Breakthrough Concepts Project Fact Sheet List

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* Factsheet Under Development

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PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

04/2008

A New Concept for the Fabrication of Hydrogen Selective Silica Membranes

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

David Lang
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4881
david.lang@netl.doe.gov

Michael Tsapatsis
Principal Investigator
University of Minnesota
Department of Chemical Engineering & Materials Science
151 Amundson Hall
421 Washington Avenue, SE
Minneapolis, MN 55455
612-626-0920
tsapatsi@cems.umn.edu

Background

As stated in the National Research Council report on Novel Approaches to Carbon Management, a novel membrane is needed that can achieve the separation of carbon dioxide (CO_2) and hydrogen (H_2) at a high temperature and pressure. Extensive efforts over the last several decades have explored high temperature H_2-selective membranes made of silicon dioxide (SiO_2) and other oxides, palladium (Pd) and other metals or alloys and, more recently, various zeolites and non-aluminosilicate molecular sieves. Although promising separation results have been reported for many of them, these technologies, they all suffer from high production costs for membrane fabrication and from long term stability problems. This project revisits the objective of high temperature H_2-selective membranes with a fresh look. It explores a new concept for the fabrication of ultrathin, hydrothermally stable, molecular sieve, H_2-selective membranes.

Description

Researchers will investigate a new method for making extremely thin, high-temperature, hydrogen-selective silica membranes with high H_2 selectivity, flux, and stability in a water gas shift reactor environment. The proposed membrane will rely on the use of layered microporous silicates that have very limited pore openings perpendicular to the layers. The largest pore openings that are perpendicular to the layers are ideal for H_2 molecular sieving membranes. The new membrane fabrication method consists of synthesis of layered silicates, preparation of thin plate-like particles from these layered silicates, and deposition of the particles using layer-by-layer assembly followed by calcination. If successfully developed, the membranes could be used for economical production of H_2 from coal-supplied synthesis gas, while simultaneously producing a concentrated carbon dioxide (CO_2) stream for capture and storage.

The project will include investigation and development of membrane synthesis techniques, membrane synthesis, and evaluation of membrane separation performance and stability. Specifically, membranes will be tested for H_2 separation from CO_2 at high temperatures and pressure and for thermal stability at high temperature and pressure in the presence of water vapor.

Primary Project Goal

The primary goal of the proposed research is to develop a new economic and easy to scale up method for the fabrication of hydrogen selective silica membranes with high hydrogen selectivity, flux, and stability in a water gas shift reactor environment.

PARTNERS

University of Minnesota

Department of Chemical Engineering and Materials Science

PERFORMANCE PERIOD

8/1/2004 to 4/30/2008

COST

Total Project Value
$267,393

DOE/Non-DOE Share
$267,393 / $ 0

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

Objectives

The specific objective is to demonstrate the fabrication of a 100 nm or thinner supported film of SiO_2 using a technique that can be easily and economically scaled up and to show that this membrane can meet the following requirements:

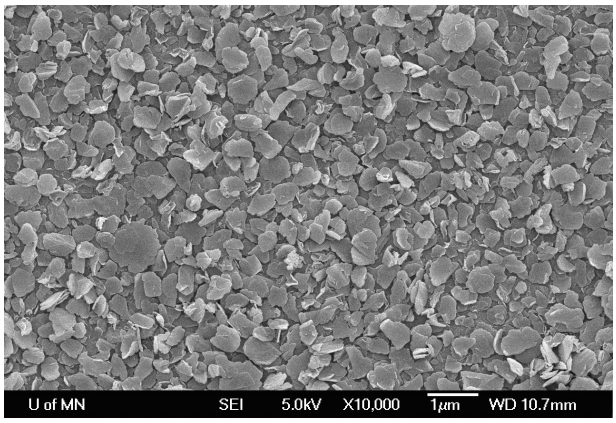
- Hydrogen permeance in excess of 10^{-7} mol/m^2-s-Pa with a H_2/CO_2 selectivity in excess of 100 at temperatures in the range of 500-700 °C, a pressure of 20 bar, and a stream composition representative of feed to a water gas shift reactor.
- Maintain stable membrane performance at the above values and conditions in the presence of steam (25 percent H_2O) for at least one month.

Benefits

Fossil fuels provide over 80 percent of the world's energy today and are expected to continue their dominance throughout the foreseeable future. Innovations in technologies that could lead to practical and cost-effective means for either reducing emissions from fossil-fueled power plants or removing CO_2 from the atmosphere could have far-reaching benefits for the economy of the United States. This project will investigate a novel alternative to current technology for the capture and sequestration of CO_2 that could result in a process for the economic production of H_2 from coal-supplied synthesis gas while simultaneously producing a concentrated CO_2 stream for sequestration. This approach has the potential to show a significant improvement in performance and cost compared to currently available technologies.

Accomplishments

- Plate-like small pore layered silicate crystals have been synthesized and calcined without significant agglomeration.
- A deposition process that leads to uniform, high-coverage (~100 percent) coating of the layered silicate particles on porous alpha-alumina supports has been developed.
- Multi-layered coatings on alpha alumina oxide discs have been obtained by repeating the deposition process.
- A permeation system has been designed and constructed to test the coated discs.
- Deposition method was extended for the film fabrication on zirconia coated stainless steel (SS) tubes.
- Permeation setup for testing the coated SS tubes was installed.
- Both coated discs and SS tubes were fabricated; permeation tests were conducted for both. For coated discs, demonstrated activated gas transport and hydrogen selectivity above one achievable by Knudsen permeation mechanism.



- Initiated investigations of the exfoliation of MCM-22(P) to single layers in order to improve the deposition procedure, reduce the membrane thickness, and/or increase the silicate particle overlap.

Coating of one layer of MCM-22 on γ-alumina coated α-alumina support

Project306.indd

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Sequestration

03/2005

NOVEL DUAL FUNCTIONAL MEMBRANE FOR CONTROLLING CARBON DIOXIDE EMISSIONS FROM FOSSIL FUELED POWER PLANTS

CONTACTS

Scott M. Klara
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4864
scott.klara@netl.doe.gov

José D. Figueroa
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4966
jose.figueroa@netl.doe.gov

C. Jeffrey Brinker
Sandia Fellow, Sandia National Laboratories
Professor of Chemical & Nuclear Engineering
The University of New Mexico
Advanced Materials Laboratory
1001 University Blvd. SE, Suite 100
Albuquerque, NM 87106
505-272-7627
cjbrink@sandia.gov

Background

There is growing concern among climate scientists that the buildup of greenhouse gases (GHG), particularly carbon dioxide, in the atmosphere is affecting the global climate in ways that could have serious consequences. One approach to reducing GHG emissions is to scrub CO_2 from the flue gas of power plants and sequester it in geologic formations. Although it is technically feasible to remove CO_2 from flue gas, current processes are too expensive. Therefore, new, less expensive processes are needed. This project is investigating the feasibility of developing a novel, dual-functional silica-based membrane for controlling carbon dioxide emissions from fossil-fuel fired power plants.

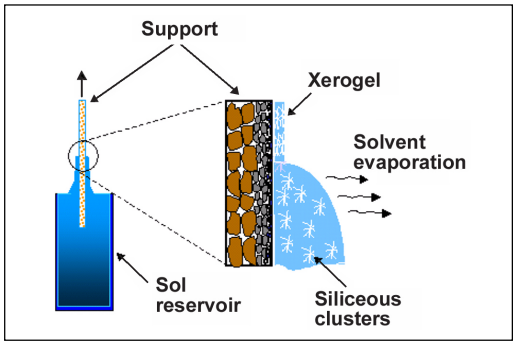


Fig. 1. Schematic representation of the sol-gel dip-coating process for depositing a microporous aminosilicate membrane on a porous tubular ceramic support.

The membrane will be prepared by a sol-gel dip-coating process on a porous support (see Fig. 1) and will consist of a microporous inorganic siliceous matrix with amine functional groups physically immobilized or covalently bonded on the membrane pore walls. It is anticipated that strong interactions between the permeating CO_2 molecules and the amine functional membrane pores will enhance surface diffusion of CO_2 on the pore wall of the membrane with subsequent blocking of the transport of other gases, such as O_2, N_2, and SO_2 (see Fig. 2). In this way, the new membrane is expected to exhibit higher CO_2 selectivity compared to prior, purely siliceous membranes that perform separations based on difference in molecular size only. The pore size of the new membranes will be controlled in the range of 4-10 Å by adjusting the precursor sol composition.

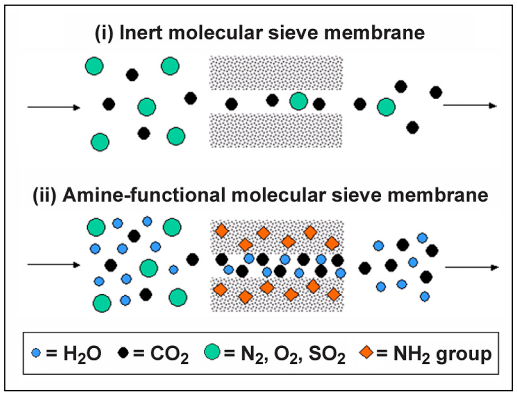


Fig. 2. Gas transport mechanism through: (i) a pure siliceous microporous membrane where separation is mainly based on size differences of permeating molecules, and (ii) a microporous aminosilicate membrane where pore blocking can be achieved by strong interactions of CO_2 and H_2O vapor with the amine groups introduced in the silica matrix.

