





Advanced Solid Sorbents and Process Designs for Post-Combustion CO₂ Capture (DE-FE0007707)

RTI International

Justin Farmer, Atish Kataria, Marty Lail, Paul Mobley, <u>Thomas Nelson</u>, Mustapha Soukri, Jak Tanthana

Pennsylvania State University

Chunshan Song, Dongxiang Wang, Xiaoxing Wang

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Energy Research at RTI International





Project Overview

Objective

Address the technical hurdles to developing a solid sorbent-based CO_2 capture process by transitioning a promising sorbent chemistry to a low-cost sorbent suitable for use in a fluidized-bed process



This project combines previous technology development efforts: RTI (process) and PSU (sorbent)



- Project management
- Process design
- Fluidized-bed sorbent



Project Funding: \$3,847,161

- DOE Share: \$2,997,038
- Cost Share: \$850,123



- PSU's EMS Energy Inst.
- PEI and sorbent improvement



Period of Performance:

• 10/1/2011 to 12/31/2015



- Masdar New Ventures
- Masdar Institute
- TEA of NGCC application



Solid Sorbent CO₂ Capture



 $\begin{array}{lll} \mbox{Primary:} & \mbox{CO}_2 + 2 R N H_2 \rightleftarrows N H_4^+ + R_2 N C O O^- \\ \mbox{Secondary:} & \mbox{CO}_2 + 2 R_2 N H \rightleftarrows R_2 N H_2^+ + R_2 N C O O^- \\ \mbox{Tertiary:} & \mbox{CO}_2 + H_2 O + R_3 N \rightleftarrows R_3 N H^+ + H C O 3 - \end{array}$

Technology Features

- Sorbent: supported polyethyleneimine
- Process: fluidized, moving-bed

Advantages

- Potential for reduced energy loads and lower capital and operating costs
- High CO₂ loading capacity; higher utilization of CO₂ capture sites
- Relatively low heat of absorption; no heat of vaporization penalty
- Avoidance of evaporative emissions
- Superior reactor design for optimized and efficient CO₂ capture performance

Challenges

- Heat management / temperature control
- Solids handling / solids circulation control
- Physically strong / attrition-resistant
- Stability of sorbent performance

Technical Approach & Scope

Start w/ process engineering analysis

 Concluded that circulating, staged, fluidized-bed design exhibits significant promise.

Development Needs:

• Optimize reactor design and process arrangement.

Development Approach:

- Detailed fluidized bed reactor modeling.
- Bench-scale evaluation of reactors designs.
- Demonstration of process concept.



Start w/ preliminary economic screening

Start w/ promising sorbent chemistry

 PSU's Molecular Basket Sorbents offer high CO₂ loading; reasonable heat of absorption (66 kJ/mol).

Development Needs:

- Improve thermal stability.
- Reduce leaching potential.
- Reduce production cost.
- Convert to fluidizable form.

Development Approach:

- Modify support selection.
- Simplify amine tethering.
- Scalable production methods.
- Conducted detailed technical and economic evaluations
- Basis: DOE/NETL's Cost and Performance Baseline for Fossil Energy Plants
- Further reduction needed \rightarrow reduced power consumption & capital cost

Technology Development Approach

Previous Work	Current Project		Future Development		
< 2011	2011-15		2016-18	2018-22	> 2022
Proof-of-Concept / Feasibility			Pilot 0.5 - 5 MW (eq)	Demo ~ 50 MW	Commercial
Laboratory Validation (2011 – 2013)		Prototype Testing (2015)			
 Economic analysis Milestone: Favorable technology fer Sorbent development Milestone: Successful scale-up of fl Process development Milestone: Working multi-physics, Milestone: Fabrication-ready design single-stage contactor 	easibility study uidized-bed sorbent CFD model of FMBR n and schedule for	 Prototype Testing Milestone: Operational prototype capable of 90% CO₂ capture Milestone: Completion of 1,000 hours of parametric and long-term testing Updated Economics Milestone: Favorable technical, economic, environmental study (i.e. meets DOE targets) 			
Polovant Environment Validation (2012 2014)					

Relevant Environment Validation (2013 – 2014)

Process development

- Milestone: Fully operational bench-scale FMBR unit capable of absorption / desorption operation
- Milestone: Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype

Sorbent development

• Milestone: Successful scale-up of sorbent material with confirmation of maintained properties and performance

Preliminary Technology Feasibility Study

TEA to be revised in 2015 using bench-scale test data and updated guidelines from NETL

