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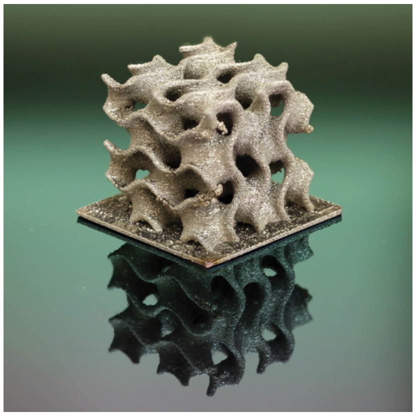
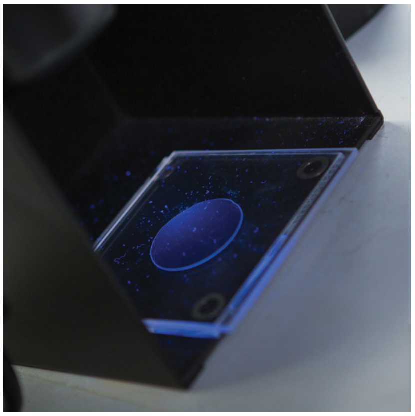


DOE/NETL CAPTURE PROGRAM R&D:

Compendium of Carbon Capture Technology



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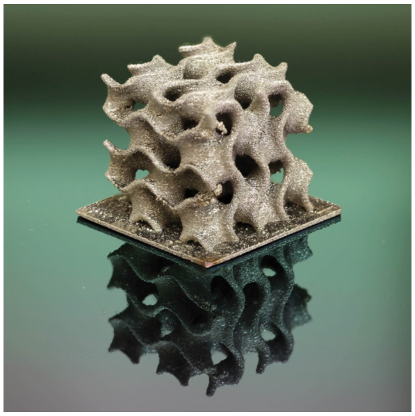
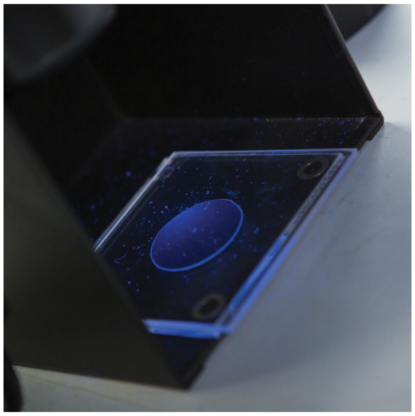


Stainless steel gyroid triply periodic minimal surface (TPMS) reactor created at Lawrence Livermore National Laboratory using 3D printing



Liquid monomers undergoing an ultraviolet light curing process creating a polymeric gas separation membrane in NETL's Polymer Synthesis Lab

MTR's Polaris plate-and-frame membrane module

DISCLAIMER

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COMPENDIUM OF CARBON CAPTURE TECHNOLOGY

OVERVIEW

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

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

The Carbon Capture program consists of two core research areas, Post-Combustion Capture and Pre-Combustion Capture, composed of projects with technology readiness levels (TRL) ranging from conceptual engineering and materials design (i.e., TRL 2) to 25 MW-electrical (MWe) equivalent pilot testing (i.e., TRL 5-7). These two core areas are focused on creating technological improvements providing a step-change in both cost and performance as compared to current state-of-the-art solvent-based capture systems. Post-combustion systems separate CO_2 from the flue gas stream produced by conventional pulverized coal power plants after fuel combustion in air. In this approach, CO_2 is separated from nitrogen (N_2), the primary constituent of the flue gas. Pre-combustion systems are designed to separate CO_2 and hydrogen (H_2) from the syngas stream produced by the gasifier in integrated gasification combined cycle (IGCC) power plants. In both cases, R&D is underway to develop solvent-, sorbent-, and membrane-based capture technologies, as well as novel technologies.

This Technology Compendium provides a technical summary of DOE/NETL's Carbon Capture program, assembling CO_2 capture technology R&D descriptions for 91 projects in a single document. As of September 1, 2017, there were 47 active projects and 44 completed projects. Descriptions of the completed projects are provided in Appendix A. It should be noted that some of the previously completed projects may differ slightly in format as they were developed for a prior version of the compendium. The following tables list the CO_2 capture technologies summarized in this Compendium as developed under DOE/NETL external R&D projects.

National Energy Technology Laboratory – Research and Innovation Center Technologies

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

Project Focus	Participant	Performance Period
ACTIVE		
Transformational Solvents	National Energy Technology Laboratory – Research and Innovation Center Technologies	01.01.2018 – 12.31.2021
Transformational Sorbents	National Energy Technology Laboratory – Research and Innovation Center Technologies	01.01.2018 – 12.31.2021
Transformational Membranes	National Energy Technology Laboratory – Research and Innovation Center Technologies	01.01.2018 – 12.31.2021
High Throughput Tools	National Energy Technology Laboratory – Research and Innovation Center Technologies	01.01.2018 – 12.31.2021
Carbon Capture Simulation for Industry Impact	National Energy Technology Laboratory – Research and Innovation Center Technologies	01.01.2018 – 03.31.2019

Post-Combustion Solvent Technologies

High levels of CO_2 capture are possible with chemical solvent-based systems but these systems also require significant amounts of energy for regeneration, which involves a temperature swing to break the absorbent-CO_2 chemical bond. Advanced solvents that have a lower regeneration energy requirement than commercially-available amine systems, no aerosol emission challenges, and that are resistant to flue gas impurities are being developed through DOE/NETL-sponsored research.

Project Focus	Participant	Performance Period
ACTIVE		
Novel Electrochemical Regeneration of Amine Solvents	Massachusetts Institute of Technology	08.01.2017 – 07.31.2020
Slipstream Demonstration Using Advanced Solvents, Heat Integration, and Membrane Separation	University of Kentucky	10.01.2011 – 03.31.2019
Biphasic CO_2 Absorption with LLPS	University of Illinois at Urbana-Champaign	10.01.2015 – 12.31.2018
Piperazine Solvent with Flash Regeneration	URS Group	10.01.2010 – 12.31.2018
Microencapsulated CO_2 Capture Materials	University of Notre Dame	10.01.2015 – 09.30.2018
Direct Air Capture from Dilute CO_2 Sources	Carbon Engineering LTD	09.19.2016 – 09.18.2018
Non-Aqueous Solvent	RTI International	10.01.2015 – 06.30.2018
Linde/BASF CO_2 Capture Process	University of Illinois at Urbana-Champaign	10.01.2015 – 10.31.2017
Low-Aqueous Solvent	ION Engineering, LLC	10.01.2010 – 09.30.2017
Phase-Changing Absorbent	GE Global Research	11.01.2014 – 09.30.2017
CO_2-Binding Organic Liquid (CO_2BOL) Solvents	Pacific Northwest National Laboratory	04.01.2014 – 09.30.2017
Aminosilicone Solvent	GE Global Research	10.01.2015 – 06.30.2017
Ammonia- and Potassium Carbonate-Based Mixed-Salt Solvent	SRI International	10.01.2013 – 06.30.2017
Amine-Based Solvent and Process Improvements	Southern Company Services, Inc.	10.01.2015 – 03.31.2017
Waste Heat Integration	Southern Company Services, Inc.	10.01.2011 – 03.31.2017
COMPLETED (in Appendix)		
Slipstream Novel Amine-Based Post-Combustion Process	Linde LLC	12.01.2011 – 11.30.2016
Chilled Ammonia Process Improvements	GE Power	10.01.2015 – 09.30.2016
Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution (“Solvents”)	Akermin, Inc.	10.01.2013 – 09.30.2016
Carbon Absorber Retrofit Equipment	Neumann Systems Group	01.02.2012 – 12.31.2015
Novel Absorption/Stripper Process	William Marsh Rice University	10.01.2011 – 12.31.2015
Gas-Pressurized Stripping	Carbon Capture Scientific	10.01.2011 – 06.30.2015
Solvent + Enzyme and Vacuum Regeneration Technology	Novozymes North America, Inc.	10.01.2011 – 06.30.2015
Optimized Solvent Formulation	Babcock & Wilcox	10.01.2011 – 04.30.2014
Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping	University of Illinois at Urbana-Champaign	01.01.2011 – 03.31.2014
Chemical Additives for CO_2 Capture	Lawrence Berkeley National Laboratory	06.01.2008 – 05.31.2013
Self-concentrating Amine Absorbent	3H Company, LLC	10.01.2010 – 01.31.2013
Ionic Liquids	University of Notre Dame	03.01.2007 – 09.30.2012
Novel Integrated Vacuum Carbonate Process	Illinois State Geological Survey	10.01.2008 – 04.30.2012
POSTCAP Capture and Sequestration	Siemens Energy Inc.	10.01.2010 – 02.29.2012
Reversible Ionic Liquids	Georgia Tech Research Corporation	10.01.2008 – 09.30.2011
Phase Transitional Absorption	Hampton University	06.15.2005 – 06.30.2009

Post-Combustion Sorbent Technologies

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

Project Focus	Participant	Performance Period
ACTIVE		
Pressure Swing Adsorption Process with Novel Sorbent	Georgia Tech Research Corporation	10.01.2015 – 09.30.2018
Porous Polymer Networks	Texas A&M University	10.01.2015 – 09.30.2018
Novel Solid Sorbent	SRI International	10.01.2013 – 09.30.2018
Alkalized Alumina Solid Sorbent	TDA Research, Inc.	02.03.2014 – 08.31.2018
Fluidizable Solid Sorbents	Research Triangle Institute	10.01.2015 – 03.31.2018
COMPLETED (in Appendix)		
Advanced Aerogel Sorbents	Aspen Aerogels, Inc.	10.01.2013 – 12.31.2016
Temperature Swing Adsorption with Structured Sorbent	NRG Energy Inc.	10.01.2015 – 09.30.2016
Rapid Pressure Swing Adsorption	W.R. Grace and Co.	10.01.2011 – 07.31.2016
Advanced Solid Sorbents and Processes for CO_2 Capture	RTI International	10.01.2011 – 12.31.2015
Cross-Heat Exchanger for Sorbent-Based CO_2 Capture	ADA-ES, Inc.	10.01.2013 – 12.31.2015
Low-Cost, High-Capacity Regenerable Sorbent	TDA Research, Inc.	10.01.2011 – 09.30.2015
Rapid Temperature Swing Adsorption	Georgia Tech Research Corporation	10.01.2011 – 03.31.2015
Novel Adsorption Process	InnoSepra, LLC	10.01.2011 – 03.31.2015
Hybrid Sorption Using Solid Sorbents	University of North Dakota	10.01.2011 – 12.31.2014
Metal Monolithic Amine-Grafted Zeolites	University of Akron	02.21.2007 – 03.31.2011
CO_2 Removal from Flue Gas Using Microporous MOFs	UOP	03.12.2007 – 06.30.2010
A Dry Sorbent-Based Post Combustion CO_2 Capture	Research Triangle Institute	03.07.2007 – 12.31.2009

Post-Combustion Membrane Technologies

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

Project Focus	Participant	Performance Period
ACTIVE		
Selective Membranes for <1% CO_2 Sources	Ohio State University	03.01.2016 – 02.28.2019
Subambient Temperature Membrane	American Air Liquide, Inc.	10.01.2015 – 12.31.2018
PolarisTM Membrane/Boiler Integration	Membrane Technology and Research, Inc.	07.01.2015 – 06.30.2017
COMPLETED (in Appendix)		
Inorganic/Polymer Composite Membrane	Ohio State University	10.01.2011 – 12.31.2015
Composite Hollow Fiber Membranes	GE Global Research	10.01.2011 – 12.31.2014
Low-Pressure Membrane Contactors (Mega-Module)	Membrane Technology & Research, Inc.	10.01.2011 – 09.30.2014
Hollow-Fiber, Polymeric Membrane	Research Triangle Institute	09.26.2008 – 09.30.2011
Biomimetic Membrane	Carbozyme	03.28.2007 – 07.31.2009
Dual Functional, Silica-Based Membrane	University of New Mexico	08.23.2004 – 04.30.2009

Post-Combustion Novel Concepts

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

Project Focus	Participant	Performance Period
ACTIVE		
Novel Concepts/Additive Manufacturing for CO_2 Capture	ORNL – Oak Ridge National Laboratory	07.01.2017 – 06.30.2019
Electrochemical Membranes	FuelCell Energy Inc.	10.01.2015 – 03.31.2019
Novel Concepts/Cryogenic Carbon Capture Process	Sustainable Energy Solutions, LLC	10.01.2016 – 03.31.2019
Hybrid GO-PEEK Membrane Process	Gas Technology Institute – GTI	10.01.2015 – 09.30.2018
Novel Concepts/ICE Membrane for Post-Combustion CO_2 Capture	Liquid Ion Solutions LLC	10.01.2015 – 09.30.2018
Novel Concepts/Integrated Temperature and Pressure Swing Carbon Capture System	Altex Technologies Corporation	06.05.2015 – 07.31.2018
Supersonic Compression	Dresser-Rand Company	03.01.2016 – 03.31.2018
Novel Concepts/Encapsulation of Solvents in Permeable Membrane for CO_2 Capture	LLNL – Lawrence Livermore National Laboratory	03.01.2015 – 02.28.2018
Supersonic Inertial CO_2 Extraction System	Orbital ATK Inc.	10.01.2013 – 03.31.2017
COMPLETED (in Appendix)		
Evaluation of Compression Efficiency Improvements	Southwest Research Institute	09.28.2005 – 06.30.2014

Pre-Combustion Solvent Technologies

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

Project Focus	Participant	Performance Period
COMPLETED (in Appendix)		
CO_2 Capture Using AC-ABC Process	SRI International	09.30.2009 – 09.30.2016

Pre-Combustion Sorbent Technologies

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

Project Focus	Participant	Performance Period
ACTIVE		
High Capacity Regenerable Sorbent	TDA Research, Inc.	10.01.2013 – 09.30.2018
COMPLETED (in Appendix)		
Sorbent Development for WGS	URS Group	01.01.2010 – 09.30.2013

Pre-Combustion Membrane Technologies

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

Project Focus	Participant	Performance Period
ACTIVE		
Zeolite Membrane Reactor	Arizona State University	10.01.2015 – 12.31.2018
Mixed Matrix Membranes	State University of New York, Buffalo	10.01.2015 – 09.30.2018
PBI Polymer Membrane	SRI International	10.01.2013 – 12.31.2017
Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane	Media and Process Technology, Inc.	10.01.2013 – 09.30.2017
COMPLETED (in Appendix)		
High-Temperature Polymer-Based Membrane	Los Alamos National Laboratory	03.01.2013 – 03.31.2016
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	10.01.2009 – 09.30.2014
Pd-Alloys for Sulfur/Carbon Resistance	Pall Corporation	10.01.2009 – 09.30.2014
Hydrogen-Selective Zeolite Membranes	University of Minnesota	10.01.2009 – 09.30.2014
Pressure Swing Membrane Absorption Device and Process	New Jersey Institute of Technology	10.01.2009 – 03.31.2013
Nanoporous, Superhydrophobic Membrane Contactor Process	Gas Technology Institute	10.01.2009 – 03.31.2012
Polymer Membrane Process Development	Membrane Technology & Research, Inc.	09.14.2009 – 09.14.2011

Pre-Combustion Novel Technologies

DOE/NETL is developing various novel concepts for the integration of CO_2 removal processes with other systems, including water gas shift and adsorption reactors, to separate CO_2 from produced syngas streams. These concepts were evaluated using computational fluid dynamics and laboratory testing, leading to prototype development and field testing.

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

R&D Collaborations

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

Project Focus	Participant	Performance Period
ACTIVE		
Carbon Capture Testing Center	Southern Company	06.06.2014 – 05.31.2019
COMPLETED (in Appendix)		
Partnership for CO_2 Capture	University of North Dakota Energy and Environmental Research Center	07.01.2013 – 06.30.2015
Analysis of CCS Technology Adoption	Argonne National Laboratory	02.01.2011 – 03.31.2014

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CARBON CAPTURE TECHNOLOGY SHEETS

RESEARCH AND INNOVATION CENTER TECHNOLOGIES

Transformational Solvents

primary project goals

The National Energy Technology Laboratory's Research and Innovation Center (RIC) is developing advanced pre- and post-combustion solvents that are able to reduce the energy penalty and cost of carbon dioxide (CO_2) separation over conventional technologies through designing, synthesizing, characterizing, and performance testing these materials.

technical goals

- Test performance of NETL Solvent 3 in 1L batches for CO_2 capacity and CO_2/hydrogen (H_2) selectivity to determine optimal chain length.
- Scale up synthesis (>60L) of NETL Solvent 3.
- Complete pilot scale testing of NETL Solvent 3 solvent using actual flue gas at host site.
- Design, build, and commission a continuously looping, pre-combustion CO_2 capture test apparatus at the NETL Pittsburgh site for evaluating physical solvents at the 10 L scale using simulated flue gas.
- Perform testing to obtain mass transfer and hydrodynamic data, using a Selexol surrogate and NETL Solvent 3.
- Complete computational fluid dynamics (CFD) and process modeling to optimize absorber/stripper equipment and process.
- Complete computational screening of additional transformational physical solvents using the CFD absorber model.

technical content

Liquid solvent processes are the most well-developed technology for CO_2 separation. A circulating solvent that passes between absorption and desorption is the most typical process configuration. However, solvent materials can be improved in several ways and may be able to serve as a drop-in replacement in a standard process. Some potential improvements include (1) reducing the required regeneration energy, (2) decreasing viscosity, (3) increasing sorption capabilities at elevated temperature, and (4) increasing the resistance to contaminants such as water or sulfur species.

Improvements in material performance can be achieved through modifications to the structure or formulation of the solvent material. When appropriate, computational methods have been used to guide structure and formulation modifications.

Solvents can be performance tested using on-site facilities such as the continuously-stirred test reactor (CSTR) or offsite at facilities using actual flue or fuel gas.

