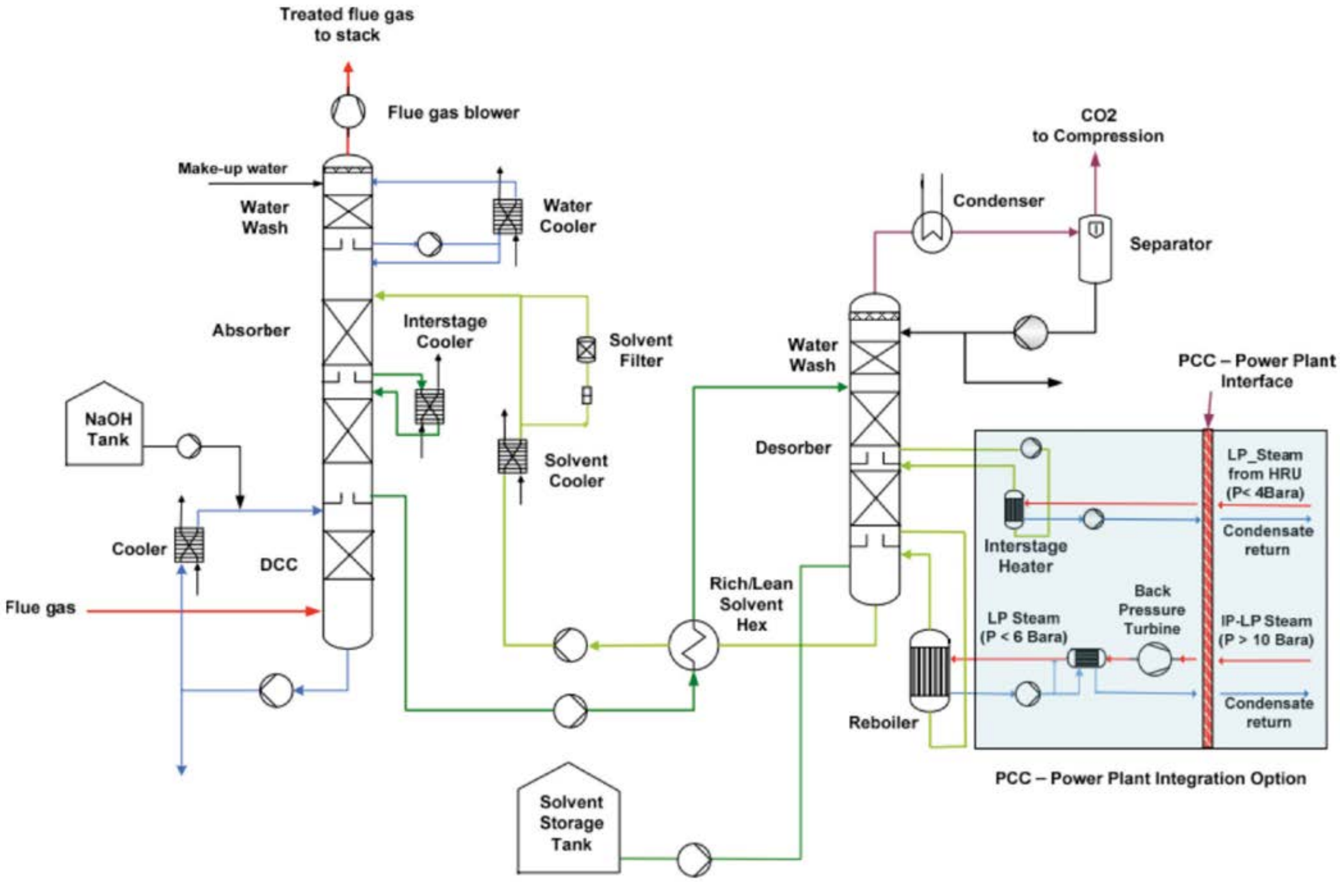


Figure 1: Linde-BASF post-combustion capture plant process concept

Techno-Economic Study Cases and Results

Three conceptual cases of pulverized coal combustion power plants with 90 percent CO_2 capture accomplished using the Linde-BASF technology were modeled to quantify expected costs and process efficiencies resulting from the improved solvent and the energy-saving process features noted above.

Linde-BASF LB1

The LB1 design employs high-performance structured packing, gravity-drain absorber intercooler, emission control system in absorber wash sections, blower downstream of absorber, novel stripper reboiler design, and elevated regeneration pressure (3.33 bar absolute). Modeling suggests this combination of features would result in a specific regeneration energy of 2.61 GJ/MT CO_2. The Wilsonville NCCC pilot plant is based on the LB1 design.

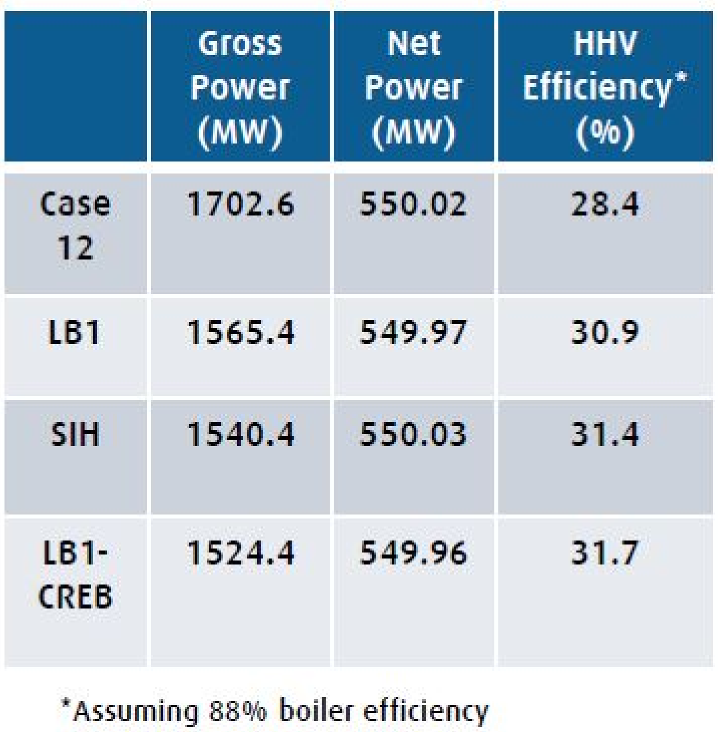
Linde-BASF SIH

The SIH design employs advanced stripper interstage heater design that improves heat recovery from CO_2-lean solution leaving stripper. Modeling suggests this combination of features would result in a specific regeneration energy of 2.30 GJ/MT CO_2.

Linde-BASF LB1-CREB

The LB1-CREB design employs novel cold CO_2-rich solution bypass exchanger and secondary CO_2-lean/CO_2-rich heat exchanger that optimizes heat recovery from hot CO_2 product vapor leaving stripper and hot CO_2-lean solution. Modeling suggests this combination of features would result in a specific regeneration energy of 2.10 GJ/MT CO_2.

Figure 2 show the overall power plant efficiencies for these cases, indicating incremental improvements over the baseline power plant case using the Linde technology, compared to conventional amine-based CO_2 capture (DOE NETL Bituminous Baseline Case 12).



	Gross Power (MW)	Net Power (MW)	HHV Efficiency* (%)
Case 12	1702.6	550.02	28.4
LB1	1565.4	549.97	30.9
SIH	1540.4	550.03	31.4
LB1-CREB	1524.4	549.96	31.7

*Assuming 88% boiler efficiency

Figure 2: Comparison of PCC plant case efficiencies from techno-economic analysis

The cost of CO_2 captured was estimated to be as follows:

DOE NETL Case 12 (baseline)	\$56.49/MT CO_2
Linde-BASF LB1	\$41.85/MT CO_2
Linde-BASF SIH	\$40.66/MT CO_2
Linde-BASF LB1-CREB	\$39.90/MT CO_2

One major reason the cost of CO_2 captured is significantly reduced in moving from Case 12 to LB1 is due to the higher inlet CO_2 gas pressure for CO_2 compression (48 psia for LB1 vs. 24 psia for Case 12) afforded by elevated regenerator pressure, which reduces downstream compression energy and capital costs. Additionally, as power plant efficiency increases, the flow rate of CO_2 produced decreases due to a reduced coal flow rate needed for the same power production. This leads to increasingly smaller incremental reductions in cost of CO_2 captured for each Linde-BASF process improvement.

Figure 3 shows the cost breakdowns for the cases relative to the baseline DOE NETL Case 12.

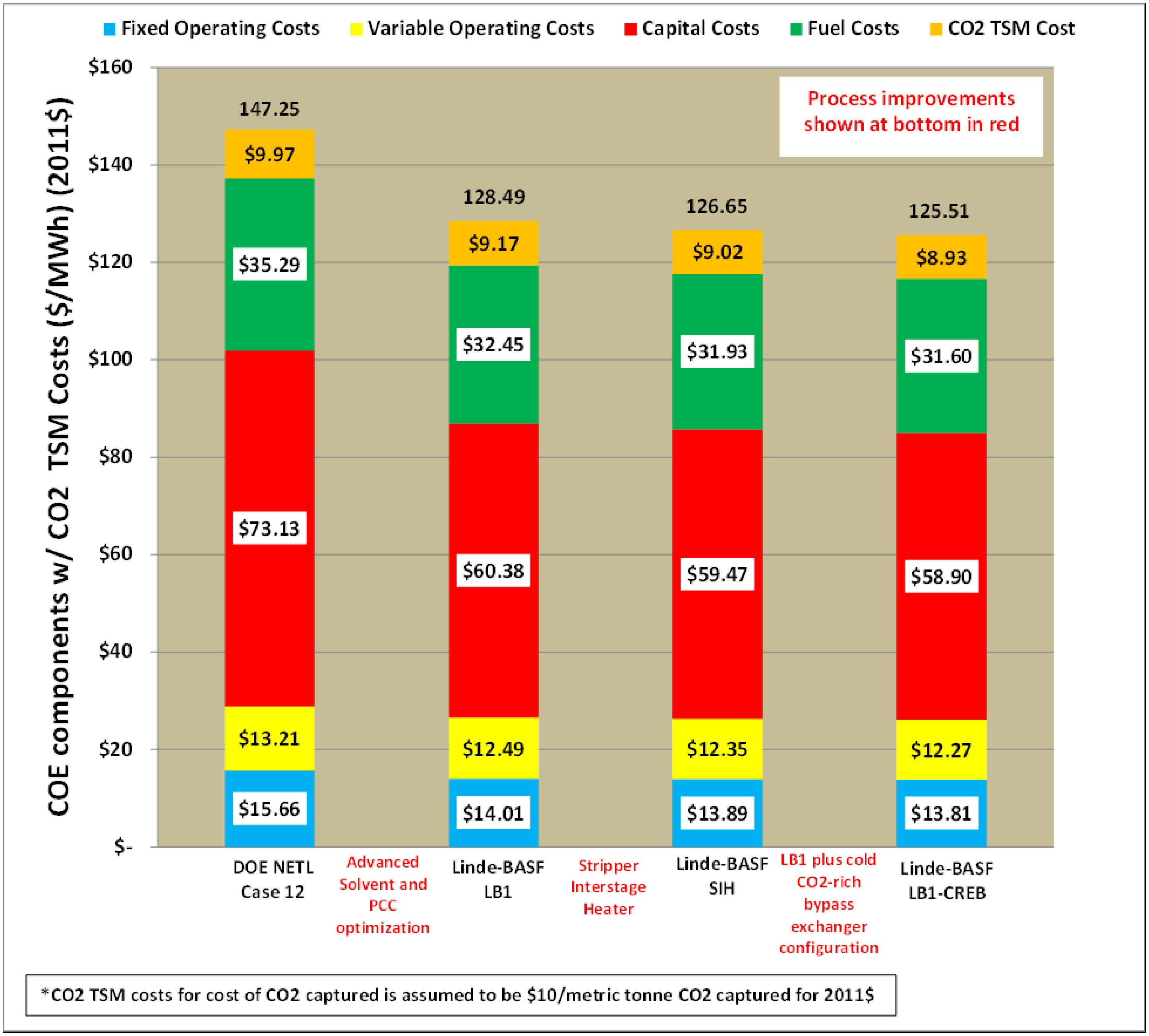


Figure 3: Cost of electricity comparisons from techno-economic analysis

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	—
Normal Boiling Point	°C	proprietary	—
Normal Freezing Point	°C	proprietary	—
Vapor Pressure @ 15 °C	bar	proprietary	—
Manufacturing Cost for Solvent	$/kg	proprietary	—
Working Solution			
Concentration	kg/kg	proprietary	—
Specific Gravity (15 °C/15 °C)	-	proprietary	—
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	—
Viscosity @ STP	cP	proprietary	—
Absorption			
Pressure	bar	≈1 atm	≈1 atm
Temperature	°C	30–70	30–60
Equilibrium CO_2 Loading	mol/mol	proprietary	—
Heat of Absorption	kJ/mol CO_2	proprietary	—
Solution Viscosity	cP	proprietary	—
Desorption			
Pressure	bar	1.6–2.5	1.6–3.4
Temperature	°C	124–132	124–140
Equilibrium CO_2 Loading	mol/mol	proprietary	—
Heat of Desorption	kJ/mol CO_2	proprietary	—
Proposed Module Design (for 550-MW_e PCC Plant)		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99.98% (dry basis), 3.4 bara	90%, 99.98% (dry), 3.4 bara
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted otherwise, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – CO_2 in the flue gas chemically binds to the OASE blue® aqueous amine-based solvent via an exothermic absorption step and this chemical bond is broken in the endothermic desorption step via heat provided by steam in the reboiler of the regenerator column, generating pure CO_2.

Solvent Contaminant Resistance – The OASE blue® solvent is highly resistant against many contaminants in the flue gas as shown in both parametric and long-term continuous tests (see EPRI report ["BASF-Linde Post Combustion Carbon Capture…"] for additional information).

Solvent Foaming Tendency – During the pilot plant operation, although anti-foaming injection was included in the design, its use was not found necessary.

Flue Gas Pretreatment Requirements – The pretreatment requirement includes reducing sulfur oxide (SO_x) in the flue gas to 2–5 parts per million (ppm) in order to limit solvent degradation and is implemented in a direct contact cooler in conjunction with flue gas cooling, typically by adding appropriate amount of sodium hydroxide corresponding to the SO_x present in the flue gas.

Solvent Make-Up Requirements – The OASE blue® solvent make-up rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low make-up rates were observed during long-term testing well below an operationally manageable threshold (see Final Testing Report ["Slipstream Pilot Plant Demonstration…"] on page 22). During the parametric testing, higher amine losses were observed and this was attributed to the lack of baghouse filter in the power plant resulting in a high density of fine aerosol particles in the flue gas that caused carryover of amine with the CO_2-depleted gas.

Waste Streams Generated – The main waste liquid stream is from the direct contact cooler where SO_x is removed; this stream is typically handled in the power plant waste water treatment facility. A small amount of solid waste is removed using carbon filters that are replaced at regular intervals. Since the degradation observed in the pilot testing is small, no solvent reclamation unit is envisioned in the large scale.

Process Design Concept – See Figure 1 above.

technology advantages

- Significant reduction in regeneration steam consumption (24–40 percent lower), electrical power (14–26 percent lower), and cooling water duty (26–43 percent lower) compared to a reference MEA plant.
- Higher plant efficiency due to a combination of advanced solvent and process improvements, including integrated absorber, down-stream gas blower, higher desorber pressure, and inter-stage gravity-flow cooler.
- Aggregate capital, O&M, fuel, and other cost reductions result in lower COE (15 percent less than the MEA-based DOE NETL reference case).
- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is a producer of the solvent in addition to being the technology owner, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.

R&D challenges

- Proving the process enhancements at the 1-MW_e plant and at larger scale.
- Validating the basis for scale up of the advanced process features and the large, single-train capability.

status

The Linde-BASF technology has been selected by DOE for Phase 1 of a large pilot plant demonstration opportunity. Linde has teamed with the University of Illinois in proposing Phase 2 work, identifying the Abbott coal fired power plant as the intended host site for the large pilot, which if selected and executed is expected to advance the technology to near-commercial readiness.

available reports/technical papers/presentations

"*Slipstream Pilot Plant Demonstration of an Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," Final Report, February 2017.

Final Techno-Economic Analysis of 550 MW_e Supercritical PC Power Plant CO_2 Capture with Linde-BASF Advanced PCC Technology," January 2017.

"*Slipstream Pilot Plant Demonstration of a Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," Final Project Review Meeting Presentation by Krish R. Krishnamurthy & Devin Bostick, Linde LLC, Pittsburgh, PA, January 2017.

"*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," presented by Krish R. Krishnamurthy, Linde LLC, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Development and Scale-Up of an Advanced Aqueous Amine-Based Post-Combustion CO_2 Capture Utilizing BASF's OASE® Blue Technology*," presented by Krish R. Krishnamurthy, Linde LLC, 2016 Carbon Capture, Utilization & Storage Conference, Tysons, VA, June 2016.

"*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*, presented by Krish R. Krishnamurthy, Linde LLC, 2015 CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

"*Pilot plant demonstration of an advanced amine-based post-combustion capture technology for CO_2 capture from power plant flue gases*," presentation at the 12th Greenhouse Gas Control Technologies (GHGT-12) Conference, October 2014.

Krishnamurthy, K., "*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," 2014 CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Krishnamurthy, K., "*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," 2013 CO_2 Capture Technology Meeting, Pittsburgh, PA.

"*Techno-Economic Analysis of 550 MWe Subcritical PC Power Plant with CO_2 Capture*," Topical Report of initial techno-economic analysis, May 2012.

"*Techno-Economic Analysis of 550 MWe Subcritical PC Power Plant with CO_2 Capture*," presentation given at NETL by S. Jovanovic & K. Krishnamurthy, Pittsburgh, PA, May 2012.

"*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," Project Kick-Off Meeting Presentation, November 2011.

"*Slipstream Pilot Plant Demo of an Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," presented by Krish R. Krishnamurthy, Linde LLC, 2011 Fall Technical Subcommittee Meeting, Pittsburgh, PA, October 31, 2011.

Krishnamurthy, K.R., "*Slipstream Pilot Plant Demo of an Amine-Based Post-Combustion Capture Technology for CO2 Capture from a Coal-Fired Power Plant Flue Gas*," presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA.

"BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

"Slipstream Pilot Plant Demonstration of an Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas," Final Testing Report to NCCC, February 2017.

Improvement of GE Power's Chilled Ammonia Process Large Pilot with the Use of Membrane Technology

primary project goals

GE Power developed several concepts for improving their existing solvent-based Chilled Ammonia Process (CAP) for capturing carbon dioxide (CO_2) from coal-fired power plants by incorporating commercially available membrane technologies to reduce energy and capital costs. Three concepts were investigated at bench-scale to determine feasibility of testing with a large pilot CO_2 validation facility at Technology Centre Mongstad (TCM).

technical goals

- Implement several improvement concepts utilizing membrane technology at an existing CAP large-scale pilot plant to lower the overall cost of CAP CO_2 capture technology.
- Leverage CAP experience in collaboration with TCM, the host site, which operates an existing CAP large pilot facility (~15 MW_e equivalent) in Norway.
- Complete a techno-economic assessment (TEA) and technology gap analysis of membrane concepts for the CAP at a full-scale 550-MW power generation facility.
- Develop key project risks.

technical content

GE Power teamed with ElectroSep™, General Electric Power and Water, and Georgia Institute of Technology, to investigate concepts for improving an existing solvent-based CAP pilot plant using liquid-liquid bipolar and reverse osmosis membrane systems to reduce energy and capital costs. GE Power's CAP uses an ammonia-based solvent for the absorption of CO_2 from flue gas at low temperature. Ammonia is an energy-efficient reagent that is stable, not susceptible to contaminants in flue gas, and is replenished in low consumption rates. The CAP has been tested at large pilot scale (20 MW_e) and is prepared for large scale demonstration in 2020. The main features of the CAP technology are:

- The flue gas leaving the CAP has no solvent degradation byproducts and the solvent can tolerate higher amounts of residual acid gases (SO_x, NO_x, etc.) in the incoming flue gas.
- The CAP technology can utilize cooler ambient conditions to lower the energy consumption of the process.
- The reactions within the CO_2 absorption process are reversible with regeneration of the solvent at elevated pressure allowing for reduced CO_2 compression.
- The CAP reagent is anhydrous ammonia—a low cost, commodity chemical that is readily available.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Chilled Ammonia Process Improvements

participant:

GE Power

project number:

FE0026589

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

David Muraskin
GE Power
david.j.muraskin@power.alstom.com

partners:

ElectroSep™; General Electric Power and Water; Georgia Institute of Technology; Technology Centre Mongstad

start date:

10.01.2015

percent complete:

100%

- The byproduct is an aqueous ammonium sulfate stream that can be used commercially as fertilizer.

Three concepts for improving the CAP CO_2 capture technology using commercially available membrane systems were previously investigated at the bench-scale level for eliminating CAP liquid ammonium sulfate effluent stream and reducing CAP energy demand. GE Power plans to modify the CAP large pilot facility at the TCM in Norway for the implementation of these membrane systems once they are validated at bench-scale.

The first concept involves eliminating ammonium sulfate byproduct and reducing the consumption of ammonia and sulfuric acid reagents. In the CAP plant, as flue gas enters the conditioning section, residual SO_x in the direct contact column (DCC) reacts with ammonia to form ammonium sulfate byproduct. In the direct contact heating (DCH) column, residual ammonia in the treated flue gas from the absorption/water wash section is reduced to form ammonium sulfate using a sulfuric acid rinse. The ammonium sulfate byproduct generated in both unit operations is then transported as a concentrated liquid solution or processed on-site using crystallization technology to form a fertilizer, which requires high operating and capital costs. In this concept, a bipolar membrane electrodialysis (ED) unit converts the byproduct to sulfuric acid and anhydrous ammonia (process reagents). Figure 1 illustrates the ion exchange process through a bipolar membrane ED unit and Figure 2 shows an ED unit implemented into the CAP plant. Through electrodialysis, ions are transported through cation and anion exchange membranes from one solution to another under the influence of an electrical driving force. The ammonium sulfate bleed stream is dissociated into acidic and basic ionic species. Bipolar membranes consisting of an anion exchange membrane and a cation exchange membrane bonded together dissociate water into hydrogen and hydroxyl ions for combining with the ionic species, forming sulfuric acid and ammonia. Eliminating the ammonium sulfate byproduct stream is beneficial for power plants that are not able to use the byproduct as commercial fertilizer and reducing process reagent consumption solves the problems of on-site storage for substantial amounts of reagents.

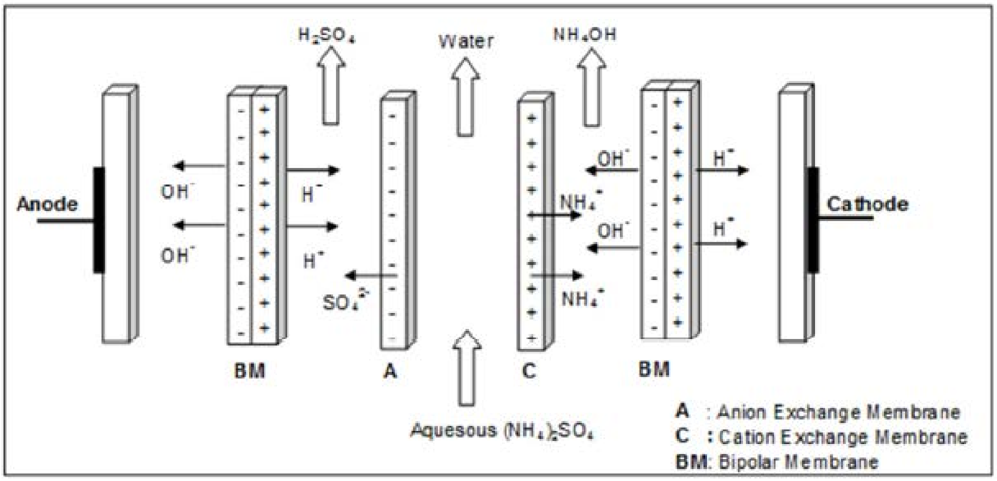


Figure 1: Bipolar membrane electrodialysis

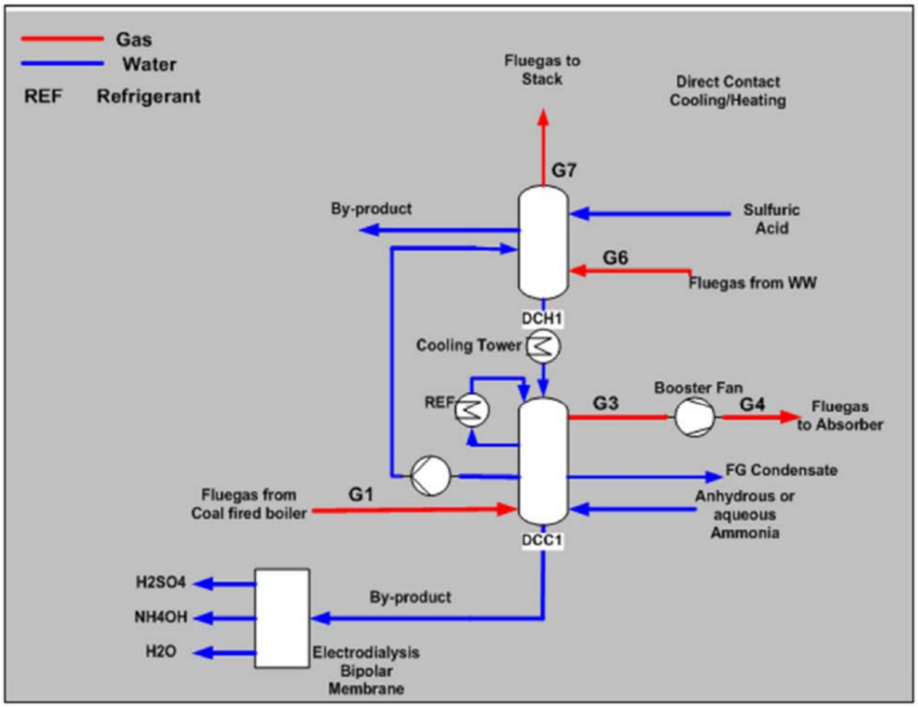


Figure 2: Bipolar membrane electrodialysis for byproduct elimination and reagent recovery

The second concept involves reducing the ammonia stripper energy. In the CAP plant, ammonia in the flue gas leaving the CO_2 absorber is first captured in a water wash vessel and then regenerated in an ammonia recovery stripper by heating the rich solution with saturated steam. In this concept, as shown in Figure 3, a reverse osmosis membrane separator is used to increase the ammonia concentration in the feed to the ammonia stripper, resulting in reduced feed flow rate, which minimizes stripper duty. As a result, stripper and heat exchanger sizes are reduced as well as steam energy demand. Also, the improvement in stripper performance potentially allows the CO_2 absorber to operate at a higher temperature resulting in lower refrigeration duty.

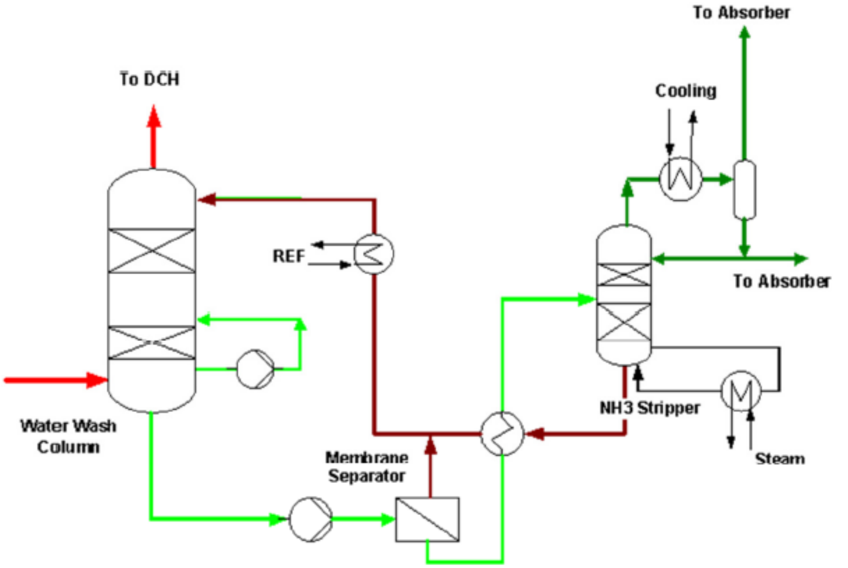


Figure 3: Reverse osmosis membrane for ammonia stripper energy reduction

The third concept involves reducing the CO_2 regeneration energy by recovering absorbent. In the CAP plant, a large amount of circulation flow between the CO_2 absorber and the CO_2 regenerator is required due to low CO_2 loading, which leads to high capital and operating costs of the plant. In this concept, as shown in Figure 4, a reverse osmosis membrane separator is used to recover the water and some portion of the ionic absorbent that passes through the CO_2 wash column after leaving the regenerator. The wash water with recovered ammonium is sent to the absorber for CO_2 capture, while the remaining carbon-containing ionic species that does not permeate through the membranes is returned to the CO_2 wash section to capture ammonia. This process allows for operation of the regenerator at lower pressure and higher ammonia emissions. In the current plant, the CO_2 is regenerated at high pressure, which reduces the ammonia content in the CO_2 product and minimizes the downstream compressor duty. However, this requires relatively high-pressure steam, which affects the power production capability of the power plant. Operating the regenerator at lower pressure allows for use of lower quality steam, which reduces the energy losses associated with high pressure steam utilization, but also increases the amount of ammonia emission from the CO_2 regenerator. This excess ammonia is captured in the CO_2 wash section and then processed in the reverse osmosis membrane system as described above.

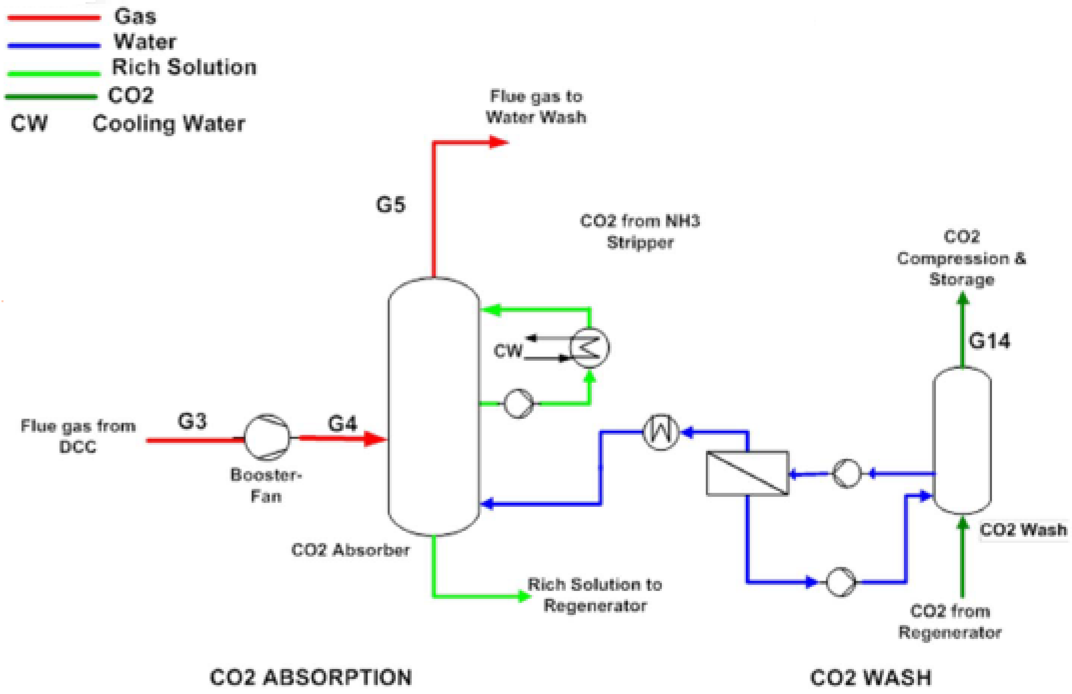


Figure 4: Reverse osmosis membrane for increased ammonium recovery from CO_2 wash

Each of these membrane systems were tested previously at laboratory-scale and bench-scale using process streams consistent with those within the CAP plant. A bench-scale electrodialysis test apparatus consisting of ion specific membranes with a total surface area of 0.152 m^2 was used to assess the first concept at ElectroSep. A sulfuric acid product tank was used to accumulate the sulfuric acid produced by the electrodialysis stack and confirmed an increase in sulfuric acid concentration, indicating that the initial membrane selection is feasible. Through testing of the commercial reverse osmosis membranes at Georgia Institute of Technology, it was determined that a higher osmotic pressure is needed; however, higher pressure membranes are not robust and are associated with high operating and capital costs. An alternate concept was developed utilizing a low-pressure reverse osmosis membrane design that is expected to improve costs by eliminating the stripper and steam consumption. The development program was revised to allow for further testing of this new concept at bench-scale and a decision was made to not proceed with modifications to the large pilot plant.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Uses ammonia—a low-cost, stable, readily available chemical—as a reagent.
- Uses commercially available membranes that can be scaled up using conventional methods.
- The incorporation of bipolar membrane technology eliminates the CAP byproduct stream (ammonium sulfate) and associated disposal/processing costs as well as recovers reagents (ammonia and sulfuric acid).
- The incorporation of reverse osmosis membrane technology minimizes the CAP regenerator steam consumption and reduces the stripper and associated heat exchanger sizes by ~50 percent.

R&D challenges

- Utilizing lower pressure membranes for reverse osmosis concept.

status

Bipolar membrane electrodialysis for the CAP is prepared for large pilot-scale testing based on the successful completion of bench-scale testing at ElectroSep, Inc. Bench-scale testing of the reverse osmosis concept determined that the low-pressure membrane rejection rate is insufficient, and therefore, modification of the initial process scheme is required along with bench-scale testing to validate the new process before proceeding to large pilot-scale testing. A preliminary techno-economic analysis was completed based on the bench-scale tests, showing an improvement in power plant steam cycle efficiency and a small reduction in cost of electricity (COE) from the DOE baseline case. The COE improvement was not sufficient to justify further development of the original reverse osmosis concept. Bench-scale testing along with an economic assessment for the alternate concept using low pressure reverse osmosis membranes is required to allow consideration of the membrane technology for CAP improvements.

available reports/technical papers/presentations

Muraskin, David, "Improvement of GE Power's Chilled Ammonia Process using Membrane Technology," Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/D-Muraskin-GE-Alstom-Chilled-Ammonia-Large-Pilot.pdf*

"Improvement of Alstom's Chilled Ammonia Process using Membrane Technology," Project kickoff meeting presentation, October 28, 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026589-Kickoff-Presentation.pdf*

Novel Flow Sheet for Low Energy CO_2 Capture Enabled by Biocatalyst Delivery System

primary project goals

Akermin developed an advanced biocatalyst enabled solvent system for lower cost carbon dioxide (CO_2) capture. The project focused on the development of encapsulated carbonic anhydrase (CA) biocatalyst technology. The project combines an improved biocatalyst delivery system (BDS), a new solvent, and process improvements tested in a modified bench-scale system incorporating these new advancements.

technical goals

- Demonstrate a second-generation biocatalyst that has lower production costs, is more readily scaled up, and enables on-stream catalyst replacement.
- Optimize production of the BDS.
- Demonstrate consistent long-term performance in lab-scale closed loop reactor.
- Design and modify bench-scale test unit to incorporate the next-generation BDS and to accommodate the novel process improvements.
- Optimize the process flow sheet to utilize low grade steam for solution regeneration and to achieve parasitic power less than 220-kWh/t CO_2.
- Evaluate performance of advanced AKM24 solvent.
- Complete field testing with the bench-scale test unit at the National Carbon Capture Center (NCCC) using coal-derived flue gas.
- Demonstrate on-stream biocatalyst maintenance.
- Perform techno-economic assessment and engineering study to demonstrate viability of the new technology, targeting at least 30 percent reduction in cost of CO_2 capture.

technical content

Akermin is developing a low-energy, enzyme-catalyzed solvent system for CO_2 capture and testing in a bench-scale unit to continue advancing the technology that was previously developed under project DE-FE0004228. The novel system combines the next-generation BDS and a non-volatile salt solution (AKM24 "solvent"). Updates to an existing 500 standard liters per minute (SLPM) bench-scale test unit incorporated the process and solvent advancements. The process scheme is shown in Figure 1.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution ("Solvents")

participant:

Akermin, Inc.

project number:

FE0012862

predecessor projects:

FE0004228

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Alex Zaks
Akermin, Inc.
zaks@akermin.com

partners:

Worley Parsons; Novozymes

start date:

10.01.2013

percent complete:

100%

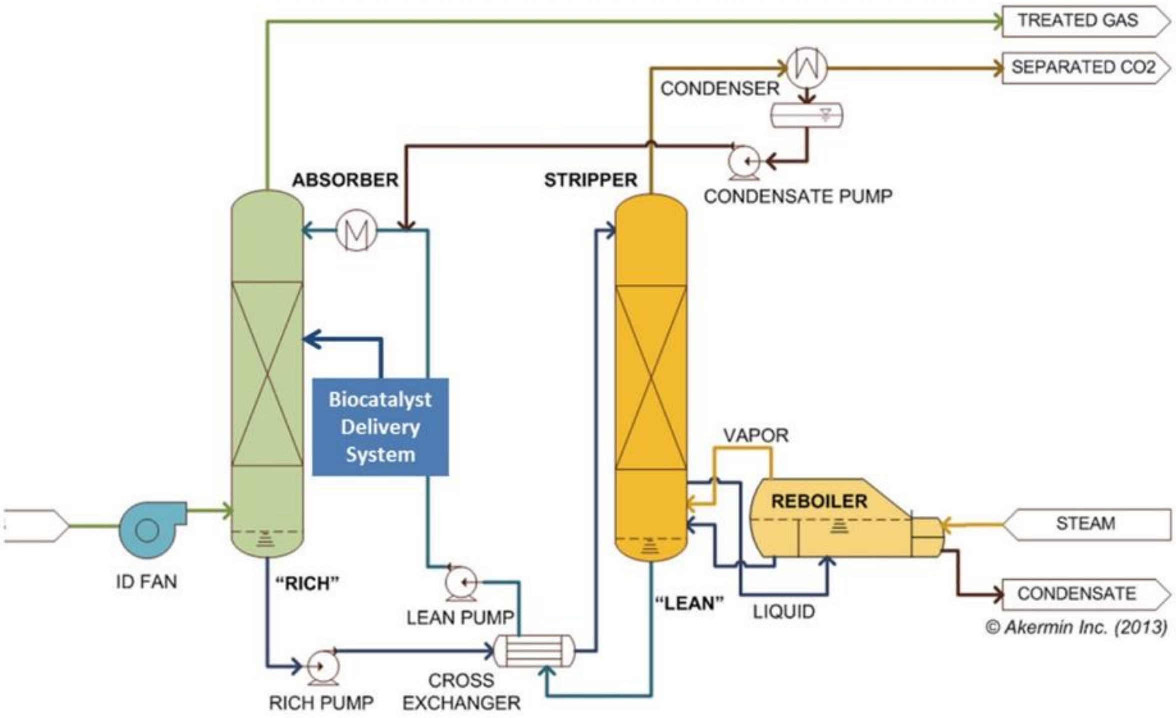


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Figure 1: Akermin's CO_2 capture process

The technology uses a next-generation BDS, in which, the CA enzyme is immobilized within proprietary polymeric microparticles. CA accelerates hydration of CO_2 to bicarbonate to enhance the performance of the solvent for CO_2 capture. The microparticles have high surface area to enable higher mass transfer rates and provide a protective environment for the enzymes against inactivation by temperature, solvent and shear forces. The catalyst can be delivered by two potential concepts: (1) by recirculation in the absorber only, which requires particle separation, or (2) by continuous circulation in the absorber and stripper, which would not require particle separation, but would require lower temperature stripping to avoid denaturation of the enzyme-based biocatalyst. By incorporating the non-volatile salt solution that has significantly lower regeneration energy combined with using lower temperature steam from the power plant, the result is significant reductions in parasitic power requirements and also lower capital costs for the power plant and integrated CO_2 capture system. Since AKM24 operates with higher CO_2 loading capacity, lower circulation rates can be realized. The modified bench-unit was operated with actual coal-derived flue gas at the NCCC to evaluate performance and validate process modeling performance estimates.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	not disclosed	not disclosed
Normal Boiling Point	°C	107	107
Normal Freezing Point	°C	-8	-8
Vapor Pressure @ 15 °C	bar	non-volatile	non-volatile
Manufacturing Cost for Solvent	$/kg	not disclosed	not disclosed
Working Solution			
Concentration	kg/kg	not disclosed	not disclosed
Specific Gravity (15 °C/15 °C)	—	1.18	1.18
Specific Heat Capacity @ STP	kJ/kg-K	3.33	3.33
Viscosity @ STP	cP	3.98	33.98
Absorption			
Pressure	bar	1.07	1.07
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	0.80	0.80
Heat of Absorption	kJ/mol CO_2	52	52
Solution Viscosity	cP	2.01	2.01
Desorption			
Pressure	bar	1.07	1.07
Temperature	°C	107	107
Equilibrium CO_2 Loading	mol/mol	0.40	0.40
Heat of Desorption	kJ/mol CO_2	70	70
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	40	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 >99 1.05	
Absorber Pressure Drop	bar	<0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Chemical/Physical Solvent Mechanism – The reaction of CO_2 with water (H_2O) in the presence of CA and base (B) is as follows:

$$H_2O + CO_2 \longleftrightarrow HCO_3^- + H \qquad \textit{(slow without catalyst)}$$

$$H^+ + B \longleftrightarrow BH^+ \qquad \textit{(fast)}$$

$$H_2O + CO_2 + B \longleftrightarrow BH^+ + HCO_3^- \qquad \textit{(overall reaction)}$$

The presence of CA increases the rate of conversion of CO_2 to bicarbonate (improving the slow step above), but does not affect the equilibrium properties of the solvent. The rate of hydration of CO_2 (i.e., the reaction with H_2O) in the absence of the enzyme is exceedingly slow; however, the enzyme provides dramatic acceleration of the reaction (kcat ≈1/microsecond) and is limited only by diffusion.

Solvent Contaminant Resistance – Studies with K_2CO_3 and CA in solution indicate that the enzyme is not inhibited by sulfate, sulfite, nitrite, nitrate, or chloride ions in solution at levels expected for coal flue gas. Divalent metal ions (e.g., mercury [Hg^{2+}], lead [Pb^{2+}]) inhibit the activity of soluble CA, because the active site in the enzyme itself contains a divalent metal ion (mainly zinc). However, the low solubility of their hydroxide and carbonate salts in carbonate solutions and the stabilizing role of the immobilization system alleviate some of the decrease in CA activity.

Solvent Foaming Tendency – The presence of soluble enzyme can contribute to foaming, especially in the stripper, whereas the tendency to foam is mitigated by using immobilized enzyme. Previous work has used small quantities of anti-foam.

Flue Gas Pretreatment Requirements – Standard sulfur oxides (SO_x), nitrogen oxides (NO_x), and mercury control systems that meet local air emission requirements will be sufficient.

Solvent Make-Up Requirements – The capture of acid gases, such as sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), will reduce carrying capacity over time. Initial tests indicated the loss of capacity to be on the order of 2 percent per year or less. K_2CO_3 is non-volatile and has excellent oxidative stability (an inorganic salt solution). Akermin's new solvent (AKM24) is based on a non-volatile salt solution; therefore, it is expected to have similar benefits.

Waste Streams Generated – In the first-generation technology, the deactivated packing would need to be replaced (recycled) to maintain CA activity on an ongoing basis. Notably, the second-generation BDS provides for on-stream biocatalyst maintenance as a microparticle, which reduces the volume and cost of solid waste management.

Process Design Concept – Figure 1 presents the basic process flow sheet.

technology advantages

- Advanced solvent in the presence of Akermin's BDS has high CO_2 absorption rates and higher capacity relative to first generation. It also has significantly lower regeneration energy compared to amine-based solvents.
- Solvent is non-volatile, oxidative stable, and environmentally benign.
- Advanced solvent uses lower-grade steam with lower regeneration temperatures than amine solvents; resulting in lower auxiliary power requirements, more power generated, lower unit capital costs, and lower CO_2 capture costs.

R&D challenges

- Scaling up and manufacturing of the immobilized biocatalyst batches that consistently achieve the critical performance metrics (cost, efficiency, ease of integration with BDS, etc.).
- Determining the optimal catalyst recirculation option.
- Demonstrating an effective BDS in the lab- and bench-scale test units to achieve stable and consistent long-term performance.

status

Akermin has produced and tested multiple biocatalyst batches on the kilogram scale. They have demonstrated an average 90 percent CO_2 capture over extended testing in the lab-scale closed loop reactor. An enzyme kinetic model was built in Aspen and validated with test data. The 500 SLPM bench unit located at the NCCC was modified and commissioned in June 2016, and testing was initiated. The project ended in July 2016, prior to the planned September 30, 2016, end date, due to unexpected circumstances.

available reports/technical papers/presentations

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Carbon Absorber Retrofit Equipment (CARE)

primary project goals

Neumann Systems Group, Inc. (NSG) has designed, constructed, and tested a 0.5-MW scale patented NeuStream® absorber at the Colorado Springs Utilities (CSU) Martin Drake #7 power plant. The absorber employs nozzle technology proven during a previously completed 20-MW NeuStream-S flue gas desulfurization (FGD) pilot project, as well as a 6-m piperazine (PZ) solvent, which is an efficient solvent for capturing carbon dioxide (CO_2). The goal of the project is to show that the absorber system is capable of significantly reducing the process equipment footprint and the CO_2 capture system cost.

Due to an unrelated turbine fire at the Martin Drake plant in May of 2014, the project scope was revised to relocate the system to NSG's facility, where a natural gas steam boiler will provide the flue gas and stripping heat. Stripped CO_2 was recycled to increase the incoming CO_2 concentration to ≈13 percent to simulate flue gas from a coal-fired boiler.

technical goals

- Design a 0.5-MW_e slipstream CO_2 scrubber to minimize parasitic power through efficient design.
- Demonstrate a 2-month steady-state operation with a three-stage absorber and a multistage stripper.
- Demonstrate 90 percent CO_2 capture efficiency utilizing the best available solvent.
- Show unit traceability/scalability to commercial scale.

technical content

The NSG Carbon Absorber Retrofit Equipment (CARE) project includes design, construction, and testing of a 0.5-MW NeuStream® CO_2 capture system, based on NSG's patented flat jet, modular absorber technology. The NeuStream® absorber uses a proven technology with an array of flat jets and an advanced solvent (6 m PZ) to capture CO_2. The CARE absorber design is based on modeling (computational fluid dynamics [CFD] and Aspen Plus™) and analysis of carbon capture data from slipstream experiments, where experimental specific surface areas of 440 m^2/m^3 have been achieved. The CARE system slipstream test includes compact NeuStream® modules, as well as sulfur oxide (SO_x) scrubbing and amine washing equipment that also utilizes the NeuStream® flat jet technology.

The SO_x scrubbing equipment uses compact modular NeuStream® technology and can be adjusted to residual SO_x level (1–30 parts per million [ppm]) prior to CO_2 capture. The CARE project employs slipstream nitrogen oxide (NO_x) removal; a four-stage, 0.5-MW_e NeuStream® high-performance absorber unit for scrubbing; a novel stripper design that reduces heat waste; and a flue gas heat-recovery method to offset a portion of steam usage.

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

Carbon Absorber Retrofit Equipment

participant:

Nuemann Systems Group

project number:

FE0007528

predecessor projects:

N/A

NETL project manager:

Andy O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Eric Klein
Neumann Systems Group
erick@neumannsystemsgroup.com

partners:

Colorado Springs Utilities, UNDEERC, Industrial Constructor Managers, University of Texas

start date:

01.02.2012

percent complete:

100%

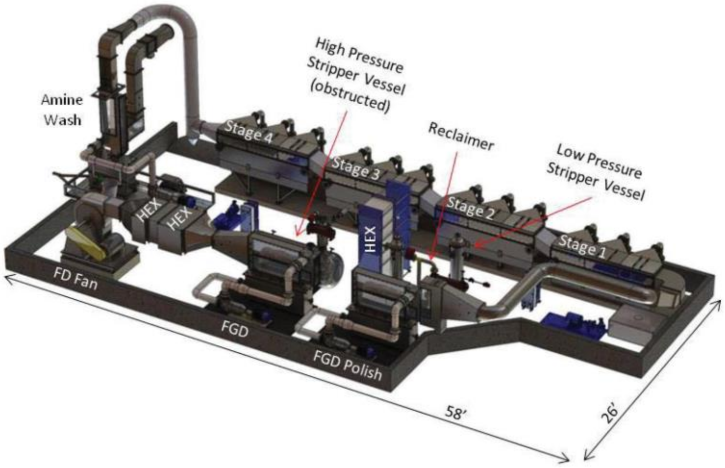

Figure 1: The system layout of the 0.5-MW NeuStream®-C demonstrator system

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	86.14	86.14
Normal Boiling Point	°C	146	146
Normal Freezing Point	°C	106	106
Vapor Pressure @ 15 °C	bar	<0.001	<0.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	34%	34%
Specific Gravity (15 °C/15 °C)	—	0.99 (50 °C)	0.99 (50 °C)
Specific Heat Capacity @ STP	kJ/kg-K	3.6 (50 °C)	3.6 (50 °C)
Viscosity @ STP	cP	3.6 cP at 50 °C	3.6 cP at 50 °C
Absorption			
Pressure**	bar	0.101	0.101
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.38	0.38
Heat of Absorption	kJ/mol CO_2	73	73
Solution Viscosity	cP	4.7	4.7
Desorption			
Pressure***	bar	2/4	2/4
Temperature	°C	150	150
Equilibrium CO_2 Loading	mol/mol	0.28	0.28
Heat of Desorption	kJ/mol CO_2	73	73
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,370	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 >95 4/8	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*unloaded PZ solution is a solid at 15 °C; **CO_2 partial pressure in the flue gas at Drake plant; ***CO_2 partial pressure exiting stripper

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine (MEA) in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135 °F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 into concentrated PZ follows a carbamate mechanism, which is typical of primary and secondary amines. The overall chemical reaction of PZ with CO_2 is

$$2PZ + CO_2 \Leftrightarrow PZH^+ + PZCOO,$$

while the full aqueous reaction pathway is [3]

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$2H_2O + CO_2 \Leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$$

$$PZH^+ + H_2O \Leftrightarrow PZ + H_3O^+$$

$$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$$

$$HPZCOO + H_2O \Leftrightarrow PZCOO^- + H_3O^+$$

$$PZCOO^- + HCO_3^- \Leftrightarrow PZ(COO)_2^{2-} + H_2O.$$

Solvent Contaminant Resistance – 6-m PZ is thermally stable at 150 °C with negligible oxidative degradation. The total amine loss is estimated to be 0.4 percent/week when stripping at 150 °C. At 135 °C, the reported thermal degradation of PZ is 0.07 percent as compared to 8.1 percent in the case of an MEA solvent.[4] The main degradation products of PZ are nitrates (0.13 mM/hr) and ethylenediamine (0.09 mM/hr).

Flue Gas Pretreatment Requirements – The flue gas is passed through a NeuStream® NO_x- and SO_x-removal system before being fed to the CARE system. The SO_x concentration is kept below 10 ppm using two stages of NeuStream® FGD absorbers. The polishing scrubber for SO_x removal has a high volumetric mass-transfer coefficient and 90 percent removal efficiency. The polishing scrubber also cools the flue gas from 57 °C to ≈32 °C by contacting the flue gas with cold sorbent. This helps maintain water balance while also reducing the volumetric flow rate through the CO_2 absorber and counteracting some of the heat from the exothermic CO_2 absorption reaction, reducing the PZ solvent temperature and decreasing the equilibrium vapor pressure, both of which help to reduce the size of the CO_2 absorber.

Waste Streams Generated —Solid waste streams are generated by the reclaimer, which removes heat stable salts formed by NO_x and SO_2 absorption, and by the inline filters. Fugitive liquid amine emissions will be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Amine slip is minimized through the use of an amine water wash absorber unit, also based on NeuStream® technology. The FGD unit generates a gypsum by-product suitable for landfill.

Process Design Concept – Process flow diagram is shown in Figure 2 below.

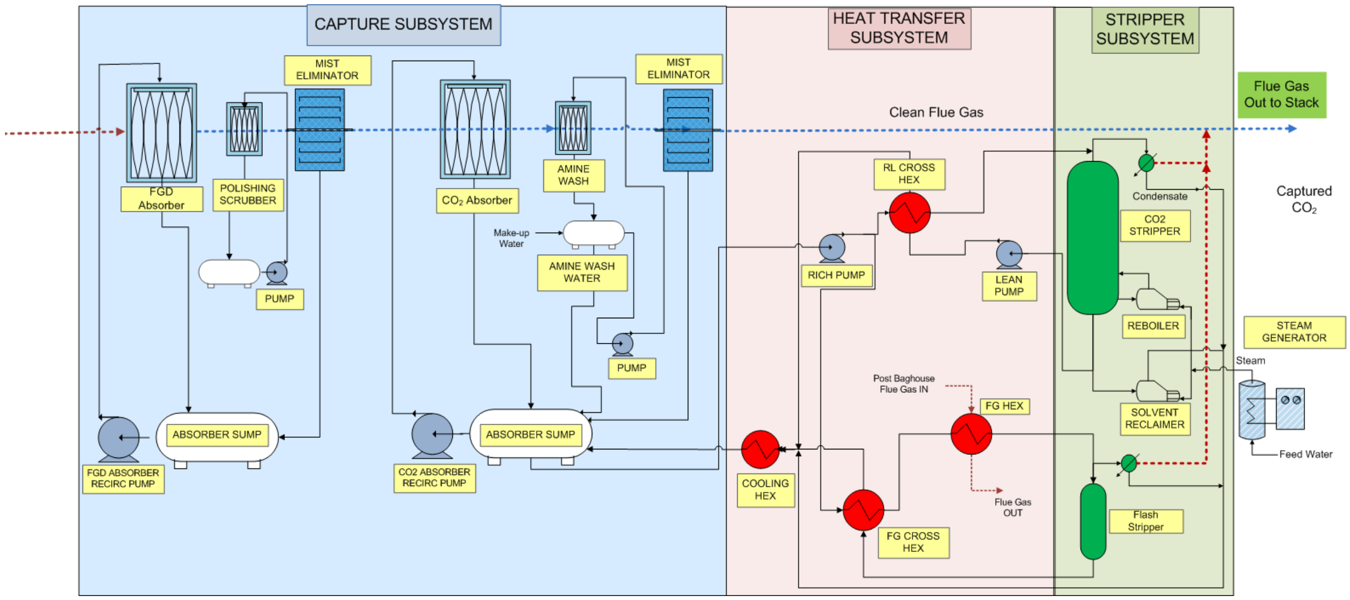

Figure 2: Process flow diagram of CARE system

Proposed Module Design – The heart of the NeuStream® system is NSG's patented, high specific surface area NeuStream® flat jet nozzle technology (shown in Figure 3) engineered into modular, scalable, and efficient cross-flow gas liquid contactor (absorber) units. The modular absorber units are arranged in parallel into full scale systems. Several areas of innovation make this gas-liquid contactor extremely effective for absorbing CO_2 from flue gas. First, a high specific surface area (400–800 m^{-1}) absorption zone is achieved over a large volume from an array of flat jets driven by low liquid-side pressure (<34 kPa). Secondly, the flat jets are aerodynamically shaped, which allows for a high gas flow parallel to the jets while maintaining a low gas-side pressure drop (0.25 kPa/m). Packaging of the NeuStream® absorber takes advantage of the high specific surface area and high gas velocities (typically 5 m/s for CO_2 capture) to reduce the footprint of the system by up to 90 percent and booster fan power requirements by up to 70 percent when compared to conventional packed towers.

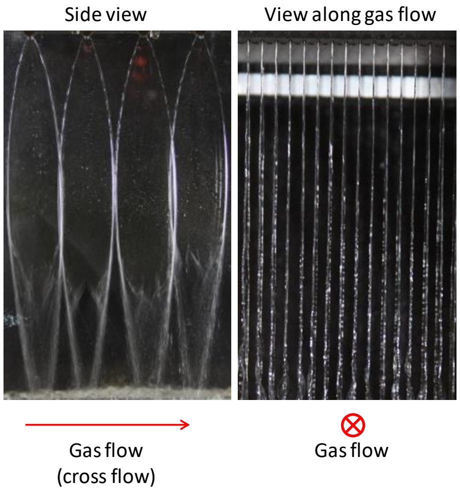

Figure 3: NeuStream® flat jet technology

The system layout is shown above in Figure 1 and the process flow diagram is shown above in Figure 2. Ozone is introduced upstream of a forced draft to oxidize NO_X to more soluble components. The fan moves the flue gas through a heat exchanger to heat the slipstream flow back up to a representative temperature (350 °F). The flue gas then passes through a second heat exchanger, which heats loaded solvent and reduces steam usage in the regeneration subsystem. The flue gas then passes through a NeuStream® FGD system to reduce the SO_x concentration to 15 ppm and the NO_x by 80–90 percent. A polishing/direct contact cooler (DCC) NeuStream® scrubber is used to further reduce the SO_x to 1 ppm, and to cool the flue gas to <35 °C. After the polishing/DDC scrubber, the gas passes through a four-unit NeuStream® CO_2 absorber (shown in Figure 4), where each unit has three stages. This 12-stage absorber reduces the CO_2 by 90 percent prior to contacting the flue gas with a NeuStream® amine wash, which cleans the amine slip from the gas before reintroducing it into the plants main flue gas stream. Due to space constraints, only 3 of the 4 absorber units were relocated to NSG's facility following the unrelated turbine fire at the Drake plant, such that the expected capture efficiency at design gas flow rates would decrease from 90 percent to ≈75 percent and the gas flow would need to be de-rated in order to realize 90 percent CO_2 capture.

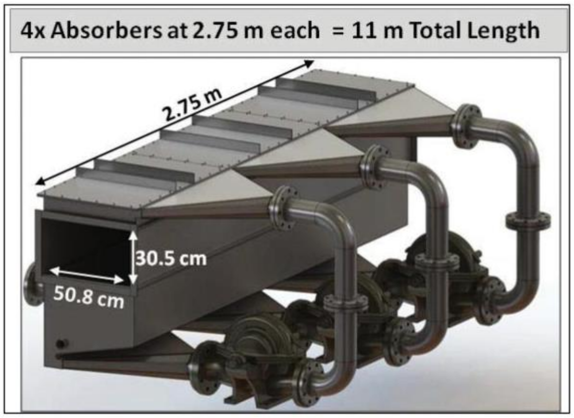

Figure 4: Solid model of one of four NeuStream® CO_2 absorber stages utilized in Project CARE (Cross-sectional area scales with system size, but length remains unchanged.)

The regeneration system contains all typical components, such as cross heat exchangers, solvent cooler exchanger, rich pump, reclaimer, and condenser. A custom-designed stripper vessel is utilized to lower steam usage during operation. Additionally, approximately 10 percent of the rich flow is directed to a lower-pressure flash vessel to desorb the CO_2 from the solvent using only heat provided by the flue gas.

technology advantages

- The NeuStream® CO_2 capture technology integrates a highly-efficient, compact absorber design with an advanced solvent, leading to substantial (≈90 percent) reduction in absorber volume as well as significant savings in both capital and operating costs compared to conventional systems.
- The high surface areas of the NeuStream® flat jets and low-pressure drop in the absorber lower the capital cost of the absorber considerably, leading to significant reductions in the increase in levelized cost of electricity (LCOE) over MEA.
- The NeuStream® technology is adaptable to a wide range of solvents encompassing a large spectrum of properties such as surface tension, viscosity and mass transfer rates.
- The NeuStream® flat jets are engineered into modular absorber units, which are arranged in parallel to meet the flue gas flow rate requirements for specific applications, facilitating rapid, low-risk scale-up of the technology.
- The NeuStream® technology incorporates PZ regeneration at high pressures, leading to lower CO_2 compression power requirements.
- The CARE system utilizes an alternative NO_x-removal strategy to demonstrate the viability of this option over selective catalytic reductions (SCRs).
- The CARE system utilizes a flue gas heat-recovery strategy to reduce the steam usage in the regeneration subsystem.
- A novel stripper design developed by NSG with Dr. Rochelle and Dr. Chen at the University of Texas is incorporated into the CARE system to minimize steam usage.

R&D challenges

- Ensuring optimal distribution of gas in the absorber and avoiding gas bypassing the jets in large-scale absorbers may be an issue, which is addressed via CFD modeling.
- Results from tests on the design verification stand indicate that the specific surface area is not fully preserved with increasing jet length; this may lead to larger absorbers, increasing capital costs. It is possible this decrease is due to the wall effects that become more prevalent at longer jet lengths in the design verification test stand.

status

NSG designed, built and tested a 0.5-MW NeuStream® CO_2 capture system using flue gas from a natural gas boiler. The system exhibited 90 percent capture at the CSU's Martin Drake PC power plant, regenerated CO_2 purity was measured to be 98.6 percent. The NeuStream® absorbers tested support a 90 percent reduction in absorber volume compared to packed towers and with an absorber parasitic power of less than 1 percent when configured for operation with a 550-MW coal plant. Figure 5 shows a size comparison between a 110-MW (net) NeuStream® CO_2 absorber and a commercial 110-MW (net) CO_2 absorber, which was recently commissioned at SaskPower's Boundary Dam Unit #3.[5] As can be seen, NeuStream® technology provides a significant size advantage over conventional CO_2 capture technology, resulting in a volume reduction of 82 percent for the 160-MW Boundary Dam application. The preliminary techno-economic analysis predicted a cost of CO_2 capture at $25.73/tonne, with a corresponding COE increase of 40 percent. Project complete as of December 31, 2015.

Figure 5: CO_2 absorber size comparison: 110 MW (net) NeuStream® vs. CanSolv's 110 MW (net) SaskPower Boundary Dam Unit #3 Project (Includes flue gas desulfurization, CO_2, and amine wash absorbers.)

available reports/technical papers/presentations

"Carbon Absorber Retrofit Equipment (CARE) Final Scientific/Technical Report," December 2015. https://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007528-Neumann-Final-Report.pdf.

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[4] Dombrowski, K, "Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas," DOE-NETL Contractor's Meeting, 2010.

[5] Couturier, Guy and DMello, Mark, (SNC-Lavalin), "From Engineering to Procurement to Construction of the Boundary Dam Carbon Capture System," SaskPower CCS Consortium, 2013 Information and Planning Symposium, May 21, 2013.

Combined Pressure, Temperature Contrast and Surface-Enhanced Separation of Carbon Dioxide for Post-Combustion Carbon Capture

primary project goals

William Marsh Rice University developed a novel process for the separation of carbon dioxide (CO_2) from flue gas from conventional, pulverized coal-fired power plants. The process combines the solvent absorber and stripper columns into a single integrated unit. The combined absorber and stripper system benefited from using a high surface area ceramic foam gas-liquid contactor for enhanced mass transfer. The project included bench-scale testing of the system.

technical goals

- Combine absorber and stripper columns into a single, integrated process unit to achieve significant cost savings in capital costs and to mitigate space availability constraints.
- Use a high surface area ceramic foam gas-liquid contactor for enhanced mass transfer.
- Use vacuum stripping in combination with waste heat for regeneration of a CO_2 solvent.
- Assess the potential to functionalize the ceramic gas-liquid contactors with solid catalyst for enhanced CO_2 desorption.
- Evaluate the use of catalysts for CO_2 desorption.
- Determine best absorbent and operating conditions for the process.
- Develop a two-dimensional (2D) model to simulate gas and liquid flow in the capture process.
- Perform a techno-economic analysis.

technical content

The technical approach involves the integration of the absorber and stripper sections into a single unit. Figure 1 shows a schematic of a combined absorber and stripper unit.

In Figure 1, the region shaded in blue represents a gas-liquid contactor on the absorption side whereas the region shaded in red represents the same on the stripping side. The gas-liquid contactor must possess a large geometric surface area for good gas-liquid contacting. For liquid to be transported from the absorption to stripping side, horizontal flow of the liquid is a requirement. This can take place in two ways, either by flow through the connected pores of a ceramic contactor or as a liquid film moving over the surface of a contactor with a complex three-dimensional structure.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Novel Absorption/Stripper Process

participant:

William Marsh Rice University

project number:

FE0007532

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Dr. Michael S. Wong
William Marsh Rice University
mswong@rice.edu

partners:

N/A

start date:

10.01.2011

percent complete:

100%

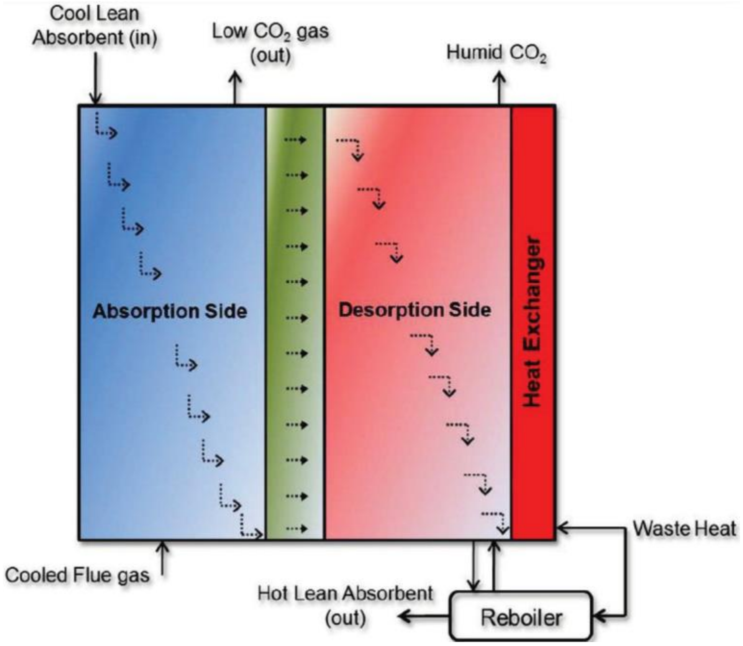

Figure 1: Schematic of combined pressure and temperature contrast and surface-enhanced separation of CO_2

A bench-scale prototype of the gas absorption process was developed to study various aspects of fluid flow in the system. A simulation model for the process was also developed to optimize the properties of ceramics being used and the process operating conditions.

The expected outcomes of this project include significant reduction in the capital and operating costs of the gas absorption process and a resulting decrease in cost of electricity (COE). The use of waste heat instead of high-quality steam provides a significant reduction in operating costs. An integrated absorber and stripper unit substantially reduces capital costs.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	86.14	86.14
Normal Boiling Point	°C	146	146
Normal Freezing Point	°C	106	106
Vapor Pressure @ 15 °C	bar	<0.001	<0.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	34%	34%
Specific Gravity (15 °C/15 °C)	—	0.99 (50 °C)	0.99 (50 °C)
Specific Heat Capacity @ STP	kJ/kg-K	3.6 (50 °C)	3.6 (50 °C)
Viscosity @ STP	cP	3.6 cP at 50 °C	3.6 cP at 50 °C
Absorption			
Pressure**	bar	0.101	0.101
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.38	0.38
Heat of Absorption	kJ/mol CO_2	73	73
Solution Viscosity	cP	4.7	4.7
Desorption			
Pressure***	bar	2/4	2/4
Temperature	°C	150	150

Equilibrium CO_2 Loading	mol/mol	0.28		0.28
Heat of Desorption	kJ/mol CO_2	73		73
Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		2,370	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	>95	4/8
Absorber Pressure Drop	bar		—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

*unloaded PZ solution is a solid at 15 °C; **CO_2 partial pressure in the flue gas at Drake plant; ***CO_2 partial pressure exiting stripper

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine (MEA) in an aqueous solution).

Manufacturing Cost for Solvent – “Current” is market price of chemical, if applicable; “Target” is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	**Temperature**	vol%					ppmv	
		CO_2	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7 psia	135 °F	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 into concentrated PZ follows a carbamate mechanism, which is typical of primary and secondary amines. The overall chemical reaction of PZ with CO_2 is

$$2PZ + CO_2 \Leftrightarrow PZH^+ + PZCOO,$$

while the full aqueous reaction pathway is [3]

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$2H_2O + CO_2 \Leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2}- + H_3O^+$$

$$PZH^+ + H_2O \Leftrightarrow PZ + H_3O^+$$

$$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$$

$$HPZCOO + H_2O \Leftrightarrow PZCOO^- + H_3O^+$$

$$PZCOO^- + HCO_3^- \Leftrightarrow PZ(COO)_2^{2-} + H_2O.$$

Solvent Contaminant Resistance –6-m PZ is thermally stable at 150 °C with negligible oxidative degradation. The total amine loss is estimated to be 0.4 percent/week when stripping at 150 °C. At 135 °C, the reported thermal degradation of PZ is 0.07 percent as compared to 8.1 percent in the case of an MEA solvent.[4]. The main degradation products of PZ are nitrates (0.13 mM/hr) and ethylenediamine (0.09 mM/hr).

Flue Gas Pretreatment Requirements – The flue gas is passed through a NeuStream® nitrogen oxides (NO_x)- and sulfur oxides (SO_x)- removal system before being fed to the CARE system. The SO_x concentration is kept below 10 ppm using two stages of NeuStream® FGD absorbers. The polishing scrubber for SO_x removal has a high volumetric mass-transfer coefficient and 90 percent removal efficiency. The polishing scrubber also cools the flue gas from 57 °C to ≈32 °C by contacting the flue gas with cold sorbent. This helps maintain water balance while also reducing the volumetric flow rate through the CO_2 absorber and counteracting some of the heat from the exothermic CO_2 absorption reaction, reducing the PZ solvent temperature and decreasing the equilibrium vapor pressure, both of which help to reduce the size of the CO_2 absorber.

Waste Streams Generated —Solid waste streams are generated by the reclaimer, which removes heat stable salts formed by NO_x and SO_2 absorption, and by the inline filters. Fugitive liquid amine emissions will be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Amine slip is minimized through the use of an amine water wash absorber unit, also based on NeuStream® technology. The FGD unit generates a gypsum by-product suitable for landfill.

Process Design Concept – Process flow diagram is shown in Figure 2 below.