Summary

- Total cost of CO₂ captured ~ 39.7 \$/T-CO₂
- > 25% reduction in cost of CO₂ capture, with > 40% reduction possible with advances in sorbent stability and reactor design
- ~ 40% reduction in energy penalty; significant reduction in total capture plant cost (compared to SOTA)

Cost Reduction Pathway

- Sorbent
 - Improve CO₂ capacity
 - Improve long-term stability; minimize losses
 - Reduce production costs
- Process
 - Heat recovery from absorber / compression train and integration into process
 - Recycle attrited sorbent particles for removal of acid gases
 - Explore lower cost MOCs and
 Compatibility

Current Status of Project

- Test Equipment
- Sorbent Scale-up
- Bench-scale Prototype Testing
- Next Steps Bench-scale Testing
- Next Steps Sorbent Development
- Application to Other Industrial CO₂ Sources

Test Equipment – PBR and vFBR

- Verify (visually) the fluidizability of PEIsupported CO₂ capture sorbents
- Operate with realistic process conditions
- Measure $\Box P$ and temperature gradients
- Test optimal fluidization conditions

"visual" Fluidizedbed Reactor

Packed-bed Reactor

- Fully-automated operation and data analysis; multi-cycle absorption-regeneration
- Rapid sorbent screening experiments
- Measure dynamic CO₂ loading & rate
- Test long-term effect of contaminants

RTI's Bench-scale Solid Sorbent CO₂ Capture Prototype System

- Flue gas throughput: 300 and 900 SLPM
- Solids circulation rate: 75 to 450 kg/h
- Sorbent inventory: ~75 kg of sorbent
- Currently conducting prototype testing to evaluate sorbent performance and process design effectiveness

Development Progress – Sorbent Scale-up

Objective

Improve the thermal and performance stability and production cost of PEI-based sorbents while transitioning fixed-bed MBS materials into a fluidizable form.

Previous Work

- Stability improvements through addition of moisture and PEI / support modifications.
- Suitable low-cost, commercial supports identified (1000x cost reduction).
- Converted sorbent to a fluidizable form.

Current Work

Gen1 Sorbent (chosen for scale-up)

- PEI on a fluidizable, commercially-produced silica support.
- Optimized Gen I sorbent through: solvent selection; drying procedure; PEI loading %; regeneration method; support selection; etc.

Gen2 Sorbent (promising next step)

- Extremely stable sorbent, high CO₂ loadings (11 wt%).
- Provisional patent application filed.

Bench-scale Prototype Testing

Prototype system has gone through full construction, shakedown, and commissioning

Prototype system operation:

- Starting temperatures: 70°C (Absorber); 110°C (Regen)
- Heat exchange: CW in Absorber; Steam in Regenerator
- Pneumatic conveying of sorbent (Regen →Absorber)
- Sorbent circulation rate controlled and monitored by measurement of the riser pressure drop

FG CO2 Composition 15 vol%	CO ₂	H ₂ O	N ₂	
	15 vol%	3 vol%	Balance	

Highlights of prototype testing (to date) *

- Cumulative testing: 350+ circulation hours; 100+ CO₂ capture hours.
- The sorbent is capable of rapid removal of CO₂ from the simulated flue gas
- Sustained 90% capture of the CO₂ in the simulated flue gas stream is possible

Bench-scale Prototype Testing

Highlights of prototype testing (cont'd)

- Sorbent has very good hydrodynamic properties
- Absorber temperature rise linked to CO₂ capture
- Immediately upon introduction of CO₂ to Absorber, a large exotherm is observed in the first stage and required ~1.5 kWth heat to be removed; Exotherm migrates up through the Absorber stages
- Heat Management Demonstration:
 - Complicated by large heat losses to environment
 - Mitigated heat loss effects through continuous heat delivery to Absorber / flue gas
 - Able to demonstrate superior CO₂ capture performance with heat management
 - 90% CO₂ capture achieved with CW heat management + heat loss to environment
- Additional parametric studies are needed to clearly correlate process variables with system performance and assumptions from economic analyses.