The current state of the art pre-combustion CO_2 capture solvent is Selexol®. This polyethylene glycol solvent is fully miscible with water, which means that water vapor must be removed prior to the absorption column by lowering the temperature of the syngas. Lowering the temperature, removing the water vapor, and then raising the temperature back is inefficient from both a cost and net electricity perspective. Hydrophobic solvents could be operated at higher temperatures and minimize the energy and cost penalties associated with cooling the syngas, but a hydrophobic solvent must also still have a CO_2 working capacity and a CO_2/H_2 selectivity that is

technology maturity:

Laboratory-Scale or Pilot-Scale, Simulated or Actual Flue Gas Slipstream

project focus:

Pre-Combustion Solvents

participant:

National Energy Technology Laboratory – Research and Innovation Center

project number:

2018 Carbon Capture FWP

predecessor projects:

2017 Carbon Capture FWP

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partners:

University of Pittsburgh

competitive with Selexol® at above ambient temperature. Other limitations of other currently available solvents include high vapor pressure, high viscosity, or low CO_2/H_2 selectivity.

As such, the research is focused on finding materials that are hydrophobic so that they can be operated at temperatures between 40ºC and 150ºC and in the presence of water vapor. A particular focus has been placed on the testing solvents to determine their CO_2 solubility, kinetics, mass transfer, regeneration energy, and stability. Each of these properties is a parameter which may be tuned in solvent development, so their effect on CO_2 separation energetics, and ultimately cost, serves to guide materials development. Equally important, system and economic studies are being conducted to determine how these material properties affect the overall performance of the pre-combustion capture system.

NETL has developed several hydrophobic physical that have shown promising performance for pre-combustion CO_2 capture by combining high absorption capacity of PEG and low viscosity of the PDMS. Using hydrophobic solvents avoids the necessity to remove water vapor from the fuel gas stream which decreases efficiency and increases capital cost. To date several solvents that were invented by NETL show improvements, and one in particular (NETL Solvent 3) has shown exceptional performance for low energy and low capital cost of CO_2 removal from fuel gas.

NETL is working is to demonstrate the NETL Solvent 3 physical solvent using actual fuel gas, complete a technoeconomic analysis to show a reduced cost of capture compared with Selexol. If successful, a second phase will investigate hybrid mixtures of high CO_2 capacity sorbents dispersed within NETL Solvent 3. These hybrid fluids can significantly enhance CO_2 capacities of the neat solvent under conditions typical for pre-combustion CO_2 capture. Work will be necessary to identify the best combination of sorbent and solvent to achieve high CO_2/H_2 selectivity and minimize water uptake.

While physical properties such as density and viscosity are easily obtained, dynamic properties require a test apparatus to determine them on the bench-scale. NETL is currently developing a test apparatus to make it possible to assess the performance parameters (including solvent stability or degradation, mass transfer coefficients, CO_2/H_2 selectivity in an absorber, pressure drop, foaming, misting, aerosol formation, energy/regeneration requirements, effect of solvent hydrophobicity on overall process performance, correlation between solvent chemical structure and overall unit performance, and effect of absorber packing) for physical solvents under simulated fuel gas conditions. This apparatus will be used to test the physical solvents developed at NETL. The experimental data can be used to improve both modeling of the capture process and technoeconomic assessments.

technology advantages

- NETL Solvent 3 has several advantages for pre-combustion CO_2 capture:
  - Simple synthesis procedure using low cost reagents
  - Hydrophobic nature allows pre-combustion capture at higher temperatures when water vapor is present in syngas, which can decrease power consumption and capital costs associated with CO_2 capture from syngas because of the better temperature match of the CO_2 process with the processes upstream (Water Gas Shift) and downstream (Combustion) of CO_2 capture.
  - High CO_2/H_2 selectivity
  - No foaming tendency
  - Can operate above room temperature due to lower vapor pressure, reducing energy penalty for chilling flue gas.
- The NETL physical solvent CO_2 capture test unit will allow for assessment of many performance parameters of physical solvents with simulated flue gas, leading to improved system modeling and technoeconomic analyses.

R&D challenges

- Challenges for physical solvent process for pre-combustion CO_2 capture include:
  - Achieving balance between required physical properties such as viscosity, density, vapor pressure, CO_2 capacity, CO_2/H_2 selectivity, and cost
  - Identify chemical functionalities for the optimal mix of physical properties and performance
  - Increasing the CO_2/H_2 selectivity of the solvent, increasing hydrophobicity, decreasing viscosity, and optimizing solvents for temperature, pressure, and gas mixture conditions specific to its application

available reports/technical papers/presentations

O. Basha, I. Gamwo, N.S. Siefert, and B. Morsi, "Computational Fluid Dynamics Modeling and Optimization of Absorber Design for Pre-combustion CO_2 Capture," International Pittsburgh Coal Conference, September 2017.

Nicholas Siefert, "*Experimental Materials Development and Bench-Scale System Design for Pre-Combustion Solvents*," 2017 NETL CO_2 CAPTURE TECHNOLOGY PROJECT REVIEW MEETING.

Shi, W., Siefert, N.S.S., and Morreale, B.D., "*Molecular Simulations of CO_2, H_2, H_2O, and H_2S Gas Absorption into Hydrophobic Poly(dimethylsiloxane) (PDMS) Solvent: Solubility and Surface Tension*," J. Phys. Chem. C, 119 (33), pp 19253–19265 (July 201).

Siefert, N.S, Agarwal, S., Shi, F., Shi, W., Roth, E.A., Hopkinson, D., Kusuma, V.A., Thompson, R.L., Luebke, D.R., and Nulwala, H.B., "*Hydrophobic physical solvents for pre-combustion CO_2 capture: Experiments, Computational simulations, and Techno-economic analysis*," International Journal of Greenhouse Gas Control, Volume 49, June 2016, Pages 364-371.

Fan Shi, Nicholas Siefert, and David Hopkinson, "Anti-foaming Study for Physical Solvents for Pre-Combustion CO_2 Capture," 2015 AIChE Annual Meeting, Salt Lake City, November 8-13, 2015.

Nicholas Siefert, Hunaid Nulwala, Wei Shi, Fan Shi, Jeffrey Culp, Elliot Roth, Victor Kusuma, David Hopkinson, "Warm Gas Precombustion CO_2 Capture Using Hydrophobic Solvents," 2015 International Pittsburgh Coal Conference, Pittsburgh, PA, October 5-8.

Fan Shi, Brian Kail, Hunaid Nulwala, Nicholas Siefert, David Luebke, "Effects of Contaminants on Pre-combustion CO_2 Capture Solvents," 18th Annual Energy, Utility & Environment Conference (EUEC), San Diego, CA, Feb 16-18, 2015.

Siefert, N., Sweta, A., Nulwala, H., Roth, E., Kusuma, V., Shi, F., Shi, W., Culp, J., Miller, D., Hopkinson, D., Luebke, D., "Hydrophobic, Physical Solvents for Pre-combustion CO_2 Capture: Experiments and System Analysis," Fourteenth Annual CCUS Conference, Pittsburgh, PA, April 30, 2015.

Siefert, N., Sweta, A., Nulwala, H., Roth, E., Kusuma, V., Shi, F., Shi, W., Culp, J., Narburgh, S., Miller, D., Hopkinson, D., "*Hydrophobic, Physical Solvents for Pre-combustion CO_2 Capture*," 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh PA, June 25, 2015.

Transformational Sorbents

primary project goals

Develop high carbon dioxide (CO_2) capacity sorbents that are chemically stable, inexpensive, and have a simple synthesis procedure.

technical goals

- Improve the CO_2 loading of the previously developed polybenzimidazole linked polymer sorbent (BILP-101) for use in post-combustion by incorporating amine moieties into the micropore structure resulting in aminated polymer sorbents.
- Perform a techno-economic analysis for these materials using the Carbon Capture Simulation Initiative (CCSI) toolset.

technical content

Porous organic polymers (POP) represent a novel class of materials targeted for CO_2 capture and separation. A promising reported POP sorbent for CO_2 capture to date is BILP-101, which was invented by NETL. This novel porous benzimidazole-linked polymer is prepared in a simple one-step reaction using commercially available building blocks. BILP-101 has a high surface area, high microporosity (Figure 1), and high chemical and thermal stability. A high nitrogen to carbon ratio in the polymer enhances CO_2 uptake and CO_2/nitrogen (N_2) selectivity (Figure 2). The CO_2 capture performance of BILP-101 (1 mmol/g at 0.15 bar and 298 K) outperforms all polybenzimidazole polymers reported to date and puts it in the category of a strong physical sorbent. High CO_2 uptake properties of BILP-101 can be explained by two key parameters: ultra-micropores and a high concentration of N-H functional groups. While the former parameter endows higher surface energy, the latter parameter dictates the strong interaction of the sorbent with CO_2 molecules.

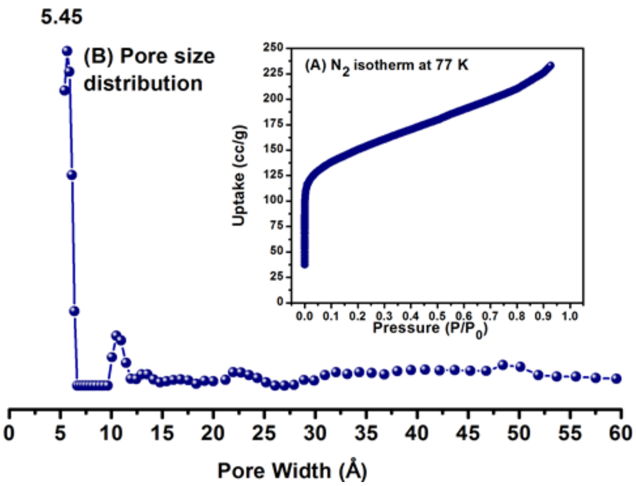

Figure 1: (A) N_2 uptake isotherm of BILP-101 at 77K
(B) Pore size distribution shows a primary pore size of 5.45 angstroms

technology maturity:

Bench Scale through Pilot Scale, Actual Flue Gas

project focus:

Pre- and Post-Combustion Solid Sorbent Materials

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

Transformational Carbon Capture FWP-1022402

predecessor projects:

RIC Carbon Capture FY2016-2020 FWP

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partners:

N/A

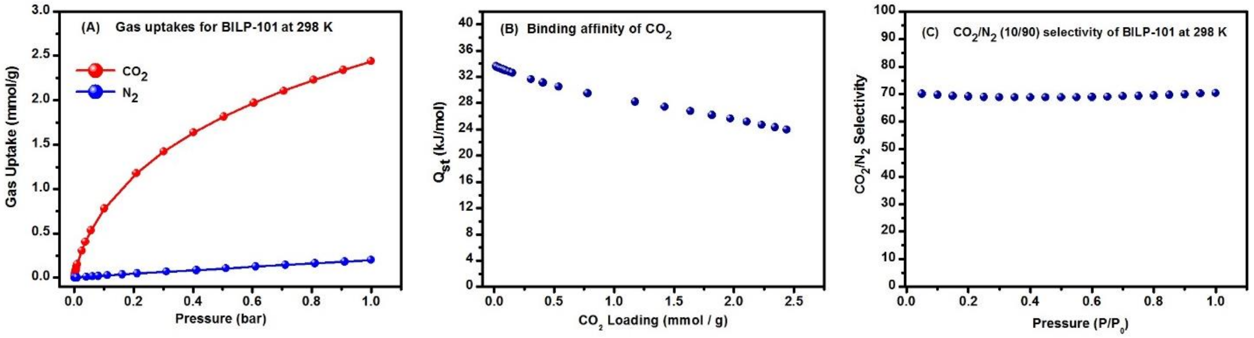

Figure 2: CO_2 and N_2 adsorption isotherm of the polybenzimidazole sorbent BILP-101 shows excellent CO_2/N_2 selectivity

When evaluated against other sorbents using the Ideal Adsorbed Solution Theory (IAST), BILP-101 shows an exceptional sorbent selection parameter, S, (S=556 for this material). This parameter S is a comprehensive figure of merit for evaluating the CO_2 capture properties of sorbents by combining the working capacity, selectivity, and regenerability criteria (Table 1 and Figure 3). Because BILP-101 is a strong physical sorbent, it can be regenerated through a swing in CO_2 partial pressure, which may not require heat and could significantly reduce the energy penalty for CO_2 capture.

Table 1: BILP-101 has the highest value for the combined selection parameter (S) for CO_2 capture of any reported sorbent. This parameter accounts for working capacity, regenerability, and CO_2/N_2 selectivity

Sorbent	**ΔN_1**	**R**	**α_{12}^{ads}**	**S**
BILP-101 (POP)	0.80	84.8	70.3	556
SNU-Cl-va[33](POP)	0.41	87.3	38.0	262
Zeolite-13X[34] (Zeolite)	1.35	54.2	86.2	128
ZIF-78[35] (MOF)	0.58	96.3	34.5	396
ZIF-82[35] (MOF)	0.38	92.5	22.7	101
MOF-4b[36] (MOF)	0.06	83.8	154	104
HKUST-1[37](MOF)	0.55	89.0	20.4	46.2
Ni-MOF-74[38](MOF)	3.20	73.7	41.1	83.5
NoritR1 extra[39] (Activated Carbon)	0.28	73.7	10.7	5.09

ΔN_1= CO_2 working capacity (mol/kg), R= Regenerability, α_{12}^{ads}= IAST selectivity, S=Sorbent selection parameter (Eq. S3). [11]

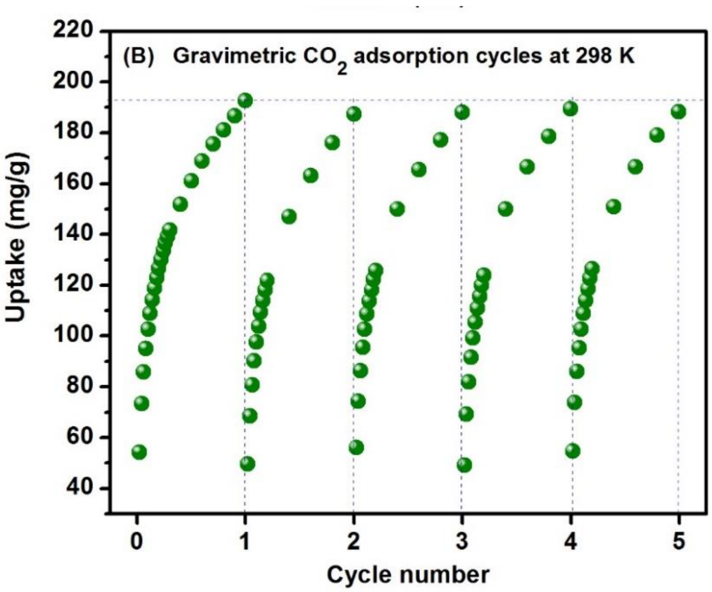

Figure 3: BILP-101 shows excellent absorption stability over a small number of cycles performed in a TGA

In this project, polymers will be impregnated and grafted with various primary amines such as ethylenediamine, diethylenetriamine, and tris(2-aminoethyl)amine (Figure 4) to afford new formulations of the BILP-101 sorbent with higher CO_2 working capacity. Sorbents will be performance tested at laboratory scale and under ideal conditions using volumetric gas sorption analysis. Sorption isotherms will be obtained for gases of interest, namely CO_2 and N_2. The effects of temperature and gas composition will be examined in the gas sorption analyzer. Once sufficient sorbent (1-2 grams) has been synthesized, more comprehensive performance testing will be conducted using a packed bed reactor. The packed bed system can provide both CO_2 and H_2O in the feed gas, and the reactor effluent is monitored using mass spectrometry, yielding single or dual gas isotherms. Experimentally measured performance parameters will then be provided to CCSI model tools, in conjunction with the systems analysis, to perform simulations and system studies as part of a techno-economic analysis to evaluate the potential to meet DOE goals. If the technoeconomic analysis demonstrates the potential to meet DOE goals, then a third year of work will include larger scale batch preparation (>100 g), pelletization, and testing in a scaled-up reactor using actual flue gas.

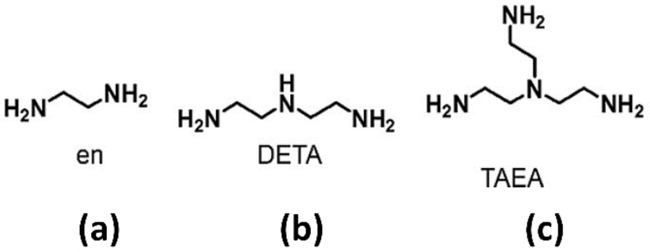

Figure 4: Chemical structures of primary amines, which will be used in the post modification of BILP-101: (a) ethylene amine, (b) diethylenetriamine, (c) tris(2-aminoethyl)amine

In the first year of this effort, BILP-101 will be modified through amine impregnation to maximize the sorbent selection parameter S for low pressure CO_2 capture. The hope is to identify an aminated BILP-101 sorbent with CO_2 adsorption working capacity >1.5 mol/kg and CO_2/N_2 selectivity >500. NETL-RIC will also complete a pre-screening economic analysis of the aminated BILP-101 sorbent. In the second year of research, NETL-RIC will produce 1–2 grams of the most promising aminated BILP-101 sorbent and will be evaluated under simulated flue gas environments in a packed bed reactor. Using techno-economic analysis, NETL-RIC will identify a sorbent and system combination capable of approaching a cost of CO_2 removed of $30/tonne. An industrial partner will be identified for further testing and licensing. Plans beyond year two include pelletizing and scaling up (100 g) the sorbent for testing in an actual flue gas.

technology advantages

- The BILP-101 sorbent consists of micro and meso pores with high surface area.
- Compared to other sorbents, the higher surface area of BILP-101 provides an optimum media for amine impregnation to increase CO_2 attractive sites in the sorbent.
- Smaller pores and intrinsic imidazole functionalities of the sorbent benefit the amine immobilization within the sorbent and, therefore, increases the material stability and cyclability.
- These materials also have a simple, one step synthesis procedure that is amenable to large-scale production.