The amount of solvent (H_2O), the type and amount of surfactant additive, and the sol aging time and their effect on membrane permeability and selectivity will be studied experimentally. The incorporation of the amine functional groups in the silica matrix will be implemented by various techniques: (1) mixing of silica sol with aqueous solution of amines; (2) using aminosilanes as a silicon source for the membrane matrix; and (3) post-grafting terminal amine groups on the pore walls of surfactant-templated membranes, using aminosilanes. The membrane microstructure (see Fig. 3) will be optimized in order to meet a targeted CO_2 permeance as high as $1x10^{-3}$ $cm^3(STP)/cm^2.sec.cmHg$, combined with a CO_2/N_2 separation factor of over 100.

The group at the University of New Mexico will be primarily responsible for laboratory-scale synthesis and testing of the proposed novel membranes, while the team at T3 Scientific will be responsible for commercialization of the technology and design/economic evaluation of an industrial-scale membrane process for CO_2 removal from power plant flue gas.

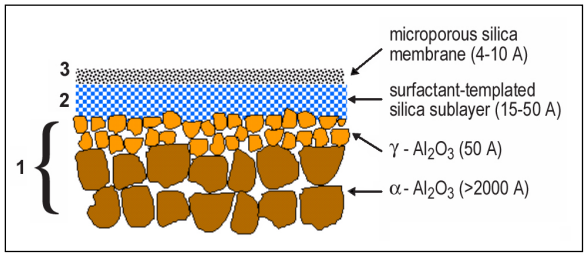


Fig. 3. Overview of the microstructure of the composite membrane comprising of: (1) a commercially available tubular or hollow fiber ceramic support; (2) a mesoporous surfactant-templated silica sub-layer with pore size 15-50 Å; and (3) a microporous aminosilicate gas separation membrane layer with pore size 4-10 Å.

Primary Project Goal

The primary goal of this project is to develop a dual functional membrane capable of removing CO_2 emissions from the flue gas of coal-fired power plants efficiently and inexpensively.

Objectives

The objectives of this project are to:

- Prepare and characterize amine functional membrane materials with a CO_2/N_2 selectivity of 100 and a CO_2 permeance of $1x10^{-3}$ $cm^3(STP)/cm^2 \cdot sec \cdot cmHg$ or greater.
- Conduct small-scale parametric testing, using a simulated multi-component gas, to determine optimum performance conditions.
- Optimize thin membrane deposition.
- Perform a preliminary systems analysis for integration of a membrane system into a 500 MW power plant.
- Perform a long-term test to estimate membrane life.
- Conduct a pilot-scale test.

Benefits

If CO_2 capture from flue gas is ever to become economically feasible, improved capture processes are needed. The use of an amine modified membrane with high CO_2 permeance and selectivity holds promise for reducing costs by avoiding the expensive absorber/stripper system required with amine based systems.

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

PARTNERS

University of New Mexico

T3 Scientific

COST

Total Project Value
$886,827

DOE/Non-DOE Share
$886,827 / $0

Project 333.pmd

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

4/2008

CARBON DIOXIDE SEPARATION WITH NOVEL MICROPOROUS METAL ORGANIC FRAMEWORKS

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4867
sean.plasynski@netl.doe.gov

David A. Lang
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4881
david.lang@netl.doe.doe

Richard Willis
Principal Investigator
UOP LLC
50 East Algonquin Road
Des Plaines, IL 60016
847-391-3190
Richard.Willis@uop.com

Background

UOP LLC, in collaboration with Vanderbilt University and the University of Edinburgh, is working to develop novel microporous metal organic frameworks (MOFs) and an associated process for the removal of CO_2 from coal-fired power plant flue gas. This innovative project will exploit the latest discoveries in an extraordinary class of materials (MOFs) having extremely high adsorption capacities. MOFs have previously exhibited exceptional adsorption capacity for methane, hydrogen, and other gases. MOFs are hybrid organic/inorganic structures – essentially scaffolds made up of metal hubs linked together with struts of organic compounds, a structure designed to maximize surface area. MOF sorption properties can be readily tailored by modifying either the organic linker and/or the metal hub.

Description

During Phase I, UOP will use its combinatorial chemistry capabilities to systematically synthesize a wide range of state-of-the-art MOFs and related materials. UOP will screen the materials for hydrothermal stability and characterize materials of particular interest. Detailed isotherm data will be collected in the low-pressure regime in order to establish a consistent, relevant baseline for subsequent development and optimization. The results of the baseline studies will be used to guide the ongoing synthesis, screening,

PARTNERS

UOP LLC

Vanderbilt University

University of Edinburgh

and measurement of new MOFs. In Phase II, up to 10 candidates will be selected for optimization, based on Phase I results. The effects of water on CO_2 adsorption will be measured in parallel with the development and validation of material scale-up and forming procedures. During Phase III, one or two of the best materials will be selected for final optimization and scale-up to pilot-scale quantities. The effects of contaminants on the performance of scaled-up, formed materials will be optimized and detailed kinetic and equilibrium data will be collected. These data will be incorporated into a process design and process economic analysis, leading to the design of a pilot study.

Primary Project Goal

The primary goal of this project is to develop a low-cost, novel sorbent and associated process to remove CO_2 from coal-fueled power plant flue gas in a cost effective manner.

Objectives

The objective of this project is to develop a low-cost novel sorbent and an associated process that demonstrates:

- High adsorption capacity
- High selectivity
- Good adsorption/desorption rates
- Ease of regeneration

- Hydrothermal and contaminant stability

- Potential to meet or exceed DOE's post-combustion CO_2 capture targets of 90% CO_2 capture at less than 20% increase in the cost of energy services by 2012

Benefits

Although oil production in the United States has been gradually declining, the nation has huge reserves of coal. Unfortunately, when coal is burned, it releases more CO_2 per unit of heat than any other fossil fuel, and anthropogenic CO_2 is believed to be contributing to global warming and climate change. Successful completion of this program could lead to a low-cost, novel sorbent to remove CO_2 from flue gas in electric power plants. The captured CO_2 could then be sequestered to prevent its emission to the atmosphere. This would enable the use of our coal reserves as an energy source without contributing to global warming, while simultaneously creating jobs and reducing our dependence on imported oil.

Accomplishments

- More than 23 different MOF materials have been prepared toward a goal of up to 50 materials.

- Prepared materials have been characterized by conventional techniques such as x-ray diffraction, thermal gravimetric analysis, and high-resolution electron microscopy to ultimately enhance the understanding of relationships among material properties and CO_2 capture performance.

- Initial CO_2 adsorption measurements have been carried out at Vanderbilt University and the University of Edinburgh.

PERFORMANCE PERIOD

4/01/2007 to 3/31/2010

COST

Total Project Value
$2,802,200

DOE/Non-DOE Share
$2,230,672 / $571,528

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

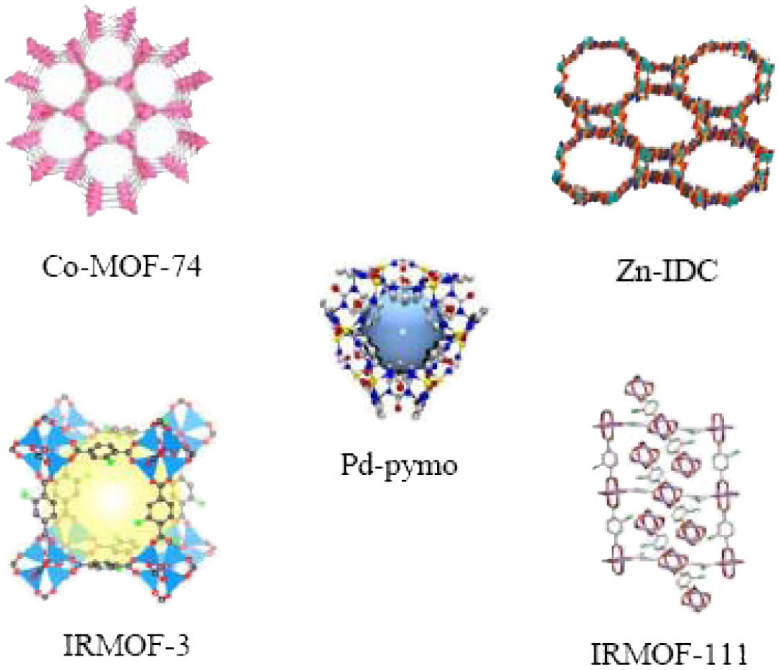
One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov



Examples of several MOFs under investigation.

PROJECT facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Carbon Sequestration

04/2008

Design and Evaluation of Ionic Liquids as Novel Absorbents

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

José Figueroa
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4966
jose.figueroa@netl.doe.gov

Edward Maginn
Principal Investigator
182 Fitzpatrick Hall
Dept. of Chem. & Biomolec. Eng.
University of Notre Dame
St. Joseph County, IN 46556
574-631-5687
ed@nd.edu

Background

There is growing concern among climate scientists that the buildup of greenhouse gases (GHG), particularly carbon dioxide (CO_2), in the atmosphere is affecting the global climate in ways that could have serious consequences. One approach to reducing GHG emissions is to scrub CO_2 from the flue gas of power plants and sequester it in geologic formations. Although it is technically feasible to remove CO_2 from flue gas, current processes are too expensive. New, less expensive processes are needed. This project is investigating the feasibility of using a novel class of compounds – ionic liquids – for the capture of CO_2 from the flue gas from coal and natural gas–fired power plants. The success of ionic liquids technology will be based on increasing the knowledge base on the chemical characteristics of ionic liquids and on the competitiveness of processes which utilize ionic liquid based absorbents for CO_2 capture from flue gas streams compared to commercial amine-based technologies. The successful ionic liquid absorbent will have high CO_2 selectivity and capacity (i.e., a Henry's law constant lower than 10 bar) with a low energy requirement for regeneration (i.e., an enthalpy of absorption less than 60 kJ/mol).