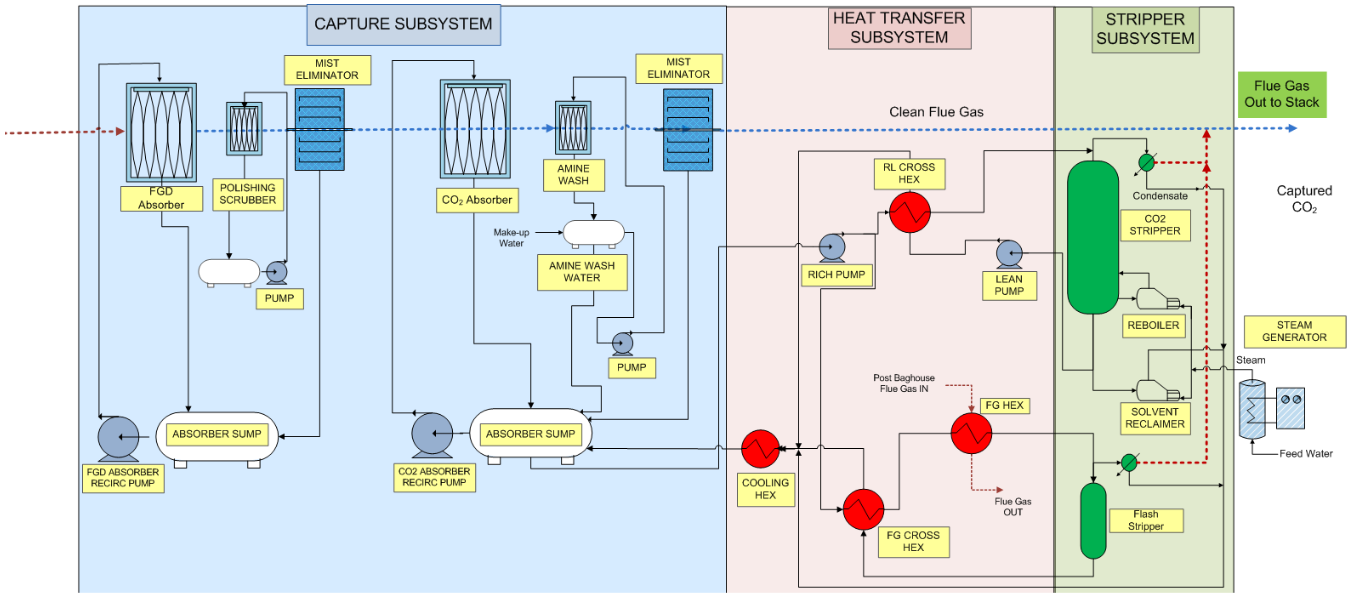

Figure 2: Process flow diagram of care system

Proposed Module Design – The heart of the NeuStream® system is NSG's patented, high specific surface area NeuStream® flat jet nozzle technology (shown in Figure 3) engineered into modular, scalable, and efficient cross-flow gas liquid contactor (absorber) units. The modular absorber units are arranged in parallel into full scale systems. Several areas of innovation make this gas-liquid contactor extremely effective for absorbing CO_2 from flue gas. First, a high specific surface area (400–800 m^{-1}) absorption zone is achieved over a large volume from an array of flat jets driven by low liquid-side pressure (<34kPa). Secondly, the flat jets are aerodynamically shaped which allows for a high gas flow parallel to the jets while maintaining a low gas-side pressure drop (0.25 kPa/m). Packaging of the NeuStream® absorber takes advantage of the high specific surface area and high gas velocities (typically 5 m/s for CO_2 capture) to reduce the footprint of the system by up to 90 percent and booster fan power requirements by up to 70 percent when compared to conventional packed towers.

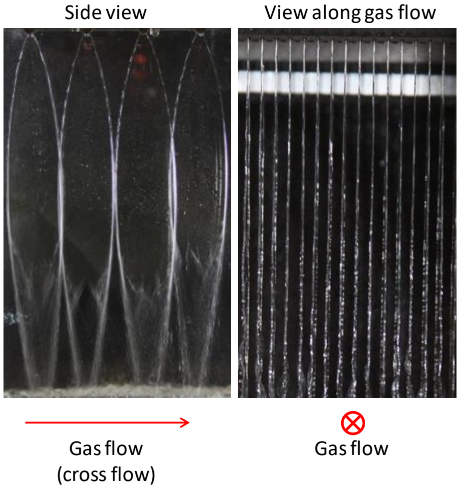

Figure 3: NeuStream® flat jet technology

The system layout is shown above in Figure 1 and the process flow diagram is shown above in Figure 2. Ozone is introduced upstream of a forced draft to oxidize NO_x to more soluble components. The fan moves the flue gas through a heat exchanger to heat the slipstream flow back up to a representative temperature (350 °F). The flue gas then passes through a second heat exchanger, which heats loaded solvent and reduces steam usage in the regeneration subsystem. The flue gas then passes through a NeuStream® FGD system to reduce the SO_x concentration to 15 ppm and the NO_x by 80–90 percent. A polishing/direct contact cooler (DCC) NeuStream® scrubber is used to further reduce the SO_x to 1 ppm, and to cool the flue gas to <35 °C. After the polishing/DDC scrubber, the gas passes through a four-unit NeuStream® CO_2 absorber (shown in Figure 4), where each unit has three stages. This 12-stage absorber reduces the CO_2 by 90 percent prior to contacting the flue gas with a NeuStream® amine wash, which cleans the amine slip from the gas before reintroducing it into the plants main flue gas stream. Due to space constraints, only 3 of the 4 absorber units were relocated to NSG's facility following the unrelated turbine fire at the Drake plant. The expected capture efficiency at design gas flow rates would decrease from 90 percent to ≈75 percent and the gas flow would to be de-rated in order to realize 90 percent CO_2 capture.

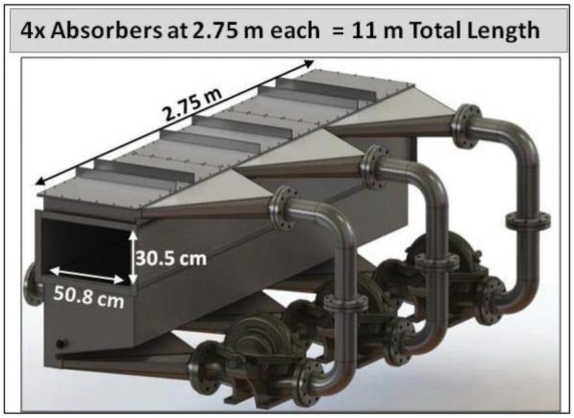

Figure 4: Solid model of one of four NeuStream® CO_2 absorber stages utilized in project CARE (cross-sectional area scales with system size, but length remains unchanged)

The regeneration system contains all typical components, such as cross heat exchangers, solvent cooler exchanger, rich pump, reclaimer, and condenser. A custom-designed stripper vessel is utilized to lower steam usage during operation. Additionally, approximately 10 percent of the rich flow is directed to a lower-pressure flash vessel to desorb the CO_2 from the solvent using only heat provided by the flue gas.

technology advantages

- The NeuStream® CO_2 capture technology integrates a highly-efficient, compact absorber design with an advanced solvent, leading to substantial (≈90 percent) reduction in absorber volume as well as significant savings in both capital and operating costs compared to conventional systems.
- The high surface areas of the NeuStream® flat jets and low-pressure drop in the absorber lower the capital cost of the absorber considerably, leading to significant reductions in the increase in levelized cost of electricity (LCOE) over MEA.
- The NeuStream® technology is adaptable to a wide range of solvents encompassing a large spectrum of properties such as surface tension, viscosity and mass transfer rates.
- The NeuStream® flat jets are engineered into modular absorber units which are arranged in parallel to meet the flue gas flow rate requirements for specific applications, facilitating rapid, low-risk scale-up of the technology.
- The NeuStream® technology incorporates PZ regeneration at high pressures, leading to lower CO_2 compression power requirements.
- The CARE system utilizes an alternative NO_x-removal strategy to demonstrate the viability of this option over selective catalytic reductions (SCRs).
- The CARE system utilizes a flue gas heat-recovery strategy to reduce the steam usage in the regeneration subsystem.
- A novel stripper design developed by NSG with Dr. Rochelle and Dr. Chen at the University of Texas is incorporated into the CARE system to minimize steam usage.

R&D challenges

- Ensuring optimal distribution of gas in the absorber and avoiding gas bypassing the jets in large-scale absorbers may be an issue which is addressed via computational fluid dynamics (CFD) modeling.
- Results from tests on the design verification stand indicate that the specific surface area is not fully preserved with increasing jet length; this may lead to larger absorbers, increasing capital costs. It is possible this decrease is due to the wall effects that become more prevalent at longer jet lengths in the design verification test stand.

status

NSG designed, built and tested a 0.5-megawatt (MW) NeuStream® CO_2 capture system using flue gas from a natural gas boiler. The system exhibited 90 percent capture at the CSU's Martin Drake PC power plant, regenerated CO_2 purity was measured to be 98.6 percent. The NeuStream® absorbers tested support a 90 percent reduction in absorber volume compared to packed towers and with an absorber parasitic power of less than 1 percent when configured for operation with a 550-MW coal plant. Figure 5 shows a size comparison between a 110-MW (net) NeuStream® CO_2 absorber and a commercial 110-MW (net) CO_2 absorber which was recently commissioned at SaskPower's Boundary Dam Unit #3.[5] As can be seen, NeuStream® technology provides a significant size advantage over conventional CO_2 capture technology, resulting in a volume reduction of 82percent for the 160-MW Boundary Dam application. The preliminary techno-economic analysis predicted a cost of CO_2 capture at $25.73/tonne, with a corresponding COE increase of 40 percent. The project was complete as of December 31, 2015.

Figure 5: CO_2 Absorber size comparison: 110-MW (net) NeuStream® vs. CanSolv's 110-MW (net) SaskPower Boundary Dam Unit #3 project (includes flue gas desulfurization, CO_2 and amine wash absorbers)

available reports/technical papers/presentations

"Carbon Absorber Retrofit Equipment (CARE) Final Scientific/Technical Report, December 2015. https://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007528-Neumann-Final-Report.pdf.

"Progress Update on the Carbon Dioxide Absorber Retrofit Equipment (CARE) Program," 2014 NETL CO_2 Capture Technology Meeting, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/A-Awtry-NSG-Progress-Update-On-NSGs-CARE.pdf*.

"Status of the Carbon Dioxide Absorber Retrofit Equipment (CARE) Program," 2013 NETL CO_2 Capture Technology Meeting, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/A-Awtry-NSG-Status-of-the-CARE-Program.pdf*

Brasseur, J., and Awtry, A., “Compact Absorber Retrofit Equipment (CARE),” presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA. *http://www.netl.doe.gov/publications/proceedings/12/CO2capture/presentations/2-Tuesday/2-Brasseur-NeumannSG.pdf*.

Awtry, A., Klein, E., and Brasseur, J., “NeuStream®-C: Carbon Capture Progress Update”, Air Quality IX, Arlington, VA, 2013.

Awtry, A., Klein, E., and Brasseur, J., “NeuStream®-C: Carbon Capture Progress Update”, Power-Gen XXV, Orlando, FL, 2013.

references

[1] Dugas, Ross E., “CO_2 Absorption, Desorption, and Diffusion in Aqueous Piperazine and Monoethanolamine,” PhD Thesis, University of Texas, 2009.

[2] Van Wagener, David H., “Stripper Modeling for CO_2 Removal Using Monoethanolamine and Piperazine Solvents,” PhD Thesis, University of Texas, 2011.

[3] Bishnoi, S., and Rochelle, G. T., “Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility,” Chemical Engineering Science 55 (2000) 5531-5543.

[4] Dombrowski, K, “Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas,” DOE-NETL Contractor’s Meeting, 2010.

[5] Couturier, Guy and DMello, Mark, (SNC-Lavalin), “From Engineering to Procurement to Construction of the Boundary Dam Carbon Capture System”, SaskPower CCS Consortium, 2013 Information and Planning Symposium, May 21, 2013.

Development of a Novel Gas Pressurized Stripping-Based Technology for CO_2 Capture from Post-Combustion Flue Gases

primary project goals

Carbon Capture Scientific has performed bench-scale development, testing, and computer simulations of a novel solvent-based carbon dioxide (CO_2) capture technology, known as gas-pressurized stripping (GPS) process. The GPS technology has the potential to significantly reduce the energy penalty associated with solvent regeneration and compression by operating the regeneration step at higher pressures, which in-turn reduces the compression requirements for CO_2 storage.

technical goals

- Computer simulation to predict GPS column performance under different operating conditions.
- Lab-scale tests of individual process units to document experimental results and obtain necessary information to progress the technology to the next level.
- Experimental investigation of selected solvents to minimize the economic risk of the proposed technology.
- Design, build, and operate a bench-scale GPS unit capable of processing about 500 standard liters of actual coal-derived flue gas per minute (SLPM) at the National Carbon Capture Center (NCCC).
- Derive a techno-economic analysis (TEA) of the GPS process on a pulverized coal plant compared to a baseline pulverized coal plant.

technical content

The project conducted lab-scale individual process unit tests and integrated continuous bench-scale GPS system tests using actual coal-derived flue gas at the NCCC. The overall objective was to reduce the energy consumption and capital cost of the CO_2 capture process.

Computer simulation tasks investigated the GPS column behavior under different operating conditions, optimizing the column design and operating conditions, leading to a capital cost increase less than five percent over the baseline monoethanolamine (MEA) case. Solvent related tasks collected information on the solvent operating cost when a modified, commercially-available solvent is used in the GPS process. Experiment related tasks with the major individual units obtained information needed for the bench-scale unit design, and the integrated continuous bench-scale GPS system tests using actual coal-derived flue gas at the NCCC provided all the necessary information for the next level pilot-scale process and engineering design along with the GPS system performance data. Testing at the NCCC demonstrated that the GPS process can

technology maturity:

Bench-Scale, Real Flue Gas

project focus:

Gas-Pressurized Stripping

participant:

Carbon Capture Scientific

project number:

FE0007567

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Shiaoguo (Scott) Chen
Carbon Capture Scientific, LLC
scottchen@carboncapturescientific.com

partners:

CONSOL Energy, Inc., Nexant, Inc., Western Kentucky University

start date:

10.01.2011

percent complete:

100%

achieve 90 percent CO_2 removal from typical coal-derived flue gas. The GPS process can produce high-pressure CO_2 product with required purity. Finally, the GPS process has an energy consumption much lower than that of the DOE MEA baseline case. A TEA of the GPS process was derived, showing that a GPS-based pulverized coal (PC) plant has net power production of 647 MW, greater than the MEA baseline study. This increase is attributed to the lower steam requirement and smaller CO_2 compression auxiliary power consumption. The TEA also found that the 20-year levelized cost of electricity for a supercritical PC plant with GPS-based PCC is 52 percent more than the baseline supercritical PC plant without CO_2 capture but 23 percent lower than the baseline supercritical PC plant with MEA. Figure 1 is a flowchart for the GPS process. Figure 2 shows the GPS-based skid developed and tested at the NCCC. Table 1 lists the process parameters relevant to the GPS process.

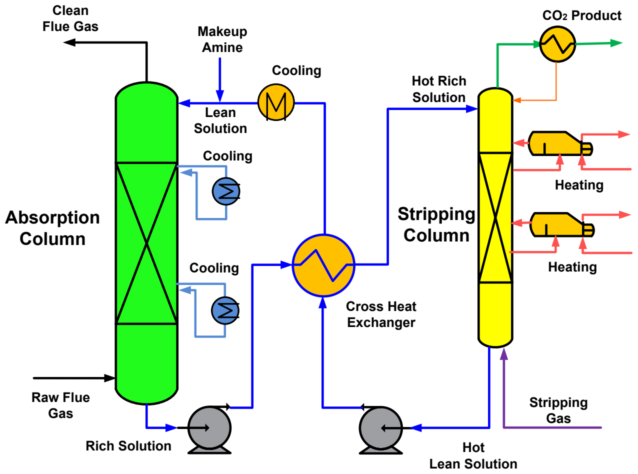

Figure 1: GPS-based absorption/stripping process

Figure 2: GPS-based skid used for bench-scale slipstream testing at NCCC

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	112.4	112.4
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15 °C	bar	<1.3E-05	<1.3E-05
Manufacturing Cost for Solvent	$/kg	3	3
Working Solution			
Concentration	kg/kg	—	—
Specific Gravity (15 °C/15 °C)	—	1.06	1.06
Specific Heat Capacity @ STP	kJ/kg-K	ca. 3	ca. 3
Viscosity @ STP	cP	N/A	
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.41	0.49
Heat of Absorption	kJ/mol CO_2	59.6	59.6
Solution Viscosity	cP	6.2	4
Desorption			
Pressure	bar	6	6
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.19	0.19
Heat of Desorption	kJ/mol CO_2	58.5	58.5
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	40	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% >95% 6 bar	
Absorber Pressure Drop	bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption **–** The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

***Pressure* –** The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

***Concentration* –** Mass fraction of pure solvent in working solution.

***Loading* –** The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

***Chemical/Physical Solvent Mechanism* –** Pressurized stripping is a process applicable to different types of solvents. Chemistry of the GPS-based absorption/stripping process depends on the solvent used in the process. In the proposed research, a modified commercially-available amine solvent will be used. Therefore, the chemistry of the amine-based CO_2 capture process will apply to the GPS-based process.

The reaction kinetics of the GPS-based process also depends on the solvent selected. With the solvent currently selected, it is believed that the reaction kinetics of the modified commercially available solvent will perform better than the baseline monoethanolamine (MEA) process.

***Solvent Contaminant Resistance* –** Since the selected solvent is an amine-based solvent, it will share common issues that other amine-based solvents have. Sulfur oxide (SO_x) and nitrogen oxide (NO_x) could be the major contaminants in flue gas, which will be detrimental to all amine-based solvents, including the solvent used in this process. Similar to other amine-based solvents, pretreatment of flue gas will be required to minimize amine degradations.

***Solvent Foaming Tendency* –** The solvent is a commercially available solvent, with different strength. The solvent forming tendency should be manageable based on industrial experience.

***Flue Gas Pretreatment Requirements* –** Similar to other amine-based solvents, pretreatment of flue gas will be required to minimize amine degradations.

***Solvent Makeup Requirements* –** Solvent stability study has demonstrated that this commercially-available solvent will have solvent makeup rate of 1 kg solvent/tonne CO_2.

***Waste Streams Generated* –** Waste stream of the GPS-based process is also similar to other amine-based absorption/stripping processes. The main waste material is amine degradation products.

Process Design Concept – Flowsheet/block flow diagram of the GPS process is shown in Figure 1. It is clear that the GPS process is virtually the same as a conventional absorption/stripping process except the two unique innovations: (1) using two side heat exchangers to replace a bottom reboiler, and (2) introducing a stripping gas (N_2 or other inert gas) into the GPS column from the bottom. This process configuration will reduce stripping heat significantly.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57 °C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

		Composition						
Pressure	Temperature	vol%					ppmv	
bara	°C	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1.014	57	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- The use of off-the-shelf process equipment will accelerate process development.
- The use of absorption/stripping technology would be suitable for low-cost, large-scale applications.
- The higher stripper operating pressure reduces the stripping heat requirement and subsequent compression work. As a result, GPS process offers higher energy efficiency.

- The GPS technology is flexible in terms of operating pressures and temperatures, and is applicable to different types of solvents.

R&D challenges

The major challenge of the GPS-based process is its capital cost. The optimal GPS-based process has almost the same capital cost as the baseline process. New process equipment, which can significantly reduce capital cost, is needed to commercialize the GPS technology.

status

The project was completed on September 30, 2015. Carbon Capture Scientific and their partners determined that a combination of experimental, computer simulation, and techno-economic analysis was effective to identify optimal process configurations and operating conditions for the GPS technology and that the GPS-based post-combustion capture process is energy-efficient and cost-effective compared with the benchmark MEA process. Integrating the GPS process into a 550-MW_e PC-fired power plant will increase cost of electricity approximately 23 percent less than that for the benchmark MEA process.

available reports/technical papers/presentations

Shiaoguo (Scott) Chen, “Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases,” Final Scientific/Technical Report, October 2015. *https://www.osti.gov/scitech/servlets/purl/1233208*.

Shiaoguo (Scott) Chen, “Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases,” Project Closeout Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007567-Final-Review-Presentation-12-18-2015.pdf*.

Shiaoguo (Scott) Chen, “Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases,” 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/S-Chen-CCS-Gas-Pressurized-Stripping.pdf*.

Shiaoguo (Scott) Chen, “Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases,” 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Chen-CCS-Development-Of-A-Novel-Gas-Pressurized-Stripping.pdf*.

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Shiaoguo (Scott) Chen, “Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases,” 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/development-novel-gas-pressurized-stripping-july2012.pdf*.

“Development of a Novel Gas Pressurized Stripping Process-Based Technology for CO_2 Capture,” Project Kick-Off Meeting Presentation, November 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/development-novel-gas-pressurized-stripping-kickoff-nov2011.pdf*.

Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Vacuum Regeneration

primary project goals

Novozymes, together with the project partners, designed, built, and tested an integrated bench-scale system that combines the attributes of an enzyme catalyst (carbonic anhydrase [CA]) with low-enthalpy absorption liquids and vacuum regeneration in a solvent-based carbon dioxide (CO_2) capture process, and evaluated a novel ultrasonically enhanced regeneration concept.

technical goals

- Conduct preliminary evaluation of the potential for ultrasonic regeneration to deliver a lean-loading equivalent to the lean loading predicted with vacuum stripping at 70 °C.
- Optimize enzyme-promoted potassium carbonate (K_2CO_3)-based solvent for maximum CO_2 absorption rate.
- Demonstrate enzyme robustness for meeting targeted bench-scale test conditions.
- Design and build an integrated bench-scale unit incorporating the vacuum regeneration component to validate stripping performance at 70–80 °C.
- Demonstrate system performance and benefits based on completion of 500 hours of testing.
- Complete a full technology assessment of the process and potential for meeting reductions in net parasitic load compared to conventional technology for post-combustion CO_2 capture.

technical content

Novozymes, together with the project partners, designed, built, and tested an integrated bench-scale system that combines the attributes of the bio-renewable enzyme carbonic anhydrase (CA) with low-enthalpy aqueous potassium carbonate-based solvent and vacuum regeneration. Preliminary evaluation of a novel ultrasonically enhanced regeneration system was also made. The objective was to develop a CO_2 capture process with improved efficiency and economics when compared with existing CO_2 technologies.

The application of CA accelerates inter-conversion between dissolved CO_2 and bicarbonate ion, which is the rate-limiting step for absorption and desorption in low enthalpy of reaction solutions that rely on reactive absorption of CO_2. The mechanism for CO_2 absorption and desorption when using potassium carbonate solvent is:

$$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2\ KHCO_3$$

The use of low enthalpy CO_2 absorption solvents offers the opportunity to regenerate the solvent at lower temperatures relative to existing CO_2 scrubber technologies. The

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Solvent + Enzyme and Vacuum Regeneration Technology

participant:

Novozymes

project number:

FE0007741

predecessor projects:

N/A

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Dr. Sonja Salmon
Novozymes

partners:

University of Kentucky CAER; Pacific Northwest National Laboratory; Doosan

start date:

10.01.2011

percent complete:

100%

system was evaluated with respect to energy requirement and enzyme effects in a process where the enzyme is dissolved and recirculates through the absorber and reduced-temperature stripper. A replenishment program to compensate for active enzyme loss while maintaining system performance was also evaluated.

One method of achieving low temperature stripping is to apply vacuum to decrease the solvent boiling point to ≈70–80 °C, and provide driving force for the regeneration. Process simulations of this approach have been made indicating that the use of low-enthalpy solvents, which could require low-pressure steam during the regeneration cycle, together with vacuum has the potential to require 43 percent less parasitic power from a coal-fired power plant compared to NETL Case 10 MEA scrubbing technology. It is recognized that application of vacuum would have a corresponding compression penalty downstream of the CO_2 capture unit. Therefore, the aim of the evaluation was to demonstrate the feasibility of the vacuum approach by a combination of bench-scale system testing and corresponding projections of feasibility at 550-megawatt electric (MW_e) scale.

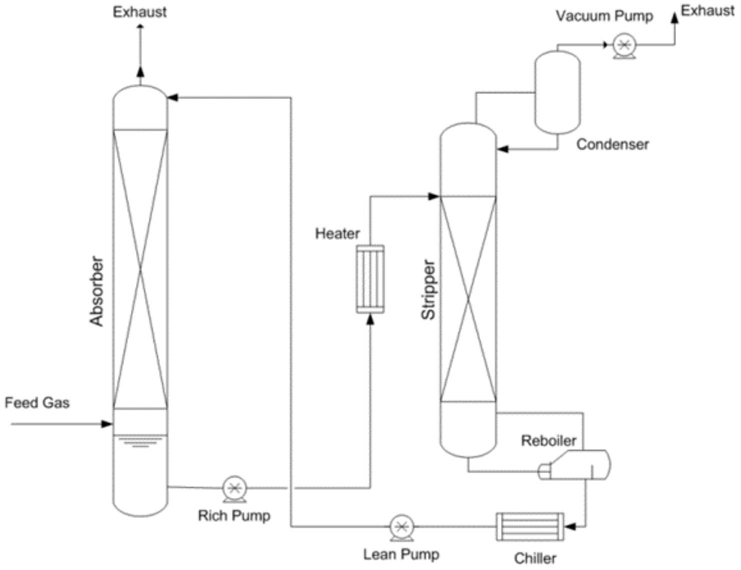

Figure 1: Bench-scale process schematic

In another method of low temperature stripping, application of ultrasonic energy transforms dissolved CO_2 into gas bubbles, thereby increasing the overall driving force of the solvent regeneration reaction. This is shown in Figure 2, where the effects of sonication can be seen on the loaded solvent. The ultrasonic effect known as rectified diffusion where expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution, could have the potential to yield lean solvent CO_2 loading equivalent to vacuum stripping. Several different configurations of the prototype ultrasonic regenerator were evaluated, including combination with vacuum and novel incorporation of a hydrocyclone to enhance gas-liquid separation. The magnitude of measured CO_2 release was within the range of temperature-dependent release, meaning that application of ultrasonics could provide thermal regeneration effects. However, additional work would be required to validate whether rectified diffusion could replace the vacuum requirement at low stripping temperatures.

Figure 2: Ultrasonic regeneration batch tests for loaded solvent at 70 °C – (L) no sonication; (R) with sonication

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	138.21	138.21
Normal Boiling Point	°C	—	—
Normal Freezing Point	°C	—	—
Vapor Pressure @ 15 °C	bar	—	—
Manufacturing Cost for Solvent	$/kg	1.3	<1.3
Working Solution			
Concentration	kg/kg	0.23	0.23
Specific Gravity (15 °C/15 °C)	-	1.21	1.21
Specific Heat Capacity @ STP	kJ/kg-K	~3.4[a]	~3.4[a]
Viscosity @ STP	cP	~1.4	~1.4
Absorption			
Pressure	bar	1	1
Temperature	°C	30–40	30–50
Equilibrium CO_2 Loading	mol/mol	0.55	0.67
Heat of Absorption	kJ/mol CO_2	27	27
Solution Viscosity	cP	~1.4	~1.4
Desorption			
Pressure	bar	0.35	0.35
Temperature	°C	77	70–80
Equilibrium CO_2 Loading	mol/mol	0.35	0.30
Heat of Desorption	kJ/mol CO_2	27	27
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Notes: Working solution additionally contains CA enzyme catalyst.

[a] Technical Data: Properties of Potassium Carbonate. Armand Products Company.

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

1. $CO_{2(g)} \leftrightarrow CO_{2(aq)}$ (gas-liquid physical mass transfer)
2. $CO_{2(aq)} + HO^- \leftrightarrow HCO_3^-$
3. $HCO_3^- + HO^- \leftrightarrow CO_3^= + H_2O$ ($pK_a = 10.3$)
4. $CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3$
5. $H_2CO_3 + HO^- \leftrightarrow HCO_3^- + H_2O$ ($pK_a = 6.4$)
6. $H_2O \leftrightarrow H^+ + HO^-$

For the solvent system in the proposed operating range (pH 9-11), Reaction 2 and reactions 4 together with 5 are responsible for the absorption of CO_2 into the liquid phase as bicarbonate. CA enzyme catalyzes Reaction 6 in the enzyme active site to produce a zinc-hydroxide nucleophile that reacts with CO_2 to produce and release bicarbonate according to Reaction 2. The proton produced during Reaction 6 is transferred from the active site to the reaction medium where the proton is neutralized by the alkalinity and buffering capacity of the medium. The transfer of proton away from the active site has been determined in the literature as the rate limiting step for CA catalysis.

The kinetics of CO_2 absorption in CA enzyme/K_2CO_3 solution were measured using the wetted-wall column technique. The current enzyme/K_2CO_3 solvent supports a mass transfer rate ≥50 percent the rate of benchmark 30 percent MEA.

Solvent Contaminant Resistance – Publications by Akermin, Inc. (DE-FE0004228 and DE-FE0012862) and the University of Illinois (DE-FC26-08NT0005498) demonstrate the robustness of enzyme-promoted K_2CO_3 solvents to typical flue gas contaminants at lab scale.

Solvent Foaming Tendency – Based on bench-scale tests, solvent foaming can be mitigated by antifoam, as necessary.

Flue Gas Pretreatment Requirements – No special requirements expected beyond conventional pretreatment for particulate, sulfur oxide (SO_x), and nitrogen oxide (NO_x) removal.

Solvent Make-Up Requirements – Preliminary feasibility study assumed a K_2CO_3 makeup rate of 0.1 ton/day and continuous enzyme reclamation from 0.05 percent lean solvent slipstream. However, lower than targeted enzyme longevity in the bench scale test resulted in significant cost impact of solvent makeup requirements in the final TEA.

Waste Streams Generated – Waste stream consists of K_2CO_3 salts and biodegradable enzyme, which could be used as compost, fertilizer or boiler fuel.

Process Design Concept – Bench-scale process schematic is shown in Figure 1.

technology advantages

- The energy required for solvent regeneration is provided by low-pressure steam and vacuum.
- Enzyme helps overcome the inherently slow reaction rates of the K_2CO_3 based solvent, which have previously made its use for atmospheric CO_2 capture prohibitive. Enzyme-enhanced rates of CO_2 absorption compared to aqueous K_2CO_3 without CA could lead to capital cost savings.
- By providing enzyme in dissolved form, conventional liquid handling approaches can be used to adjust enzyme dose and replenishment rates to achieve optimal system performance.
- K_2CO_3 has chemical handling advantages due to negligible vapor pressure, no flash point, no odor, no degradation, good safety and environmental profile, and ready availability.

R&D challenges

- Scale-up of the vacuum and ultrasonic regeneration systems from lab- to bench-scale (10–30 standard liters/minute [SLPM] gas, 0.1–0.30 LPM solvent) to provide sufficient lean loading to support 90 percent capture.
- Ultrasonic test system showed tendency towards rapid CO_2 re-dissolution of generated gases and foaming phenomena, which pointed to the need for specialized gas removal in the continuous system. Further work is needed to verify predicted ultrasonic advantages.
- Enzyme dose required to achieve and maintain 90 percent capture.
- Accurate scale up of bench scale data to full scale predictions using process models.
- Practicality of vacuum equipment to handle CO_2 gas flow at 550-MW_e scale.
- Utilization of a very low pressure (VLP) turbine for extracting the solvent regeneration steam at 8 psia (and 85 °C).

status

This project was completed on June 30, 2015. A novel flow-through ultrasonic regenerator was designed and tested, confirming that CO_2 was released, however the release values were below the equilibrium projections. The highest ultrasonic results were explainable by the localized temperature increases in the liquid caused by the ultrasonic energy alone, therefore the remainder of the project focused on the use of vacuum regeneration. The fully integrated bench-scale system including vacuum regeneration was designed and fabricated, with parametric and alternative solvent testing completed. Overall, the system was operated successfully for an accumulated 500 hours of operation with vacuum conditions. An average of 84 percent CO_2 capture efficiency was attained during the period using enzyme replenishment. The presence of enzyme caused foaming in the stripper, which was controlled via antifoam addition. There was a faster decay rate of the enzyme activity at longer residence time at elevated temperatures in the cycle. TEA studies of the system indicated higher COE, higher cost of CO_2 captured, and slightly lower energy requirement compared to DOE Case 10 (Econamine solvent process), with the difference in costs primarily due to higher variable costs.

available reports/technical papers/presentations

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *http://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007741-Final-Project-Meeting-09-23-15.pdf*

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *http://netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*

House, A., "Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," AIChE 2014 Meeting, Atlanta, GA, November 17, 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007741-AIChE-2014-Presentation-11-17-2014.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*.

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Salmon, S., "Lab-Scale Assessment of a Post-Combustion Carbon Dioxide Capture Process Enabled by a Combination of Enzymes and Ultrasonics," 2012 Pittsburgh Coal Conference, Pittsburgh, PA, October 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/ipcc-oct2012-session11-salmon.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Ultrasonics," 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. July 2012. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/enzymes-ultrasonics-july2012.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Ultrasonics," Project Kick-Off Meeting, November 2011. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/enzymes-ultrasonics-kickoff-nov2011.pdf*.

DEVELOPMENT OF AN ENERGY-EFFICIENT, ENVIRONMENTALLY FRIENDLY SOLVENT FOR THE CAPTURE OF CO_2

primary project goals

This Babcock & Wilcox Power Generation Group, Inc., (B&W) project focuses on identifying concentrated piperazine (PZ)-based solvent formulations that improve overall solvent and system performance.

technical goals

- Improve system operability and reliability.
- Minimize environmental impacts.
- Reduce corrosion potential.
- Maximize solvent durability.

technical content

B&W is characterizing and optimizing the formulation of a novel solvent for the capture of carbon dioxide (CO_2) at coal-fired utility plants. The solvent of interest has been identified through a 5-year solvent development program conducted at B&W. The solvent formulations of interest comprise concentrated solutions of a cyclic diamine, PZ. Testing at B&W indicates that blends of concentrated PZ with other compounds have the potential to perform substantially better than PZ itself. The objective is to lower the total cost of solvent-based CO_2 capture systems by identifying formulations that improve overall solvent and system performance.

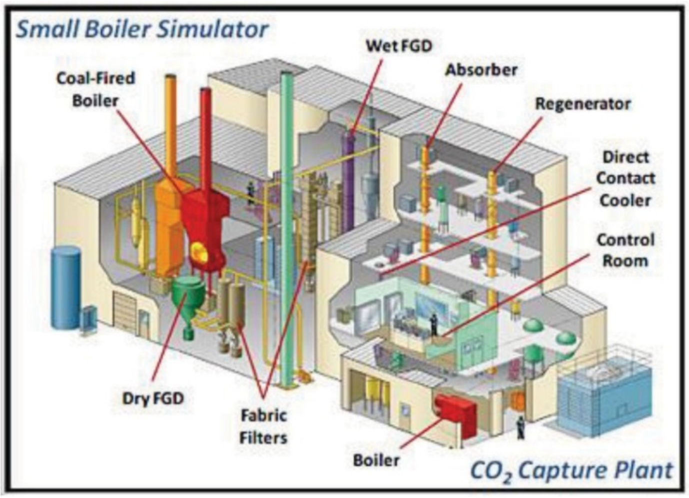

Figure 1: B&W 7-Ton/Day Pilot Facility

technology maturity:

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Optimized Solvent Formulation

participant:

Babcock & Wilcox

project number:

FE0007716

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

George Farthing
Babcock & Wilcox
gafarthing@babcock.com

partners:

University of Cincinnati, First Energy

performance period:

10/1/11 – 4/30/14

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The CO_2-reactive species (there may be other non-reactive species) in the solvent formulation may include amines, carbonates, or amino acid salts in combination with concentrated PZ. Amine solvents are grouped according to their molecular structure. Carbonate and amine reactions with CO_2 can be summarized as follows:

Carbonates: $CO_3{=} + CO_2 + H_2O \leftrightarrow 2\ HCO_3^-$

Hindered and tertiary amines: $CO_2 + R_3N + H_2O \leftrightarrow HCO_3^- + R_3NH^+$

Primary and secondary amines: $CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+$

Solvent Contaminant Resistance – Amine solvents chemically degrade in a variety of ways (thermal degradation due to exposure to the high temperatures of the regeneration process, oxidative degradation due the presence of oxygen in the flue gas, carbamate polymerization, etc.). Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals (possibly originating with the coal fly ash). Minimizing solvent degradation and the attendant production of potentially hazardous chemical species is a central objective of this project.

Flue Gas Pretreatment Requirements – Flue gas supplied to the CO_2 capture system must be cooled to approximately 40°C and relatively free of contaminants. Concentrations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) must be less than about 10 parts per million (ppm)—preferably around 1 ppm.

Solvent Makeup Requirements – Solvent makeup is required to offset solvent losses due to volatility, degradation, the formation of heat stable salts, etc. PZ-based solvents are expected to minimize such losses due to the lower volatility and better resistance to thermal degradation exhibited by PZ relative to solvents such as monoethanolamine (MEA). This project is focused on minimizing solvent losses in the system.

Waste Streams Generated – Waste streams generated by the process will be similar to those generated by convention amine processes, including reclaimer waste solids, spent carbon and particulate filter cake from solvent filtration equipment, and potentially waste water. It is an objective of this project to minimize the environmental impact of these streams through careful selection of the solvent formulation and operating conditions.

Process Design Concept – The CO_2 capture process, illustrated in Figure 2, comprises a relatively conventional absorption/stripping process.

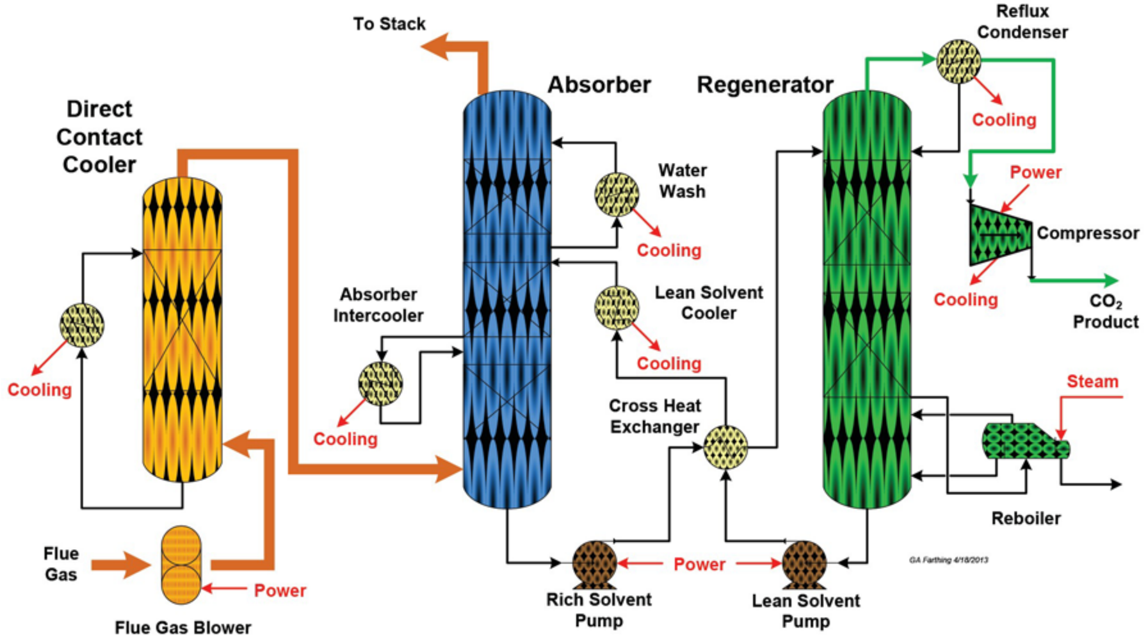

Figure 2: Schematic of Solvent-Based CO_2 Capture Process

technology advantages

Piperazine, used alone, has demonstrated high rates of absorption and low regeneration energy. Recent testing at B&W indicates that blends of concentrated PZ with other organic compounds may perform substantially better than PZ alone.

R&D challenges

- Selection of a solvent formulation involves compromises that seek to optimally balance competing effects. Using limited and potentially non-representative data generated in laboratory-scale equipment is extremely challenging. Previous solvent development work supports correlation of laboratory results with pilot-scale performance estimation to optimize solvent formulation.
- Goals include improved system operability and reliability, minimizing environmental impacts, reducing corrosion potential, and maximizing solvent durability.

results to date/accomplishments

- A list of candidate solvent formulations was developed and refined. This work comprised evaluations regarding overall solvent performance criteria, identification of primary active components, and verification of wet chemistry analytical techniques for CO_2 loading and alkalinity.
- Several modeling approaches were identified. Tools considered include equilibrium models, semi-empirical rate-based models, and rigorous rate-based models. Tools for the prediction of process economics were also evaluated.
- Characterization tests in B&W's wetted-wall column (WWC) were completed on a baseline concentrated PZ solvent and 12 candidate solvent formulations. The liquid film mass transfer coefficient (kg), as well as equilibrium partial pressure of CO_2 (P_{CO2}*), were obtained from each WWC test. Other parameters, such as heat of absorption and CO_2 working capacity, were also derived from these experimental data. Preliminary solvent formulation performance was then estimated with in-house, semi-empirical models.
- Solvent volatility and solubility testing was performed on several candidate formulations of concentrated PZ solutions containing salts of amino acids, carbonates, and other amines. Also evaluated were organic additives designed to improve the solubility of PZ and its carbamates. In addition, it was found necessary to characterize candidate formulations with respect to their viscosities in order to ensure good mass transfer performance and acceptable operability.
- Installation of the bench-scale continuous solvent degradation system (CSDS) was completed. The CSDS will enable comprehensive investigations of proposed solvent formulation degradation under representative operating conditions. It is intended to simulate key features of industrial CO_2 capture processes, including cyclical absorption and regeneration process conditions. The CSDS is designed for continuous, unattended operation for tests lasting 100 to 1,000 hours or more.

next steps

This project ended on April 30, 2013.

available reports/technical papers/presentations

Final Report, "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," June 2014. *http://www.osti.gov/scitech/servlets/purl/1136527*.

Farthing, G., "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

BENCH-SCALE DEVELOPMENT OF A HOT CARBONATE ABSORPTION PROCESS WITH CRYSTALLIZATION-ENABLED HIGH-PRESSURE STRIPPING FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

The University of Illinois at Urbana-Champaign (UIUC) is performing a proof-of-concept study that will generate process engineering and scaleup data to optimize the Hot Carbonate Absorption Process (Hot-CAP) with crystallization-enabled, high-pressure stripping technology. The study seeks to demonstrate its capability to achieve the U.S. Department of Energy (DOE) goals of at least 90 percent carbon dioxide (CO_2) removal from coal-fired power plant flue gas with less than a 35 percent increase in the cost of electricity (COE), helping to advance the process to pilot-scale level within 3 years.

technical goals

- Perform laboratory- and bench-scale tests to measure thermodynamic and reaction engineering data that will be used to evaluate technical feasibility and cost-effectiveness, performance of scaleup, and commercial competitiveness of the Hot-CAP with monoethanolamine (MEA)-based processes and other emerging post-combustion CO_2 capture technologies.
- Perform a combination of experimental, modeling, process simulation, and technical and economic analysis studies.

technical content

UIUC and Carbon Capture Scientific, LLC are investigating a Hot-CAP to overcome the energy use disadvantage of MEA-based processes. A preliminary technical-economic evaluation shows that the energy use of the Hot-CAP is about 40 percent less than that of its MEA counterpart, and the process has the potential to meet or exceed DOE's technical and cost goals of greater than or equal to 90 percent CO_2 removal and less than or equal to a 35 percent increase in the COE.

The Hot-CAP is an absorption-based, post-combustion CO_2 technology that uses a carbonate salt (K_2CO_3 or Na_2CO_3) as a solvent. The process integrates a high-temperature (70–80 °C) CO_2 absorption column, a slurry-based high-pressure (up to 40 atm) CO_2 stripping column, a crystallization unit to separate bicarbonate and recover the carbonate solvent, and a reclaimer to recover $CaSO_4$ as the byproduct of the sulfur dioxide (SO_2) removal.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping

participant:

University of Illinois at Urbana-Champaign

project number:

FE0004360

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Yongqi Lu
University of Illinois at Urbana-Champaign
yongqilu@illinois.edu

partners:

Carbon Capture Scientific, LLC

performance period:

1/1/11 – 3/31/14

Project objectives include performing a proof-of-concept study aimed at generating process engineering and scaleup data to help advance the Hot-CAP technology to pilot-scale demonstration level. The project tasks employ lab- and bench-scale test facilities to measure thermodynamic and reaction engineering data that can help evaluate technical feasibility and cost-effectiveness, performance of scaleup, and commercial competitiveness of the Hot-CAP compared to the MEA-based processes and other emerging post-combustion CO_2 capture technologies.

To meet project objectives, lab- and bench-scale tests include measurement of the kinetics and phase equilibrium data associated with the major reactions and unit operations in the Hot-CAP, including CO_2 absorption, bicarbonate crystallization, sulfate recovery, and CO_2 stripping. The results from the lab- and bench-scale studies support development of a process flow diagram, equipment and process simulations, and a techno-economic study for a conceptual 550-MWe high-sulfur coal-fired power plant retrofitted with the Hot-CAP.

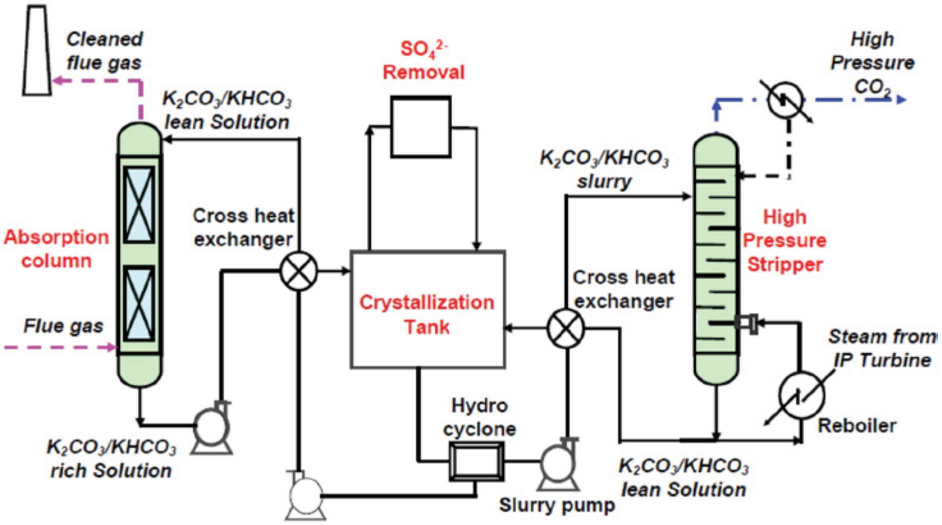

Figure 1: Hot Carbonate Absorption Process with High-Pressure Stripping Enabled by Crystallization (Hot-CAP)—Process Flow Diagram

TABLE 1: PROCESS PARAMETERS FOR CARBONATE SALT SOLVENT
(based on 40 wt% [K_2CO_3 equivalent] $K_2CO_3/KHCO_3$ solution)

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	138 g/mol	N/A
Normal Boiling Point	°C	105–115 (depending on % K_2CO_3 to $KHCO_3$ conversion, i.e., CO_2 loading)	N/A
Normal Freezing Point	°C	<0 (estimated)	N/A
Vapor Pressure at 15 °C	bar	N/A (not volatile)	N/A
Manufacturing Cost for Solvent	$/kg	0.4–1.0 (dry, pure K_2CO_3)	0.8
Working Solution			
Concentration	kg/kg	0.4	0.4
Specific Gravity (15 °C/15 °C)	—	1.42	N/A
Specific Heat Capacity at STP	kJ/kg-K	2.72	N/A
Viscosity at STP	cP	5.1	N/A
Absorption (Rich Solution at Bottom)			
Pressure (CO_2 partial)	bar	0.09 (1.32 psia)	<0.1
Temperature	°C	60–80	60–80
Equilibrium CO_2 Loading	mol/mol	0.4–0.45	0.4–0.45
Heat of Absorption	kJ/kg CO_2	609	609
Solution Viscosity	cP	1.5	N/A

TABLE 1: PROCESS PARAMETERS FOR CARBONATE SALT SOLVENT

(based on 40wt% [K_2CO_3 equivalent] K_2CO_3/$KHCO_3$ solution)

	Units	Current R&D Value	Target R&D Value
Desorption (Lean Solution at Bottom)			
Pressure (CO_2 partial)	bar	0.3-1.7 (4-12 total pressure)	>0.6 (>6 total pressure and CO_2/H_2O>3:1)
Temperature	°C	140–200	<200
Equilibrium CO_2 Loading	mol/mol	0.20-0.40 (60 wt% slurry concentration)	0.20-0.40
Heat of Desorption	kJ/kg CO_2	600–1,500 (including heat of crystallization)	<1,500
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	1,600,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99%, 10 bar	
Absorber Pressure Drop	bar	0.07 (structured packing)	

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

The overall reaction for CO_2 absorption into potassium carbonate solution at 70–80 °C is:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$

The CO_2-rich solution from the absorber is cooled to 30–35 °C to crystallize $KHCO_3$:

$$KHCO_3\ (aq) = KHCO_3(s)$$

The overall reaction for CO_2 stripping using $KHCO_3$ slurry at 140–200 °C is:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O$$

Solvent Contaminant Resistance – K_2CO_3 reacts with the flue gas contaminants (e.g., SO_2, nitrogen oxide [NO_x], and hydrogen chloride [HCl]), to form K_2SO_4, KNO_3, and KCl, respectively, resulting in solvent losses if the salts are not reclaimed.

Solvent Foaming Tendency – $K_2CO_3/KHCO_3$ solution itself does not have a foaming problem. If an organic promoter is used, foaming may occur for the $K_2CO_3/KHCO_3$ + promoter solution. However, the foaming tendency is expected to be less severe than the conventional amine-based processes because the promoter concentration is generally low.

Flue Gas Pretreatment Requirements – If an organic promoter is used, pretreatment of the flue gas is required to reduce the concentration of SO_2 to below 30 parts per million by volume (ppmv). If an inorganic promoter or a catalyst is used, flue gas pretreatment can be eliminated by a K_2SO_4 reclamation process under development in this project.

Solvent Makeup Requirements – Stoichiometric loss of K_2CO_3 due to reactions with acidic gases in the flue gas (SO_2, NO_x, etc.) is estimated 1.46 kg K_2CO_3/tonne CO_2 captured based on the assumed 42 ppmv SO_2 and 74 ppmv NO_x in the flue gas exiting a wet flue gas desulfurization (FGD) unit.

If an organic promoter is used, the promoter has tendency to degrade. Since the promoter concentration is low and most of the promoter does not enter the Hot-CAP stripping column, nominal losses due to promoter degradation is estimated to be less than10 percent of that in the conventional MEA-based processes.

Waste Streams Generated – Waste streams include sludge of inorganic salts (e.g., sulfate, nitrate, chloride, etc.) as a result of $K_2CO_3/KHCO_3$ reactions with acid gases in the flue gas and liquid blowdown from the process to avoid accumulation of chlorine, metals, etc.

Process Design Concept – Shown in Figure 2 below.

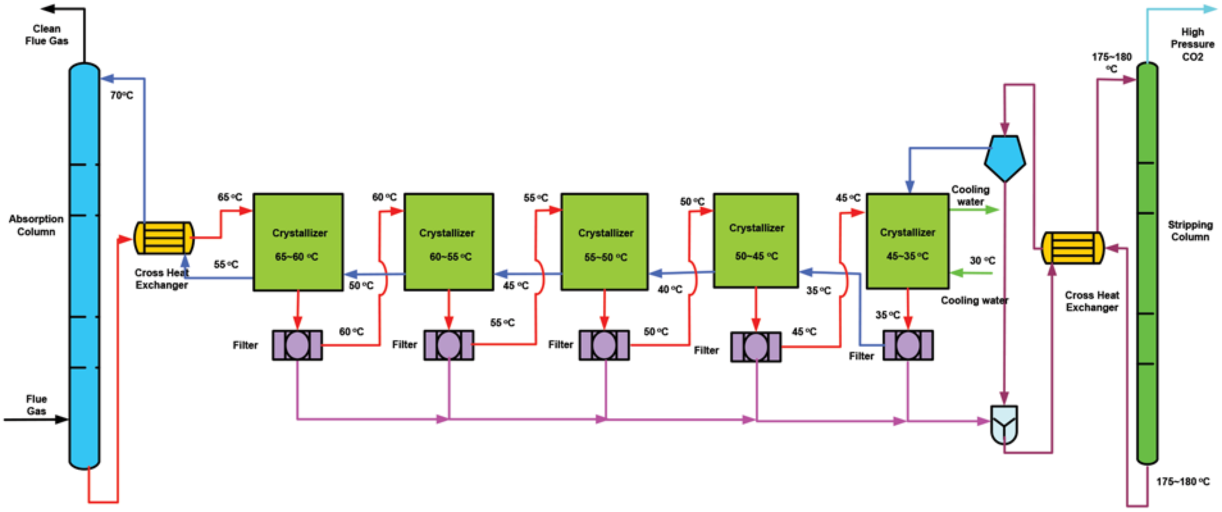

Figure 2: Process Design Concept

technology advantages

- High stripping pressure, which equates to low compression work and low stripping heat (high CO_2/H_2O ratio).
- Low sensible heat as a result of higher working capacity and lower Cp (1/2) compared with MEA.
- Low heat of absorption: 7–17 kcal/mol CO_2 (crystallization heat included) versus 21 kcal/mol for MEA.
- Increased absorption rate by employing high K_2CO_3 concentration and high absorption temperature.
- FGD may be eliminated.
- No degradation of the carbonate solution and low degradation of the promoter.
- Low-cost solvent.
- Less corrosiveness.

R&D challenges

- Identifying favorable process conditions and promoters/catalysts for achieving fast absorption kinetics in carbonate solution.
- Identifying process conditions and solution properties for achieving a fast crystallization rate and a desirable crystal size for solid separation.
- Identifying process conditions for potassium bicarbonate slurry to achieve stripping pressure ≥6 bar.
- Identifying process conditions for >95 percent SO_2 removal and continuous reclamation of the sulfate.
- Identifying risk mitigation strategies to prevent fouling on surfaces of heat exchangers and crystallizers due to bicarbonate crystallization.

results to date/accomplishments

- Three inorganic catalysts and five amine and three amino acid salt promoters were evaluated using a batch-stirred tank reactor.
- A bench-scale, packed-bed column was designed and fabricated to investigate the kinetics, mass transfer, and hydrodynamic performance of CO_2 absorption. Absorption column tests revealed that CO_2 removal efficiency by 40 wt% $K_2CO_3/KHCO_3$ solution promoted by either of two selected promoters at 70 °C was higher than that of the counterpart 5M MEA solution at 50 °C at the CO_2 loading levels typical of the two processes.
- Absorption column tests also showed that $KHCO_3$ precipitation could occur when the CO_2 loading reached a level equivalent to 40–45 percent of K_2CO_3 conversion. However, the accumulation of precipitates in the solution did not result in a pronounced decrease in CO_2 removal efficiency.
- Mixed suspension-mixed product removal (MSMPR) crystallization tests revealed that pure $KHCO_3$ crystals could be obtained and the crystallization of $KHCO_3$ was kinetically fast and a residence time of as few as 15 minutes was sufficient to obtain large crystal particles (>80 µm) required for efficient solid-liquid separation.
- Vapor Liquid Equilibrium (VLE) measurements for concentrated $KHCO_3/K_2CO_3$ aqueous systems with high levels of K_2CO_3 conversion at temperatures of 140–200 °C revealed the thermodynamic feasibility of high-pressure stripping (achieving both a high total pressure and a low H_2O/CO_2 pressure ratio).
- Parametric tests of reclaiming the potassium sulfate desulfurization byproduct were performed and results provided guidance for developing a modified process concept for the combined SO_2 removal and CO_2 capture. The feasibility of the modified process was preliminarily demonstrated. A bench-scale, packed-bed stripping column with a temperature rating of 200 °C and pressure rating of 500 pounds per square inch absolute (psia) was fabricated and installed at the UIUC laboratory.
- Parametric testing of high-pressure CO_2 stripping with concentrated bicarbonate-dominant slurries at high temperatures (≥140 °C) in the bench-scale stripping column demonstrated lower heat use than with MEA. For example, it was observed that compared with the 5 M MEA solution at 120 °C, the heat duty for CO_2 stripping at 160 °C from the 30 to 50 wt% $KHCO_3/K_2CO_3$ feed solutions with the CO_2 loading equivalent to 80 percent of carbonate conversation was two-to-three times lower.

- In addition to the experimental studies, the technical challenges pertinent to fouling of slurry-handling equipment and the design of the crystallizer and stripper were addressed through consultation with vendors and engineering analyses.
- A techno-economic analysis for the baseline Hot-CAP integrated with a 550-MWe power plant showed that the net power produced in the PC + Hot-CAP is 609 MWe, greater than the PC + MEA (550 MWe). The LCOE (levelized cost of electricity) increase for the Hot-CAP, including CO_2 transportation and storage, incurs a 60 percent increase over the base PC plant without CO_2 capture. The LCOE increase caused by the Hot-CAP is 29 percent lower than that for MEA.

next steps

This project ended on March 31, 2014.

available reports/technical papers/presentations

Shihan Zhang, Xinhuai Ye, Yongqi Lu. Development of a Potassium Carbonate-based Absorption Process with Crystallization-enabled High-pressure Stripping for CO_2 Capture: Vapor–liquid Equilibrium Behavior and CO_2 Stripping Performance of Carbonate/Bicarbonate Aqueous Systems. *Energy Procedia* 2014, 63: 665-675.

Final Report, "Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High-Pressure Stripping for Post-Combustion CO_2 Capture," April 2014.

Final Project Review Presentation, May 2014.

Lu, Y., O'Brien K.; and Chen, S., "Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture," presented at the Project Review Meeting, Pittsburgh, PA, February 15, 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/HotCAP-review-meeting-021513.pdf*.

Lu, Y., "Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture," 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/Y%20Lu-ISGS-Hot%20CAP.pdf*.

Lu, Y., "Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture," 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

POST-COMBUSTION CO_2 CAPTURE FOR EXISTING PC BOILERS BY SELF-CONCENTRATING AMINE ABSORBENT

primary project goals

3H Company set out to experimentally and analytically confirm the feasibility of the proposed Self-Concentrating Absorbent CO_2 Capture Process, with the goal of developing a sound engineering design, supported by laboratory data and economic justification, for a flue gas slipstream-testing unit.

technical goals

- Perform laboratory screening experiments to identify different absorbent/solvent combinations that can exhibit the “self-concentrating” carbon dioxide (CO_2) absorption effect, and conduct fundamental absorption/regeneration rates and physical and chemical property measurements to allow its process design and techno-economic feasibility to be evaluated.
- Conduct experiments to demonstrate the process under dynamic column testing conditions and to develop a process design package for a slipstream testing facility.

technical content

This project examined an innovative and proprietary CO_2 capture technology developed by 3H Company. The process is based on amine and/or other chemical absorbents in a non-aqueous solvent that can phase separate into a distinct CO_2-rich liquid phase upon reaction with CO_2. The process was demonstrated using commercially available amines and solvents. The technology has the potential of not only greatly reducing the energy penalty associated with regeneration compared to conventional monoethanolamine (MEA)-based processes, but it can also increase the amine CO_2 absorption rate. Preliminary experimental data shows that the proposed Self-Concentrating Amine Absorbent process has the potential of reducing the total regeneration energy by as much as 70 percent.

The technology removes CO_2 from power plant flue gas, using an absorbent (e.g., amine or special designed chemical species) and a matched solvent, which rapidly forms two immiscible liquid phases upon absorbing CO_2 (Figure 1). The process has been demonstrated in the laboratory for a number of specific amine/solvent pairs. The solvents employed are non-aqueous. The novelty of the concept rests on the duel hydrophobic/hydrophilic functionality of the CO_2 absorbents (e.g., amine), the stability of the “CO_2-rich” reaction product, and its solubility behavior within the non-aqueous solvent system employed. When an amine is used as the CO_2 absorbent, it is reasonable to assume that the chemistry follows that for an aqueous-based system. However, in the presence of a Self-Concentrating Solvent, the CO_2:amine reaction forms a stable product that can be solvated in higher concentration within the solvent system. The chemistry and mechanism of the process requires additional research and development (R&D).

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

CO_2 Capture with Self-Concentrating Amine Absorbent

participant:

3H Company

project number:

FE0004274

NETL project manager:

Morgan Mosser
morgan.mosser@netl.doe.gov

principal investigator:

Liang Hu
3H Company
lianghu59@yahoo.com

partners:

Nexant, Inc.
LG&E and KU Energy LLC
EPRI

performance period:

10/1/10 – 1/31/13

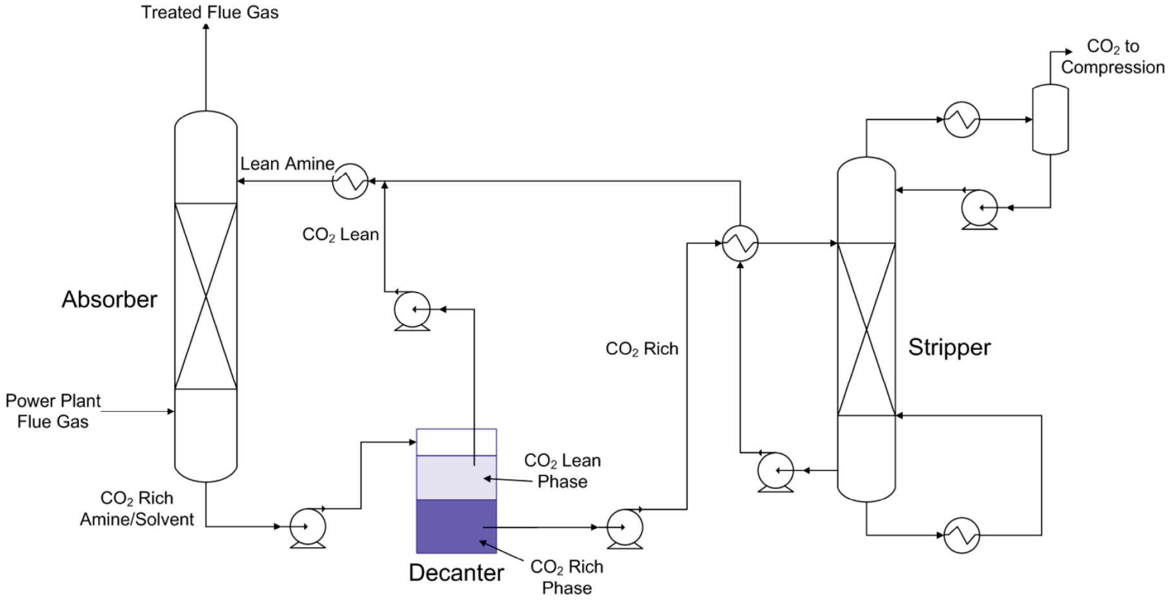

Figure 1: Concept of the Proposed Self-Concentrating Amine Absorbent Process

Conventional 30 wt% MEA-based CO_2 capture is considered to be the benchmark for performance. A typical heat of regeneration for a 30 percent MEA CO_2 capture process is about 1,934 Btu/lb CO_2, as cited in the literature, and only about 1/3 of the regeneration energy is used to break the amine:CO_2 bonds. Minimizing the overall heat of regeneration by using a unique absorbent/ solvent system is the key to the Self-Concentrating Absorbent process. Figure 2 shows a flow scheme for the concept, using amine as the CO_2 absorbent. The flow scheme is similar to a conventional MEA process, with the exception that a decanter is incorporated downstream of the absorber to allow the "rich CO_2 liquid" to be fully phase separated before sending it onto the stripper. Only the "rich CO_2 liquid" is subjected to regeneration, at a significant reduced volume as compared to a conventional MEA process. Overall, a 70 percent reduction in heat of regeneration can be achieved with the Self-Concentrating Absorbent process, taking into consideration that (1) only the "rich CO_2/solvent liquid" will be sent onto regeneration with minimum excess solvent, and (2) the solvent has a lower heat capacity and heat of vaporization than water. Because the process uses a non-aqueous system, many of the problems associated with MEA, including degradation due to corrosion, oxygen degradation, and the formation of stable salts, are expected to be mitigated. These types of effects, along with the potential environmental emissions and health problems associated with the use of the non-aqueous process, will need to be investigated in more detail.

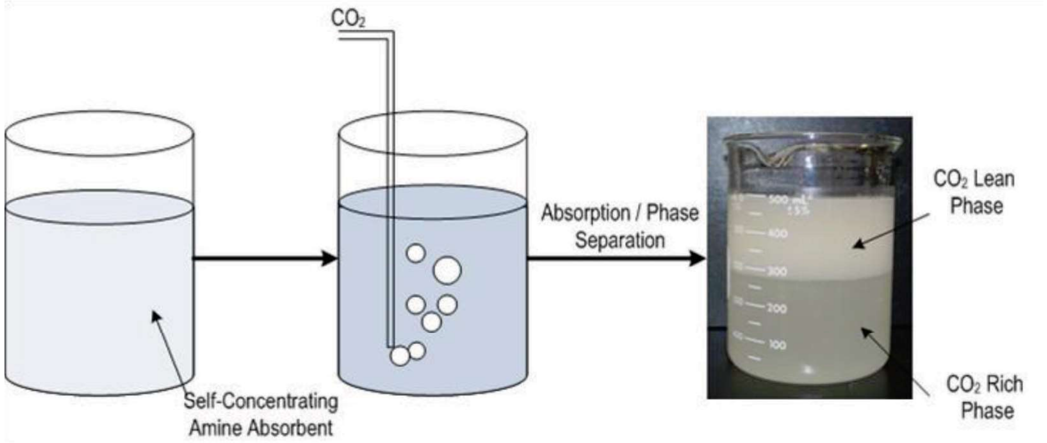

Figure 2: Simplified Flow Scheme of the Proposal Self-Concentrating Amine Absorbent Concept

technology advantages

- Lower regeneration energy requirements.
- Minimal degradation due to corrosion, oxygen degradation, and the formation of stable salts.

R&D challenges

- The chemistry, kinetics, and mass-transfer characteristics governing the diffusion of CO_2 into the liquid phase where it reacts with amine within the non-aqueous solvent, etc., are unknown.
- The self-concentrating process involves the phase separation of the "CO_2 rich" reaction product from the solvent system, of which its stability, composition, phase behavior, thermodynamic miscibility, and solubility limit are unknown.
- It is necessary to develop some basic theoretical and mechanistic understanding of the process so that R&D will not have to be based purely on an empirical approach.

results to date/accomplishments

- Completed preliminary system analysis and process design study comparing the 3H process to 30 percent MEA.
- Completed bench-scale screening, property measurement, and testing to identify all four promising Self-Concentrating Absorbent/Solvent pairs for more detailed characterization and evaluation.
- Completed down-selection to two promising Self-Concentrating Absorbent/Solvent pairs and commenced detailed characterization and analysis of these two final absorbent/solvent pairs.

next steps

This project ended on January 31, 2013.

available reports/technical papers/presentations

Hu, L., "Post-Combustion CO_2 Capture for Existing PC Boilers by Self-Concentrating Absorbent," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/L%20Hu-%203H%20Company-Self-concentrating%20Absorbent.pdf*.

IONIC LIQUIDS: BREAKTHROUGH ABSORPTION TECHNOLOGY FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

The University of Notre Dame set out to develop a new ionic liquid (IL) solvent capture process resulting in a small increase in cost of electricity (COE) compared to currently available capture technologies by overcoming viscosity and capacity issues impacting cost and performance of ILs via "proof-of-concept" exploration and laboratory-/bench-scale testing of a variety of IL formulations.

technical goals

- Design and synthesize one or more IL absorbents tailored for post-combustion carbon dioxide (CO_2) capture.
- Perform atomistic-level classical and quantum calculations to engineer IL structures maximizing CO_2 carrying capacity with minimal regeneration costs.
- Measure or accurately estimate all physical solvent properties essential for detailed engineering and design calculations:
    - Gas solubility, viscosity, heat of absorption, heat capacity, mass transfer coefficients, thermal decomposition, chemical stability, and corrosivity.
- Complete detailed systems and economic analysis.
- Demonstrate CO_2 capture technology on a continuous lab-scale unit.

technical content

ILs are salts that are liquid at room temperature. They are known to have high intrinsic physical solubility for CO_2. Examples of ILs are illustrated in Figure 1.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Ionic Liquids

participant:

University of Notre Dame

project number:

FC26-07NT43091

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Edward J. Maginn
University of Notre Dame
ed@nd.edu

partners:

Babcock and Wilcox
DTE
Trimeric Corporation
Koei Chemical

performance period:

2/28/07 – 9/30/12

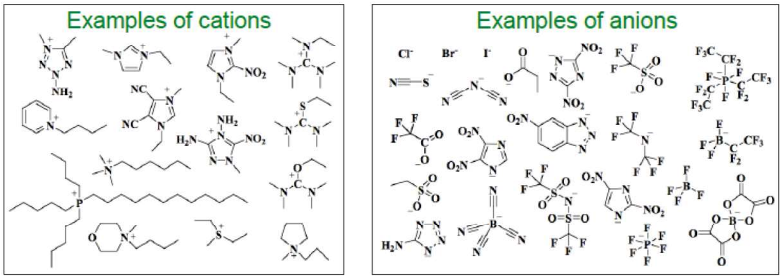

Figure 1: Examples of Ionic Liquids

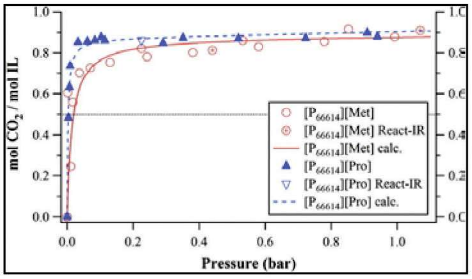

Figure 2: Isotherms confirming 1:1 binding

A close-to-conventional absorber/stripper process is assumed for process modeling and costing. Process simulation has been used to evaluate the sensitivity of a representative 500-MW (gross capacity), coal-fired power plant CO_2 capture process for the properties of ILs. The results were used to guide the development of the next generation of ILs. Salient project details include:

- Anion/cation functionalization: Notre Dame has developed both 1:1 and 2:1 (IL:CO_2) stoichiometries by adding chemical functionality to the anion and cation, respectively. Molecular modeling calculations were used to identify anion-functionalized ILs with minimal increase in solvent viscosity after CO_2 absorption. Two ILs (NDIL0046 and NDIL0157) were identified. NDIL0046 was used for lab-scale experimental tests, and data on NDIL0157 was used for techno-economic analysis.
- Enthalpy of reaction: Process modeling indicated that the binding strength of NDIL0046 needed to be improved, and a new IL (NDIL0157) with optimal enthalpy of reaction and lower heat capacity was identified. Optimal reaction enthalpy leads to higher CO_2 solvent capacities, reduced solvent circulation rate, and lowered sensible heating load.

Results show much lower parasitic energy compared with a monoethanolamine (MEA) system. From techno-economic analysis, it was estimated that the parasitic electricity losses in the reboiler are reduced by 36 percent, compression load increased by 14 percent, and the auxiliary losses in CO_2 capture are lowered by 34 percent. The best-case IL (NDIL0157) has almost the same increase in levelized cost of electricity (LCOE) compared with MEA due to higher capital costs for the CO_2 capture system.

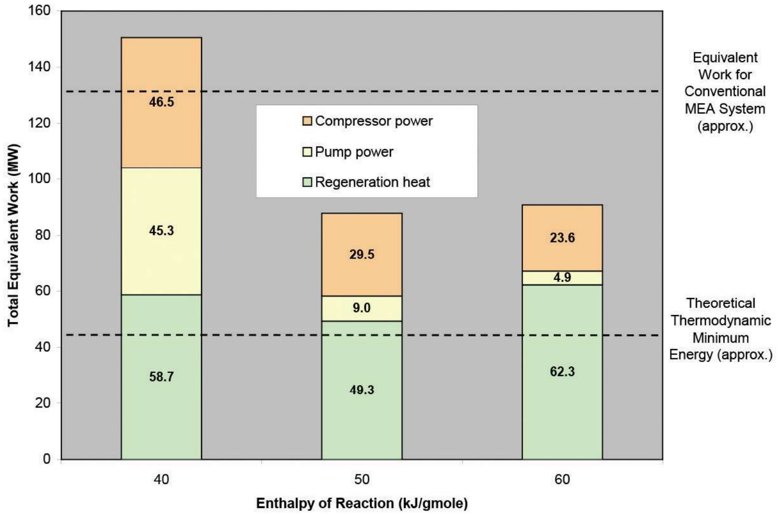

Figure 3: Results from Sensitivity Studies on the Parasitic Power Requirement of Ionic Liquid Solvents

TABLE 1: PROCESS PARAMETERS FOR IONIC LIQUID SOLVENTS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	575	322
Normal Boiling Point	°C	N/A - does not boil	N/A - does not boil
Normal Freezing Point	°C	< -10oC	< -10oC
Vapor Pressure @ 15°C	bar	Essentially zero	Essentially zero
Manufacturing Cost for Solvent	$/kg	$20/kg	< $15/kg
Working Solution			
Concentration	kg/kg	0.998	> 0.9
Specific Gravity (15°C/15°C)	-	0.907	≈1.0
Specific Heat Capacity @ STP	kJ/kg-K	2.25	<2.3
Viscosity @ STP	cP	158 @40 c	< 100
Absorption			
Pressure	bar	1.03	1
Temperature	°C	40-52	40-52
Equilibrium CO_2 Loading	mol/mol	0.167	0.988
Heat of Absorption	kJ/mol CO_2	43	54
Solution Viscosity	cP	129	< 100
Desorption			
Pressure	bar	1.3	1-3
Temperature	°C	120-188	120-204
Equilibrium CO_2 Loading	mol/mol	0.041	0.51
Heat of Desorption	kJ/mol CO_2	43	54
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A	
Adsorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized-coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – A 1:1 reaction with CO_2 and the basic group on the anion of the IL.