R&D challenges

- Improving CO_2 working capacity while retaining CO_2/N_2 selectivity.
- Immobilization of primary amines in the sorbent media.
- Reduced CO_2 uptake performance in presence of humidity due to competitive absorption by H_2O.
- Preventing amine leaching from the sorbent pores.
- The optimization of device and process to fully take and exploit sorbent technology advantages.
- The evaluation of sorbent technology at scales and under environments needed to transfer technology to market.

status

In previous work, a novel polybenzimidazole linked polymer sorbent (BILP-101) was invented by NETL for the capture of CO_2 from flue gas. This physical sorbent had many desirable qualities including high CO_2/N_2 selectivity, low regeneration energy, and a simple synthesis procedure, but the CO_2 working capacity was only moderate. NETL-RIC plans to improve the CO_2 loading of BILP-101 by incorporating amine moieties into the micropore structure resulting in aminated polymer sorbents.

available reports/technical papers/presentations

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"Ultra-micro Porous Organic Polymer for High Performance Carbon Dioxide Capture and Separation" Chem. Commun. 2015 DOI: 10.1039/C5CC04656D, Sekizkardes, A; Culp, J. T.; Islamoglu, T.; Marti, A.; Hopkinson, D.; Myers, C.; El-Kaderi, H. M.; Nulwala, H.

Ali Sekizkardes, David Hopkinson, "Ultramicroporous Polybenzimidazole for Selective Gas Capture", Report of invention filed with NETL, September 23, 2015.

James Hoffman, Gray, M., Wilfong, C., Kail, B. "Basic Immobilized Amine Sorbents (BIAS) for Post Combustion CO2 Capture." Poster presented at 2015 NETL CO2 Capture Technology Meeting, June 23 – June 26, 2015, Pittsburgh, PA.

Pennline, H., Hoffman, J., Gray, M., Siriwardane, R., Fisher, J. "NETL/ORD Sorbent Research for the Capture of Carbon Dioxide." NETL topical report (final draft) submitted for review December 2015.

Transformational Membranes

primary project goals

NETL's Research and Innovation Center is developing new, ultra-high-performance membranes and membrane modules for post-combustion carbon dioxide (CO_2) capture. Membrane types under investigation include polymer membranes and mixed matrix membranes (MMMs); also, development of low pressure drop hollow fiber membrane modules is underway. Development efforts are consistent with overall goals of reducing the energy penalty and cost of CO_2 separation relative to conventional technologies.

technical goals

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

technical content

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

Advanced Polymer Membranes

Fundamentally, polymer membranes are bounded by their performance, known as the Robeson upper bound (permeability must be sacrificed for selectivity and vice

technology maturity:

Bench Scale, Actual Flue Gas

project focus:

Post-Combustion Membrane Materials

participant:

National Energy Technology Laboratory - Research and Innovation Center

project number:

RIC Capture FY2018-2021 FWP

predecessor projects:

RIC Capture FY2017 FWP

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partners:

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

versa). This intrinsic trade-off between permeability and selectivity is a significant limitation of using polymer membranes in the challenging application of capture of relatively dilute CO_2 from flue gas. Incremental improvements in polymer performance continue to advance the trade-off curve towards more selective, more permeable materials, but a step change over current technology would facilitate wider implementation of membrane technology.

Recently, NETL-RIC developed several novel polymer materials with CO_2/N_2 separation performance on the Robeson Upper Bound (Figure 1). NETL Polymer 1 is a cross-linked rubbery polymer that contains a free ionic liquid, trapped within the polymer matrix. Unlike a supported ionic liquid membrane, NETL Polymer 1 is a dense film that is stable under pressure. However, by adding an ionic liquid to the rubbery polymer, CO_2 permeability increased by 150 percent compared with the neat polymer. Furthermore, this performance can be tuned depending on the ionic liquid used.

NETL Polymer 2 is a photo cross-linked polyphosphazene material. The native polyphosphazene is known to have high gas separation performance, but is an unstable, gel-like material. Previous attempts by other research groups to thermally cross-link this material failed. NETL developed the first effective photo cross-linking procedure for this polyphosphazene, which resulted in a durable, flexible film.

NETL Polymer 3 is a polymer blend that consists of a high CO_2 permeability, glassy polymer, and a high CO_2/N_2 selectivity, rubbery polymer. Either polymer on its own is not well optimized for post-combustion carbon capture. The high permeability glass polymer has a selectivity that is too low for this application and is mechanically very brittle. The high selectivity, rubbery polymer has a permeability that is too low and it has a gel-like consistency. However, this proprietary blend forms a strong, flexible film that is perfectly suited for post-combustion carbon capture.

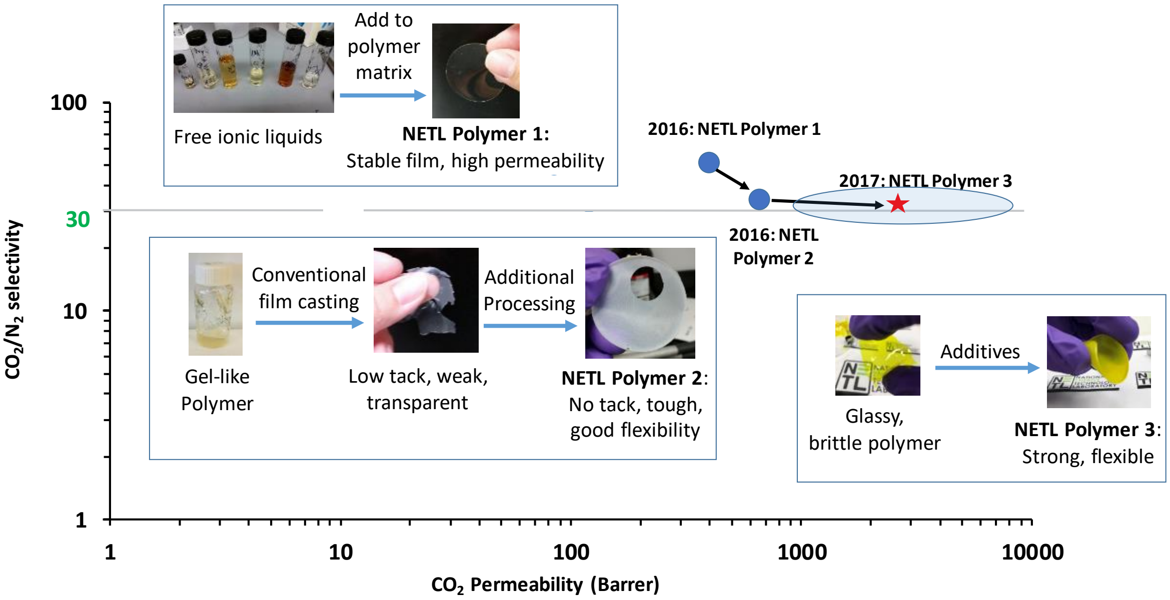

Figure 1: Gas transport performance for NETL Polymers 1, 2, and 3

NETL will pursue a phased approach in future technology development, featuring lab demonstration/testing of the several types of membrane materials discussed above, followed by fabrication of at least one of the most promising materials into a hollow fiber module, and testing of this on a slipstream of actual flue gas at the National Carbon Capture Center.

Mixed Matrix Membranes

Mixed matrix membranes are a technology which could potentially achieve a step change in gas separation performance. MMMs are composite structures that make use of a polymer matrix and a porous filler particle. Metal organic frameworks (MOFs) are commonly used as the filler particle because of their high CO_2 uptake and the tunability of their pores for achieving selective mass transfer of CO_2 relative to the other species in post-combustion flue gas (primarily N_2). In general, MOFs will have more desirable gas transport properties than a polymer, but are very difficult to form into a free-standing and defect-free membrane film. By integrating MOFs into a polymer film, the selectivity and permeance of the film are enhanced. This makes the system more capable of dealing with a low partial pressure driving force than conventional polymers, while also retaining the processability of a polymer. The MMM concept, challenges and development are depicted in Figure 2.

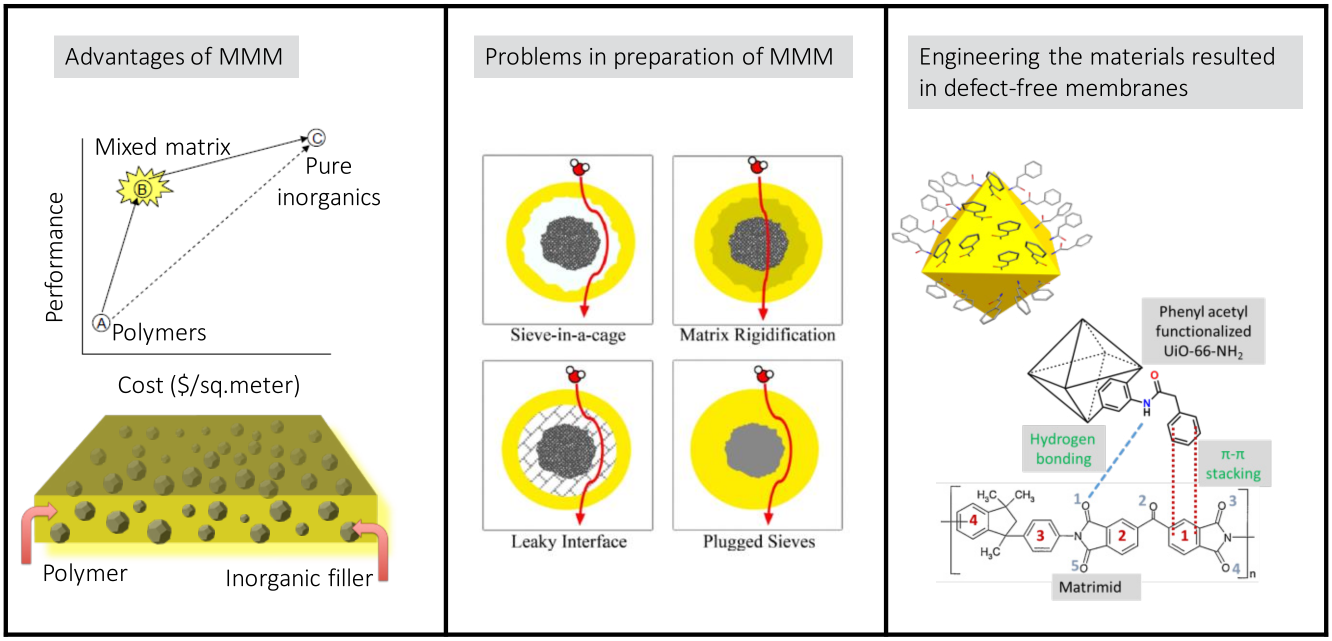

Figure 2: MMMs characteristics and development

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

NETL has previously developed the foundational knowledge needed for successful MMM fabrication and materials selection. For example, NETL used surface functionalized UiO-66 MOF materials with the polymer Matrimid to prove the concept of improved polymer-particle interfacial interactions by particle functionalization. Later, NETL used ionic cross-linked polyether to pursue a higher performance polymer coupled with silica gel, an inexpensive and commercially available filler particle. Subsequently, polyphosphazenes polymers were paired with SIFSIX MOFs to achieve even higher performance.

Most recently, NETL has taken a unique approach to MMM design by using high throughput computational tools to predict the gas permeability of a large database of MOF materials and make predictions of the gas permeation behavior of more than a million hypothetical MMMs (Figure 3). Predictions are compared with experimental measurements in Figure 4, showing excellent agreement. The model was expanded by coupling it with process analysis tools to calculate the cost of capture for the hypothetical MMMs. This represents the first known attempt at a true rational design of MMMs for post-combustion carbon capture. It was found that a well-designed MMM can lead to dramatic improvement of performance over a neat polymer, and reduce the cost of capture by $15/tonne.

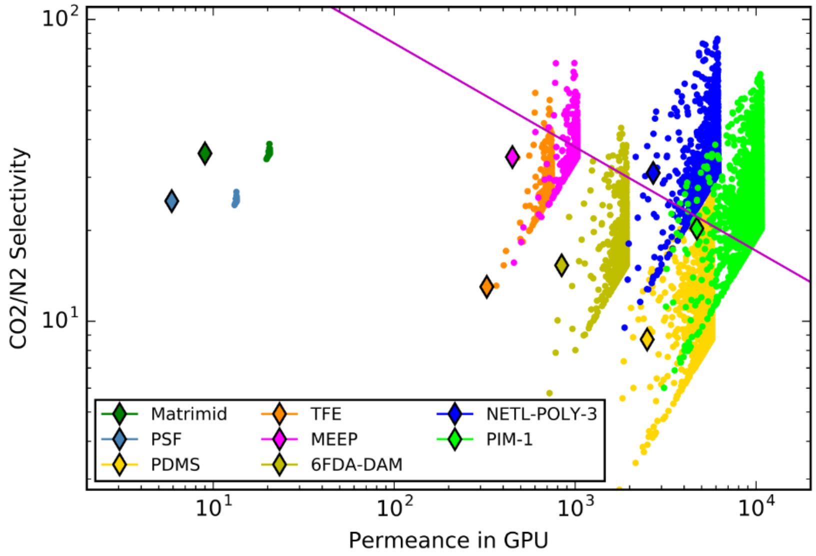

Figure 3: Predictions of MMM permeance and selectivity performance compared with neat polymers show potential for vast improvement beyond the Robeson Upper Bound. Diamond markers = neat polymer performance; dot markers = predicted MMM performance for various MOFs; purple line = Robeson Upper Bound

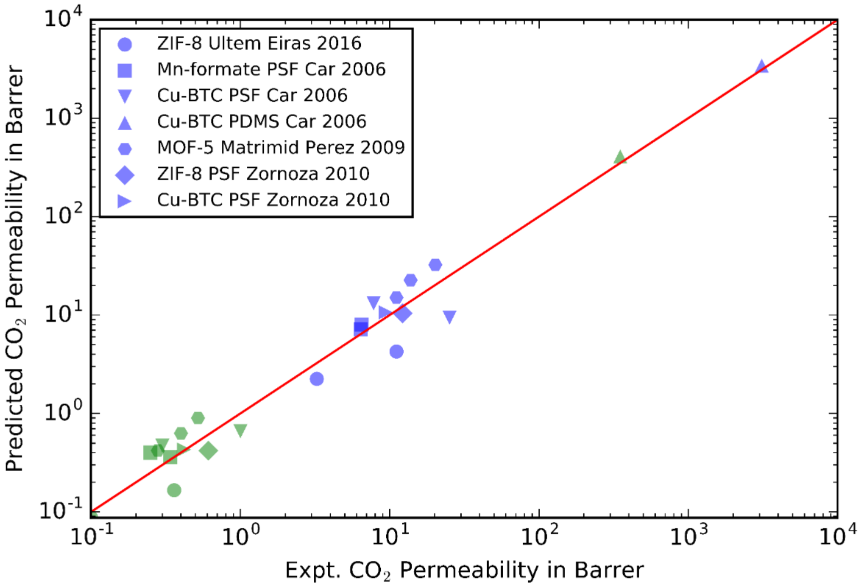

Figure 4: Comparison of literature reports of experimental performance for MMMs with performance predicted using NETL computational modeling tools showing excellent agreement. Blue markers = CO_2 permeability; green markers = N_2 permeability

In ongoing work, NETL will validate the multi-scale computational tools that were developed to optimize MMM materials by experimentally demonstrating the best predicted MMMs using actual flue gas. The most promising MOFs that were identified through computational modeling will be incorporated into polymer films and tested to prove that the performance of the MMM can exceed the Robeson Upper Bound under actual flue gas conditions.

technology advantages

- Membranes separate mixed gas streams according to differences in gas permeability across a membrane film, enabling steady-state operation with no energy-intensive regeneration step required: this creates potential for energy savings using this technology.

- Higher permeability membranes lead to a reduced membrane area requirement, smaller capital cost, and a smaller equipment footprint.
- NETL-developed polymers have enhanced mechanical stability.
- High-throughput computational methods have identified MMMs capable of breaking the Robeson Upper Bound.

R&D challenges

- Increasing membrane permeability and selectivity for CO_2.
- Identifying compositions that have durable mechanical properties and good thin film forming properties.
- Maintaining low cost of fabrication, particularly in membranes that involve complex synthesis procedures.
- Maintaining robust performance under harsh operating conditions such as elevated temperature or pressure.
- Increasing the resistance of membranes and membrane materials to contaminants including water, sulfur species, or particulates.
- Increasing the compatibility between composite membrane materials.
- Realizing good membrane separation performance even under low driving forces for separation associated with energy-saving configurations.
- Achieving defect-free thin film selective layer coatings that are <<1 µm in thickness.

available reports/technical papers

Ionic Cross-Linked Polyether and Silica Gel Mixed Matrix Membranes for CO_2 Separation from Flue Gas, Ali K. Sekizkardes, Xu Zhou, Hunaid B. Nulwala, David Hopkinson, Surendar R. Venna, Separation and Purification Technology, 191 (2018) 301-306.

Ionic Liquid Compatibility in Polyethylene Oxide/Siloxane Ion Gel Membranes, Victor A. Kusuma, Megan Macala, Jian Liu, Anne M. Marti, Rebecca Hirsch, Lawrence J. Hill, David Hopkinson, Journal of Membrane Science, 545 (2018) 292-300.

Active Response of Six-Coordinate Cu^{2+} on CO_2 Uptake in Cu(dpa)2SiF6-i from In Situ X-Ray Absorption Spectroscopy, Jeffrey B. Kortright, Anne M. Marti, Jeffrey Culp, Surendar Venna, David Hopkinson, Journal of Physical Chemistry Part C, 121 (2017) 11519-11523.

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An Automated Lab-Scale Flue Gas Permeation Membrane Testing System at the National Carbon Capture Center, Victor Kusuma, David Hopkinson, Journal of Membrane Science, 533 (2017) 28-37.