Description

The fundamental factors influencing the absorption of CO_2 and other gases present in flue gas streams will be determined, relevant thermo-physical and phase behavior properties measured, and a preliminary process design for the use of ionic liquids in an absorption separation system developed.

Primary Project Goal

The primary goal of this project is to provide a comprehensive evaluation of the feasibility of using a novel class of compounds – ionic liquids – for the capture of CO_2 from the flue gas of coal and natural gas – fired power plants.

Objectives

The objectives of the project are to:

- Produce a range of ionic liquid sorbents for further evaluation.
- Determine the fundamental factors influencing the absorption of CO_2 and other gases present in flue gas streams.

PARTNERS

University of Notre Dame

PERFORMANCE PERIOD

07/16/2004 to 07/15/2007

COST

Total Project Value
$434,076

DOE/Non-DOE Share
$434,076 / $0

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

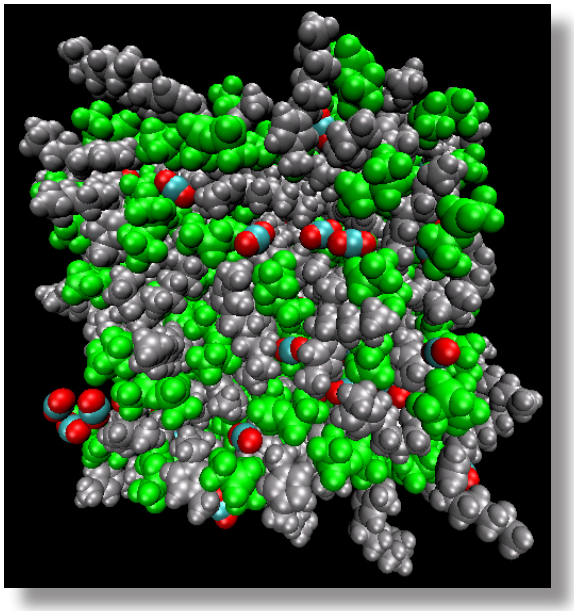
CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

- Determine relevant thermo-physical and phase behavior properties.
- Develop a preliminary process design that uses ionic liquids in an absorption separation system.



Model of CO_2 absorption by an ionic liquid. The model shows that the anions are controlling absorption in ionic liquids. The green units represent anions and the grey units represent cations.

Benefits

If CO_2 capture from flue gas is to become economically feasible, improved capture processes are needed. The use of ionic liquids as CO_2 absorbents holds promise for reducing costs by developing a process with higher CO_2 loading in the circulating liquid and lower heat requirements for regeneration. Both of these effects would lower process costs.

Accomplishments

Eleven ionic liquids have been synthesized or acquired. CO_2 solubility has been measured for five of these compounds, with 1-n-hexyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate showing the best performance to date, having a Henry's constant of 25 bar at 25 °C. By measuring the solubility of other gases in these liquids, including oxygen, ethylene and ethane, it was found that CO_2 is significantly more soluble in these ionic liquids than any of these other gases, Figure 1. Other physical properties, including viscosity and density, have been measured for these compounds. The viscosities vary widely at low temperature, but all fall to reasonable values above 40 °C.

First principles quantum mechanics calculations have been conducted to understand the nature of CO_2 absorption in these liquids. The calculations have shown that CO_2 associates primarily with the anion, but that the anion primarily associates with the cation. Thus, the CO_2 interacts most strongly with the secondary negatively charged regions of the anion, suggesting that greater negative charge delocalization could lead to enhanced CO_2 solubility. These concepts are being used to identify new targets for synthesis and testing.

Research has also demonstrated that SO_2 is highly soluble in ionic liquids, being 8 to 25 times more soluble than CO_2, depending upon pressure. NETL researchers have proven that ionic liquids can be used as the separating media in supported liquid membranes to separate CO_2.

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

4/2008

NEUTRALIZING CARBONIC ACID IN DEEP CARBONATE STRATA BELOW THE NORTH ATLANTIC OCEAN

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4867
sean.plasynski@netl.doe.gov

Heino Beckert
Project Manager
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507
304-285-4132
heino.beckert@netl.doe.gov

Daniel Schrag
Principal Investigator
Harvard University
20 Oxford Street
Cambridge, MA 02138
617-495-7676
schrag@eps.harvard.edu

Background

The eastern seaboard of the United States is the most densely populated region in the country and generates a large fraction of all U.S. anthropogenic carbon dioxide (CO_2) emissions. Disposal options for this large volume of CO_2 are limited, and land transport and disposal are difficult due to high population density. From geographical considerations, offshore disposal might seem a reasonable approach. However, a number of technical uncertainties and environmental concerns make this option difficult to implement at this time.

The Atlantic Ocean is the site of most of the world's deep sea carbonate deposition, with a wide range of sediment compositions ranging from almost pure limestone to marly shales and claystones occurring at a wide range of water depths. A number of potential disposal sites are within 200 miles of the U.S. coastline. Thus, it is essential to the Department of Energy's Carbon Sequestration Program to evaluate the suitability of CO_2 storage in deep-sea carbonate sediments as part of an overall strategy of carbon storage and management.

The major advantage of CO_2 injection into carbonate sediments beneath the sea floor is the natural chemical buffer created by the reaction between calcium carbonate and carbonic acid, producing high-alkalinity pore fluid. Unfortunately, the reaction kinetics of CO_2/water mixtures with natural carbonate sediments is not well understood at the pressures and temperatures of interest.

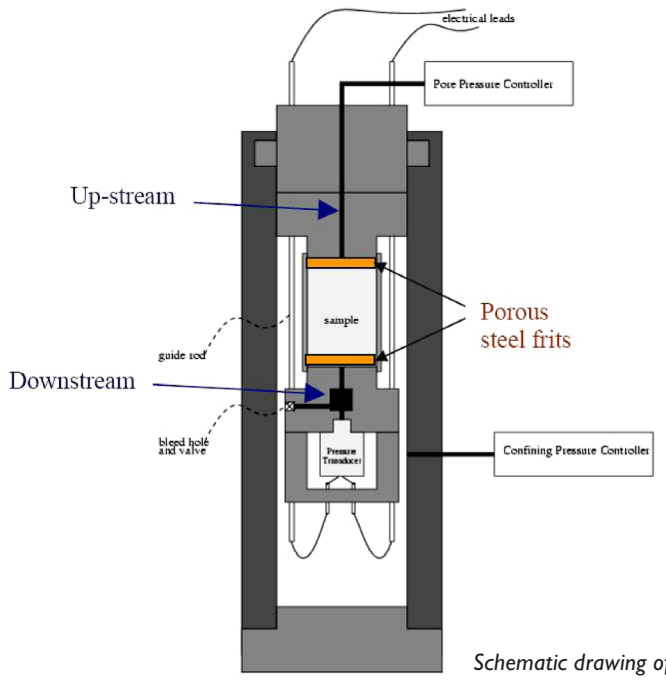
The technical issues of injection are relatively straightforward, although some questions do exist. Drilling into carbonate sediments is relatively easy. At shallow depths below the ocean floor, these deposits have high porosity but very little structural integrity. At greater depths, deposits have lower porosity and would allow little flow. However, oil extraction from such fields shows that hydrofracturing is a viable option. Also, after a relatively short period of injection, dissolution of carbonate material could provide greatly increased permeability. The calcium carbonate present will be consumed in neutralizing carbonic acid and leave behind an increased pore volume filled with calcium bicarbonate solution.

PARTNERS

Columbia University

Massachusetts Institute of Technology

Rensselaer Polytechnic Institute

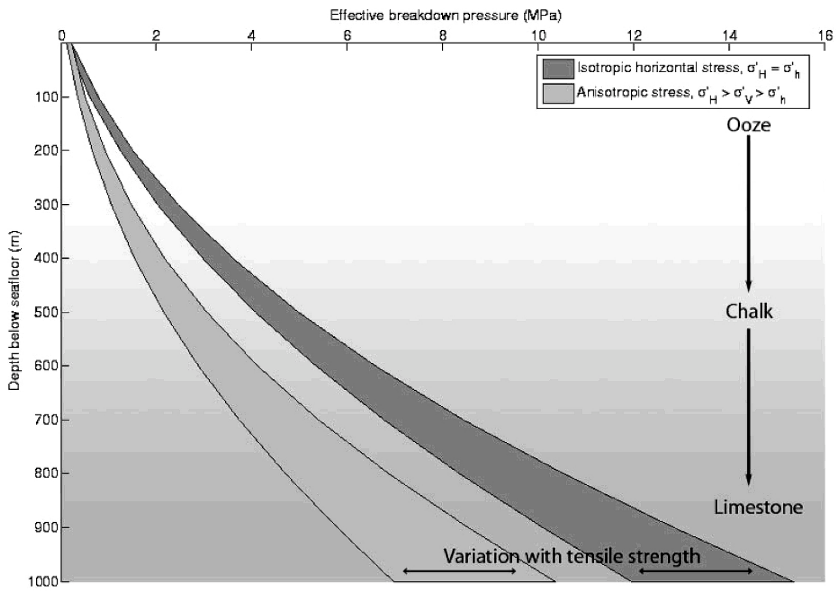


Schematic drawing of the experimental system.