Solvent Contaminant Resistance – Resistant to air; have not evaluated resistance to other contaminants.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – Flue gas desulfurization (FGD) plus polishing column to get to 10 parts per million (ppm) sulfur oxide (SO_x).

Solvent Make-Up Requirements – 3.15 tons/day for a 550-MW net plant.

Waste Streams Generated – Degraded solvent waste; negligible vapor emissions.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

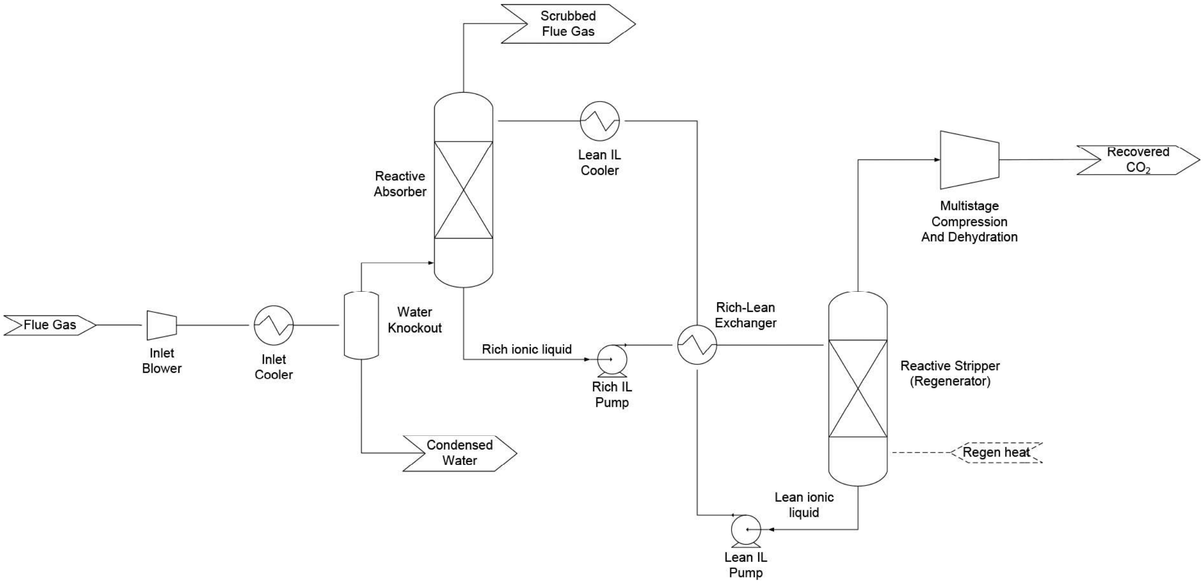

Figure 4: Schematic of Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Low volatility and good thermal stability.
- Wide liquidus range.
- Net-CO_2 uptake by solvent can be varied by tuning the enthalpy of CO_2 absorption (10 to 80 kJ/mol) through a combination of computational methods and experimental synthesis.
- Anhydrous absorption process.
- The viscosity of the current generation of ILs (NDIL0046) does not change significantly with CO_2 absorption.

R&D challenges

- The solvent CO_2 capacity (on a weight basis) should be higher than that for the best-case scenario (NDIL0157) to lower-solvent recirculation rates and reduce absorber costs.
- The effects of water on the corrosion behavior and CO_2 reactivity of the ILs need to be examined in greater detail, though preliminary results show negligible corrosion for NDIL0046 + carbon steel.
- The chemically functionalized IL solvent mass-transfer characteristics/viscosity need to be improved to lower capital and operating costs.
- Low-cost commercial synthesis routes for Generation III ILs are required to lower operating costs.

results to date/accomplishments

All project phases (I, II, and III) are complete. Key accomplishments to date include:

- Discovered and synthesized a new class of non-aqueous ILs reacting with 1:1 stoichiometry, and with no increase in viscosity following CO_2 absorption.
- Developed molecular modeling techniques that enabled the computation of key properties of ILs from first principles, and tuned the binding strength of ILs to optimize process economics.
- Demonstrated that the NDIL0046 IL had significantly lower corrosion rates compared to aqueous MEA, indicating that lower-cost materials could be used for absorber and heat exchangers.
- Techno-economic analysis on the best IL to date (NDIL0157) suggests favorable COE and significantly lower parasitic energy losses compared to aqueous MEA (U.S. Department of Energy [DOE]/National Energy Technology Laboratory [NETL] Baseline Case 12).
- Developed unique experimental techniques, including the ability to monitor the infrared spectrum of the IL as it absorbs CO_2, and then use this information to determine reaction rates and mechanisms.

next steps

The project ended on September 30, 2012. Recommendations for further steps include:

- Scale-up of experiments to the next level using synthetic flue gas and slipstream tests.
- The operating performance of ILs (mass-transfer characteristics, viscosity) would be improved.
- Process chemistry improvements needed to make ILs at tonne-scales for lower cost would be investigated.
- IL toxicity and long-term stability would also be examined.

available reports/technical papers/presentations

M. McCready et al., “Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO_2 Capture,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July, 2012. Available at: *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/M%20McCready-Notre%20Dame-Ionic%20Liquids.pdf*.

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K. E. Gutowski and E. J. Maginn, “Amine-Functionalized Task Specific Ionic Liquids for CO_2 Capture,” Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 17-21, 2008.

Joan F. Brennecke, “CO_2 Capture – Challenges and Opportunities,” Energy, Citizens and Economic Transformation for Indiana and America, University of Notre Dame, July 7, 2008.

Joan F. Brennecke, Jessica L. Anderson, Alexandre Chapeaux, Devan E. Kestel, Zulema K. Lopez-Castillo, and Juan C. de la Fuente, “Carbon Dioxide Capture Using Ionic Liquids,” 236th ACS National Meeting, Philadelphia, Pennsylvania, August 17, 2008.

E. M. Mindrup and W. F. Schneider, “Comparison of Functionalized Amine Energetics for CO_2 Capture,” poster presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

Wei Shi and E. J. Maginn, “Molecular simulation of pure and mixture gases absorption in ionic liquids,” presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

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Xiaochun Zhang, Feng Huo, Zhiping Liu, Wenchuan Wang, Edward Maginn and Wei Shi, “Absorption of CO_2 in the Ionic Liquid 1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FEP]): A Molecular View by Computer Simulations,” Journal of Physical Chemistry B, 2009, 113, 7591-7598.

Keith Gutowski and Edward J. Maginn, “Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity Upon Complexation with CO_2 from Molecular Simulation,” Journal of the American Chemical Society, 2008, 130, 14690-14704.

E. J. Maginn, Developing New Ionic Liquids for CO_2 Capture: A Success Story for Thermodynamics and Computational Molecular Design, GE Global Research Symposium on Emissions and Aftertreatment, GE Global Research Center, Niskayuna, New York, Sept. 17, 2009.

Marcos Perez-Blanco and Edward J. Maginn, "Molecular Dynamics Simulations of CO_2 at an Ionic Liquid Interface: Adsorption, Ordering and Interfacial Crossing," Journal of Physical Chemistry B (cover article), 2010, 36, 11827.

W. F. Schneider, "Ionic Liquids for CO_2 Capture from First-Principles," CECAM workshop on Carbon Capture, Lausanne, Switzerland, July 26-28, 2010.

W. F. Schneider and E. Mindrup, "AHA! Computational design of aprotic heterocyclic anions for ionic-liquid-based CO_2 separations," Division of Fuel Chemistry, American Chemical Society National Meeting, Boston, Massachusetts, August 22-26, 2010.

Burcu E. Gurkan, Juan C. de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, and Joan F. Brennecke, "Equimolar CO_2 absorption by anion-functionalized ionic liquids," J. Am. Chem. Soc., 132, 2010, 2116-2117.

Burcu E. Gurkan, Juan de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, Edward J. Maginn and Joan F. Brennecke, "Chemically Complexing Ionic Liquids for Post-Combustion CO_2 Capture," Clearwater Clean Coal Conference, Clearwater, FL, June 6-10, 2010.

Edward J. Maginn, "Molecular engineering of new ionic liquid sorbents for CO_2 capture" at the 9th Annual Carbon Capture and Sequestration Meeting, Pittsburgh, Pennsylvania, May 2010.

Edward J. Maginn, Joan F. Brennecke, William F. Schneider, and Mark J. McCready, "Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture," presented at the NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September, 2010.

DEVELOPMENT AND EVALUATION OF A NOVEL INTEGRATED VACUUM CARBONATE ABSORPTION PROCESS

primary project goals

The Illinois State Geological Survey (ISGS) set out to prove the novel Integrated Vacuum Carbonate Absorption Process (IVCAP) concept and further improve the energy efficiency of the process for post-combustion carbon dioxide (CO_2) capture.

technical goals

- Test the proof-of-concept of the IVCAP.
- Identify an effective catalyst for accelerating CO_2 absorption.
- Identify an effective additive for reducing the stripping heat.
- Evaluate a modified IVCAP as a multi-pollutant control process for combined sulfur dioxide (SO_2) and CO_2 capture.

technical content

The proposed IVCAP employs a potassium carbonate (K_2CO_3) aqueous solution for CO_2 absorption. While the absorption takes place at atmospheric pressure, the stripper is operated under a vacuum condition. As seen in Figure 1 and Table 1, the low heat of reaction between CO_2 and K_2CO_3 favors a stripping process operated at a low temperature and the low-quality steam (close to the exhaust end of low-pressure turbine in the power plant) can be used as a heat source for the stripping process as a result.

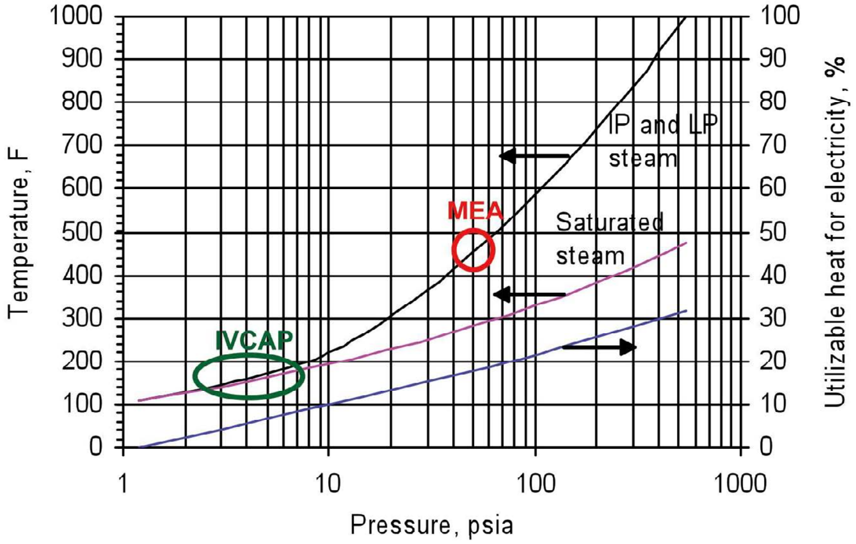

Figure 1: Steam Properties During Expansion in the Intermediate- and Low-Pressure Turbines

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Novel Integrated Vacuum Carbonate Process

participant:

Illinois State Geological Survey

project number:

NT0005498

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Yongqi Lu
Illinois State Geological Survey
yongqilu@illinois.edu

partners:

Calgon Carbon Corporation
Illinois Clean Coal Institute
University of Illinois

performance period:

10/1/08 – 4/30/12

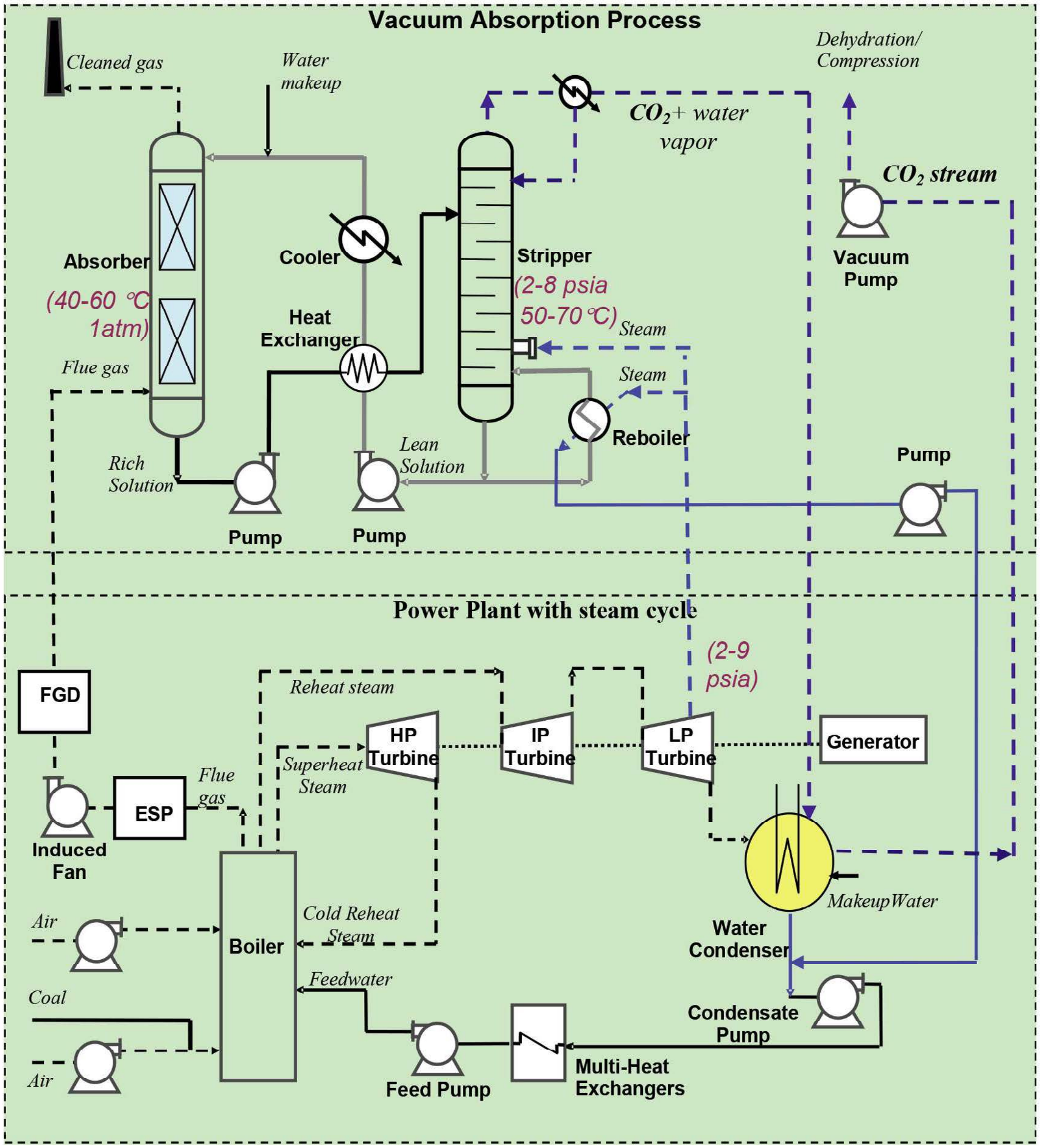

Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low-Quality Steam From the Power Plant

TABLE 1: A COMPARISON OF HEATS OF ABSORPTION FOR CO_2 SOLVENTS

Solvent	Main Reaction	Heat of Absorption
Primary/Secondary Amines	$2RR'NH + CO_2 = RR'NCOO^- + RR'NH_2+$	MEA: 1,900 kJ/kg
Tertiary Amine	$RR'R''N + CO_2 + H_2O = HCO_3^- + RR'R''NH^+$	MDEA: 1,200 kJ/kg
Carbonate	$CO_32- + CO_2 + H_2O = 2\ HCO_3^-$	600 kJ/kg

The intrinsic rate of CO_2 absorption into the K_2CO_3 solution is much slower than that in a monoethanolamine (MEA) solution; therefore, enzyme catalysts were developed to promote the absorption rate. Unlike the mixing of another solvent into a primary solvent, a catalyst accelerates the absorption rate without increasing the heat of absorption of the solvent.

The enzyme catalysts will need to be immobilized in order to:

- Reduce enzyme leakage in a flow system.
- Improve chemical stability of enzymes.
- Improve thermal stability of enzymes.

Three supportive matrices (i.e., carbon-, controlled pore glass [CPG]-, and silica-based materials) were evaluated for enzyme immobilization.

Since more than 60 to 70 percent of the process heat in the IVCAP is the stripping heat, an additive able to suppress water vaporization of the CO_2-loaded solution can reduce the stripping heat in the stripper. Successful screening and development of an additive can further reduce the heat use in the IVCAP.

The IVCAP has the flexibility to integrate SO_2 removal in the CO_2 capture process. In the amine-based and amine-promoted absorption processes, the flue gas must be treated to reduce the concentration of SO_2 and other acid gases to below 20 parts per million (ppm) to prevent/minimize the formation of heat-stable salts that are difficult to reclaim. In the IVCAP, SO_2 can be removed by the reaction with the solvent to form a sulfate salt that can be further processed to reclaim the solvent.

TABLE 2: PROCESS PARAMETERS FOR IVCAP PROCESS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	138	N/A
Normal Boiling Point	°C	103	N/A
Normal Freezing Point	°C	≤0	N/A
Vapor Pressure @ 15°C	bar	Not volatile	N/A
Manufacturing Cost for Solvent	$/kg	0.4-1.0	≤0.8
Working Solution			
Concentration	kg/kg	0.2	0.2
Specific Gravity (15°C/15°C)	-	1.24	N/A
Specific Heat Capacity @ STP	kJ/kg-K	3.34	N/A
Viscosity @ STP	cP	1.9	N/A
Absorption (Rich Solution at Bottom)			
Pressure	bar	0.06-0.08 (0.8-1.2 psia)	<0.1
Temperature	°C	40-60	40-60
Equilibrium CO_2 Loading	mol/mol	0.5	0.5
Heat of Absorption	kJ/mol CO_2	600	N/A
Solution Viscosity	cP	0.95 (at 50°C)	N/A
Desorption (Lean Solution at Bottom)			
Pressure (CO_2 equilibrium pressure)	bar	0.007-0.02 (0.1-0.3 psia)	≥0.01
Temperature	°C	50-70	50-70
Equilibrium CO_2 Loading	mol/mol	0.12-0.20	≤0.2
Heat of Desorption	kJ/mol CO_2	600	N/A
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	500,000 (100,000 kg/hr CO_2)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 99%, 0.14–0.54 (prior to vacuum pump)	
Adsorber Pressure Drop	bar	0.04 (structured packing)	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The main reactions involving in the IVCAP include:

CO_2 absorption: $CO_2+H_2O^+K_2CO_3 = 2KHCO_3$
Solvent regeneration: $2KHCO_3=K_2CO_3+H_2O^+CO_2$

Solvent Contaminant Resistance – Since the potassium carbonate solution is used as a solvent, no solvent degradation and little corrosion problems are expected. The $K_2CO_3/KHCO_3$ solution reacts with the flue gas contaminants (e.g., SO_2, nitrogen oxides [NO_x], hydrogen chloride [HCl], etc.). No SO_2 scrubbing pretreatment is needed prior to the IVCAP, since SO_2 removal can be combined with CO_2 capture and the potassium sulfate desulfurization product can be potentially reclaimed in the IVCAP.

Solvent Foaming Tendency – The $K_2CO_3/KHCO_3$ solution itself does not have a foaming problem. The addition of a carbonic anhydrase (CA) enzyme biocatalyst in the $K_2CO_3/KHCO_3$ solution will not incur a foaming tendency due to its low dosage (<3 g/l) and low contents of impurities.

Flue Gas Pretreatment Requirements – Sulfur dioxide removal can be combined with CO_2 capture in the IVCAP. The carbonate solution absorbs SO_2 to form a sulfate salt, which is reclaimable using a reclamation approach developed in this project. Therefore, a separate flue gas desulfurization (FGD) unit currently required in the power plant can be potentially downsized or even eliminated in the IVCAP. No other flue gas pretreatments (such as for particulate matter [PM], NO_x) are required either.

Solvent Make-Up Requirements – A thermophilic CA enzyme tested in the project demonstrated to be stable at 40°C. At 50°C, the enzyme had a half-life of approximately two months. After immobilization, the thermal stability of the enzyme has been significantly improved. The enzyme also demonstrated excellent chemical stability against the most abundant flue gas impurities. It is estimated that two to three replacements of the enzyme is required annually if the absorption operates at 50°C and 30 percent replacements is required at 40°C.

Waste Streams Generated – Waste streams mainly include the process blowdown streams, such as the carbonate/bicarbonate aqueous solution from the absorber/stripper and water condensate saturated with CO_2.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Uses lower-quality steam than amine-based processes (e.g., MEA), consequently increasing net power output.
- Lower heat of absorption.
- Less energy required for CO_2 stripping.
- Modified IVCAP may be able to remove SO_2 without an FGD unit.
- Approximately 25 percent lower electricity loss.

R&D challenges

- Slow kinetics of CO_2 absorption into the K_2CO_3 solution; thus, a high-activity catalyst is required.
- Potentially large capital and operating cost of the vacuum pump and vacuum stripper.
- Suppressing water vaporization in the stripper.
- Chemical and thermal stability of the absorption enzymes.

results to date/accomplishments

- Reactivity tests of two CA enzymes (ACA1 and ACA2) from a leading enzyme manufacturer and eight inorganic and organic catalysts commercially available were evaluated in a laboratory-stirred tank reactor (STR). The CA enzymes were identified to be the most-effective catalyst for promoting CO_2 absorption into $K_2CO_3/KHCO_3$ solution.
- Rates of CO_2 absorption into a 20 wt% $K_2CO_3/KHCO_3$ solution were increased by approximately three to nine times at temperatures between 25 and 50°C with the addition of 300 mg/l CA enzyme. Further increase in absorption rate was observed at higher CA concentrations (>300 mg/l CA). Absorption rates into CO_2-rich $K_2CO_3/KHCO_3$ solutions were comparable to those into CO_2-lean $K_2CO_3/KHCO_3$ solutions at the same CA dosage. Modeling predictions suggested that in a packed-bed column configuration, the IVCAP absorber at 2 g/l CA dosage was 23 to 40 percent larger than the equivalent equipment for the MEA process employing 5M MEA as a solvent.
- The CA enzymes demonstrated excellent chemical stability to resist flue gas impurities. Presence of flue gas impurities at their typical concentrations resulted in <11 percent loss of initial CA activity.
- The ACA1 enzyme had satisfactory stability at 25°C, but not at temperatures higher than 40°C. The ACA2 enzyme (a thermophilic CA) demonstrated excellent thermal stability at 40°C, losing only about 15 percent of its initial activity after six months. At 50°C, the ACA2 enzyme had a half-life of about two months.
- Covalent bonding methods were successfully developed to immobilize the CA enzymes onto different carbon-, CPG-, and silica-based support materials. All of the immobilized CA enzymes exhibited significantly improved thermal stability.
- Process simulation studies showed that the IVCAP integrated with a 528 MWe (gross) coal-fired, subcritical power plant at a baseline condition lowered parasitic power losses by 24 percent compared to the conventional MEA process.

- Techno-economic studies showed that the capital cost of the baseline IVCAP was about 33 percent higher than that for the MEA process due to the requirements for a vacuum pump and a larger stripper under a vacuum condition, but its operation and maintenance (O&M) cost was about 40 percent lower due to its lower solvent cost and reduced parasitic power losses. The levelized cost of electricity (LCOE, about $46/MWh) of the baseline IVCAP was a 71 percent increase over the reference power plant without CO_2 capture, about 17 percent less than that of the MEA process.

next steps

This project ended on April 30, 2012.

available reports/technical papers/presentations

Zhang, S., et. al, "Catalytic Behavior of Carbonic Anhydrase Enzyme Immobilized onto Nonporous Silica Nanoparticles for Enhancing CO_2 Absorption into a Carbonate Solution," Int. J. Greenhouse Gas Control 2013, 13: 17-25.

Lu, Y., et. al, "Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process," Final Project Closeout Review, Pittsburgh, Pennsylvania, July 13, 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/IVCAP-Closeout-Mtg-0713.pdf*.

Lu, Y., et al, "An Integrated Vacuum Carbonate Absorption Process Enabled with an Enzyme Biocatalyst for CO_2 Absorption," proceedings of the Clearwater Clean Coal Conference, Tampa, Florida, June 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Clearwater-IVCAP-YLu.pdf*.

Zhang S., et. al, "Activity and Stability of Immobilized Carbonic Anhydrase for Promoting CO_2 Absorption into A Carbonate Solution for Post-Combustion CO_2 Capture," Bioresources Technology 2011, 102(22): 10194-10201.

Lu, Y., et. al, "Development of a Carbonate Absorption-Based Process for Post-Combustion CO_2 Capture: The Role of Biocatalyst to Promote CO_2 Absorption Rate," Energy Procedia 2011, 4: 1286-1293.

Lu, Y., et. al, "Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011.

Lu, Y., et.al, "Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010.

Lu, Y., "Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.

SLIPSTREAM DEVELOPMENT AND TESTING OF SIEMENS POSTCAP CAPTURE AND SEPARATION TECHNOLOGY

primary project goals

Siemens Energy set out to design, install, and operate a pilot plant to treat a 2.5-megawatt (MW) flue gas slipstream from an operating coal-fired power plant to demonstrate the aqueous amino acid salt (AAS) solvent-based, post-combustion carbon dioxide (CO_2) gas capture technology.

technical goals

- Demonstrate the ability of Siemens Energy's POSTCAP technology to achieve 90 percent CO_2 removal while approaching a 35 percent increase in the cost of electricity (COE).
- Demonstrate the scalability and feasibility of developing the technology to a full-scale, commercial, post-combustion CO_2 capture (550 MW) application for coal-fired power plants and to full-scale commercial application for industrial sources of CO_2 emissions.

technical content

Siemens Energy worked to design, install, and operate an advanced CO_2 capture, solvent-based pilot plant. The Siemens POSTCAP CO_2 capture process utilizes an aqueous AAS solution as the solvent that offers cost and performance advantages when compared to state-of-the-art, amine-based solvents. The POSTCAP pilot plant was to be installed at Tampa Electric Company's (TECO) Big Bend Station and treat a flue gas slipstream equivalent to approximately 2.5 megawatt electric (MWe). Although the CO_2 source for this slipstream pilot-scale testing is from a coal-fired power plant flue gas, it would have provided an appropriate design and performance baseline for direct scale-up to many industrial applications.

The project encompassed the complete design, engineering, procurement, installation, operation, data analysis, and decommissioning of the CO_2 capture system and was to be completed in four phases. In Phase I, the engineering design and permitting for the project were completed. POSTCAP system mass and energy balances and pilot plant process flow diagrams were to be generated, and the host site was to be analyzed for integration of the pilot plant. Phase II was to encompass the equipment procurement, fabrication, delivery, and installation of the components at the host site with required tie-ins to plant interfaces. In Phase III, the pilot plant was to be commissioned and started up, the pilot program test campaigns were to be conducted, and the resulting data were to be analyzed. Phase IV was to cover the pilot plant decommissioning and disassembly.

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

POSTCAP Capture and Separation

participant:

Siemens Energy

project number:

FE0003714

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

John Winkler
Siemens Energy, Inc.
john.winkler@siemens.com

partners:

Siemens AG

performance period:

10/1/10 – 2/29/12

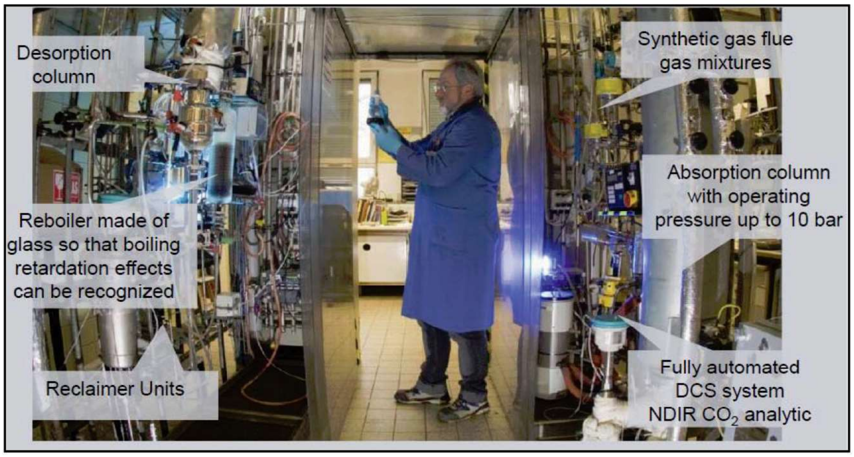

Figure 1: Siemens Lab Plant for CO_2 Capture Tests at Frankfurt Hoechst Industrial Park

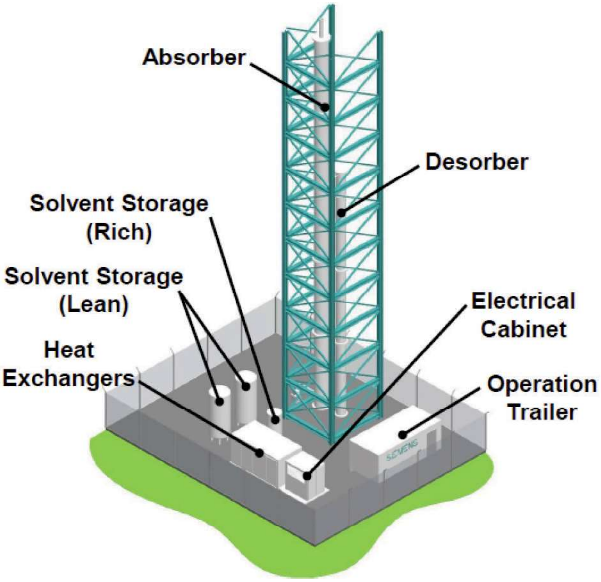

Figure 2: Basic POSTCAP Pilot Layout

technology advantages

- Lower energy consumption.
- Negligible solvent emission and degradation.
- High absorption capacity.
- Low environmental impact.

R&D challenges

- Developing solvent suppliers on a large, commercial scale.
- Minimize energy consumption.
- Available footprint for large-scale carbon capture retrofits.
- Combined cycle challenges to be overcome:
    - Low CO_2 concentration in flue gas.
    - High oxygen content in flue gas.
    - Operation with frequent load changes.
    - Fewer integration options for low-temperature heat from the capture plant.

results to date/accomplishments

Completed a preliminary design for a 2.5-MW POSTCAP pilot plant that was to be installed at the TECO Big Bend Power Station.

next steps

This project ended on February 29, 2012.

available reports/technical papers/presentations

Winkler, J.L., "Slipstream Development & Testing of Post Combustion CO_2 Capture and Separation Technology for Existing Coal-Fired Plants," presented at 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/2-Tuesday/23Aug11-Winkler-Siemens-Technology%20Slipstream%20Testing.pdf*.

DEVELOPMENT OF CHEMICAL ADDITIVES FOR CO_2 CAPTURE COST REDUCTION

primary project goals

Lawrence Berkeley National Laboratory (LBNL) is investigating a novel mixed solvent system that integrates amine-based, potassium-based, and ammonia-based solvents to provide benefits of three systems while avoiding many of their drawbacks.

technical goals

- Develop chemical additives for solvent systems to reduce the cost of post-combustion capture of carbon dioxide (CO_2).
- Determine the optimal process configuration and operating condition for the transfer of CO_2 in amine solvent to potassium carbonate (K_2CO_3), and then to an ammonium species, resulting in the production of NH_4HCO_3.

technical content

The new solvent system uses a novel solvent transfer approach after the capture of CO_2 from flue gas. Using this approach, the energy demand and the capital cost of solvent regeneration are expected to be significantly reduced compared to the monoethanolamine (MEA) system.

An aqueous solution of amine is used as an absorbent to facilitate favorable CO_2 absorption kinetics. The amine is chosen such that the CO_2 absorbed in an absorber can be readily transferred to potassium carbonate (K_2CO_3) in a recirculation tank to produce $KHCO_3$ solids. Subsequently, $KHCO_3$ solids enter into a regenerator by gravitation, where it reacts with an ammonia catalyst to regenerate K_2CO_3 for reuse and generate a concentrated CO_2 stream suitable for sequestration.

The approach contains the benefits of three solvent systems: amine, K_2CO_3 and ammonia systems. The benefits are: (1) amine's fast CO_2 absorption kinetics; (2) K_2CO_3 and ammonium species' low reagent cost, high chemical stability, and small heat capacity; and (3) ammonium bicarbonate's low decomposition temperature, fast decomposition kinetics, and amenable for high-pressure CO_2 production. The employment of solids significantly reduces the sensible and latent heat consumed by water in solvent regeneration. The low decomposition temperature of ammonium bicarbonate enables waste heat and/or low-quality steam to be used for the production of concentrated CO_2 gas.

technology maturity:
Bench-Scale, Simulated Flue Gas

project focus:
Chemical Additives for CO_2 Capture

participant:
Lawrence Berkeley National Laboratory

project number:
FWP-ED33EE

NETL project manager:
Elaine Everitt
elaine.everitt@netl.doe.gov

principal investigator:
Shih-Ger (Ted) Chang
LBNL
sgchang@lbl.gov

partners:
N/A

performance period:
6/1/08 – 5/31/13

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	100–212	100–212
Normal Boiling Point	°C	165–252	165–252
Normal Freezing Point	°C	(-50)–28	(-50)–28
Vapor Pressure at 15 °C	bar	0–0.0013	0–0.0013
Manufacturing Cost for Solvent	$/kg	30–250	30–250
Working Solution			
Concentration	kg/kg	0.3–0.6	0.3–0.6
Specific Gravity (15 °C/15 °C)	-	0.9–1.7	0.9–1.7
Specific Heat Capacity at STP	kJ/kg-K	3–4	3–4
Viscosity at STP	cP	20–40	20–40
Absorption			
Pressure	bar	1.01	1–1.5
Temperature	°C	40–70	30–80
Equilibrium CO_2 Loading	mol/mol	0.7–0.9	0.7–0.9
Heat of Absorption	kJ/mol CO_2	65–75	65–75
Solution Viscosity	cP	10–15	10–15
Desorption			
Pressure	bar	2.7	1–75
Temperature	°C	80–120	80–300
Equilibrium CO_2 Loading	mol/mol	0.4–0.6	0.4–0.6
Heat of Desorption	kJ/mol CO_2	85–92	85–92
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99%, 75 bar	
Absorber Pressure Drop	bar		

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

Absorber: Amine + $CO_2 \leftrightarrow$ Amine-CO_2

Recirculation tank: Amine-$CO_2 + K_2CO_3 + H_2O \leftrightarrow$ Amine + $2\ KHCO_3\downarrow$

Regenerator: $2\ KHCO_3 + (NH_4+) \rightarrow K_2CO_3 + H_2O + CO_2\uparrow + (NH_4+)$

Solvent Contaminant Resistance – Sulfur dioxide (SO_2) has little impact to the amine. The amine is regenerated by chemical rather than thermal methods. The amine employed should be much more resistant to oxygen (O_2) and nitrogen oxides (NO_x) than MEA. Nevertheless, the reaction kinetics and products of O_2 and NO_x with amine need to be investigated.

Solvent Foaming Tendency – Solvent foaming was not observed in laboratory experiments.

Flue Gas Pretreatment Requirements – Flue gas from coal-fired power plants equipped with conventional pollution control systems does not require additional pretreatment. Residual SO_2 after dissolution can be separated from the liquid stream as K_2SO_3/K_2SO_4 precipitates. The formation of heat-stable salts with amine should not be an issue, as amine is regenerated by chemical rather than thermal methods involving steam.

Solvent Makeup Requirements – Amine is confined in the low-temperature absorber and recirculation tank loop. As a result, the thermal degradation, chemical degradation (due to the reactions with flue gas trace constituents), and emission loss (due to the volatility) are expected to be insignificant compared to the benchmark MEA process. Absorber is not expected to exhibit a plugging problem resulting in operation breakdown and reagent loss as $KHCO_3$ solid is produced in the recirculation tank located above the K_2CO_3 regeneration tank (i.e., the stripper). A long-term integration test that lasts a significant number of hours will be needed to determine the amine's makeup requirements. $KHCO_3$ and K_2CO_3 are stable chemicals and do not degrade under high-temperature operation in the regenerator.

Waste Streams Generated – Waste streams from the absorber/recirculation tank low-temperature loop may contain trace amount of fly ash, dissolved NO_x, and amine degradation products. Waste streams from the stripper are expected to contain K_2SO_3 and K_2SO_4, if SO_2 polishing is not equipped ahead of the CO_2 capture system.

Process Design Concept – Shown in Figure 1 below.

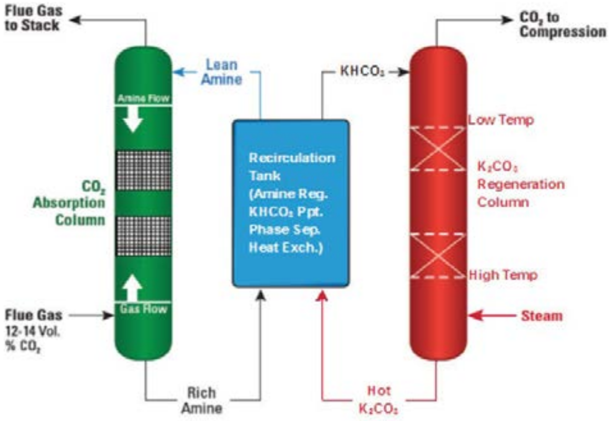

Figure 1: Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bar, temperature is 57 °C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Possession of high-CO_2 absorption kinetics, resulting in an acceptable absorber capital cost.
- Reduction of processing water, resulting in reduced solvent regeneration energy demands.
- Employment of low-heat capacity $KHCO_3$/K_2CO_3, resulting in reduced sensible heat demands.
- Reduction of reagent loss and equipment corrosion, resulting in reduced operation costs.
- Reduction of emission as $KHCO_3$ can be treated at high temperature without any emissions of heat degradable harmful products.
- Reduction of CO_2 compression ratio, resulting in reduced CO_2 compression energy and compressor capital costs.

R&D challenges

- Development of a new system for the transfer of $KHCO_3$ solid from the recirculation tank to the stripper by the gravitation method and with pressurized steam.
- Determination of the optimal operation condition to regenerate K_2CO_3 and to produce high pressure CO_2 gas for enhanced oil recovery (EOR) or methanol production.

results to date/accomplishments

- Evaluated more than 50 amines and amino acid salts for CO_2 absorption amenable for the new solvent regeneration approach.
- Compared relative CO_2 absorption efficiencies of various lean amines regenerated by chemical methods.

- Investigated conditions required for phase separation and determined phase diagrams following chemical regeneration of lean amine in the recirculation tank in attempt to understand its chemical and physical behaviors.
- Elucidated the kinetics and mechanisms of CO_2 absorption and chemical regeneration involved in the new solvent system.
- Constructed a stripper system equipped with a calorimeter for the determination of K_2CO_3 regeneration rates and energy demands. Preliminary results indicated that K_2CO_3 regeneration energy demand was 2,079 kJ/kg CO_2 at steady-state conditions, which is approximately 40 percent less than that of MEA.
- Performed a semi-continuous integration test encompassing CO_2 absorption in the absorber, amine regeneration in the recirculation tank, and K_2CO_3 regeneration and CO_2 production in the stripper.
- Performed mass and water balances, and developed a stream table of the bench-scale new solvent system.

next steps

Project completed May 31, 2013.

available reports/technical papers/presentations

“Developing Chemical Additives for Aqueous Ammonia to Reduce CO_2 Capture Cost,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants Meeting, Pittsburgh, PA, March 2009.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/monday/Ted%20Chang-LBNL.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/CO2capture/presentations/2-Tuesday/23Aug11-Chang-LBNL-Additives%20for%20Reducing%20CO2%20Capture%20Costs.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2012. *http://www.netl.doe.gov/publications/proceedings/12/CO2capture/presentations/2-Tuesday/T%20Chang-LBNL-Additives.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/events/2013/CO2%20capture/Y-Li-LBNL-Additives-for-Reducing-CO2-Capture-Costs.pdf*.

REVERSIBLE IONIC LIQUIDS AS DOUBLE-ACTION SOLVENTS FOR EFFICIENT CO_2 CAPTURE

primary project goals

The primary project goal was to develop a novel class of solvents for the recovery of carbon dioxide (CO_2) from post-combustion flue gases that would achieve a substantial increase in CO_2 working capacity with a reduction in cost.

technical goals

- Synthesis of silyl amine-based ionic liquids (ILs) with minimal viscosity.
- Measure heat of absorption and desorption.
- Measure rates of CO_2 absorption and desorption.
- Identify solvents that will consume the minimal amount of energy.
- Use simulation tools, such as ASPEN, to design an economic absorption/desorption process.

technical content

Reversible ionic liquids (RevILs) are neutral molecules that react with CO_2 to form an IL, which then dissolves additional CO_2 by a physisorption mechanism. Subsequently, modest elevations in temperature reverse the reaction and yield pure CO_2 for disposal; because of this dual mode, capacity can be large.

In a two-component RevIL, CO_2 at 1 atmosphere acts as a "switch," as shown in Figure 1.

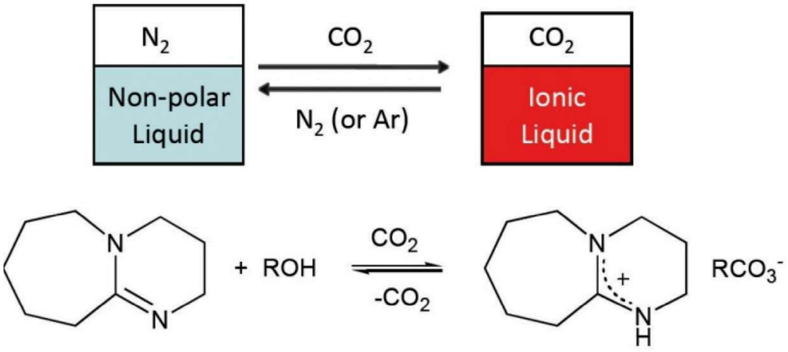

Figure 1: CO_2 Will Switch a Non-Polar Liquid to an Ionic Liquid

Two-component RevILs have the disadvantage of being too complex and requiring alcohol. Light alcohol would evaporate with the CO_2, while a heavy alcohol would have too much heat capacity. A single-component RevIL would eliminate the need for alcohol.

Figure 2 shows an example based on silylated amine. The chemistry must work well in the presence of water, considering that water is a component of flue gas. The RevILs will be tested for their chemical stability with 0 and 10 % water present. Stability will also be tested

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Reversible Ionic Liquids

participant:

Georgia Tech Research Corporation

project number:

NT0005287

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Charles A. Eckert
Georgia Tech Research Corporation
charles.eckert@chbe.gatech.edu

partners:

N/A

performance period:

10/1/08 – 9/30/11

at 4, 25, and 50°C. High viscosity could also be an issue; however, viscosity in RevILs is highly nonlinear (as shown in Figure 3) and can be reduced with impurities, such as water or dissolved gases.

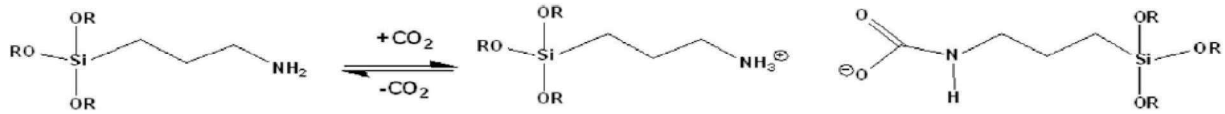

Figure 2: An Example of a Single-Component RevIL

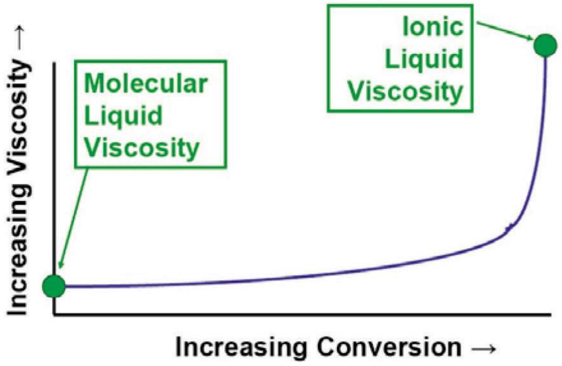

Figure 3: Ionic Liquids are More Viscous Than Their Respective Molecular Liquids

TABLE 1: PROCESS PARAMETERS FOR REVIL SOLVENTS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	170-220	150
Normal Boiling Point	°C	150 or greater	200
Normal Freezing Point	°C	< -77	
Vapor Pressure @ 15°C	bar	0.5-1x10-3	
Manufacturing Cost for Solvent	$/kg	TBD	
Working Solution			
Concentration	kg/kg	0.95	
Specific Gravity (15°C/15°C)	-	≈0.82	
Specific Heat Capacity @ STP	kJ/kg-K	2.2	<4.2
Viscosity @ STP	cP	>1,000	<80
Absorption			
Pressure	bar	1.2	1.2
Temperature	°C	25-40	>50
Equilibrium CO_2 Loading	mol/mol	Avg. 0.63	
Heat of Absorption	kJ/mol CO_2	80-90	
Solution Viscosity	cP	Variable (often <1,000)	<1,000
Desorption			
Pressure	bar	2	2
Temperature	°C	115	75
Equilibrium CO_2 Loading	mol/mol	< 0.01	
Heat of Desorption	kJ/mol CO_2	≈120	

TABLE 1: PROCESS PARAMETERS FOR REVIL SOLVENTS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical reaction for the CO_2 capture process is shown in Figure 2.

Solvent Contaminant Resistance – Since amine groups are involved in the reaction, sulfur oxides (SO_x) and nitrogen oxides (NO_x), as well as other acid gases, have to be removed. However, solvents have been shown to be stable in wet and oxygen-rich environments for a period of two months.

Solvent Foaming Tendency – No foaming observed.

Flue Gas Pretreatment Requirements – Flue gas pretreatment should be similar to the amine-based absorption processes since the RevIL is resistant to moisture.

Solvent Make-Up Requirements – Only required for process leakage in large plant.

Waste Streams Generated – None anticipated.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Use both physical absorption (dissolution in RevILs) and chemical absorption (reaction with RevILs); amines utilize only chemical absorption.
- Structure can be modified to optimize properties.
- Silylation will decrease viscosity.
- Function in the presence of water.
- Greater capacity than current solvents.
- Smaller energy penalty than current solvents.

R&D challenges

- New compounds must be designed, synthesized, and characterized.
- Optimum equilibria and heats must be achieved.
- Rapid reaction rates must be achieved.
- Favorable transport rates must be achieved.
- Results from new process must meet U.S. Department of Energy goals.

results to date/accomplishments

- Have demonstrated greater capacity than current solvents.
- Successful synthesis and chemical characterization of 10 precursors for novel RevILs:
    - (3-aminopropyl) trimethoxysilane.
    - (3-aminopropyl) triethoxysilane.
    - (3-aminopropyl) triethylsilane.
    - (3-aminopropyl) tripropylsilane.
    - (3-aminopropyl) trihexylsilane.
    - (3-aminopropyl) diisopropyl silane.
    - (3-aminopropyl) cyclohexyldimethyl silane.
    - (3-aminopropyl) phenyldimethyl silane.
    - (E)-3-(triethylsilyl) prop-2-en-1-amine.
    - 4-(triethylsilyl) butan-2-amine.
- Completed examination of the chemical and physical absorption of CO_2 in the six silyl-amine-based RevILs at operating pressures of up to 1,000 pounds per square inch (psi) and temperatures of 35, 50, 75, and 100°C.
- Established recyclability of silyl-amine-based reversible ILs.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

Rohan, A. L., et.al, “The Synthesis and the Chemical and Physical Properties of Non-Aqueous Silylamine Solvents for Carbon Dioxide Capture,” Chemsuschem 2012, 5 (11), 2181-2187.

Eckert, C. A., and Liotta, C. L., “Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture,” Final Report, December 2011. *http://www.osti.gov/bridge/servlets/purl/1048880/1048880.pdf*.

Eckert, C. A., and Liotta, C. L., “Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture,” presented at 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Charles%20Eckert-NT0005287.pdf*.

Blasucci, V., et.al, “Single Component, Reversible Ionic Liquids for Energy Applications,” Fuel, 89, 1315–1319, 2010.

Blasucci, V., et.al, “Reversible Ionic Liquids Designed for Facile Separations,” Fluid Phase Equilibria, 294, 1-6, 2010.

Hart, R., et.al, “Benign Coupling of Reactions and Separations with Reversible Ionic Liquids,” Tetrahedron, 66, 1082-1090, 2010.

Eckert, C. A., and Liotta, C. L., “Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO_2/pdfs/5287%20Georgia%20Tech%20reversible%20IL%20solvent%20%28Eckert%29%20mar09.pdf*.

Blasucci, V., et.al, “One Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines,” Chem Comm, 116-119, 2009.

CO_2 CAPTURE FROM FLUE GAS BY PHASE TRANSITIONAL ABSORPTION

primary project goals

Hampton University set out to conduct the kinetic study for its novel technology, phase transitional absorption, which has the potential to reduce operation costs by at least half (possibly by 80%) and significantly cut capital investment (compared with current monoethanolamine [MEA]-carbon dioxide [CO_2] absorption technologies).

technical goals

To understand the mechanisms of phase transitional absorption by measuring absorption kinetics, regeneration rate, and loading capacity, as well as to further compare with other methods, such as the state-of-art MEA absorption.

technical content

The phase transitional absorption process is radically different from the conventional absorption processes. It uses an activated agent, which, when mixed with a special solvent, forms a special phase transitional absorbent for CO_2 capture. The absorbent, after absorbing CO_2 from flue gas in an absorber, flows into a settler where it is separated into two phases: a CO_2-rich phase and a CO_2-lean phase. The CO_2-rich solvent is then sent to a regenerator for regeneration. After regeneration, the solvent is cooled and mixed with the CO_2-lean phase and sent to an absorber to complete the cycle.

A schematic diagram of the process is shown in Figure 1. It may be noted that the process is similar to a conventional MEA process, except that a settler is added for separating the two phases.

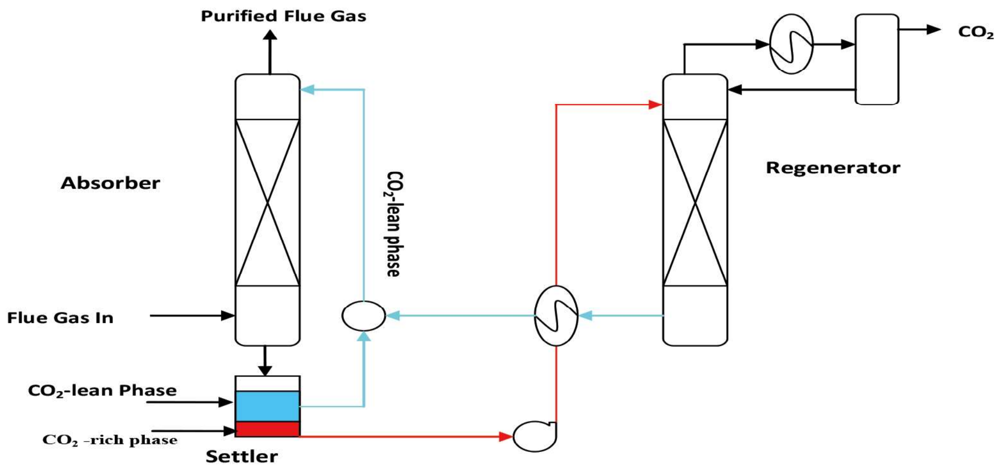

Figure 1: Concept Flow Diagram of Phase Transitional Absorption

In the conventional absorption process, such as an MEA process, the entire solvent is sent to the regenerator for regeneration, which necessitates a large circulation pump and a large amount of regeneration energy. In contrast, in the phase transitional absorption process, the

technology maturity:

Laboratory-Scale, Using Simulated Flue Gas

project focus:

Phase Transitional Absorption

participant:

Hampton University

project number:

FG26-05NT42488

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Liang Hu
Hampton University
lianghu59@yahoo.com

partners:

None

performance period:

6/15/05 – 6/30/09

absorbent separates into two phases, and only the CO_2-rich phase needs to be regenerated. The CO_2-rich phase is only approximately 20 percent of the total absorbent. Thus, the pumping and heating requirements are significantly less compared to the MEA process.

Another important feature of the phase transitional absorption is that the absorption rate of CO_2 will be enhanced by selecting the proper solvent, as shown in Figure 2.

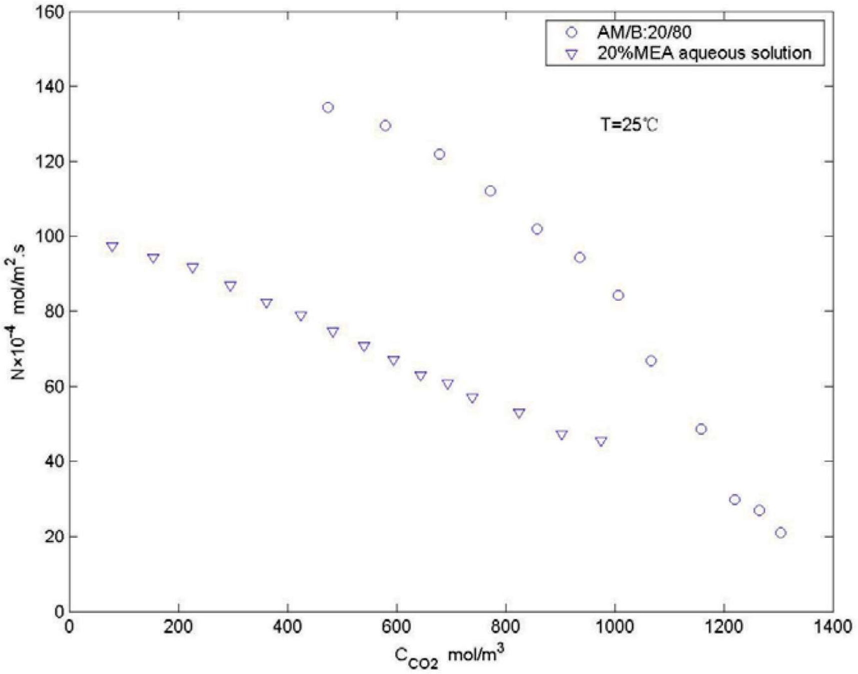

Figure 2: Absorption Rate Comparison (Phase Transitional Absorption vs. MEA Technology)

T = 25°C; P_{CO2} = 1 atm; N=60 rpm; VL = 900 ml.
Phase Transitional Absorption: activated agent: AM 20 percent by volume; solvent: B 80 percent.
MEA Technology: 20 percent (by volume) MEA aqueous solution.

Experimental results also showed that the temperature did not have strong impact on the absorption rate for the several absorbents studied. The small effect on the absorption rate by temperature could be attributed to the much smaller reaction heat.

The highest absorption rate is found when the activated agent was in the range of 30 to 40 percent by volume. The range may vary if the different activated agents and solvents are used. The range of activated agents with the highest absorption rate is highly related to the physical and chemical properties of the absorbent (i.e., activated agents and solvents), as well as the combination.

It was determined from these results that the mechanism of the absorption is a fast chemical reaction controlled by the liquid-side mass transfer. Therefore, an absorber with large gas-liquid interface and sufficient liquid turbulence is recommended in order to have a higher absorption rate, such as a packed column.

TABLE 1: PARAMETERS FOR PHASE TRANSITIONAL ABSORPTION PROCESSES

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	varies	
Normal Boiling Point	°C	varies	
Normal Freezing Point	°C	N/A	
Vapor Pressure @ 15°C	bar	N/A	
Manufacturing Cost for Solvent	$/kg	N/A	

TABLE 1: PARAMETERS FOR PHASE TRANSITIONAL ABSORPTION PROCESSES

	Units	Current R&D Value	Target R&D Value
Working Solution			
Concentration	kg/kg	20/80 by volume	
Specific Gravity (15°C/15°C)	-	N/A	
Specific Heat Capacity @ STP	kJ/kg-K	N/A	
Viscosity @ STP	cP	N/A	
Absorption			
Pressure	bar	1	
Temperature	°C	25-50	
Equilibrium CO_2 Loading	mol/mol	0.4 – 0.5	
Heat of Absorption	kJ/mol CO_2	N/A	
Solution Viscosity	cP	N/A	
Desorption			
Pressure	bar	1	
Temperature	°C	90-120	
Equilibrium CO_2 Loading	mol/mol	≈ 0	
Heat of Desorption	kJ/mol CO_2	N/A	
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A	
Adsorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine MEA in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The mechanism of the absorption is a fast chemical reaction controlled by the liquid-side mass transfer.

technology advantages

- Greatly reducing regeneration energy compared with the MEA process.
- Higher absorption rate, resulting in lower capital investment for absorption equipment.
- Higher CO_2 working capacity, which will reduce sensible heat and solvent volume in circulation.
- Low corrosion rate to carbon steel compared to the MEA process.
- Potentially less solvent loss.
- Non-toxic, environmentally safe.

R&D challenges

- Process exists only at the laboratory scale and needs to be scaled-up.
- Moisture in flue gas may have impact on the process.

results to date/accomplishments

- Measured the absorption rate at 15, 25, 35, 45, and 55 °C.
- Measured the effect of absorbent concentration in solution (from 10 to 50 percent by volume) on absorption rate and loading capacity.
- Measured the effect of solution agitation speed (30, 60, and 90 rpm) on absorption rate.
- Measured the absorption rate at 1 atm of CO_2 partial pressure.
- Conducted the regeneration tests; measured the regeneration rate at different temperature.
- Conducted the corrosion tests for carbon steel coupon.
- Conduct the initial process evaluation based on the lab results and made the comparison with MEA absorption.

next steps

This project ended on June 30, 2009.

available reports/technical papers/presentations

Hu, L., "CO_2 Capture from Flue Gas by Phase Transitional Absorption." Final Report June 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/phase-transitional-absorption-final-report-june2009.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: POST-COMBUSTION SORBENT TECHNOLOGIES

Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture

primary project goals

SRI International operated a bench-scale test unit for post-combustion carbon dioxide (CO_2) capture to demonstrate their process using a novel low-cost, low-energy, and high-capacity carbon sorbent in a single column integrating both the absorber and desorber. SRI also designed a 0.5-megawatt electric (MW_e) pilot-scale test unit.

technical goals

- Operate SRI's 40-kilowatt electric (kW_e) sorbent test unit on actual flue gas at the National Carbon Capture Center (NCCC) to provide data for initial techno-economic assessment and for pilot plant design.
- Design 0.5-MW_e slipstream pilot plant for post-combustion CO_2 capture using the novel sorbent.
    - Complete preliminary techno-economic assessment and environment, health, and safety (EH&S) assessment based on data from testing.
- Develop sorbent formulation and method of manufacture.

technical content

SRI International tested their process for post combustion CO_2 capture on the bench-scale using their novel carbon sorbent. The technology is based on the sorbent developed in a previously funded DOE project NT0005578. This novel sorbent, manufactured by ATMI, Inc., is composed of carbon microbeads, as shown in Figure 1. These microbeads show excellent CO_2 capacity and selectivity, fast adsorption/desorption kinetics, and good resistance to agglomeration and attrition, allowing for reductions in both capital and operating expenses. Reduced steam regeneration requirements in the process can reduce the parasitic power load.

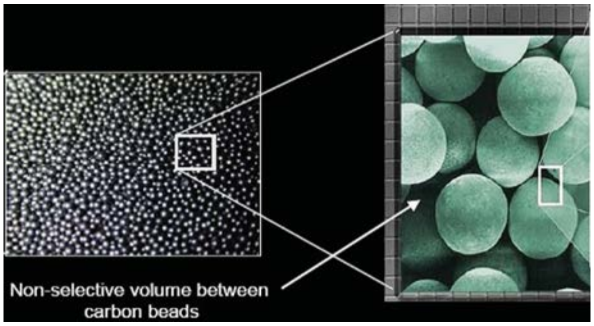

Figure 1: Graphic displays of novel carbon pellets sorbent

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Novel Solid Sorbent

participant:

SRI International

project number:

FE0013123

predecessor projects:

NT0005578

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Marc Hornbostel
SRI International
marc.hornbostel@sri.com

partners:

ATMI, Inc.; Linde, LLC; Electric Power Research Institute

start date:

10.01.2013

percent complete:

100%

Figure 2 depicts the proposed sorbent system for an existing coal-fired power plant. Flue gas first enters an existing flue gas desulfurization (FGD) system where most of the sulfur content is removed. The gas is then cooled before entering the continuous falling-bead sorbent reactor which integrates the adsorber and stripper in a single vertical column, providing a low pressure drop for gas flow and minimizing physical handling of the high capacity carbon sorbent (0.05–0.08 kg of CO_2 per kg of sorbent). As the gas stream passes over the lean sorbent, CO_2 is removed from the gas and adsorbed by the sorbent. The loaded sorbent cascades down the separation column and is heated by low-pressure steam, causing the sorbent to release the adsorbed CO_2. The CO_2 is siphoned off to a compressor where it can be prepared for sequestration. The sorbent is then dried, cooled, and sent back into the separation column for reuse and the cycle begins again.

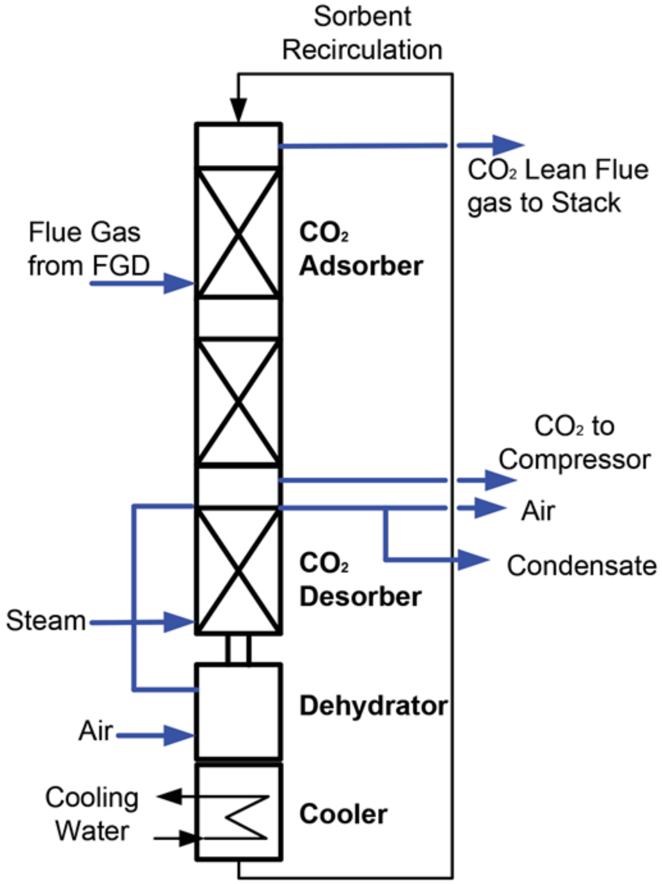

Figure 2: Sorbent system

SRI also designed a 0.5-MW_e pilot-scale system based on this technology. The system includes a heat exchanger for recovering sensible heat from the hot, regenerated sorbent for use to preheat the sorbent from the adsorber. The system is designed for a nominal flue gas flow of 70 cubic feet per minute (cfm) and a CO_2 capture capacity of approximately 1 ton/day.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,100	1,100
Bulk Density	kg/m^3	700	700
Average Particle Diameter	mm	0.2	0.2
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.1 x 10^9	1.1 x 10^9
Solid Heat Capacity @ STP	kJ/kg-K	1.0	1.0
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	proprietary	proprietary
Adsorption			
Pressure	bar	1	1
Temperature	°C	20	20
Equilibrium Loading	g mol CO_2/kg	4	4
Heat of Adsorption	kJ/mol CO_2	27	27
Desorption			
Pressure	bar	1	1
Temperature	°C	100	100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.96	0.96
Heat of Desorption	kJ/mol CO_2	27	27
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	continuous, moving bed	
Flue Gas Flowrate	kg/hr	1,860	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 1	
Adsorber Pressure Drop	bar	0.005	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
psia	°F	vol%					ppmv	
		CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Rapid physical adsorption and desorption rates: The adsorption of CO_2 occurs on the micropores of the sorbent with low activation energy (<5 kJ/mole), allowing rapid equilibrium. Similarly, the adsorbed CO_2 is desorbed rapidly at the regeneration temperature (≈100 °C), and the sorbent performance can be predicted by equilibrium models.

Sorbent Contaminant Resistance – The sorbent is pure carbon and generally resistant to many contaminants. The sulfur dioxide (SO_2) needs to be reduced to <10 parts per million (ppm) levels, preferably to 1 ppm level. Nitrogen oxides (NO_x) can be present at ≈50 ppm levels. Fly-ash particles in flue gas downstream of an electrostatic precipitator do not appear to interfere with CO_2 adsorption.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent granules are hard and attrition-resistant. No observable attrition was noticed in a recent field test conducted over 7,000 cycles of adsorption and regeneration. The sorbent has a high hydro-thermal stability and direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.

Flue Gas Pretreatment Requirements – Reduce SO_2 levels to <5 ppm. The flue gas needs to be cooled to ≈25 °C.

Sorbent Makeup Requirements – Preliminary data suggest multi-year lifetime for sorbent makeup.

Waste Streams Generated – The sorbent particles are hard and attrition-resistant, and no fine sorbent particles are generated during operation. Steam condensate from the dehydrator may need to be treated before cycling back to the steam boiler.

Process Design Concept – The module will be located between FGD and flue gas chimney.

technology advantages

- Low cost carbon sorbent.
- Low activation energy and rapid cycling for adsorption/desorption.
- Reduced capital and operating costs.
- The sorbent has a high capacity for CO_2 adsorption (20 wt% at 1 atm CO_2) and good selectivity for CO_2 over other flue gas components (CO_2-N_2 separation factor >20).
- Low heat capacity minimizes thermal energy required to heat the sorbent to regeneration temperature.
- Carbon sorbent particles have excellent attrition resistance, minimal dust generation, and high resistance to agglomeration.
- High hydrothermal stability: Direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.
- High thermal conductivity: The thermal conductivity of 0.8 W/m-K enables rapid thermal equilibrium between the surface and interior of the microbeads.

- The sorbent is essentially hydrophobic, indicating little interaction between the condensed water and the sorbent. The thermal energy required to desorb the condensed water is significantly less than that required to evaporate water from oxide surfaces such as those found in molecular sieves (zeolites), alumina, and silica.
- Continuous, falling microbead sorbent reactor geometry integrates the adsorber and stripper in a single vertical column.
  - Low pressure drop for gas flow.
  - Minimal physical handling of solvent.

R&D challenges

- Other elements of the flue gas, such as sulfur oxides (SO_x), may compete with CO_2 in being adsorbed by the sorbent, reducing the amount of CO_2 that is adsorbed as the gas passes through the reactor.

status

The project was completed on June 30, 2016. SRI completed approximately 250 hours of testing on their 40-kW_e bench-scale unit using actual flue gas at the NCCC. The project achieved CO_2 purity of 93 percent and CO_2 capture efficiency of 67 percent. SRI indicated that 90 percent capture is achievable by decreasing the sorbent temperature and increasing the adsorber height. A basic engineering design package was completed for the 0.5-MW_e pilot unit.

available reports/technical papers/presentations

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," presented at Project Review Meeting, Pittsburgh, PA, June 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0013123-Project-Review-Presentation-06-21-2016.pdf*

Hornbostel, M. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," presented at 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/M-Hornbostel-SRI-Pilot-Advanced-Sorbent-Process.pdf*

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," Project Review Meeting, Pittsburgh, PA, October 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0013123-Project-Review-Presentation-10-28-2014.pdf*

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/G-Krishnan-SRI-Pilot-Scale-Evaluation.pdf*

Krishnan, G., "Development of Novel Carbon Sorbents for CO_2 Capture," Final Technical Report, March 2014. *http://www.osti.gov/scitech/servlets/purl/1132602*.

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture", presented at Project Kickoff Meeting, Pittsburgh, PA, December 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/FE0013123-Kickoff-Presentation-12-04-2013.pdf*

Krishnan, G. "Development of Advanced Carbon Sorbents for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO$_2$%20Capture/G-Krishnan-SRI-Advanced-Carbon-Sorbents.pdf*.

Krishnan, G. "Development of Advanced Carbon Sorbents for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO$_2$/development-of-advanced-carbon-sorbents-july2012.pdf*.

Hornbostel, M. "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.
http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/22Aug11-Hornbostel-SRI-Novel-Carbon-Sorbents.pdf.

Krishnan, G. "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.
http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/monday/Gopala%20Krishnan-NT0005578.pdf.

Krishnan, G, "Development of Novel Carbon Sorbents for CO_2 Capture – Project Overview," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.
http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5578%20SRI%20carbon%20sorbent%20%28Hornbostel%29%20mar09.pdf.

Bench-Scale Development and Testing of Aerogel Sorbents for CO_2 Capture

primary project goals

Aspen Aerogels designed an innovative aerogel sorbent for carbon dioxide (CO_2) capture with improved CO_2 capacity, high adsorption/desorption cyclic stability, and resistance to contaminants in the flue gas, improving the performance and economics of CO_2 capture.

technical goals

- Optimize Amine Functionalized Aerogel (AFA) to maximize CO_2 adsorption, decrease regeneration temperature, maintain kinetics for fluidized bed operation, and maintain high cyclic-adsorption stability.
- Develop pellet- and bead-forming processes.
- Develop a sulfur oxide (SO_x)-resistant coating to minimize aerogel degradation due to flue gas contaminants.
- Develop optimum AFA pellet/binder (SO_x coating) formulations.
- Develop aerogel production process.
- Test and evaluate aerogel sorbent technology at the bench-scale to determine CO_2 capture performance and optimize operating conditions.
- Complete a techno-economic analysis of the system.

technical content

Aspen Aerogels has designed an AFA sorbent for CO_2 capture with improved CO_2 capacity, high adsorption/desorption cyclic stability, and resistance to contaminants in the flue gas to achieve an overall reduction in total carbon capture cost. The AFA contains amine groups bonded to an aerogel backbone. AFA benefits include high surface area, high porosity, hydrophobicity to enhance CO_2 adsorption selectivity, low specific heat for lower energy regeneration, and high temperature stability. The unique, specific aerogel structural morphology is shown in Figure 1, along with the AFA beads, shown in Figure 2.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Advanced Aerogel Sorbents

participant:

Aspen Aerogels, Inc.

project number:

FE0013127

predecessor projects:

SC0004289

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Redouane Begag
Aspen Aerogels, Inc.
rbegag@aerogel.com

partners:

University of Akron; ADA Environmental Solutions, Longtail Consulting, LLC

start date:

10.01.2013

percent complete:

100%

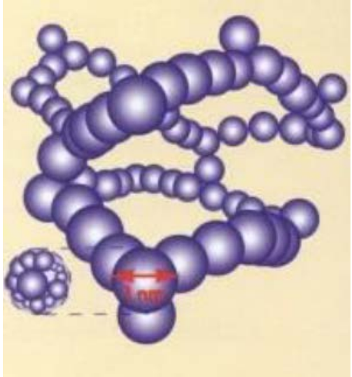

Figure 1: Structural morphology of an aerogel

Figure 2: AFA sorbent in bead form

This project maximized those benefits via bench-scale evaluation of the aerogel sorbents. Optimization of the initial sorbent formulations aimed to increase CO_2 loading capacity, improve resistance to flue gas contaminants, maintain kinetics for fluidized bed operation, and maintain high cyclic stability. Initial testing on aerogel powders provided performance data to determine optimal formulations. For use in larger scale applications, the use of AFA pellets or beads is necessary instead of powders. The AFA pellets are formed by adding binder to the aerogel powder. Further development optimized the process of aerogel bead fabrication. Bead performance was compared to AFA pellet performance, with not only the optimization of CO_2 capacity, cycle life, and stability to contaminants, but also for parameters important to high performance in a fluidized bed, including particle size, density, attrition index, and crush strength. Bench-scale cold-flow fluidized bed testing on the final AFA formulations provided hydrodynamic properties and heat transfer coefficients.