Continuous Flow Processing of ZIF-8 Membranes on Polymeric Porous Hollow Fiber Supports for CO_2 Capture, Anne M. Marti, Shan Wickramanayake, Ganpat Dahe, Ali Sekizkardes, Tracy Banks, David Hopkinson, and Surendar Venna, ACS Applied Materials & Interfaces, 9 (2017) 5678-5682.

Carbon Dioxide Separation from Flue Gas by Mixed Matrix Membranes with Dual Phase Microporous Polymeric Constituents, Ali K. Sekizkardes, Victor A. Kusuma, Ganpat Dahe, Elliot A. Roth, Lawrence J. Hill, Anne Marti, Megan Macala, Surendar R. Venna, and David Hopkinson, Chemical Communications, 52 (2016) 11768-11771.

Interactions at the Interface of Polymer Matrix-Filler Particle Composites, Jie Feng, Surendar Venna, and David Hopkinson, Polymer, 103 (2016) 189-195.

High Throughput Tools

primary project goals

The Research and Innovation Center (RIC) at NETL is developing high throughput screening tools to design advanced materials and processes that are able to reduce the energy penalty and cost of carbon dioxide (CO_2) separation as compared to conventional technologies.

technical goals

- Develop tools for rapid screening of novel carbon capture materials through computational approaches.
- Identify solvents for pre-combustion capture with high CO_2 loading, low hydrogen (H_2) loading, and low volatility using high-throughput computational screening tools.
- Use high-throughput computational tools to design mixed matrix membranes for post-combustion capture with desirable mechanical properties, CO_2 permeability of >2,000 Barrers and selectivity of >25 under a simulated mixed gas environment.
- Use computational methods developed at NETL to design novel polymer materials and investigate their gas separation properties.

technical content

The discovery of transformational new separation materials (solvents, mixed matrix membranes and polymer membranes) could dramatically lower the cost of carbon capture. In the design of new materials, it is common to have an extremely large number of possible variations in the chemistry of a compound. Predicting which variation will have the most desirable properties is not always obvious. High-throughput computational methodology is well-suited to the task of large surveys of existing or hypothetical materials. NETL is designing tools for rapid screening and characterization of a large number of membrane, solvent and polymer materials. An equivalent amount of data would take years or decades to acquire experimentally. NETL has established expertise in the development of new, high performance physical solvents and polymer membrane materials as well as the development of high throughput computational screening tools for carbon capture materials.

At NETL, computational data tools have been developed to screen thousands of physical solvents for carbon capture. Solvents are being designed for pre-combustion capture of CO_2 from integrated gasification combined-cycle power plants. The ideal solvent will exhibit low foaming behavior, low viscosity, low volatility, hydrophobicity, and the ability to operate above room temperature with high CO_2 capacity and CO_2/H_2 selectivity. In a first-round screening, a large number of promising, low-cost solvents have been identified. Using high-throughput methods, properties such as CO_2 loading, density, CO_2/H_2 selectivity, viscosity, and CO_2 diffusivity have been calculated. It is important to note that several of the most promising novel solvents are hydrophobic. Hydrophobicity is highly advantageous for a pre-combustion solvent. Phosphate-based solvents were identified as particularly promising for CO_2 separation and are in the early stages of experimental evaluation. Techno-economic evaluations will aid in the down-selection of promising solvents. Foaming behavior could be the downfall of an otherwise-perfect solvent and is notoriously difficult to predict. NETL has developed

technology maturity:

Modeling

project focus:

High-Throughput Computational Tools

participant:

National Energy Technology Laboratory – Research and Innovation Center

project number:

RIC Capture FY 2018 FWP

predecessor projects:

RIC Capture FY 2017 FWP

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partners:

Professor Christopher E. Wilmer and Professor Nathaniel Rosi (University of Pittsburgh) computational methods for the prediction of foaming in solvents and solvent mixtures. The prediction of foaming in solvents is accomplished based on dimensionless measures (e.g., Reynold's number), molecular dynamic simulations of the force required to break a thin layer of solvent, the use of energy minimization methods to determine the equilibrium structure of a foam bilayer, and potential of mean force calculations.

Post-combustion carbon capture is an application in which membrane-based processes are predicted to have a cost advantage. For a process to achieve success, the membrane needs to be highly permeable to CO_2 as well as highly selective. Mixed matrix membranes (MMMs) are formed from combining the low cost and good mechanical properties of polymer membranes with the superior gas separation properties of inorganic porous solids such as metal organic frameworks (MOFs). It has been demonstrated that pure polymer membranes have a trade-off between permeability and selectivity; this trade-off is known as the Robeson bound. Inclusion of high-selectivity MOF particles in MMMs creates the potential to overcome the Robeson bound. We have carried out high-throughput atomistic simulations on 112,888 real and hypothetical MOF structures in order to calculate their CO_2 permeabilities and CO_2/N_2 selectivities. The real MOFs are structures obtained from the CoRE database, while the hypothetical MOF structures were created by Professor Christopher E. Wilmer of the University of Pittsburgh. Using experimentally-measured polymer properties and the Maxwell model, we predicted the properties of all of the hypothetical MMMs that could be made by combining the MOFs with each of nine polymers, resulting in over one million possible MMMs. We used tools developed in the Carbon Capture Simulation Initiative (CCSI) to carry out twelve individually optimized techno-economic evaluations of a three-stage membrane-based capture process. For each evaluation, capture process variables such as flow rate, capture fraction, pressure and temperature conditions were optimized and the resultant cost data were interpolated in order to assign cost based on membrane selectivity and permeability. This work makes a connection from atomistic simulation all the way to techno-economic evaluation for a membrane-based carbon capture process. The carbon capture performance of MMMs formed from CoRE MOFs and the polymer PIM-1 are presented in Figure 1, where the color of the background indicates the predicted cost of carbon capture. The performance of a membrane composed of neat PIM-1 ($64 per tonne CO_2 removed) is indicated by the location of the blue diamond. The Robeson bound is indicated by a black line. We have shown that the inclusion of MOF particles in the PIM-1 polymer can either improve or degrade the performance of the polymer membrane, depending on the identity of the individual MOF particles. This gives us a tool for selecting a good MOF to pair with a given particle, and thus a way to design MMMs that have the properties that we seek. We find that a large number of MMMs are predicted to have performance that exceeds the Robeson bound, with several predicted to yield a cost of carbon capture less than $50 per tonne CO_2 removed. NETL is collaborating with Professor Wilmer and Professor Nathaniel Rosi of the University of Pittsburgh to continue the development of mixed matrix membranes.

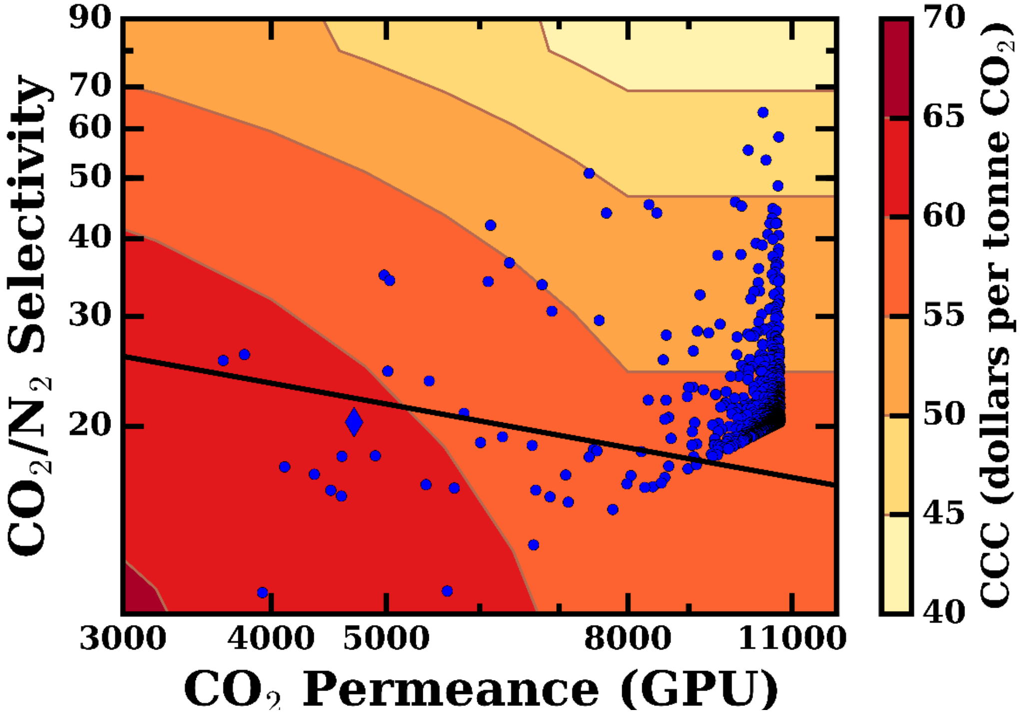

Figure 1: Performance of MMMs formed from CoRE MOFs and PIM-1. The performance of a membrane composed of neat PIM-1 ($64 per tonne CO_2 removed) is indicated by the location of the blue diamond. The Robeson bound is indicated by a black line.

technology advantages

- Computational high-throughput approaches allow for property predictions for a large number of hypothetical or real materials to determine material characteristics that lead to high performance.
- Structure-property relationships can be studied using computational methods and leveraged to design new materials with desirable characteristics.

R&D challenges

- Absence of mature computational methodology for the prediction of foaming in solvents.
- Incomplete or inaccurate data in databases or literature sources.
- Developing appropriate force fields, coarse grained models, solubility parameters, or group contribution models.
- Limitations in size and run-time for simulations of large systems.
- Accounting for polymer swelling that is associated with the sorption of CO_2.
- Large computational demands associated with production-scale computer simulations.

Carbon Capture Simulation For Industry Impact (CCSI^2)

primary project goals

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

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

technical goals

Carbon capture is critical to significantly reducing domestic and global carbon dioxide (CO_2) emissions. However, the energy and capital cost associated with carbon capture systems is prohibitive for any meaningful deployment. Today's cost to capture CO_2 using state-of-the-art carbon capture technologies must be reduced to competitive levels more rapidly and at lower risk. Fossil Energy goals are for technologies under development to be ready for commercial deployment by 2030 and must be on a pathway to achieve a price of \$30/tonne of CO_2 captured or a reduction in cost of electricity (COE) of a state of the art supercritical PC plant with CCS (excluding transportation and storage) by 30 percent. Strict requirements for 90 percent CO_2 capture have been relaxed, which provides technology developers the opportunity to further reduce the cost to capture CO_2. Balancing cost reduction with a level of CO_2 capture meaningful enough to contribute to climate change mitigation is critical in this new approach, yet this balance introduces a great deal of additional complexity. CCSI^2, with world-class expertise in process modeling and proven cost-performance optimization frameworks, is ideally positioned to provide well-informed perspective on the most impactful areas of research and development when capture percentage is free to vary.

The CCSI^2 team provides fundamental analysis, modeling and optimization of carbon capture technology by working closely with industry partners. The CCSI^2 team will efficiently identify data collection needs, characterize carbon capture materials, design and optimize devices and processes, and fully propagate uncertainty in model predictions for a complete perspective on model accuracy. The team will assist the Capture Program and technology developers by providing:

- More detailed understanding of capture materials through system performance under parametric uncertainty.
- Designs for high performance and intensified unit operations.
- Synthesis of processes optimized for novel materials; characterization of dynamic system behavior.
- More informed design, operating, and control decisions.
- Optimized processes under the intrinsic uncertainty.

technology maturity:

Practical Application of Modeling to Pilot-Scale

project focus:

Carbon Capture Simulation

participant:

National Energy Technology Laboratory–Research and Innovation Center

project number:

FWP1022422

predecessor projects:

FWP-FY16_CCSI2

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- A framework for intelligent design of experiments at all technology readiness levels (TRLs) for model refinement and system optimization.

CCSI^2 is in the process of disseminating the CCSI Toolset to the public. Specifically, CCSI^2 will prepare the tools for public release, document capabilities and instructions for use, manage a public repository, and implement a release management system for subsequent versions of the Tools.

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

technical content

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

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

- Lawrence Berkeley National Laboratory (LBNL) Metal Organic Framework (MOF) Sorbent Materials
- Pacific Northwest National Laboratory (PNNL) CO_2 Binding Organic Liquids (CO_2BOL)
- Lawrence Livermore National Laboratory (LLNL) Advanced Device Manufacturing

The Computational Support for the Capture Program task will focus on increasing the impact of research and development across the Capture Program by generating and applying computational frameworks to support carbon capture technology research. The subtasks for this task include:

- Sequential Design of Experiments (DoE)
- Multi-scale Modeling and Optimization
- Development and Application of Advanced Process Control (APC)

The Open Source Toolset Community Support task will coincide with the CCSI Toolset scheduled for open source release in 2018. A centralized open source repository will be created and maintained to facilitate public access to the CCSI Toolset. Prior to release, the CCSI computational tools must also be conditioned and documented to reduce the need for ongoing support of the public release. This task will develop a software and management framework for interoperability of the underlying simulation tools, ongoing development of the software and management of public tools for CCSI^2 Tool and information access (i.e., CCSI^2 Website Management).

technology advantages

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

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

R&D challenges

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

status

The tasks of CCSI² will have four thrusts for the Initiative:

1. To provide direct, low TRL support to the projects awarded under the Discovery of Carbon Capture Substances and Systems (DOCCSS) Initiative. The DOCCSS Initiative integrates contributions from national laboratory developers and industrial stakeholders to accelerate the commercialization process of advanced carbon capture materials, requires a multi-hierarchical characterization which embodies materials through systems level performance. Specifically, this work will ensure advanced materials development efforts are integrated with advanced systems design, analysis and optimization. Work will first focus on CO_2BOL and MOF based modeling frameworks to enable multi-scale, integrated materials, device and process optimization, move to generalized solvent and sorbent frameworks for program year (PY) 2019, and solvent and packing agnostic effective area calculation validations in PY 2020.

2. To develop a formalized Design of Experiments (DoE) methodology that will strive for data generation at all TRLs that is optimized for a variety of objectives including model refinement, process optimization, etc. In PY 2018, this thrust will work towards developing a methodology that will optimize the experimentation required at any scale, maximizing learning while reducing the time and cost of experimental testing at lab scale through pilot scale. In PY 2019 the project teams will work to build additional capability for Computational DoE into FOQUS (Framework for Optimization and Quantification of Uncertainty and Sensitivity, a validated CFD (computational fluid dynamics) model to predict particle attrition) which will cover computational experimental design, maximizing learning while reducing the time and computational cost of generating results from computationally-intense simulations; develop constrained DoE to consider operational and/or safety restrictions in the DoE; and investigate the feasibility of DoE generation based on output-based requirements. In PY 2020, the initiative will work to implement dynamic DoE which will substantially increase the speed and amount of data that can be generated at the pilot scale.

3. To inform research and development efforts in projects supported by the Capture Program through fundamental modeling, analysis and optimization, including: an Advanced Flash Stripper (AFS) modeling framework which is capable of acceptable performance predictions for generic solvents; identification of an optimal system for the LLNL Micro-Encapsulated Carbon Sorbent (MECS) technology; and demonstration of an Advanced Process Control (APC) strategy predicted to reduce settling time by 80 percent. Once underway, the efforts will expand in PY 2019 to work on a superstructure-based AFS process synthesis framework for generic solvents; accurate wetted area framework for estimating generic packing and generic solvents to inform device performance; and APC for full shut-down/startup scenarios and enhanced disturbance-rejection by refined disturbance-model development. The PY2020 focus is on the device scale intensification and optimization.

4. To prepare and release the full CCSI Toolset to the open domain, namely to complete a fully operational Toolset Release and launch of a repository for both open source and internal CCSI² modeling products. The following year's focus will include launch of the system for evaluation, testing and release management of open source contributions to the CCSI² Toolset. In PY 2020, the project will seek to use the Toolset for continued capture program support.

The CCSI² team will work to release the management system as a fully operational open source community with toolset revision evaluation and distributed toolset management by PY 2020.

available reports/technical papers/presentations

N/A

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION SOLVENT TECHNOLOGIES

Electrochemically Mediated Amine Regeneration in CO_2 Scrubbing Processes

primary project goals

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

technical goals

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

technical content

MIT terms their technology as Electrochemically-Mediated Amine Regeneration (EMAR). In conventional amine regeneration-based capture processes, a standard amine solvent such as monoethanolamine is contacted in countercurrent flow with CO_2-containing flue gas in an absorption column at relatively low temperature (<60 °C). At lower temperatures, CO_2 readily reacts with the amine forming an amine-CO_2 complex, and given suitable contact time and solvent flow in the absorption column, high levels of CO_2 removal (>90 percent) can be attained. The rich amine solvent (containing elevated levels of absorbed CO_2) exiting the absorber column is preheated in a countercurrent heat exchanger and introduced into the desorber column, where it is further heated with low-pressure steam withdrawn from the power plant's steam cycle, to reach temperatures greater than 110 °C. At elevated temperatures, the CO_2 is released from the solvent as a relatively pure stream of CO_2 that can be recovered. Hot lean solvent is cooled and returned to the absorption column. This conventional thermal regeneration-based process is depicted in the top half of Figure 1.