Disposal by injection into carbonate sediments below the sea floor could provide a very large sink for CO_2, and the CO_2 would be neutralized in a chemical reaction that turns solid calcium carbonate into dissolved bicarbonate. The physical characteristics of the reservoir could provide a series of barriers to the escape of the CO_2. If the bicarbonate-rich pore fluid did mix with seawater, the ocean would provide an additional safeguard by buffering pH changes. Effects on the atmosphere, even on the time scale of millennia, would be extremely small, and the process should qualify as a near-permanent sequestration method.

Description

This project investigated several technical issues associated with carbon dioxide sequestration in calcium carbonate sediments below the sea floor through laboratory experiments and chemical transport modeling. The goal was to evaluate the basic feasibility of this approach, including an assessment of optimal depths, sediment types, and other issues related to site selection. Researchers studied the flow of liquid carbon dioxide and carbon dioxide-water mixtures through calcium carbonate sediments to better understand the geo-mechanical and structural stability of the sediments during and after injection. The research included investigations of the kinetics of calcium carbonate dissolution in the presence of CO_2-water fluids (a critical feature of the system as it allows for increased permeability during injection) and the possibility of carbon dioxide hydrate formation in the pore fluid. Hydrate formation may complicate the injection procedure by reducing sediment permeability but might also provide an upper seal in the sediment-pore fluid system, preventing release of CO_2 into the deep ocean, particularly if depth and temperature at the injection point rule out immediate hydrate formation. Finally, the investigators performed an economic analysis to estimate costs of drilling and gas injection, and site monitoring, as well as the availability of potential disposal sites with particular emphasis on those sites within the 200-mile Exclusive Economic Zone of the United States.



Graph showing the effective breakdown pressure as a function of burial depth.

Primary Project Goal

The primary goal was to investigate the feasibility of carbon dioxide disposal by injection and neutralization in calcium carbonate sediments below the ocean floor.

Objectives

The research objectives for this project were to:

- Understand the mechanical and chemical behavior of CO_2 and CO_2/water mixtures injected into carbonate sediments of various compositions under a range of pressures and temperatures.
- Investigate the kinetics of calcium carbonate dissolution in the presence of CO_2/water.
- Investigate the possibility of CO_2 hydrate formation in the pore fluid.
- Conduct an economic analysis to estimate costs of drilling, gas injection, and site monitoring

Benefits

Modeling and experimental results suggest that injection of carbon dioxide in deep sea sediments below 3000 meters (m) of water depth, and then 300 to 400 m deep within the underlying sediment should provide for permanent storage of carbon dioxide. Data and conclusions developed by this research provide key background information necessary to further evaluate this CO_2 mitigation option.

PERFORMANCE PERIOD

1/12/2004 to 1/14/2008

COST

Total Project Value

$801,374

DOE/Non-DOE Share

$801,374/ $0

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

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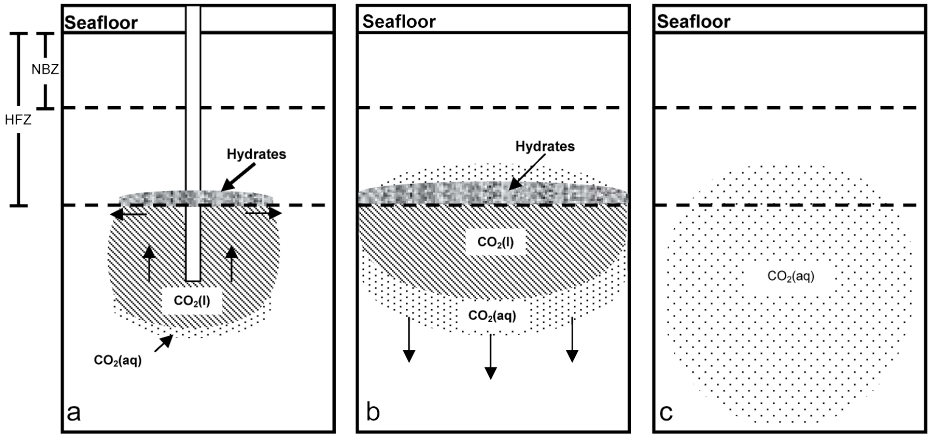
WEBSITE

www.netl.doe.gov

Accomplishments

Through a variety of modeling and laboratory efforts, researchers examined the feasibility of CO_2 injection into deep-sea sediments for permanent storage. Calculations show that once injected, the higher density of liquid CO_2 at appropriate pressures and temperatures, as well as the potential to form CO_2 hydrates that will impede the migration of CO_2 upward towards the sea floor, make this approach essentially a leak-proof method for CO_2 storage. Thermal modeling shows that continued injection of CO_2 will not perturb the local geothermal gradients to allow an escape route. The actual evolution of the CO_2 in the sub-seafloor is a complex, multiphase flow problem that will require further study. Analysis of the porosity and permeability of deep-sea sediments shows that some places have high enough permeability for direct injection, but finding such sediments represents one of the challenges associated with this strategy of ocean sequestration of CO_2. Hydrofracturing of the sediments is probably not a viable strategy as this may propagate upwards and allow some CO_2 to escape. Instead, an approach that involves injection through a network of horizontal wells that increases the effective surface area during injection would be preferable, allowing adequate flow rates even in lower permeability sediments. Additional work has also demonstrated that calcium carbonate dissolution is not an important factor in the process, and that karstification will not be an important process, nor can collapse of karst structures result in escape of injected CO_2.



The expected long-term evolution of injected CO_2: (a) 1 year; (b) 100 years, and (c) 10,000 years.

Planned Activities

This research project has recently ended and a final report will be completed in the near future. This report will include the results of the economic and site analysis.

Project317.indd

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

4/2008

A Novel Approach to Mineral Carbonation: Enhancing Carbonation While Avoiding Mineral Pretreatment Process Cost

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

David A. Lang
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4881
david.lang@netl.doe.gov

Andrew Chizmeshya
Arizona State University
Center for Solid State Science
Tempe, AZ 85287-1704
480-965-6072
chizmesh@asu.edu

Background

Carbonation of the widely occurring minerals of the olivine group, such as forsterite (Mg_2SiO_4), is a potential large-scale sequestration process that converts CO_2 into the environmentally benign mineral magnesite ($MgCO_3$). Because the process is exothermic, it inherently offers low-cost potential. Enhancing carbonation reactivity is the key to economic viability. Previous studies at the U.S. DOE Albany Research Center (ARC) established that aqueous-solution carbonation using supercritical CO_2 is a promising process; even without olivine activation, 30–50 percent carbonation has been achieved in an hour. Mechanical activation by attrition accelerated the carbonation process to an industrial timescale (near completion in less than an hour) at reduced pressure and temperature. However, the activation cost is too high to be economical and lower-cost pretreatment options are needed. The Arizona State University Center for Solid State Science proposes a novel approach that offers the potential to dramatically enhance carbonation reactivity while bypassing any pretreatment/activation.

Mechanistic investigations have shown that robust silica-rich layers form on an olivine surface during carbonation. As carbonation proceeds, these passivating layers thicken, fracture, and eventually exfoliate, exposing fresh olivine surfaces. Particle-particle and particle-wall collisions within the slurry stream can dramatically impact both the exfoliation rate and the extent of carbonation. Order of magnitude increases in the extent of carbonation have been observed for different flow systems. In order to identify key parameters that can enhance carbonation, it is proposed to explore exfoliation mechanisms and their relationship to enhanced carbonation using three innovative approaches:

PARTNERS

Arizona State University
Project Team

Michael J. McKelvy

Andrew V.G. Chizmeshya

Kyle Squires

Ray W. Carpenter

Hamdallah Bearat

PERFORMANCE PERIOD

06/22/2004 to 06/21/2007

- Carry out multiphase hydrodynamics fluid simulations and experimental investigations to elucidate key fluid-flow parameters that facilitate the slurry interactions that enhance exfoliation.

- Chemical studies to establish the potential for controlling passivating layer effectiveness and exfoliation rate by adjusting aqueous cation size (e.g., Li+, Na+, K+).

- Sonic investigations to elucidate the potential that controlled sonication offers to enhance exfoliation and particle cracking.

Once the key parameters for each approach are identified, they will be integrated to evaluate their combined potential to synergistically enhance exfoliation and carbonation. The above studies will be complemented by detailed morphological, structural, and compositional investigations of their intermediate and final reaction products down to the nanoscale. These studies will be further integrated with advanced computational modeling of key phenomena to develop an atomic-level understanding of the mechanisms that govern carbonation reactivity and exfoliation.

Primary Project Goal

The primary goal is to develop the understanding needed to engineer a new low-cost mineral carbonation process that avoids the cost of pretreatment and/or activation.

Objectives

Explore and assess the effectiveness of novel, low-cost pathways to enhance olivine passivating layer exfoliation and carbonation.

Benefits

Mineral sequestration processes have the potential to permanently dispose of CO_2 in geologically stable mineral carbonate rocks that will not require continuous monitoring, which is required with many other CO_2 sequestration technologies. The technology to be developed under this proposal will hasten the natural mechanism of turning CO_2 into a solid. The solidification process could be accomplished in less

than an hour rather than in hundreds of thousands of years via natural mineral weathering. Methods for economically sequestering CO_2 will allow for continued use of our abundant coal reserves.

Accomplishments

- Multi-phase slurry-flow studies have been integrated with multiphase hydrodynamic simulations to identify key parameters that control exfoliation and carbonation of feedstock particles. Simulations indicate that wall roughness and particle size distribution can significantly affect cross-stream transport, particle-particle collisions, and carbonation.