Upon testing, both the AFA bead and pellet forms demonstrated comparable CO_2 capture performance. Pellets showed superior stability during long term CO_2 capture testing. The pellet form was chosen moving forward primarily due to scale-up production capabilities of the aerogel at Aspen and the pelletization capabilities at the University of Akron for future large-scale production.

Opportunities to improve the sorbent in terms of advancing the production process include: (1) reducing the mass of the pellet binder to increase the CO_2 mass loading by using lightweight aerogel beads, needing minimal binder as coating for SO_2 resistance, and (2) lowering density of AFA and using the bead form to reduce capital costs and sorbent circulation rate, directly tied to sorbent costs due to attrition.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,150	1,200–1,300
Bulk Density	kg/m^3	250-800	≈1,000
Average Particle Diameter	mm	0.2–1.0	0.3–0.6
Particle Void Fraction	m^3/m^3	0.56	
Packing Density	m^2/m^3	not measured	
Solid Heat Capacity @ STP	kJ/kg-K	≈1.3	0.7
Crush Strength	kg_f	3.8–6.4	
Manufacturing Cost for Sorbent	$/kg	N/A	7- 10
Adsorption			
Pressure	bar	0.8 (in Colorado)	1.0
Temperature	°C	40	<70
Equilibrium Loading	g mol CO_2/kg	100-200	>250
Heat of Adsorption	kJ/mol CO_2	55-62	60
Desorption			
Pressure	bar	0.8 (in Colorado)	1.0
Temperature	°C	100-120	<130
Equilibrium CO_2 Loading*	g mol CO_2/kg	20–100	<100
Heat of Desorption	kJ/mol CO_2	55–62	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*Under 100 percent CO_2

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The primary mechanism of CO_2 capture on AFA sorbents occurs by chemisorption. The homogenous distribution of amine grafted on the high surface area aerogel structure facilitates mass transfer of CO_2 to and from receptor sites. Adsorption/desorption of CO_2 occurs by temperature swing, between 40 °C and 100–120 °C.

Sorbent Contaminant Resistance – Development of a series SO_2 resistant coatings was initiated. Preliminary studies of the performance of the coatings were carried out. These coatings reduced the effect of SO_2 poisoning on the AFA sorbent and increased the stability of the sorbent in the presence of SO_2. The effectiveness of the newly developed coatings shows a CO_2 capacity reduction of only 4 percent after 20-cycle exposure to 40 ppm SO_2 in simulated flue gas, versus 55–61 percent reduction with no coating on the sorbent.

Sorbent Attrition and Thermal/Hydrothermal Stability – Selected AFA pellets were subjected to ASTM D5757 (Standard Test Method for Determination of Attrition and Abrasion of Powdered Catalysts by Air Jets), to measure the attrition index (AI). The initial sizes of the tested pellets are above 500 µm. AI is lower for AFA pellets relative to a reference of fluidized catalytic cracker (FCC). The attrition index was higher for < 20 micron particles at 300 ft/s than the reference FCC sample. The AI index indicates that the sorbent is suitable for a fluidized bed process where it will not only encounter mechanical attrition from the fluidized bed at relatively low velocities, but it will also be subject to high gas velocity cyclones needed to separate the sorbent from the gas flow.

Flue Gas Pretreatment Requirements – Protecting sorbents from SO_2 poisoning and generating high-purity CO_2 from the process are two unavoidable tasks for CO_2 Capture and Sequestration (CCS). The economic feasibility considerations are also important to the scale-up and commercialization of the CO_2 capture process. SO_2-resistant coating was verified effective to reduce the SO_2 poisoning of the AFA sorbent pellets. However, it was determined that a SO_2 polishing scrubber was needed prior to the CO_2 capture process, based on the maximum SO_2 concentration that the AFA sorbent can tolerate.

As for temperature of the flue gas entering the adsorber, for example for an adsorption temperature of 40 °C, some cooling was required due to inevitable gas heating in the blower (to overcome the pressure drop of the sorbent bed in the adsorber).

Sorbent Makeup Requirements – This has not yet been determined.

Waste Streams Generated – None known.

Process Design Concept – The solid sorbent capture case utilizing AFA sorbent was modeled using ADA-ES's general process design reported in their 1 MW pilot testing report[1] (Figure 3). However, individual reactors were specifically designed and sized for use with Aspen Aerogel's sorbent (AFA).

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[1] Sjostrom, S. (2016). *Evaluation of Solid Sorbents as a Retrofit Technology for CO2 Capture*. ADA-ES, Inc. U.S. Department of Energy

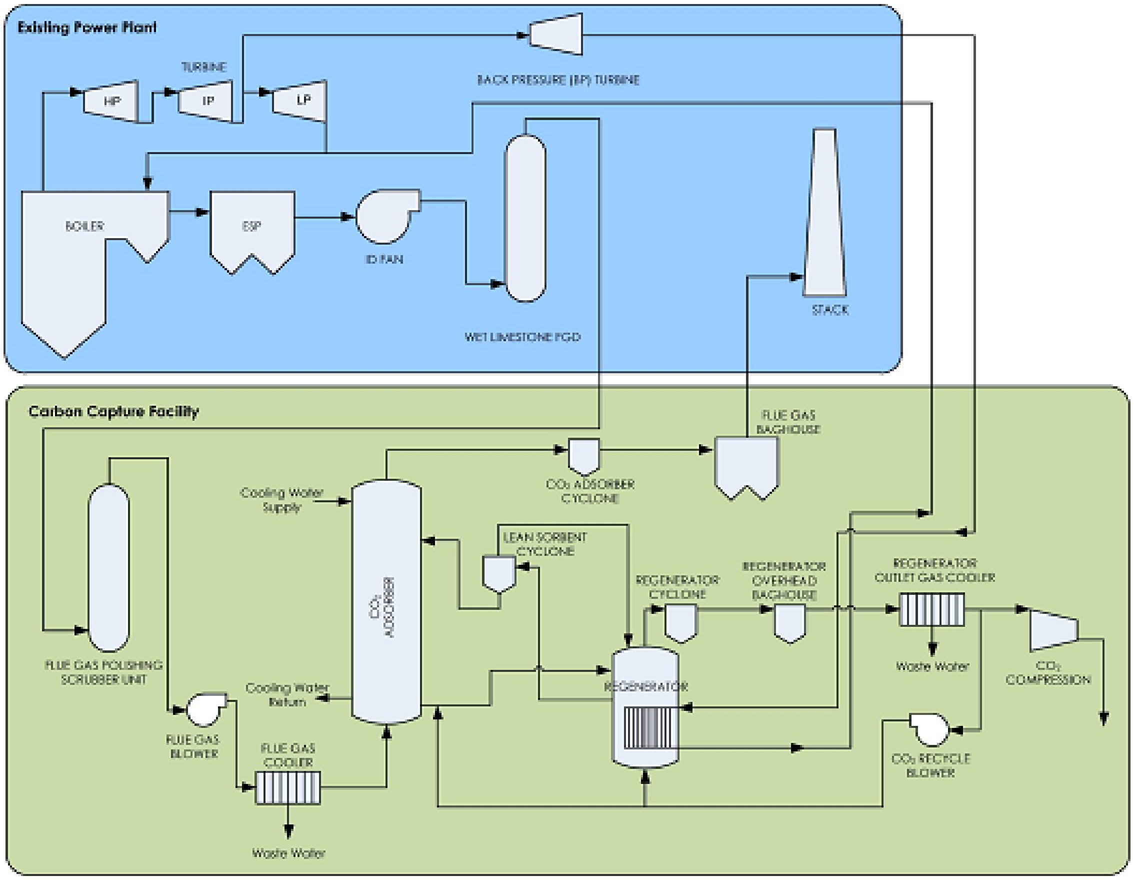

Figure 3: ADA-ES solid sorbent CO2 capture process flow diagram

technology advantages

- AFA sorbent has high CO_2 capacity and long life, reducing equipment size requirements and process costs.
- High sorbent selectivity allows for reduced sorbent cycling times, which allows for reductions in sorbent quantity, reactor size, and cost.
- Low specific heat results in low energy regeneration.
- High moisture resistance.
- High temperature stability.
- Reduced delta T for adsorption/desorption.

R&D challenges

- Optimizing pellet formulation to balance properties for optimum performance, including CO_2 capacity, attrition and SO_x resistance, thermal conductivity to improve kinetics, as well as selecting the optimal particle size and density for use in a fluidized bed.
- Optimizing pellet and bead fabrication to match performance of the aerogel powder.
- Reducing attrition.
- Overcoming the issue of reduced CO_2 capacity for AFA beads due to some amine leaching out during the fabrication process.

status

The project was completed on December 31, 2016. Aspen Aerogels tested bead and pellet formulations of the AFA, with both showing comparable CO_2 capture performance, with total CO_2 capacity between 11–14 wt%, CO_2 working capacity between 6.0–6.5 wt%, and cyclic stability over 500 cycles in a fixed bed. The AFA production and pelletization processes were scaled up, with 30 kg of pelletized sorbent prepared. The pellet form was chosen for scale-up and testing based primarily on the pelletization capabilities at the University of Akron for future large-scale production. The pelletized AFA sorbent was tested on the bench-scale in a cold-flow fluidized bed and showed good fluidization could be attained at bed velocity of 1.5 ft/s and pellet density of 1150 kg/m^3.

available reports/technical papers/presentations

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/R-Begag-Aspen-Testing-of-Aerogel-Sorbents.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/R-Begag-AAI-Aerogel-Sorbents.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Gould-AAI-Bench-Scale-Development.pdf*

Begag, R., et al. "Development and Testing of Aerogel Sorbents for CO_2 Capture," presented at BP1 Review Meeting, July 2014. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/BP1-NETL-presentation-Final-Rev-2-nonproprietary.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbent for CO_2 Capture," presented at Project Kick-Off Meeting, Pittsburgh, PA, November 8, 2013. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/Aspen-Aerogels-NETL-DOE--Kick-Off-Final-Non-proprietary.pdf*

NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology

primary project goals

NRG Energy proposed to develop a post-combustion carbon dioxide capture project utilizing the Inventys VeloxoThermTM technology utilizing a structured adsorbent in a rotary bed adsorber using rapid cycle temperature swing adsorption. The project would have included developing the scope, configuration, and design basis of a pilot-scale system.

technical goals

- Develop the scope, configuration, and design basis for a pilot plant using the VeloxoThermTM process sized for a 10-megawatt electric (MW_e) or greater slipstream of flue gas from an NRG coal plant.
- Determine optimal size and host site location at one of NRG's coal plants.
- Complete a techno-economic analysis and identify technology gaps.

technical content

NRG Energy was working to establish the technical and economic feasibility of the Inventys VeloxoThermTM post-combustion carbon dioxide (CO_2) capture process. VeloxoThermTM is an intensified temperature swing adsorption process using a proprietary combination of structure sorbent and process design using a rotary adsorption machine, as depicted in Figure 1.

The structured sorbents provide high surface area along with mass and heat transfer kinetics allowing for low pressure drop, immobilization with no fluidization, and high surface area. The VeloxoThermTM process is based on rotary air preheaters, which have been used in process industries. The process implements a cycle design without the need of discrete vessels, multiple large switching valves, and complicated interconnecting piping and ducting. The VeloxoThermTM technology has previously been validated for capturing CO_2 from a natural gas-fired boiler. The current project is aimed at determining the size, scope, configuration, and design basis for a pilot plant using a slipstream of flue gas from one of NRG Energy's coal plants.

technology maturity:

Conceptual Design of Pilot-Scale, Actual Flue Gas Slipstream (equivalent to 10 MW_e or greater)

project focus:

Temperature Swing Adsorption with Structured Sorbent

participant:

NRG Energy, Inc.

project number:

FE0026581

predecessor projects:

N/A

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

David Greeson
NRG Energy, Inc.
david.greeson@nrg.com

partners:

Inventys

start date:

10.01.2015

percent complete:

100%

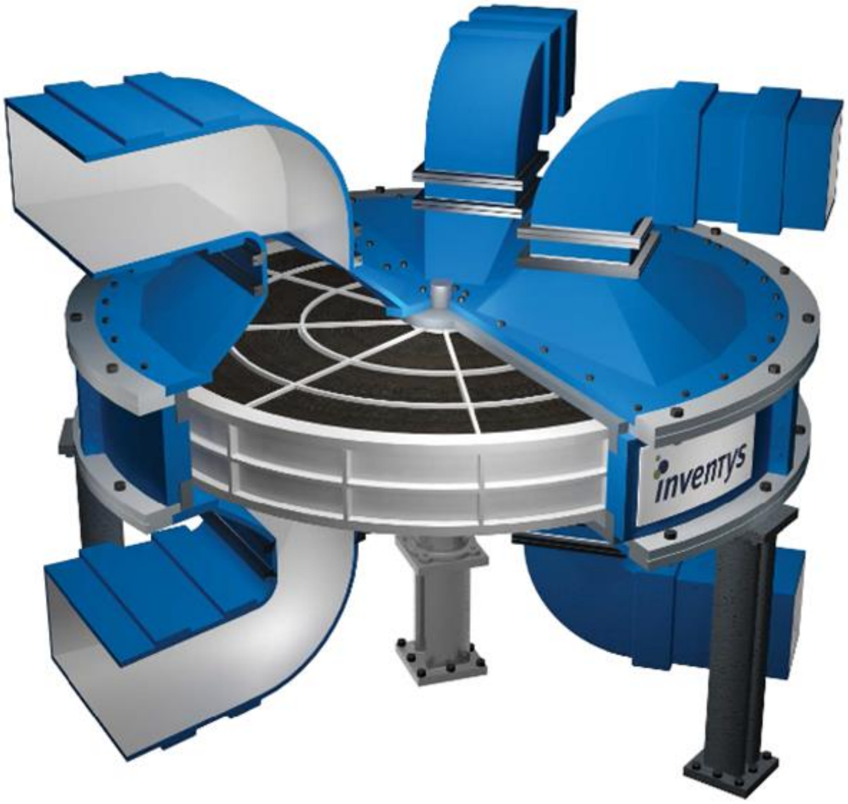

Figure 1: Inventys VeloxoTherm™ rotary adsorption machine concept

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	**Temperature**	**Composition**						
		vol%					ppmv	
psia	°F	**CO_2**	**H_2O**	**N_2**	**O_2**	**Ar**	**SO_x**	**NO_x**
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- Technology proven at 0.5 MW_e pilot scale using natural gas feed.
- Structured adsorbents have high surface area per reactor volume and low pressure drop.
- Structured adsorbents allow for high heat and mass transport due to short diffusion paths within structured materials.
- High heat retention due to anisotropic heat transfer properties.
- Laminate design allows degrees of freedom for adjusting void fraction, packing densities, and hydrodynamics.
- Rapid cycle temperature swing adsorption (TSA) with structured adsorbents shows good resistance to sulfur oxides (SO_x) and other flue gas contaminants.

R&D challenges

- Risk of scale up to a large-scale rotary adsorption machine.
    - Maintaining flow distribution.
    - Size of adsorbent beds.
    - Scale-up of gas seal design.
    - Rotor imbalances/process asymmetry.
- Developing the technology for a coal-based flue gas feed.

status

During the initial phase of the project NRG and Inventys conducted a six-week test exposing the adsorbent to flue gas from one of NRG coal-fired boilers and determined that further work was needed to improve the economics before a large scale pilot demonstration could be attempted. Consequently, the project was wrapped up September 30, 2016. NRG completed conceptual design of a 15 m diameter large scale pilot rotary adsorption machine, along with a preliminary EH&S risk assessment and technology gap analysis. Increased structured adsorbent bed density and use of a vacuum-assisted regeneration strategy was determined to be necessary to achieve process performance targets for the coal flue gas TSA cycle.

available reports/technical papers/presentations

Armpriester, A. and Stevenson, M. "NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/A-Armpriester-NRG-CO2NCEPT.pdf*

Armpriester, A. "NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology," presented at the Project Kickoff Meeting, Pittsburgh, PA, November 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026581-NRG-Inventys-DOE-Kickoff-Meeting.pdf*

Bench-Scale Development and Testing of Rapid Pressure Swing Adsorption for Carbon Dioxide Capture

primary project goals

W.R. Grace developed a rapid pressure swing adsorption (rPSA) process to evaluate concept cost and performance benefits by testing a bench-scale system using a low-cost, structured adsorbent with low-pressure drop, high mass-transfer rates, high capacity, and high availability that will enable large feed throughputs.

technical goals

- Develop an attrition-resistant and low-pressure drop structured adsorbent based on a commercial zeolite that is compatible with the high velocities associated with rapid PSA operation.
- Design, develop, and test a bench-scale rapid PSA process using the structured adsorbent to deliver efficient and cost-effective separation of carbon dioxide (CO_2) from flue gas.

technical content

W.R. Grace worked to develop a rapid PSA process with a much shorter cycle time compared to conventional PSA, which could potentially reduce the cycle time from 300 seconds (conventional PSA cycle) to 30 seconds or less. This would increase the feed throughput, and thus decrease the size of the columns by a factor of 10 or more, significantly reducing both the capital and operating costs, as well as the plant footprint. Pressure swing adsorption is attractive because it requires only electricity and not any of the power plant's steam.

The key challenge to the success of this concept is two-fold: (1) an attrition-resistant and low-pressure drop structured adsorbent must be developed based on commercial zeolite that is compatible with the high velocities associated with rapid PSA operation; and (2) a rapid PSA cycle configuration must be developed in concert with the structured adsorbent so that the resulting rapid PSA process achieves necessary cost and performance metrics.

One advantage of a rapid PSA process over other CO_2 adsorption processes is simplified heat management. The rapid cycle times minimize temperature swings. Thus, the columns will heat up only slightly during adsorption and cool down only slightly during desorption, approaching nearly isothermal operation, which is optimal.

Management of water will provide some operational challenges. Degradation of the PSA process performance in the presence of water is well documented. It is anticipated that for a rapid PSA CO_2 removal process, up to 95 percent of the water in the flue gas will need to be removed using commercial desiccant technology. This will increase capital and operating costs; however, any increases are more than offset by cost savings in other parts of the process.

The structured adsorbent to be developed will consist of zeolite crystals coated on a

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid Pressure Swing Adsorption

participant:

W.R. Grace and Co.

project number:

FE0007639

predecessor projects:

N/A

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

James A. Ritter
University of South Carolina
ritter@cec.sc.edu

partners:

University of South Carolina;
Catacel Corporation;
Battelle Memorial Institute

start date:

10.01.2011

percent complete:

100%

metal support. This process has been successfully demonstrated using metal foil, as shown in Figure 1.

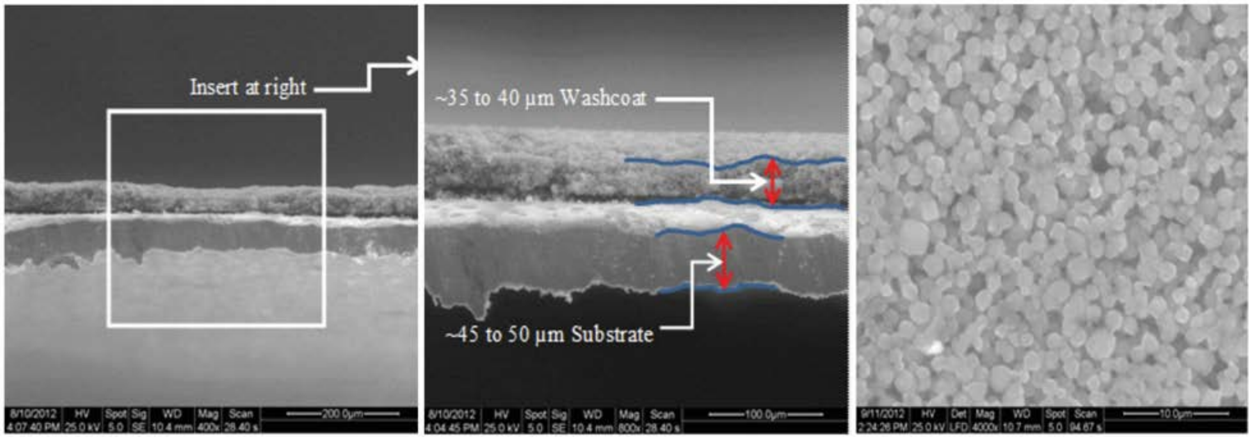

Figure 1: Edge view of zeolite-coated metal substrate at 400x magnification (left); edge view of zeolite-coated metal substrate at 800x magnification indicating washcoat is 35–40 µm thick (center); top view of zeolite-coated metal foil substrate at 4,000x magnification (right)

Corrugated cores have been fabricated (Figure 2) to serve as the metal substrate for testing the rapid PSA process. These cores were tested to evaluate pressure drop, and coated with zeolite crystals for process testing.

Figure 2: Side view of 1.5" x 6" x 289 psi corrugated cores

In addition, a dynamic volumetric frequency response (DVFR) apparatus (Figure 3) that is being used to characterize adsorbate mass-transfer rates in various adsorbents at cycle times up to 10 Hz, as well as a single-column rapid pressure swing adsorption (S-C rPSA) system (Figure 4), is being used to study the effect of cycle time on the mass-transfer rates at step times as short as 0.25 seconds.

Figure 3: Photograph DVFR apparatus

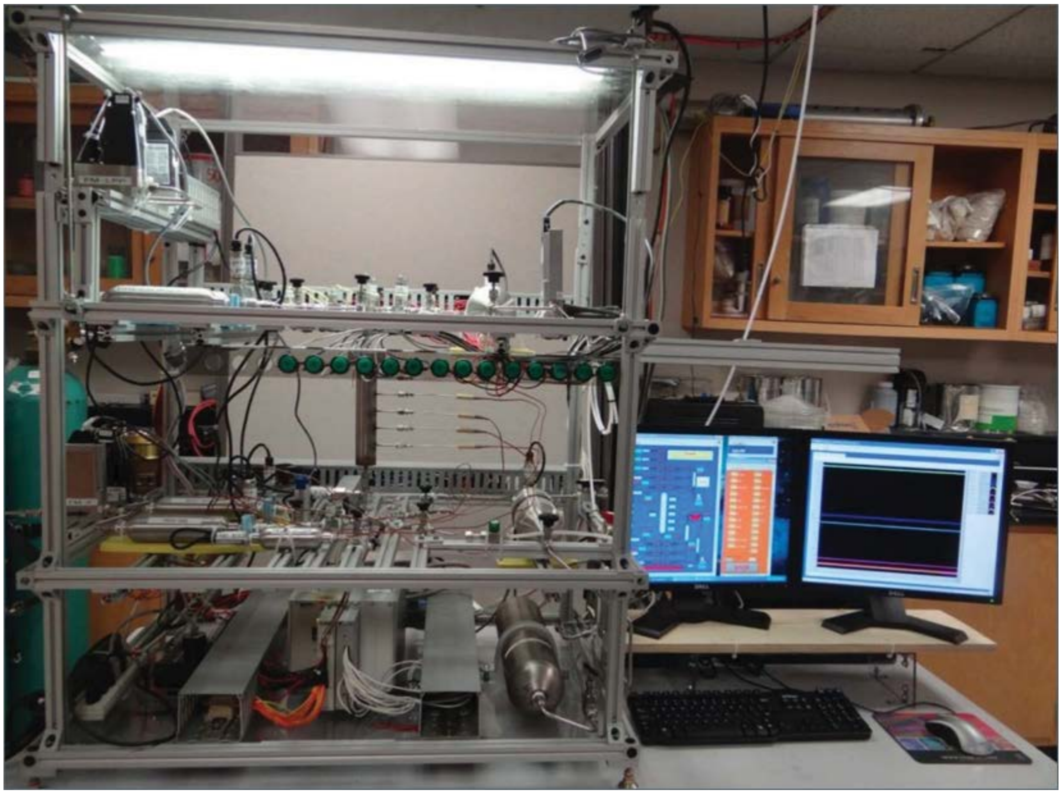

Figure 4: Photograph of S-C rPSA system

TABLE 1: SORBENT PROCESS PARAMETERS[1]

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP[2]	kg/m^3	1,090	2,518
Bulk Density[3]	kg/m^3	688	400
Average Particle Diameter[4]	mm	5.0	0.100
Particle Void Fraction	m^3/m^3	0.47	0.47
Packing Density	m^2/m^3	750	6,070
Solid Heat Capacity @ STP[2]	kJ/kg-K	0.92	0.82
Crush Strength[5]	kg$_f$	3.6	N/A
Manufacturing Cost for Sorbent	$/kg	20	37.4
Adsorption[6]			
Pressure[7]	bar	1.2/1.14	1.2/1.14
Temperature	°C	50	50
Equilibrium Loading[8]	g mol CO_2/kg	4.18	4.18
Heat of Adsorption	kJ/mol CO_2	37.5–46.0	37.5–46.0
Desorption			
Pressure[7]	bar	0.05/0.00085	0.05/0.00085
Temperature	°C	50	50
Equilibrium CO_2 Loading[9]	g mol CO_2/kg	0.14	0.14
Heat of Desorption	kJ/mol CO_2	37.5–46.0	37.5–46.0
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed bed/cyclic	
Flue Gas Flowrate	kg/hr	2.32×10^6	
CO2 Recovery, Purity, and Pressure	% / % / bar	90 95 1.38	
Adsorber Pressure Drop	bar	0.15	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

1. For the Current R&D Value, the calculation is based on 5-mm 13X beads. For the Target R&D Value, the calculation is based on a 52-micron thick stainless steel support containing a 100-micron thick zeolite crystal coating at each side.
2. The Target R&D Value includes the stainless steel support.
3. The Target R&D Value corresponds to mass of adsorbent (zeolite) per volume of bed.
4. The Target R&D Value corresponds to coating thickness.
5. The structured support for the target will be unaffected by PSA dynamic stresses.
6. The adsorption step is considered as the Heavy Reflux step, which follows the feed step in the PSA cycle and is highly enriched in CO_2 and obtained from another desorption step in the PSA cycle.
7. First value is total pressure; second value is partial pressure of CO_2.
8. The value corresponds to conditions of the heavy product gas.
9. The value corresponds to conditions of the light product gas.

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The relative thermodynamic adsorption selectivity toward CO_2 over other gases such nitrogen (N_2), oxygen (O_2), and argon (Ar) on a commercial zeolite at partial pressures of CO_2 at around or below 1.0 bar.

Sorbent Contaminant Resistance – The effect of the contaminant sulfur dioxide (SO_2) is not clear yet; tests are planned. It is expected, however, that the 42 parts per million (ppm) in the fresh flue gas will be significantly reduced at the condensing heat exchanger that will be located upstream of the PSA unit. It is not expected that the zeolite will be irreversibly affected by nitrogen oxides (NO_x).

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent will be deposited on the surface of a metal structured support; thus, thermal or mechanical stresses present in pelletized/beaded systems will not be observed.

Flue Gas Pretreatment Requirements – The flue gas requires a blower to bring the pressure up to 120 kPa and then a condensing heat exchanger followed by a dryer to bring the content of water to less than 0.1 vol% prior to entering the PSA unit.

Sorbent Makeup Requirements – There are no sorbent makeup requirements in PSA units. The structured adsorbent is expected to last at least 5 years and possibly 10 years before it needs to be replaced. This is common in commercial PSA systems.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensing heat exchanger will produce about 460,000 lb/h of condensed water that is recycled back as makeup water for the flue gas desulfurization (FGD) unit. It may contain up to 1,125 mg/L of dissolved SO2 and no other contaminants. In addition, about 3.69 x 106 lb/h of N_2-rich product at about 80 °C is vented into the air. This stream will contain, by volume, about 1.8 percent CO_2, 4.0 percent H_2O, 3.3 percent O_2, 1.09 percent Ar, and balance N_2.

technology advantages

- Established large-scale technology for other applications.
- Requires no steam or water, only electricity.
- Tolerant to trace contaminants; possibly with use of guard or layered beds.
- Zeolite adsorbent is commercial and widely available.
- Increase in cost of electricity (COE) lower than other capture technologies.
- If research and development (R&D) is successful, beds could be installed under a parking lot.

R&D challenges

- Energy-intensive (but better than current amines).
- Reducing bed size; larger bed implies large pressure drop, requiring more power.
- Minimizing pressure drop, mass transfer issues, and adsorbent attrition.

status

The project has ended. Three 6-inch Catacel core structures were successfully coated with a 50 μm thick layer of Zeolite crystals, with a density of 240 kg/m^3. One-bed and three-bed bench-scale PSA apparatuses were constructed. Testing of the structured adsorbent began using these units. The dynamic adsorption process simulator was validated with experimental data from the testing.

available reports/technical papers/presentations

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Ritter-USCarolina-Rapid-PSA.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/J-Ritter-USCarolina-Rapid-Pressure-Swing-Adsorption.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO$_2$%20Capture/J-Ritter-USC-Rapid-Pressure-Swing-Adsorption.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-july2012.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the Project Kickoff Meeting, Pittsburgh, PA, May 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-kickoff-july2012.pdf*

Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration

primary project goals

ADA Environmental Solutions (ADA-ES) investigated heat recovery for a temperature-swing-adsorption (TSA) capture process, including the use of a cross-heat exchanger to recover sensible heat from the sorbent leaving the regenerator. Recovering heat generated by the sorbent during the capture process reduces the energy penalty and overall cost for carbon dioxide (CO_2) capture.

technical goals

- Evaluate options to reduce the plant heat rate and levelized cost of electricity (LCOE) associated with the ADAsorb™ process through heat integration with the plant and use of a cross-heat exchanger.
- Optimize approach temperature and cross-heat exchanger design.
- Assess two different sorbents with preliminary design and techno-economics.
- Assess two cross-heat exchanger designs with laboratory testing, preliminary design and techno-economics.

technical content

ADA-ES, along with partners Solex Thermal Science, Technip Stone and Webster Process Technologies, and the Energy Research Center at Lehigh University, optimized its promising dry sorbent-based post-combustion capture process—the ADAsorb™ process—developed under another DOE-funded project (DE-FE0004343), by evaluating heat integration opportunities as well as working to develop an overall optimized process. In prior project DE-NT0005649, ADA-ES evaluated multiple solid sorbents at the lab- and bench-scale. In prior project DE-FE0004343, ADA-ES evaluated the ADAsorb™ process at the 1 megawatt electric (MW_e) pilot-scale. The ADAsorb™ process is shown in Figure 1. The concepts, however, will be applicable to other TSA processes. The optimization study includes a sensitivity analysis across a range of sorbent properties to identify cost and energy demand trends so that the general conclusions can be applied to most sorbent-based CO_2 capture processes.

technology maturity:

Bench-Scale Testing at Simulated Full-Scale Process Conditions

project focus:

Cross-Heat Exchanger for Sorbent-Based CO_2 Capture

participant:

ADA-ES, Inc.

project number:

FE0012914

predecessor projects:

FE0004343
NT0005649

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Sharon Sjostrom
ADA-ES, Inc.
sharons@adaes.com

partners:

Solex Thermal Science; Lehigh University–Energy Research Center; Technip Stone and Webster Process Technologies

start date:

10.01.2013

percent complete:

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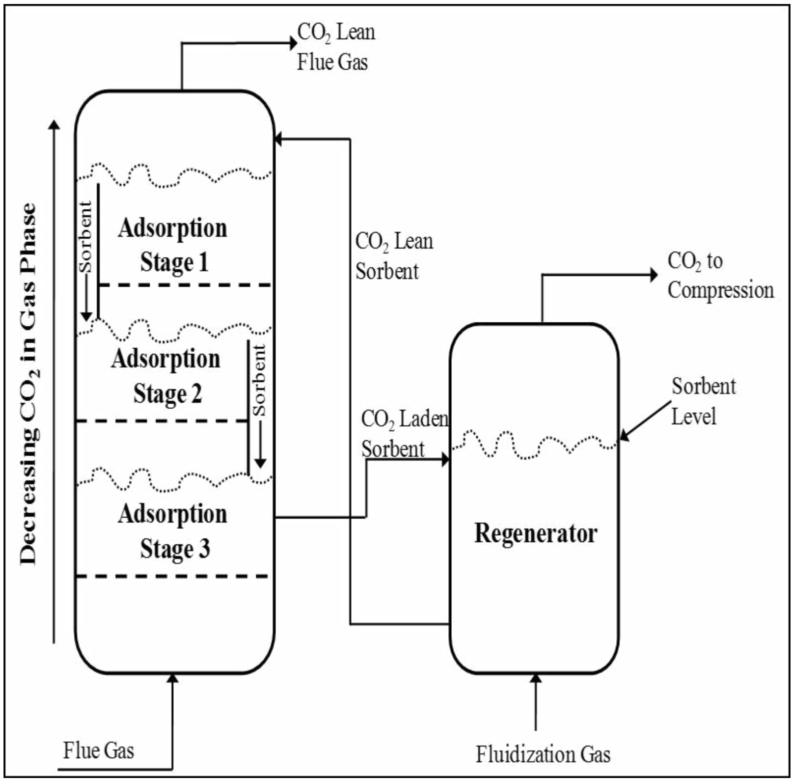

Figure 1: ADAsorb™ process overview

Cross-heat exchangers are standard features of solvent-based processes; large-scale heat exchangers appropriate for solids in this application currently do not exist. Although the fundamental components for solids-based heat exchangers are commercially available, the design details and integration approach are being developed and optimized to ensure that the additional equipment capital costs do not outweigh benefits associated with reduced overall energy penalty. Figure 2 is a concept drawing for the cross-heat exchanger.

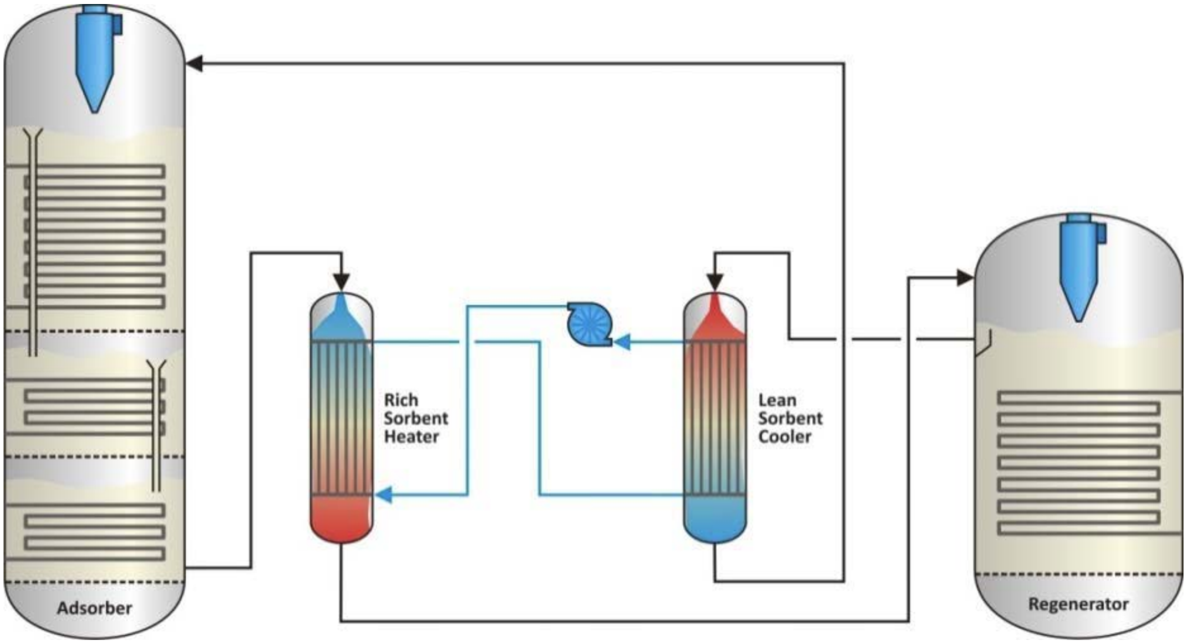

Figure 2: Cross-heat exchanger concept

The team evaluated heat integration opportunities and optimizing the process by:

- Bench-scale testing the heat exchanger concept with a single sorbent to collect the data required for scale-up modeling and the subsequent computational modeling.
- Modeling using ASPEN Plus and custom tools to determine the optimal operating conditions for the heat exchanger in a moving-bed and fluidized bed arrangements integrated into the overall CO_2 capture process to minimize capital and operating cost.
- Process modeling to assess the viability of heat integration options (with the power plant and the CO_2 compressors).
- Optimization of the flue gas moisture level.
- Adsorber and regenerator design assessment to reduce pressure drop.

The sorbent and process properties are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	646	646
Bulk Density	kg/m^3	453	453
Average Particle Diameter	mm	0.18	0.18
Particle Void Fraction	m^3/m^3	0.418	0.418
Packing Density	m^2/m^3	N/A	N/A
Solid Heat Capacity @ STP	kJ/kg-K	1.05	1.05
Crush Strength	kg_f	2.2	2.2.
Manufacturing Cost for Sorbent	$/kg	150	10
Adsorption			
Pressure	bar	1	1
Temperature	°C	40	40
Equilibrium Loading	g mol CO_2/kg	2.4	7.2
Heat of Adsorption	kJ/mol CO_2	-60	-60
Desorption			
Pressure	bar	1	1
Temperature	°C	120	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.8	0.6
Heat of Desorption	kJ/mol CO_2	60	60
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fluidized bed, temperature swing adsorption	
Flue Gas Flowrate	kg/hr	3,500	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 85(CO_2)/15(H_2O) ambient	
Adsorber Pressure Drop	bar	0.55	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism **–** The sorbent selected for this project is an ion exchange resin with a primary benzyl amine that removes CO_2 in a TSA process. It is important to note that other supported amine sorbents with similar enthalpy of adsorption and physical properties could also be used in the same process without major equipment changes.

One of the most important sorbent properties for post-combustion CO_2 capture is the CO_2 working capacity. Isotherms were generated using experimental data and the Langmuir isotherm model, which are provided in Figure 3. To calculate the CO_2 working capacity of this sorbent, the adsorption conditions are assumed to be 40 °C and pCO_2 (partial pressure of carbon dioxide) = 0.15 bar, while the regeneration conditions are assumed to be 120 °C and 0.81 bar (note that the CO_2 in the regenerator exhaust will be slightly diluted with desorbing moisture). Using the isotherms provided in Figure 3, the CO_2 loading under adsorption conditions is approximately 10.5 g CO_2/100 g fresh sorbent, while the CO_2 loading under the regeneration conditions is approximately 3.5 g CO_2/100 g fresh sorbent; the CO_2 working capacity is approximately 7 g CO_2/100 g fresh sorbent, which is nearly an 80 percent improvement versus the working capacity of aqueous monoethanolamine provided in the 2010 version of the DOE baseline report.

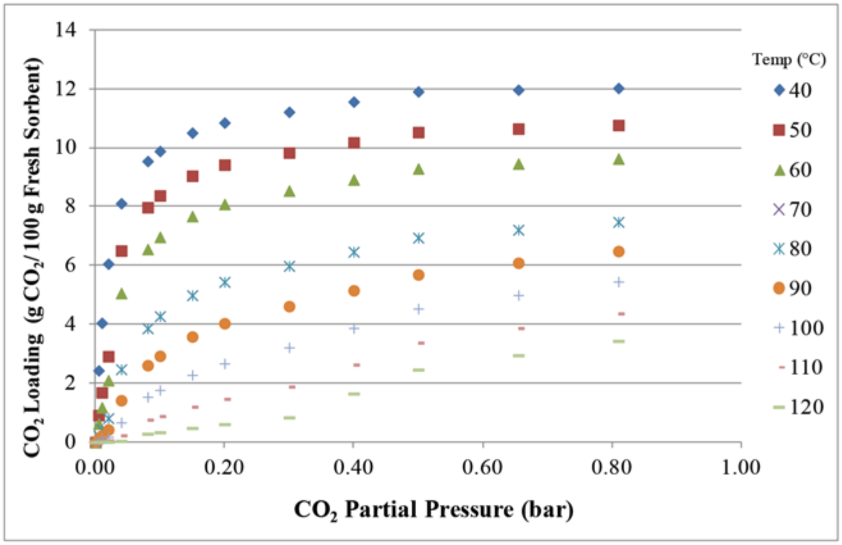

Figure 3: Sorbent isotherms

Sorbent Contaminant Resistance – Amines will react with sulfur dioxide (SO_2) in the flue gas. The selected sorbent will react with SO_2 and, as a result, the overall working capacity for CO_2 will decrease. However, this is a reversible reaction and the sorbent can be regenerated to recover CO_2 capture effectiveness.

Sorbent Attrition and Thermal/Hydrothermal Stability – Based on laboratory testing, the selected sorbent is expected to have low mechanical attrition. Comparisons to fluid catalytic cracking (FCC) catalyst attrition are favorable. The moisture uptake on the sorbent is important because it results in an increase in the regenerator heat duty due to the enthalpy of vaporization/condensation (assuming that the water (H_2O) is physically adsorbed). In addition, in the regenerator, the released H_2O will necessitate the addition of condensers to separate the H_2O from the CO_2 exhaust. This sorbent demonstrates a small (≈0.9 g H_2O/100 g fresh sorbent under expected 1-MW_e pilot operating conditions) H_2O working capacity.

Flue Gas Pretreatment Requirements – A secondary scrubber has been incorporated into the pilot design to reduce the flue gas SO_2. An assessment of the cost-benefit of scrubbing SO_2 versus regenerating the sorbent that has reacted with SO_2 to recover CO_2 capture effectiveness must be conducted to determine the commercial process design and operating details. Additional work has examined the possibility of regenerating sorbents contaminated by acid gases such as SO_2 so that the sorbents may be reused in the process.

Sorbent Makeup Requirements – Current estimates used in cost projections are to replace the sorbent nominally once per year. Further testing is required, including pilot testing to refine the makeup requirements.

Waste Streams Generated – Waste streams will include spent sorbent, flue gas scrubber blow-down, and flue gas cooler condensate.

Process Design Concept – Flowsheet/block flow diagram included above.

Proposed Module Design – The CO_2 capture module will be located downstream of the plant's existing SO_2 scrubber. The gas stream from which CO_2 will be removed is representative of that from a coal-fired power plant with nominal conditions of $pCO_2 = 0.13$ bar and T = 55 °C. The adsorber is designed to operate isothermally at 40 °C. The exhaust pressure for regeneration is approximately ambient pressure. The minimum superficial velocity of the flue gas will be limited to 1.2 m/s (4.0 ft/s) to minimize the number and footprint of reactors, and thus capital costs. Pneumatic conveying will be utilized for all required material conveying to increase reliability, decrease operations and maintenance (O&M) costs, and increase technology acceptance. Because the sorbent and flue gas are contacted in a system that approaches counter-current flow, CO_2 working capacity can be maximized. In addition, the heat transfer has been optimized through the use of bubbling fluidized beds. The optimal mixing that is characteristic of bubbling fluidized beds also translates into effective gas/solids contacting. The design of the system employed established methods and principles used for gas-solid systems, including gas distribution, in-bed heat transfer, risers, standpipes, cyclones, and diplegs. Large-scale, two-stage fluidized beds have been used commercially for FCC processes. However, not all aspects of the design are commercially available.

In addition, the cross-heat exchanger module will consist of a further module based upon two concepts. The first concept is a moving bed plate and frame heat exchanger which transfers sensible heat from the hot CO_2 lean sorbent to cold CO_2 rich sorbent via a working fluid within the plates. As the sorbent flows between the plates heat is either transferred from hot sorbent to cool plates and the working fluid in the plates or cool sorbent flows past plates being warmed by the hot heat transfer fluid circulating within the plates.

The second concept uses a fluidized bed system with heat exchanger coils to extract heat from the hot CO_2 lean sorbent and transfer heat to the cold CO_2 rich sorbent. This system is analogous to a shell and tube heat exchanger where the fluidized sorbent in a vessel flows past coils with a heat transfer fluid circulating through the coils. The sensible heat of the hot CO_2 lean sorbent is then rejected to the heat transfer fluid in the coils which then is used in another exchanger to heat the cool CO_2 rich sorbent before it enters the regenerator.

technology advantages

- Sensible heat recovery.
- Reduced adsorber pressure drop.
    - Sorbent is currently cooled in top adsorber bed.
    - Reduced cooling requirements, smaller bed, reduced flue gas blower power, and reduced thermal regeneration input and cooling duty.
- Reduced regenerator pressure drop.
    - Sorbent enters regenerator at higher temperature.
    - Less heat transfer surface required.

R&D challenges

- Benefits of heat recovery must outweigh the increase in capital costs.
- The addition of a cross-heat exchanger may increase the footprint of the existing capture unit.
    - For many existing power plants, overall site footprint may be a limiting factor.
- A heat exchanger will necessitate more sorbent residence time and increase the amount of sorbent required for the process.
- Sorbent cycling time flexibility will be limited by heat exchange requirements.

status

The project ended on December 31, 2015. Two cross-heat exchanger designs—moving bed and fluidized bed—were evaluated for use between the adsorber and regenerator. The initial assessment indicated that the fluidized bed concept was not a practical approach due to the prohibitively high additional electric load associated with fluidization. The techno-economic assessment indicated that addition of a cross-heat exchanger and heat integration significantly improved net unit heat rate, but the additional equipment costs required almost always outweighed the performance improvement. Sorbent BN with the cross-heat exchanger had lower cost of electricity (COE) than for the case without. Sorbent OJ with cross-heat exchanger alone lowered the COE by 0.2 percent, however it showed thermodynamic benefits over the other sorbent. The lowest cost sorbent OJ case had a 15 percent lower COE than the lowest cost sorbent BN case.

available reports/technical papers/presentations

Sjostrom, S. "Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration," presented at Project Closeout Meeting, Pittsburgh, PA, March 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/7017-DOE-Closeout-DE-FE0012914-Final.pdf*

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Sjostrom, S. “Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration,” Project Kick Off Meeting, Pittsburgh, PA, November 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/NETL-ADA-Heat-Integration-Project-Kickoff-Meeting.pdf*.

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Sjostrom, S., “Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture,” presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/S-Sjostrom-ADA-Solid-Sorbents.pdf*

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Sjostrom, S., “Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture,” presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Sjostrom-ADA-Solid-Sorbents-as-Retrofit-Technology.pdf*.

Sjostrom, S., “Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *https://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/22Aug11-Starns-ADAES-Solid-Sorbents-Retrofit.pdf*

Sjostrom, S.; Krutka, H.; Starns, T.; and Campbell, T., “Pilot Test Results of Post-Combustion CO_2 Capture Using Solid Sorbents,” Energy Procedia, 2011, 4, 1584-1592.

Sjostrom, S., and Krutka, H., “Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture,” Fuel, 2010, 89, 1298-1306. *http://www.sciencedirect.com/science/article/pii/S0016236109005286*.

Sjostrom, S., “Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture from Coal-Fired Power Plants,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/Sharon-Sjostrom---ADA-Environmental-Solutions.pdf*.

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ADA-ES Inc., “Evaluation of Solid Sorbents as Retrofit Technology for CO_2 Capture from Coal-Fired Power Plant,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/evaluation-of-solid-sorbents-nt0005649-mar2009.pdf*

Bench-Scale Development of an Advanced Solid Sorbent-Based CO_2 Capture Process for Coal-Fired Power Plants

primary project goals

RTI International addressed the technical and economic hurdles to developing a sorbent-based carbon dioxide (CO_2) capture process by transitioning a promising sorbent chemistry, based on molecular basket sorbent (MBS) materials, to a low-cost sorbent suitable for use in a fluidized-bed process and developing a scalable circulating fluidized, moving-bed reactor (FMBR) process arrangement.

technical goals

- Improve the thermal and chemical stability of the base polyethyleneimine (PEI) reactant while transitioning the current fixed-bed form MBS material into a fluidizable form.
- Collect critical process engineering data using a bench-scale test unit to allow for a detailed design of a CO_2 capture prototype system based on improved MBS materials.
- Improve reactor design, optimize operability, and optimize heat integration strategies for the FMBR system.
- Scale-up advanced MBS materials production for use in the CO_2 capture prototype system.
- Demonstrate the technical and economic feasibility of a commercial embodiment of the MBS-based CO_2 capture process through a detailed technology feasibility study.

technical content

The project team developed an advanced sorbent process that utilizes a polymeric amine-based CO_2 sorbent developed by Pennsylvania State University (PSU) under a previous project (DE-FE-0000458) to capture CO_2 from coal-fired power plant flue gas. This molecular basket sorbent consists of a high-surface area support, such as silica, impregnated with branched PEI polymer, as exhibited in Figure 1.

The branched polymer contains primary, secondary, and tertiary amine sites that adsorb CO_2. Carbon dioxide absorption is favored between 50 and 90 °C (122 and 194 °F), with a heat of reaction of $\Delta Habs = 66$ kJ/mol- CO_2 (645 Btu/lb- CO_2). At temperatures greater than 110 °C (230 °F), the reverse reactions predominate and the sorbent releases CO_2.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Advanced Solid Sorbents and Processes for CO_2 Capture

participant:

RTI International

project number:

FE0007707

predecessor projects:

N/A

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Thomas Nelson
RTI International
tnelson@rti.org

partners:

Pennsylvania State University; Masdar New Ventures; Masdar Institute

start date:

10.01.2011

percent complete:

100%

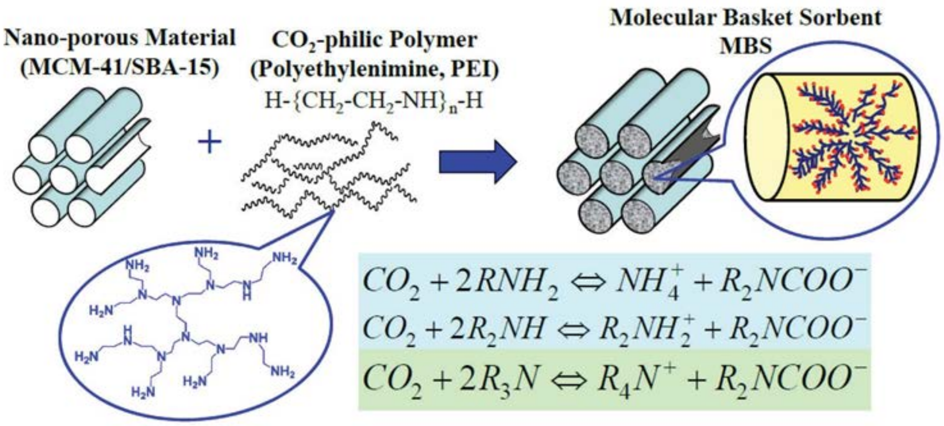

Figure 1: Molecular basket sorbent concept

This advanced sorbent CO$_2$ capture process operates as a cyclic adsorption-regeneration thermal swing process where the solid sorbent is continuously circulated between two FMBRs—a CO$_2$ adsorber and a sorbent regenerator. A basic block flow diagram of this process, installed within a pulverized coal (PC)-fired power plant, is provided in Figure 2.

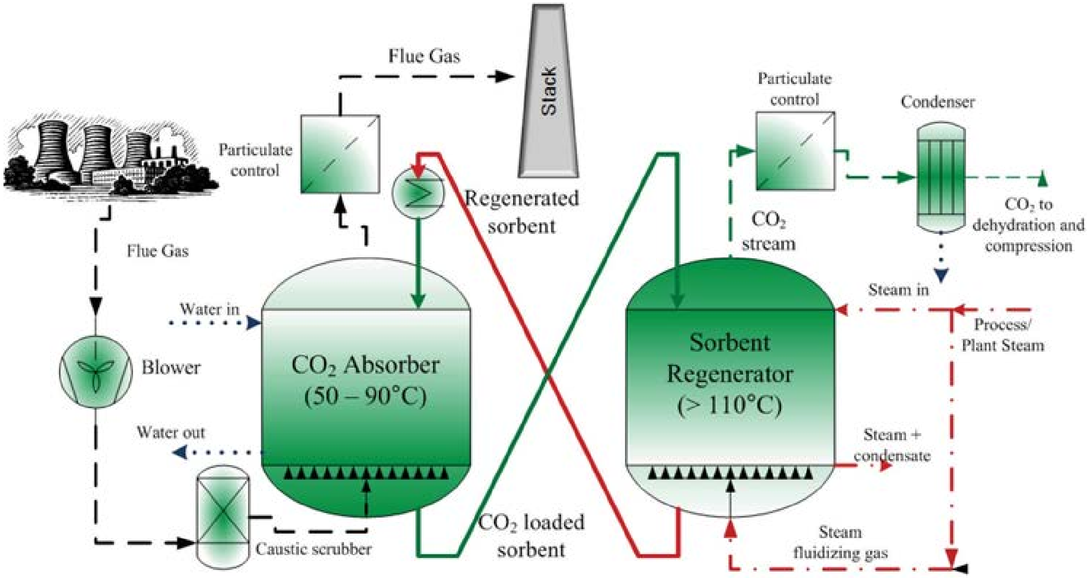

Figure 2: Block flow diagram of advanced solid sorbent CO$_2$ capture process

Carbon dioxide-rich flue gas from the PC power plant goes through a caustic scrubbing system to remove strong acid gases prior to entering the CO$_2$ adsorber. The CO$_2$ adsorber is designed as an FMBR. Within the adsorber, flue gas comes in contact with lean sorbent that is fed to the adsorber from the sorbent regenerator. The sorbent selectively removes CO$_2$ and generates heat due to the heat of reaction for CO$_2$ removal. In order to control the sorbent bed temperature, cooling water is used to cool the sorbent through indirect contact. Treated flue gas exits the CO$_2$ adsorber and enters a baghouse filter for removal of particulates, primarily attrited sorbent particles. Following particulate removal, the flue gas is then directed to the stack and vented.

The CO$_2$-rich sorbent exits the adsorber and is transported to the sorbent regenerator. The sorbent regenerator design and operation is similar to the CO$_2$ adsorber, except that the sorbent bed is indirectly heated with condensing steam in order to strip the sorbent of the adsorbed CO$_2$. The regenerated sorbent produces a concentrated CO$_2$ gas stream that is swept out of the sorbent regenerator with a CO$_2$ sweep gas. The concentrated CO$_2$ gas stream is then sent to a dehydration and compression unit, and the sorbent is transferred through a sorbent cooling unit and on to the CO$_2$ adsorber for continued CO$_2$ removal. Fresh sorbent is added to this stream to make up for attrited sorbent and diminished sorbent performance.

RTI led an effort to conduct process evaluations in a bench-scale, single-stage, fluidized-bed unit capable of sustained CO_2 capture and sorbent regeneration, followed by the design and fabrication of a bench-scale, continuous-flow CO_2 capture prototype system. This system is integrated and commissioned at RTI's Energy Technology Development Facility (ETDF) using simulated flue gas.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	N/A	N/A
Bulk Density	kg/m^3	≈500	≈1,000
Average Particle Diameter	mm	≈0.1	0.05 to 0.2
Particle Void Fraction	m^3/m^3	not measured	TBD
Packing Density	m^2/m^3	not measured	TBD
Solid Heat Capacity @ STP	kJ/kg-K	1.53	1.1 to 1.5
Crush Strength	kg_f	N/A	N/A
Manufacturing Cost for Sorbent	$/kg	N/A	<10
Adsorption			
Pressure	bar	1.01	1.01
Temperature	°C	75	60 to 90
Equilibrium Loading	g mol CO_2/kg	2.27	3.18
Heat of Desorption	kJ/mol CO_2	66	60 to 70
Desorption			
Pressure	bar	1.01	1.01
Temperature	°C	100	>110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.68	0.45
Heat of Desorption	kJ/mol CO_2	78	70 to 80
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— —	—
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the FGD (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – see Figure 1.

Sorbent Contaminant Resistance – Most, if not all materials used for CO_2 capture, including aqueous amine solvents, alkaline and alkali-based solvents and sorbents, and the amine-based sorbents being developed in this project, have a high affinity for strong acid gases, including sulfur oxide (SO_x), nitrogen oxide (NO_x), and hydrogen chloride (HCl). Considerations have been made regarding how to implement contaminant control within the overall CO_2 capture system. Resistance to trace metal contaminants is unknown at this point.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition will be a function of the process operating environment and physical strength of the sorbent. These will be measured and observed during larger-scale testing campaigns. The base PEI reagent suffers from performance instability at temperatures greater than 110 °C. One of the focuses of this project is to improve the sorbent performance stability.

Flue Gas Pretreatment Requirements – Most likely, the flue gas will require a scrubbing of acid gases prior to entering the CO_2 adsorber containing the sorbent being developed in this project.

Sorbent Makeup Requirements – Continuous sorbent makeup will be required during operation of a commercial system in order to replenish sorbent lost to attrition, entrainment, and deactivation by reaction with contaminants.

Waste Streams Generated – As a whole, the process generates few waste streams. It is expected that a continuous purge of sorbent will be required to maintain a desired level of CO_2 removal within the sorbent bed. In addition, sorbent will be lost from the process through attrition and entrainment. The sorbent can either be treated and reused, or disposed of following minimal treatment.

Process Design Concept – See Figure 2.

technology advantages

- Potential for reduced parasitic loads and lower capital and operating costs than conventional technology.
- High CO_2 loading capacity.
- Relatively low heat of absorption with no heat of vaporization penalty.
- Reactor design offers superior gas-solid heat and mass transfer characteristics.

- Counter current gas-solids flow maximizes CO_2 driving force.
- Required process equipment exists and is used industrially.

R&D challenges

- Heat management / temperature control.
- Solids handling / solids circulation control.
- Sorbent attrition resistance.
- Stability of sorbent performance.
- Heat management and novel heat integration strategies are critical to reduce parasitic power losses.

status

The project was completed on December 31, 2015. RTI has produced a fluidizable form of a high capacity sorbent and has optimized and scaled up sorbent production to 135 kg scale. The multi-stage fluidized bed bench-scale test unit with a flue gas processing capacity of 13 standard cubic feet per minute (scfm) was operated with several hundred hours of parametric and long-term performance testing, identifying optimal operating conditions and achieving 90 percent CO_2 capture using a simulated flue gas. The sorbent maintained CO_2 working capacity between 4 and 7 wt% during 100+ hours of continuous testing. The techno-economic analysis indicated an estimated cost of CO_2 capture for a conceptual commercial layout of the process to be approximately \$45.0/tonne CO_2.

available reports/technical papers/presentations

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/T-Nelson-RTI-Solid-Sorbent-Based-CO2-Capture.pdf*

Nelson, T., et al. "Bench-Scale Development of an Advanced Solid Sorbent-Based CO_2 Capture Process for Coal-Fired Power Plants," Final Scientific/Technical Report, June 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/fe0007707-final-report.pdf*

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Low-Cost High-Capacity Regenerable Sorbent for Carbon Dioxide Capture from Existing Coal-Fired Power Plants

primary project goals

TDA Research, Inc. (TDA) developed a low-cost, high-capacity carbon dioxide (CO_2) adsorbent to demonstrate its technical and economic viability through sorbent evaluation and optimization, development of sorbent production techniques, and bench-scale testing of the process using actual flue gas.

technical goals

- Optimize sorbent chemical composition.
- Optimize physical properties and mechanical integrity of the sorbent to meet the specific requirements of the process.
- Design and test performance on moving-bed and fixed-bed units.
- Identify optimum operating conditions and process parameters for design calculations.
- Assess the economic viability of the new carbon capture process.

technical content

TDA developed a low-cost, high-capacity CO_2 adsorbent and demonstrated its technical and economic viability for post-combustion CO_2 capture for existing pulverized coal (PC)-fired power plants. The sorbent consists of a carbon material modified with surface functional groups that remove CO_2 via physical adsorption. It exhibits a much higher affinity to adsorb CO_2 than nitrogen, water, or oxygen, enabling effective CO_2 separation from the flue gas. The sorbent binds CO_2 more strongly than common adsorbents, providing the chemical potential needed to remove the CO_2. However, because CO_2 does not form a true covalent bond with the surface sites, regeneration can be carried out with only a small energy input. The heat input to regenerate the sorbent is only 4.9 kcal/mol of CO_2, which is much lower than that for chemical absorbents (e.g., 29.9 kcal/mol CO_2 for sodium carbonate) or amine-based solvents (e.g., 14.2 kcal/mol CO_2 for monoethanolamine [MEA]).

Initial sorbent testing under conditions simulating the environment downstream of a wet flue gas desulfurization unit showed stable CO_2 capacity for more than 220 cycles with no sign of degradation (Figure 1).

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Low-Cost, High-Capacity Regenerable Sorbent

participant:

TDA Research, Inc.

project number:

FE0007580

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Gokhan Alptekin
TDA Research, Inc.
galptekin@tda.com

partners:

Babcock & Wilcox; Gas Technology Institute; University of California, Irvine

start date:

10.01.2011

percent complete:

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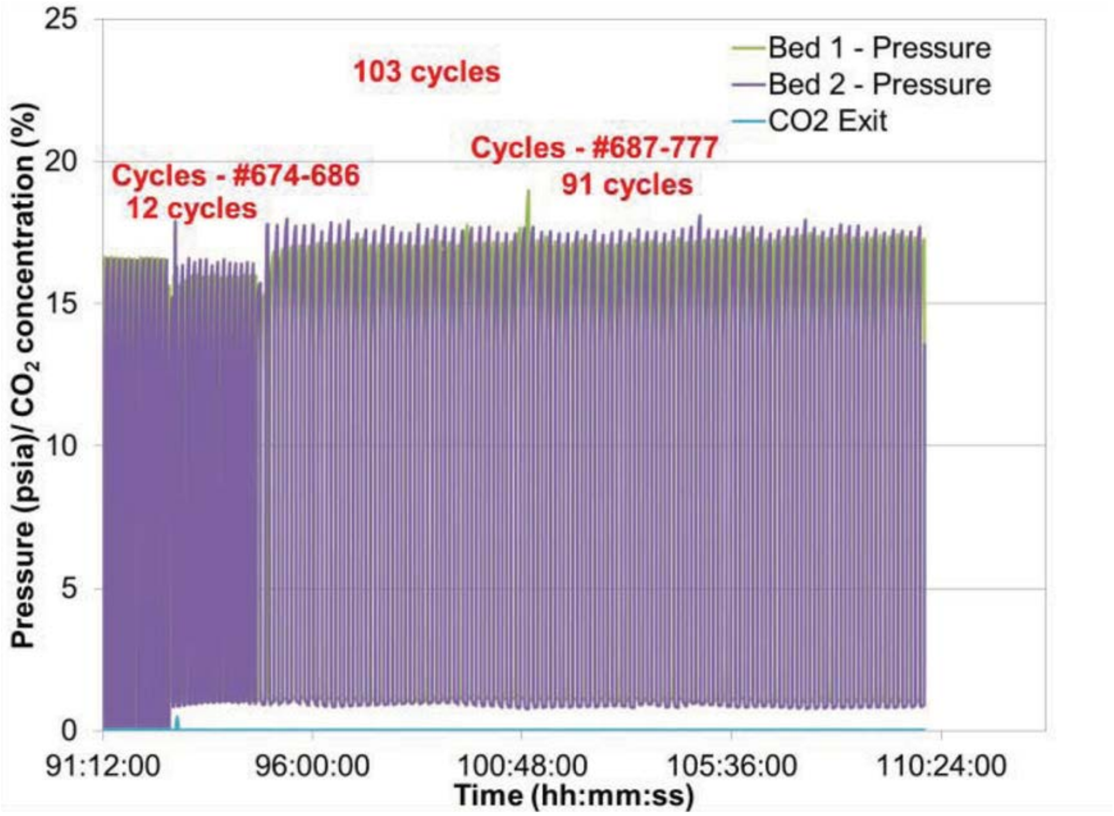

Figure 1: Capacity testing under multiple VSA cycles—capacity maintained over 770 cycles (T = 22 °C; half-cycle time = 4–8 min.; P_{ads} = 16 psia; P_{des} = 1 psia; simulated flue gas, 17 vol% CO_2, H_2O = 1.2 vol%)

The presence of acid gases, such as sulfur dioxide (SO_2) and nitrogen oxide (NO_x), and water (H_2O) vapor up to 15 vol% caused no adverse effect on the CO_2 capacity (Figure 2).

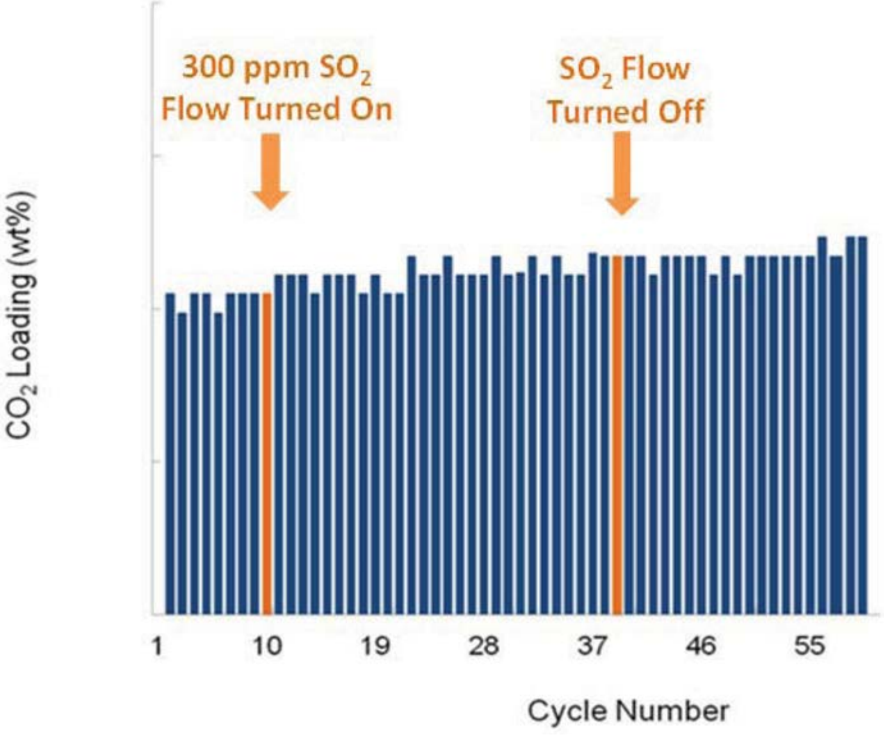

Figure 2: Capacity analysis in presence of SO_2 and water (adsorption T = 62 °C, 15.2 percent CO_2, 2.8 percent O_2, bal. N_2, sat. with H_2O, 300 ppmv SO_2)

Both a moving-bed and fixed-bed vacuum swing adsorption unit were designed for proof-of-concept testing. The 4-bed vacuum swing adsorption (VSA) system is shown in Figure 3.

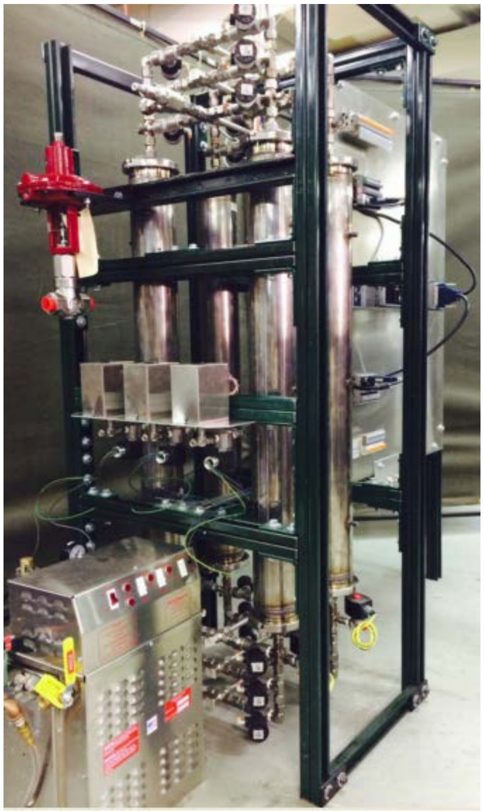

Figure 3: 4-bed VSA prototype

The regeneration of the sorbent and the recovery of CO_2 and its pressurization can then be achieved by several approaches, including temperature swing and vacuum swing. Figure 4 shows a schematic diagram of the process. The sorbent and process parameters are shown in Table 1.

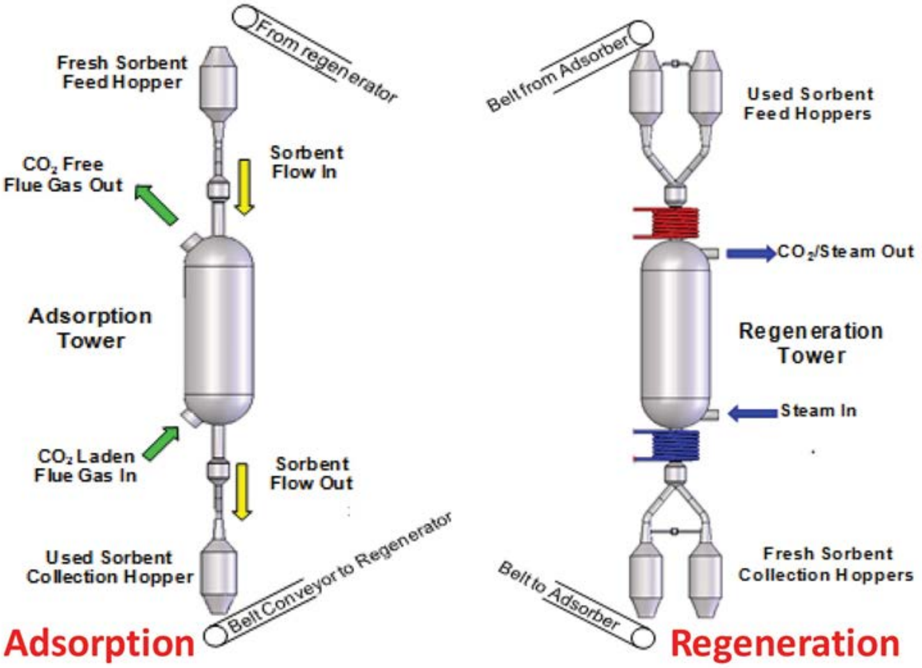

Figure 4: TSA process schematic

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	—	—
Average Particle Diameter	mm	—	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	1.02	1.02
Temperature	°C	70	58
Equilibrium Loading	g mol CO_2/kg	0.3	0.4
Heat of Adsorption	kJ/mol CO_2	-20.5	-20.5
Desorption			
Pressure	bar	0.204	0.15–0.2
Temperature	°C	70	58
Equilibrium CO_2 Loading	g mol CO_2/kg	—	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

		Composition						
Pressure	Temperature	vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- The sorbent competitively adsorbs CO_2 over water.
- The heat of adsorption of CO_2 is low (much lower than amine-based solvents; comparable to that of Selexol).
- The net energy loss in sorbent regeneration is expected to be lower than amine scrubbers.