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 1 MW_e)

project focus:

Novel Electrochemical Regeneration of Amine Solvents

participant:

Massachusetts Institute of Technology

project number:

FE0026489

predecessor projects:

N/A

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partners:

N/A

start date:

08.01.2017

percent complete:

<10%

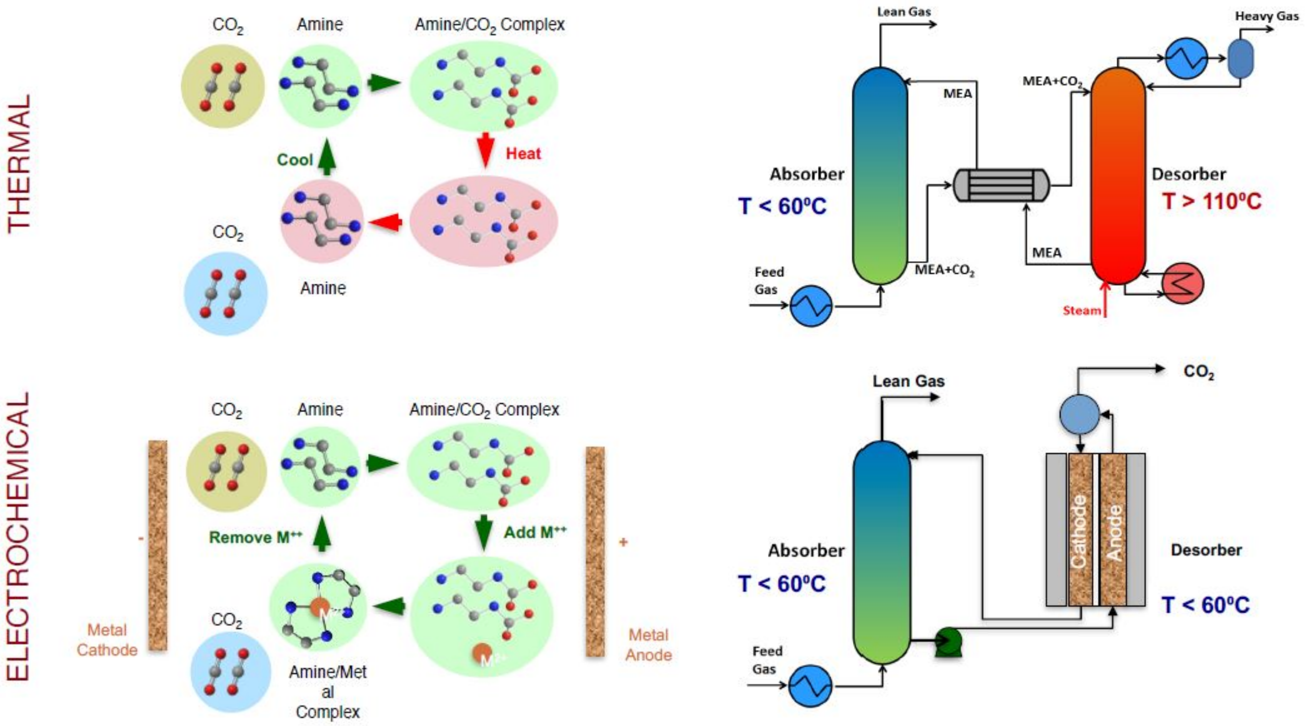

Figure 1: Electrochemically-mediated vs. thermal amine regeneration

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

Because the EMAR process requires only a limited amount of electrical power to operate the electrochemical processes in the cells, it avoids the need to use steam withdrawn from the power plant's steam cycle, minimizing parasitic energy consumption. This is depicted in Figure 2, which compares the theoretical minimum of CO_2 capture work (units of kJ/mol CO_2 captured), the amount associated with the EMAR system concept, and that of a conventional thermal amine system. These are all set on an equivalent non-thermal work basis. Note the significant energy advantage of the EMAR system in regeneration.

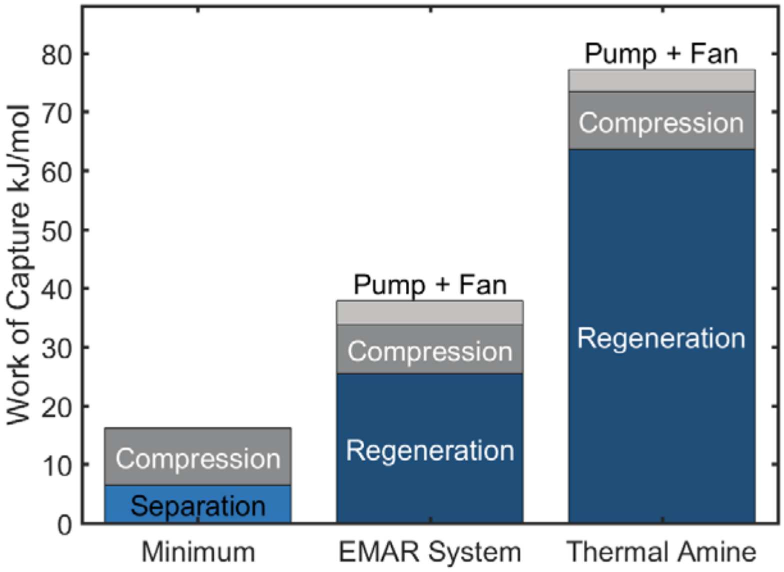

Figure 2: Comparison of Capture Work of Conventional Amine and EMAR Systems

Although this process concept has been proven at lab-scale, further work is required to refine/optimize the technology. Some of the technical points needing attention are as follows:

Amine Selection—Binding energies of metal ions with amines are specific to the amine. The binding energies must be strong enough to overcome the amine/CO_2 complexing, but higher binding energies demand high power consumption in the electrochemical cell to remove metal ions from the amine/metal complexes. Therefore, amine selection will be important in optimizing the process. Adequate amine stability in the process is required. Candidate amines include EDA, DETA, piperazine, MDEA, AEEA, to name a few. Ionic liquids with amine functionalities may also be suitable for utilization in this technology.

Metal Ions—Species such as Zn(II), Co(II), Fe(III), Fe(II), Ni(II), Cr(III), Cu(II) are under investigation. Most importantly, the metal-amine complex must meet certain criteria:

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

Screening of amine/metal complexes will be important in ongoing developmental work.

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

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

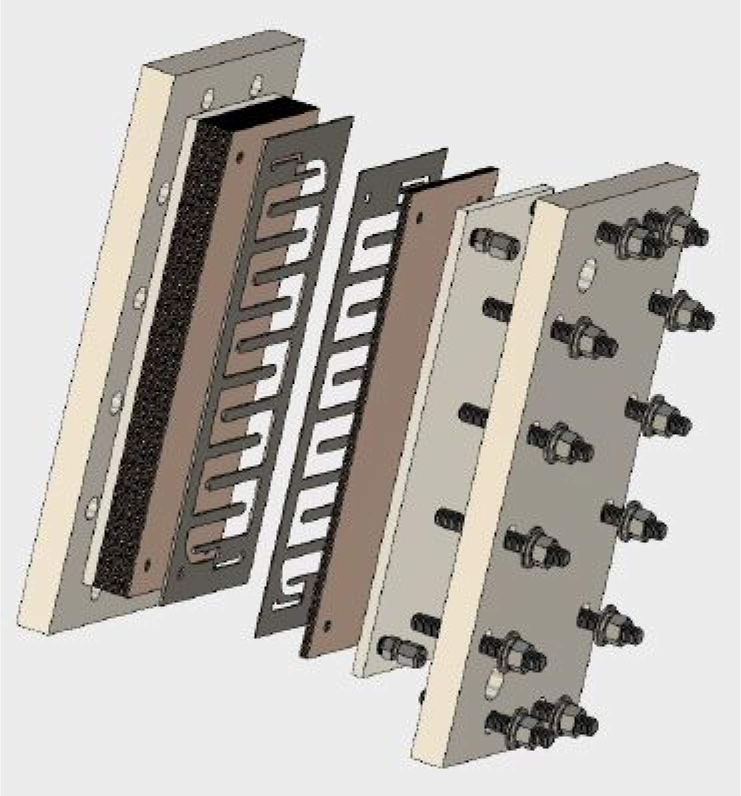

Figure 3: Electrochemical cell engineering

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	g mol^{-1}	60.2172	60.2172
Normal Boiling Point	°C	116	116
Normal Freezing Point	°C	11	11
Vapor Pressure @ 15 °C	bar	0.037	0.037
Manufacturing Cost for Solvent	$/kg	<50	<50
Working Solution			
Concentration	kg/kg water	0.06	0.24
Specific Gravity (15 °C/15 °C)	-	1	<1
Specific Heat Capacity @ STP	kJ/kg-K	4	4
Viscosity @ STP	cP	1.3	
Absorption			
Pressure	bar	1	1
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	1	1
Heat of Absorption	kJ/mol CO_2	85	85
Solution Viscosity	cP	1.3	
Desorption			
Pressure	bar	1	1–10
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol		<.2
Heat of Desorption	kJ/mol CO_2		89
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	466	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%/99%/1–10bar	
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent

(e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

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

Flue Gas Pretreatment Requirements – Sulfur removal.

Process Design Concept – See Figure 1 above.

technology advantages

- Amine scrubbing with electrochemically-mediated amine regeneration offers a combination of fast kinetics, low parasitic energy requirements, and process flexibility.
- CO_2 gas recovered from the regenerator is at elevated pressure (5–10 bar), lessening downstream compression requirements and saving energy.
- An initial techno-economic analysis indicates that the electrochemically mediated capture technology has a significant economic advantage over state-of-the-art thermal amine processes, cutting capture costs by 30 to 60 percent.

R&D challenges

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

status

MIT's electrochemically mediated amine regeneration technology has been previously developed from concept to a proof-of-concept lab-scale device, validating the feasibility and potential of the approach. Currently, additional lab-scale work is underway to further optimize the performance of the technology through screening, modeling, and experimental testing of various metals ions and candidate amine solvent types.

available reports/technical papers/presentations

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

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

Application of a Heat Integrated Post-Combustion CO_2 Capture System with Hitachi Advanced Solvent into Existing Coal-Fired Power Plant

primary project goals

The University of Kentucky Center for Applied Energy Research (UKy-CAER) team is developing a post-combustion carbon dioxide (CO_2) capture technology using advanced solvents and incorporating innovative heat integration methods to utilize heat typically rejected to environment, via a two-stage solvent regeneration configuration, increased solvent capacity, and lowered reboiler specific duty, thereby ultimately improving power plant efficiency. Related bench-scale project work (FE0012926) has extended the technology to include membrane pretreatment to enrich the flue gas stream entering the absorber, increasing absorber performance. This method has the potential to meet the U.S. Department of Energy (DOE) CO_2 capture performance and cost targets of 90 percent CO_2 capture, 95 percent CO_2 purity, and an increase in the cost of electricity (COE) of no more than 35 percent.

UKy-CAER has also recently prepared a pre-FEED study for a 10-megawatt electric (MW_e) large pilot plant (FE0026497) based on the technology demonstrated at 0.7 MW_e scale. If the proposed 10 MW_e pilot moves forward to later phases, this would contribute towards the goal of advancing the technology to near-commercial readiness.

technical goals

- 90 percent CO_2 capture with 99.9 percent purity and a cost of electricity (COE) of \$119/MWh, a 47 percent reduction on incremental COE from DOE Reference Case (RC) 12.
- CO_2 capture cost of \$35/tonne CO_2, excluding transportation, storage, and monitoring (TS&M) costs.
- Solvent regeneration energy of <1,000 British thermal unit (Btu)/lb CO_2 captured and heat rejection from CCS block reduced to 1540 MBTU/hr, a 51 percent decrease compared to DOE RC 12.
- Capital cost of \$3,039/MWh (2011\$), a 15 percent decrease compared to DOE RC 12.
- Generation plant efficiency of 32 percent, higher heating value (HHV) basis, a 13 percent increase compared to DOE RC 12.
- Solvent makeup rate of 0.3 kg/tonne CO_2 captured.
- Minimal water makeup with no deionized water requirement.

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 0.7 MW_e or 2 MW_{th})

project focus:

Slipstream Demonstration Using Advanced Solvents, Heat Integration, and Membrane Separation

participant:

University of Kentucky

project number:

FE0007395

predecessor projects:

FE0012926
FE0026497

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partners:

Mitsubishi Hitachi Power Systems America (MHPSA), Electric Power Research Institute (EPRI), Koch Modular Process Systems (KMPS), Smith Management Group (SMG), Membrane Technology Research (MTR), Louisville Gas and Electric and Kentucky Utilities (LG&E and KU)

start date:

10.01.2011

percent complete:

80%

technical content

UKy-CAER's technology has evolved over a series of projects in recent years. Currently, the proposed capture process system incorporates several energy-saving and performance-increasing features, among which the most notable are as follows:

- A two-stage solvent regeneration configuration, consisting of a steam-driven first-stage primary stripper removing most of the CO_2, followed by a secondary stage designed as an air stripper, powered by recovered heat from the CCS block. This reduces the carbon loading in the lean solvent to very low levels, and the exiting CO_2-laden air is fed into the boiler as combustion air to boost CO_2 concentration at the absorber inlet.
- A system integration and heat recovery scheme demonstrated through experimentation and simulation. Heat is recovered from the CO_2 compressor intercoolers and the primary and secondary stripper overhead streams, and used to effectively power the secondary stripper, thereby minimizing exergy loss from the steam supply.
- An optimized two-stage cooling tower concept to reduce the condenser temperature, thereby improving steam turbine efficiency.
- Use of advanced solvents for CO_2 absorption from flue gas. The Hitachi solvent H3-1 had been under investigation for application in this process and has figured prominently in small pilot slipstream testing, but corporate restructuring has resulted in H3-1 becoming commercially unavailable. Other proprietary, commercial solvents will be available for utilization in this technology moving forward; these will be suitable for UKy-CAER CO_2 capture process which can function with various advanced solvents as demonstrated by bench and pilot scale studies. To balance the cost of commercial solvents and the gain in performance benefits, the advisable approach to solvent development focuses on striking a good balance of moderate solvent cost with CO_2 absorption performance and kinetics including but not limited to cyclic capacity, solvent emissions and degradation. This can be achieved by blending amines that are functionalized so as not to result in formation of nitrosamine, and by using additives with catalytic kinetic function, and additives which inhibit solvent degradation and corrosion.
- A hybrid process including a membrane unit in the flue gas inlet to the absorption column, working as a CO_2 pre-concentrating separator for the entering flue gas. Outputs consist of retentate enriched in CO_2 and permeate depleted in CO_2. These two flue gas streams are introduced at different levels in the column, with the lean stream injected higher in the column where fresher solvent is present, and the rich stream injected farther down. In effect, this increases the number of theoretical stages in the absorption column for a given height and amount of packing, improving column separation performance.

Figure 1 depicts the general process arrangement of the UK CAER technology; most of these features are depicted here.

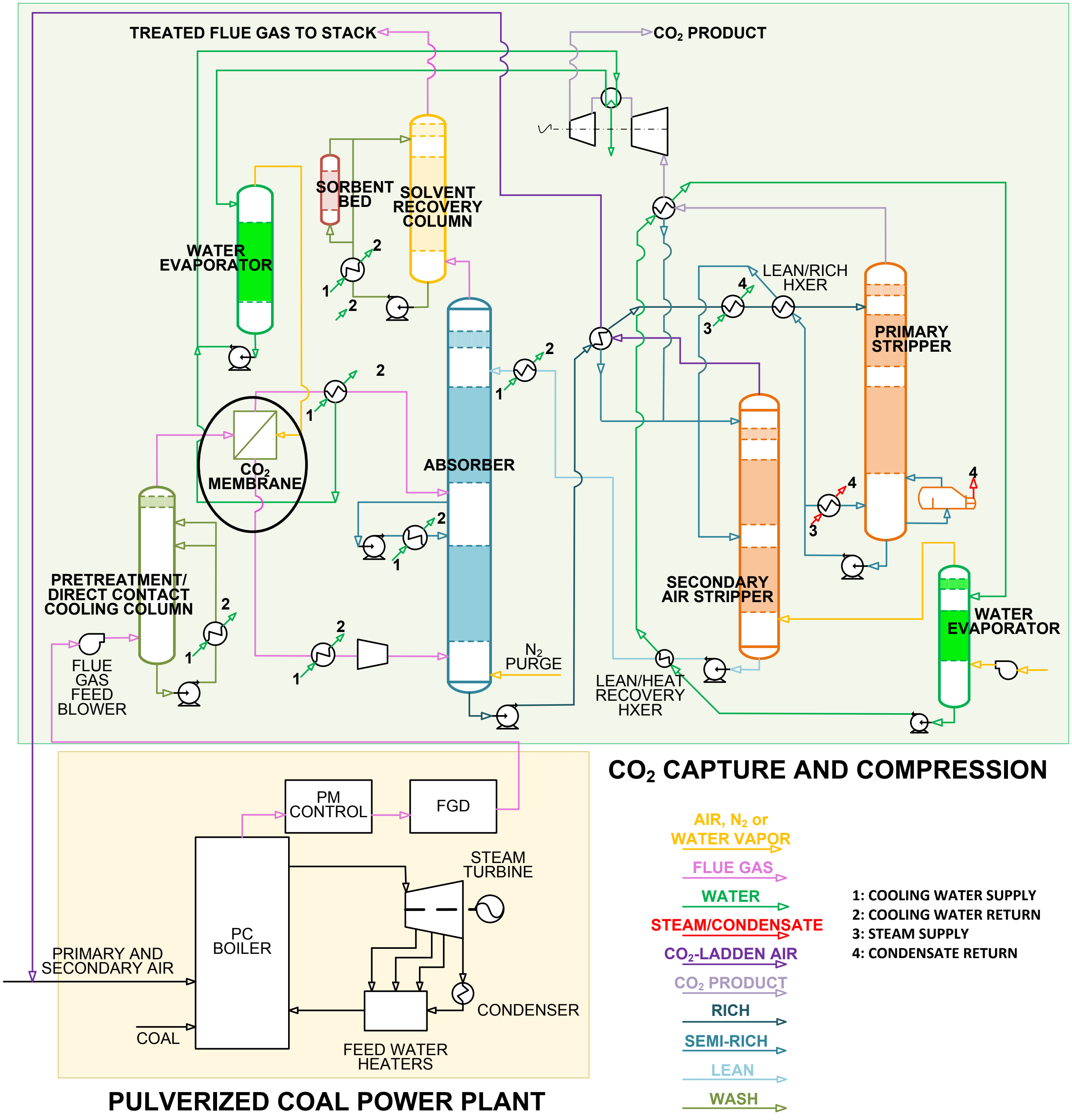


Figure 1: UK CAER carbon capture system process flow diagram

Note: Black oval indicates the CO_2 pre-concentrating membrane unit investigated in FE0012926.