- A detailed systematic search for alternative aqueous solution buffers has led to the discovery that 5.5M $KHCO_3$ produces nearly twice the extent of carbonation as does the standard 0.64M $NaHCO_3$ + 1M NaCl aqueous solution, significantly enhancing the efficiency of the one-step "feedstock dissolution + aqueous carbonation" process.

- Mechanistic investigations suggest that silica-rich passivating layers (PL) formed via incongruent dissolution possess significant permeability to key reaction species during carbonation. Exfoliation behavior and structural morphology of the PL vary greatly, depending on the specific choice of halide salt and alkaline bicarbonate buffer species.

- Large-scale molecular dynamics simulations of the olivine PL predict a continuous transition zone that extends from the bulk olivine solid through the amorphous PL-solution interface and a "glassy" metastable PL nanostructure that possesses significant permeability for reactant species.

- A sonication system was developed and used to explore the effects of sonication on the extent of carbonation as a function of the weight percentage olivine present, particle size distribution, volume fraction of aqueous solution present, and sonication power, time, temperature, and CO_2 pressure. None of the conditions investigated to date significantly enhanced carbonation.

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

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1-800-553-7681

WEBSITE

www.netl.doe.gov

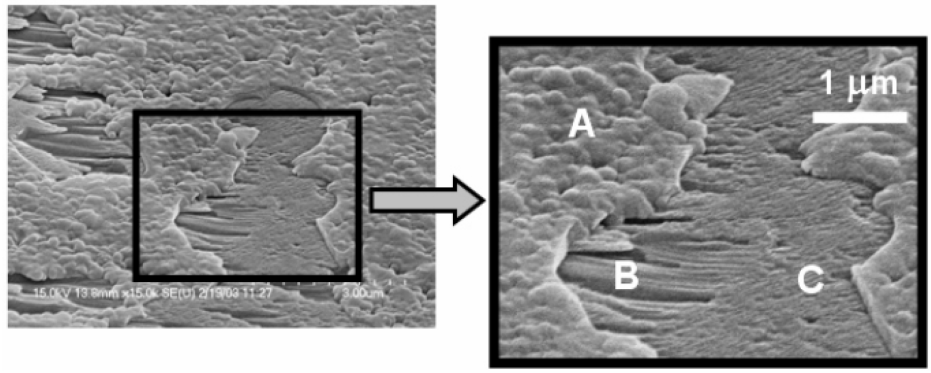

FIGURE 1
Scanning electron micrograph showing silica-rich passivating layer exfoliation. A) the passivating layer; B) a recently fractured and exfoliated region exposing part of the olivine particle core; C) a new passivating layer beginning to grow in the exfoliated region.

PROJECT facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Carbon Sequestration

04/2008

A Novel Approach to Experimental Studies of Mineral Dissolution Kinetics

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

David A. Lang
Project Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4881
david.lang@netl.doe.gov

Chen Zhu
Indiana University
Department of Geological Sciences
1001 East 10th Street
Bloomington, IN 47405
812-856-1884
chenzhu@indiana.edu

Background

DOE is conducting pilot CO_2 injection tests to evaluate the concept of geologic sequestration. One strategy that has the potential to enhance CO_2 solubility and reduce the risk of CO_2 leaking back to the surface is dissolution of indigenous minerals in the geological formation and formation of secondary carbonate precipitates. This both increases the brine pH and immobilizes the CO_2. Clearly, the rates at which these dissolution and precipitation reactions occur directly determine the efficiency of this option. However, one of the fundamental problems in modern geochemistry is the persistent two to five orders of magnitude discrepancy between laboratory-measured and field-derived feldspar dissolution rates.

To date, there is no real guidance on how to predict silicate reaction rates for use in quantitative models. Current models for assessment of geological carbon sequestration have generally opted to use laboratory rates in spite of the dearth of such data for compositionally complex systems and the persistent disconnect between laboratory and field applications. Therefore, a firm scientific basis for predicting silicate reaction kinetics in geological formations containing injected CO_2 is urgently needed to ensure the reliability of the geochemical models used for the assessment of carbon sequestration strategies.

Feldspar is the most abundant mineral in earth's crust.

PARTNERS

Indiana University

University of Minnesota

PERFORMANCE PERIOD

09/01/2004 to 08/31/2008

COST

Total Project Value

$426,701

DOE/Non-DOE Share

$426,701/$0

ADDRESS

National Energy Technology Laboratory

1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

The proposed experimental and theoretical study attempts to resolve this outstanding scientific issue by a novel experimental design and theoretical interpretation to measure silicate and dawsonite dissolution rates and iron carbonate precipitation rates at conditions pertinent to geological carbon sequestration. Additionally, this project will experimentally test the novel idea of storing CO_2 together with SO_2 contaminants in redbed sandstones that contain both feldspars and iron oxides. It is expected that SO_2 will reduce ferric iron to ferrous iron, which reacts with CO_2 and precipitates iron carbonate. If the SO_2 impurity in flue gas has a beneficial use in geological carbon sequestration, this represents a major cost reduction in front-end processing. The proposed experimental design and data interpretation depart significantly from the state-of-the-art practice, and the results will provide a guide to the evaluation of geological sequestration. Furthermore, an atomic scale, or near atomic scale, electron microscopic study will reveal reaction mechanisms that will also benefit the ongoing mineral carbonation and brine carbonation programs.

Primary Project Goal

The primary goal of this project is to resolve a long-term controversy that laboratory measured silicate dissolution rates are consistently two to five orders of magnitude faster than field-derived rates. This controversy is one of the major obstacles to quantitatively evaluating the efficacy of geological carbon sequestration.

Objectives

- To develop an experimental design and an interpretation of results to determine the rate of feldspar dissolution in geologic formations.
- To experimentally test the novel idea of storing CO_2 together with SO_2 contaminants in redbed sandstones that contain both feldspars and iron oxides.

Benefits

The results of this work will provide guidance relative to the rates and rate laws that should be used in performance assessments and will also benefit the mineral carbonation and brine carbonation programs. This may lead to improvements in the geologic sequestration of CO_2. Any reduction in the cost of CO_2 sequestration would have a positive effect on the economy should it become necessary to reduce the emissions of CO_2 to the atmosphere.

Accomplishments

- Completed three batch-type feldspar dissolution experiments, two batch-type and one flow-through Navajo sandstone experiments, and validation runs
- Characterized the reaction products of the feldspars using scanning electron microscopy, transmission electron microscopy, x-ray photoelectron spectroscopy, and x-ray diffraction
- Conducted geochemical modeling to interpret the results
- Established the coupling between the dissolution and precipitation reactions
- Completed a dawsonite experiment including preliminary electron microscopy

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

08/2007

MEMBRANE PROCESS TO SEQUESTER CO_2 FROM POWER PLANT FLUE GAS

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

Heino Beckert
Project Manager
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4132
heino.beckert@netl.doe.gov

Tim Merkel
Principal Investigator
1360 Willow Road
Menlo Park, CA 94025-1516
650-328-2228
tcmerkel@mtrinc.com

Background

Carbon dioxide emissions from coal-fired power plants are believed to contribute significantly to global warming climate change. The direct approach to address this problem is to capture the carbon dioxide in flue gas and sequester it underground. However, the high cost of separating and capturing CO_2 with conventional technologies prevents the adoption of this approach. This project investigates the technical and economic feasibility of a new membrane process to capture CO_2 from power plant flue gas.

Description

Direct CO_2 capture from power plant flue gas has been the subject of many studies. Currently, CO_2 capture with amine absorption seems to be the leading candidate technology—although membrane processes have been suggested. The principal concern with previous membrane processes has been the enormous membrane area required for separation because of the low partial pressure of carbon dioxide in flue gas.

Recently, MTR has developed membranes with 10 times the CO_2 permeance of conventional gas separation membranes. The combination of these membranes with a novel countercurrent module design that utilizes incoming combustion air to generate separation driving force greatly reduces the projected cost of CO_2 capture from flue gas with membranes. In this project, the goal is to optimize the membrane and module performance for flue gas treatment.

Primary Project Goal

The overall technical objective of this project is to develop high CO_2 permeance, high CO_2/N_2 selectivity composite membranes that can be used for the economic capture of CO_2 from post-combustion flue gas.

Objectives

- Develop high-performance membranes with a CO_2 permeance of at least 3,000 gpu (where 1 gpu = 1 x 10^{-6} $cm^3(STP)/cm^2 \cdot s \cdot cmHg$) and a CO_2/N_2 selectivity of at least 50 at 50-80°C (where selectivity is the ratio of gas permeances).
- Optimize the membrane structure to maximize CO_2 permeance and the effectiveness of countercurrent sweep operation.
- Optimize module design to minimize pressure drop in the permeate side channels and maximize countercurrent flow patterns.

PROJECT DURATION

04/01/2007 to 03/31/2009

COST

Total Project Value

$985,333

DOE/Non-DOE Share

$788,266 / $197,067

ADDRESS

National Energy Technology Laboratory

1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

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1-800-553-7681

WEBSITE

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- Construct a bench-scale module test skid for countercurrent sweep operation.
- Perform parametric tests with countercurrent sweep modules using a simulated coal power station flue gas.
- Perform a technical and economic analysis of the commercial viability of scale-up and use of counterflow modules for flue gas treatment at power stations.

Benefits

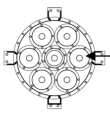
Membranes for CO_2 sequestration will likely consume less parasitic energy and be less expensive than amine wet scrubbing, which is the current carbon capture technology.