R&D challenges

- Mechanical integrity of the sorbent material at the conditions of use must be demonstrated.
- The gas-solid contactor design must be proven with full capabilities to be demonstrated.

status

The project was completed on September 30, 2015. Proof-of-concept testing was completed on both a moving-bed and a fixed-bed VSA unit. B&W estimated the total plant cost for the moving-bed system as approximately $424 million (2011 basis) and a total plant cost for the fixed-bed system to be approximately $276 million. A 4-bed VSA system was tested for over 750 hours on a 4-standard cubic feet per minute (scfm) slipstream of actual flue gas at Gas Technology Institute's Combustion Facility, showing stable performance and achieving >90 percent CO_2 capture.

available reports/technical papers/presentations

Alptekin, G., Jayaraman, A., and Copeland, R., "Post-Combustion CO_2 Capture System for Existing Coal-Fired Power Plant," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/G-Alptekin-TDA-New-Sorbent-Process.pdf.*

Alptekin, G., Jayaraman, A., and Copeland, R., "Post-Combustion CO_2 Capture System for Existing Coal-Fired Power Plant," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/G-Alptekin-TDA-A-New-Sorbent-For-Post-Combustion.pdf.*

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Rapid Temperature Swing Adsorption Using Polymeric/Supported Amine Hollow Fiber Materials

primary project goals

Georgia Tech Research Corporation developed a rapid temperature swing adsorption (RTSA) carbon dioxide (CO_2) process and evaluated the cost and performance benefits of this novel hybrid capture approach via bench-scale testing of a module containing polymeric/supported amine hollow fibers, which are loaded with supported adsorbents and surround an impermeable lumen layer that allows for cooling and heating.

technical goals

- Produce polymeric hollow fiber contactors loaded with amine adsorbent particles for post-combustion (CO_2 capture.
- Develop a computational model of the fiber module and validate it in parallel with the experimental program.
- Assess adsorption/desorption and heat-exchange performance of hollow fiber modules using simulated clean and simulated dirty flue gas.

technical content

Supported amine adsorbents have many promising properties with regard to CO_2 capture from post-combustion flue gas. However, most previous studies of supported amine materials focus only on CO_2 adsorption, ignoring desorption. In addition, essentially all published studies describe the use of supported amine materials in fixed beds. This process configuration is difficult to use at practical scales due to heat integration challenges. This is especially important for supported amines; whose heats of adsorption are among the highest of known CO_2 adsorbents (50–80 kJ/mol), but which enables large swings in capacity with temperature. Thus, practical process designs for amine sorbents must include effective heat transfer.

Recently, the use of novel polymeric hollow fiber contactors loaded with CO_2 adsorbents has been introduced as a scalable process configuration for CO_2 capture. In this approach, polymeric hollow fibers, similar to those used for commercial-scale membrane gas separation, are prepared and loaded with large volumes of solid CO_2 adsorbing materials. However, unlike those used for membrane applications, these hollow fibers have several unique aspects. First, high volumes of adsorbent materials are included, typically 60–75 percent by volume. Second, the polymeric phase is designed to have many large voids, allowing rapid mass transfer to the sorbent particles. Third, a dense lumen layer is installed in the fiber bore to largely shutdown transport from the shell side of the fibers to the bore. This design yields fibrous structures that are ideally suited for application as combined sorption and heat transfer modules in an RTSA process. Total cycle times are in the order of 3 minutes.

In the amine-hollow-fiber RTSA process, flue gases flow over the shell of the fibers while cooling water flows through the bore. Given the small diameter of the fibers, the fibers

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid Temperature Swing Adsorption

participant:

Georgia Tech Research Corporation

project number:

FE0007804

predecessor projects:

N/A

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Christopher W. Jones
Georgia Tech
christopher.jones@chbe.gatech.edu

partners:

Trimeric Corporation; Algenol Biofuels; Southern Company Services; GE Energy

start date:

10.01.2011

percent complete:

100%

and adsorbents can be maintained in nearly isothermal conditions, with the cooling fluid providing an effective reservoir for heat of adsorption (Figure 1). At the appropriate time, the flue gas can be rerouted to another bed and the fibers can be switched to desorption mode by passing hot water through the fiber bore, driving off the CO_2.

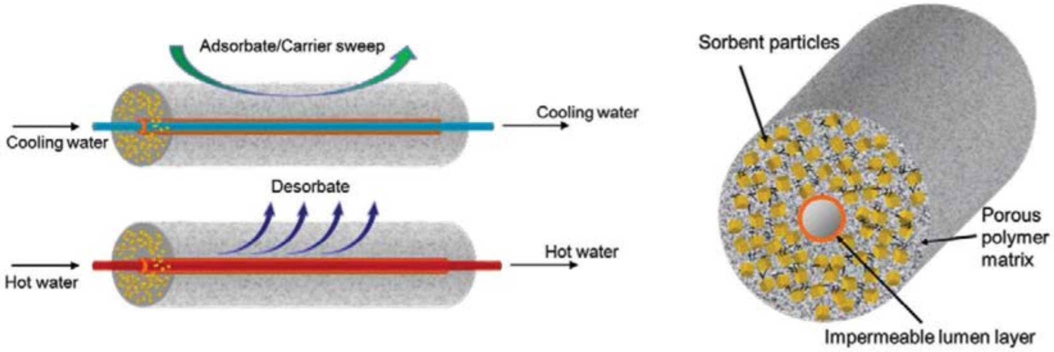

Figure 1: Sorption (top) and desorption (bottom) modes in hollow fiber sorbents

This RTSA approach was previously demonstrated using cellulose acetate fibers and zeolite 13X as the adsorbent in the fibers. Zeolite 13X is not an ideal sorbent for wet post-combustion CO_2 capture streams, but supported amines may be well suited for the task.

The hollow fiber architecture has three key attributes: (1) it provides the adsorption surface area needed to handle large volumes of flue gas, (2) it enables efficient heat transfer needed to handle the high heat of adsorption of supported amines, and (3) it is readily scalable given the current commercial capability to produce large surface area hollow fibers on an industrial scale.

The RTSA process based on hollow fibers containing supported amine adsorbents represents a novel new process configuration for post-combustion CO_2 capture. In a commercial process, multiple hollow fiber modules would be used, and modules would cycle synergistically between adsorption and desorption modes in a continuous process, as shown in Figure 2.

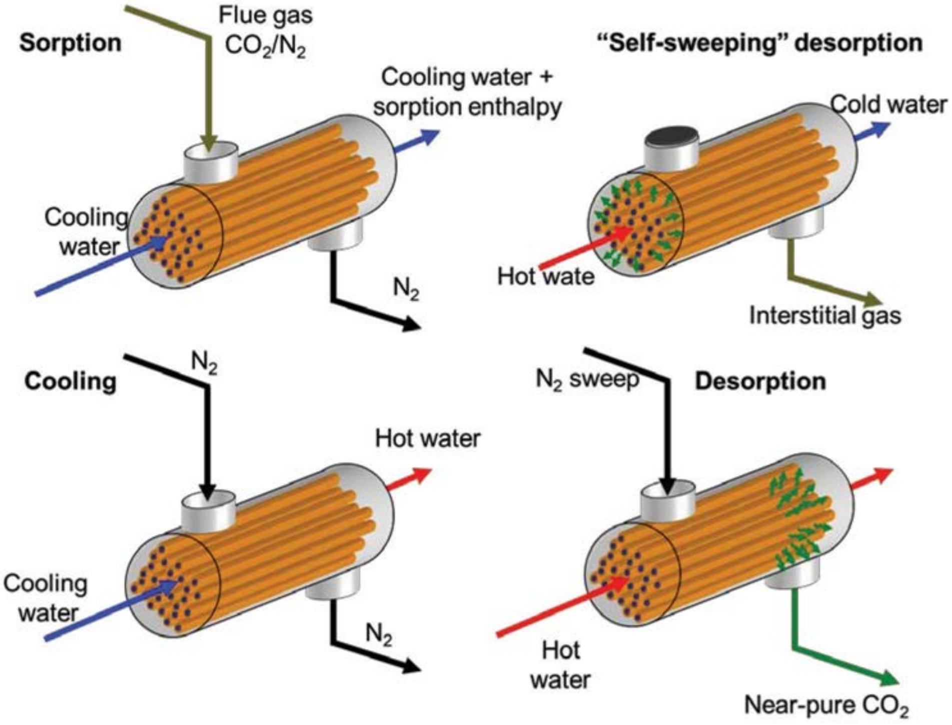

Figure 2: Potential RTSA process configuration

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,100	1,100
Bulk Density	kg/m^3	1,100	1,100
Average Particle Diameter	mm	1.2	1.0
Particle Void Fraction (void fraction of fiber bed)	m^3/m^3	0.4–0.5	0.28–0.3
Packing Density (packing density of fiber bed)	m^2/m^3	1,000	1,600
Solid Heat Capacity @ STP	kJ/kg-K	1,800	3,000
Crush Strength	kg_f	1.140	1.140
Manufacturing Cost for Sorbent	$/kg	unknown	unknown
Manufacturing Cost for Fiber Module (includes hardware, fibers, sorbent)	$/kg	unknown	$10/m^2 or $25–$35/kg
Adsorption			
Pressure (partial pressure of CO_2)	bar	0.159	0.13
Temperature	°C	55	35
Equilibrium Loading	g mol CO_2/kg fiber	0.84	1.0–1.5
Heat of Adsorption	kJ/mol CO_2	59	55–65
Desorption			
Pressure	bar	0.2	1.0
Temperature	°C	120	90
Equilibrium CO_2 Loading	g mol CO_2/kg fiber	0.34	0.1
Heat of Desorption	kJ/mol CO_2	59	55–65
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	shell and tube	
Flue Gas Flowrate	kg/hr	200 sccm (lab), ≈2,900 (full scale, per module)	0.5 (lab), ≈2,900 (full scale, per module)
CO_2 Recovery, Purity, and Pressure	% / % / bar	91%/96 mol%/0.2 bar (0.19 bar partial pressure)	90%/95 mol%/1 bar or 80 mol% at 5.5 bar
Adsorber Pressure Drop	bar	<0.1	<0.15
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The underlying mechanism is primary and secondary amines reacting with CO_2 to produce carbamates or (bi)carbonates, depending on the nature of the amines, amine loading, and humidity level. Under most conditions, a mixture of species is formed on the adsorbent surface.

Sorbent Contaminant Resistance – Thus far, the solid supported amines developed for this project have displayed excellent oxidative stability, stability in humid conditions (5–90 percent relative humidity [RH]), and resistance to nitric oxide. The active amine fillers are poisoned by high concentrations of sulfur oxide (SO_x, 200 parts per million [ppm]), and extensive sulfur removal is needed.

Sorbent Attrition and Thermal/Hydrothermal Stability – Due to the sorbents being "protected" within the walls of the hollow fiber sorbents, the Georgia Institute of Technology has yet to experience any mechanical issues (such as attrition) in their studies. The fibers themselves are quite temperature-resistant, but the amines have a realistic upper temperature limit of ≈130 °C. The amines contained within the fiber walls exhibit higher CO_2 uptake capacities in the presence of water; moreover, the fibers themselves have been continuously cycled between 35°C and 120°C without damage to the fiber structure. These suggest that the materials are hydrothermally stable within the operating ranges of the RTSA process.

Flue Gas Pretreatment Requirements – Current analysis indicates that flue gas cooling to approximately 35 °C is required for low-cost CO_2 capture. Experimental work suggests that partial dehydration of the flue gas may prolong fiber lifetimes (i.e., 90 percent RH vs. 100 percent RH). Finally, further wet FGD may be required for additional SO_x removal for optimum long-term performance of the amines.

Sorbent Makeup Requirements – Analyses investigating the amine loss rates are needed. It has been demonstrated that deactivated amines can be removed when required, and fresh amines redeposited in the fibers, allowing fiber recycling and reuse.

Waste Streams Generated – Spent fiber sorbents represent the only process waste stream. Currently, the fibers are assumed to last 3 years before replacement is required. With appropriate flue gas scrubbing, such lifetime may be achievable.

Process Design Concept – See Figure 2.

technology advantages

- Deleterious thermal effects typically associated with packed-bed sorption can be mitigated and higher sorption efficiencies can be achieved by utilizing the hollow fiber morphology to supply cooling agents in the bore of the fiber during adsorption.
- The thin porous walls of the fiber sorbent allow for rapid heat and mass transfer equilibration, thereby allowing for more rapid thermal cycles and thus reducing device volume.
- Pressure drops through these beds will be correspondingly lower than those of packed or fluidized solid sorbent beds, which will reduce draft fan costs.
- Heat transfer fluids in the bore of the fibers can be as simple as hot water and cold water, providing an environmentally friendly overall process.
- Rapid heat transfer enables potential recovery of heat of adsorption and reuse of sensible heat of the bed. This affords heat integration both within the capture process and may facilitate heat integration with the boiler feed water preheat. This can dramatically reduce the overall parasitic thermal load of the RTSA process.

R&D challenges

- High heat of adsorption, with heat management improved by contactor design.
- Deactivation of sorbents upon exposure to SO_x and exposure to saturated humidity and temperature.
- Low-working capacity in more conventional contactors.
- Efficient heat integration with power plant.
- Long-term operation of complete cycles with bore-side heating and cooling.
- Manufacturing cost estimates of fibers have significant uncertainty.
- Design of efficient multibed cycles to improve recovery and purity.
- Adaptive scheduling and control to manage slow degradation over many cycles and variability between modules.

status

The project was completed on March 31, 2015. Georgia Tech has developed a post-spinning amine infusion method to create and recharge sorbents. A dual layer spinning method was developed for constructing a barrier lumen layer in the fiber bore, which allows the fiber to be used as an adsorbing shell-in-tube heat exchanger. Testing has been completed on hollow fiber RTSA modules. Heat integration in the RTSA process has allowed for up to 70 percent recovery of the heat of adsorption and the RTSA cycle time has been reduced to 3 minutes. A detailed process model of the cyclic pressure temperature swing adsorption module was developed and validated against experimental data. The process model was integrated with costing models for the overall process that included compression and flue gas conditioning. The CO_2 capture cost was estimated to be $44.8/tonne CO_2.

available reports/technical papers/presentations

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EVALUATION OF CARBON DIOXIDE CAPTURE FROM EXISTING COAL-FIRED PLANTS BY HYBRID SORPTION USING SOLID SORBENTS

primary project goals

The University of North Dakota (UND) and Envergex LLC are developing a solid sorbent technology—Capture from Existing Coal-Fired Plants by Hybrid Sorption (CACHYS™)—that is based on the following principles:

- Reduction of energy for sorbent regeneration.
- Utilization of novel process chemistry.
- Contactor conditions that minimize sorbent-CO_2 heat of reaction and promote fast CO_2 capture.
- Low-cost method of heat management.
- Low-cost, carbon-based sorbent impregnated with an alkali carbonate salt and an active promoter.

technical goals

- Sorbent selection and formulation, as well as the determination of heat of sorption, sorbent capacity (CO_2 loading), and sorbent physical properties for process design definition.
- Conduct lab-scale, fixed-bed tests to investigate adsorption and desorption kinetics, working capacity, heats of adsorption and desorption and a relative measure of attrition during multiple cycles.
- Establish the optimum process conditions (e.g., temperatures, pressures, and residence times), preferred sorbent compositions, and bench-scale equipment design (e.g., size, energy duties, and material feed rates).
- Design, build, and operate a bench-scale CACHYS™ adsorption and desorption system designed for a flue gas flow rate of 30 actual cubic feet per minute (acfm) obtained as a slipstream from a sub-bituminous coal-fired stoker boiler at the UND campus steam plant.

technical content

The project was intent on developing key information for the CACHYS™ process - sorbent performance, energy for sorbent regeneration, physical properties of the sorbent, the integration of process components, sizing of equipment, and overall capital and operational cost of the integrated CACHYS™ system. The bench-scale CACHYS™ test unit includes a flue gas conditioning system to remove particulate matter and sulfur dioxide via a fabric filter and a wet packed-bed scrubber using sodium hydroxide solution, respectively. Two circulating fluidized beds are employed for CO2 adsorption. The Solex Thermal regenerator system consists of three functional units capable of operating at elevated pressure—the

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Solid Sorbent-Based CO_2 Capture

participant:

University of North Dakota

project number:

FE0007603

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Steven A. Benson
University of North Dakota
steve.benson@engr.und.edu

partners:

Industrial Commission of North Dakota
Envergex LLC
Barr Engineering
Solex Thermal Science Incorporated
ALLETE Incorporated
SaskPower

performance period:

10/1/11 – 12/31/14

preheater, the regenerator, and the cooler. Sorbent transferred from the adsorber system is heated to the desired regeneration temperature in the preheater and transferred to the regenerator unit where the CO_2 is desorbed from the sorbent. The sorbent then transfers to the cooler, where the temperature of the sorbent is returned to the adsorption temperature. The sorbent is then transferred back to the adsorber system via pneumatic conveyance.

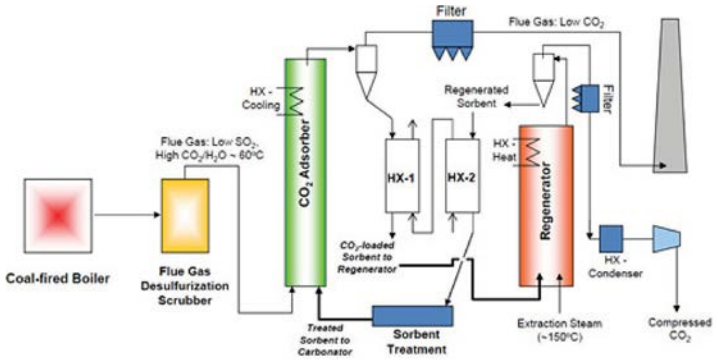


Figure 1: CACHYS™ Sorption Process

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density at STP	kg/m^3	1,800–2,200	1,800–2,200
Bulk Density	kg/m^3	400–700	400–700
Average Particle Diameter	mm	0.1–1	0.1–1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	230	230
Solid Heat Capacity at STP	kJ/kg-K	1.2	1.2
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg	1.65	1.00
Absorption			
Pressure (partial of CO_2)	bar	0.1	0.1
Temperature	°C	50–80	50–80
Equilibrium CO_2 Loading	g mol CO_2/kg	2.1	2.1
Heat of Absorption	kJ/mol CO_2	30–80	30–80
Desorption			
Pressure (partial of CO_2)	bar	1.9	1.9
Temperature	°C	140–160	140–160
Equilibrium CO_2 Loading	mol/mol	0.5	0.5
Heat of Desorption	kJ/mol CO_2	30–80	30–80
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fluidized bed	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 95–99%	
Adsorber Pressure Drop	bar		

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

technology advantages

- Low heat of sorption.
- Increased sorption kinetics.
- Low-cost sorbent.
- Commercially-available and easily-scalable equipment.

R&D challenges

- Confirmation of energetics.
- Sorbent integrity.
- Sorbent handling.
- Achievement of 90% CO_2 capture.

results to date/accomplishments

- Performed laboratory-scale testing that showed heat of desorption was 30–80 kJ/mol CO_2, depending on process conditions. Sorbent CO_2 working capacity ranged from 70–100 g/kg sorbent. Both metrics exceeded the target levels.
- 100-cycle tests demonstrated excellent chemical stability and no detectable loss in capacity.
- The CACHYS™ bench-scale test facility was constructed at UND's coal-fired steam plant. The system captures CO_2 from 30 acfm of flue gas with a sorbent throughput of 200-400 lb/hr.
- Bench-scale parametric testing resulted in a maximum CO_2 capture of 85 percent and demonstrated the significant benefits of hybrid sorption compared to standard carbonate sorption: Much higher capture and reaction rates (≈2–3X) and excellent control of exothermic heat of adsorption.
- Continuous and integrated bench-scale testing demonstrated sustainable (5–7 hours) capture of 70–80 percent with 4 percent CO_2 in flue gas and 40–60 percent with 8 percent CO_2 in flue gas. A 15-hour continuous test with stable operations was completed.
- Based on the testing data gathered over the course of the project, a final technical and economic feasibility study was completed. Results indicate a modest improvement over the benchmark MEA process and progress towards the DOE goals.

next steps

This project ended December 31, 2014.

available reports/technical papers/presentations

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Benson-UNDakota-S-Srinivasachar-Envergex-Evaluation-of-CO2.pdf*.

Presentation at the Thirteenth Annual Conference on Carbon Capture, Utilization, and Storage, Pittsburgh, PA, April 28–May 1, 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/2014-CCUS-Presentation-7603.pdf*.

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2013, *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Benson-UND-Hybrid-Sorption-Using-Solid-Sorbents.pdf*.

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

Preliminary Carbon Dioxide Capture Technical and Economic Feasibility Study—Topical Report (November 2012).

Project Review Meeting Presentation (September 2012). *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/und-CO2-capture-budget-period1.pdf*.

Evaluation of CO_2 Capture from Existing Coal-Fired Power Plants by Hybrid Sorption Using Solid Sorbents (CACHYS™) Project Kick-Off Meeting Presentation, November 21, 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/und-CO2-capture-budget-period1.pdf*.

METAL MONOLITHIC AMINE-GRAFTED SILICA FOR CO_2 CAPTURE

primary project goals

The University of Akron set out to develop a low-cost carbon dioxide (CO_2) capture technology by integrating metal monoliths with a grafted amine sorbent.

technical goals

- 1.5 mmol-CO_2/g-sorbent.
- 1.0 mmol-sulfur dioxide (SO_2)/g-sorbent.
- 500 repeated thermal cycles of sorbent between CO_2 adsorption at 25°C and desorption at 110°C with less than a 10 percent degradation in original CO_2 capture capacity.

technical content

The key innovation of this project is the utilization of metal foils with amine-grafted porous silica to fabricate a highly efficient and low-cost CO_2 adsorption system. Porous silica, alumina, zeolite, and carbon, which are used as commercial adsorbents for a wide range of applications, are impregnated with alkyl amine molecules such as monoethanolamine (MEA)/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was determined to be greater than 1.5 mmol-CO_2/g-sorbent because of the abundance of available amine functional groups on the amine-grafted silica. The adsorption and desorption can be further optimized by the sorbent preparation procedures with additives.

The metal monolithic structure allows the rapid removal of heat of CO_2 adsorption. The surface of the metal monolith is coated with a layer of silica, carbon fibers, and a binder. Calcination of the metal monolith with this coating produces the silica or zeolite layers structure with 10-µm diameter channels. The binder and carbon fiber concentration is fine-tuned to optimize the number of the micro channel pathways for CO_2 diffusion into the amine-grafted silica and zeolite.

The University of Akron, as part of this project, has also investigated using coal fly ash treated first with sodium hydroxide (NaOH) and/or hydrochloric acid (HCl), and then impregnated with the amine tetraethylenepentamine. Coal fly ash was investigated as a support for amine due to its ready availability and low cost.

technology maturity:

Pilot-Scale Using Simulated Flue Gas, 15 kW

project focus:

Metal Monolithic Amine-Grafted Zeolites

participant:

University of Akron

project number:

FC26-07NT43086

NETL project manager:

I. Andrew Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Steven Chuang
University of Akron
chuang@uakron.edu

partners:

FirstEnergy

performance period:

2/21/2007 – 3/31/11

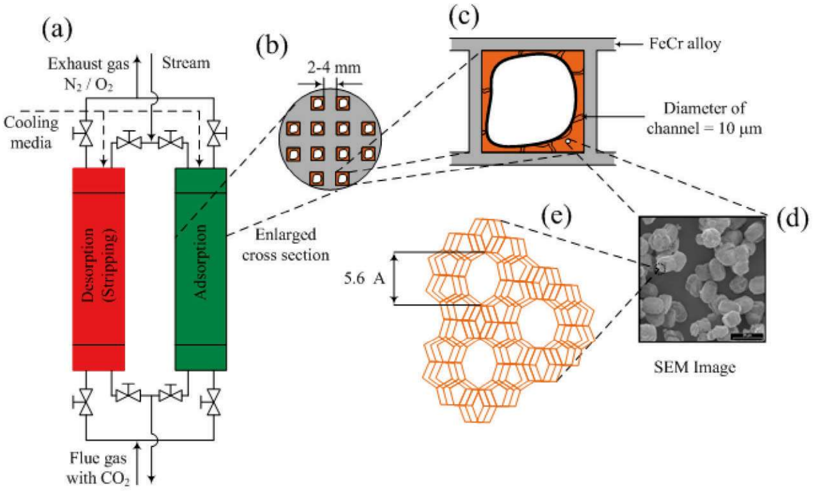


Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

Figure 1 displays the amine-grafted zeolite structure (5.6 Angstroms in length) inside an adsorption unit. The amine is located in the adsorption (a) chamber within holding tubes. The tubes housed in the adsorption unit holds the individual metal (b) tubes with the amine approximately 2 to 4 mm apart. The silica or zeolite is coated inside the square metal tube. Gas enters the tube and flows through the channels (d) of the amine grafted silica, which are 10 µm in diameter. Heating for CO_2 desorption (i.e., regeneration) and cooling for adsorption are achieved by 40 pounds per square inch gauge (psig) steam and cooling water flowing through the jacket side of the adsorber. Desorbed CO_2 is purged from the channels of metal monoliths by pulses of steam and hot air. The goal is that CO_2 and SO_2 adsorption capacity of the amine will be greater than 1.5 mmol-CO_2/g-sorbent and 1.0 mmol-CO_2/g-sorbent, respectively. The amine is capable of greater than 500 times regeneration with less than 10 percent degradation in CO_2 capacity. The amine-grafted silica sorbent is expected to exhibit a heat capacity of 1.5 kJ/kg K. The CO_2 will be captured at an approximate temperature of 50°C (140°F) and then released at approximately 110°C (230°F).

TABLE 1: PROCESS PARAMETERS FOR METAL MONOLITHIC AMINE-GRAFTED SILICA SORBENTS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3		
Bulk Density	kg/m^3	0.5	0.5
Average Particle Diameter	mm	0.05-1	<1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	.43	<0.5
Solid Heat Capacity @ STP	kJ/kg-K		
Crush Strength	kg$_f$		
Manufacturing Cost for Sorbent	$/kg	14	12
Adsorption			
Pressure	bar	1	1
Temperature	°C	50	<55
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Adsorption	kJ/mol CO_2	60	55
Desorption			
Pressure	bar	1-1.05	1-1.05
Temperature	°C	100-110	100-110
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Desorption	kJ/mol CO_2		

TABLE 1: PROCESS PARAMETERS FOR METAL MONOLITHIC AMINE-GRAFTED SILICA SORBENTS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – $CO_2 + R\text{-}NH_2 \rightarrow$ Carbamate/ammonium ions and Carbamic acid

Sorbent Contaminant Resistance – Sorbent capacity decreased by more than 50 percent after 30 cycles in 15 percent CO_2 and 250 parts per million (ppm) SO_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent capacity decreased by less than 10 percent after more than 500 cycles under thermal/hydrothermal conditions.

Flue Gas Pretreatment Requirements – Less than 20 ppm SO_2.

Sorbent Makeup Requirements – Less than 10 percent after 500 cycles.

Waste Streams Generated – Degraded sorbents will be re-activated.

Proposed Module Design –

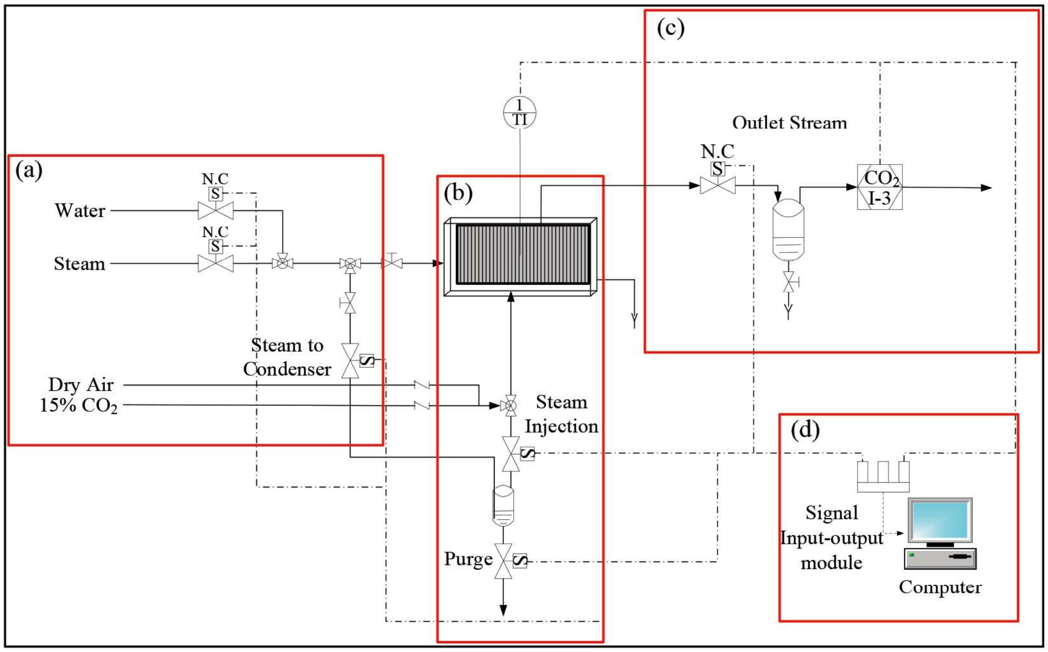


Figure 2: Process Schematic of the Monolith Adsorber

Adsorption temperature: < 40°C; desorption temperature: 105 to 115°C; pressure: 1 to 1.3 atm.

technology advantages

- High stability for CO_2 adsorption and desorption.
- Accelerated removal of the heat of adsorption.
- Low regeneration heat duty due to the low heat capacity of the sorbent.
- Low-cost immobilized amine sorbent.

R&D challenges

- The scale-up transition from lab- to bench-scale tests.
- Temperature swing adsorption requires a long cycle time due to the heating and cooling of the sorbent.
- Contaminants, such as sulfur oxides (SO_x), will react with amine functional groups similar to the MEA process.
- Currently, the CO_2 capture capacity of the sorbent is too low.

results to date/accomplishments

- The first generation of immobilized amine sorbents underwent 500 CO_2 capture cycles with less than 15 percent degradation. Refining in composition and preparation method resulted in sorbents with high stability for more than 1,100 CO_2 capture cycles, but lower capture capacity.
- Zeolite was shown to not be an effective support because of its hydrophilicity and small pore sizes.
- Developed a pilot-scale sorbent manufacturing process at a rate of 1 kg/hr.
- Enhanced the sorbent resistance to SO_2 poisoning by adding a proprietary additive to the CO_2 sorbent.

- A binder agent allows to agglomerate powder sorbents into rod or spherical pellets while maintaining the CO_2 capture capacity of the sorbent and yielding to low attrition rates.
- The operation under fixed-bed conditions present limitations in heat transfer: (1) slowing down the CO_2 capture process and (2) causing the sorbent to degrade.
- The CO_2 capture capacity could be increased 1.6 to 1.9 times when H_2O is present in the flue gas as compared to capture in dry conditions.
- Demonstrated the sorbent at pilot-scale, a 5-kg fixed bed. Adsorption was carried out at 55°C and desorption was with steam at 110°C.

next steps

This project ended on March 31, 2011.

available reports/technical papers/presentations

Chuang, S.S.C., "Amine absorber for carbon dioxide capture and processes for making and using the same,"

US 8377173 B_2, US Patent, Publication date: Feb. 19, 2013.

Chuang, S.S.C., "Metal Monolithic Amine-Grafted Zeolites for CO_2 Capture Power Plants," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Steven%20Chuang-NT43086.pdf*.

Chuang, S.S.C.; Fisher, J.; and Tanthana, J., "Metal Monolithic Amine-grafted Zeolites for CO_2 Capture," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO₂/pdfs/43086%20Akron%20amine-zeolite%20sorbent%20%28Chuang%29%20mar09.pdf*.

Tanthana, J., and Chuang, S.S. C., "In Situ Infrared Study of the Role of PEG in Stabilizing Silica-Supported Amines for CO_2 Capture," Chemical & Sustainability Energy & Materials, 3, 957-964, 2010. *http://onlinelibrary.wiley.com/doi/10.1002/cssc.201000090/abstract*.

Fisher II, J.C.; Tanthana, J.; and Chuang, S.S.C., "Oxide-supported Tetraethylenepentamine for Carbon Dioxide Capture," Environmental Progress & Sust Energy, 28 (4), 589-598, 2009. *http://onlinelibrary.wiley.com/doi/10.1002/ep.10363/abstract*.

CO_2 REMOVAL FROM FLUE GAS USING MICROPOROUS METAL ORGANIC FRAMEWORKS

primary project goals

UOP set out to design and develop a carbon dioxide (CO_2) removal system that employs metal organic framework (MOF) sorbents.

technical goals

- Use combinatorial chemistry to systematically synthesize and characterize a wide range of MOF and related materials.
- Screen materials for hydrothermal stability.
- Collect isotherm data for subsequent development and optimization.
- Determine the effects of water on CO_2 adsorption.
- Develop and validate material scale-up and forming procedures.
- Select the best one or two materials for final optimization and scale-up.
- Determine the effects of contaminants on the performance of scaled-up materials.
- Understand detailed kinetic and equilibrium data for incorporation in a process design and an economic analysis.

technical content

MOFs are extremely high surface area, crystalline, microporous, and thermally stable materials that have shown exceptional storage capacity for CO_2, methane, hydrogen, and other gases. MOFs typically consist of transition metal vertices, or hubs, attached three-dimensionally to other metal vertices by organic "linker" molecules. After removal of reaction solvent, the resulting porosity can be adjusted by simply changing the length or composition of the molecules used to link the metal vertices. Well-ordered openings, channels, and pockets in the structures are from a few angstroms to tens of angstroms. Figure 1 represents the building blocks used to create prototypical MOF-5, in which the green ball represents the metal-containing hub, and the yellow cylinder represents the organic linker.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

CO_2 Removal from Flue Gas Using Microporous MOFs

participant:

RTI International

project number:

FC26-07NT43092

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Richard Willis
UOP LLC
richard.willis@uop.com

partners:

University of Edinburgh
University of Michigan
Vanderbilt University
Northwestern University

performance period:

3/12/07 – 6/30/10

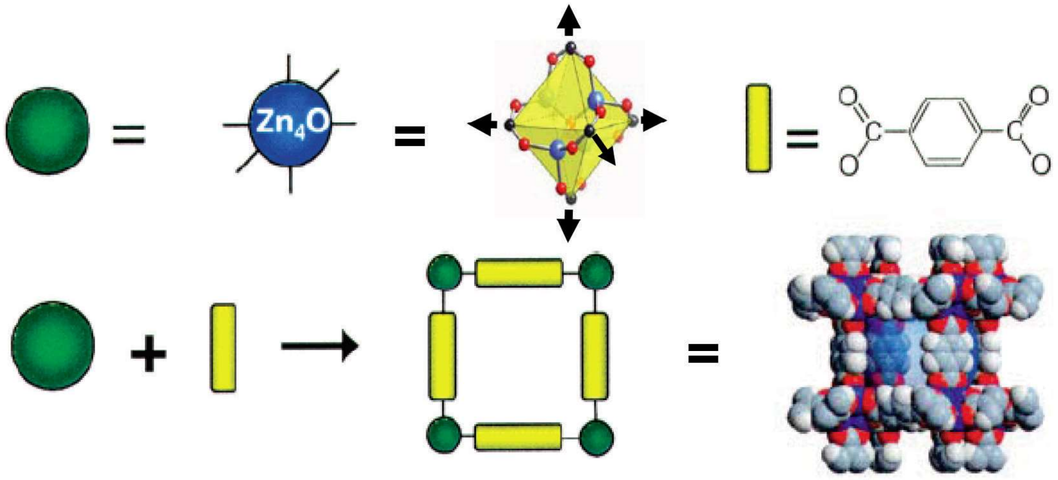


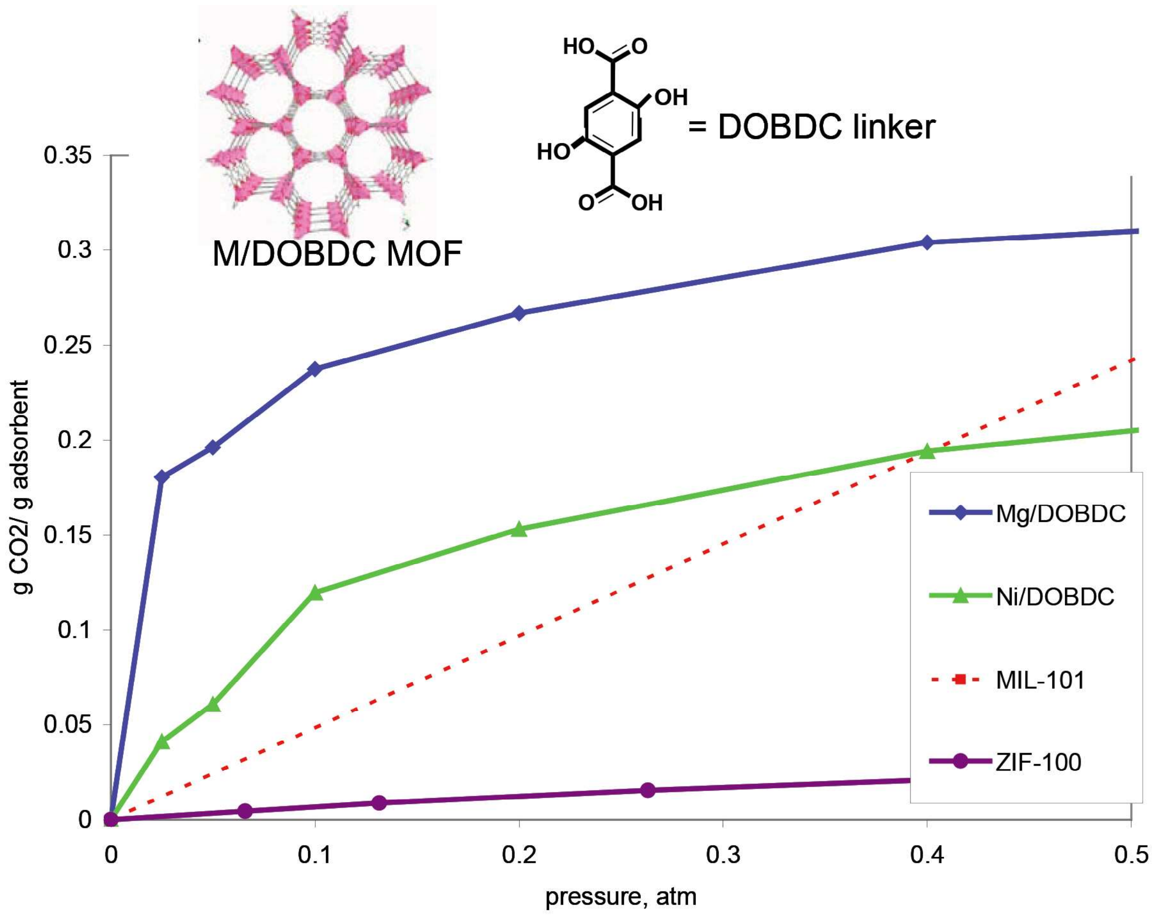
Figure 1: Building Blocks Used to Create Prototypical MOF-5

More than 50 MOFs for CO_2 adsorption were prepared from literature reports or designed by the experimenters. Table 1 displays the top MOFs for CO_2 capture.

TABLE 1: TOP 10 MOFS FOR CO_2 CAPTURE

Sample	Loading (mol/kg)	Loading (wt%)	Heat of Absorption (kJ/mol)
Mg\DOBDC (2)	4.73	20.9	60.1
Ni\DOBDC	3.40	15.0	27.2
Co\DOBDC	1.84	8.1	19.9
Mg\DOBDC (1)	1.28	5.6	21.3
HKUST-1 (CuBTC)	0.42	1.8	23.3
Zn\DOBDC	0.41	1.8	22.9
A1-MIL-110	0.24	1.1	21.7
Cr-MIL-101	0.18	0.8	13.3
Tb-MOF-76	0.18	0.8	21.7
A1-MIL-53	0.17	0.7	26
Zn-IRMOF-1	0.13	0.6	13.5

MOF-based adsorbents will be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO_2 from flue gas. Figure 2 represents an example of MOF CO_2 adsorption capabilities as a function of pressure (for M/DOBDC, M represents the metal).



ZIF-100 data from Wang, et al, *Nature* **2008**, *453*, 207

Figure 2: Example of MOF CO_2 Adsorption Capabilities as a Function of Pressure

The MOF-based VPSA CO_2 recovery system will be located after a contaminant-removal section and before the final CO_2 compression and drying section. The nitrogen (N_2)-rich waste stream (raffinate) will be sent to the stack. A process schematic is provided in Figure 3.

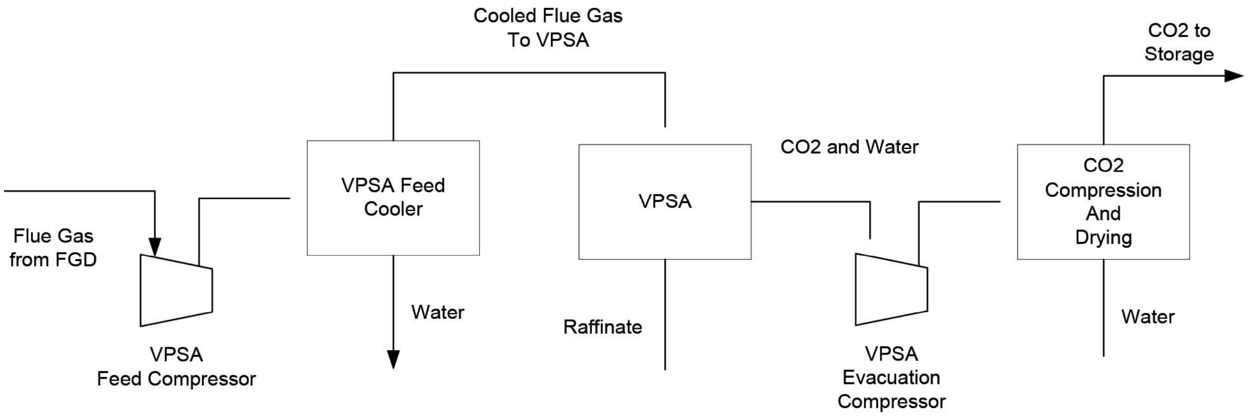


Figure 3: The MOF-Based CO_2 Capture System Process Schematic

Downstream from the flue gas desulfurization (FGD) and polishing scrubber, flue gas pressure is boosted in the VPSA feed compressor by approximately 4.8 pounds per square inch (psi) to make up for pressure drop in the contaminant-removal section and to maximize the adsorption of CO_2 in the VPSA unit. The VPSA feed compressor will be followed by a VPSA feed cooler to lower the temperature of the flue gas to approximately 100°F. It is likely that two parallel operating VPSA feed compressor and VPSA feed cooler trains will be required. Compressing and cooling the flue gas to 100°F will reduce the flue gas volume flow rate (actual cubic feet per minute [ACFM]) by up to 35 percent, and concurrently knock out at least 75 percent of the water vapor originally present in the flue gas. The combined lower-volume, lower-temperature, and lower-water content will allow the VPSA unit to operate more efficiently and effectively on the resultant flue gas stream.

The cooled flue gas enters the VPSA unit and will flow in a radial fashion through a short bed of adsorbent in either a vertical or horizontal configuration, depending upon the particular power plant's requirements. The adsorbent beds will consist of alumina for moisture polishing, and MOF for CO_2 removal. In the VPSA conceptual design at the end of the adsorption step, the vessel first vents N_2 raffinate to the stack to reduce the bed pressure to atmospheric pressure; pressure then equalizes with another vessel that had just completed the vacuum regeneration step. This would reduce the bed pressure to 7 to 8 pounds per square inch absolute (psia). These steps also reduce the N_2 stored in the vessel voids and minimize the amount that would be co-produced with the CO_2. The adsorbent bed would then be evacuated to 0.5 psia to produce the CO_2. For the purposes of the calculations, it was assumed that there was negligible co-adsorption of N_2 on the CO_2-loaded adsorbent and that the N_2 was primarily stored in the voids of the adsorbent vessel. The target CO_2 delta loadings were based on producing a >90 percent CO_2 purity stream during the regeneration step. The parasitic load for regeneration of the adsorbent is the compression energy associated with evacuating the vessel to 0.5 psia and compressing the contents to at least 8.8 pounds per square inch gauge (psig). The contribution of the N_2 stored in the voids is quite small compared to the compression energy associated with desorbing the CO_2. A purge step was not used in this process since the primary concern is producing a high-purity CO_2 stream.

The VPSA evacuation compressor will be used to remove CO_2 streams at 95 to 97 percent purity from the adsorbent beds. The water that comes along with the CO_2 will be removed during the CO_2 compression and drying stage of the process. In order to facilitate the gas compression and drying section CAPEX estimate, the VPSA evacuation compressor discharge pressure is 8.8 psig. This is the same pressure that the Econamine process delivers captured CO_2 to the gas compression and drying section. In the compression section, the CO_2 is compressed to 2,215 psia by a six-stage centrifugal compressor with inter-stage cooling to 100°F. The discharge pressures of the stages were balanced to give reasonable power distribution and discharge temperatures across the various stages. During compression in the multiple-stage, intercooled compressor, the CO_2 stream is dehydrated to a dew point of -40°F with triethylene glycol. The virtually moisture-free supercritical CO_2 stream is delivered to the plant battery limit as sequestration-ready.

There are no heating or cooling steps within the VPSA unit operation, which is typical of VPSA processes. Since this is still a conceptual design, however, there remain other types of processes to consider depending upon future pilot study and other experimental results. In a VPSA process, the heat of adsorption is released and is stored in the bed by a sensible temperature rise. The heat is removed during the desorption step as the adsorbent bed cools. Approximately 90 percent of the CO_2 in the feed gas is adsorbed onto the MOF adsorbent, and the rest leaves the VPSA section to the stack. Further, other than spent adsorbent, there is no waste generated in this process. The MOF-based VPSA process should generate little waste because the adsorbent itself is not hazardous waste, nor is it expected that the MOF will generate any hazardous waste products via degradation.

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	0.8	1.0
Bulk Density	kg/m^3		
Average Particle Diameter	mm	0.5 – 2.0	1.0
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	0.5	0.7
Solid Heat Capacity @ STP	kJ/kg-K	≈ 1	< 1
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg		

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Adsorption			
Pressure	bar	0.1	0.1 – 0.15
Temperature	°C	25 – 45	25 – 45
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Adsorption	kJ/mol CO_2	45	45 – 55
Desorption			
Pressure	bar	0.01 – 0.05	0.05
Temperature	°C	Ambient	Ambient
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	—-	—-
Flue Gas Flowrate	kg/hr	—-	—-
CO_2 Recovery, Purity, and Pressure	% / % / bar	90–98	
Adsorber Pressure Drop	bar	—-	—-
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—-	—-

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical pulverized coal (PC) power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

technology advantages

- High CO_2 adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D challenges

- Effects of water, sulfur oxides (SO_x), and nitrogen oxides (NO_x) on the MOF material.
- Need for large vacuum pumps to compress the CO_2 from the outlet of the VPSA.

results to date/accomplishments

- More than 50 MOF materials were evaluated; two were selected for further development and testing. The CO_2 capacity for these MOFs was determined in the presence of water and other contaminants and measured at several temperatures. Hydrothermal stability testing at accelerated conditions was also carried out for these MOFs.
- Mg/DOBDC outperformed all MOF and zeolite materials evaluated, with about 25 wt% CO_2 captured by this MOF at flue gas conditions (≈0.13 atm CO_2 pressure, 311°K).
- UOP's techno-economic analysis indicated that an MOF-based VPSA process has potential to be a less-expensive option than using amines to capture CO_2. Their analysis indicated a 65 percent increase in cost of electricity (COE) compared to a reference power plant without CO_2 capture.

next steps

This project ended on June 30, 2010. The final report was issued in October 2010.

available reports/technical papers/presentations

Carbon Dioxide Removal from Flue Gas Using Microporous Metal Organic Frameworks [PDF-2.7MB] (Oct 2010) Final Technical Report.

Benin, A., et al., "CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO₂/pdfs/43092%20UOP%20MOF%20sorbent%20%28Benin%29%20public%20version%20mar09.pdf*

DEVELOPMENT OF A DRY SORBENT-BASED POST-COMBUSTION CO_2 CAPTURE TECHNOLOGY FOR RETROFIT IN EXISTING POWER PLANTS

primary project goals

Research Triangle Institute (RTI) developed and tested a carbon dioxide (CO_2) capture process that utilizes a dry sodium carbonate (Na_2CO_3) sorbent that is based on the reaction of Na_2CO_3 with CO_2 and water vapor present in the flue gas from a coal-fired power plant.

technical goals

- Determine the optimal process configuration for the dry carbonate process.
- Construct and demonstrate a bench-scale CO_2 capture process using Na_2CO_3.
- Construct and demonstrate a pilot-scale, dry carbonate process that captures 0.9 tonnes of CO_2/day (1 ton of CO_2/day).
- Demonstrate the long-term chemical and mechanical stability of the sorbent.
- Update the economic analyses of the CO_2 sorbent capture process.
- Develop a commercialization plan for instituting the CO_2 capture process.

technical content

In an effort to develop a pre-pilot scale facility, RTI has been collecting data needed for designing, constructing, and operating the dry sorbent-based capture unit. RTI has designed and constructed a bench-scale heat transfer evaluation unit, shown in Figure 1, which is used to experimentally determine realistic gas and solid circulation rates and overall heat transfer coefficients for new reactor designs. A schematic diagram of the process is shown in Figure 1.

technology maturity:

Bench-Scale/Small Pilot-Scale

project focus:

A Dry Sorbent-Based Post Combustion CO_2 Capture

participant:

RTI International

project number:

FC26-07NT43089

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Thomas Nelson
RTI International
tnelson@rti.org

partners:

Arcadis
ADA-ES
BOC
EPA
EPRI
Nexant
Süd-Chemie, Inc

performance period:

3/7/07 – 12/31/09

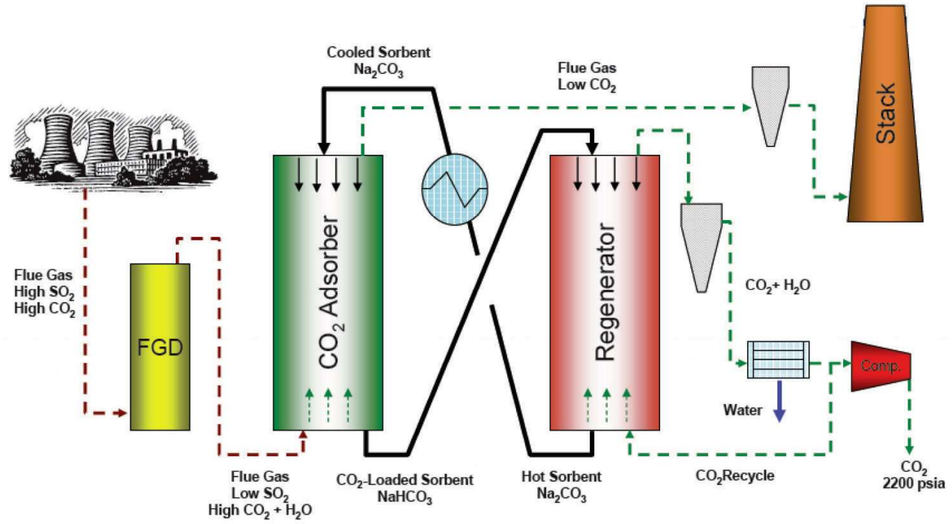


Figure 1: Schematic Diagram of CO_2 Capture Process

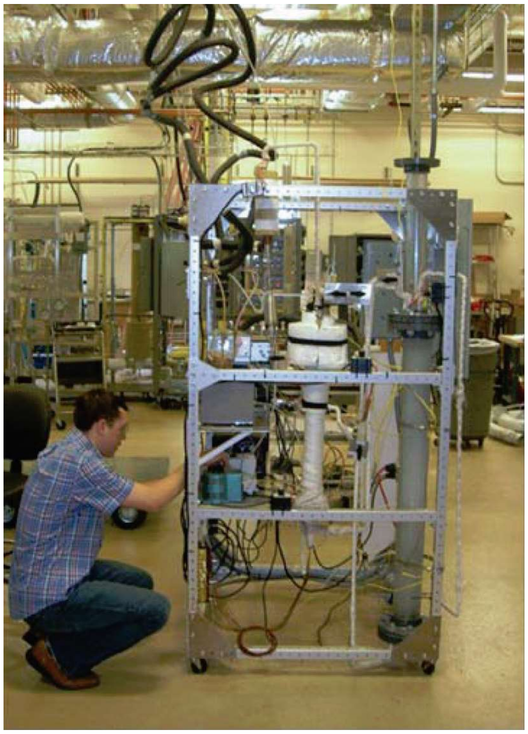


Figure 2: Lab-Scale CO_2 Absorption Reactor Skid

Pilot-scale testing will be performed on a slipstream from the air-blown gasifier at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. SRI has designed a pilot-scale, continuous, integrated test system. The equipment is being procured and will be assembled. The pilot-scale test will emphasize stability of integrated operation. The effects of trace contaminants will be observed, as the pilot tests will use a gas stream from an operating gasifier that has undergone minimum cleanup and will contain trace contaminants.

The CO_2 capture unit is located after the wet flue gas desulfurization (FGD) unit. The Na_2CO_3 sorbent reacts with the CO_2 and water (H_2O) located in the gas stream through a cyclic temperature swing cycle by adsorbing the CO_2 and H_2O at 60°C and releasing the constituents at 120°C during the sorbent regenerating stage. Considering the high exothermic heat of absorption (3.08 MJ/kg), significant cooling fluid is required to maintain the adsorption temperature at the desired value.

Utilizing the information gathered from the bench-scale unit, as well as the lab-scale unit shown in Figure 2, RTI has developed engineered sorbents that exhibit improved CO_2 capture rate and physical characteristics (e.g., attrition resistance, fluidizibility, and density) over the supported (multi-layer) sorbents. These improvements will have a significant impact on a commercial, dry carbonate system by lowering the solids handling requirements and minimizing the heating and cooling duties in a commercial process. A long-term, multi-cycle testing of these sorbents to demonstrate chemical stability has been undertaken. Initial results indicate that the engineered sorbents are highly stable in the presence of contaminates such as hydrochloric acid (HCl), nitrous oxides (NO_x), H_2O, and oxygen (O_2). While sulfur dioxide (SO_2) forms irreversible chemical bonds to the sorbent, it is considered a minor issue, considering the rate of attrition is generally greater than the rate of deactivation due to SO_2.

TABLE 1: PHYSICAL PROPERTIES OF SODIUM CARBONATE SORBENTS

Property	Value
Bulk Density	1.0 – 1.1 g/mL
Average Particulate Size	65 – 75 µm
Surface Area	100 – 120 m^2/g
Physical Strength (A)	0.77
Na_2CO_3 Strength	10 – 40 wt%
Heat of Absorption	3.08 MJ/kg
Regeneration Energy	3.08 MJ/kg

The heat transfer experiments will be conducted in a fluidized bed contactor, as shown in Figure 2. The conveyors (one heated, the other cooled) will be used to move the Na_2CO_3 through the fluidized bed to introduce a simulated flue gas (from coal or natural gas) to the sorbent. The instrument is used to analyze the adsorption effectiveness and the attrition rate of the Na_2CO_3 sorbent. Data from the fluidized bed will be used to validate and develop the computational fluid dynamic (CFD) model called MFIX.

Some physical properties of the sorbent are provided in Table 1.

As seen in the aforementioned table, the theoretical maximum CO_2 loading for the sorbent is ≈40 wt%. While RTI has achieved loading as high as 30 wt%, it requires a cycle time much greater than would be practical. Allowing only 30 minutes per cycle phase results in loading capacities of ≈20 to 25 percent.

technology advantages

- Lower capital and operating costs for CO_2 removal.
- Sorbent is inexpensive and easy to acquire (≈$200/ton).
- Sorbent is non-hazardous, non-toxic, and does not produce hazardous waste.

R&D challenges

- Circulation of solids may be problematic.
- The reaction of Na_2CO_3 with H_2O is highly exothermic and requires effective heat transfer.
- Removal of CO_2 requires equimolar amounts of H_2O.
- Irreversible reactions of Na_2CO_3 with SO_2 and HCl during process conditions.
- Raw Na_2CO_3 is not a physically strong material, leading to high attrition rates.
- Raw Na_2CO_3 agglomerates upon contact with condensed H_2O.

results to date/accomplishments

- Constructed a heat transfer evaluation system used to evaluate the hydrodynamics and heat transfer characteristics of the reactor designs.
- Constructed a packed-bed reactor system to demonstrate sorbent stability over many adsorption and regeneration cycles and provide insight into reaction kinetics.
- Validated the operation of a bench-scale, coupled cold-flow system and collected data on gas-solid contactor bed height control, range of operability, sorbent bed densities, bed void volumes, and fluidization characteristics.
- Measured the heat transfer limitations of the existing screw conveyor system and determined that the screw conveyors cannot be used for sorbent regeneration in a 1-ton/day CO_2 capture pre-pilot system.
- Developed updated process simulations for the new dry carbonate process design using ASPEN Plus.

next steps

This project ended on December 31, 2009. The final report was completed in April 2010.

available reports/technical papers/presentations

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants – Final Report – April 2010.

Nelson, T., et al., "Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology Retrofit in Existing Power Plants," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO$_2$/pdfs/43089%20RTI%20sorbent%20%28Nelson%29%20mar09.pdf*.

The Dry Carbonate Process: Carbon Dioxide Recovery from Power Plant Flue Gas, 7th Annual Conference on Carbon Capture and Sequestration in Pittsburgh, Pennsylvania, May 2008.

The Dry Carbonate Sorbent Technology for CO_2 Removal from Flue Gas of Existing Coal-Fired Power Plants – Power Plant Air Pollutant Control "Mega" Symposium in Baltimore, Maryland, August 2008.

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants Fact Sheet, April 2008.

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents, Topical Report, November 2004.

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: POST-COMBUSTION MEMBRANE TECHNOLOGIES

Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

primary project goals

Ohio State University developed an inorganic/polymer composite membrane consisting of a thin, selective inorganic-containing layer embedded in a polymer structure. The project developed the new membrane design to improve system performance through laboratory, bench-scale, and pilot-scale testing, and developed a continuous manufacturing process to decrease costs.

technical goals

- Develop membrane synthesis process that incorporates a thin, selective inorganic-containing layer embedded in a polymer structure.
    - Membranes were developed and down-selected to achieve the Department of Energy (DOE) target of <$40/tonne carbon dioxide (CO_2) captured for 2025 (for a CO_2/nitrogen [N_2] selectivity of >100 and a CO_2 permeance of >800 gas permeation units [GPU]).
    - Continuous fabrication of the proposed hybrid membrane morphology was performed with the use of a continuous membrane fabrication machine.
- Conduct membrane characterization via bench-scale testing.
    - Functional hybrid membranes were synthesized for incorporation into three prototype membrane modules for parametric and continuous testing with simulated or actual flue gas.
- Complete system and cost analysis of the membrane system.

technical content

Ohio State University developed a cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas. In one approach, the membranes are comprised of a thin, selective inorganic particle-containing layer embedded in a polymer structure so that it can be made in a continuous manufacturing process. In another approach, a continuous zeolite membrane is rapidly synthesized on a polymer support. Figures 1 and 2 show the two hybrid membrane concepts studied in this project. The membrane of the first approach was incorporated in spiral-wound modules for testing with simulated and actual coal-fired flue gas. Preliminary cost calculations showed that a single-stage membrane process is economically unfavorable, primarily because of the low concentration of CO_2 (≈14 percent) in the flue gas stream. A two-stage process is more economical, but requires plant operation with a CO_2-enriched recycle stream. An important cost driver in current carbon capture membrane technologies is the energy requirement for maintaining the driving force for the membrane separation. The flue gas must be kept at atmospheric pressure and the concentrated CO_2 stream kept under vacuum (approximately 3 pounds per square inch [psi]) conditions. Preliminary calculations showed that the carbon capture energy requirement can be sufficiently reduced in a two-stage process. In the first stage, CO_2 is removed from flue gas by evacuation; in the second stage, remaining CO_2 is removed using an air-sweep such that the 90 percent capture target is met.

technology maturity:
Pilot-Scale, Actual Flue Gas

project focus:
Inorganic/Polymer Composite Membranes

participant:
Ohio State University

project number:
FE0007632

predecessor projects:
N/A

NETL project manager:
José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:
Dr. Winston Ho
Ohio State University
ho.192@osu.edu

partners:
Gradient Technology, TriSep Corporation, American Electric Power (AEP)

start date:
10.01.2011

percent complete:
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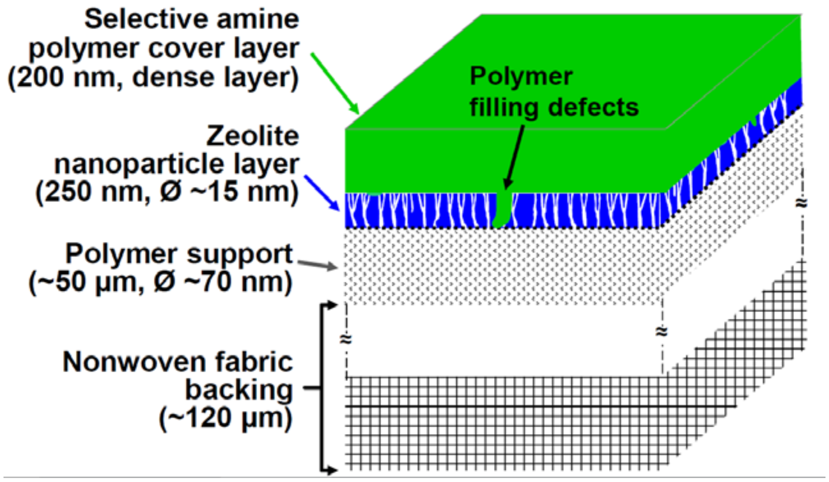

Figure 1: Membrane concept with selective amine polymer layer on zeolite nanoparticles embedded in polymer support

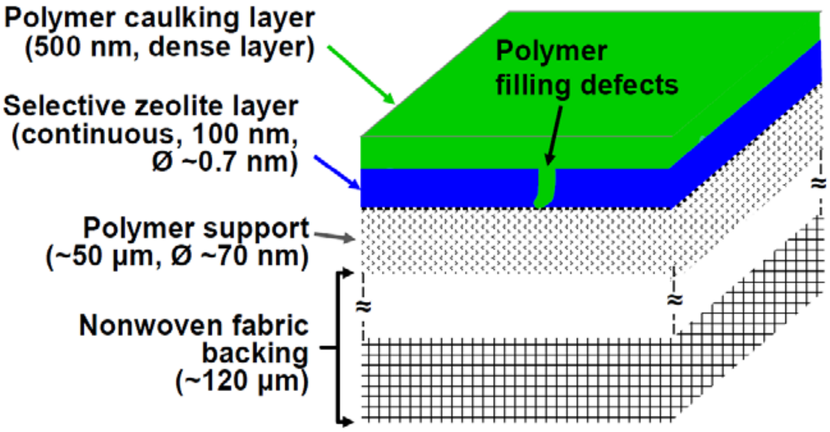

Figure 2: Membrane concept with polymer caulking layer on selective zeolite membrane grown on polymer support

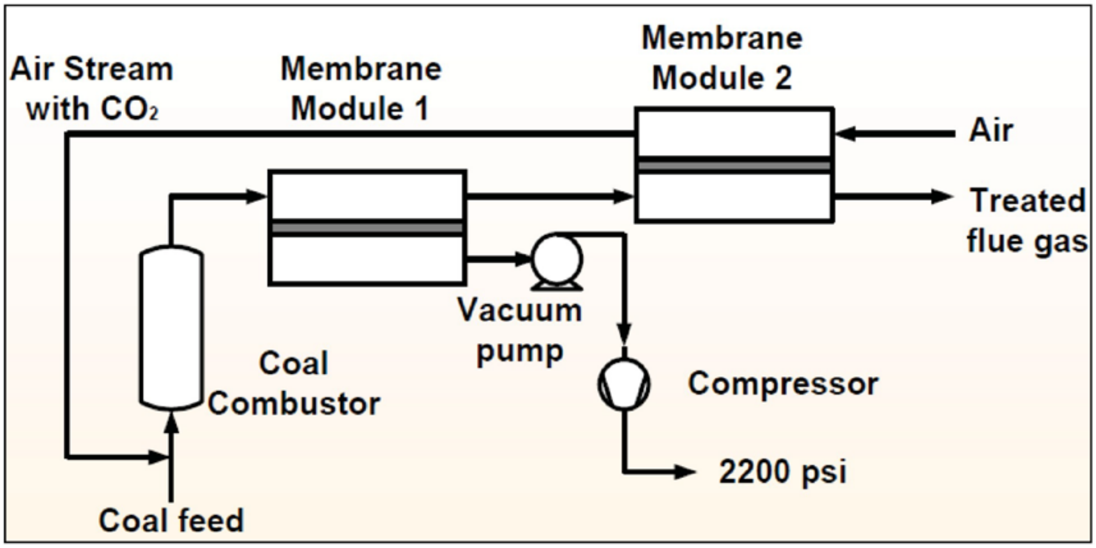

Figure 3: Process concept for two-stage membrane system

The entrance sweep flow is the same as the combustion air used in the current plant; the now CO_2-enriched stream is subsequently used for combustion. The 95 percent pure CO_2, captured in the first stage, is then compressed to 15 MPa (≈2,200 psi). DOE's cost targets can be met with a membrane that has a selectivity ≈170, a permeance of 1,100 GPU, and full stability against flue gas contaminants. This combination cannot be achieved with fully polymeric membranes. Fully inorganic, micro-porous membranes are sufficiently selective and stable, but generally too expensive due to high manufacturing costs. The focus of this project was a design that combines favorable inorganic membrane selectivity with the cost-effectiveness resulting from the manufacture of a composite membrane in continuous mode. The micro-porous membranes are aluminosilicates. Fully inorganic structures have CO_2/N_2 selectivities of >200, and permeances of <3,000 gas GPU. The latter can be improved by reducing membrane thickness, in combination with defect abatement with a thin polydimethylsiloxane (PDMS) layer. Two types of inorganic selective layers including alumina and zeolite Y (zeolite Y has a silica-to-alumina ratio of their framework of three or greater) were investigated. Membrane fabrication with growth of zeolite Y (ZY) into a continuous layer offers better selectivity, lower processing cost, and is easier to scale-up than membrane fabrication with rapid modification of the top aluminum oxide layer to form a microporous layer. A zeolite Y/polymer composite membrane was down-selected for further studies. Zeolite Y layers can be grown from solutions at 95 °C; however, the zeolite Y layer requires long growth time, which was reduced to 1 hour via application of a novel zeolite synthesis approach. The membrane system can be deposited on available polyethersulfone supports, which are fabricated into 14-inch supports with a continuous fabrication machine.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	zeolites and/or amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone or polysulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	150–250	150–250
Membrane Geometry	—	flat sheet	spiral-wound sheet
Max Trans-Membrane Pressure	bar	can be 0.2–50	0.2–1.5
Hours Tested without Significant Degradation	—	200 hours	200 hours
Manufacturing Cost for Membrane Material	$\$/m^2$	20	20
Membrane Performance			
Temperature	°C	57 °C and 102 °C	57 °C
CO_2 Pressure Normalized Flux	GPU or equivalent	800 GPU	>800 GPU
CO_2/H_2O Selectivity	—	not determined	not determined
CO_2/N_2 Selectivity	—	α = 140–800 for 20 CO_2/80 N_2 with p_{tot} = 101 kPa	α >100 for flue gas conditions
CO_2/SO_2 Selectivity	—	not determined	not determined
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	about 1800	
Shell-Side Fluid	—	air sweep	
Flue Gas Flowrate	kg/hr	about 0.2	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90%, >95%, 0.2–1.2 bar	
Pressure Drops Shell/Tube Side	bar	about 0.05/0.05	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) should be assumed as:

Pressure	Temperature	Composition						
		vol%					ppmv	
psia	°F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Surface adsorption and diffusion and molecular sieving for the zeolite selective layer; solution-diffusion for the polymer cover layer; facilitated transport for amine-containing selective layer.

Contaminant Resistance – Fully resistant polymer and inorganic materials.

Flue Gas Pretreatment Requirements – Removal of particulates, possibly dehydration.

Membrane Replacement Requirements – Estimated approximately 4 years.

Waste Streams Generated – N_2 with water (H_2O), about 1 percent CO_2 and minor impurities.

Process Design Concept – See Figure 3.

technology advantages

High CO_2/N_2 selectivity and cost-effective separation principle.

R&D challenges

Synthesis and scale-up of sufficiently selective and permeable membranes.

status

The project was completed on December 31, 2015, resulting in the development of a pilot-scale continuous casting machine for the fabrication of 14-inch polymer substrates and the development of a pilot-scale continuous membrane fabrication machine for the deposition of zeolite particles on polymer substrates using a vacuum-assisted dip coating method, followed by coating of the amine-containing polymer cover layer on the zeolite/polymer substrates. The pilot-scale amine-containing composite membranes were rolled into spiral-wound modules and implemented in a two-stage CO_2 capture process. These membrane modules were tested with real flue gas at the National Carbon Capture Center (NCCC), achieving >800 GPU of CO_2 permeance and >150 CO_2/N_2 selectivity. A process for rapid (1 hour) zeolite membrane growth, involving a continuous zeolite layer grown within polymer support, was also developed.

available reports/technical papers/presentations

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," Final project review meeting presentation, Pittsburgh, PA, February 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007632-Project-Meeting-Final-public-release-2-26-16.pdf.*

Ho, W. "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the Continuation Application Status Meeting, Pittsburgh, PA, August 2014. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007632-Continuation-Application-Status-Mtg-public-release-8-11-14.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

Verweij, H., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/events/2012/co2%20capture%20meeting/H-Verweij-OSU-Composite-Membranes.pdf.*

Verweij, H., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," project kickoff meeting presentation, December 2011. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/NETL-kick-off.pdf.*

BENCH-SCALE, HIGH-PERFORMANCE, THIN FILM COMPOSITE HOLLOW FIBER MEMBRANE FOR POST-COMBUSTION CARBON DIOXIDE CAPTURE

primary project goals

General Electric Global Research (GE) is developing high-performance, thin film polymer composite hollow fiber membranes and advanced processes for economical post-combustion carbon dioxide (CO_2) capture. The project includes bench-scale testing to tune the properties of a novel phosphazene polymer membrane and decrease costs through development of innovative fabrication techniques.

technical goals

- Optimize phosphazene polymer and coating solution: Synthesize phosphazene polymer, optimize separation performance, and develop processable coating solutions.
- Fabricate hollow fiber support layer: Produce highly porous, robust hollow fiber supports with controlled surface porosity from commercially available materials.
- Fabricate composite coated hollow fiber membranes: Develop processes to apply thin layer coatings on hollow fiber supports and elucidate fundamental polymer properties.
- Test membranes at bench-scale under flue gas conditions: Exposure and performance test materials and membranes under flue-gas conditions.
- Conduct process evaluation and module design: Conduct technical and economical process evaluation and module design and fabrication.

technical content

GE and partners are developing a high-performance, thin film polymer composite hollow fiber membrane and advanced process for economical post-combustion CO_2 capture. The project utilizes novel phosphazenepolymeric materials to produce an economical and scalable composite hollow fiber membrane module.