UKy-CAER’s Advanced Solvents

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

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

UKy-CAER designates catalytic solvents currently under investigation with codes, reflecting permutations of proprietary commercial amine solvents (Solvent A, Solvent B, etc.), maintaining confidentiality. One of the solvents much investigated of late is CAER-B3. In future technology evolution, none of these will be based on the now unavailable Hitachi H3-1 solvent.

CO_2 Pre-Concentrating Membrane

Figure 2 shows the membrane separator for enriching CO_2 in the flue gas, and an actual polymeric membrane unit produced by MTR which was used in bench-scale testing.

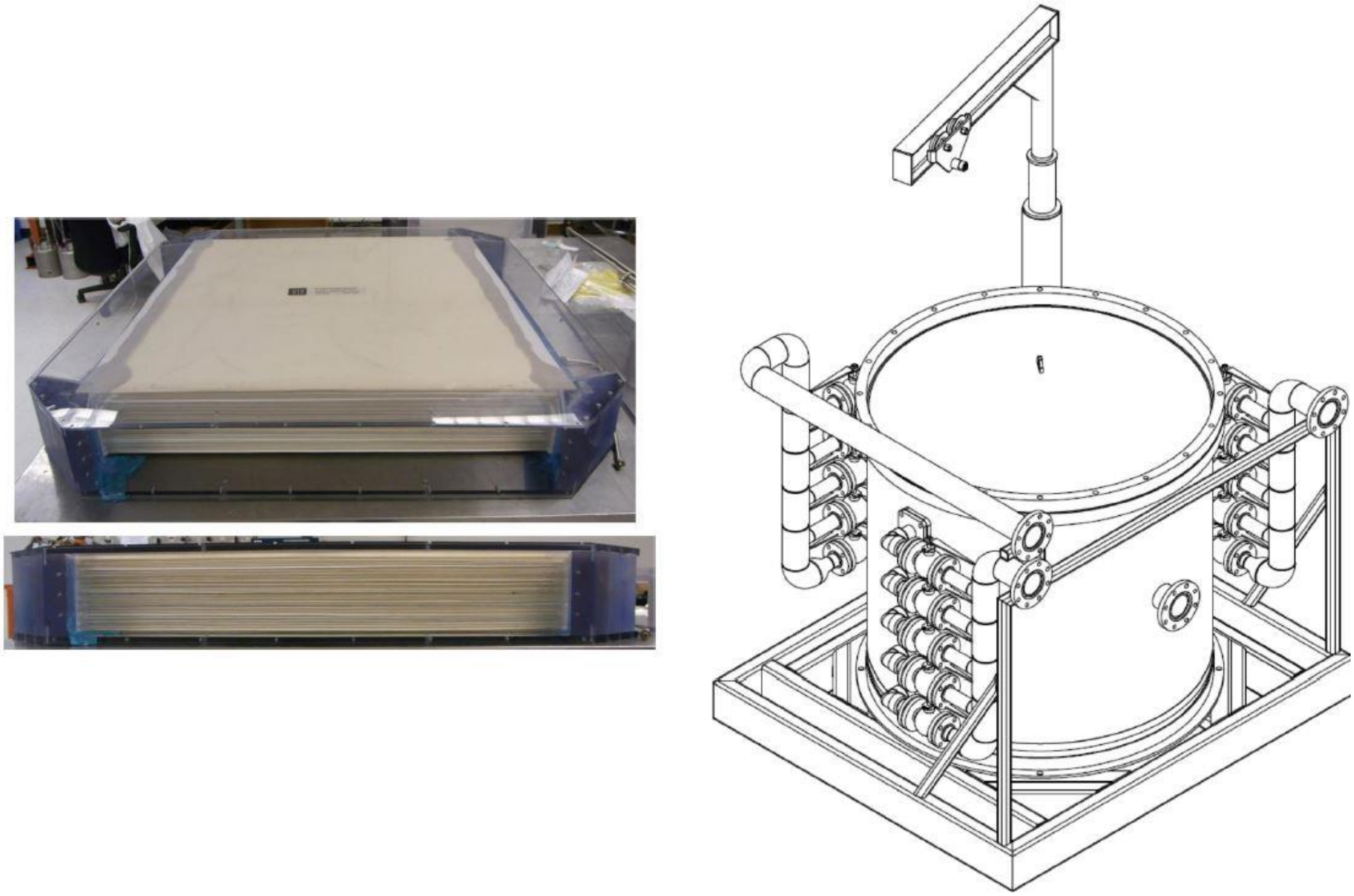


Figure 2: CO_2 pre-concentrator membrane unit (MTR-supplied product on right)

Membrane-Based Dewatering of Rich Amine Solvent

Figure 1 does not include one process feature that UKy-CAER has investigated in the context of Project FE0012926, and is currently still interested in. This feature is an integrated membrane concentrator unit intended to provide dewatering of the CO_2 rich amine solvent/solution exiting from the absorber/scrubber, either before or after the lean-rich heat exchanger. The membrane separator would selectively permeate water from the stream for recycle to the absorber through a zeolite-based membrane, as shown in Figure 3, effectively concentrating the CO_2 rich stream and increasing the CO_2 partial pressure, which can further reduce process energy demand. This membrane should be designed to maximize water permeability and carbon/amine rejection, while maintaining stable performance over time. UK CAER has investigated zeolites as the material of choice for this membrane. Currently, given the membrane surface area required and the high cost of zeolite membranes, it is not practical to include it in process scenarios as currently envisioned. However, through the use of lower-cost hollow fiber support materials and increasing the packing density of the active membrane surface area up to >200 m^2/m^3, the economics of this enrichment process can be improved. In addition, through modifications to the active membrane layer and the permeability of the support layer, water flux through the membrane can be enhanced to further reduce the cost and implementation of this system in a CO_2 capture process.

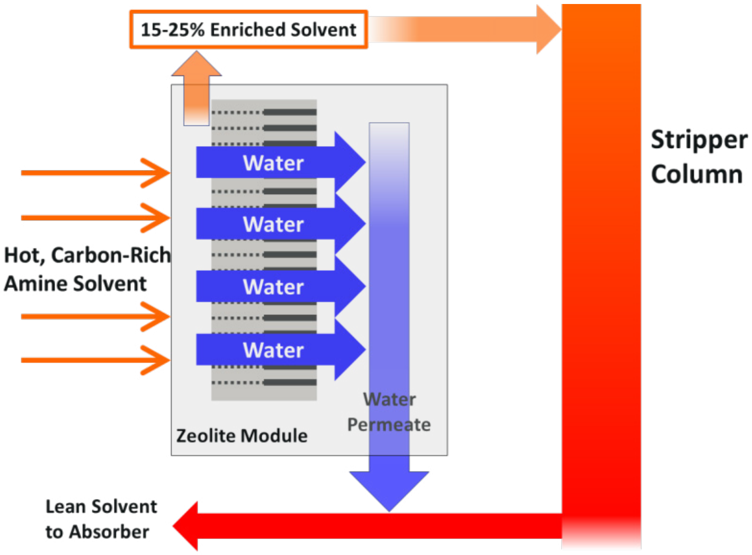


Figure 3: CO_2 membrane dewatering for CO_2 enrichment

Findings from Slipstream Testing

0.7 MW_e small pilot testing has been performed at Kentucky Utilities E.W. Brown Generating Station in Harrodsburg, Kentucky, using a process configuration including much of the scheme depicted in Figure 1. Performance of the capture system was baselined using a generic 30 wt% monoethanolamine (MEA) solvent to obtain data for direct comparison with the National Energy Technology Laboratory (NETL) Reference Case 12. Also, Hitachi's proprietary solvent H3-1 and the CAER blended solvent were tested. Parametric test campaigns, system transient dynamic studies, and long-term continuous verification tests of the heat integration process enabled characterization of systems response in terms of load demand following, varying flue gas conditions, and individual component operation. Evaluation of solvent degradation, process emissions, and corrosion studies of materials in the circulating solvent were accomplished. See below, and also in the Other Parameters section following Table 1 for findings in these areas. Data were collected to support a full techno-economic and environmental health and safety (EH&S) analysis for a 550-MW commercial-scale carbon capture plant.

Notable findings are as follows:

- The process can easily capture 90 percent of CO_2 in flue gas using either MEA or H3-1 or CAER solvent as the working capture solvent.
- MEA solvent regeneration energy was determined to be 1,200–1,750 Btu/lb CO_2 captured, ~13 percent lower than NETL Reference Case 10.
- H3-1 solvent regeneration enegy was determined to be 900–1,600 Btu/lb CO_2 captured,~36 percent lower than RC10. Overall, low regeneration energies are possible over a range of solvent concentrations.

- The secondary air stripper is capable of regenerating >10 percent of the CO_2 captured as depicted in Figure 4. At the commercial scale, the exhaust CO_2-laden air (8-12 vol% CO_2, dry) will be recycled back to the boiler as combustion secondary air, yielding a higher absorber inlet CO_2 concentration (15-17 vol%), which has been observed to always correspond to a low solvent regeneration energy.

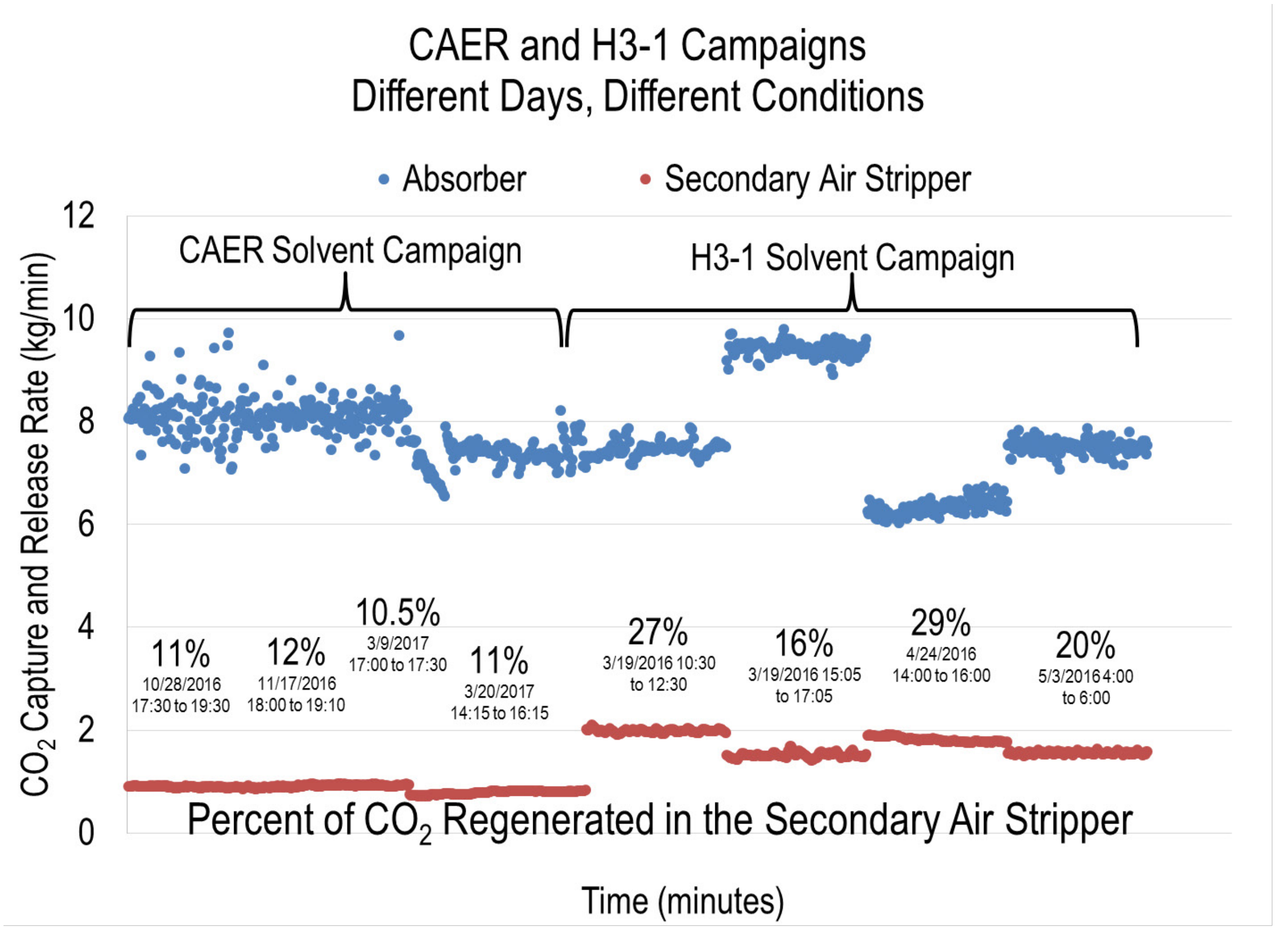


Figure 4: UKy-CAER secondary air stripper CO_2 regeneration

- Varying ambient conditions have an impact on CO_2 capture, attributable to cooling water temperature variations which impact the capture system process stream temperatures at any point where heat exchange with cooing water is involved.
- Good absorber liquid/gas distribution has to maintained to keep absorber efficiency from being reduced.
- Lean/rich exchanger performance is critical to the energy efficiency of the cycle: if the approach temperature in the exchanger is not kept low, the efficiency suffers. This is depicted in Figure 5, showing that an increase in approach temperature to 35 °F from 20 °F degrees increases the solvent regeneration energy demand by about 400 Btu/lb CO_2.

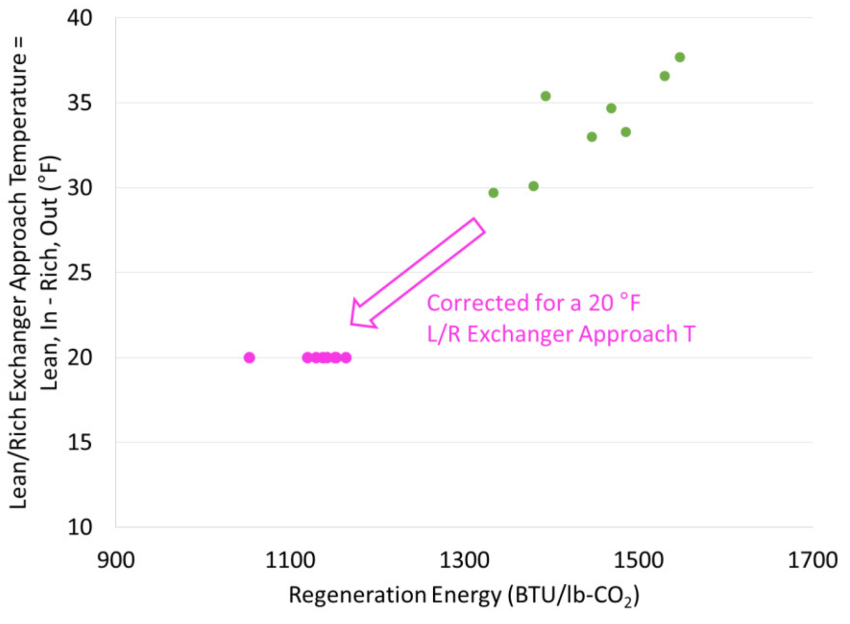


Figure 5: Effect of lean/rich heat exchanger approach temperature on solvent regeneration energy demand