Other Lessons Learned

Concept Lab

Bench-scale testing

- Sorbent circulation and fluidization
 - Identified process conditions to pressure balance circulation loop
 - Calibrated circulation rate using extraction probes / ΔP measure
 - Optimized loop seal aeration approach to maximize solids circulation
 - Eliminated static electricity build-up which was causing solids agglomeration
 - Added pneumatic vibrators to downcomers to improve circulation reliability
 - Added larger diameter downcomers for additional circulation reliability
- Mechanical
 - Experienced cracking of polycarbonate viewing section due to thermal expansion differences– replaced with a SS pipe section
 - Identified need for cyclone maintenance to eliminate sorbent back-up potential
 - Modified gas entrance arrangement to primary cyclone and added secondary cyclone to improve sorbent recovery
 - Replaced rotameters with more reliable / less burdensome MFCs
- Performance
 - Minimal PEI leaching or vapor-phase degradation observed
 - Observed heat loss to the environment requiring additional heat tracing
 - Observed oxidative degradation of sorbent which is being eliminated through modification of bench-scale riser section

Pilot

Demo

Mechanical failure of PC viewpo

Fouling of bench system filters

Next Steps – Parametric Testing

Parametric testing to be focused on key economic performance variables and assumptions

Process Variable	Range Evaluated	Notes			
Focus Areas Studied					
Temperature profiles	65 to 95 °C (Absorber) 100 to 130 °C (Regen.)	 Regeneration performance improved at higher temperatures (> I20C) Additional work will attempt to evaluate performance impact while maintaining Absorber stages at different temperatures. 			
Sorbent circulation rate	50 to 350 lbs/hr	• Additional work will focus on optimizing performance based on S/G ratios and will evaluate if higher circulation has impact on attrition.			
Absorber temperature	65 to 95 °C	 CO₂ capture clearly improves with heat removal in Absorber. Additional work to be performed while heat loss to environment is minimized 			
Focus Areas to be Studied					
% CO ₂ Capture	10 to 99% capture	 Work will focus on improving S/G ratio, maximizing sorbent capacity, maximizing heat removal, and improving regenerator performance. 			
Sorbent stability	Stability indicators; 3 to 5 wt% loading	 PEI sorbent fluidizable under relevant process conditions. Attrition to be quantified in parametric and long-term tests. 			
Sorbent bed height	Total bed height is 156"	• Work will correlate bed height with pressure drop in Absorber.			
Flue gas velocity	0.4 to 0.65 ft/s	 There will be an optimization point which maximizes FG velocity > 1 ft/s, but does not entrain a significant amount of solids. 			
Pressure drop	3 to 4 psia	Work will focus on minimizing pressure drop.			
Heat transfer coefficient	Calc. 500-800 W/m ² K	• Work will continue to evaluate HX coefficient at different conditions.			

Next Steps – Long-term Testing

- Parametric tests
- System modification: Regenerator
 - McCabe-Thiele method used to estimate optimal number of vessel stages needed for ideal CO₂ capture performance
 - Staging accomplished through separate vessels or effective staging using internals in a single column
 - Staged design is analogous to trayed columns used extensively in gas-liquid absorption/desorption processes.
 - Current regenerator configuration (single-stage) is not optimal for achieving very high sorbent working capacities.
 - Current regenerator will be replaced with staged column mimicking design of the absorber column.
- 500 hrs long-term testing goal
 - Conduct testing under optimal process conditions.

Next Steps – Sorbent Development

Supported PEI Sorbent Improvement ("Gen1")

- Fresh sorbent scale-up batch
 - 130 kg batch incorporated lab-scale improvements
 - ~ 20% increase in CO₂ loading capacity (preliminary data)
- Identifying additional optimization approaches
 - Preparation/manufacturing variables
 - Support modifiers
 - Blended amines
- Working with commercial manufacturers on silica support modifications/tailoring and to streamline production process

Water-stable Sorbents (Potential "Gen2" materials)

- Two key benefits
 - Stability in presence of liquid water
 - Very high CO₂ loading capacities (> 11 wt%)
 - Other applications (e.g. water treatment)
- These materials have other applications (potentially in water treatment applications)
- Development efforts for these water-stable sorbents are focused on key challenges:
 - Increase density and physical strength
 - Convert to fluidizable form

Application to Other Industrial CO₂ Sources

Objective

Demonstrate the technical and economic feasibility of RTI's advanced, solid sorbent CO₂ capture process in an operating cement plant

Period of Performance:

• 5/1/2013 to 10/31/2016

NORCEM

- Location: HEIDELBERGCEMENTGroup
- Cement plant in Brevik, Norway

Project is structured in two phases:

Phase I - Complete

- Evaluate sorbent performance using simulated and actual cement plant flue gas (testing in Norway)
- Prove economic viability of RTI's technology through detailed economic analyses
- Develop commercial design for cement application

Phase II

- Design, build, and test a pilot-scale system of RTI's technology at Norcem's Brevik cement plant
- Demonstrate long-term stability and effective CO₂ capture performance
- Update economic analyses with pilot test data

RTI's Lab-scale Test Unit in Norway

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