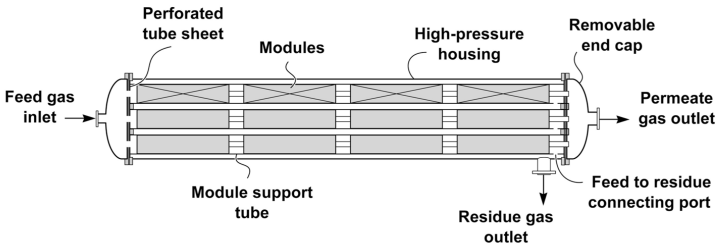
Accomplishments

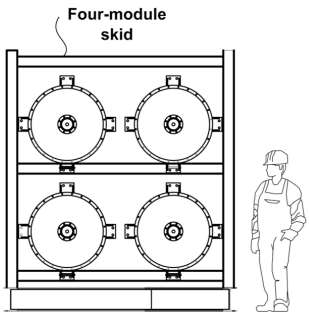
- Composite membranes with CO_2 permeances of 2,000 gpu and CO_2/N_2 selectivities of 50 have been prepared.
- Membranes have been fabricated into spiral-wound modules that operate in countercurrent/sweep mode.
- Module performance data have confirmed the benefit of sweep operation.
- A new module test system dedicated to this project was built to perform parametric vacuum and countercurrent module experiments.
- A lower-cost, more efficient membrane process design has been identified. CO_2 recovery of 90% and >99% water recovery is possible at a cost of ~$25/ton CO_2 using about 18% of power plant energy.

Planned Activities

MTR is currently working through the tasks described in the Statement of Project Objectives document. The focus at this time is on membrane module fabrication and parametric testing, as well as analysis of different possible membrane process designs. The first semi-annual report describing these activities will be available in October 2007.







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Project475.indd

PROJECT facts

U.S. DEPARTMENT OF ENERGY
OFFICE OF FOSSIL ENERGY
NATIONAL ENERGY TECHNOLOGY LABORATORY

Carbon Sequestration

08/2007

METAL MONOLITHIC AMINE-GRAFTED ZEOLITES FOR CO_2 CAPTURE

CONTACTS

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

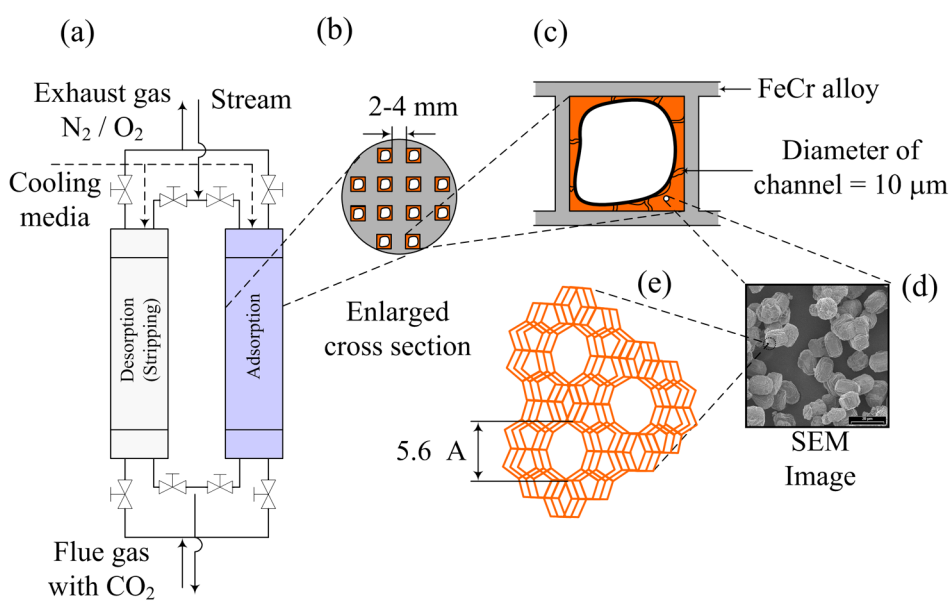
Timothy Fout
Project Manager
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-1341
timothy.fout@netl.doe.gov

Steven Chuang
Principal Investigator
University of Akron
200 E. Buchtel Common
Akron, OH 44325-3906
330-972-6993
schuang@uakron.edu

Background

Current aqueous amine and membrane technologies are cost-effective for separation of CO_2 from natural gas in liquefaction process and ammonia synthesis process due to the high value of end products. These current technologies, when applied for CO_2 capture from coal-fired power plants, result in significant increases in the cost of electricity produced. The cost of CO_2 capture and storage can be reduced if an effective CO_2 capture sorbent is developed which has:

- High CO_2 adsorption capacity.
- Long term regeneration capacity in power plant flue gas environment.
- Low energy requirement for regeneration compared to large amount of energy required for aqueous amine process.



CO_2 capture unit with metal monolithic amine-grafted zeolites

COST

Total Project Value
$1,119,257

DOE/Non-DOE Share
$764,995 / $354,262

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

This project is investigating a CO_2 capture system that involves the novel integration of a metal monolith with amine-grafted zeolites. Key features of this CO_2 capture system are the use of metal monoliths coated with a low cost amine-grafted zeolite which eliminates the use of corrosive liquid amine and decreases the energy required for sorbent regeneration. The metal monoliths consist of straight channels: one row of channels coated with amine-grated zeolite; one used for heat transfer media for either cooling for adsorption or heating for regeneration. The alternative arrangement of CO_2 adsorption and cooling media (i.e., water or air) channels will allow effective removal of adsorption heat.

Primary Project Goal

The primary goal of this project is to develop a highly efficient and low-cost CO_2 capture system consisting of metal monoliths with parallel square channels of which the surface is coated with a nanostructured/hydrophobic zeolite-grafted amine.

Objectives

- Prepare and test the performance of various amine-grafted zeolite sorbents. Performance testing will evaluate CO_2 and SO_2 capacity along with long term stability.
- Develop an optimized amine-grafted zeolite based upon stability and capture capacity.
- Design, fabricate, and test a metal monolithic absorber coated with the optimal sorbent.
- Determine the performance capabilities of final CO_2 capture system through the development of an engineering system model and economic analysis of a large scale system.

Benefits

The low cost of raw materials for the synthesis of zeolite-grafted amine sorbents combined with the innovative application of metal monoliths as an adsorber structure may lead to a breakthrough technology for the effective capture of CO_2 from flue gas of coal-fired power plants.

Planned Activities

- Prepare, characterize, and determine the CO_2 capture capacity of at least 15 alkyl amine-grafted zeolites.
- Prepare, characterize, and determine the long term CO_2 capture capacity of at least 12 alkyl amine-grafted zeolites.
- Prepare, characterize, and determine the SO_2 capture capacity of at least 3 aryl amine-grafted zeolites.
- Fabricate metal monolith CO_2 absorber coated with amine-grafted zeolites.

R & D facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Carbon Sequestration

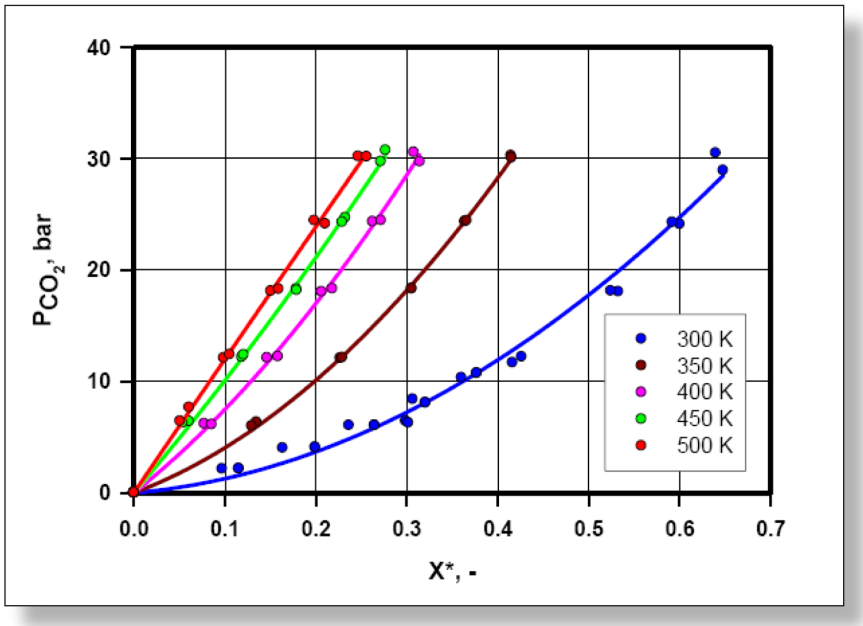
09/2007

Solvents for CO_2 Capture

Background

Large point sources from power generation systems, both conventional and advanced, are key locations for CO_2 capture. With respect to advanced systems, such as Integrated Gasification Combined Cycle (IGCC), precombustion capture is advantageous because of the high partial pressure of CO_2. Additionally, CO_2 removal at higher temperatures, as compared to cooler conventional scrubbing temperatures, provides a thermal efficiency advantage. If improved, one capture technique that may provide additional benefits is higher temperature solvent scrubbing for CO_2.

The most attractive physical solvents for CO_2 capture are those having such properties as high thermal stability, extremely low vapor pressures, nonflammability, and nontoxicity. Such materials not only have the potential to capture CO_2 with minimal solvent loss in the gas stream but are expected to be environmentally benign. In collaboration with the University of Pittsburgh, NETL conducted a study involving one general type of solvent—ionic liquids—with these physical properties. The results of that study will serve as the basis for a conceptual design and system analysis of a new CO_2 capture technique.