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

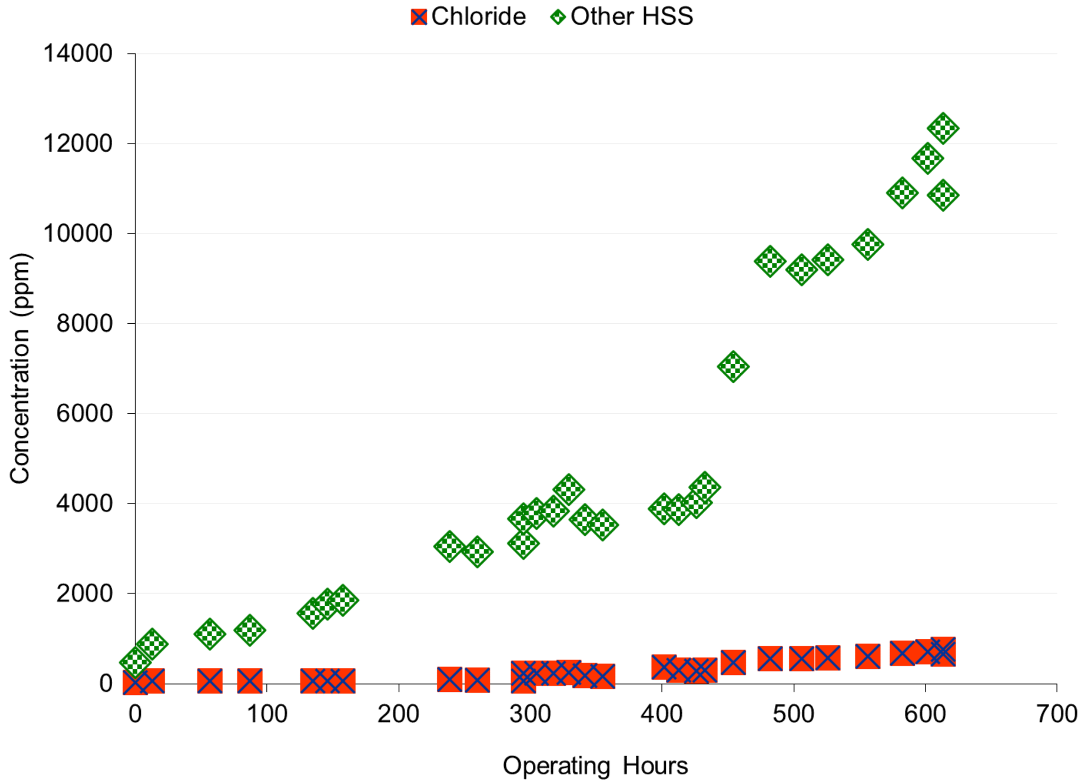


Figure 6: Accumulation of contaminants in solvent

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

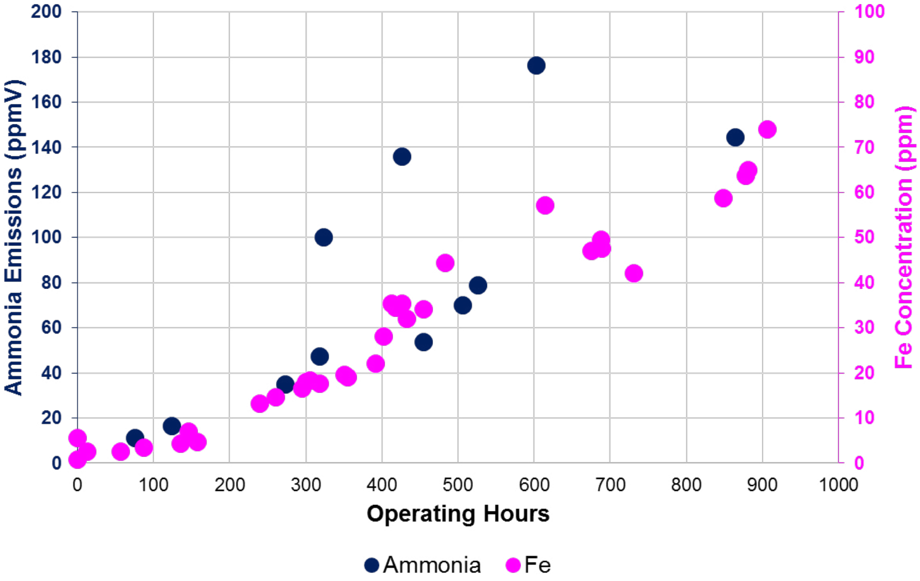


Figure 7: Ammonia emissions and iron

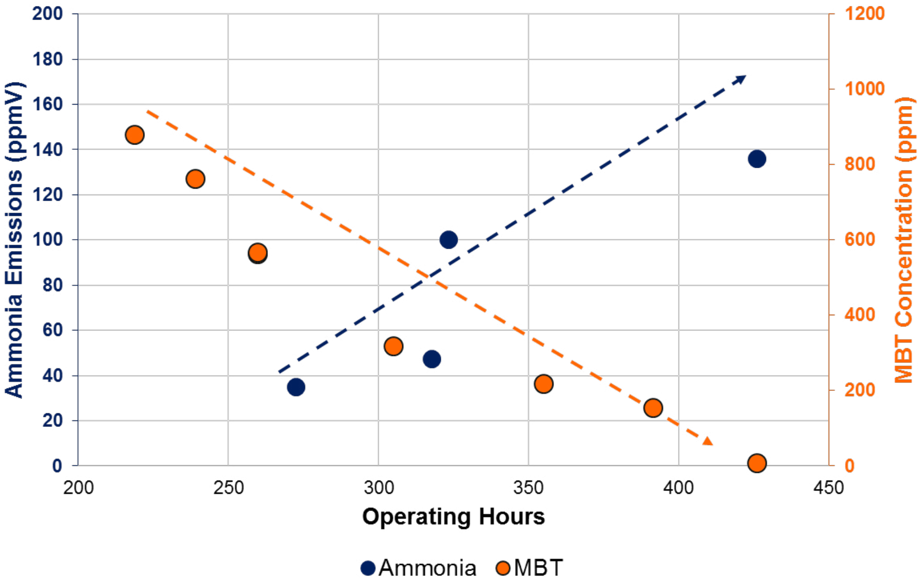


Figure 8: Ammonia emissions versus additive (MBT) in the solvent

Techno-Economic Analysis Findings

The preliminary TEA conducted and experimentally validated under FE0007395 shows that application of the improved process cycle (with MEA as the solvent) would reduce COE by about 8 percent over the conventional 90 percent capture case, and that use of H3-1 in the improved process cycle would reduce COE 12 percent. Taking into account equipment sizing findings from the UKy-CAER 0.7 MWe small pilot study, the overall reduction in COE is 19 percent when UKy-CAER technology is deployed to commerical scale, as depicted in Figure 9. This shows that the cost of CO_2 capture (excluding T&SM) is reduced from \$56.52 to \$34.51 per tonne CO_2 captured, a reduction of 38.9 percent.

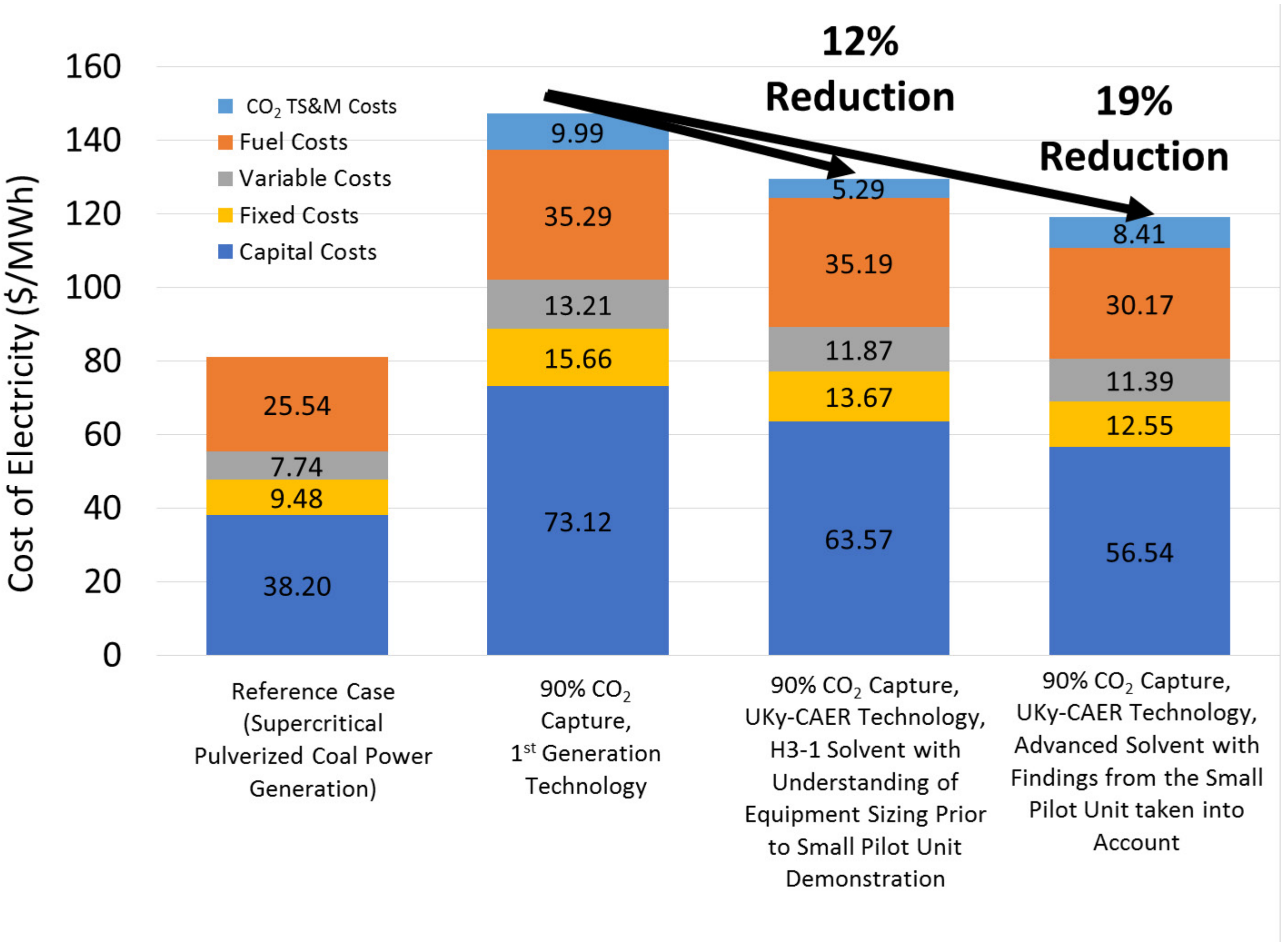


Figure 9: Cost of electricity estimates from techno-economic analysis

However, additional cost reductions will be necessary to attain ultimate DOE program targets. For this, UKy-CAER reckons that a combination of a further improved 3rd generation solvent will be critical, combined with the pre-concentrating membrane and absorption enhancement technologies via optimial absorber temperature profile and gas-liquid interface mixing. To illustrate the issue, the current 2nd generation solvents are simply too expensive compared to conventional MEA as shown below (Solvent B is 10 times the cost of MEA on a unit basis). In these cases the energy savings are less than the additional solvent makeup cost.

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

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	<90	<90
Normal Boiling Point	°C	160–165	160–220
Normal Freezing Point	°C	-2	-2–5
Vapor Pressure @ 15 °C	bar	$6.3x10^{-4}$	$6.3x10^{-4}$-$6.3x10^{-3}$
Manufacturing Cost for Solvent	$/kg	4–6 (estimated)	3–5
Working Solution			
Concentration	kg/kg	<0.4	<0.45
Specific Gravity (15 °C/15 °C)	-	1.01	1.01
Specific Heat Capacity @ STP	kJ/kg-K	3.7	3.7
Viscosity @ STP	cP	3.04	3.5
Absorption			
Pressure	bar	1	1
Temperature	°C	40	0
Equilibrium CO$_2$ Loading	mol/mol	0.42	0.51–0.65
Heat of Absorption	kJ/mol CO$_2$	74	<60
Solution Viscosity	cP	4.88	8-10
Desorption			
Pressure	bar	3.1	3.0
Temperature	°C	125	120
Equilibrium CO$_2$ Loading	mol/mol	0.23	0.30
Heat of Desorption	kJ/mol CO$_2$	84	<75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate @ 10 MWe equivalent	kg/hr	43,000	
CO$_2$ Recovery, Purity, and Stripper Pressure	%/%/bar	90 99.9 3.0	
Absorber Pressure Drop	bar	<0.1–0.15	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~200	

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

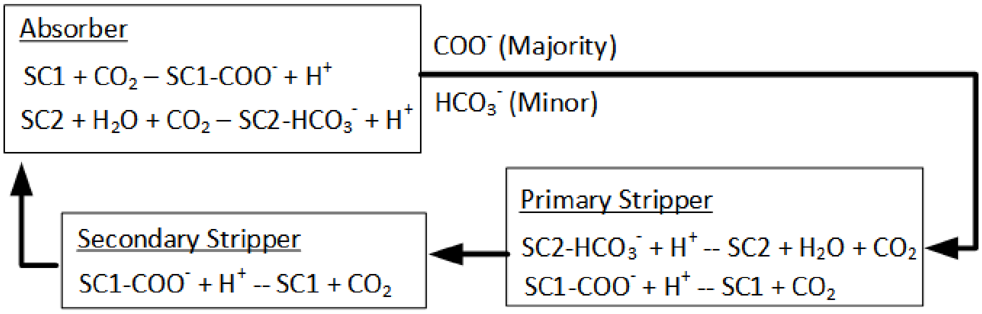
Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

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

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

Other Parameters

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



In the illustration:
SC1 – The constituents of primary and secondary amines in the solvent
SC2 – The constituents of tertiary and hindered amines in the solvent

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

Solvent Contaminant Resistance – The CAER-B3 solvent shows analogous behavior towards oxidation and flue gas components as 30 percent MEA. We anticipate similar levels or less of oxidation and degradation due to flue gas components.

Solvent Foaming Tendency – The addition of anti-foam to solvent scan help control foaming tendencies by lowering the solvent surface tension. Any new solvent additive will need to be evaluated for its foaming potential and those that to increase foaming tendency should be avoided. The catalytic solvent has very low foaming tendencies due to a low surface tension of <40 dyn/cm. The foaming observed is less than 30 percent MEA, but more than 30 percent MEA with antifoam added.

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

Solvent Make-Up Requirements – Long-term stability is an ever-present concern of all solvent developers. The CAER solvent is composed of amines that are inherently more stable than MEA and has a higher thermal stability than MEA. As seen in Figure 11, a 50–70 percent decrease in rate of amine loss as percent of initial is observed at the high temperatures associated with stripper conditions over a 2-week period. Regression of the data compared to reference MEA predicts a thermal degradation rate similar to MEA at a 10 °C higher stripper operating temperature. It is expected that the makeup requirements will be similar to that of MEA under the proposed process conditions of a higher stripper temperature/pressure.

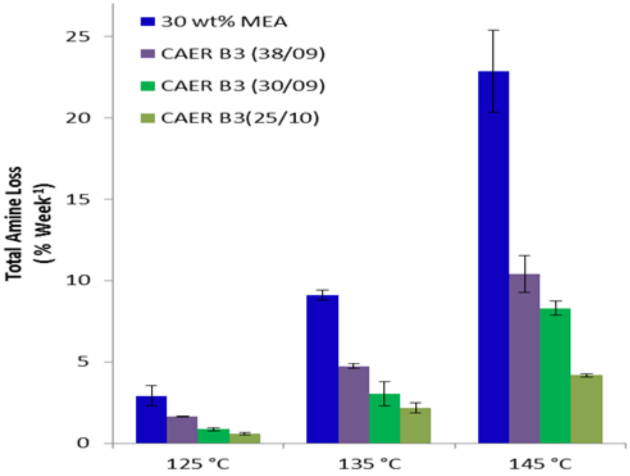


Figure 11: Rate of amine loss as total percent amine under stripper conditions of 30 wt% MEA (Blue) and various combinations of CAER-B3

Waste Streams Generated – The waste streams generated from the process are the spent soda ash solution and CAER-B3 solvent used for SO_2 removal and the absorption of CO_2, respectively. The loss of performance and how quickly the solvent is spent is impacted by the rate of degradation and heat stable salts formation in the solvent.

Process Design Concept – Flowsheet/block flow diagrams are included above in Figure 1. In brief, the SO_2-polished flue gas (from the pre-treatment tower) enters the CO_2 pre-concentration membrane to produce two streams which are injected into the CO_2 absorber at separate locations. After gaseous CO_2 is converted into aqueous carbon species, the carbon-rich solution exits the scrubber bottom, is pressurized, and is sent to the rich-lean solution heat exchanger (Crossover EHX) prior to the dewatering membrane unit. The permeate stream of the dewatering membrane unit with low amine concentration combines with the regenerated lean solution stream exiting at the outlet of the stripper. The reject stream which has higher carbon loading than the feed stream is sent to the top of pressurized stripper for solvent regeneration. This stage will require an energy source to drive the reboiler. At the stripper exit, the gas stream consists primarily of CO_2 and water vapor at a pressure of approximately 3 bar. After exiting the heat recovery unit at the top of stripper, the CO_2 gas stream with purity of 99.9 percent will be pressurized to about 135 bar and intercooled for downstream utilization or sequestration. The carbon-lean solution exiting the primary stripper is sent to the Crossover EHX, where heat will be recovered with the carbon rich solution. After the Crossover EHX, this heat depleted stream will be cooled to approximately 40 °C and recycled to the scrubber.

technology advantages

- The two-stage stripping unit, including the deployment of an air-based secondary stripper, will regenerate an exceptionally CO_2-lean solvent, increasing the rate of CO_2 absorption and solvent cyclic capacity.
- Cooling water temperature with the heat-integrated cooling tower can be decreased by more than 2 °C compared to conventional evaporative cooling towers, leading to improved steam turbine and power plant efficiency and lower levelized cost-of-electricity (LCOE).
- The solvent recovery column at the outlet of the gas stream leaving the CO_2 absorber uses water from the in-duct cooler as make-up to minimize the freshwater withdrawal, and recover solvent vapor in this stream.
- The advanced solvent used in this system has (1) a higher mass-transfer flux, (2) a higher net cycle carbon capacity, (3) less energy demand for CO_2 stripping, and (4) lower corrosion rates than a 30 wt% MEA solution, leading to lower capital and operational costs.
- The advanced solvent also has 89 percent lower thermal and oxidative degradation rates compared to MEA, leading to lower capital costs and low solvent makeup costs.
- Potential for reduced capital cost for post-combustion CO_2 capture, chiefly through increased absorption kinetics which allow for a smaller absorber and regeneration columns coupled with a lower solvent circulation rate and smaller associated equipment (blowers, pumps and piping systems).
- Potential for reduced energy consumption compared to conventional MEA-based scrubbing, chiefly attributable to:
    - High cyclic capacity
    - High stripper temperatures/pressure: the primary CO_2 stripper can be operated at approximately 3 bars in order to maximize the energy benefit while minimizing system capital and solvent degradation, which could lead to low compressor capital and operating costs
    - Lower solvent makeup rate

R&D challenges

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

- Absorption enhancement techniques must be demonstrated to reduce the size of the absorption column and lower the solvent circulation rate. These include mass transfer enhancement and column temperature and CO_2 absorption profile management.
- Two-stage solvent regeneration has been successfully demonstrated at the small pilot scale, but intensification in the strippers can be applied to reduce the column height and steam requirement.
- The UKy-CAER solvent recovery from the absorber exit gas stream has been demonstrated at lab scale and bench scale, but needs to be demonstrated at the pilot scale.
- Use of a CO_2 pre-concentrating membrane in the absorber flue gas feed has been demonstrated at bench scale, but needs to be demonstrated at pilot scale.
- Implementation of a smart process control scheme needs to be demonstrated to reduce the solvent regeneration energy while also responding quickly to the dynamic load and ambient conditions.
- Absorber liquid/gas maldistribution has been shown to significantly affect CO_2 absorption. Due to the high volume and low CO_2 absorption driving force in utility flue gas and the highly viscous nature of 2nd-gen + solvents, the low pressure drop structured packing suffers from a lack of macro-mixing/turbulence between the bulk solvent and the gas-liquid interface, which results in localized channel flow and significantly reduces column effectiveness which has to address prior to deployment in commercial scale.
- Waste minimization techniques need to be demonstrated at large pilot scale. Accumulation of elements such as Se and As in the CO_2 capture solvent can result in a hazardous classification of the material.
- The relationship between thermal compression and L/R HXER size needs to be understood and included when reporting solvent and process performance. It is generally accepted that the stripper is equilibrium controlled, and in-situ thermal compression via high temperature operation will drop the H_2O/CO_2 ratio at the stripper outlet, lowering the specific reboiler duty. 0.7 MWe small pilot experimental data indicate this holds true only for systems with a relatively large L/R HXER (low ΔT between hot lean from stripper and hot rich to stripper).