The membrane will be optimized at bench-scale, including tuning the properties of the phosphazene polymer in a coating solution and fabricating highly engineered porous hollow fiber supports. The project will also define the processes for coating the fiber support to manufacture thin, defect-free composite hollow fiber membranes.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Composite Hollow Fiber Membranes

participant:

General Electric Global Research Center

project number:

FE0007514

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Paul Glaser
General Electric
paul.glaser@ge.com

partners:

Idaho National Laboratory,
Western Research Institute,
Georgia Institute of Technology

performance period:

10/1/11 – 12/31/14

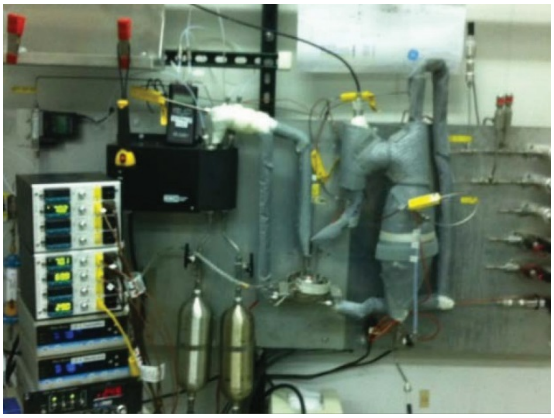

Figure 1: GE Test Rig – Flat Sheet and Hollow Fiber Membranes

The physical, chemical, and mechanical stability of the materials (individual and composite) to flue gas components will be evaluated using exposure and performance tests. Membrane fouling and cleanability studies will define long-term performance.

GE and the Georgia Institute of Technology (Georgia Tech) will work together on developing processes to apply the thin layer coating formulations onto the hollow fiber supports. GE will leverage the knowledge gained from using its flat sheet film coating apparatus to enable development of the continuous dip process for coating of hollow fiber membrane supports. Georgia Tech will use the in situ process developed to coat porous cellulose acetate hollow fibers with defect-free layers as a benchmark, which will be further adapted to obtain thin, defect-free coated layers. Both the continuous dip coating and batch in situ processes will be optimized to provide economical and scalable coated composite hollow fiber membranes.

Figure 2: Georgia Tech Hollow Fiber Fabrication Line

Working with Idaho National Laboratory, Georgia Tech will characterize phosphazene material properties in films cast on porous polymer supports to elucidate polymer properties including aging, membrane fouling, and cleanability. The characterization techniques will enable a better understanding of polymer and composite membrane performance. Membrane performance validation testing under flue-gas conditions will be performed at Western Research Institute's coal combustion test facility. Module design and technical and economic feasibility analyses will be conducted to evaluate the overall performance and impact of the process on the cost of electricity.

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	phosphazene	
Materials of Fabrication for Support Layer	—	polymer	
Nominal Thickness of Selective Layer	µm	1–10	<1
Membrane Geometry	—	flat sheet/hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	2–5	up to 10
Hours Tested Without Significant Degradation	—	200 (flat sheet) 100 (hollow fiber)	100–1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	—	—
Membrane Performance			
Temperature	°C	30 and 65	30 and 60
CO_2 Pressure Normalized Flux	GPU or equivalent	50–275 Barrer (flat sheet 30 °C) 100–425 Barrer (flat sheet 65 °C) up to 70 GPU (hollow fibers 35 °C)	1,000–2,500 GPU (hollow fibers)
CO_2/H_2O Selectivity	—	8–10	8–10
CO_2/N_2 Selectivity	—	15–20 (65 °C) flat sheet 30–40 (30 °C) flat sheet 10–35 (35 °C) hollow fibers	30–40
CO_2/SO_2 Selectivity	—	not tested	non tested
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	>1,000	
Shell-Side Fluid	—	retentate	
Flue Gas Flowrate	kg/hr	<1	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90%, 60–80%, 0.2–1 bar	
Pressure Drops Shell/Tube Side	bar	1–4	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cmHg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Phosphazene-based membranes have been tested to be resistant to contaminant species such as oxygen (O_2), nitrogen oxide (NO_x), sulfur dioxide (SO_2), and moisture present in coal flue gas.

Flue Gas Pretreatment Requirements – Fly ash particulate removal.

Membrane Replacement Requirements – Membranes found to be stable with up to 200 hours of testing. Long-term stability tests are currently in progress.

Waste Streams Generated – Acidic water condensate stream.

technology advantages

- Surface property optimization to reduce fly ash adhesion.
- Highly scalable, low-cost hollow fiber support platform.
- Ease of cleaning should provide longer membrane life.
- Phosphazene polymer with high permeability and selectivity.

R&D challenges

- Fouling potential from fly ash/particulates.
- Permeability and selectivity at 60 °C lower than anticipated.
- Large membrane area requirements and process integration.

results to date/accomplishments

- Synthesized phosphazene polymer, characterized separations performance under realistic flue gas conditions, and developed hollow fiber support coating solutions.
- Developed engineered, high-porosity, hollow fiber supports.
- Built/upgraded bench-scale membrane coating and testing facilities.
- Completed initial process technical and economic feasibility study.
- Fabricated phosphazene coated defect-free hollow fiber membranes.
- Membrane performance studies conducted showed stability over >100 hours of testing.

next steps

- Optimize phosphazene polymer coatability on hollow fiber supports.
- Optimize the continuous dip and batch coating processes to provide economical and scalable coated composite hollow fiber membranes.
- Continue testing of coated composite hollow fiber membranes at bench scale under flue gas conditions.
- Conduct final technical and economic feasibility analyses and an environmental, health, and safety assessment.

available reports/technical papers/presentations

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/D-Ajit-Bhandari-GE-Composite-Hollow-Fiber-Membranes.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO$_2$/DBhandari-GEGR-2013-CO$_2$-NETL-Conference.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2013 North American Membrane Society Meeting, Boise, ID, June 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO$_2$/GEGR-2013-CO$_2$-NAMS-Conference.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

LOW-PRESSURE MEMBRANE CONTACTORS FOR CO_2 CAPTURE

primary project goals

Membrane Technology and Research (MTR) is developing a new type of membrane contactor (or mega-module) to decrease capture costs, energy use, and system footprint through bench-scale testing of a module with a membrane area that is 100 m^2, 5 times larger than that of current modules used for carbon dioxide (CO_2) capture.

technical goals

- Develop a module design to reduce energy cost by lowering module pressure drop.
- Develop a module design with a large membrane area.
- Develop a module design to reduce manifold complexity, footprint, and cost.

technical content

MTR is developing a new type of membrane contactor (or mega-module) to separate CO_2 from power plant flue gas. This module membrane area is 100 m^2, which is 4–5 times larger than that of current modules used for CO_2 capture. The countercurrent sweep module is crucial to the MTR-developed CO_2 removal from flue gas process, as this membrane module permits the use of air as a sweep gas, which increases the CO_2 flux through the membrane without requiring additional compression energy. This means the CO_2 concentration in the flue gas is increased at a minimal energy cost.

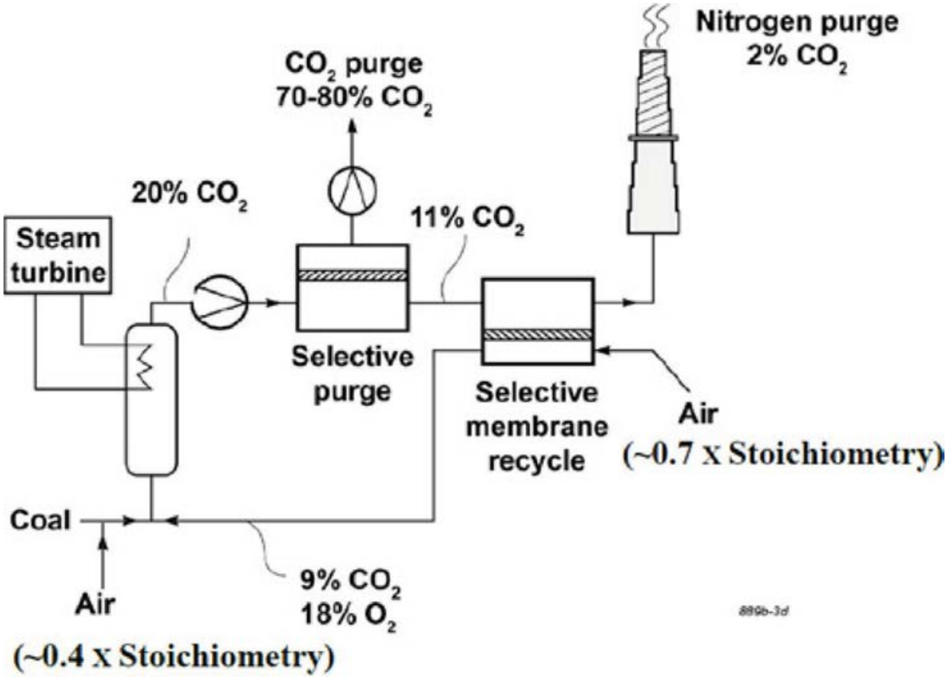

Figure 1: Two-Stage Membrane CO_2 Capture Process

technology maturity:
Bench-Scale, Simulated and Actual Flue Gas

project focus:
Low-Pressure Membrane Contactors (mega-module)

participant:
Membrane Technology and Research, Inc.

project number:
FE0007553

NETL project manager:
Morgan Mosser
morgan.mosser@netl.doe.gov

principal investigator:
Richard Baker
Membrane Technology and Research, Inc.
richard.baker@mtrinc.com

partners:
University of Toledo

performance period:
10/1/11 – 9/30/14

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		proprietary polymer	
Materials of Fabrication for Support Layer		proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry		plate-and-frame	plate-and-frame
Max Trans-Membrane Pressure	bar	70	70
Hours Tested Without Significant Degradation		500	500
Manufacturing Cost for Membrane Material	$\$/m^2$	100	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,500	>2,500
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	pure gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	cross-flow	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	5,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.1; sweep:0.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as mercury, arsenic, etc., is unknown and is being examined in the ongoing field demonstration at the National Carbon Capture Center (NCCC) in Wilsonville, AL, under a different U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL)-sponsored project (DE-FE0005795).

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown. The current demonstration tests at NCCC treat post-flue gas desulfurization (FGD) flue gas and will help determine the need for gas treatment prior to entering the membrane system. The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. Particulate filters that can achieve an order of magnitude better ash removal than a standard bag house, and are used today to treat refinery and gasification streams, may be needed.

Waste Streams Generated – The membrane process will recover >95 percent of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

technology advantages

- In flue gas applications, the novel countercurrent sweep module recycles CO_2 to the boiler with an air sweep, which increases the CO_2 concentration in the flue gas with minimal energy input.
- The recycle of CO_2 to the boiler increases the concentration of CO_2 in the flue gas, which could make the CO_2 capture process easier for technologies other than membranes.
- The novel countercurrent sweep module design has low-pressured drop, which reduces the energy costs.
- Mega-modules (500 m^2 or larger) reduce the manifolding complexity, footprint, and cost of the membrane system.

R&D challenges

- The novel sweep plate and framed design will need to overcome several issues, including sweep-side pressure drop, poor utilization of the membrane area due to module geometry, and non-uniform flow patterns.
- Spacer design and selection needs to maximize packing density and mechanical support while minimizing pressure drop.
- Scaleup issues associated with building membrane modules 10–20 times larger than conventional modules.

results to date/accomplishments

- Completed design and fabrication of various 20-m^2 prototype membrane modules.
- Completed pressure drop and CO_2 separation performance testing of various 20-m^2 prototype membrane modules with bench-scale lab test system
- Completed design and construction of larger lab test system, sized for parametric studies of 100-m^2 membrane modules.
- Conducted CFD simulations of various sweep module designs that incorporate pressure drop, velocity profiles, and mass transfer.
- A large sweep module test unit was designed and assembled at MTR for all pure-gas, pressure drop, and CO_2 separation performance testing of 100 m^2 modules. The pressure drop through the plate-and-frame module is more than 10-fold lower than that through the best modified spiral module, significantly lower than the project target of 1.5 psi, and demonstrate substantial energy savings for the membrane capture process.
- A CFD comparative analysis of crossflow and countercurrent sweep membrane modules demonstrated that countercurrent/sweep modules require 35 percent less membrane area than crossflow modules to remove the same amount of CO_2, but the pressure drop through crossflow modules was lower.
- A 500-m^2 sweep membrane module skid was designed and fabricated for field testing. A pressure vessel with five 100-m^2 membrane modules can be run individually or as a group. The skid was designed for integration into the existing MTR 20-tpd CO_2 capture pilot test unit for testing at NCCC in Wilsonville, AL. The 500-m^2 sweep module skid is to be tested at NCCC in early 2015.

- A detailed performance and economic analysis of the MTR membrane CO_2 capture process with low-pressure sweep modules was performed. The methodology used by MTR to evaluate the membrane process is consistent with Case 10 of the 2010 DOE report: Econamine was used to capture 90 percent of the flue gas CO_2. The "all membrane" case demonstrates savings over the Econamine CO_2 capture process, but the cost is still higher than the DOE target of $40/tonne CO_2 captured.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/R-Baker-MTR-Low-Pressure-Membrane-Contactors.pdf*.

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/R-Baker-MTR-Low-Pressure-Membrane-Contactors.pdf*.

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

CO_2 CAPTURE MEMBRANE PROCESS FOR POWER PLANT FLUE GAS

primary project goals

Research Triangle Institute (RTI) set out to develop an advanced hollow-fiber, polymeric membrane-based process that can be cost-effectively retrofitted into current pulverized coal (PC)-fired power plants to capture at least 90 percent of the carbon dioxide (CO_2) from the plant's flue gas.

technical goals

- Develop new fluorinated polymers as membrane materials that have superior CO_2 separation properties compared to conventional and competitive membrane platforms. A minimum selectivity of 30 for CO_2 over nitrogen (N_2) and CO_2 permeance in excess of 300 gas permeance unit (GPU) are targeted. Fluorinated polymers are a promising material platform because they exhibit excellent chemical stability to moisture, sulfur dioxide (SO_2), and nitrogen oxide (NO_x) contaminants present in flue gas.
- Develop next-generation polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current commercial polycarbonate membranes.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and high CO_2 permeate flow rates with minimal pressure drop.
- Identify and develop CO_2 capture membrane process design and integration strategies suitable for retrofit installation.

technical content

Project research efforts include development of membrane materials and membrane hollow fibers, membrane module design and fabrication, and process design.

RTI pursued the development of two membrane material platforms. As a near-term membrane platform solution, RTI worked with Generon to develop next-generation, high-flux polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current-generation, commercial polycarbonate membranes. Hollow-fiber membranes made from the high-flux polycarbonate have been successfully developed, scaled up, and fabricated into module separation devices. Laboratory-scale membrane modules have been studied with simulated flue gas mixtures with and without flue gas contaminants.

For a longer-term membrane platform solution, RTI worked with Arkema to develop improved CO_2 capture membrane materials based on the polymer chemistry of polyvinylidene fluoride [PVDF], the chemical structure of which is shown in Figure 1 and comprises the [CH_2-CF2]n repeat unit. PVDF is well suited for contact with flue gas, possessing high chemical resistance to acids and oxidants, specific affinity for CO_2 for high CO_2 solubility, and high thermal stability (Td ≈ 340°C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the fiber extrusion process used to fabricate mem-

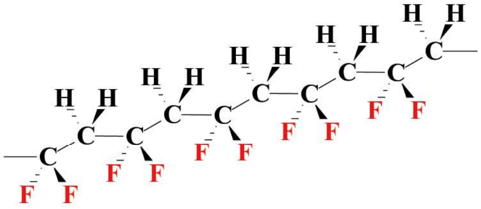

Figure 1: Chemical Structure of PVDF

technology maturity:

Bench-Scale, Using Simulated Flue Gas

project focus:

Hollow-Fiber, Polymeric Membrane

participant:

Research Triangle Institute

project number:

NT0005313

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Lora Toy
Research Triangle Institute
ltoy@rti.org

partners:

Arkema
Generon IGS

performance period:

10/1/08 – 9/30/11

brane hollow fibers. However, conventional PVDF is a homopolymer that is semicrystalline and has CO_2/N_2 selectivity of ≈23 and low CO_2 permeance of ≈10 GPU. Arkema has pursued synthesizing and developing advanced, PVDF based copolymers possessing improved CO_2 permeance and selectivity.

In this project, the membrane under development was in the form of hollow fibers that are packaged into compact, high surface area-to-volume module devices. Multiple modules were utilized in a given CO_2 capture membrane system for power plant applications due to the large quantity of flue gas to be processed. The modularity of the membrane separation devices allows for easy adaptation to different levels of CO_2 removal desired by simply adding or subtracting the number of membrane modules used. Figure 2 shows a cross-section of a hollow-fiber membrane module. A single-membrane module consists of hundreds of thousands to more than a million micron-sized diameter hollow fibers bundled together. A couple of individual membrane hollow fibers, a small bundle loop of fibers, and modules of different sizes are shown in Figure 3. As flue gas flows through the membrane fibers, the feed is split into two streams. A permeate stream enriched in CO_2 is produced by the preferential transport of CO_2 across the fiber walls. The remaining flue gas (non-permeate) flows out of the membrane module as a CO_2-depleted retentate stream that is sent to the plant stack for discharge to the atmosphere.

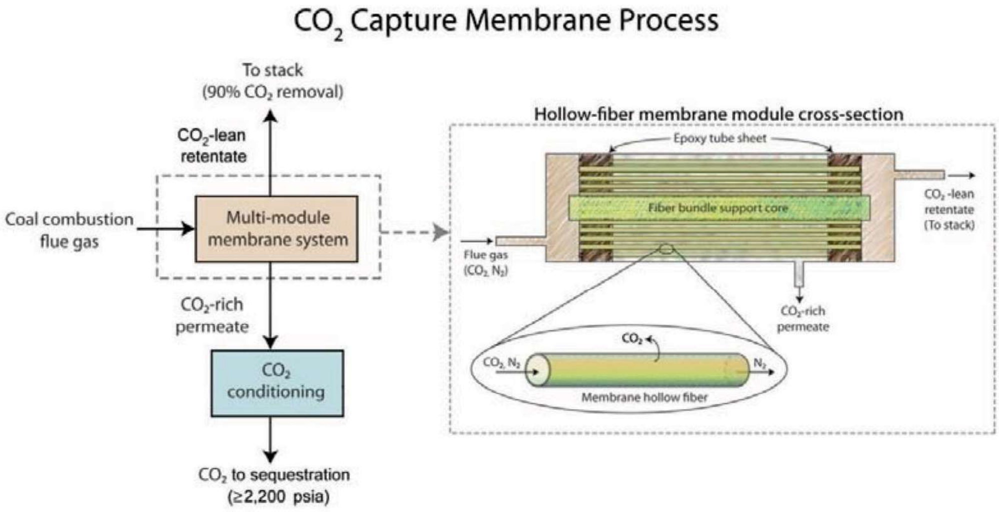

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

Individual Membrane Hollow Fibers **Small Bundle Loop of Hollow Fibers** **Various Membrane Module Sizes**

Figure 3: Membrane Hollow Fibers

Process simulations for a single-stage membrane process were conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity to different parameters, including membrane flux (permeance), membrane selectivity, membrane fiber dimensions, and membrane pressure driving force. An important outcome of this sensitivity analysis was the understanding that membrane property development should focus on improving both permeance and selectivity together rather than individually.

To achieve high levels of CO_2 capture and purity, RTI developed the three-stage membrane process shown in Figure 4, where the membrane stages are represented by M1, M2, and M3. The flue gas is compressed and fed to the first membrane stage M1. To obtain a net 90 percent removal of CO_2 from the stream ultimately sent to the stack, the CO_2-depleted retentate exiting M1 is fed to M3, which is operated with a permeate-side air sweep to enhance removal of more CO_2. Before being released into the stack, the pressurized M3 retentate is sent to an expander to recover the energy associated with high pressure. The resulting M3 permeate is a CO_2 enriched air stream that is sent back to the boiler. In the second membrane stage M2, the CO_2 captured in the M1 permeate is further concentrated. The resulting CO_2-rich M2 permeate is then compressed and dehydrated to produce the final, sequestration-ready CO_2 capture stream. The M2 retentate is recycled and fed back to M1. The numbers shown in Figure 4 are for a 550-MW coal-fired power plant to achieve 90 percent CO_2 capture and 95 percent CO_2 purity in the capture stream using the high-flux polycarbonate membrane (400 GPU; CO_2/N_2 = 35).

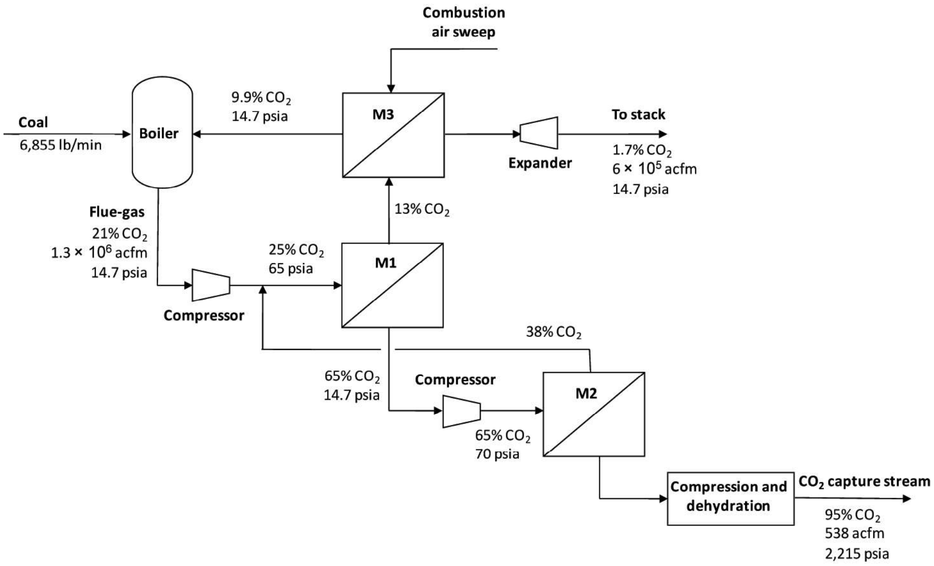

Figure 4: RTI's Three-Stage CO_2 Capture Membrane Process Design

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Polycarbonate-based and Vinylidene fluoride-based	
Materials of Fabrication for Support Layer	-	N/A	
Nominal Thickness of Selective Layer	µm	0.05	0.05
Membrane Geometry	-	Hollow-fiber	Hollow-fiber
Max Trans-Membrane Pressure	bar	15 (Not tested higher)	15
Hours Tested Without Significant Degradation	-	165	300 (coal)
Manufacturing Cost for Membrane Material	$/m²	32	8
Membrane Performance			
Temperature	°C	25 – 30	50
CO_2 Pressure Normalized Flux	GPU or equivalent	400	1,000
CO_2/H_2O Selectivity	-	0.04	0.01 – 0.02
CO_2/N_2 Selectivity	-	35	50
CO_2/SO_2 Selectivity	-	≈1	<0.5 or >2
Type of Measurement	-	Ideal and mixed	Ideal and mixed
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m^2/m^3	9,000	
Shell-Side Fluid	-	Permeate	
Flue Gas Flowrate	kg/hr	(Unknown at this stage)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95+%, 1 bar	

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pressure Drops Shell/Tube Side	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	(Unknown at this stage)	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Gas permeation in the high-flux polycarbonate and PVDF-based membrane platforms occurs due to a partial pressure driving force across the membrane. The specific permeation mechanism obeyed is the solution-diffusion model for gas transport in nonporous polymers. According to this model, preferential permeation of certain gas species occurs because they are more soluble in the polymer membrane, have a higher diffusion coefficient in the polymer membrane, or both. In this project, the preferentially permeated species CO_2 has both greater diffusivity and greater solubility than N_2 in the polycarbonate- and PVDF-based membranes.

Contaminant Resistance – Membrane resistance to contaminant species (NO_x, SO_2, moisture) found in flue gas was investigated in continuous, seven-day, bench-scale separation performance stability tests with contaminant-containing CO_2/N_2 mixtures. The permeance of the high-flux polycarbonate membrane showed some sensitivity to contaminants such as NO_x, but its selectivity was stable. The new PVDF-based membrane material platform, because of its intrinsically high-chemical resistance, exhibited excellent permeability (permeance) and selectivity stability in the contaminant tests.

Flue Gas Pretreatment Requirements – Before being fed to the membrane system, the flue gas from the plant stack must be conditioned to remove solid particulates and any condensed/entrained liquids (essentially liquid water).

Membrane Replacement Requirements – Based on seven-day, bench-scale contaminant resistance testing results, replacement cycle for high-flux polycarbonate membranes is anticipated to be roughly every five years. In the presence of flue-gas contaminants, the high-flux polycarbonate membrane has shown gradual permeance loss without loss in selectivity in continuous, seven-day testing. For PVDF-based membranes, the replacement cycle is anticipated to be every 10 years because of the excellent chemical and separation performance stability exhibited by them in the presence of flue-gas contaminants in seven-day tests. Much longer-term contaminant exposure testing of these membranes to real coal-derived flue gas, however, is recommended to confirm/refine the above membrane replacement requirements.

Waste Streams Generated – Because the membrane permeates and concentrates water into the CO_2 capture stream, a liquid water stream is recovered by the membrane process during compression of the capture stream to sequestration pressure. A water condensate stream is also produced upstream of membrane stages M1 and M2 because of compression of their feed gas streams, followed by cooling of this compressed gas with cooling water to the optimum membrane operating temperature. The quality of these liquid water streams is not known and will need to be determined.

technology advantages

Membrane-based processes have the potential to provide PC-fired power plants with a cost-effective technology option for CO_2 capture. They are inherently energy-efficient because the membrane enables passive separation of gases. Their compact footprint and modular nature allows for easy installation into an existing PC-fired plant, and, with no moving parts, they are simple to operate and maintain. In addition, the hollow fiber membrane approach taken in this project is particularly well suited for high-volume applications such as the large flue gas volumes that must be handled in post-combustion carbon capture. Hollow-fiber modules have much higher membrane packing density and lower cost-per-membrane area than other module types. The hollow-fiber membrane tubes are economically produced on a commercial scale by using existing fiber manufacturing equipment technology.

R&D challenges

Flue gas properties, such as low CO_2 concentration of 13 to 15 percent, low flue gas pressure of 1 atm, large flue gas volumes, and the presence of moisture and contaminants (sulfur oxides [SO_x], NO_x, and particulate matter), can pose certain challenges for a conventional membrane separation process. These technology challenges are being addressed in this project through the development of new membrane materials with improved CO_2 separation properties and chemical resistance, improved membrane module design and engineering, and novel process design and integration strategies.

results to date/accomplishments

- Development and scale-up of Generon next-generation, high-flux polycarbonate membrane hollow fibers with up to four times higher CO_2 flux (410 GPU) than that of Generon standard polycarbonate membrane fibers.
  - CO_2/N_2 selectivity of high-flux polycarbonate hollow-fiber membrane was comparable to that of standard (current-generation) polycarbonate hollow-fiber membrane. However, it was only 60 to 70 percent of its intrinsic CO_2/N_2 selectivity (35 to 37), meaning that the high-flux polycarbonate membrane properties could still be improved.
  - Fibers of high-flux polycarbonate with 25 percent larger dimensions were successfully spun as an option for managing parasitic axial pressure drops in the module.
  - High-flux polycarbonate membrane would be best operated at temperatures below room temperature to benefit from substantial increase in CO_2/N_2 selectivity without much decrease in CO_2 permeance due to its weak temperature dependence.
  - High-flux polycarbonate membrane displayed some sensitivity to flue-gas contaminants (NO_x and SO_2), which led to a permeance decline but had minimal to no effect on CO_2/N_2 selectivity. This observed sensitivity did not seem to degrade the membrane as it recovered much of its original properties when the contaminants were removed. In practice, therefore, feed pretreatment should be considered for this membrane.
- Successful formation of Generon high-flux polycarbonate membrane fibers into lab-scale modules and larger prototype (2,200 ft^2) modules.
- Development and synthesis of novel Arkema VDF-based copolymers with improved CO_2 permeance and improved CO_2/N_2 selectivity.
  - Copolymerization of a bulky, low-dipole Comonomer A into the VDF chain backbone can increase gas permeability by disrupting chain packing density and crystallinity in the polymer matrix.
  - VDF-co-A copolymer family was developed with up to 17 to 18 times higher CO_2 permeability than the base PVDF homopolymer, while maintaining the CO_2/N_2 selectivity of 24 of the base PVDF.
  - Copolymerization of a bulky, high-dipole Comonomer B into the VDF chain backbone can increase CO_2/N_2 selectivity by enhancing the CO_2 affinity of the polymer while also improving gas permeability relative to the base PVDF homopolymer.

  - VDF-co-B copolymer family was developed with 2.5 to 3 times higher CO_2/N_2 selectivity and six times higher CO_2 permeability than base PVDF homopolymer.
  - Strong temperature dependence of CO_2 permeance in VDF-based polymers could be exploited as a key process variable for increasing and optimizing CO_2 permeance to increase gas processing throughput in the capture process while maintaining reasonable CO_2 removal.
  - VDF-based polymer platform demonstrated excellent stability of its gas separation properties to contaminants SO_2, NO_x, and water vapor.
- Fabrication of the first developmental hollow fibers from new Arkema VDF-based copolymer platform.
  - VDF-A.2 was down-selected for fiber development because it had among the best balance of CO_2 permeability and selectivity of the new copolymers in this fluorinated platform.
  - Synthesis of VDF-A.2 was successfully scaled up to pilot scale to prepare 200 pounds of this resin for fiber development.
  - Fiber tackiness, fiber shape stability, and solvent extraction kinetics were identified as key issues that must be addressed and managed for the VDF-based polymers.
  - Hollow-fiber cores of the VDF-based materials were successfully spun on commercial fiber-spinning equipment. Fibers had good gas flux but exhibited no gas selectivity. Development of a membrane structure with gas selectivity will require additional research and development (R&D) effort.
- Development of three-stage CO_2 capture membrane process design to achieve 90 percent CO_2 capture and 95 percent CO_2 purity.
- Completed techno-economic evaluation of three-stage CO_2 capture membrane process design based on Generon's high-flux polycarbonate hollow-fiber membrane assuming a CO_2 permeance of 400 GPU and CO_2/N_2 selectivity of 35.
  - Increase in levelized cost of electricity (LCOE) estimated for subcritical coal power plant with RTI membrane process was estimated to be ≈73 to 82 percent over that of a plant with no capture, with the LCOE increase depending strongly on compressor cost.
  - Compressor costs made up the majority of equipment costs for the process, with 64 percent of costs attributed to compressors needed for the CO_2 separation process and 10 percent to the compressor for compression/drying of the captured CO_2 product.
  - Cost of CO_2 capture was estimated to be ≈\$42/ton-CO_2.
  - The energy penalty was the biggest contributor to the LCOE.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

"CO_2 Capture Membrane Process for Power Plant Flue Gas," Final Report, April 2012. *http://www.netl.doe.gov/publications/factsheets/program/05313%20Final%20Report%20April%202012.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Toy-RTI-CO2-Capture-Membrane-Process.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Lora-Toy---NT0005313.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/5313-RTI-membrane--Toy--mar09.pdf*.

DEVELOPMENT OF BIOMIMETIC MEMBRANES FOR NEAR-ZERO PC POWER PLANT EMISSIONS

primary project goals

Carbozyme set out to develop an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO_2) from coal and natural gas combustion flue gas. Carbozyme also set out to evaluate a state-of-the-art electrodialytic (EDI) method for CO_2 capture, comparing its performance with that of the CLM.

technical goals

- Scale-up the enzyme-catalyzed, CLM permeator design (4 to 400 m^2) to include multiple units organized as a skid (3×40 m^2) for testing with various coal ranks and natural gas.
- Implement a pretreatment conditioner to ensure that the flue gas constituents will not adversely impact the CLM permeator.
- Validate technology to cost-effectively produce carbonic anhydrase (CA) enzymes for the CLM.
- Test and analyze three different EDI test cells: a controlled pH resin wafer, a hollow fiber fed bipolar membrane (BPM), and an ion exchange membrane-resin wafer (IEM-RW).
- Conduct a commercialization study for both the CLM and EDI technologies.

technical content

The enzyme-based CA CLM membrane process mimics the natural process for removing CO_2 from an organism. An organism's blood stream is used to transport oxygen (O_2) and CO_2 to and from its cells, respectively. CA is an enzyme in the blood that captures the CO_2 from the cells and converts it to bicarbonate (HCO_3^-). The enzyme reverses this reaction in the lungs, allowing the CO_2 to be exhaled. Figure 1 shows the configuration for the enzyme-based CA CLM membrane process Carbozyme set out to develop. The CA CLM membrane is able to incorporate the absorption and stripping processes into a single unit. A membrane module consists of two groups of hollow fibers – one group contains the incoming CO_2 lean flue gas, and the second group contains the CO_2 rich permeate stream. The CA enzyme is contained in a thin-film liquid between the two groups of fibers. The CA helps catalyze the CO_2 to HCO_3^- to pro-

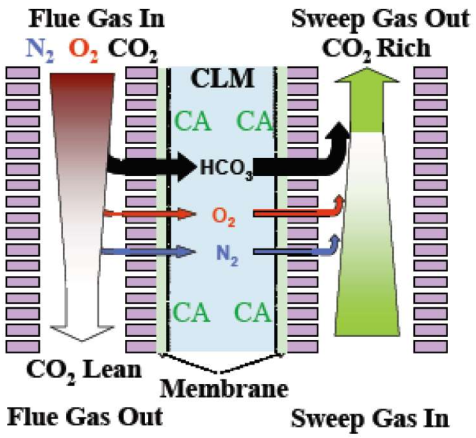

Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

technology maturity:

Laboratory/Bench-Scale, Using Simulated Flue Gas

project focus:

Biomimetic Membrane

participant:

Carbozyme

project number:

FC26-07NT43084
FG26-06NT42824

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Michael Trachtenberg
Carbozyme, Inc.
mct@cz-na.com

partners:

Argonne National Laboratory
EERC
Electrostep
Kansas State University
Siemens
SRI
Visage Energy

performance period:

3/28/07 – 7/31/09

mote permeation across the CO_2 lean membrane and reverses the process, promoting permeation across the CO_2-rich membrane. CA is one of the fastest acting enzymes with a turnover rate of 600,000 katals (catalyzes the hydration of 600,000 molecules of CO_2 per second per molecule of CA).

Figure 2 shows a process schematic for the CA CLM. Pretreated combustion flue gas from the boiler enters the membrane. A vacuum system is used to provide the driving force across the membrane. After the CO_2 is separated from the flue gas, it goes through a knockback condenser for water removal prior to compression. The resulting product is a 95 percent pure CO_2 stream. The remaining flue gas is sent to the plant stack.

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This technique reduces the size of the CO_2 stripper and operates at high pressure, reducing CO_2 compression needs; both reduce electric power consumption. AC has high net CO_2 loading, is a low-cost and readily available reagent, and requires little solvent makeup; the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in absorber solution is extremely low.

The project, in its first phase, constructed a bench-scale batch reactor unit to test the technology at SRI's facility in California. Testing was performed to validate the concept and to determine the optimum operating conditions.

Absorber testing was conducted to first determine the solubility of shifted-gas components (H_2, CO, nitrogen [N_2], argon [Ar]), then to determine the reactivity of CO_2 and H_2S; mixed-gas testing was performed to determine the relative reaction kinetics.

Regenerator testing was conducted to determine CO_2 and H_2S release characteristics, as well as the relative kinetics of CO_2 and H_2S release. Optimal operating conditions derived in bench-scale testing will be used at the pilot-scale test.

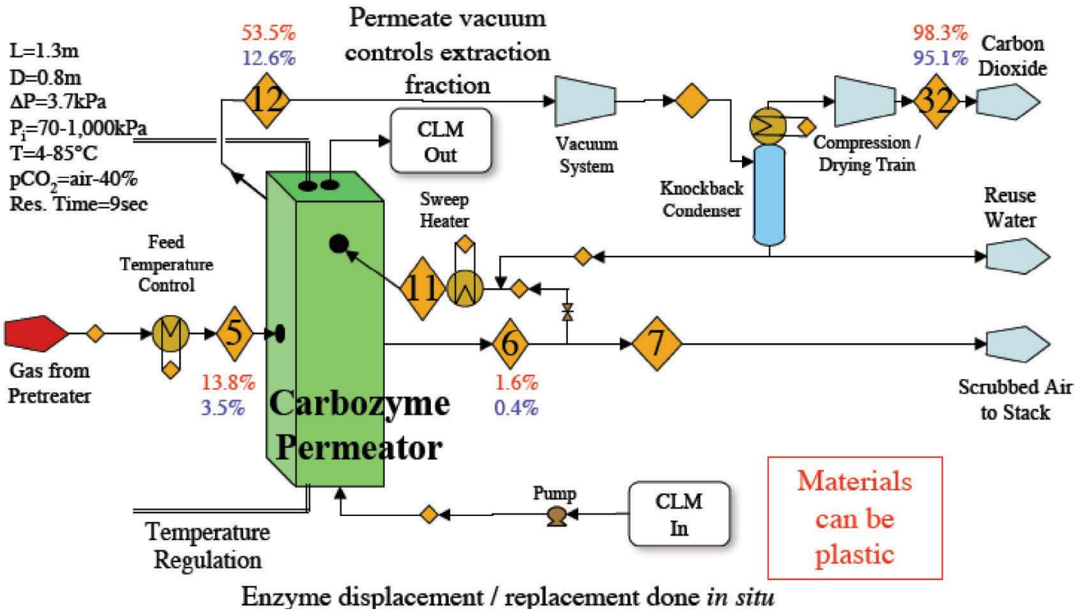

Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

technology advantages

- The CA enzyme catalyst does not contain any toxic chemicals or byproducts, making it more environmentally friendly than competing technologies.
- The CA enzyme catalyst has a fast CO_2 production rate with low energy requirements and boosts separation and purification due to its low nitrogen (N_2) and O_2 solubility.
- The enzyme catalyst is not vulnerable to oxidation or the formation of stable salts.
- The CA CLM system requires only minimal pumping and no heat exchangers, allowing it to consume 30 to 50 percent less energy compared to competing technologies.
- The CA CLM system recycles nearly all of its water and a portion of its waste heat.
- The modular design of the membrane makes it easy to manufacture, install, and scale up.

R&D challenges

- The cost of the purified CA enzyme remains high and production costs will need to be reduced in order to be considered economically viable.
- Early immobilization of the CA enzyme needs to be addressed.
- Sulfur dioxide (SO_2) acidification of the carbonate carrier fluid needs to be addressed via flue gas pretreatment.
- Ionized mercury in the flue gas could reduce enzyme activity.

results to date/accomplishments

Development progress for the CA CLM process was made in several categories, such as flue gas stream analysis and conditioning, enzyme selection, enzyme immobilization, membrane module construction, and economic analysis.

Specific accomplishments include:

- Developed an immobilized CA enzyme catalyst based on a thermophilic form of CA that can maintain a high activity at elevated temperature (≈50°C). The enzyme was immobilized using a proprietary surface activation method using an ultrathin polyamino acid (PAA) layer that can be removed and replaced, as needed. Enzyme testing indicated up to 80 percent of initial activity was retained over a 60-day period.
- Developed a 0.5-m^2 bench-scale CLM permeator that combines absorption and desorption in a single house through use of dual hollow-fiber, spiral-wound, polymer membranes. In this configuration, CO_2 capture is driven by a combination of pressure, vacuum, and temperature. More than 90 percent CO_2 capture was achieved during testing.
- Developed an alternate process technology based on separate absorption/desorption modules using single hollow-fiber, spiral-wound, polymer membranes.
- Fabricated an 11-m^2 CLM module for scale-up testing.
- Developed and tested a flue gas pre-treatment system for the CLM process.
- Developed computer modeling for CLM process components and integrated systems.
- Developed and tested a second technology based on a resin-wafer EDI system that uses a pH shift to accomplish CO_2 absorption/desorption.

next steps

This project ended on July 31, 2009.

available reports/technical papers/presentations

"Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions," Final Report for Project #43084, March 2011.

"Capture of CO_2 by the Carbozyme Permeator," 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2009.

"Development of Biomimetic Membranes for Near-Zero Power Plant Emissions," Annual NETL CO_2 Capture Technology for Existing Plants R&D meeting, Pittsburgh, Pennsylvania, March 2009.

"Membrane-based, Enzyme Facilitated, Efficient, Carbon Dioxide Capture," 9th International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 2008.

"Progress on Carbozyme's HFCLM Permeator Technology Scale-up Project," 7th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2008.

"Biomimetic Membrane for CO_2 Capture from Flue Gas," Final Report for Project #42824, August 2007.

NOVEL DUAL FUNCTIONAL MEMBRANE FOR CONTROLLING CARBON DIOXIDE EMISSIONS FROM FOSSIL-FUELED POWER PLANTS

technology maturity:

Laboratory-Scale, with Simulated Flue Gas

project focus:

Dual Functional, Silica-Based Membrane

participant:

University of New Mexico

project number:

FG26-04NT42120

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

C. Jeffrey Brinker
University of New Mexico
cjbrink@sandia.gov

partners:

T3 Scientific LLC

performance period:

8/23/04 – 4/30/09

primary project goals

The University of New Mexico set out to develop a new, dual-functional, silica-based membrane for carbon dioxide (CO_2) emissions capture from coal-fired power plants.

technical goals

- Achieve a membrane CO_2/nitrogen (N_2) selectivity of 100 and a CO_2 permeance of 1,000 gas permeance units (GPU) or greater.
- Formulate a sol-gel composition to be used in the preparation of clear aminosilicate coatings for membrane deposition onto the siliceous support matrix.
- Setup multi-component gas separation tests for preliminary membrane performance analysis.
- Refine the sol-gel compositions for optimal membrane deposition.
- Study the influence of sulfur dioxide (SO_2), water vapor, and trace oxygen (O_2) on membrane performance.
- Optimize membrane deposition on alternative economical membrane supports.
- Conduct preliminary economic analysis of the membrane process for post-combustion CO_2 capture.
- Identify a processing window that allows reproducible preparation of an asymmetric microporous silica membrane.
- Stabilize membrane performance through a nickel (Ni)-doping approach.
- Prepare an ultra-thin silica membrane using a plasma-assisted, atomic layer deposition technique (PA-ALD).

technical content

The dual-functional, silica-based membrane is prepared by a unique sol-gel dip-coating process for depositing a microporous amino-silicate membrane on a porous tubular ceramic support. It consists of a microporous inorganic siliceous matrix, with amine functional groups

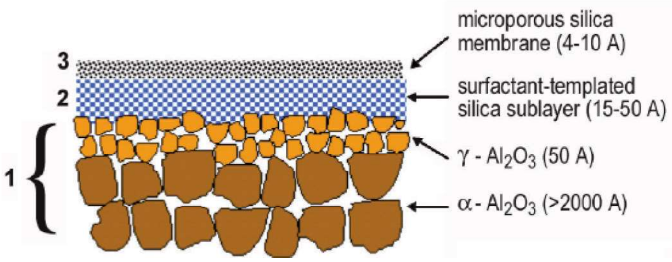

Figure 1: Cross-Section of Membrane

physically immobilized or covalently bonded on the membrane pore walls. Strong interactions between the permeating CO_2 molecules and the amine functional membrane pores enhance surface diffusion of CO_2 on the pore wall of the membrane, subsequently blocking other gases. The membrane is composed of three distinct layers as shown in Figure 1: (1) a commercially available tubular or hollow-fiber ceramic support; (2) a mesoporous surfactant-templated silica sub-layer with pore size 15-50 Å; and (3) a microporous aminosilicate gas separation membrane layer with pore size 4-10 Å.

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Aminosilicate/doped-silicate	
Materials of Fabrication for Support Layer	-	Surfactant-templated silica on alumina	
Nominal Thickness of Selective Layer	μm		
Membrane Geometry	-	Plate-and-frame	Hollow-fiber
Max Trans-Membrane Pressure	bar	3 bar	N/A
Hours Tested Without Significant Degradation	-	168 hrs	100 hrs
Manufacturing Cost for Membrane Material	$\$/m^2$		
Membrane Performance			
Temperature	°C	25 – 250°C	25 – 80°C
CO_2 Pressure Normalized Flux	GPU or equivalent	CO_2: 400 GPU	CO_2: 1,000 GPU
CO_2/H_2O Selectivity	-		
CO_2/N_2 Selectivity	-	CO_2/N_2=80-100 (dry feed); CO_2/N_2 = 50-60 (humidified feed)	CO_2/N_2 = 100
CO_2/SO_2 Selectivity	-		
Type of Measurement	-	Mixed gas	Mixed gas
Proposed Module Design			
Flow Arrangement	-		
Packing Density	m^2/m^3	980	
Shell-Side Fluid	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90%	
Pressure Drops Shell/Tube Side	bar	0.01 – 0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Contaminant Resistance – $SO_2 > 10$ parts per million (ppm).

Flue Gas Pretreatment Requirements – Particulate removal.

Waste Streams Generated – None.

technology advantages

The dual-functional, silica-based membrane will have a higher CO_2 selectivity and permeance compared to conventional membranes that separate gases based on differences in molecular size only.

R&D challenges

- The permeance of the new membrane will need to be increased by a factor of five to meet the research and development (R&D) target.
- The selectivity for the new membrane must remain constant under temperatures of 50 to 70°C and high humidity conditions.
- The presence of particulates in the flue gas could adversely affect membrane performance.
- Previous membrane designs suffered from a gradual reduction in permeance and selectivity under elevated temperature and humidity conditions due to pore shrinkage/blockage.

results to date/accomplishments

- Three classes of microporous, sol-gel derived, silica-based membranes were developed for CO_2 removal under simulated flue gas conditions.
- A novel class of amine-functional, microporous silica membranes was prepared using an amine-derivatized alkoxysilane precursor, exhibiting enhanced CO_2:N_2 selectivity (>70) in the presence of water vapor, but its CO_2 permeance (<1.25 cm^3[STP]/cm^2-min-atm [≈275 GPU]) was below the target.
- Pure siliceous membranes showed higher CO_2 permeance (1.5-2 cm^3[STP]/cm^2-min-atm [≈330-440 GPU]), but subsequent densification occurred under prolonged simulated flue gas conditions.
- Nickel oxide (NiO) was incorporated into the membrane's microporous network to retard densification and achieved CO_2 permeance of 0.5 cm^3(STP)/cm^2-min-atm (≈110 GPU) and CO_2:N_2 selectivity of ≈50 after 163 hours exposed to simulated flue gas conditions.
- The implementation of a novel ALD processing scheme shows evidence that a vapor-processed membrane can exhibit higher thermal/structural stability combined with higher flux and selectivity compared to the traditional liquid phase processing approach (sol-gel).

next steps

This project ended on April 30, 2009.

available reports/technical papers/presentations

“Novel Dual-Functional Membrane for Controlling Carbon Dioxide Emissions from Fossil Fuel Power Plants,” Final Scientific/Technical Report, August 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/2009Novel-Dual-Functional-Membrane-for-Controlling-Carbon-Di.pdf*.

“Tubular Ceramic-Supported Sol-Gel Silica-Based Membranes for Flue Gas Carbon Dioxide Capture and Sequestration,” J. Memb. Sci., 341 (2009) 30-36.

“Novel Dual-Functional Membrane for CO_2 Capture,” Seventh Annual Carbon Capture and Sequestration Conference, Pittsburgh, Pennsylvania, May 2008.

“Anodic Alumina Supported Dual-Layer Microporous Silica Membranes,” J. Memb. Sci., 287, (2007) 157-161.

“Microporous Sol-Gel Derived Aminosilicate Membrane for Enhanced Carbon Dioxide Separation,” Separation and Purification Technology, 42(3) (2005) 249-257.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: POST-COMBUSTION NOVEL CONCEPTS

Supersonic Post-Combustion Inertial CO_2 Extraction System

primary project goals

Orbital ATK, Inc. (OA) developed an inertial carbon dioxide (CO_2) extraction system (ICES) that converts CO_2 from flue gas to solid CO_2 (dry ice) using supersonic expansion followed by inertial separation. The project included bench-scale testing of the system with simulated flue gas.

technical goals

- Demonstrate ICES at bench-scale including condensation, migration, CO_2 removal, and diffusion of the CO_2-depleted flue gas to atmospheric pressure.
- Develop approach to obtain condensed CO_2 particle size required for effective migration and separation.
- Demonstrate pressure recovery efficiency of system consistent with economic goals.
- Demonstrate CO_2 capture efficiency.

technical content

Orbital ATK, Inc. designed an inertial CO_2 extraction system (ICES) that aims to achieve an overall reduction in total carbon capture cost for post-combustion CO_2 capture. The ICES system, shown in Figure 1, is derived from aerospace applications and is based on supersonic inertial separation technology. Compressed flue gas is directed to a converging-diverging nozzle and undergoes supersonic expansion (high velocity, low pressure and temperature), which results in CO_2 desublimation. Turning the supersonic flow in the curved flow path causes inertial separation of the dense, solid CO_2 particles, which are collected in a CO_2-rich stream through a duct in the wall into a cyclone separator where the CO_2 solids are collected. The CO_2-depleted stream is diffused and sent to the stack.

Factors for improved performance of the ICES system included controlling and increasing CO_2 particle size to increase migration and capture, pre-cooling of the flue gas to enable subsonic condensation and promote heterogeneous nucleation for larger particles, and efficient pressure recovery. The compact design, along with efficiencies in CO_2 capture, reduces costs of the carbon capture system. An initial techno-economic assessment by Worley Parsons estimated a $41.80/tonne CO_2 captured for an ICES plant, with cost savings coming from lower capital costs (smaller equipment), lower operating costs (no moving parts, chemicals or media), and improved capture efficiency compared to a typical amine solvent-based plant. However, further studies found that more compression is required due to lower pressure recovery than predicted and, therefore, a cost of >$50/tonne CO_2 captured is anticipated. ICES is expected to have comparatively favorable economics for applications requiring less capture and/or applications with lower CO_2 concentration since compression costs scale with these parameters.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Supersonic Inertial CO_2 Extraction System

participant:

Orbital ATK, Inc.

project number:

FE0013122

predecessor projects:

N/A

NETL project manager:

Andrew O'Palko
andrew.opalko@netl.doe.gov

principal investigator:

Dr. Vladimir Balepin
Alliant Techsystems Operations LLC
vladimir.balepin@orbitalatk.com

partners:

ACENT Laboratories LLC; Electric Power Research Institute; Ohio State University, New York State Energy Research and Development Authority, WorleyParsons Group, Inc.

start date:

10.01.2013

percent complete:

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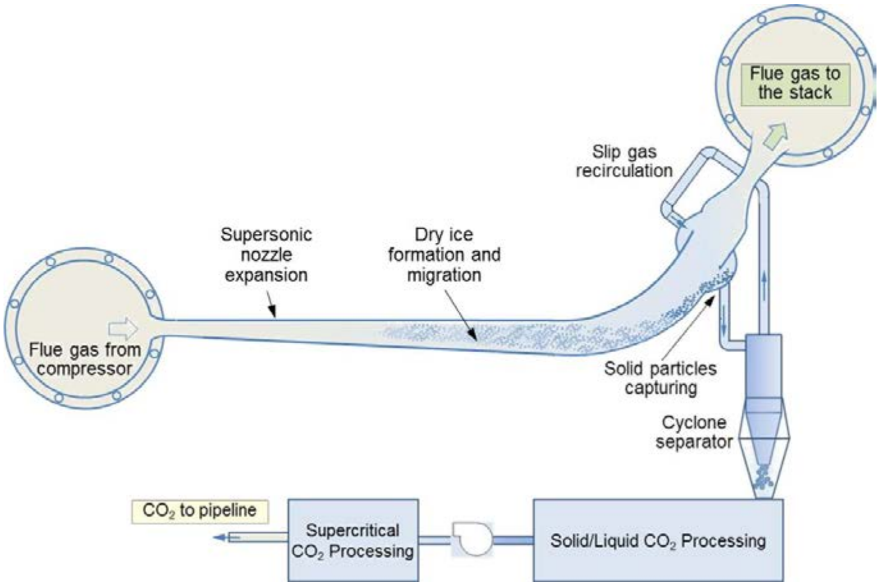

Figure 1: ICES system

Lab-scale testing of the system in a previous project has shown that CO_2 particles of >2.5 μm is required to ensure efficient inertial migration. Initial test results also proved that CO_2 only condenses on solid or liquid media in the flow (heterogeneous condensation). This led to the conclusion that solid CO_2 seeding is the most viable path to 90 percent CO_2 capture by causing flue gas CO_2 to condense on particles that are already >2.5 μm. Preliminary testing on a bench-scale apparatus (Figure 2) using a liquid throttle to inject CO_2 of a controlled particle size in the duct demonstrated >50 percent capture of solid CO_2 and indicated a higher amount of CO_2 captured with a lower inlet temperature. An approach was developed to recirculate a fraction of the collected liquid CO_2 back to the inlet to achieve additional cooling at the inlet along with the creation of large "seeded" particles to promote heterogeneous nucleation capable of migration. However, compression requirements would further increase with this method since more energy would be needed to accelerate the added mass of the recycled CO_2 to high speed. Based on thermodynamic analyses, a method for pre-cooling of the flue gas using captured CO_2 as a "cold sink" was determined to be the best approach. This pre-cooling enables subsonic condensation of a small quantity of CO_2 (and trace water) resulting in "in situ" seeding without the need to recirculate solid CO_2. Testing of a subsonic ICES system with pre-cooling by liquid nitrogen showed that a significant amount of CO_2 condensed into large CO_2 particles with an average size of 30–40 μm.

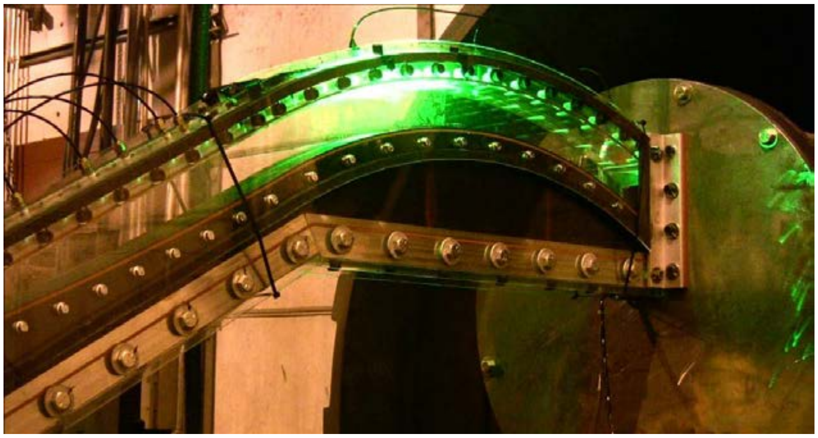

Figure 2: Bench-scale ICES test apparatus illuminated with laser sheet

Scaling the technology for use in a full-scale power plant involves combining multiple ICES units for increased capacity. The compactness of the group of ICES units, as shown in the proposed plant configuration in Figure 3, leads to substantial reductions in the footprint capture plant compared to a similar capacity capture plant using amine solvent capture technology (8,000 m^2 vs. 20–30,000 m^2). Stacking the ICES nozzles and compressors further reduces the footprint.

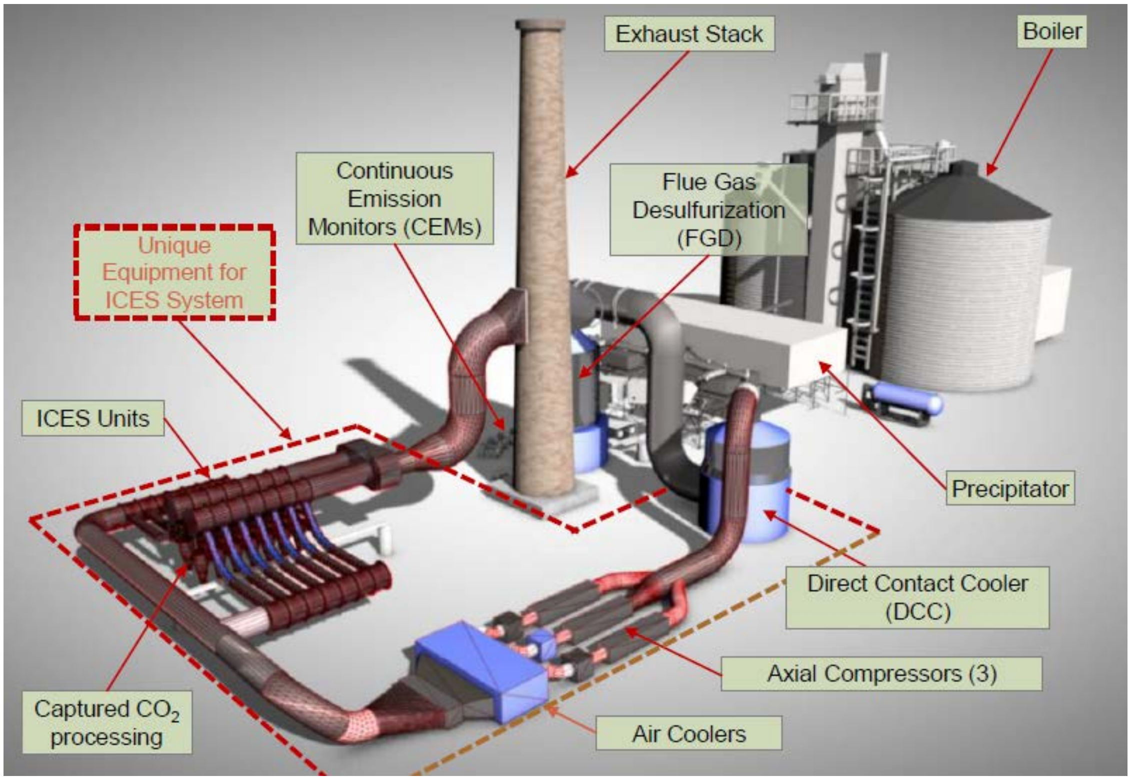

Figure 3: ICES plant layout and footprint

Definitions:

Inertial Separation – Method that uses a rapid change in air direction and principles of inertia to separate particulate from an air stream.

Heterogeneous nucleation **–** Process that occurs in the formation of a crystal from a solution, liquid, or vapor, in which particles become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.

technology advantages

- No moving parts, chemicals/additives, or consumable media.
- No refrigeration expense—low temperatures from supersonic expansion.
- Inexpensive construction based on sheet metal and concrete.
- Small equipment footprint.
- "Cold sink" available from accumulated solid CO_2.
- Costs driven by flue gas compression.

R&D challenges

- Development of optimized supersonic contour to maximize particle size and migration and minimize pressure losses.
- Minimization of slip gas that is removed with solid CO_2.
- CO_2 purity—condensable flue gas impurities removed along with CO_2.
- Solid CO_2 processing.
- Optimization of flow path pressure recovery.

status

Testing of a bench-scale capture duct/diffuser system achieved ≥50 percent CO_2 capture. Testing of a subsonic ICES test article demonstrated large CO_2 particle formation through partial subsonic condensation enabled by pre-cooling of the flue gas. The pre-cooling approach addresses the increase in compression requirements that evolved from thermodynamic modeling efforts. Future work will continue optimization of the ICES for a range of CO_2 concentrations and/or CO_2 capture levels to identify the most favorable operating conditions.

available reports/technical papers/presentations

"Supersonic Post-Combustion Inertial CO_2 Extraction System," Final Report, April 2017.
https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/Final-Report-ATK-FE0013122-April-2017.pdf

Castrogiovanni, A., Balepin, V., Robertson, A., Calayag, B., "Supersonic Post-Combustion Inertial CO_2 Extraction System," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016.
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Balepin, V., Castrogiovanni, A., Robertson, A., Calayag, B., "Supersonic Post-Combustion Inertial CO_2 Extraction System," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.
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NOVEL CONCEPTS FOR THE COMPRESSION OF LARGE VOLUMES OF CO_2

primary project goals

Southwest Research Institute (SwRI) is developing novel compression technology concepts to reduce carbon dioxide (CO_2) compression power requirements by 10 percent compared to conventional compressor designs. The basic concept is a semi-isothermal compression process where the CO_2 is continually cooled using an internal cooling jacket rather than using conventional interstage cooling. The project includes thermodynamic testing (Phase I), prototype testing (Phase II), and a full-scale demonstration of a multistage, internally cooled diaphragm pilot test (Phase III).

technical goals

Phase III

- Design and construct a pilot-scale demonstration of a multistage internally cooled compressor diaphragm design.
- Complete a comprehensive thermodynamic and cost analysis of both pulverized coal (PC) and integrated gasification combined cycle (IGCC) plant incorporating the new compression technology.
- Design a multistage diaphragm and test loop.
- Design, fabricate, and test a third-generation cooled diaphragm and test in a single-stage test rig.

technical content

In the cooled diaphragm concept, the gas is continually cooled after each stage in the flow path through the compressor. A cooling jacket insert is used in the diaphragm of each stage to provide continuous cooling. Figure 1 shows a conceptual design for an internally cooled compressor. The flow of the CO_2 is shown in red, while the cooling liquid is shown in blue.

SwRI examined a number of different compression options to find the ones that would consume the least amount of power. Figure 2 shows how two hypothetical compression processes can achieve the same pressure, but still consume different quantities of power. The isothermal compression, even at 60 percent efficiency, requires less power than the isentropic compression at 100 percent efficiency. Therefore, efficiency alone cannot be used as a figure of merit for the compression process.

Figure 3 shows the pressure/enthalpy curves for six of the options examined by SwRI. While liquefaction and pumping is a viable option and may be superior to a pure compression route in cold climates, the semi-isothermal compression proved to be superior when all of the heat exchanger performance and other losses were taken into account.

technology maturity:
Pilot-Scale, 90 tonnes/hr

project focus:
Evaluation of Compression Efficiency Improvements

participant:
Southwest Research Institute

project number:
FC26-05NT42650

NETL project manager:
Travis Shultz
travis.shultz@netl.doe.gov

principal investigator:
Jeffery Moore
Southwest Research Institute
jeff.moore@swri.org

partners:
Dresser-Rand

performance period:
9/28/2005 – 6/30/2014

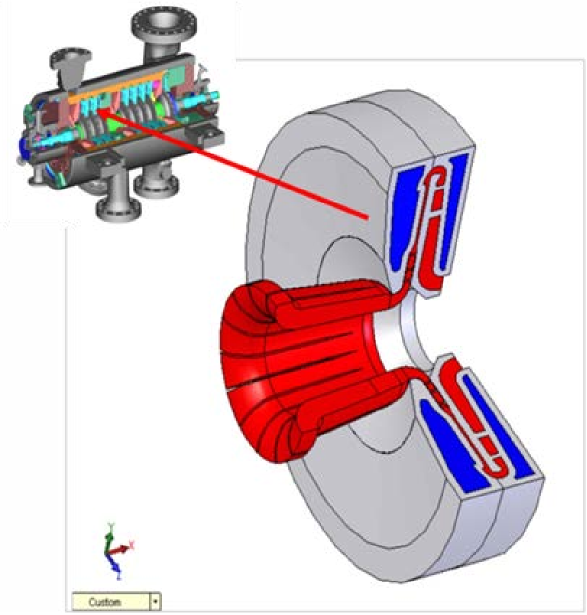

Figure 1: Design for an Internally Cooled Compressor

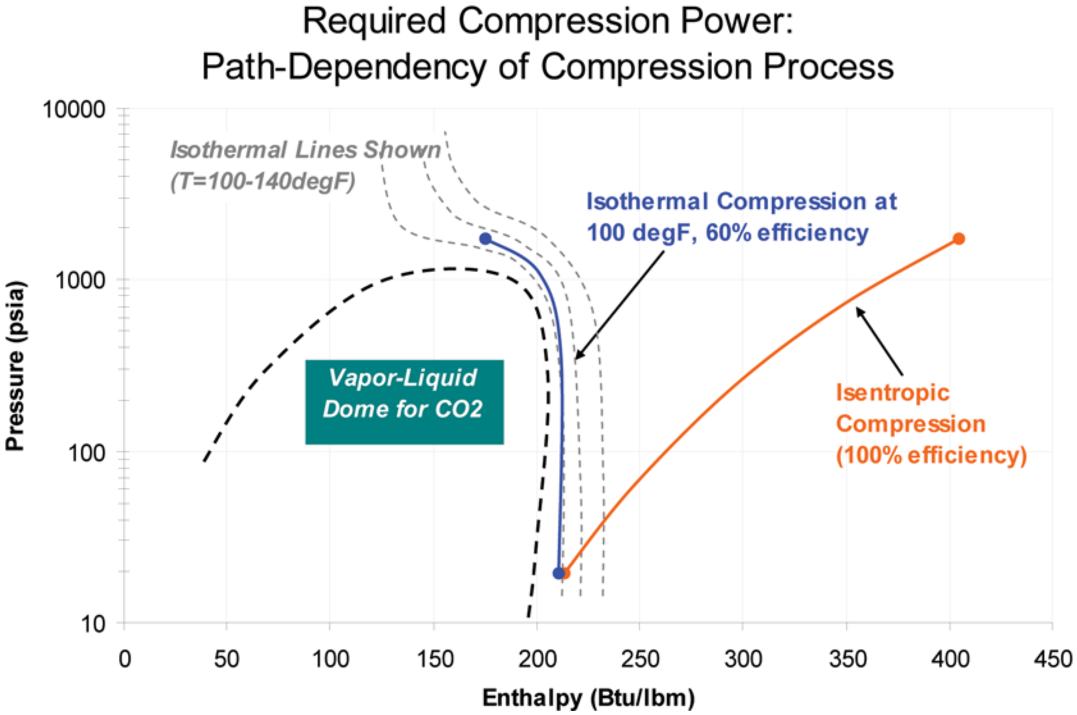

Figure 2: Example of Path Dependency of Compression Power

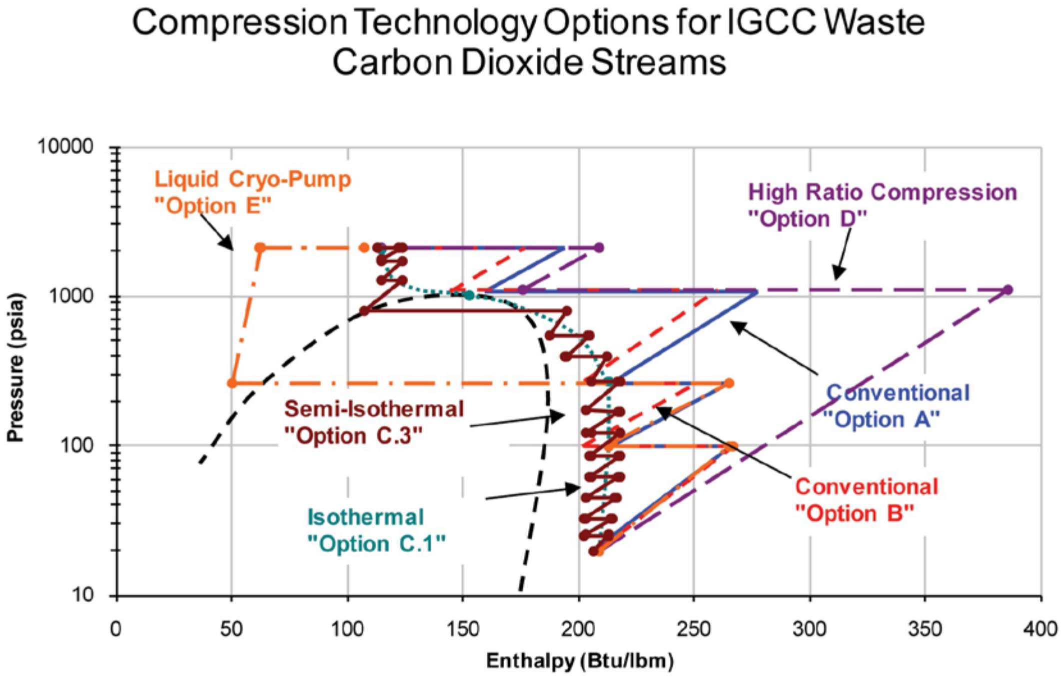

Figure 3: Required Compression Power for the Investigated Technology Options

Table 1 presents a description of the compression and cooling technology options and the resultant power requirements for the U.S. Department of Energy (DOE) 550-megawatt (MW) PC reference power plant with carbon capture using an amine process (≈1.3 million lb/hr CO2 stream, Ramezan 2007)

- Single stream inlet pressure/temperature = 14.8 psia/115 °F
- Discharge pressure = 2,150 psia
- Intercooler/after-cooler exit temperature = 115 °F

The following configurations were analyzed for power comparisons:

1. DOE baseline (efficiencies and refrigeration/ liquefaction cycle performance calibrated to match data in [1])
2. Back-to-back LP and HP compressors with uncooled diaphragms
3. Back-to-back LP and HP compressors with cooled diaphragms, 15 percent effectiveness, 85 °F cooling water
4. Back-to-back LP and HP compressors with cooled diaphragms, 20 percent effectiveness, 85 °F cooling water

The power calculations in this analysis include gas horsepower for compression, cooling horsepower required for liquefaction, pumping horsepower, and gearbox power losses of 2 percent. The estimates exclude bearing and windage losses and power required for the pumping and chilling of cooling water.

The overall compression system analysis results for the methods shown above are displayed in Table 1. A back-to-back compressor with a cooled diaphragm is expected to achieve 10.4–11.7 percent power savings (15–20 percent effectiveness) relative to the DOE baseline case.

TABLE 1. OVERALL COMPRESSION POWER SAVINGS ANALYSIS RESULTS

Case Description	Assumed HX Effectiveness	Power Savings
DOE Baseline	NA	0%
D-R B2B LP and HP Uncooled Diaphragm	0%	6.6%
D-R B2B LP and HP with Cooled Diaphragm	15%	10.4%
D-R B2B LP and HP with Cooled Diaphragm	20%	11.7%

The goal of the current work was to develop and construct a pilot-scale demonstration compression plant to optimize CO_2 compression, as well as perform a balance of plant measurement for total power required and savings realized by improving on the technology developed in Phase II, but in a multi-stage version of the cooled diaphragm design. A new compressor, based on a Dresser-Rand DATUM® D12 frame size, consisted of a six-stage, back-to-back centrifugal compressor (D12R6B) that incorporated the cooled diaphragms. A new test loop with required coolers, valves, and piping was constructed to test this new compressor. The cooled diaphragm, compressor, and loop design, commissioning, and testing will be discussed in this paper. The compressor impeller selection was made for an adiabatic compressor for the design point of 15 psia (1.03 bara) to 250 psia (17.2 bara) for a mass flow of 15.1 lbm/sec (6.85 kg/s). This flow is equivalent to the CO_2 produced by a 35 MW coal fired power plant. The design speed of the compressor is 11,403 rpm and is driven by a 3 MW electric motor through a speed increasing gearbox.

The compressor package was delivered and set, leveled, and bolted to 20 sub-sole plates (Figure 4). Hand valves, control valves, orifice plates, flow conditioners, strainers, and the cooling tower were received and installed. The heat exchangers and piping were assembled and the cooling water supply was tested through the process heat exchangers. The completed pipe assembly is shown in Figure 5. A venting control valve is also used to maintain the desired suction pressure to the compressor. Cooling water was provided to the heat exchangers and compressor diaphragm via an 800 gpm evaporative cooling tower.

Figure 4. Installed Dresser-Rand Datum Compressor Package

The compressor package and pipe loop were commissioned, including oil flush, pipe alignment, shaft alignment, and mechanical testing. All mechanical parameters of the compressor met manufacturer’s specifications.