CO_2 Solubility in Candidate Ionic Liquid

CONTACTS

Kenneth Jones
Project Leader
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-5703
kenneth.jones@netl.doe.gov

George Richards
Focus Area Leader
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507
304-285-4458
george.richards@netl.doe.gov

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

PARTNER

University of Pittsburgh

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street, Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

Objective

The overall objective of this research is to test and develop physical solvents to selectively capture CO_2 from fuel gas streams, particularly those containing CO_2, CO, H_2S, H_2O, and H_2 in amounts typically produced after the water-gas shift reaction. Ultimately, the technical and economic feasibility of using physical solvents for CO_2 capture from synthesis gas produced in a post-shift reaction IGCC context will be determined. A comparison between the ability of these solvents to selectively capture CO_2 from fuel gas and those of existing processes, will be performed.

Accomplishments

Three ionic liquids (ILs) were screened as potential solvents for CO_2 capture. The screening process involved measuring the viscosity and density of these materials at various temperatures and pressures, as well as determining their abilities to dissolve CO_2.

The most significant accomplishment was the identification of a CO_2 capture solvent (a commercially available ionic liquid) that contains molecular constituents that give it a strong affinity toward CO_2, is thermally stable, is environmentally benign, and has a very low vapor pressure. During the screening process, it was found to be a fairly good CO_2 solvent at 500 K, an IGCC-like temperature, while, surprisingly, being a significantly better CO_2 solvent than the existing solvent benchmark at 300 K.

Following the screening measurements, the best-performing ionic liquid solvent was advanced to the next phase of experimental work, which involved the completion of a Central Composite Statistical Design matrix, a parametric study involving the measurement of CO_2 solubility and mass transfer coefficient (k_La) and other hydrodynamic parameters in the solvent as a function of temperature, pressure, liquid height, and mixing speed in a 1-gallon agitated autoclave. This study involved the ability of the solvent to capture CO_2 from a multi-component synthetic fuel gas mixture consisting of CO_2, H_2, Ar, CH_4, and CO. The data collected from this study, after the effects of H_2O and H_2S are determined, will be used as input parameters for a future system analysis.

Benefits

One goal of the carbon sequestration program is to develop capture/sequestration systems that capture at least 90% of emissions and result in a small increase in the cost of energy services for gasification-based processes. To attain such benefits, NETL's CO_2 separation and capture research is aimed at developing technologies that have low capital cost, low parasitic load, high percent reduction in emissions, and the capability to integrate with pollutant controls. Additionally, its gasification technology area is focusing on achieving greater acid-gas removal, improved hydrogen economy, zero emissions, integrated systems with lower costs due to fewer subsystems, lower parasitic losses, and smaller plant footprints. The successful development of a higher-temperature physical solvent process will produce a capture technique that can certainly make it possible for the Department of Energy to fulfill the goals of its various technology areas.

R & D facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Carbon Sequestration

12/2007

Novel Membranes for CO_2 Removal

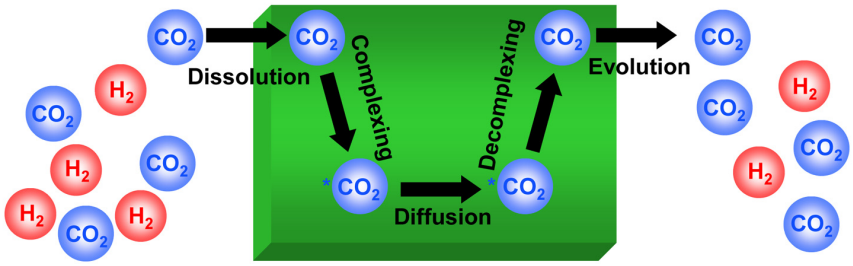
Background

As the stabilization of CO_2 concentrations in the atmosphere becomes increasingly important, the capture and sequestration of CO_2 emissions from advance power generation systems will become a necessity. In the current carbon sequestration concept, separation and capture represent the greatest expense in the overall capture and storage process. Improvements in capture and separation have the greatest potential to affect the cost of CO_2 mitigation, and membrane technology holds significant promise in this area.

Membranes have a number of innate advantages over other separation techniques, including simple design with no moving parts, limited maintenance, lower energy requirements due to lack of phase transitions, single-step separation, and exceptional reliability. These advantages have allowed membranes to make significant commercial advances in other CO_2 removal applications, such as natural gas sweetening. In fuel gas streams where pressures and CO_2 concentrations are high, membranes seem a natural choice for carbon capture.

Primary Project Goal

This research is aimed at developing robust membranes capable of selective CO_2 removal in reducing environments, such as in Integrated Gasification Combined Cycle (IGCC) power plant fuel gas. Capture in these gasification systems will most likely take place after the low-temperature water gas shift reaction. Carbon dioxide technologies for the shifted fuel gas should work at elevated temperature (260 °C or above) to maximize the efficiency of the power generation process and should be able to handle other components in the fuel gas. Current research focuses on a class of organic salts known as ionic liquids. Certain ionic liquids have high solubility for CO_2 compared to H_2 and other light gases. When ionic liquids are combined with porous substrates, the resulting supported liquid membranes (SLMs) have already demonstrated the capability to separate CO_2 in various applications and systems. They have greater diffusivities than polymeric membranes and are stable to temperatures above 300 °C. Recently, membranes have been developed based on ionic liquids that interact with gases to form chemical complexes. These membranes have the potential for better selectivity through facilitated transport diffusion, making them a promising capture technology.



In facilitated transport diffusion, the CO_2 desorbs into the membrane, reacts with the ionic liquid and forms a complex, diffuses across the membrane, decomplexes, then the CO_2 desorbs.

CONTACTS

David Luebke
Project Leader
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4118
david.luebke@netl.doe.gov

Abbie Layne
Director - Separations and Fuels Processing Division
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507
304-285-4603
abbie.layne@netl.doe.gov

Sean Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15326
412-386-4867
sean.plasynski@netl.doe.gov

PARTNERS

University of Notre Dame

University of Pittsburgh

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street,
Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

Objectives

The project examines the development of techniques and materials that can be used to stabilize ionic liquids for use in membrane applications. Ionic liquids used in this project are supplied by researchers at the University of Notre Dame under a Cooperative Research and Development Agreement (CRADA). Work has centered on optimization of the materials for CO_2 selective membrane applications. It is hypothesized that the use of ionic liquids, including those that form chemical complexes with CO_2, could improve performance at the elevated temperatures. NETL researchers incorporate the ionic liquids into commercially available and fabricated polymer supports and examine the performance of the resulting membranes to determine whether or not particular liquid/support combinations meet gas separation performance objectives. Beyond simply meeting high-performance goals, the membranes are expected to perform at high temperatures in the presence of trace contaminants, such as H_2S. Future testing will include testing other complexing ionic liquids and supports as high as 300 °C and also in the presence of contaminants.

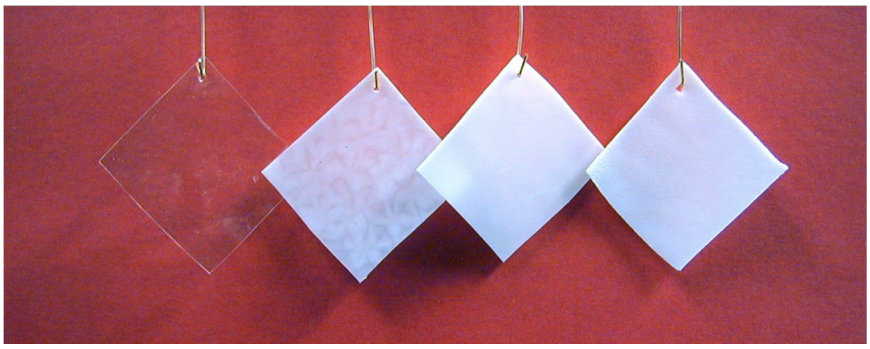
Accomplishments

Since its conception, the project has reached some very important milestones:

- Membranes have been prepared using both commercially available and fabricated polymer supports.
- Membranes have proven to be stable to temperatures above 300 °C.
- CO_2/H_2 selectivities as high as 15 have been measured with associated CO_2 permeabilities an order of magnitude greater than those observed for conventional polymeric membranes at 75 °C.

Benefits

The successful development of a commercially viable membrane would have several benefits. Industry would gain a simplified separation technique for CO_2/H_2 mixtures leading the way toward adoption of advanced power generation processes as part of an overall carbon abatement strategy. Membranes produced in this project may also have applicability to other separation problems, such as the removal of CO_2 from crude natural gas and the capture of CO_2 from stack gas produced by conventional pulverized coal combustion.



Series of polymeric films with increasing ionic liquid content.

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R & D facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Carbon Sequestration

04/2008

Molecular Design and Evaluation of CO_2 Sorbents

Background

The capture and separation of carbon dioxide (CO_2) has been identified as a high-priority topic within DOE's Carbon Sequestration Program. The costs of separation and capture, including compression to the required pressure for the storage step, are generally estimated to be a significant percentage of the total cost of the sequestration process. Improvement in CO_2 separation and capture is necessary to reduce the total cost required for sequestration.

Description

The objective of this project is to develop novel amine-enriched sorbents for the capture of CO_2 from flue gas streams generated by the utility industry. These novel CO_2 capture sorbents will be prepared by chemical treatment of the high surface area materials with various amine compounds.

The implanting of amine groups on a high surface area material will increase the needed contact area between CO_2 and amine by several magnitudes. Therefore, only a small amount of sorbent used in the typical amine process is needed for capturing the same amount of CO_2. A significant improvement in the efficiency of the process is due to the increased contact area and therefore less energy consumption in regenerating the sorbents.

Primary Project Goal

This research is aimed to incorporate and graft the amino-functionality onto various high-surface substrates for the capture of CO_2 from flue gas streams produced by the combustion of coal. These sorbents must be regenerable, durable, and cost-effective to create a CO_2 capture system that can be used in the utility industry.

CONTACTS

George A. Richards
Focus Area Leader
National Energy Technology Laboratory
3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507
304-285-4458
george.richards@netl.doe.gov

McMahan L. Gray
Physical Scientist
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4826
mcmahan.gray@netl.doe.gov

Sean I. Plasynski
Sequestration Technology Manager
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4867
sean.plasynski@netl.doe.gov

PARTNERS

University of Hartford

University of Pittsburgh

Georgia Institute of Technology

Tennessee Valley Authority

ADDRESS

National Energy Technology Laboratory

1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street, Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

1-800-553-7681

WEBSITE

www.netl.doe.gov

Objectives

- Design a sorbent that will bind CO_2 at greater than 3 moles CO_2 per kg of sorbent and ideally greater than 5 moles CO_2 per kg of sorbent.
- Allow for adsorption temperatures between 55 and 75 °C.
- Allow for CO_2 release at temperatures less than 120 °C, and with release complete in a short period of time.
- Provide for a low pressure drop across the adsorbent bed.
- Allow for adsorption at gas flow rates and with gas mixtures (up to 8 percent water, 14 percent CO_2, 50 ppm SO_x, 25 ppm NO_x) that are industrially realistic.
- Provide the information to develop a new environmental control technology for the reduction of CO_2, a greenhouse gas emission.

Benefits

The cost of CO_2 capture should be significantly reduced as a result of decreasing the amount of amine required to recover the CO_2. Ease of regeneration of the amine will also help to lower costs. The application of this, or similar CO_2 capture units, to older pulverized coal- (PC) fired power plants will also be very useful in reducing the total amount of CO_2 to the atmosphere. Retrofitting of capture units in the 5- to 10-thousand ton range with older PC-fired power plant units will lower costs for the removal and reduction of CO_2.

Accomplishments

The atmospheric pressure performance of these amino-sorbents was obtained in a temperature swing adsorption (TSA) system after exposure to a 10 percent CO_2 and 2 percent H_2O and He experimental gas stream. Their ability to capture CO_2 over the temperature range of 25–65 °C was detailed.

After the adsorption stage, desorption of CO_2 from these sorbents was determined at 90 °C, and the sorbents were regenerated for additional cycles. According to TSA/mass spectrometer analysis, all of the sorbents were successful in the capture of CO_2 from the moist experimental gas streams. The best performing sorbents are summarized in the table below.

Sorbent Type	Researchers	Temperature °C	Mole CO_2/kg Adsorbent
Immobilized	NETL	25-65	2.0-3.5
Polymeric	NETL/Georgia Tech	25-65	2.5-3.0

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R & D facts

U.S. Department of Energy
Office of Fossil Energy
National Energy Technology Laboratory

Sequestration

4/2006

Bauxite Residue/Brine for CO_2 Sequestration

Background

An ever-increasing amount of scientific evidence suggests that anthropogenic release of CO_2 has led to a rise in global temperatures over the past several hundred years. Assuming this is true, unabated release of greenhouse gasses will result in global warming that may lead to significant and possibly catastrophic alteration of climate and natural cycles throughout the world. One feasibility study underway at the National Energy Technology Laboratory (NETL) involves sequestration of CO_2 from the atmosphere by promoting the trapping of CO_2 as mineral carbonates using Ca, Mg, and Fe-bearing caustic waste streams.

More than 70 million tons of bauxite residues are generated annually when alumina is extracted from bauxite ore. The residue is mostly composed of iron and titanium oxides, silica, calcium carbonate, and unrecoverable alumina and soda. The pH of the liquid can be as high as 13.5, and the solids also contain high alkalinity. The caustic nature of the residue causes concerns associated with long-term environmental liability and impact. Worldwide, there are about 200 million tons of bauxite residues; these are mostly stored in tailings ponds. For decades, the aluminum industry has been investigating options for treating, disposing, and utilizing these bauxite residues. Traditionally, dewatering and impoundment of these residues has been the only viable management option. Recently, the addition of CO_2 has been used to achieve partial neutralization of liquid and solid phase alkalinity (to a pH of approximately 10) of this caustic material prior to impoundment. In addition to partial neutralization, carbonation promotes a limited amount of CO_2 trapping through dissolution and mineral carbonate formation. Carbonation, therefore, helps to decrease the threat of environmental impact posed by storage of large volumes of the caustic residue. However, direct carbonation does not succeed in fully neutralizing the bauxite residue byproduct.

Currently 20 to 30 billion barrels of saline wastewater are produced annually with the production of oil and gas in the USA. About 35 percent of this acidic wastewater (pH 3 to 5) is treated and discharged as surface water. Many of the gas/oil-field brines have high concentrations of dissolved Ca, Mg, and Fe ions. Carbonate minerals could be formed in the presence of CO_2 under certain conditions. This suggests the possibility of using Ca, Mg, and Fe ions from saline wastewater for CO_2 sequestration *via* the formation of carbonate minerals.

CONTACTS

Yee Soong
Research Group Leader
Geosciences Division
National Energy Technology Laboratory
626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236
412-386-4925
yee.soong@netl.doe.gov

Robert Kleinmann
Division Director
Geosciences Division
National Energy Technology Laboratory
P.O. Box 10940
626 Cochrans Mill Road
Pittsburgh, PA 15236
412-386-6555
robert.kleinmann@netl.doe.gov

ADDRESS

National Energy Technology Laboratory
1450 Queen Avenue SW
Albany, OR 97321-2198
541-967-5892

2175 University Avenue South
Suite 201
Fairbanks, AK 99709
907-452-2559

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880
304-285-4764

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940
412-386-4687

One West Third Street, Suite 1400
Tulsa, OK 74103-3519
918-699-2000

CUSTOMER SERVICE

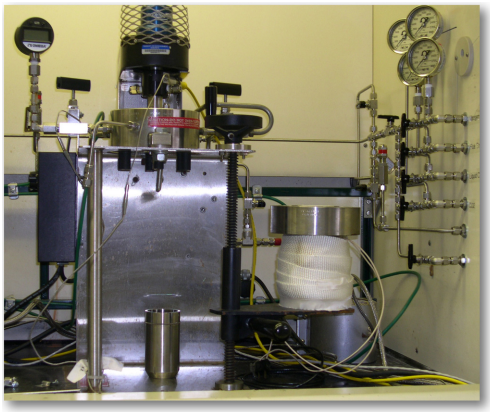
1-800-553-7681

WEBSITE

www.netl.doe.gov

Primary Project Goal

This project is designed to explore the applicability of bauxite residue/brine reactant mixtures to absorb and sequester CO_2 from both concentrated gas streams and as a component of a mixed flue gas.



Autoclave Reactor

Objectives

The objectives of this project are to provide initial assessment of CO_2 and SO_2 sequestration in bauxite residue/brine/CO_2 mixtures and bauxite residue/brine/flue gas mixtures.

Accomplishments

Alcoa and NETL have entered a Cooperative Research and Development Agreement to further advance a novel concept that achieves full neutralization of bauxite residue through reaction with acidic oil and gas field wastewater brines with subsequent carbonation. Experiments are being conducted to determine the ability of bauxite residue/brine mixtures to absorb and sequester CO_2 both from a concentrated CO_2 stream and as a component of a mixed flue gas. The use of bauxite residue/brine mixtures to capture and store CO_2 will serve to not only help mitigate the impact of anthropogenic CO_2 on global warming but will also serve to achieve complete neutralization of the caustic industrial waste for safe storage and potential reuse. Finally, the ability to sequester SO_2 in the reactive slurry and the fate of the absorbed sulfur is also under investigation. Geochemical equilibrium modeling will be used to predict precipitation and mineralization phenomena. An internal NETL report of possible invention has been filed and reviewed by the internal patent review panel. Collected data provide a preliminary assessment of process feasibility and probe the influence of several variables on treatment efficiency. Maximum observed initial sequestration capacities ranged from 2 to 7.2 grams of CO_2 per liter of reactant for mixtures ranging from pure brine to pure bauxite residue, respectively. Product pH for CO_2 carbonated mixtures of bauxite and brine varying in composition from 10 percent brine/90 percent bauxite residue by volume to 90 percent brine/10 percent bauxite residue by volume resulted in product slurry neutralization to pHs of between 7.37 and 5.99, respectively. Geochemical equilibrium modeling was conducted to predict the composition, pH, and CO_2 solubility of bauxite residue/brine mixtures. Despite the relatively short duration of batch experiments (hours), results of preliminary equilibrium modeling efforts compare favorably with experimental results while observing CO_2-absorbing capacity and trends in dissolved constituent concentration in agreement with model results over the range of bauxite/brine mixtures. Experiments conducted to date have proved the concept of CO_2/SO_2 absorption and bauxite residue neutralization.

Benefits

- Solubility and potential mineral trapping of CO_2 from industrial waste gas with concomitant neutralization of reactive byproduct.
- NETL opportunity to collaborate with industry.

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