Figure 5. Pipe Loop Assembly Aerial View

Several compressor operating configurations were tested in order to verify compressor performance and determine the effects of the cooled diaphragms. The adiabatic tests (with no cooling water) showed close correlation to the predicted aerodynamic performance maps. These tests established a baseline temperature distribution and power. The liquid cooling system was commissioned and tuned to provide the correct flow distribution to the diaphragms. The subsequent cooled diaphragm testing showed similar head-flow characteristic curves, but slightly higher head and pressure ratio for a given flow due to the increased volume reduction caused by lower stage discharge temperatures.

The polytropic head for varying flow rates from Test 1 is plotted in Figure 6 for the two sections. The adiabatic test points are shown in blue, and the data points for testing with cooling water at the two different flow rates are shown in red and green. The solid black line denotes the predicted adiabatic curve. All data are normalized with respect to the adiabatic test data at the design flow.

The measured adiabatic data were reasonably close to the predicted adiabatic curve, with polytropic head for Sections 1 and 2 measured to be slightly lower and higher than predicted near the design point, respectively. The data also showed that diaphragm cooling changed the characteristics of the speed line slightly by increasing the volume flow capacity for each section, particularly near the choke side of the map. This performance change is attributed to the gas volume reduction that occurred as the gas was cooled in the diaphragm, which caused the latter stages in each section to stay out of choke and operate closer to their design point. The opposite would be true at low flow operation allowing the flow range to be extended by shutting off cooling flow when operating near the surge line. Since the introduction of cooling water affected the head characteristics, the speed during the cooled tests was reduced to match identical discharge pressure as the adiabatic test in order to allow a direct comparison on power.

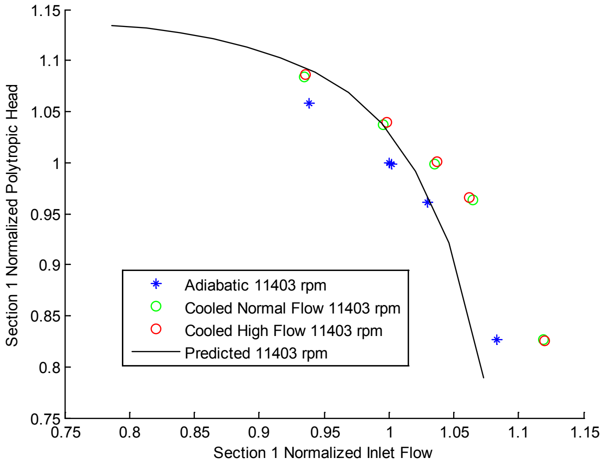

Figure 6. Section 1 Normalized Polytropic Head vs. Normalized Flow (Test 1)

Internal temperature measurements were taken at various points along the compressor. At each of these points, several temperature and pressure measurements were taken at different circumferential locations. These data points were averaged to get a temperature and pressure at each location. For both the adiabatic and cooled cases, the predicted design point temperature was plotted against the actual design point temperature in Figure 7 for Section 1. These results indicate that the adiabatic temperature rise was slightly higher than predicted and cooled temperatures were slightly lower than predicted but showed good agreement overall. The measured discharge temperature was over 100 °F lower for the cooled case.

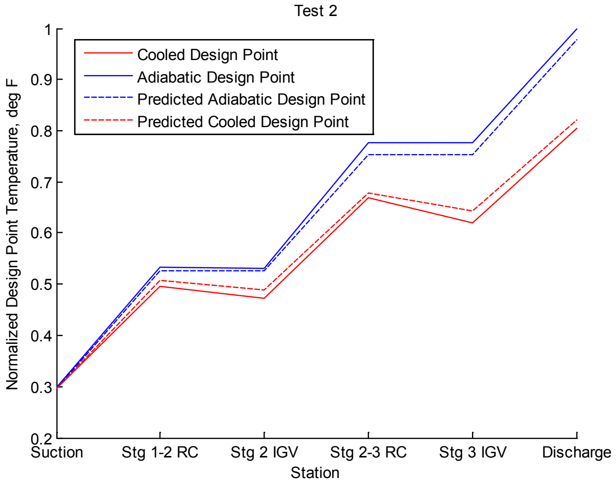

Figure 7. Section 1 Comparison with Predicted Normalized Temperature for Design Flow Conditions

The data show that the cooled diaphragms reduce power consumption by 3–8 percent when the compressor is operated as a back-to-back unit, with the higher power savings at high flow operating points using the high speed torquemeter for reference as shown in Table 2. Additional performance savings could be realized by adding more stages and running the compressor at a slower speed.

TABLE 2. HORSEPOWER PERCENT SAVINGS WITH INTERCOOLER

Point	Adiabatic versus Cooled Diaphragm Difference (%)
1	7.99
2	6.28
3 (design PR)	3.24 (predicted 2.9%)
4	3.03
5	3.01
6	3.32

The results from Test 3 (no intercooling to simulate a straight-through compressor), as shown in Table 3, showed even higher power savings of 9 percent at the design point when matching pressure ratio and speed. Based on the trends seen in back-to-back testing, power savings are expected to be even higher at higher flows exceeding the 10 percent goal of this program.

TABLE 3. HORSEPOWER PERCENT SAVINGS WITH NO INTERCOOLER

Power Savings (%) A. Matching speed and pressure ratio	Power Savings (%) B. Matching flow and pressure ratio
5.64	9.00

technology advantages

- New compression process could use up to 10 percent less power compared to commercially available inline centrifugal compressors.
- Applicable to all types of power plants, including PC, IGCC, and oxy-fuel.
- Could result in significant capital savings and reliability improvement compared to an integrally geared compressor.
- Inline compressors are scalable to large power plants, and their reliability is well proven in LNG and Ethylene service.

R&D challenges

- The wide range of CO_2 output from the power plant based on required electrical output.
- Carbon dioxide compression technology must have high reliability.
- IGCC plants contain multiple CO_2 streams at different pressures.
- The volume reduction during the compression can exceed 500:1.

results to date/accomplishments

- Development complete of multistage internally cooled diaphragm.
- Detailed design of Dresser-Rand DATUM compressor with multistage cooled diaphragms is complete.
- Design of a closed-loop to test back-to-back compressor is complete.
- Pilot-scale demonstration compression plant was developed and constructed.
- Measured the CO_2 baseline compressor performance with and without diaphragm cooling.
- Comparative testing of adiabatic and cooled tests at equivalent inlet conditions shows that the cooled diaphragms reduce power consumption by 3–8 percent when the compressor is operated as a back-to-back unit and over 9 percent when operated as a straight-through compressor with no intercooler.
- The power savings, heat exchanger effectiveness, and temperature drops for the cooled diaphragm were all slightly higher than predicted values.

next steps

This project ended on June 30, 2014.

available reports/technical papers/presentations

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2," presented at the 2013 NETL CO_2 Capture Technology Meeting, July 2013. *http://www.netl.doe.gov/File%20Library/events/2013/CO2%20capture/J-Moore-SWI-Concepts-for-Compression-of-Large-Volumes-of-CO2.pdf*.

Moore, J.J.; et al., "Advance Centrifugal Compression and Pumping for CO_2 Applications," presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012. *http://www.netl.doe.gov/File%20Library/Events/2012/CO2%20Capture%20Meeting/J-Moore-SRI-CO2-Compression.pdf*.

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2 – Phase II," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: PRE-COMBUSTION SOLVENT TECHNOLOGIES

CO_2 Capture from IGCC Gas Streams Using the AC-ABC Process

primary project goals

SRI International (SRI)'s goal was development of a carbon dioxide (CO_2) capture technology for integrated gasification combined cycle (IGCC)-based power plants that uses a high-capacity and low-cost aqueous solution containing ammonium carbonate (AC) that reacts with CO_2 to form ammonium bicarbonate (ABC). SRI partnered with Bechtel Hydrocarbon Technology Solutions (BHTS) to use the Bechtel Pressure Swing Claus (BPSC) process to remove sulfur species from the recovered CO_2 stream.

technical goals

- Test the technology on a bench-scale batch reactor to validate the concept.
- Determine the optimum operating conditions for a small pilot-scale reactor.
- Design and build a small pilot-scale reactor capable of continuous, integrated operation.
- Perform pilot-scale tests to evaluate the process in a coal gasifier environment.
- Perform a technical and economic evaluation of the technology.

technical content

The technology is based on the use of an aqueous ammoniated solution containing AC, which reacts with CO_2 to form ABC.

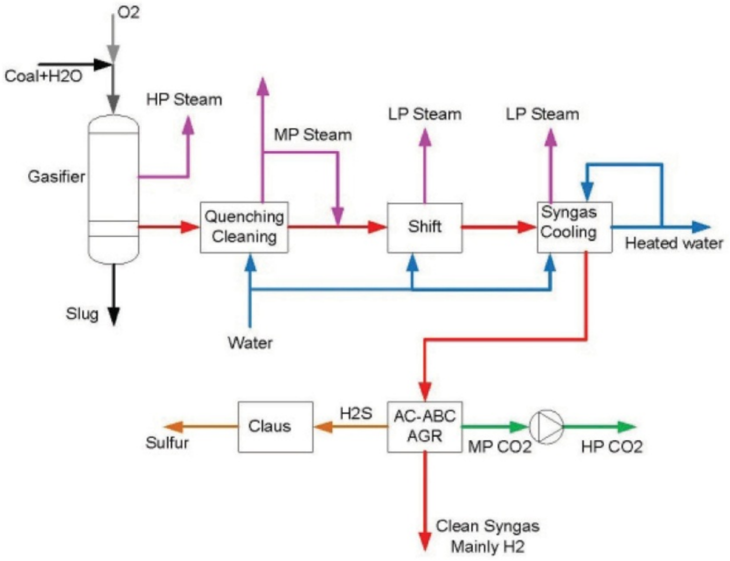

Figure 1: Acid gas removal in a gasification system

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This high-pressure separation technique reduces the size of the CO_2 stripper, the CO_2 compression needs, and the

technology maturity:

Pilot-Scale, Actual Syngas (equivalent to 0.15 MW_e)

project focus:

CO_2 Capture Using AC-ABC Process

participant:

SRI International

project number:

FE0000896

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

Anoop Nagar
SRI International
anoop.nagar@sri.com

partners:

Bechtel Hydrocarbon Technology Solutions, Inc.; EIG, Inc.; National Carbon Capture Center

start date:

09.30.2009

percent complete:

100%

electric power consumption relative to capture at lower syngas pressures. Figure 1 depicts the AC-ABC acid gas removal process in the larger context of a coal gasification and syngas cleanup system.

Figure 2 depicts the flows within the AC-ABC process, showing how acid gases are removed from the syngas in the absorber column, and how they are recovered as a separate gas stream in the stripping column. AC is a low-cost and readily available reagent with high net CO_2 loading capacity, requiring relatively low circulation of solvent between the CO_2/H_2S absorber and CO_2/H_2S stripper. The ammonium carbonate is highly selective to CO_2 and H_2S at the lower temperatures of the gas and solvent in the absorber (solvent entering column at 85 °F), while the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in the absorber solution is extremely low, resulting in minimal losses of syngas species in the absorber. Rich solvent exiting the absorber is regenerated in the stripping column by increasing its temperature (solution entering column at 250 °F), causing the CO_2 and H_2S to evolve as a relatively pure gas stream from the stripper. The pressure is relatively constant in this cycle, with only the temperature being varied, classifying this a temperature-swing absorption cycle for acid gas removal from syngas.

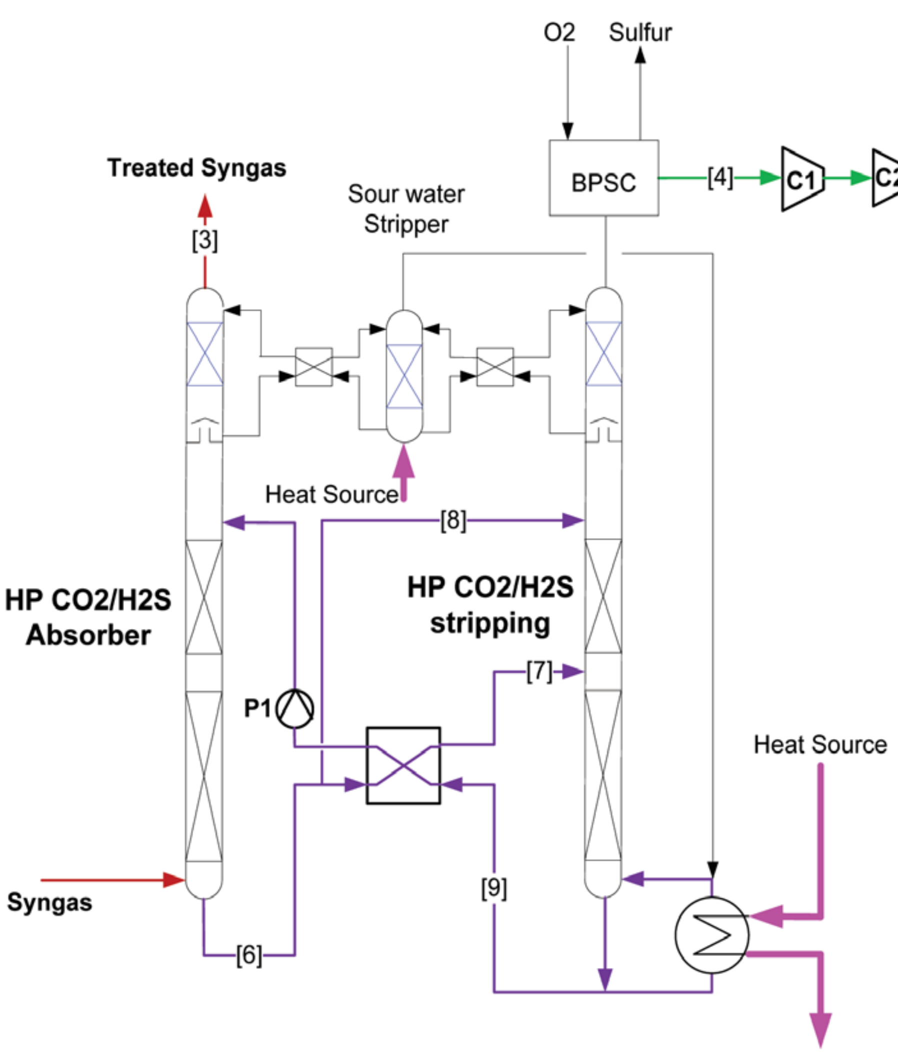

Figure 2: Schematic of the CO_2 and H_2S capture system

Because the AC-ABC process removes a mixture of CO_2 and H_2S, it is necessary to separate the H_2S to enable utilization or storage of the CO_2. Accordingly, the BPSC process was chosen for this purpose downstream from the AC-ABC unit. BPSC is a high-pressure, sub dew point Claus system which recovers H_2S directly from an acid gas stream in the form of elemental molten sulfur, using SO_2 as an oxidant. In this technology, multiple sub dew point reactors are used in rotation (Lead/Lag/Regeneration) similar to a molecular sieve dehydration unit, a pressure swing absorption unit, or a low-pressure sub dew point Claus system. BPSC allows recovery of sulfur species as elemental sulfur while maintaining system pressure. Due to the higher pressures compared to traditional Claus units, equipment size is reduced. Figure 3 shows the basic process scheme of the BPSC system.

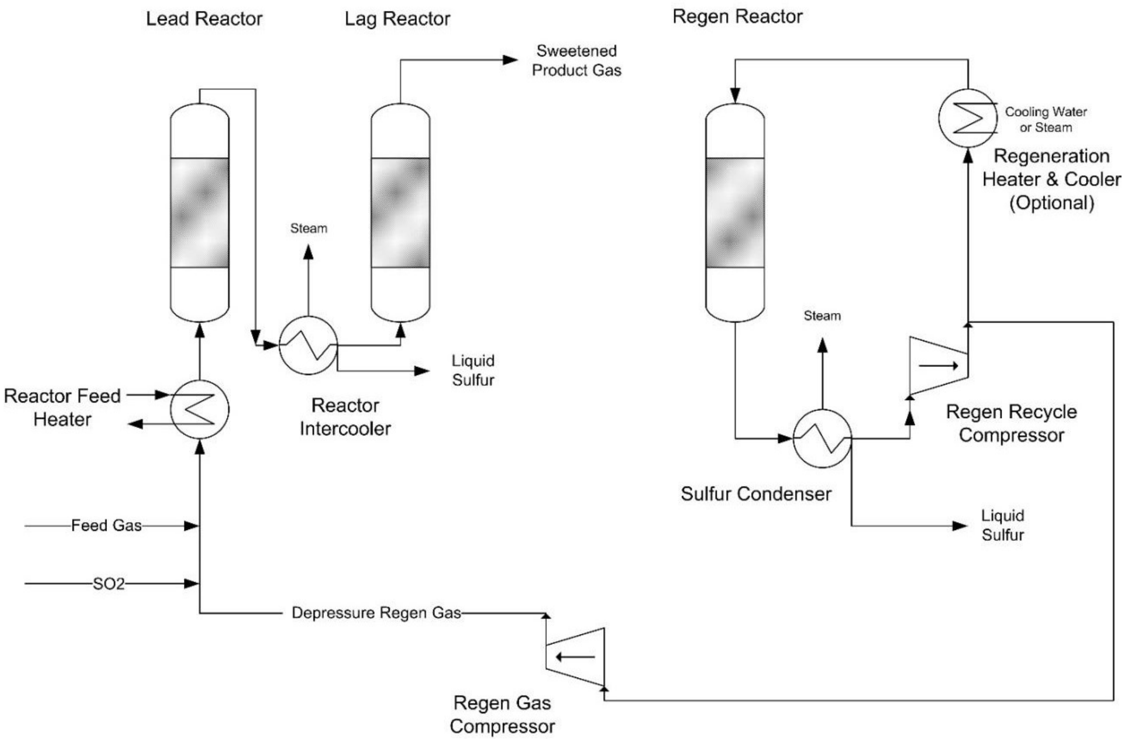

Figure 3: Schematic of the Bechtel pressure swing Claus H_2S removal system

In the BPSC process, SO_2 (produced by oxidizing some of the product sulfur) is introduced to the acid gases ("feed gas") and they are heated indirectly by steam in the "reactor feed heater". Then the mixture is fed to the first or primary on-line reactor ("primary reactor"), where most of the H_2S, carbonyl sulfide (COS), and SO_2 are converted to sulfur and adsorbed on the catalyst. The gas flows through a cooler ("reactor intercooler"), where it is cooled by generating steam. Provisions are made to accommodate any sulfur that may condense at this location. Any recovered sulfur drains to a sulfur pit, and the vapor goes to the next reactor ("secondary reactor/sulfur trap"), which acts as a sulfur trap/guard bed. The product gas is returned to the facility for compression. After about 8–12 hours online, the primary reactor is rotated to regeneration, the secondary reactor moves up to the primary position, and the regenerated reactor is switched to the secondary reactor position. The sulfur-loaded bed is partially regenerated by pressure let down. Flash gas passes through a sulfur condenser and is recompressed in the Regen Recycle Compressor and Regen Gas Compressor prior to being mixed into the BPSC feed stream. There is a heating and cooling cycle ("Regeneration Heater & Cooler") using recycled sweep gas to complete the reactor regeneration.

In 2016, SRI International and EIG Inc. were awarded a patent on the technology for simultaneous high-efficiency capture of CO2 and H2S from pressurized gas, which is at the core of the AC-ABC Process. For further information, refer to U.S. Patent No. 9,463,416 B2, dated October 11, 2016.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	nominal 18	nominal 18
Normal Boiling Point	°C	varies with pressure: 100 °C at 1 atm	varies with pressure: 100 °C at 1 atm
Normal Freezing Point	°C	nominal 0 °C, varies with composition	nominal 0 °C, varies with composition
Vapor Pressure @ 15°C	bar	NH_3 vapor pressure varies with composition and temperature	NH_3 vapor pressure varies with composition and temperature
Manufacturing Cost for Solvent	$/kg	—	cost of anhydrous ammonia typically \$200–\$400/ton
Working Solution			
Concentration	kg/kg	0.1 kg NH_3/kg	0.15 kg NH_3/kg
Specific Gravity (15 °C/15 °C)	-	1.1	1.1
Specific Heat Capacity @ STP	kJ/kg-K	3.5	3.5
Viscosity @ STP	cP	nominal 1	nominal 1
Absorption			
Pressure	bar	20	30
Temperature	°C	25	25–40
Equilibrium CO_2 Loading	mol/mol	varies with the composition of the solution	varies with the composition of the solution
Heat of Absorption	kJ/mol CO_2		40-60
Solution Viscosity	cP	nominal 1	nominal 1
Desorption			
Pressure	bar	30	30
Temperature	°C	<200°C	—
Equilibrium CO_2 Loading	mol/mol	varies with the composition of the solution	varies with the composition of the solution
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr	225	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90% / >95% / 30 bar	
Absorber Pressure Drop	bar	<1 bar	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

STP – Standard temperature and pressure (15 °C, 1 atm).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of MEA and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

$$NH_4OH + CO_2 \leftrightarrow NH_4HCO_3$$

$$(NH_4)_2CO_3 + CO_2 + H_2O \leftrightarrow 2NH_4HCO_3$$

$$NH_4(NH_2CO_2) + CO_2 + 2H_2O \leftrightarrow 2NH_4HCO_3$$

Solvent Contaminant Resistance – The solvent is expected to be resistant to several contaminants nominally present in an IGCC gas stream. Hydrogen sulfide reacts with the solvent, but it can be removed during the regeneration. The ammonia (NH_3) in the IGCC may negate any NH_3 loss from the solvent. The resistance of the solvent to trace metals is not known yet.

Solvent Foaming Tendency – Solvent foaming tendency was not observed in the bench-scale tests.

Syngas Pretreatment Requirements – The IGCC gas stream needs to undergo a water gas shift (WGS) reaction to convert CO to CO_2 and to be cooled to a temperature of 25–50 °C.

Solvent Makeup Requirements – The AC is a readily available commodity chemical, and the makeup requirements are estimated to be small. However, the actual amount will be determined in the field test.

Waste Streams Generated – Ammonium sulfate solution from the capture of trace residual NH_3 in the gas.

Process Design Concept – See Figures 1–3.

Proposed Module Integration – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module.

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	Ar	H_2S
185	68	13.4	0.03	0.6	74.4	10.1	0.6	2000

technology advantages

- Low-cost and stable reactive solution/solvent—low ammonia loss demonstrated in testing.
- Ammoniated solution is very effective in rapid absorption of CO_2 at elevated pressure—CO_2 capture efficiency greater than 99 percent demonstrated in testing.
- The reactive ammoniated solution has a high CO_2 loading capacity (12 percent CO_2 effective loading).
- H_2S can be simultaneously absorbed along with CO_2 in a single absorber column—H_2S capture efficiency greater than 99 percent demonstrated in testing.

- The absorption/loss of fuel gas species like H_2, CO, and CH_4 was very low as shown in testing—therefore high conversion of CO in the syngas is not required to achieve 90 percent reduction of carbon emissions.
- CO_2 stripping in the AC-ABC process can be accomplished at elevated pressures in the range of 20–50 bar, resulting in a 3–7.5 pressure ratio to compress the gas to the pipeline pressure of 150 bar pressure—i.e., the availability of regenerated CO_2 at elevated pressure significantly reduces the compressor requirements for CO_2 sequestration.
- The AC-ABC process does not require compressors other than the CO_2 compressor.
- Both the absorber and regenerator are operated at similar elevated pressure, reducing the need for pumping solvents across pressure boundaries.
- Hot syngas from the shift reactor can be used as the main heat source for the CO_2 stripping, reducing the power output penalty.
- The BPSC process removes H_2S from the high-pressure CO_2 (or syngas) stream with minimal reduction in pressure, which reduces the power output penalty.
- The BPSC process combines the function of three units (solvent, Claus, and Claus tail gas) into one. The thermal oxidizing unit needed for the traditional approach is not needed with BPSC, reducing total carbon footprint.

R&D challenges

- Possible sulfating problem on beds of BPSC process catalyst.
- Difficulty in measurement/quantification of sulfur produced in the BPSC process at pilot scale.
- Difficulties in engineering packing or trays to effectively control ammonia emissions from the absorber at pilot scale.

status

The project was completed in September 2016. In the culmination of project activities, a 0.15-megawatt electric (MW_e) integrated pilot plant was constructed and operated, processing 500 lb/hr of shifted syngas from an air blown gasifier at the National Carbon Capture Center in Wilsonville, Alabama, with total testing duration of over 700 hours. This successfully demonstrated use of the AC-ABC process for carbon dioxide and sulfur capture from actual coal-derived syngas. System availability was considered to be favorable, even at the pilot-scale level.

The results of the techno-economic analysis (with baseline case 750-MW IGCC plant using CO_2 capture using conventional Selexol and traditional Claus plant) indicate that the increase in cost of electricity (COE) with the AC-ABC process will be ~30 percent, and the cost of CO_2 captured is projected to be less than $27/metric ton of CO_2 while meeting DOE's 90 percent CO_2 capture goal.

available reports/technical papers/presentations

Nagar, A. et al., "*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process,*" Final Report, SRI Project P19207 and P21321, Cooperative Agreement No. DE-FE0000896, SRI International, Menlo Park, CA, 16 February 2017.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.

"CO_2 Capture from IGCC Gas Streams Using the AC-ABC Process," presented at the Pre-Combustion CO_2 Capture Kick-Off Meetings, Pittsburgh, PA, November 2009.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: PRE-COMBUSTION SORBENT TECHNOLOGIES

EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE- COMBUSTION CO_2 CAPTURE

primary project goals

URS Group and the University of Illinois at Urbana-Champaign (UIUC) are developing dry carbon dioxide (CO_2) sorbent materials, through the coupling of thermodynamic, molecular simulation, as well as process simulation modeling with novel synthesis methods, that possess superior adsorption and regeneration properties at conditions applicable to water gas shift (WGS) systems. If successful, this project will demonstrate that one or more sorbent materials are able to remove greater than 90 percent of the CO_2 from a simulated synthesis gas (syngas) at conditions applicable to a WGS reactor, thus meeting a key U.S. Department of Energy (DOE) program objective.

technical goals

Specific technical objectives of this project include:

- Determination of optimal CO_2 sorbent properties and operating conditions for CO_2 removal and regeneration and carbon monoxide conversion in a simulated syngas using a combination of computational and experimental methods.
- Development of one or more sorbents that recover high-quality heat during CO_2 adsorption, regenerate at elevated pressure, have minimal deactivation over multiple cycles, have high selectivity at high temperatures, have high adsorption capacity, and have acceptable thermal stability and mechanical integrity. This will result in sorbents capable of 90 percent CO_2 removal with high loading capacities and able to operate at the high temperatures and pressures typically encountered upstream of a WGS reactor. If successful, the sorbents developed in this program will augment or replace the carbon monoxide conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.
- Determine the techno-economic feasibility of the sorption-enhanced WGS (SEWGS) process for removing CO_2.

technical content

URS Group is leading development of a dry sorbent process configured to combine the WGS reaction with CO_2 removal for coal gasification systems. The result will be an SEWGS technology.

A novel approach integrates the use of multiple computational models with sorbent synthesis and characterization activities to develop sorbents with optimal CO_2 removal properties at high temperatures and pressures applicable to WGS applications. Tests evaluate sorbent performance in simulated WGS gas mixtures at commercially relevant conditions. Appropriate data reduction and analysis provides suitable data for a techno-economic analysis to evaluate the feasibility and scaleup potential of the SEWGS technology.

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Sorbent Development for WGS

participant:

URS Group, Inc.

project number:

FE-0000465

NETL project manager:

Elaine Everitt
elaine.everitt@netl.doe.gov

principal investigator:

Carl Richardson
URS Group, Inc.
carl.richardson@urs.com

partners:

Illinois Clean Coal Institute University of Illinois at Urbana-Champaign

performance period:

1/1/10 – 9/30/13

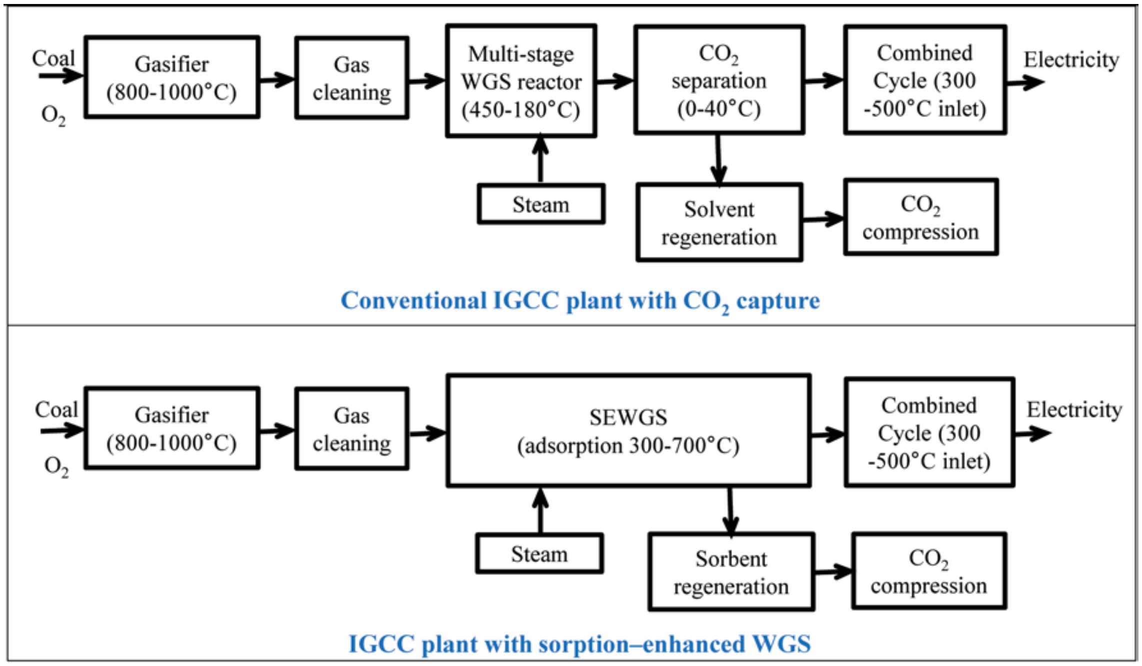

Figure 1: IGCC with SEWGS vs. Conventional IGCC

Process simulation modeling and sorbent molecular and thermodynamic analyses by UIUC allow prediction of optimal sorbent properties and identification of optimal operating temperature and pressure windows to maximize the energy efficiency of the combined WGS and CO_2 capture processes. The thermodynamic study includes developing phase equilibrium diagrams for potential sorbents, identifying optimum operating conditions for CO_2 capture, understanding impacts of syngas impurities, and identifying promising sorbents. Molecular simulation predicts isotherms and properties, kinetics, and dynamics, and identifies sorbents with desired properties using quantum chemistry/mechanics, force field-based molecular dynamics (MD), and reactive dynamics (RD) simulations. Process simulation analyzes various process scenarios for heat integration between SEWGS and integrated gasification combined cycle (IGCC) and process energy performance for individual sorbents.

The first phase testing and modeling efforts guide the synthesis of sorbents with desired pore structure and composition. Synthesis includes use of various precursors, including calcium, magnesium, and other metal oxides, as well as zirconates, titanates, silicates, aluminates, and adsorbent-shift catalyst hybrid. The sorbent down-selection process is guided by the decision tree shown in Figure 2.

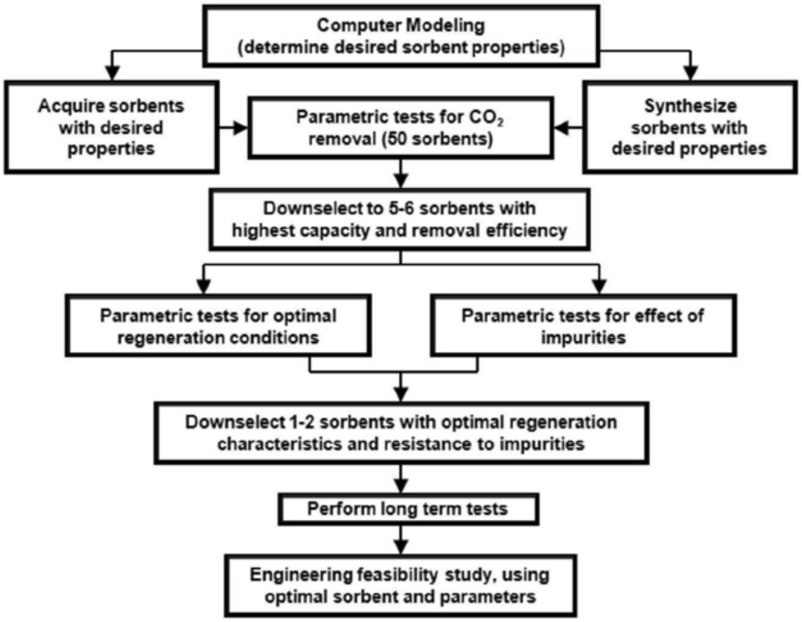

Figure 2: Sorbent Development and Analysis Decision Tree

An atmospheric-pressure thermogravimetric analyzer (TGA) and high temperature and pressure reactor (HTPR) system, capable of 300 pounds per square inch gauge (psig) and 950 °C, are UIUC's primary tools for screening sorbents for CO_2 removal. A URS HTPR provides the capability to evaluate five to seven down-selected sorbents' adsorption performance in the presence of syngas impurities and regeneration performance. Long-term testing is limited to a down-selection of one to two sorbents.

A preliminary engineering study of process feasibility for adsorbing and removing CO_2 as part of the WGS process, and comparison to base WGS operation and other CO_2 removal strategies, is informed by the preceding laboratory test results. Parameters under evaluation include costs of >90 percent removal (cost of electricity [COE], operation and maintenance [O&M]), sorbent costs, anticipated lifetime (i.e., replacement rate), estimated future market costs of precursor materials, handling equipment, sorbent regeneration costs, heat/energy integration, compression costs with SEWGS, unit footprint, and capital costs and scalability.

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density at STP	kg/m^3		TBD
Bulk Density	kg/m^3		TBD
Average Particle Diameter	mm	nano (20–70 nm) or micro meter (0.5–10 µm) level; particles can be pelletized if needed	TBD based on the reactor design analysis
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3		
Solid Heat Capacity at STP	kJ/kg-K	<1	<1
Crush Strength	kg$_f$		
Manufacturing Cost for Solvent	$/kg		
Absorption			
Pressure	bar	30–40	40
Temperature	°C	300–700	550–650
Equilibrium CO_2 Loading	g mol CO_2/kg		
Heat of Absorption	kJ/mol CO_2	100–200	TBD

Desorption			
Pressure	bar	up to 30	highest possible up to 30
Temperature	°C	depends on individual sorbent and highest regeneration pressure achievable	TBD; optimization based on minimal energy limit
Equilibrium CO_2 Loading	mol/mol		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	temperature swing	temperature swing
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 percent, 99 percent	
Adsorber Pressure Drop	bar	depending on sorbent properties, to be determined during project	TBD

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – "Current" is market price of material, if applicable; "Target" is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column. These may be assumed to be 1 atm total flue-gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40 °C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2. Note that for a typical PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

This is a research and development (R&D) program involving fairly immature technology. As such, many target R&D values will be determined during execution of the test program and will be impacted by a number of key process parameters, including sorbent type and cost, sorbent performance and loading capacity, sorbent lifetime, regeneration conditions and cycling parameters, and complexity of integration of optimal adsorption and regeneration processing steps.

Sorbent Heating/Cooling Method – For sorbent regeneration, the sorbent is heated in a fluidized-bed or moving-bed configuration with heat supplied by either hydrogen (H_2) (or syngas) oxy-combustion or steam extracted from the gasification plant steam cycle. Before entering the adsorption bed, the regenerated sorbent is cooled by exchanging heat with inlet regeneration H_2/oxygen (O_2) or syngas. In the adsorption bed, a heat exchanger (such as a boiler tube bundle used in the fluidized-bed boiler) is used for recovering heat generated from CO_2 adsorption.

Heat of Adsorption Handling – Adsorption heat is recovered during CO_2 adsorption by using a heat exchanger to generate steam, which is combined into the gasification plant's steam cycle for electricity generation.

Heat Supply Method for Regeneration – Two methods are considered. One is to burn a small amount of the H_2 or syngas using O_2 to supply heat directly. Another approach is to use the steam from the gasification plant's steam cycle if the regeneration temperature is below 1,000 °F.

Contamination Resistance – This program will evaluate the impact of various syngas impurities on the adsorption and regeneration performance of promising CO_2 sorbents. Sorbents may not be resistant to sulfur species (hydrogen sulfide [H_2S], carbon disulfide [CS_2], etc).

Syngas Pretreatment Requirements – The pretreatment of H_2S/CS_2 is needed for sorbents with no sulfur resistance. If it is determined that the performance of identified sorbents is inhibited by sulfur species present in the syngas, additional work will focus on the development of sorbents materials that are resistant to sulfur; the objective will be to avoid the need for syngas pretreatment associated with this technology.

Waste Streams Generated – Desulfurization byproducts.

technology advantages

- High carbon monoxide conversion with reduced stream addition.
- No or limited WGS catalyst use.
- High-quality adsorption heat usable for generation of high-quality steam.
- Limited gas cooling/reheating requirement downstream.
- No separate CO_2 capture unit required.
- Reduced energy requirement for CO_2 compression.

R&D challenges

- Sorbent pores may be plugged during adsorption, causing capacity and activity loss.
- Long-term capacity and activity stability after multiple cycles.
- Selectivity at high temperature.
- System/reactor issues, such as material transport and handling at high temperature and pressure.

results to date/accomplishments

- More than 40 sorbents were modeled and subsequently down-selected to seven candidates (magnesium oxide [MgO], calcium oxide [CaO], lithium zirconate [Li_2ZrO_3], calcium zirconium oxide [$CaZrO_3$], barium zirconate [$BaZrO_3$], barium titanate [$BaTiO_3$], and barium silicate [$BaSiO_3$]) for further development.
- Process simulations were performed for a baseline IGCC plant with WGS and a Selexol process and compared to an IGCC with SEWGS. These showed a 0.5–2.4 percentage point increase in net thermal efficiency for the simulated plant with SEWGS.
- Molecular simulation studies included quantum chemical (QC) calculations and MD simulations with reactive field force
- (ReaxFF). Molecular simulation was successfully applied to assess carbonation and calcination reactions (CaO).
- The impacts of sorbent structure and the sintering of calcium oxide particles with and without CO_2 chemisorption, and the role of a dopant in reducing the sintering of CaO particles, were also determined.
- More than 60 SEWGS sorbents were synthesized using mechanical alloying (MA), ultrasonic spray pyrolysis (USP), and flame spray pyrolysis (FSP) techniques.
- CaO sorbents prepared by dry and wet ball-milled MA methods exhibited improved CO_2 adsorption capacities and stabilities over commercial $CaCO_3$ materials. The performance of $CaCO_3$ sorbents was improved by doping with inert MgO.
- Hollow, porous $CaCO_3$ sorbents synthesized using the USP method were spheres of ≈1 µm with a shell thickness of 50–100 nm. The CaO generated upon calcination of the $CaCO_3$ exhibited a high surface area (up to 75 m^2/g).

- A 75:25 w/w CaO:$Ca_{12}Al_{14}O_{33}$ (mayenite) sorbent retained 91 percent of its initial CO_2 capacity after 15 cycles and 79 percent after 50 cycles, while a USP CaO only retained 43 percent after 15 cycles.
- The surface area of nano-sized (<70 nm) CaO, ZrO_2-doped CaO, MgO, MgO-doped CaO, and ZrO_2-doped MgO sorbents synthesized using the FSP method ranged between 21 and 54 m^2/g. ZrO_2 was found to be an effective dopant to improve the stability of CaO-based sorbents. A ZrO_2-CaO (Zr:Ca=0.2:1) sorbent maintained its capacity at 0.5 g CO_2/g sorbent over 15 adsorption-desorption cycles.
- An HTPR tube reactor with quarter-inch ID and 1-foot length was also used to test sorbents at UIUC. These tests were performed at 650 °C and CO_2 partial pressures up to 4 bar adsorption conditions.
- Results from the HTPR testing showed sorbents with as high as 0.4 grams of CO_2 per grams of sorbent capacity with the ability to initially shift the WGS completely toward CO_2/H_2.
- A longer term experiment with a simple syngas matrix and N_2/steam regeneration stream showed a USP sorbent (#199) to be stable through 50 adsorption-regeneration cycles, though the sorbent tested had a somewhat diminished initial capacity.

next steps

This project ended on September 30, 2013.

available reports/technical papers/presentations

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"Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture," Pre-Combustion CO_2 Capture Kick-Off Meetings, Pittsburgh, PA, November 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2capture/7-URS%20Dry%20Sorbent%20Kickoff%20Presentatin-111309.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: PRE-COMBUSTION MEMBRANE TECHNOLOGIES

Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery

primary project goals

The Media and Process Technology Inc. (MPT) project objective has been to develop a dual-stage membrane-based process (DSMP) for pre-combustion carbon dioxide (CO_2) capture in an Integrated Gasification Combined Cycle (IGCC) power plant. The process utilizes MPT hydrogen (H_2)-selective carbon molecular sieve (CMS) membranes, in conjunction with conventional water gas shift (WGS) reactors, in the first stage for enhanced production and bulk recovery of H_2. Following cold gas clean-up, a palladium alloy-based membrane is used in the second stage for efficient residual hydrogen recovery from the high-pressure CO_2 gas stream just prior to sequestration.

technical goals

- Characterize the performance of the proposed CMS and Pd-alloy membrane technologies for H_2-CO_2 separations from simulated coal and biomass derived syngas in laboratory scale testing.
- Verify the membrane performance under extreme pressure conditions to qualify the technology for pre-combustion capture.
- Demonstrate the performance stability of the CMS and Pd-alloy multiple tube membrane bundles in actual gasifier syngas in bench-scale testing at the National Carbon Capture Center (NCCC).
- Develop the mathematical model from the performance database obtained in lab and bench-scale work.
- Perform techno-economic assessment (TEA) and environment, health, and safety (EH&S) analysis for the process using the performance database and models developed under this project.

technical content

The technological approach utilizes MPT's commercial ceramic tubular ultrafilter shown in Figure 1 as a support for the high performance H_2 selective membranes. Ultrathin CMS and Pd-alloy layers are deposited to form composite membranes and then packaged into high packing density multiple tube membrane elements as illustrated. In this bundle configuration, the membranes can be operated at high temperatures (up to 500 °C) and pressures (up to at least 1,200 pounds per square inch gauge [psig]) to support warm syngas cleanup in pre-combustion CO_2 capture.

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 0.01 MW_e)

project focus:

Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane

participant:

Media and Process Technology, Inc.

project number:

FE0013064

predecessor projects:

FC26-07NT43057

NETL project manager:

Andrew Jones
andrew.jones@netl.doe.gov

principal investigator:

Paul Liu
Media and Process Technology, Inc.
pliu@mediaandprocess.com

partners:

Technip USA Corporation, University of Southern California

start date:

10.01.2013

percent complete:

100%

Figure 1: MPT ceramic ultrafiltration membranes as supports for high performance H_2 selective CMS and Pd-alloy membranes shown packaged into multiple tube membrane elements

MPT's Dual Stage Membrane Process (DSMP) is illustrated in Figure 2. In the process, the CMS and Pd-alloy membranes are used in distinctly different roles, taking advantage of their specific performance capabilities, to deliver high H_2 and CO_2 recovery from IGCC gasifier syngas. In the DSMP, the CMS membrane is deployed in a multiple step serial arrangement with the WGS reactors in two roles, specifically, (i) to recover the bulk H_2 from the gasifier off-gas and (ii) to enhance the equilibrium conversion in WGS reactors to improve net power output. The CMS membrane is operated at temperatures in the range of 250–300 °C and no syngas pretreatment is necessary, making them complementary to the WGS reactors in terms of operating conditions window and reactor performance enhancement.

In the 1st Stage CMS membrane section, only about 85 percent of the H_2 is recovered due to the "low" pressure (~800 psig) of the syngas and excessive carbon losses to the permeate at higher H_2 recovery levels. Hence, considerable H_2 remains that must be recovered to deliver adequate power output and to meet the cost of capture targets. For this purpose, a Pd-Ag alloy membrane is used in the 2nd stage of the process. Due to the well-known deficiencies of the Pd-based membrane, most specifically its vulnerability to sulfur poisoning and the resultant irreversible damage, it is deployed downstream of the CO_2 compressors. At this location in the process, the syngas has been processed through the Cold Gas Cleanup Unit (CGCU) to remove various contaminants (Hg, sulfur, tar, water, etc.) as required for storage; thus, potential membrane poisons are eliminated. Hence, the major limitation of the Pd membrane technology is avoided while the major benefit, specifically its ultra-high (potentially infinite) selectivity of H_2-to-CO_2, is brought to bear. With the addition of this 2nd stage, >99 percent of the produced H_2 is ultimately recovered.

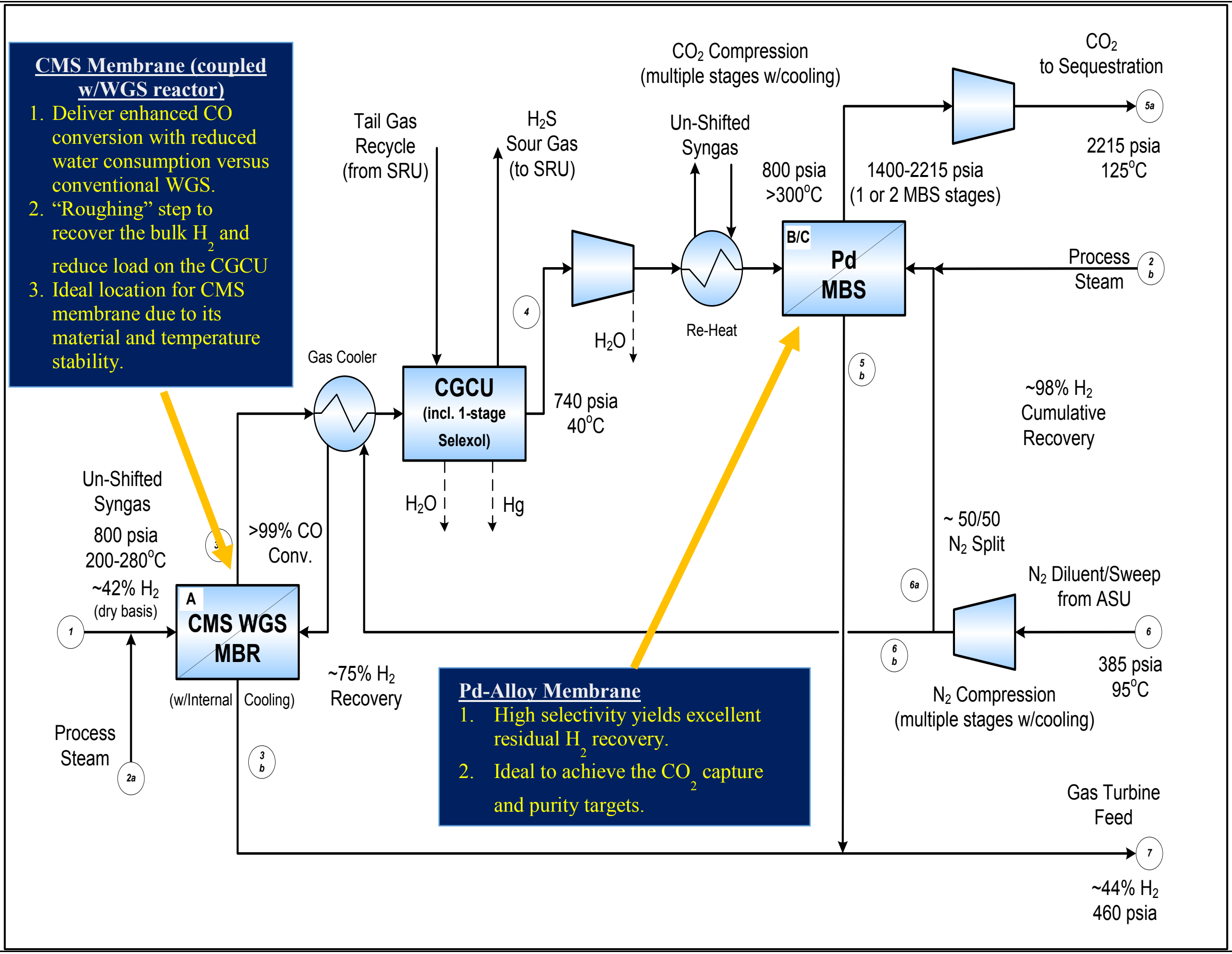

Figure 2: MPT Dual Stage Membrane Process for pre-combustion CO_2 capture

By replacing the dual-stage Selexol unit of the DOE baseline design with the proposed highly efficient and robust membrane technology, the DSMP achieves the DOE carbon capture targets, delivering 90 percent CO_2 capture at 94.5 percent purity, while producing higher net power output (+3 percent, 559 MW) at reduced cost of CO_2 captured (-14 percent, $33.2/tonne) in comparison with the base case.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$\$/m^2$	<1,200	<750
Membrane Performance			
Temperature	°C	250–300	250–300
H_2 Pressure Normalized Flux	GPU or equivalent	500	900
H_2/H_2O Selectivity	—	2–4	>3
H_2/CO_2 Selectivity	—	35	>50
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>10,000	>10,000
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	co/counter-current or cross-flow	
Packing Density	m^2/m^3	>450	
Shell-Side Fluid	—	permeate	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 95 >60	
H_2 Recovery, Purity, and Pressure	%/%/bar	.>80 >90 Up to 20	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	1,500	

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	palladium-alloy	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2 to 5	2 to 5
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82	>82
Hours Tested without Significant Degradation	—	>35,000 hours lab 150 hours at NCCC	—
Manufacturing Cost for Membrane Material	$\$/m^2$	1,800	<1,000
Membrane Performance			
Temperature	°C	250 to 400	250 to 400
H_2 Pressure Normalized Flux	GPU or equivalent	2,000 to >5,000	1,000 to >5,000
H_2/H_2O Selectivity	—	1,000 to >5,000	1,000 to >5,000
H_2/CO_2 Selectivity	—	1,000 to >5,000	1,000 to >5,000
H_2/H_2S Selectivity	—	N/A	N/A
Sulfur Tolerance	ppm	<10	<10
Type of Measurement	—	mixed gas.	mixed gas
Proposed Module Design			
Flow Arrangement	—	co- or counter-current	
Packing Density	m^2/m^3	450	
Shell-Side Fluid	—	feed/retentate	
Syngas Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	>99 93 to 94 >1,000	
H_2 Recovery, Purity, and Pressure	%/%/bar	>99 >99 1.2	
Pressure Drops Shell/Tube Side	bar	N/A	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	260	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – CMS: molecular sieving. Pd-alloy: H_2 dissolution and permeation.

Contaminant Resistance –.CMS: stable in gasifier raw syngas testing conducted at NCCC. Pd-alloy: stable in gasifier syngas with the removal of sulfur and tar species.

Syngas Pretreatment Requirements – CMS: No syngas pretreatment required. Pd-alloy: sulfur and tar-like species removal required.

Membrane Replacement Requirements – Unknown but lifetimes of >16,000 hours for the CMS and >35,000 hours for the Pd-alloy membranes have been demonstrated with no apparent loss in performance.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

Proposed Module Integration –

Membrane Material	Pressure psia	Temperature °F	Composition						
			vol%						ppmv
			CO_2	CO	CH_4	N_2, Ar	H_2	H_2O	H_2S
CMS	800	440–540	27.4	5.5	<1	~1	40.8	24.5	>5,000
Pd-alloy	>1,000	480–570	87.8	0.5	<1	~3	8.4	0.17	<10

technology advantages

- The proposed DSMP matches specific capabilities and properties of the CMS (high material stability) and Pd-alloy (high H_2 selectivity) membranes to different separation requirements at separate stages in the process, enabling efficient gas separations performance.
- The proposed DSMP delivers significant cost savings in cost of CO_2 captured due to reduced capital and parasitic compression costs relative to conventional technology. Further, since significant H_2 recovery is achieved in the first stage, the required size and cost of the cold gas cleanup unit is significantly reduced due to the nearly 50 percent reduction in gas volume processed.
- The CMS membranes exhibited excellent performance stability in the presence of untreated gasifier syngas in testing conducted at the NCCC. This makes them highly suitable for first-stage service in pre-combustion H_2 and CO_2 gas production and separations.
- The Pd-alloy membranes were also demonstrated to be highly stable in second stage residual H_2 recovery following cold gas clean-up prior to CO_2 sequestration. The high selectivity of the Pd-alloy permitted excellent residual H_2 recovery to achieve CO_2 capture and purity targets at higher power output and lower cost of CO_2 captured.
- By limiting the Pd-alloy membrane to residual H_2 recovery and fabricating it as an ultra-thin film on a ceramic support, the Pd metal demand/consumption is significantly reduced over CO_2 capture schemes that rely solely on Pd membrane use in flat sheet geometry, thereby addressing both issues of the very high cost and limited availability of Pd metal.

R&D challenges

- Develop the multiple tube membrane bundle suitable for the high-pressure gas processing.
- Fabricate CMS and Pd-alloy membrane bundles for bench-scale testing at the NCCC.
- Demonstrate performance stability of the multiple tube membrane bundles in actual gasifier syngas at the NCCC.
- Develop the mathematical model and confirm applicability to the proposed process in live gas testing.

status

Multiple tube CMS and Pd-alloy membrane bundles were tested at NCCC, exposed to synthetic and actual coal gasifier syngas for hundreds of hours, and found to be stable in this environment. Given this and their stability at elevated temperature and pressure, the technology is expected to be viable for CO_2 capture in IGCC process scenarios. Techno-economic analysis of proposed DSMP in pre-combustion CO_2 capture for an IGCC power has been completed. The TEA shows that net power production is improved by 3 percent and the cost of CO_2 captured is reduced by 14 percent over the NETL base plant case (IGCC with dual stage Selexol CO_2 capture). An EH&S assessment has been completed for the proposed process, and based upon this assessment, there is no reason to believe that a production process and operation meeting the EH&S satisfaction cannot be established to commercialize the proposed technology and process.

available reports/technical papers/presentations

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2015 NETL CO_2 Capture Technology, Pittsburgh, PA, June 2015.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Capture*," NETL Fact Sheet, February 2014.

"*Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery*," Project Kickoff Meeting Presentation.

Doug Parsley, Richard J. Ciora, Jr., Diane L. Flowers, John Laukaitaus, Amy Chen, Paul K.T. Liu, Jiang Yu, Muhammad Sahimi, Alex Bonsu, Theodore T. Tsotsis, "Field evaluation of carbon molecular sieve membranes for the separation and purification of hydrogen from coal-and biomass-derived syngas", *J. Membrane Science*, *450, 81* (2014)

M. Abdollah, J. Yu, H.T. Hwang, P.K.T. Liu, R.J. Ciora Jr., M. Sahimi, T. Tsotsis, "Process Intensification in Hydrogen Production from Biomass Derived Syngas", Ind. Eng. Chem. Res., **49**, 10986, (2010).

Abdollahi, M., et al., "Hydrogen Production from Syngas, using a Catalytic Membrane Reactor," presented at the North American Membrane Society, Charleston, SC, June 2009.

Abdollahi, M., et al., "Integrated One-Box Process for Hydrogen Production from Syngas," presented at the 2009 Annual Meeting, American Institute of Chemical Engineers (AIChE), November 2009.

Polymer-Based Carbon Dioxide Capture Membrane Systems

primary project goals

Los Alamos National Laboratory (LANL) developed and demonstrated polymer-based membrane structures, deployment platforms, and sealing technologies for attaining a combination of high selectivity, high permeability, chemical stability, and mechanical stability at elevated temperatures (>150 °C) and packaged in a scalable, economically viable, high area density system amenable to incorporation into an integrated gasification combined cycle (IGCC) plant for pre-combustion carbon dioxide (CO_2) capture.

technical goals

- Minimize membrane support costs, maximize membrane flux, retain thermo-mechanical and thermo-chemical stability characteristics, and increase the area density achievable in a commercial module design.
- Produce an asymmetric polybenzimidazole (PBI) hollow fiber comprised of a thin, dense, defect-minimized PBI selective layer and an open, porous underlying support structure with morphology characteristics tailored to optimize transport and mechanical property requirements (use and lifetime).
- Develop materials and methods to further mitigate defects in ultra-thin selective layers for use under process relevant conditions.
- Reduce perceived technical risks of utilizing a polymeric membrane based technology in challenging (thermal, chemical, mechanical) syngas environments.

technical content

LANL work, from a previously funded project FWP-10-002, demonstrated that PBI and other benzimidazole-based materials show promise as membranes for pre-combustion-based capture of CO_2. PBI is a unique polymer family that is stable to temperatures approaching 500 °C. PBI possesses excellent chemical resistance, a high glass transition temperature (>460 °C), good mechanical properties, and an appropriate level of processability. The PBI-based membranes developed by LANL have demonstrated operating temperatures significantly higher than 150 °C (up to 450 °C) with excellent chemical, mechanical, and hydrothermal stability, and outperformed any polymer-based membrane available commercially or reported in the literature for separations involving hydrogen. This achievement is validated via membrane productivity (separation factor and flux) comparisons (Figure 1). The improved performance of this technology in an application such as IGCC-integrated capture is further substantiated by the accessible operating temperature range (up to 400 °C), long-term hydrothermal stability, sulfur tolerance, and overall durability of the proposed membrane materials in these challenging pre-combustion environments. These characteristics have been validated via extensive evaluations of LANL's polymer-based membrane in simulated syngas environments containing hydrogen (H_2), CO_2, methane (CH_4), nitrogen (N_2), carbon monoxide (CO), steam (H_2O), and hydrogen sulfide (H_2S), from 25 to 400 °C, and demonstration of the membrane's thermal stability

technology maturity:

Bench-Scale, Simulated Syngas (single hollow fiber testing)

project focus:

High-Temperature Polymer-Based Membrane

participant:

Los Alamos National Laboratory

project number:

FWP-FE-308-13

predecessor projects:

FWP-FE-10-002
04FE13-AC24

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Kathryn A. Berchtold
Los Alamos National Laboratory
berchtold@lanl.gov

partners:

PBI Performance Products, NETL

start date:

10.01.2008

percent complete:

100%

via 300-plus days in operation at 250 °C. These achievements and material/membrane property validations were largely conducted on flat sheet and tubular platform membranes.

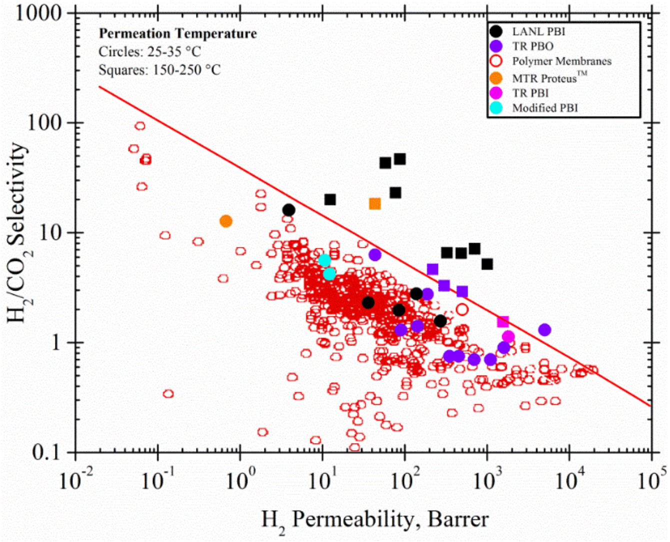

Figure 1: Robeson plot comparing PBI composite membrane with other polymeric membranes tested for H_2/CO_2 separation

The line represents the 2008 upper bound and Red symbols are the corresponding experimental data from Robeson JMS 320 (2008) 390-400. Data taken from LANL PBI: Berchtold *et al.*, JMS 415 (2012) 265-270, Xin *et al.*, JMS 461 (2014) 59-68 & Pesiri *et al.*, JMS 218 (2003) 11-18; Modified PBI: Kumbharkar *et al.*, JMS 286 (2006) 161-169; Membrane Technology & Research (MTR) Proteus: Merkel *et al.*, JMS 389 (2012) 441-450; Thermally Rearranged Polybenzoxazole (TR PBO): Han *et al.*, PCCP 14 (2012) 4365-4373 & Park *et al.*, JMS 359 (2010) 11-24; TR-PBI: Hans *et al.*, JMS 357 (2010) 143-151.

Previous R&D efforts were focused on the utilization of the PBI formulations as a selective layer deposited on and supported by a unique porous metal substrate (fabricated by Pall Corporation). Systems, economic, and commercialization analyses conducted by NETL, LANL, and others, combined with in- and out-of-laboratory testing, established the technical viability of the technology and indicated the strong potential for the membrane-based capture technology to meet and exceed the DOE Carbon Capture Program goals. However, these analyses also made clear the need to cut the costs of the support material and increase the area density realized by the ultimate module design in order to realize the desired step-change in both performance and cost of CO_2 capture associated with the use of this membrane-based capture technology. One promising option for achieving a substantial increase in active membrane area density and mitigating the cost of a metal or inorganic material-based support is the use of a hollow fiber membrane (HFM) platform. A HFM is the membrane configuration with the highest achievable packing density (i.e., the highest membrane selective area density). Commercial HFM modules have been fabricated to obtain selective area densities as high as 30,000 m^2/m^3. This affords the opportunity to achieve several orders of magnitude improvement over the density achievable with the previous polymeric-metallic membrane platform (ca. 250 m^2/m^3) which will reduce the size requirement of the costly, high temperature-tolerant membrane module housings, will minimize membrane support costs through their all-polymeric design, and will facilitate membrane flux maximization through processing facilitated selective layer thickness minimization (Figure 2). Realization of such increases in membrane area density and flux with the materials previously developed would lead to substantial economic and technical benefits.

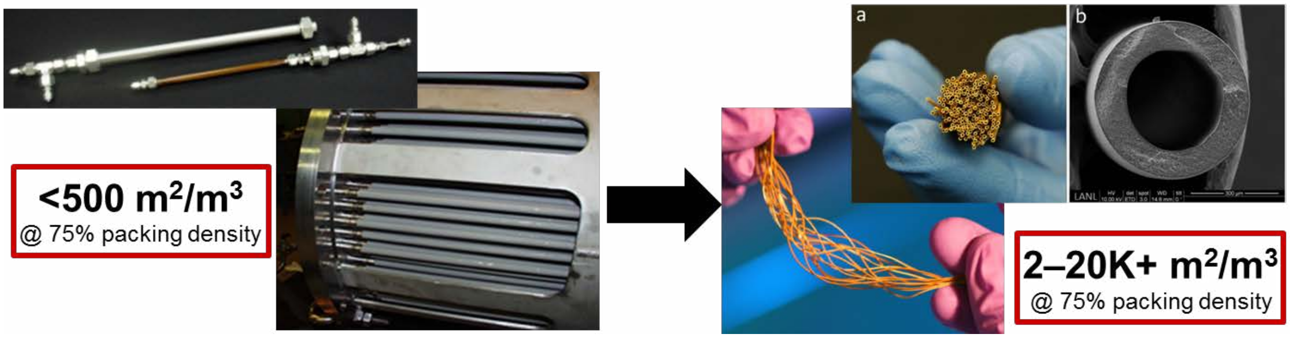

Figure 2: Illustration of the transition from the technology development state at project onset (PBI-metallic composite membrane in a tubular platform) to the technology end state (high area density all-polymeric PBI hollow fiber membrane platform)

The focus of recent technology development has been translation of the previously developed membrane materials chemistries into a high area density HFM platform via commercially viable HFM manufacturing methods; developing and deploying defect mitigation strategies for optimizing membrane performance and durability; and demonstrating the produced membranes in simulated and actual process environments with the overarching goal of technology progression toward commercialization.

Technology advancement has now been extended to realization of polybenzimidazole (PBI)-based membrane chemistries, structures, deployment platforms, and sealing technologies that achieve the critical combination of high permselectivity and durability at elevated temperatures (up to 350 °C, the highest ever reported viable operating temperature of a polymer based membrane). The work conducted as part of this development and demonstration effort includes the translation of these unique PBI materials into a commercially viable, all polymeric HFM platform (Figure 3). Results also demonstrated that the developed materials not only function at significantly higher temperatures than current commercially available polymeric membranes (which are limited to <150 °C) but also provide improved performance while exhibiting long-term temperature stability, sulfur tolerance, and overall durability in industrially relevant operating conditions. For the most detailed documentation of recent work available, the reader is referred to the project final report for FWP-FE-308-13 (see the list of available reports below).

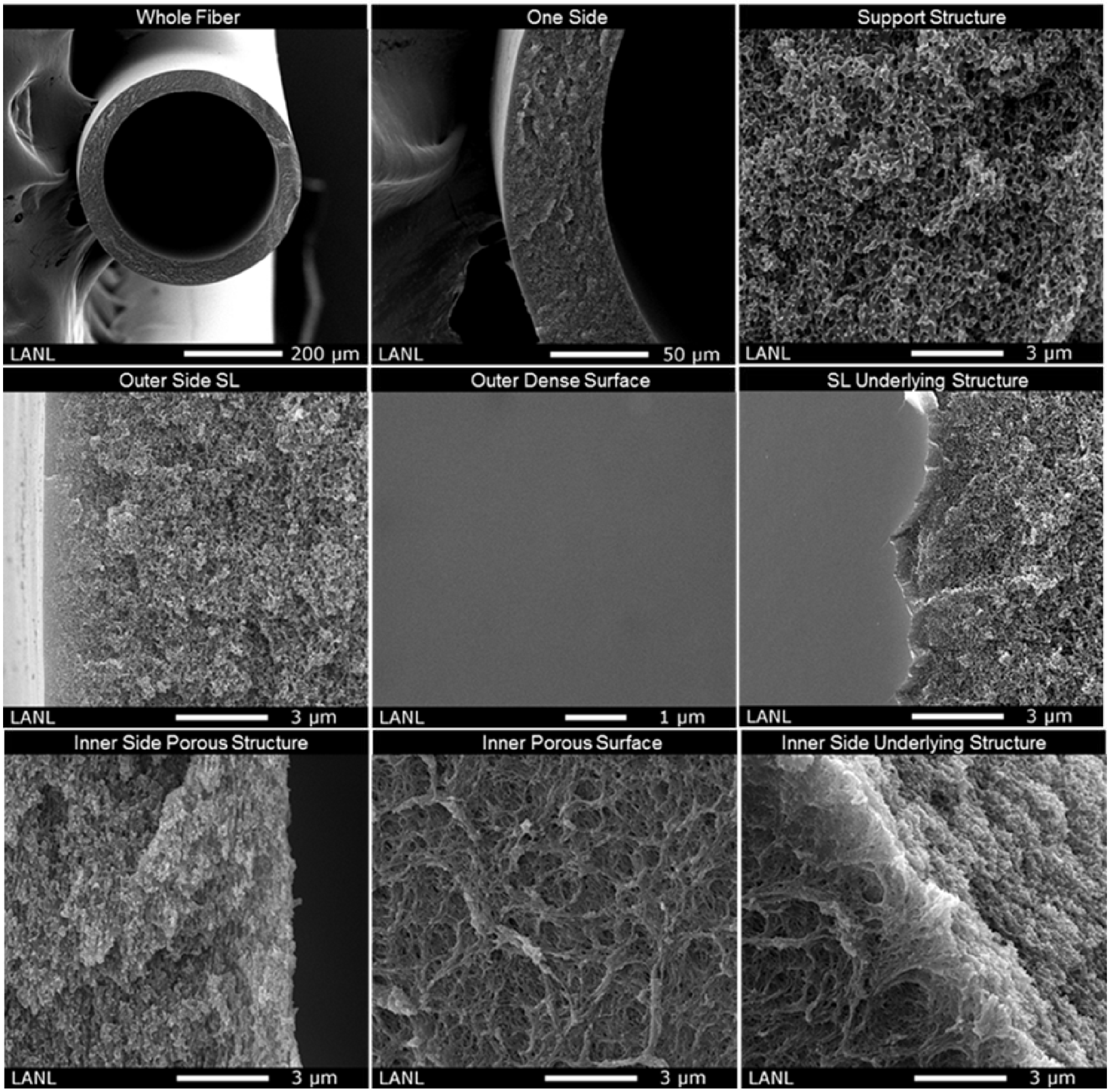

Figure 3: The state-of-the-art PBI HFM having ideal morphology: thin (ca. 160 nm) selective layer, macrovoid free, porous inner surface and fiber wall, and fabricated in an environmentally benign external coagulant (water).

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value		Target R&D Value
Materials of Fabrication for Selective Layer	—	m-PBI, high T_g polymer		
Materials of Fabrication for Support Layer	—	metallic composite	high T_g polymer	high T_g polymer
Nominal Thickness of Selective Layer	µm	0.6	0.2–0.5	0.1–0.5
Membrane Geometry	—	tubular	hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	30[1]	12.5[1]	30
Hours Tested without Significant Degradation	—	8,400 (at 250 °C)[2]	3,000 (at ≥250 °C)[2]	1,000
Manufacturing Cost for Membrane Material	\$/m²	>100	≤15	15
Membrane Performance				
Temperature	°C	250	150–350	150–350
H_2 Pressure Normalized Flux	GPU or equivalent	170	200–275	250
H_2/H_2O Selectivity	—	≈1	≈0.3	
H_2/CO_2 Selectivity	—	42	25	25–40
H_2/H_2S Selectivity	—	>1,800	>1,800	>1,800
Sulfur Tolerance	ppm	10,000[3]	10,000[3]	1,000
Type of Measurement	—	mixed and pure	mixed[4] and pure	mixed
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement	—	counter	counter/complex	
Packing Density	m²/m³	250	2,000–15,000	
Shell-Side Fluid	—	feed/retentate		
Syngas Flowrate	kg/hr	210-240		
CO_2 Recovery, Purity, and Pressure	%/%/bar	75-90%[6], HPD[5,6], 50 bar[6]		
H_2 Recovery, Purity, and Pressure	%/%/bar	80-99%[6,7], HPD[5,7], 20 bar[7]		

[1] Max TMP tested, not max achievable TMP.

[2] No degradation observed during testing.

[3] Max sulfur content tested with current generation HFMs was 100 ppm, not a measure of sulfur tolerance. Materials testing in other platforms indicates a tolerance to ≥10,000 ppm

[4] Typical Mixed gas conditions: simulated syngas 50.3% H_2, 19.2% H_2O, 29.4% CO_2, 1.1% CO with 0, 20, & 100 ppm H_2S.

[5] Highly process dependent (HPD).

[6] Gasifier, coal feedstock, upstream unit operation (e.g., water gas shift [WGS]), and downstream unit operation (e.g., CO_2 purification) specifications dependent.

[7] Tailored to match the turbine inlet specifications (e.g., 125 LHV Btu/ft³ and 20 bar permeate).

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm³ (1 atm, 0 °C)/cm²/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm³ (1 atm, 0 °C)/cm²/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m²-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution diffusion where at the proposed elevated separation temperatures, permeability is dominated by gas diffusivity in the selective layer.

Contaminant Resistance – Excellent resistance to syngas contaminants.

Syngas Pretreatment Requirements – Particulate removal.

Waste Streams Generated – Particulate removal.

Process Design Concept – Multiple location possibilities largely influenced by gasifier type (syngas pressure and quality), the employed WGS technology, and the presence or lack thereof of a warm temperature gas cleanup for sulfur removal prior to the capture step. For performance benchmark purposes, the membrane separation is conducted post-low temperature (250 °C) WGS. Nitrogen from the air separation unit (ASU) is used as a membrane sweep gas, with the sweep flows specified based on the turbine inlet heating value specification. Initial evaluations have utilized GE F-class turbine specifications and GE (Texaco) gasifier-radiant operation.

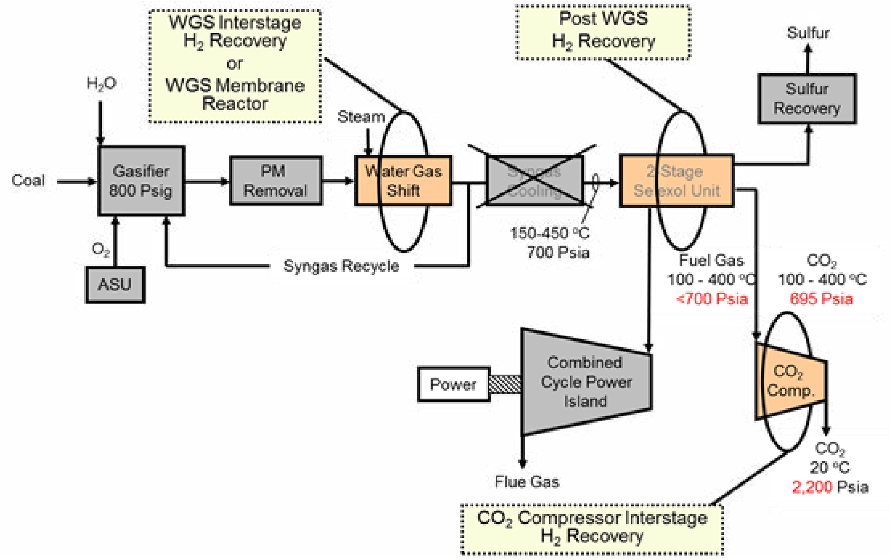

Figure 4: Proposed design concept identifying multiple location opportunities for PBI membrane separation technology integration

Proposed Module Integration – Hollow fiber module design comprised of high-pressure, high-temperature housings and components. The syngas will be processed at process temperature and pressure (see conditions and composition below). The conditions of the primary separation position will be matched to those at the exit of the low-temperature WGS reactor. The pressure drop utilized will be tailored based on the turbine inlet pressure. This process favors conditions created by gasifiers that operate at higher pressure.

technology advantages

- Broad accessible membrane operating temperature range (150–350 °C) facilitating increased opportunity for process integration/optimization.
- Demonstrated long-term hydrothermal stability, sulfur tolerance, and overall durability of selective layer materials.
- Membrane-based technology competitive advantages: modularity, low-maintenance operations, small footprint, low/no waste process, and flexible design opportunities.
- CO_2 produced at higher pressure enables reduced compression costs.

R&D challenges

- Design, control, prediction, and synthesis of tailored material morphologies in hollow fiber format.
- Realizing high-permeance, defect-free gas separation viable hollow fibers.
- Realizing sealing materials and methods compatible with the target material and process thermal, chemical, and mechanical characteristics/environments.

status

At the project's end, production of mechanically robust PBI hollow fibers suitable for industrial use was attained, taking advantage of a novel continuous spinning process, defect sealing layer material and deposition method, and environmentally benign coagulation solvent and modified commercial dope to ensure macro-void free fiber fabrication. A novel potting material for multi-fiber module fabrication with promising properties to withstand typical syngas operating conditions and chemical environments was developed. In fiber testing, long-term stable performance in simulated syngas containing H_2S, steam and CO at elevated temperatures (250–350 °C) of syngas was demonstrated.

Challenges remaining for successful industrial deployment include (1) further development and demonstration of potting material for multi-fiber modules (current industrial materials lack hydrothermal stability, material developed in this work requires further development and demonstration), and (2) further improvement in H_2/CO_2 selectivity is needed to meet carbon capture targets without relying on supplemental downstream processing/purification.

available reports/technical papers/presentations

Berchtold, K. A. and Singh, R. P., "*Polymer-Based Carbon Dioxide Capture Membrane Systems*," Final Technical Report DOE/NETL FWP-FE-308-13, 2017.

"*High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Rajinder P. Singh & Kathryn A. Berchtold, NETL Final Project Review Meeting, January 2017.

"*High-Temperature Polymer Based CO_2 Capture Membrane Systems for Pre-Combustion CO_2 Capture*," presented by Rajinder Singh, Los Alamos National Laboratory, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

Berchtold, K. A., Dudeck, K. W., Singh, R. P., and Dahe, G. J., "Polybenzimidazole hollow fiber membranes and method for making an asymmetric hollow fiber membrane," US 15/190,011, 2016

Radcliffe, A. J., Singh, R. P., Berchtold, K. A., and Lima, F., "Modeling and Optimization of High-Performance Polymer Membrane Reactor Systems for Water–Gas Shift Reaction Applications," Processes, 4 (2016) 8.

"*High-Temperature Polymer Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Kathryn A. Berchtold, Los Alamos National Laboratory, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

Singh, R. P and Berchtold, K. A., "H_2 Selective Membranes for Pre-combustion Carbon Capture," in: F.S. Morreale (Ed.) Novel Materials for Carbon Dioxide Mitigation Technology, Elsevier, Amsterdam, 2015, pp. 177-206.

"*High-Temperature Polymer Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Kathryn A. Berchtold, Los Alamos National Laboratory, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Singh, R. P., Dahe, G. J., Dudeck, K. W., Welch, C. F., and Berchtold, K. A., "High Temperature Polybenzimidazole Hollow Fiber Membranes for Hydrogen Separation and Carbon Dioxide Capture from Synthesis Gas," *Energy Procedia* **63** (2014) 153-9.

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Krishnan, G.D.; Steele, D.; O'Brien, K.C.; Callahan, R.; Berchtold, K.A.; and Figueroa, J.D., "Simulation of a Process to Capture CO_2 from IGCC Syngas Using a High-Temperature PBI Membrane," *Energy Procedia* **1** (2009) 4079-88.

O'Brien, K.C.; Krishnan, G.; Berchtold, K.A.; and Figueroa, J.D., et al., "Toward a Pilot-Scale Membrane System for Pre-Combustion CO_2 Separation," *Energy Procedia* **1** (2009) 287-94.

PRE-COMBUSTION CARBON DIOXIDE CAPTURE BY A NEW DUAL-PHASE CERAMIC-CARBONATE MEMBRANE REACTOR

primary project goals

Arizona State University is developing a dual-phase, membrane-based separation device that will separate carbon dioxide (CO_2) from typical water-gas shift (WGS) mixture feeds and produce hydrogen (H_2), which can be introduced into the combustion turbines of integrated gasification combined cycle (IGCC) plants.

technical goals

- Synthesize chemically and thermally stable dual-phase, ceramic-carbonate membranes with CO_2 selectivity (with respect to [H_2], carbon monoxide [CO], or water [H_2O]) larger than 500 and CO_2 permeance larger than 5×10^{-7}mol/m^2/s/Pa.
- Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications.
- Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93 percent purity and the CO_2 stream with at least 95 percent purity.

technical content

A membrane separation device consisting of a porous metal phase and a molten carbonate phase can conduct carbonate ions (CO_3^{2-}) at a high rate. The metal-carbonate membranes only conduct electrons implying oxygen (O_2) should be mixed with CO_2 in the feed in order to convert CO_2 to $CO_3^=$ ions. However, the presence of O_2 can also oxidize the metallic support and reduce its electronic conductivity, and thus CO_2 permeability. The problem is addressed by the proposed dual-phase, ceramic-carbonate membrane configuration consisting of a porous ionic conducting ceramic phase and a molten carbonate phase.

At the upstream surface, CO_2 reacts with oxygen ions supplied from the ceramic phase to form $CO_3^=$, which transports through the molten carbonate phase towards the downstream surface of the membrane. On the downstream surface, the reverse surface reaction takes place, converting $CO_3^=$ to CO_2, with $O^=$ released and transported back through the ceramic phase towards the upstream surface of the membrane. The net effect is permeation of neutral CO_2 through the membrane driven by the CO_2 pressure gradient. The dual-phase membrane will be made of continuous thin mesoporous oxygen ionic-conducting ceramic layer filled with a molten carbonate, supported on porous stainless steel or other metal, with an intermediate layer of sub-micron, pore-sized oxygen ionic conducting material.

technology maturity:

Lab-Scale Using Simulated Syngas

project focus:

Dual-Phase Ceramic-Carbonate Membrane Reactor

participant:

Arizona State University

project number:

FE0000470

NETL project manager:

Elaine Everitt
elaine.everitt@netl.doe.gov

principal investigator:

Jerry Y.S. Lin
Arizona State University
jerry.lin@asu.edu

partners:

None

performance period:

10/1/09 – 9/30/14

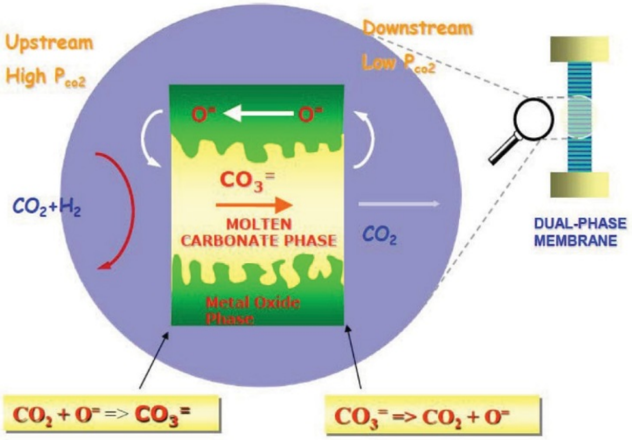

Figure 1: Concept of Dual-Phase Membrane

Development of this dual-phase membrane will be divided in to two phases. Phase I work will include identifying optimum conditions for synthesis of adequate membrane supports and the dual-phase membranes in disk geometry and studying gas permeation properties of the membranes. The second part of the Phase I work will be focused on fabrication of the dual-phase membranes in tubular geometries and the study of permeation, chemical, and mechanical stability of the tubular membranes relevant to their uses in membrane reactors for WGS reaction.

Phase II work will be directed towards studying the dual-phase membrane reactor performance for WGS reaction for hydrogen production and CO_2 capture. The work includes synthesis and kinetic study of a high-temperature WGS catalyst and experimental and modeling study of WGS reaction on the dual-phase membrane reactors. The experimental data will be compared with modeling results to identify optimum operating conditions for WGS reaction. The project will perform an economic analysis using the dual-phase membrane as a WGS reactor for hydrogen production and CO_2 capture for an IGGC plant.

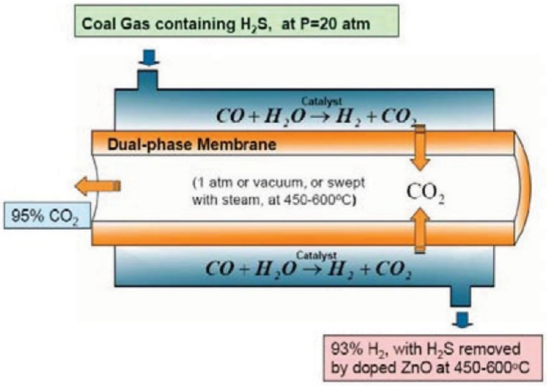

Figure 2: Proposed Membrane Reactor for WGS Reaction

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	Li_2/K_2CO_3	doped Li_2/K_2CO_3
Materials of Fabrication for Support Layer	—	porous stainless steel	fast-ionic conductors (doped ZrO_2, CeO_2)
Nominal Thickness of Selective Layer	µm	2,000	10-200
Membrane Geometry	—	disk	tube
Max Trans-Membrane Pressure	bar	2	>6
Hours Tested Without Significant Degradation	—	N/A	>700
Manufacturing Cost for Membrane Material	$\$/m^2$	/	500
Membrane Performance			
Temperature	°C	700–900	700–900
CO_2 Pressure Normalized Flux	GPU or equivalent	600	>1,000
CO_2/H_2O Selectivity	—	300	>500
CO_2/H_2 Selectivity	—	300	>500
CO_2/SO_2 Selectivity	—	—	>500
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	flat disk	Tube – counter-flow
Packing Density	m^2/m^3	10	>60
Shell-Side Fluid	—		steam
Syngas Flowrate	L(STP)/min (per tube)	>0.2	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%/99.5%/1 atm	
H_2 Recovery, Purity, and Pressure	%/%/bar	99.9%/93%/>6 atm	
Pressure Drops Shell/Tube Side	bar	>6	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Carbon dioxide permeates through by combined transport of carbonate ions in the molten carbonate phase and oxygen ions in the solid metal-oxide phase.

Contaminant Resistance – The membrane to be stable in 0.1–1 percent atmosphere containing hydrogen sulfide (H_2S).

Proposed Module Design – Shell-tube module.

technology advantages

- WGS reaction at one temperature (above 400 °C).
- Separation of CO_2 and H_2 mixture in one step.
- Production of high-pressure hydrogen stream.

R&D challenges

- Failure to obtain sufficiently high CO_2 permeance due to a rate-limiting surface reaction.
- Undesired surface properties of ceramic supports resulting in instability of the carbonate in the support pores.

results to date/accomplishments

- Synthesis of dual-phase membrane disks.
- Tubular membranes were prepared via pressing technique using graphite powders.
- Fabrication techniques of pressing-sintering and centrifugal casting were successfully modified to optimize support microstructure.
- Thin, dual-phase membranes on porous support of disk and tubular geometries were successfully fabricated.
- High CO_2 selectivity and good CO_2 permeance through the membranes were demonstrated.
- Separation and permeation properties of dual-phase membranes under syngas conditions was modeled and analyzed. CO_2 permeation mechanism and factors affecting CO_2 permeation of the dual-phase membranes have been identified.
- WGS reaction in the dual-phase membrane reactor was studied. Conditions to produce hydrogen of 93 percent purity and CO_2 stream of >95 percent purity, with 90 percent CO_2 capture were identified.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Lin, Jerry, Final Technical Report, "Pre-Combustion Carbon Dioxide Capture by a New Dual Phase Ceramic-Carbonate Membrane Reactor," *http://www.osti.gov/scitech/biblio/1172599*, publication date September 30, 2014.

Lin, J.Y.S., Final Project Presentation. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/pre-combustion/2014-12-05-Closeout-Presentation-FE0000470.pdf*.

Lin, J.Y.S.; Norton, T.; Ortiz-Landeros, J.; Lu, B.; and Anderson, M; "Pre-Combustion Carbon Dioxide Capture by a New Dual-Phase Ceramic-Carbonate Membrane Reactor," presented at 2014 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20*CO_2*%20Capture/X-Dong-ASU-Dual-Phase-Ceramic-Carbonate-Membrane-Reactor.pdf*.

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Lu, B.; and Lin, Y.S., "Sol-Gel Synthesis and Characterization of Mesoporous Yttria Stabilized Zirconia Membranes with Graded Pore Structure," *J. Materials Sci*., 46, 7056-7066 (2011).

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Anderson, M.; and Lin, Y.S., "Carbon Dioxide Separation and Dry Reforming of Methane for Synthesis of Syngas by a Dual- Phase Membrane Reactor," *AIChE J*., 59, 2207-2218 (2013)

Lu, B.; Lin, Y.S., "Synthesis and characterization of thin ceramic-carbonate dual-phase membranes for carbon dioxide separation", *J. Membr. Sci*., 444, 402-411 (2013)

Dong, X.; Ortiz-Landeros, J.; Lin, Y.S., "An asymmetric tubular ceramic-carbonate dual phase membrane for high temperature CO_2 separation", *Chem. Commun*, 49, 9654-9656 (2013)

Ortiz-Landeros, J., Norton, T.; Lin, Y.S., "Effects of support pore structure on carbon dioxide permeation of ceramic-carbonate dual-phase membranes", *Chem. Eng. Sci*., 104, 891-898 (2013)

Norton, T.T., Ortiz-Landeros, J., Lin, Y.S., "Stability of La-Sr-Co-Fe oxide-carbonate dual-phase membranes for carbon dioxide separation at high temperatures", *Ind. Eng. Chem. Res.,* 53, 2432-2440 (2014)

Norton, T.T.; Lu, B.; Lin, Y.S., "Carbon dioxide permeation properties and stability of samarium-doped-ceria carbonate dual-phase membranes", *J. Membr, Sci*., 467, 244-252(2014)

Norton, T.T., Lin, Y.S., "Ceramic-carbonate dual-phase membrane with improved chemical stability for carbon dioxide separation at high temperature", *Solid State Ionics*, 263, 172-179 (2014)

DESIGNING AND VALIDATING TERNARY PD-ALLOYS FOR OPTIMUM SULFUR/CARBON RESISTANCE

primary project goals

Pall Corporation is developing an economically viable hydrogen (H_2)/carbon dioxide (CO_2) separation membrane system that would allow efficient capture of CO_2 at high temperature and pressure from gasified coal in the presence of typical contaminants using a ternary palladium (Pd)-alloy. Membranes were fabricated and tested in simulated coal gasification conditions. The final objective is a membrane with high hydrogen flux and excellent resistance to syngas contaminants.

technical goals

- Create an advanced Pd-alloy for optimum H_2 separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability under long-term testing of a pilot membrane in laboratory-scale.
- Understand long-term effects of the coal gasifier environment on the metallurgy of the membrane components by comparing controlled diffusion studies with in-service membranes.

technical content

The project developed an advanced Pd-alloy for optimum H_2 separation performance to demonstrate long-term durability under coal synthesis gas (syngas) conditions. Ternary Pd-alloys with potential for favorable performance were selected based on a literature search. This large set of ternary Pd-alloys underwent combinatorial alloy spreads on thin film support disks. These disks were tested in a syngas environment using in situ Raman spectroscopy to measure H_2 separation factor and permeability, as well as characterize sulfur and carbon resistance of best candidate alloys. These alloys were compared to baseline tests of traditional Pd-gold (Au) alloy membranes.

The best alloys were fabricated into 15-cm^2 tubular membranes and tested. As with the combinatorial disks, the 15-cm^2 active area tubes were exposed to conditions representative of a coal gasifier environment: high temperature and high pressure in the presence of contaminating species. Emphasis was placed on identification and characterization of membrane defects, surface analysis of the regions affected by the contaminants, and assessment of the surface quality of the ceramic substrate

technology maturity:

Laboratory-Scale Using Simulated Syngas

project focus:

Pd-Alloys for Sulfur/Carbon Resistance

participant:

Pall Corporation

project number:

FE0001181

NETL project manager:

Jason Hissam
jason.hissam@netl.doe.gov

principal investigator:

Scott Hopkins
Pall Corporation
scott_d._hopkins@pall.com

partners:

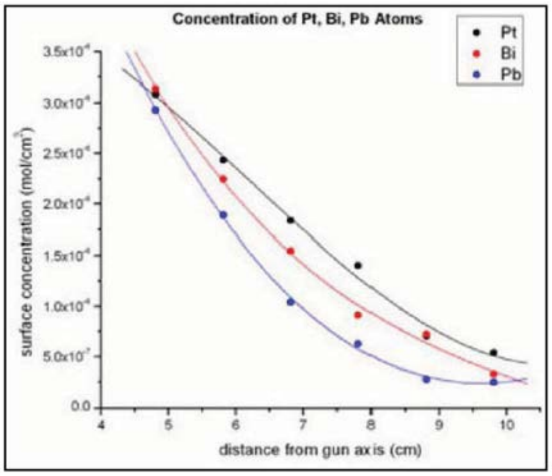
Cornell University,
Georgia Institute of Technology,
Colorado School of Mines,
Southern Company

performance period:

10/1/09 – 9/30/14

Figure 1: A Co-Sputtering Chamber

Scale-up of membranes to75-cm^2 was initially planned but was not conducted. The 15-cm^2 active area tubes were subjected to a 100+ hour continuous testing.



Membrane Figure 2: Graph of Atom Concentration as a Function of Distance from the Gun Axis for Pt, Bi, and Pb Targets

Figure 3: A 75-cm^2

Technical Targets:

- Membrane would be tolerant of up to 20 parts per million (ppm) hydrogen sulfide (H_2S).
- Hydrogen flux of 200 ft^3/hr/ft^2 at 400 °C and 20 pounds per square inch (psi) H_2 partial pressure differential.
- Total pressure differential operating capability 400 psi.
- The membrane cost must be in the range of \$500/ft^2.
- Permeate H_2 purity should be at a level of 99.5 percent.
- The membrane must be resistant to coking with relatively low steam-to-carbon ratio.
- The system should be stable for a minimum of 3 years in service.

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	palladium-gold alloys	palladium alloys
Materials of Fabrication for Support Layer	—	zirconia coated porous stainless steel tubes	zirconia coated porous stainless steel tubes
Nominal Thickness of Selective Layer	µm	3–5 µm	3–7 µm
Membrane Geometry	—	shell and tube	shell and tube
Max Trans-Membrane Pressure	bar	400 psi at 400 °C	400 psi at 400 °C
Hours Tested Without Significant Degradation	—	1,000	5,000
Manufacturing Cost for Membrane Material	$/m²	1,000	500
Membrane Performance			
Temperature	°C	400	450
H_2 Pressure Normalized Flux	GPU or equivalent	170	200
H_2/H_2O Selectivity	—		
H_2/CO_2 Selectivity	—		
H_2/SO_2 Selectivity	—		
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	outside – in	
Packing Density	m^2/m^3		
Shell-Side Fluid	—		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – Palladium-based alloy membranes should tolerate moderate levels of coal gas contaminants after advanced hot syngas cleanup. Primary contaminants include H_2S and carbon monoxide (CO). A typical hot gas cleanup process can bring residual level of sulfur into the range of 0.5–20 parts per million volume (ppmv). After a single-stage water-gas shift (WGS) reactor, CO can be as low as a few percent.

Waste Streams Generated – No waste streams are generated since H_2 is extracted by a Pd-alloy membrane system with primarily CO_2 and water (H_2O) left at high pressure. After steam is condensed, CO_2 is sent for sequestration.

technology advantages

- Researchers use a proprietary process to create ultrathin, economical, Pd-alloy membranes in virtually any alloy system.
- The project applied combinatorial methods to continuous ternary alloy spreads and use a novel characterization method to rapidly scan the alloys after syngas exposure to identify the most resistant compositions.
- A customized composite substrate from Pall was used to deposit ultrathin Pd-alloy membranes. The substrate is porous stainless steel tubes with ceramic coating on the outside surface as a diffusion barrier; thus, membrane elements can be assembled into the module by a conventional welding technique.

R&D challenges

- Hydrogen separation performance may not achieve target performance by membrane design alone. Supplements such as additional gas reforming capabilities may be required either upstream or downstream of the membrane module.
- Scale-up of the Pd-alloy surface area from 15 to 75 cm^2; was planned but will not be conducted under this project.
- Membrane durability during thermal cycling and its effect on stability; the stability of the ceramic coated support has been demonstrated, but not the long-term stability with a Pd-alloy membrane in place.

results to date/accomplishments

- Identified six candidate ternary alloys that had little adsorption of sulfur and carbon after exposure.
- Added Colorado School of Mines as a subcontractor to create six ternary alloys for hydrogen permeance testing and sulfur/carbon exposure testing.
- Made 5 cm^2 membranes for exposure testing.
- Conducted preliminary tests on active area membranes.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Lewis, A., Hopkins, S.; and H. Zhao "Identifying Pd-Based Ternary Membranes for Carbon and Sulfur Applications," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/A-Lewis-Pall-Pd-Based-Ternary-Membranes.pdf*.

Hopkins, S.; and H. Zhao. "High Throughput Design of Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems," presented at 2013 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO$_2$%20Capture/H-Zhao-Pall-Ternary-Pd-Alloys.pdf*.

Hopkins, S.; and H. Zhao. "High Throughput Design of Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems," presented at 2012 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2012.

Hopkins, S. "Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance," presented at 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, August 2011.

Henkel, D., "Combinatorial Design of Pd Ternary Alloys for Sulfur/Carbon Tolerant Hydrogen Separation," presented at 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, September 2010.

HYDROGEN-SELECTIVE EXFOLIATED ZEOLITE MEMBRANES

primary project goals

The University of Minnesota researchers are further developing exfoliated zeolite coating technology for hydrogen (H_2) separation membranes, including membrane production methodology, and determining the feasibility of integration of the membrane into a water-gas shift (WGS) reactor model.

technical goals

- Develop and optimize a membrane production method for the exfoliated zeolite coating.
- The membrane must demonstrate high flux, high selectivity, and stable performance.
- Determine the feasibility of integrating these membranes in WGS reactors and integrated gasification combined cycle (IGCC) flow sheets.
- Perform a techno-economic analysis.

technical content

This project will further develop a novel silica molecular sieve membrane using exfoliated zeolite coatings with the potential to contribute to carbon capture by high-temperature separation of H_2 from carbon dioxide (CO_2) and other gases present in shifted synthesis gas (syngas). The project will establish procedures for the production of the required supply of these layered silicates, first optimizing the synthesis process of the exfoliated zeolite, then the layer-by-layer coating process.

The pore structure of the zeolite that is currently studied (MCM-22) includes ultra-small (potentially H_2-selective) sized pores defined by six SiO_4 tetrahedra (6-Member Ring pores: 6MR) along the c-axis. Therefore, c-out-of-plane oriented films are promising for H_2-separation membranes. MCM-22 has highly anisotropic plate or disk-like crystal shape, thin along the c-crystallographic axis and appropriate for achieving c-oriented films. Among available compositions, an all-silica and potentially hydrothermally stable composition has been reported, which could enable H_2-separations in applications like WGS reactors.

Membrane Microstructures Achieved Currently: MCM-22/silica composite films were fabricated using layer-by-layer deposition towards a nanoscale realization of the selective flake concept. The repetition of appropriate deposition cycles (i.e., particle deposition and subsequent silica coating) led to the gradual increase of separation performance achieving H_2/nitrogen (N_2) ideal selectivity as high as 120. The scanning electron microscope (SEM) cross-section image of a five-layer membrane along with its schematic is shown in Figure 1. The aim of the ongoing work is to improve performance using thinner flakes (exfoliated zeolite layers).

technology maturity:

Bench-Scale, Simulated Syngas

project focus:

Hydrogen-Selective Zeolite Membranes

participant:

University of Minnesota

project number:

FE0001322

NETL project manager:

Elaine Everitt
elaine.everitt@netl.doe.gov

principal investigator:

Michael Tsapatsis
University of Minnesota
tsapatsis@umn.edu

partners:

None

performance period:

10/1/09 – 9/30/14

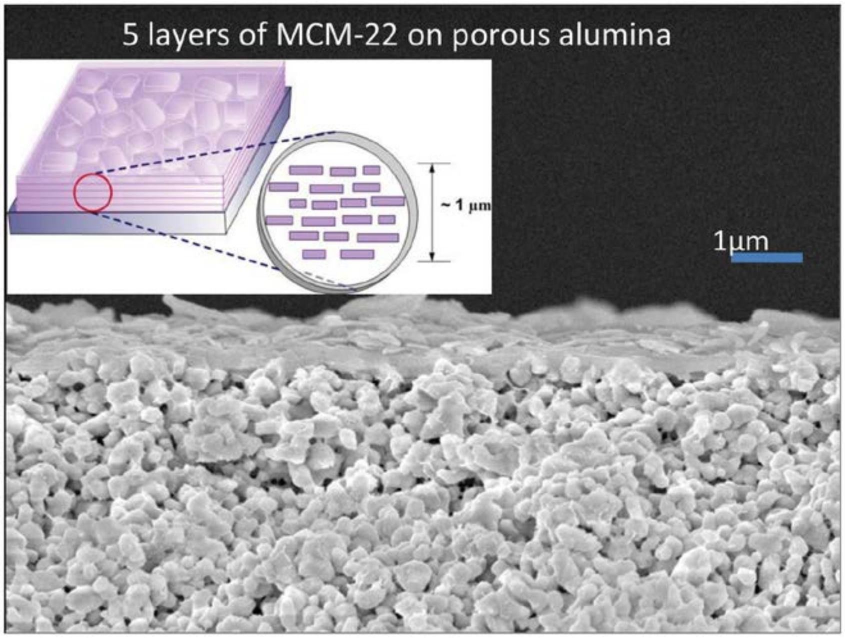


Figure 1: SEM Cross-Section Image of a Five-Layer Membrane Along with Schematic

The H_2 permeance and selectivity to CO_2 and other gases, as well as hydrothermal stability, will be determined for the developed membrane. A series of tests will determine membrane separation performance. Performance testing configurations will include flat alumina supports up to 220 °C; tubular membrane testing using single gases up to 600 °C; tubular membrane testing using simulated feeds up to 600 °C; and high-temperature, high-pressure testing of tubular supports. The membrane stability will be determined in a WGS environment. The three stability test configurations are in steam containing simulated feeds for exfoliated powders; in steam containing simulated feeds for alumina supported films; and in steam containing simulated feeds for stainless steel supported films.

The project will also integrate the membrane into a WGS membrane reactor model, integrate the model in an IGCC flow sheet, and perform techno-economic analysis and operability evaluation and analysis.

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	MCM-22 plate like crystals	exfoliated MCM-22 layers
Materials of Fabrication for Support Layer	—	porous alumina discs (homemade)	porous stainless steel tubes (commercial)
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	—		
Max Trans-Membrane Pressure	bar		
Hours Tested Without Significant Degradation	—	48	250
Manufacturing Cost for Membrane Material	$/m^2		
Membrane Performance			
Temperature	°C	200	500
H_2 Pressure Normalized Flux	GPU or equivalent		
H_2/H_2O Selectivity	—		
H_2/CO_2 Selectivity	—	20	80–800
H_2/H_2S Selectivity	—		
Sulfur Tolerance			
Type of Measurement	—		

Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—		
Packing Density	m^2/m^3		
Shell-Side Fluid	—		
Syngas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar	1–2	10

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – These materials are crystalline silicates and the main issue is stability to steam. Other contaminants are not expected to create problems.

Syngas Pretreatment Requirements – To be determined as project progresses.

Waste Streams Generated – To be determined as project progresses.

technology advantages

This membrane technology will form the selective film using a coating process and premade components, and will have high selectivity, flux, and stability.

R&D challenges

- Dispersible exfoliated layers.
- Simple and efficient coatings process.

results to date/accomplishments

- Synthesis of high aspect ratio exfoliated MCM-22 layers while preserving structure.
- Layer-by-layer coatings of exfoliated MCM-22 layers were fabricated.
- Membranes were tested for separation performance.
- Stability testing was conducted on exfoliated MCM-22 membranes in WGS environment.
- Simulation and optimization studies for IGCC-Membrane Reactor (MR) plant were performed and a techno-economic assessment of IGCC-MR process was completed.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Tsapatis, M; Daoutidis, P.; Elyassi, B.; Lima, F; Iyer, A.; Agrawal, K.; Sabnis, Sanket, Final Report, “Hydrogen Selective Exfoliated Zeolite Membranes,” *http://www.osti.gov/scitech/biblio/1178537*, Publication date 09/30/2014.

Tsapatsis, M.; Daoutidis, “Hydrogen Selective Exfoliated Zeolite Membranes,” Final Project Presentation. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/pre-combustion/2014-12-12-Final-Presentation-DOE-CO$_2$.pdf*.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. Iyer, A, “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2014 NETL CO$_2$ Capture Technology Meeting in Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/A-Iyer-UMinnesota-Zeolite-Membranes.pdf*.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. Iyer, A, “ Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2013 NETL CO$_2$ Capture Technology Meeting in Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO$_2$%20Capture/A-Iyer-UMinnesota-H$_2$-Selective-Exfoliated-Zeolite-Membranes.pdf*.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. “ Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2012 NETL CO$_2$ Capture Technology Meeting in Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Events/2012/CO$_2$%20Capture%20Meeting/F-Lima-UMn-Exfoliated-Zeolite-Membranes.pdf*.

Lima, Fernando V.; Daoutidis, Prodromos; Tsapatsis, Michael; et al., “Modeling and Optimization of Membrane Reactors for Carbon Capture in Integrated Gasification Combined Cycle Units,” Industrial & Engineering Chemistry Research, Volume: 51 Issue: 15 Pages: 5480-5489, April 18, 2012. Tsapatsis, Michael, Toward High-Throughput Zeolite Membranes, Science, Volume: 334 Issue: 6057 Pages: 767-768, November 11, 2011.

Varoon, Kumar; Zhang, Xueyi; Elyassi, Bahman; et al., “Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane,” Science, Volume: 333 Issue: 6052 Pages: 72-75, October 7, 2011.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2011 NETL CO$_2$ Capture Technology Meeting in Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/File%20Library/Events/2011/CO$_2$capture/26Aug11--Lima-UMinn-H$_2$-Selective-Zeolite-Membranes.pdf*.

Tsapatsis, M.; Daoutidis, P., “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2010 NETL CO$_2$ Capture Technology Meeting in Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/File%20Library/Events/2010/CO$_2$capture/Michael- Tsapatsis-FE0001322.pdf*.

Maheshwari, S.; Kumar, S.; Bates, F.S.; Penn, R.L.; Shantz, D.F.; Tsapatsis, M. Journal of the American Chemical Society 130, 1507-1516 (2008), “Layer Structure Preservation during Swelling, Pillaring and Exfoliation of a Zeolite Precursor.”

Choi, J.; Tsapatsis, M. Journal of the American Chemical Society 132(2), 448-449 (2010), “MCM-22/Silica Selective Flake Nanocomposite Membranes for Hydrogen Separations.”

PRESSURE SWING ABSORPTION DEVICE AND PROCESS FOR SEPARATING CO_2 FROM SHIFTED SYNGAS AND ITS CAPTURE FOR SUBSEQUENT STORAGE

primary project goals

The New Jersey Institute of Technology (NJIT) is developing, via laboratory-scale experiments, a pressure swing membrane absorption-based (PSMAB) device using a non-dispersive, membrane-based gas-liquid contactor that produces hydrogen at high pressure for integrated gasification combined cycle (IGCC), as well as a carbon dioxide (CO_2) stream, between 1 and 5 atm, that contains at least 90 percent of the CO_2 from a feed gas at ≈200 °C and 300 pounds per square inch gauge (psig).

technical goals

- Develop, via laboratory experiments, an advanced PSMAB device and a cyclic process to produce helium (He) (a surrogate for hydrogen) at high pressure from low-temperature, post-shift reactor synthesis gas (syngas), as well as a CO_2 stream containing at least 90 percent of the CO_2 and suitable for sequestration.
- Provide data and analysis of the cyclic process and device to facilitate subsequent scaleup.
- Develop a detailed analysis for the process and device to allow economic evaluation for potential larger-scale use.

technical content

In the first phase of research, an experimental setup will be developed for studying the PSMAB process. NJIT will work with Media and Process Technology, Inc., Porogen Inc. and Applied Membrane Technologies (AMT), Inc. to develop microporous hydrophobized ceramic tubule-based, microporous hydrophobized Polyetheretherketone (PEEK) hollow fiber-based and microporous Polytetrafluoroethylene (PTFE) hollow fiber-based absorption devices. The absorption device will be explored on a preliminary basis for performance of PSMAB separation of a moist CO_2-He gas mixture at 150–200 °C and 200–300 psig, simulating a low-temperature, post-shift reactor syngas stream.

technology maturity:

Laboratory-Scale Using Simulated Syngas

project focus:

Pressure Swing Membrane Absorption Device and Process

participant:

New Jersey Institute of Technology

project number:

FE0001323

NETL project manager:

Steven Markovich
markovis@netl.doe.gov

principal investigator:

Dr. Kamalesh K. Sirkar
New Jersey Institute of Technology
sirkar@njit.edu

partners:

Applied Membrane Technologies,
Media and Process Technology,
Porogen,
Techverse

performance period:

10/1/09 – 3/31/13

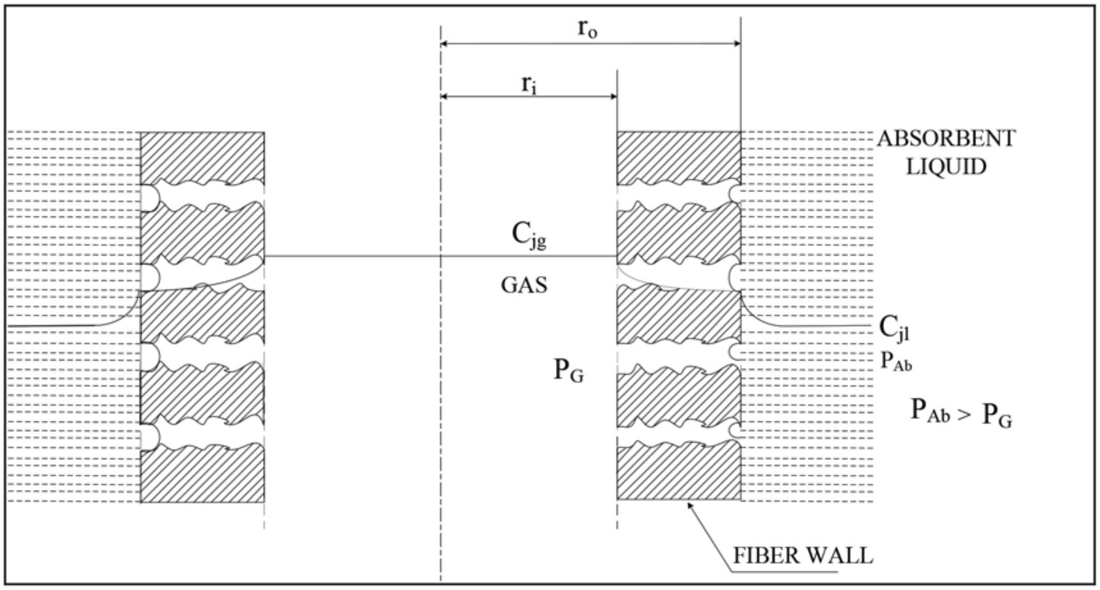


Figure 1: Concentration Profile of Absorbed Species in Gas and Liquid Phases.

In Phase II, NJIT will explore, in detail, the purification and separation performance of the PSMAB process for selected absorbents vis-à-vis purification of the feed gas stream to obtain a high-pressure, purified He stream and a low-pressure, purified CO_2 stream.

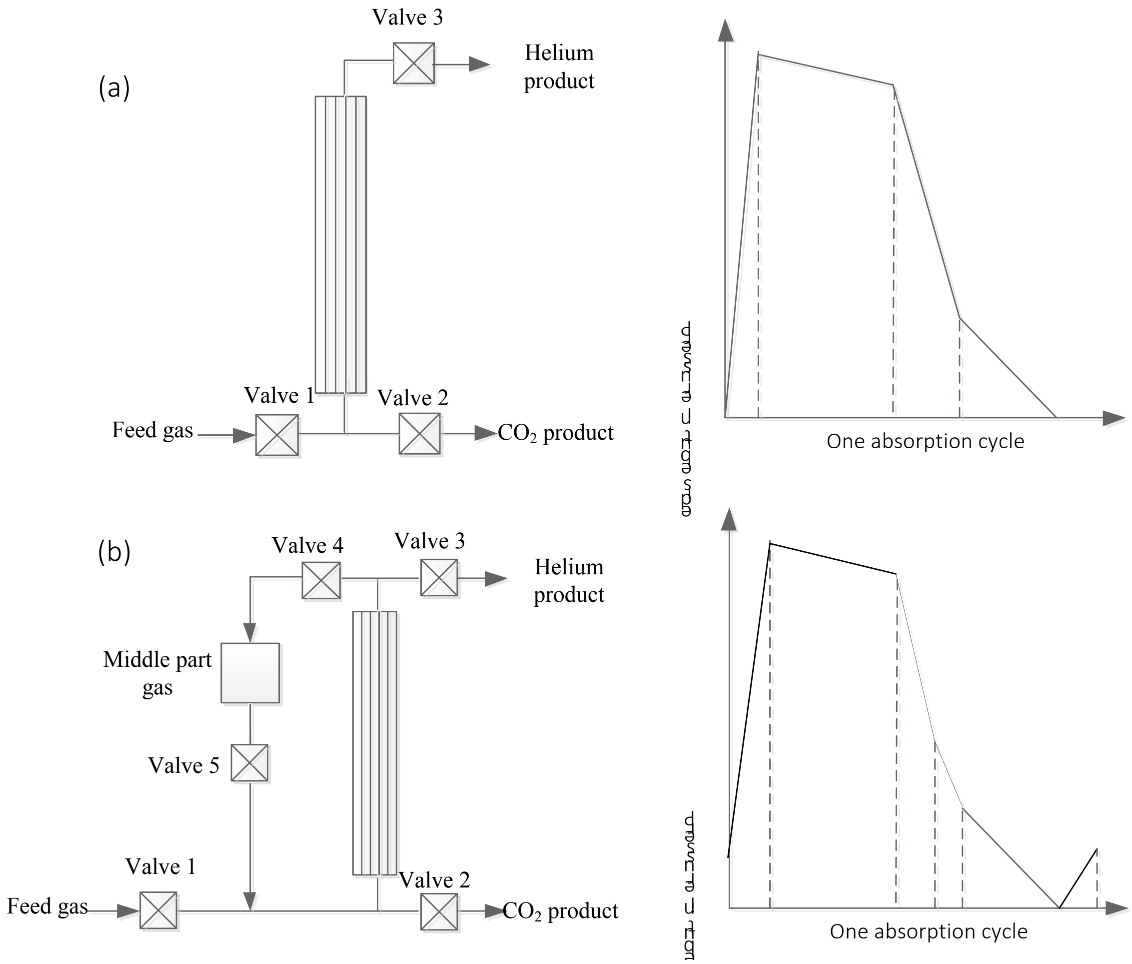


Figure 2: Schematic Diagrams of (a) 3-Valve and (b) 5-Valve Pressure Swing Membrane Absorption Process and the Corresponding Pressure vs. Time Profile in the Bore of the Tubule or Hollow Fiber.

Experimental setups will be developed to measure the solubility and diffusion coefficients of CO_2 and He at the appropriate ranges of temperature and pressure for selected absorbents. Researchers will develop a mathematical model of the PSMAB device and process.

In Phase III, NJIT will generate experimental data on the solubility and diffusion coefficient for CO_2 and He for the selected absorbents. This will allow comparison of the results of simulation of the mathematical model with the observed purification and separation in the PSAB process and device for selected absorbents. Simulations of the model will be performed to explore scale up of the process and facilitate process evaluation. The extent of loss/deterioration of the absorbents over extended periods of operation will be determined.

TABLE 1: LIQUID SORBENT BED PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pure Sorbent			
Molecular Weight	mol^{-1}	205.26	205.26
Normal Boiling Point	°C	N/A	N/A
Normal Freezing Point	°C	-6	-6
Vapor Pressure at 15 °C	bar	None	None
Manufacturing Cost for Sorbent	$/kg	Not available	
Working Solution			
Concentration 20% PAMAM dendrimer Gen 0 in [bmim]	Kg/kg	0.25 (dendrimer/[bmim][DCA])	
Specific Gravity (15 °C/15 °C)	g/cm^3	1.08 at room temp.; 1.06 at 65 °C 1.092 (20 wt% dendrimer-[bmim][DCA] mixture) at room temperature	
Specific Heat Capacity at STP	kJ/kg-K	N/A	N/A
Viscosity at STP	cP	106.7 at room temp	
Absorption			
Pressure	bar	13.8–17	13–20
Temperature	°C	100–125	150–200
Equilibrium CO_2 Loading	mol/mol	0.13	
Heat of Absorption	kJ/mol CO_2		
Solution Viscosity	cP	25.4 at 65 °C	
Desorption			
Pressure	bar	0.9	1.0
Temperature	°C	100–125	150–200
Equilibrium CO_2 Loading	mol/mol	0.019	
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar		

TABLE 2: MEMBRANE-CONTACTOR PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	fluoropolymer	
Materials of Fabrication for Support Layer	—	ceramic, Teflon, PEEK	
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	—	hollow fiber, shell and tube	
Max Trans-Membrane Pressure	bar	20.4 bar	21 bar
Hours Tested Without Significant Degradation	—	100	1,000
Manufacturing Cost for Membrane Material	\$/m^2	100	
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—		
Packing Density	m^2/m^3		ceramic: 900 Teflon: 2,000 PEEK: 5,000
Shell-Side Fluid	—		
Syngas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	N/A/85≈90.7/0.2≈1.0	90/95/1.0
H_2 Recovery, Purity, and Pressure	%/%/bar	N/A/93≈95/5.0≈6.0	95/98/6.0–10.0
Pressure Drops Shell/Tube Side	bar	N/A	N/A

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – Hydrogen sulfide (H_2S) will not affect the ceramic substrate, nor will it affect the fluoropolymer coating on ceramic and PEEK materials; the Teflon hollow fibers will also remain unaffected. PEEK material is also unlikely to be affected.

Syngas Pretreatment Requirements – Syngas may need to be cooled to 100–125 °C, unless the next round of membrane modules can withstand higher temperature on a continuous basis.

Membrane Replacement Requirements – Device has not been run long enough continuously to define the replacement time. Device will need to run for at least 1,000–3,000 hours.

Waste Streams Generated – Degraded absorption solvent.

Proposed Module Design – Porous hydrophobic hollow-fiber based membrane modules having very limited dead volume at the tube-side headers and tube sheets and connections; the outside diameters of contiguous hollow fibers should not touch each other to allow absorbent in between at the closest distance between adjacent hollow fibers

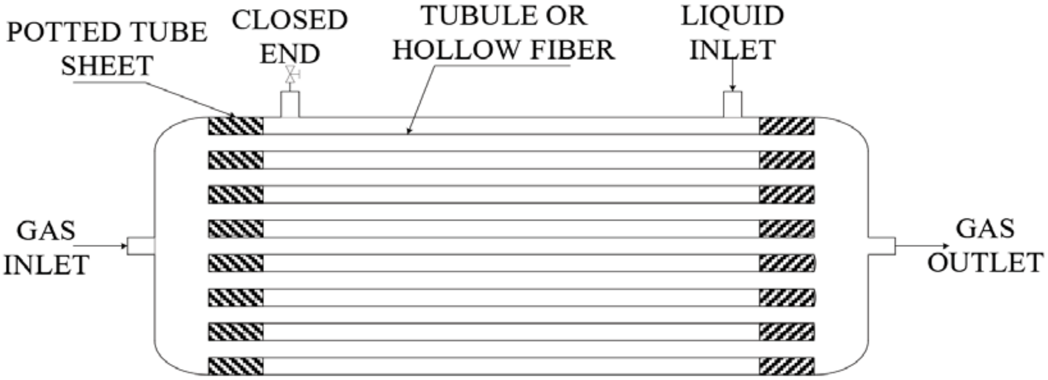


Figure 3: Schematic of Absorber Containing Ceramic Tubules or Hollow Fibers

technology advantages

- High solubility selectivity of novel selected liquid absorbents, high purification ability of the PSA process, and high gas-liquid contacting surface area per unit device volume.
- Compact, membrane-like device.
- Will deliver highly purified hydrogen (H_2) at nearly its partial pressure and temperature in the post-shifted reactor syngas feed.
- Purified CO_2 stream (>90 percent CO_2) will be available at 1 atm.

R&D challenges

- Continuous production of both a higher-purity He stream and a highly purified CO_2 stream requires more modules and altered module configurations. The PEEK hollow-fiber module design has to be changed to achieve higher purification. There is considerable dead volume in the design provided to us resulting in lower CO_2 concentration in the CO_2-rich stream and higher CO_2 concentration in the He-rich stream.
- Absorbent leaks through microporous PTFE hollow fibers that have a plasma polymerized microporous fluorosilicone coating. These fibers did not develop a high-enough pressure capability and need further development.
- The ceramic tubules have considerable pressure capability but have low surface area per unit volume and are therefore not suitable with current tubule dimensions.

results to date/accomplishments

- Successful testing of PEEK membrane in lab at 250 psig and 100 °C with He/CO_2 stream.
- Successful testing of ceramic membrane modules in lab at 300 psig without any leakage; extended operation at 120 °C.
- Scale-up of process and device was conducted, including implementation of improved hollow-fiber module design with regard to inter-fiber spacing and fiber surface area in a given module.
- Absorbent liquid was characterized and degradation determined.
- Polyethylene glycol (PEG) 400 is capable of replacing the ionic liquid as the solvent especially in the presence of the dendrimer.
- The PSMAB process was stable with time; the PEEK membrane modules performed much better than ceramic membrane modules to separate CO_2 since PEEK hollow fibers had much higher gas-liquid contacting area per unit gas volume.
- A mathematical model was developed to describe the pressure swing membrane absorption process.

next steps

This project ended on March 31, 2013.

available reports/technical papers/presentations

Jie, X., Chau, J., Obuskovic G. and Sirkar, K. K., "Preliminary Studies of CO_2 Removal from Precombustion Syngas through Pressure Swing Membrane Absorption Process with Ionic Liquid as Absorbent," I&EC Res., 52, 8783-8799 (2013).

Chau, J., Obuskovic, G., Jie, X., Mulukutla, T. and Sirkar, K. K., "Solubilities of CO_2 and Helium in an Ionic Liquid Containing Poly(amidoamine) Dendrimer Gen 0," I&EC Res., 52, 10484-10494 (2013).

Chau, J., Obuskovic, G., Jie, X. and Sirkar, K.K., "Pressure Swing Membrane Absorption Process for Syngas Separation in a 3-valve System: Modeling vs. Experiments," J. Membrane Sci., 453, 61-70 (2014).

Jie, X., Chau, J., Obuskovic, G. and Sirkar, K.K., "Enhanced Pressure Swing Membrane Absorption Process for CO_2 Removal from Shifted Syngas with Dendrimer-Ionic Liquid Mixture as Absorbent," I&E Chem. Res., 53(8), 3305-3320 (2014).

Sirkar, K; Jie, X; Chau, J; Obuskovic, G.; Final Technical Report, June 2013, "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage." *http://www.osti.gov/scitech/servlets/purl/1097081*.

Sirkar, K.K., "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage," presented at 2012 NETL CO_2 Capture Technology Meeting, July 2012.

Chau, J.; Xingming, J.; Obuskovic, G.; and Sirkar, K.K., "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage," presented at 2011 NETL CO_2 Capture Technology Meeting, August 2011. *http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/26Aug11-Sirkar-NJIT-PSA-CO_2-from-Syngas.pdf*.

PRE-COMBUSTION CARBON CAPTURE BY A NANOPOROUS, SUPERHYDROPHOBIC MEMBRANE CONTACTOR PROCESS

primary project goals

Gas Technologies Institute set out to develop cost-effective separation technology for carbon dioxide (CO_2) capture from synthesis gas (syngas) based on a hollow-fiber membrane contactor.

technical goals

- Design an energy-efficient, CO_2 recovery process that minimizes hydrogen loss.
- Tailor highly chemical-inert and temperature-stable, superhydrophobic, hollow-fiber poly (ether ether ketone) (PEEK) membrane for pre-combustion CO_2 capture.
- Manufacture a low-cost integrated membrane module.

technical content

The membrane contactor is a novel gas separation technology, advanced mass transfer device that operates with a liquid on one side of the membrane and gas on the other. Unlike gas separation membranes where a differential pressure across the membrane provides the driving force for separation, the membrane contactor can operate with pressures that are almost the same on both sides of the membrane. The driving force is the chemical potential of CO_2 absorption into the liquid. This process is thus easily tailored to suit the needs for pre-combustion CO_2 capture.

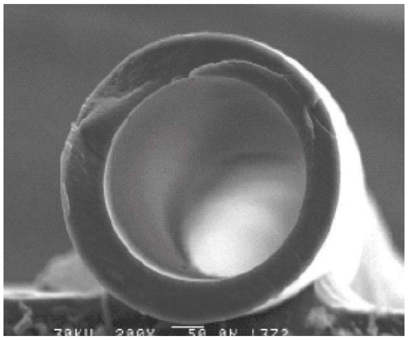


Figure 1: PEEK Hollow Fiber

The hollow-fiber membrane is manufactured from an engineered material, called PEEK by PoroGen Corporation, using a patented process. Some key characteristics that make PEEK attractive for this process are: high heat resistance, high rigidity, high dimensional stability, good strength, excellent chemical resistance, excellent hydrolytic stability, an average pore size of 1 to 50 nm, an average porosity of 40 to 70 percent, and an 800-pound per square inch (psi) water breakthrough pressure.

The PEEK hollow-fiber membrane is nanoporous and can be surface modified to achieve superhydrophobicity; fiber OD can range from 200µm to 1mm; and fibers can be made with thin wall (<25µ) due to the strength of PEEK. The PEEK membrane pore size can be controlled from 1 to 50 nm, and asymmetric membrane structures can be utilized for high performance. The hollow fiber has a high burst pressure of greater than 500 pounds per

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Nanoporous, Superhydrophobic Membrane Contactor Process

participant:

Gas Technology Institute

project number:

FE0000646

NETL project manager:

Arun Bose
arun.bose@netl.doe.gov

principal investigator:

Howard Meyer
Gas Technology Institute (GTI)
howard.meyer@gastechnology.org

partners:

PoroGen Corporation
Aker Process Solutions

performance period:

10/1/09 – 3/31/12

square inch gauge (psig), and a high collapse pressure of greater than 1,000 psig.

The advanced hollow-fiber module is constructed by computer-controlled helical winding. The modules exhibit favorable flow dynamics with minimal pressure drop, high uniform packing density, and thermodynamically efficient counter-current flow configuration.

The project was divided into two phases. The activities of Phase I included the development of hollow-fiber membranes suitable for the membrane contactor application with improved mass transfer, establishing feasibility of the proposed technology for syngas CO_2 separation, and performing initial process design and economic analysis based on test data.

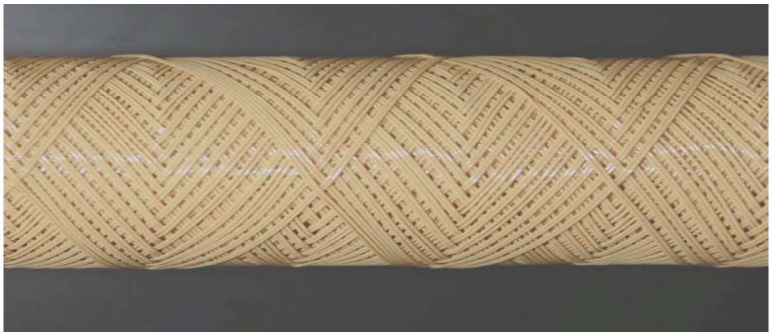


Figure 2: Advanced Hollow-Fiber Module Design

The focus of the Phase II activity was to scale-up the process from lab to bench scale. This included scale-up of the membrane module fabrication process so that membrane modules of the size suitable for large-scale application could be manufactured; bench-scale testing of the membrane contactor process stability and sensitivity to process variations; and refinement of the process economics based on bench-test data.

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Perfluoro-oligomer	Perfluoro-oligomer/Polymer
Materials of Fabrication for Support Layer		PEEK	PEEK
Nominal Thickness of Selective Layer	µm	100	100
Membrane Geometry		Hollow Fiber	Hollow Fiber
Maximum Trans-Membrane Pressure	bar	3.4	Maximize
Hours Tested Without Significant Degradation		120	120
Manufacturing Cost for Membrane Material	$\$/m^2$	Proprietary	Proprietary
Membrane Performance			
Temperature	°C	0 – 50	Maximize
H_2 Pressure Normalized Flux	GPU or equivalent		
CO_2 Removal Rate	$kg/m^2/h$	6	1.5
H_2/H_2O Selectivity	-	$3.7x10^{-6}$	$3.7x10^{-6}$
H_2/CO_2 Selectivity	-	$2.65x10^{-7}$	$2.65x10^{-7}$
H_2/H_2S Selectivity	-	7.5x10-5	7.5x10-5
Sulfur Tolerance	ppm	>100,000	>100,000
Type of Measurement	-	Equilibrium Calculation	Gas Analysis
Proposed Module Design		-	
Flow Arrangement	-	Counter-Current	Counter-Current
Packing Density	m^2/m^3	500 – 1,000	500 – 1,000
Shell-Side Fluid	-	Water, methanol, aMDEA	Water, methanol, Selexol

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Membrane Area/Module	m^2	1	100
Syngas Gas Flowrate	L/min	12	1,200
Solvent Flowrate	L/min	1.2	120
CO_2 Recovery, Purity, and Pressure	% / % / bar	90/96/5	90/96/5
H_2 Recovery, Purity, and Pressure	% / % / bar	99/91/50	99/91/50
Pressure Drops Shell/Tube Side	bar	0.4/0.04	0.4/0.04
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	$100	$40

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Contaminant Resistance – Membrane is resistant to all contaminants. Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column.

technology advantages

- Counter-current flow allows for the most efficient mass transfer, thermodynamically.
- Computer-controlled winding provides structured packing to enable enhanced turbulence flow at fiber surface.
- High temperature stability for the desorption step.
- High liquid breakthrough pressure (no liquid wet out), high membrane integrity.
- High membrane productivity.

R&D challenges

- Membrane hydrophobic properties change with solvent contact, causing leakage.
- Mass transfer coefficient of 1.5 kg/m^2hr used in the economic evaluation was not sufficiently high for gas absorption in the membrane contactor.

results to date/accomplishments

- Membrane contactor stability and life testing completed.
- 90 percent CO_2 removal from simulated syngas demonstrated.
- High mass transfer coefficients achieved.
- Commercial size membrane contactor designed.
- Slipstream testing completed.

next steps

- The project ended on March 31, 2012.
- Additional module design and testing required to operate with more viscous solvents.
- Scale-up testing with 8-in diameter modules with coal-derived syngas.

available reports/technical papers/presentations

Meyer, H.; Zhou, J.; Bikson, B.; and Ding, Y., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/5-Friday/26Aug11-Meyer-GTI-Pre-Combustion%20Capture%20by%20Nanoporous%20Membr.pdf*.

Zhou, J.; Meyer, H.; and Bikson, B., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/friday/Shaojun%20Zhou%20-%20FE0000646.pdf*.

Meyer, H.; Zhou, J.; and Leppin, D., "Advanced H_2S and CO_2 Removal Technologies for Synthesis Gases", presented at the 4th International Freiberg Conference of IGCC and XtL Technologies, Dresden, Germany, May 2010. *http://www.gasification-freiberg.org/PortalData/1/Resources/documents/paper/IFC_2010/14-2-Meyer.pdf*.

Zhou, S.J.; Meyer, H.; Bikson, B.; and Ding, Y., "Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture." AIChE Spring Meeting, San Antonio, Texas, March 2010. *http://www.aiche.org/cei/resources/chemeondemand/conference-presentations/hybrid-membrane-absorption-process-post-combustion-co2-capture*.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: R&D COLLABORATIONS

Advancing CO_2 Capture Technology: Partnership For CO_2 Capture

primary project goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) conducted pilot-scale testing to evaluate and validate a range of carbon dioxide (CO_2) capture technologies to develop key technical and economic information that can be used to examine the feasibility of capture technologies as a function of fuel type and system configuration.

technical goals

- Integrate a high-efficiency, flexible post-combustion capture system with existing pilot-scale combustion and emission control systems to evaluate the performance of several capture techniques and technologies in flue gas streams derived from selected fossil fuels, biomass, and blends.
- Conduct testing of oxy-combustion for selected fuels and blends in one or more of UNDEERC's existing pilot-scale units.
- Evaluate the performance of emerging CO_2 capture technologies under development and identify key challenges associated with each for both pre-combustion and post combustion platforms
- Perform systems engineering modeling to examine efficient and cost-effective integration of CO_2 capture technologies in existing and new systems.

technical content

UNDEERC constructed two pilot-scale systems and performed experiments on several advanced CO_2 capture technologies and compared them to monoethanolamine (MEA). Flue gas derived from one of two pilot combustors was used as the CO_2 source. The pilot combustors are highly versatile; able to fire virtually any fuel and configurable with all of the primary pollution control devices including electrostatic precipitators, fabric filters, selective catalytic reduction for nitrogen oxide (NO_x) control, and flue gas desulfurization.

Baseline testing was conducted using MEA to gather information to characterize each of the units. The results obtained by using MEA in the CO_2 absorption system were used as a standard by which all other solvents were compared. Data collected included CO_2 removal, CO_2 purity, required regeneration heat, and effects of sulfur oxide (SO_x), NO_x, particulate matter, and trace metals.

Baseline testing of the oxy-combustion system followed similar procedures as the absorption system. The data collected can be used to identify potential challenges concerning this technology. These challenges include effects of mercury (Hg) capture, flame stability, fouling, slagging, and heat-transfer issues.

technology maturity:

Pilot Scale

project focus:

Partnership for CO_2 Capture

participant:

University of North Dakota
Energy and Environmental
Research Center

project number:

FC26-08NT43291

predecessor projects:

N/A

NETL project manager:

Andrew Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

John Kay
UNDEERC
jkay@undeerc.org

partners:

Arthur Gallagher, Atco Power, Black & Veatch, Baker Hughes, Cansolv Technologies, CO_2 Capture Project Consortium, Constellation Power Source Generation, C-Quest Technologies, GE Global Research, Hitachi, Huntsman Petrochemical, Metso Power, Midwest Generation, Minnesota Power, Nebraska Public Power District, North Dakota Industrial Commission, Neumann Systems Group, PPL Montana, Saskatchewan Power, Sulzer, TransAlta Utilities, and University of Wyoming

start date:

05.01.2008

percent complete:

100%

Figure 1: UNDEERC post-combustion CO_2 capture test facility

Carbon dioxide capture technologies were selected and tested. Two flue gas pretreatment technologies were evaluated. The Partnership for CO_2 Capture worked with Cansolv Technologies Inc. to test the operability of a benchmark solvent and an improved formulation for sulfur dioxide (SO_2) removal. The testing indicated that choice of solvent should be made based on both SO_2 removal effectiveness and energy input required for regeneration rather than on solvent operability. The second pretreatment technology tested was a flue gas filtration technology manufactured by Tri-Mer Corporation which combines particulate, NO_X, and SO_2 control. This test showed that their capture was highly dependent on temperature, ammonia injection rate, and amount of sorbent used. The Sorbacal sorbent SPS achieve higher levels of SO_2 removal than their SP sorbent, and the Tri-Mer system effectively removed impurities prior to post-combustion CO_2 capture (though SO_2 levels may need additional trimming).

Two post-combustion solvents were also tested. Korea Carbon Capture and Sequestration R&D Center's (KCRC) Solvent-B showed 90 percent capture with approximately 40 percent lower liquid/gas ratio and 30 percent lower regeneration energy input than MEA at the same capture level. CO_2 Solutions Incorporated proprietary technology uses the enzyme carbonic anhydrase as a catalyst with a salt solution. Testing showed no degradation in performance of the enzyme catalyst, no generation of toxic waste by-products, and showed the ability to use low-grade heat for regeneration, allowing for reduction of cost of CO_2 capture.

Nine membranes for hydrogen/CO_2 separation were provided by Commonwealth Scientific and Industrial Research Organization (CSIRO) for pre-combustion testing using syngas from EERC's fluidized-bed gasifier with warm-gas cleanup. Membrane performance increased with increases in temperature.

A detailed process-modelling effort was undertaken using Aspen Plus software to develop the basis for determining cost of CO_2 capture using advanced post-combustion capture technologies and techniques including the solvents from KCRC and CO_2 Solutions. Also, three power plants were modeled using Carnegie Mellon's Integrated Environment Control model to show the effects that capture would have on net power production, water usage, and revenue requirements for various levels of capture.

Laboratory testing was performed to determine the feasibility of measuring residual amine and nitrosamines potentially emitted in stack flue gases using Fourier transform infrared spectroscopy (FT-IR).

This project placed a strong emphasis on the integration of total systems so that the economic and environmental benefits of carbon capture could be further understood and potentially implemented by utility stakeholders.

Testing of proprietary solvents was conducted on a small industrial 1 tonne/day CO_2 catch and release test system. The system utilized real combustion flue gas generated in a pilot combustor located adjacent to the capture system with typical flue gas conditions given in Table 1. Proprietary membrane testing was conducted utilizing UNDEERC's gasification pilot systems. Table 2 lists the typical conditions of the syngas for membrane testing.

Table 1: Typical Flue Gas Conditions

Flue Gas Flow 250 kg/hr		Composition						
Pressure	Temperature	vol%				ppmv		
psia	°C	CO_2	H_2O	N_2	O_2	CO	SO_x	NO_x
14.7	40	15.6	11.0	80.1	4.2	25	295	200

Table 2: Typical Syngas Conditions

Syngas Flow 2,200 kg/hr		Composition							
Pressure	Temperature	vol%							ppmv
psig	°C	CO	H_2	O_2	N_2	CO_2	CH_4	hydrocarbons	H_2S
309	325	2.63	37.64	0.12	11.96	47.92	2.83	0.04	4,095

technology advantages

UNDEERC has obtained experimental data for a variety of advanced CO_2 capture technologies and oxy-combustion systems. Beyond showing a clear comparison of various approaches, this work has resulted in several improvements to solvents and membranes. Data from this program led directly to an improved sulfur capture solvent being produced by Cansolv Technologies. KCRC took the data obtained to focus their development pathway, focusing on a solvent which displays potential for future performance improvement. CO_2 Solutions Incorporated utilized data generated to further develop their technology to take advantage of waste heat availability which shows potential to reduce capture costs. Finally, CSIRO advanced their early stage development of a membrane that shows great promise for pre-combustion CO_2 capture. These advancements are moving concepts toward application, producing concepts and technologies that reduce the cost of CO_2 capture.

R&D challenges

Retrieving enough information on existing technologies to make appropriate selections for testing and integrating the technologies into total systems.

status

Final report is completed.

available reports/technical papers/presentations

SUBTASK 2.18 – ADVANCING CO_2 CAPTURE TECHNOLOGY: PARTNERSHIP FOR CO_2 CAPTURE (PCO_2C) PHASE III, Final Report, J.P. Kay, at al. March 2016.*https://www.osti.gov/scitech/servlets/purl/1320560*

Kay, J.P.; Jensen, M.D.; Fiala, N.J., "Pilot-Scale Evaluations of Advanced Solvents for Postcombustion CO_2 Capture," Energy Procedia 2014, 63, 1903–1910.

Kay, J.P.; Fiala, N.J., "Comparative Evaluation of Advanced Postcombustion CO_2 Capture Technologies," Paper presented at the 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, June 2–6, 2013.

Pavlish, B.M.; Kay, J.P.; Laumb, J.D.; Strege, J.R.; Fiala, N.J.; Stanislowski, J.J.; Snyder, A.C., "Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II", Final Report (September 1, 2010–April 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-08-17; Energy & Environmental Research Center: Grand Forks, ND, August 2013.

Hildebrandt, K.; Kay, J.P., "Integration of Postcombustion CO_2 Capture into Existing Coal-Fired Power Plants," Topical Report for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; Energy & Environmental Research Center: Grand Forks, ND, March 2012.

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FUTURE OF CCS TECHNOLOGY ADOPTION AT EXISTING PC PLANTS

primary project goals

Argonne National Laboratory (ANL) is constructing scenarios that affect carbon capture and storage (CCS) adoption as combinations of cases for the following dimensions: electricity demand, nuclear growth, renewable energy growth, higher or lower gas price factors, and alternative policies.

technical goals

- Extension of ANL's previous work in project FWP49539, "Evaluation of CO_2 Capture/ Utilization/Disposal Options."
- Simulate oxy-combustion and amine-based processes using ASPEN.
- Expand the scenario analyses to focus on the value of coal-based CCS for existing pulverized coal (PC) plants and for other technologies, such as coal-to-liquids with CCS.
- ANL will examine pathways that expedite CCS adoption, such as accelerated research and development (R&D) and carbon dioxide (CO_2) utilization for enhanced oil recovery (EOR).
- ANL will examine opportunities for R&D related to shale gas, such as developing CCS specifically for natural gas combined cycle (NGCC) units.

technical content

In a previous project (FWP49539), ANL conducted engineering assessments and economic evaluations on retrofitting PC boilers with oxy-combustion, and then eventually repowering the site with integrated gasification combined cycle (IGCC). The engineering assessment for oxy-combustion was conducted with the ASPEN process model and the economic evaluations with the AMIGA macroeconomic model. The assessment investigated the entire life cycle of the plant, which included the mining of the coal, coal transportation, coal preparation, power generation, environmental controls, water use, pipeline CO_2 conditioning, and pipeline transport of CO_2 for sequestration.

ANL also conducted ASPEN modeling for 18 different oxy-combustion and air-fired cases. Three different power production ratings (150 MW, 300 MW, and 450 MW) were investigated. The model included a selective catalytic reduction (SCR) system and a flue gas desulfurization (FGD) system for flue gas cleanup.

technology maturity:

Systems Analysis and Macroeconomic Modeling

project focus:

Analysis of CCS Technology Adoption

participant:

Argonne National Laboratory

project number:

FWP49806
continued from
FWP49539

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

Donald Hanson
ANL
dhanson@anl.gov

partners:

None

performance period:

2/1/11 – 3/31/14

The analysis in the current project will demonstrate and, to the extent possible, quantify the role and benefit of R&D related to the utilization and environmental control of fossil fuels. The impacts of R&D will be shown by comparing model results such as deployment rates, emissions reductions, and electricity costs across various scenarios. The scenarios will capture a number of CO_2 control regimes, R&D programs, and economic conditions in order to fully understand the role that R&D plays in each. With widespread deployment of CCS under a CO_2 reduction target, R&D that lowers cost of CO_2 capture and increases efficiency will be shown to have a high economic payoff.

Other topics to be analyzed with the ANL model are as follows: the value of coal-based CCS in high natural gas price scenarios; opportunities and obstacles for R&D, on NGCC with CCS, including cost and performance parameters; the conditions under which CO_2-EOR enables faster deployment of CCS systems; the market opportunity for coal and biomass to liquid fuels and power co-production with CCS; and impacts on PC units, especially those retrofitted with CCS, from cycling due to intermittent grid generation from renewables.

technology advantages

The ANL model is especially designed to analyze the issues and scenarios described above.

R&D challenges

Capturing the impacts and costs of high intermittent renewable generation as it affects dispatchable coal generators, especially those that have adopted CCS.

results to date/accomplishments

- Ran Electricity Supply and Investment Model (ESIM) for high, mid, and low gas supply scenarios to identify retirement of existing PC power plants which do not retrofit with CCS and to identify the retrofit with CCS of other current PC plants.
- Modeled predicted increased CO_2 capture and decreased CO_2 emissions for the scenarios.
- Simulated the benefit of higher utilization (i.e., capacity factor) for PC plants that retrofit CCS because of rising up the loading order (i.e., dispatch order).
- Analyzed the value of coal-based CCS in high natural gas price scenarios.
- Analyzed opportunities and obstacles for R&D, specifically regarding CCS, including cost and performance parameters.
- Analyzed market opportunity for coal and biomass to liquid fuels and power co-production with CCS.
- Analyzed impacts on PC units, especially those retrofitted with CCS, from cycling due to intermittent grid generation from renewables.
- Concluded funding for R&D for CCS, nuclear, and biochemical technologies can help meet CO_2 reduction goals.
- Concluded credits for reducing CO_2 or small price on emitting CO_2 will provide incentive to operate units with CCS at higher utilization than units without capture.
- Concluded electricity prices can be moderated for consumers and businesses if revenue from a modest price on CO_2 is recycled back to help fund investments in advanced generation capacity.

next steps

This project ended on March 31, 2014.

available reports/technical papers/presentations

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Doctor, R.; Hanson, D. A.; and Molburg, J. C., "Evaluation of CO_2 Capture and Sequestration Using Oxyfuels with AMIGA Economic Modeling," presented at 2009 NETL Capture Technology Meeting, March 2009.

U.S. DEPARTMENT OF ENERGY

NATIONAL ENERGY TECHNOLOGY LABORATORY

1450 Queen Avenue SW
Albany, OR 97321
541-967-5892

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4687

Program staff are also located in
Houston, TX and **Anchorage, AK**

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