- Long term, low cost advanced solvent performance needs to be demonstrated. While several solvents are currently in use at the commercial scale, they are costly and improved performance may not justify this cost.
- Lower cost corrosion-resistant materials of construction need to be demonstrated. In general, most amine solvents have the tendency to corrode metal surfaces, especially in high carbon loading and/or high temperature locations. Sections of the CCS that are specifically impacted are the absorber bottom, lean/rich heat exchanger and the top of the stripper. Currently, most CCS systems deployed in the utility environment use stainless steel for locations where wetted surfaces are expected, while some are using concrete with a plastic/polymer or ceramic liner for the CO_2 absorber, which results in a higher capital investment.

status

Small pilot-scale testing results and recent identification of process improvements, such as the pre-absorber membrane concentrator, have shown promise of this technology to attain DOE program goals. The UKy-CAER CO_2 capture process represents a third-generation in development, with transformational technologies demonstrated at the lab and bench being validated with modifications made to the E.W. Brown Generating Station small pilot facility. Additional advancement to meet ultimate performance and cost goals will rely on identification of a third-generation advanced solvent that can be produced at reasonable cost, and subsequent large-pilot demonstration at the proposed 10-MW_e plant scale.

available reports/technical papers/presentations

Wei Li, James Landon, Bradley Irvin, Liangfu Zheng, Keith Rugh, Liang Kong, Jonathan Pelgen, David Link, Jose D. Figueroa, Jesse Thompson, Heather Nikolic, Kunlei Liu. *"Use of Carbon Steel for Construction of Post-Combustion CO_2 Capture Facilities: A Pilot-Scale Corrosion Study*," Industrial & Engineering Chemistry Research. 56. 16. 4792-4803. 2017.

Jesse G. Thompson, Megan Combs, Keemia Abad, Saloni Bhatnaga, Jonathan Pelgen, Matt Beaudry, Gary Rochelle, Scott Hume, David Link, Jose Figueroa, Heather Nikolic, Kunlei Liu. *"Pilot Testing of a Heat Integrated 0.7 MWe CO_2 Capture System with Two-stage Air-stripping: Degradation and Amine Emissions,"* International Journal of Greenhouse Gas Control. 64. 267-275. 2017.

Jesse Thompson, Keemia Abad, Heather Nikolic, Jonathan Pelgen, Jose Figueroa, Davis Link, Saloni Bhatnagar, Megan Combs, Femke Onneweer, Kunlei Liu. *"Pilot testing of a heat integrated 0.7 MWe CO_2 capture system with two-stage air-stripping: Amine degradation and metal accumulation,"* International Journal of Greenhouse Gas Control. 64. 22-33. 2017

J.R. Heberle, Heather Nikolic, Jesse Thompson, Kunlei Liu, Lora L. Pinkerton, David Brubaker, James C. Simpson, Song Wu, Aboyjit S. Bhown. "*Techno-Economic Analysis of a Secondary Air Stripping Process. 13th International Conference on Greenhouse Gas Control Technologies,".* GHGT-13, 14-18 November 2016, Lausanne, Switzerland. Energy Procedia. 114. 2017.

Jesse Thompson, Heather Nikolic, Megan Combs, Saloni Bhatnagar, Jonathan Pelgen, Keemia Abad, Kunlei Liu. "*Solvent degradation and emissions from a 0.7 MWe pilot CO_2 capture system with two-stage stripping. 13th International Conference on Greenhouse Gas Control Technologies,"* GHGT-13, 14-18 November 2017, Lausanne, *Switzerland. Energy Procedia. 114. 2017.*

Widger, L. R.; Sarma, M.; Bryant, J. J.; Mannell, D. S.; Thompson, J. G.; Lippert, C. A.; Liu, K., "Enhancements in Mass Transfer for Carbon Capture Solvents Part I: Homogeneous Catalyst" Int. J. Greenhouse Gas Control, 2017, 63, 249-259.

Mannel, D. S.; Qi, G.; Widger, L. R.; Bryant, J.; Liu, K.; Fegenbush, A.; Lippert, C. A.; Liu, K., " Enhancements in Mass Transfer for Carbon Capture Solvents Part II: Micron-Sized Solid Particles" Int. J. Greenhouse Gas Control, 2017, 61, 138-145.

Leland Widger, Cameron Lippert, Moushumi Sarma, and Kunlei Liu "Method of Development and Use of Catalyst-Functionalized Catalytic-Particles to Increase the Mass Transfer Rate of Solvents Used in Acid Gas Cleanup" Patent Pending (Published August 17, 2017, 2017/0232380)

Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture

primary project goals

The University of Illinois at Urbana-Champaign (UIUC) is developing and evaluating a novel biphasic carbon dioxide (CO_2) absorption process (BiCAP), with multiple stages of liquid-liquid phase separation (LLPS) using a solvent blend for post-combustion CO_2 capture. The overall goal of the project is to demonstrate the technical advantages of the process and to generate engineering and scale-up data.

technical goals

- Develop biphasic solvents desirable for the BiCAP process.
- Generate thermodynamic and reaction engineering data required for process engineering and scale-up.
- Demonstrate the performance of CO_2 absorption with multiple stages of phase separation.
- Demonstrate the performance of high-pressure CO_2 desorption.
- Assess the techno-economic performance of the process if integrated with a 550-megawatt electric (MW_e) coal-fired power plant.

technical content

UIUC is developing a CO_2 absorption process that uses a biphasic solvent that allows the formation of dual liquid phases, with the absorbed CO_2 concentrated in one phase and lean in the other. The phase transition behavior of a biphasic solvent is illustrated in Figure 1. The process features multiple stages of LLPS during CO_2 absorption to maximize the CO_2 absorption kinetics and minimize the increase in solvent viscosity.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Biphasic CO_2 Absorption with LLPS

participant:

University of Illinois at Urbana-Champaign

project number:

FE0026434

predecessor projects:

N/A

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Illinois State Geological Survey, University of Illinois at Urbana-Champaign
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partners:

Trimeric Corporation

start date:

10.01.2015

percent complete:

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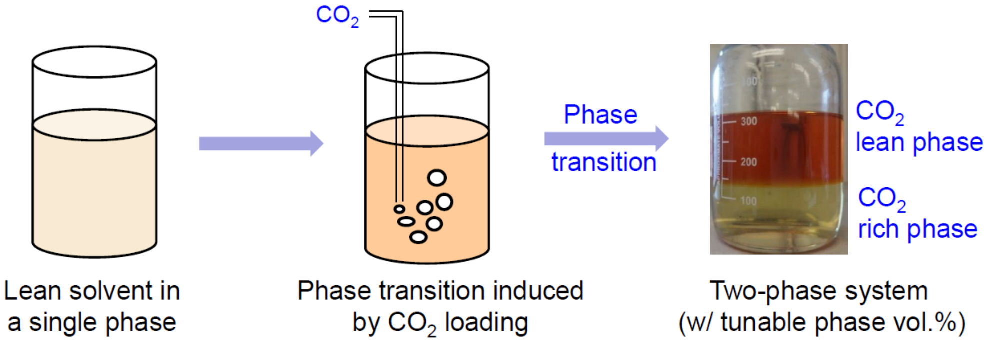

Figure 1: Phase transition behavior of a biphasic solvent

A schematic diagram of the BiCAP process is shown in Figure 2. The flue gas, after the desulfurization and SO_2 polishing stages, enters the absorption column, which contains multiple stages of packed beds, and the CO_2 is absorbed into a biphasic solvent. At each stage, upon CO_2 loading, the biphasic solvent undergoes a phase transition and forms dual liquid phases. The CO_2-enriched phase is separated and collected in a rich solvent tank. The CO_2-lean phase then flows to a heat exchanger to reduce the solvent temperature before entering the next stage of the packed bed. At the last stage, the solvent exiting the absorber is sent to an LLPS tank, in which the CO_2-enriched phase is pumped into the rich solvent tank and fed to a flash/stripper to remove CO_2, while the CO_2-lean phase is mixed with the regenerated solvent from the CO_2 stripper before recycling to the absorber. The CO_2 product streams from both the flash and stripper are cooled and compressed. Key features of this process include 1) a unique process configuration of multi-stage CO_2 absorption and phase transition allows continual separation and removal of the CO_2-enriched liquid phase, maintaining rapid kinetics and low solvent viscosity throughout CO_2 absorption; 2) only the CO_2-enriched liquid phase is used for CO_2 desorption, thus lowering the mass flow of solvent required for regeneration; and 3) a combination of flash and CO_2 stripping operations allows the high pressure of CO_2 desorption to further improve the energy efficiency.

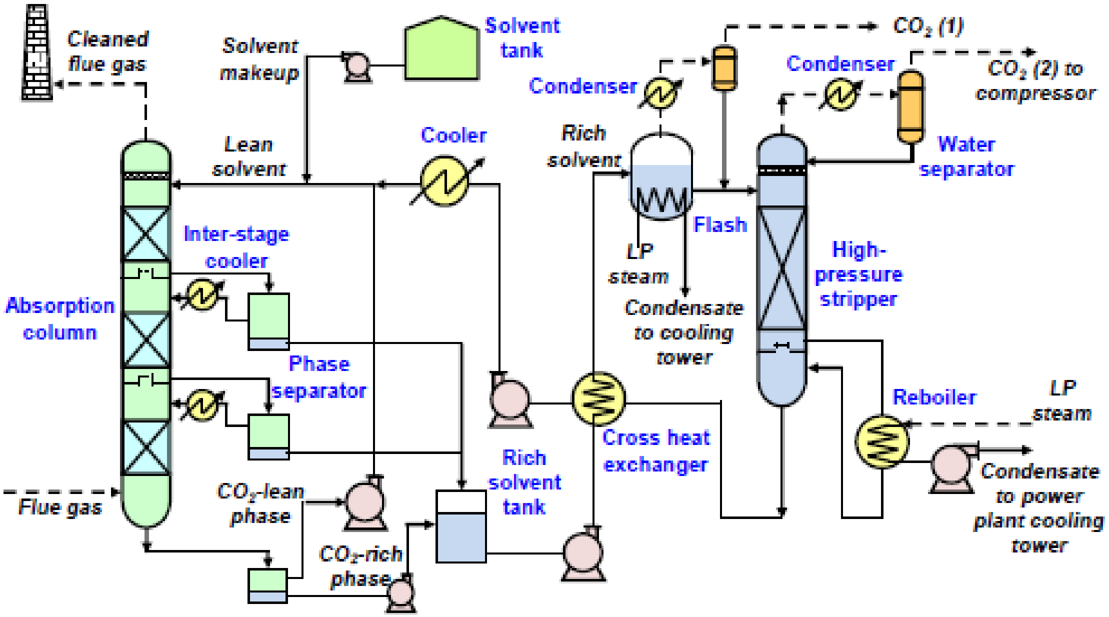

Figure 2: Schematic diagram of the biphasic CO_2 absorption process with multiple stages of LLPS

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	60-240	<230
Normal Boiling Point	°C	140-300	>170
Normal Freezing Point	°C	-30 to 110	<20
Vapor Pressure @ 20 °C	bar	1×10^{-5} to 4×10^{-3}	$<1.0 \times 10^{-3}$
Manufacturing Cost for Solvent	$/kg	3-10	<15
Working Solution			
Concentration	kg/kg	0.6-0.8	>0.5
Specific Gravity (15 °C/15 °C)	-	~1.0	0.9–1.4
Specific Heat Capacity @ STP	kJ/kg-K	2.5–3.5	<3.5
Viscosity @ STP	cP	2-15	<20
Absorption			
Pressure*	bar	0.05 (equilibrium P_{CO_2} at absorber bottom)	<0.07
Temperature	°C	40	30–50
Equilibrium CO_2 Loading	mol/mol	0.375-0.625 (0.7-1.0 in rich phase)	>0.375
Heat of Absorption	kJ/mol CO_2	65-85	~75
Solution Viscosity	cP	5–10/30–50 (upper/lower phases)	<100 (CO_2-enriched phase)
Desorption			
Flash			
Pressure**	bar	7.2	≥10
Temperature	°C	100-140	<140
Equilibrium CO_2 Loading	mol/mol	0.5-0.7	
Stripping (lean solution)			
Pressure***	bar	3.0 (4.0 in total)	≥3
Temperature	°C	120-150	<150
Equilibrium CO_2 Loading	mol/mol	0.05-0.30	<0.25
Heat of Desorption (flash + stripping)	kJ/mol CO_2	65-85	~75
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	not available	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% / >99% / >4	
Absorber Pressure Drop	Bar	0.14	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	not available	

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

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

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

Solvent Contaminant Resistance – The developed biphasic solvent is resistant to oxygen and heat. Experiments revealed that the oxidative degradation of the biphasic solvent was 10 times slower than the benchmark MEA under similar absorption conditions and its thermal stability at 150°C was comparable to the benchmark MEA at 120 °C.

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

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

Solvent Make-Up Requirements – Laboratory solvent stability experiments indicate that the makeup requirement of the biphasic solvent is lower than the benchmark MEA, i.e., <2 kg/ton CO_2 captured.

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

Process Design Concept – See Figure 2.

technology advantages

- BiCAP can significantly reduce both the energy use and equipment cost for CO_2 separation and compression compared with the benchmark MEA process.
- BiCAP maintains rapid kinetics throughout the CO_2 absorption process and thus can reduce the footprint and cost of absorption equipment compared with either MEA or other biphasic solvent-based processes.
- BiCAP is able to maintain the solvent at a lower viscosity and thus retain rapid mass transfer in the absorber, potentially increasing the CO_2 working capacity of the solvent and reducing the footprint and capital cost of the absorber.
- The combination of flash and stripping operations achieves high-pressure CO_2 desorption and thus lowers the energy use for CO_2 separation and compression.

R&D challenges

- Achieving the high pressure target for CO_2 desorption.
- Reducing the severity of solvent oxidation, thermal degradation, and corrosion tendency.
- Achieving a fast liquid-liquid phase separation of solvent to reduce the phase separator size.
- Attaining a low viscosity of the CO_2-loaded rich-phase solvent.

status

Two top-performing solvents were identified based on laboratory testing, demonstrating an acceptable viscosity of CO_2-loaded rich-phase solvent (≤50 cP), ~98 percent of absorbed CO_2 concentrated in the rich liquid phase, a CO_2 working capacity of rich phase solvent ~2 times higher than 5M MEA, CO_2 removal rates and absorption rates comparable or faster than 5M MEA, desorption pressure ~2–4 times higher than 5M MEA, thermal and oxidative stability better than 5M MEA, and a lesser corrosion effect on either stainless steel or carbon steel than 5M MEA. Laboratory testing of these two solvents in an absorption system with multiple stages of packed beds arranged side by side was completed, achieving steady and reliable operation for either 1, 2, or 3 stages of CO_2 absorption and complete phase separation in less than 5 minutes. A 10-kW_e, laboratory CO_2 desorption system comprising of a flash vessel and 2-stage packed bed stripper was assembled, and testing of the CO_2 desorption performance of the selected biphasic solvents is ongoing.

available reports/technical papers/presentations

Du, Y., et al., "A Novel Water-Lean Biphasic Solvent System for CO_2 Capture," presented at the 4th University of Texas Conference on Carbon Capture and Storage, Austin, Texas, February 2018.

Sachde, D., et al., "Economic Analysis of a Water-Lean Biphasic Solvent," presented at the 4th University of Texas Conference on Carbon Capture and Storage, Austin, Texas, February 2018.

Du, Y., et al., "A Novel Biphasic Solvent for Post-Combustion CO_2 Capture," presented at the 4th Post-Combustion Capture Conference, Birmingham, Alabama, September 2017.

Lu, Y., "Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/Y-Lu-ISGS-Biphasic-CO2-Absorption-Process.pdf*

Lu, H., et al., "Bench-Scale Testing of CO2 Absorption with a Biphasic Solvent in an Absorption Column with Staged Phase Separations," presented at the 2017 Carbon Capture, Utilization & Storage Conference, Chicago, IL, April 2017.

Lu, Y., "Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," Budget Period 1 Project Review Meeting presentation, Pittsburgh, PA, June 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/FE0026434-BP1-Review-Presentation-06-08-17.pdf*

Lu, Y., "Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/Y-Lu-ISGS-Biphasic-CO2-Absorption-Process.pdf*

"Development of a Novel Biphasic CO_2 Absorption Process with Multiple Stages of Liquid-Liquid Phase Separation for Post-Combustion Carbon Capture," Project Kickoff Meeting presentation, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/FE0026434-Kick-off-Presentation-12-11-15.pdf*

Ye, Q., et al., "Screening and Evaluation of Novel Biphasic Solvents for Energy-Efficient Post-Combustion CO_2 Capture," International Journal of Greenhouse Gas Control, Volume 39, August 2015, pp. 205-214.

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

primary project goals

URS Group, Inc. (URS) is investigating the use of a high-temperature flash regenerator using concentrated piperazine (PZ) solvent to capture carbon dioxide (CO_2) from coal-fired flue gas more economically. Pilot tests and analyses will be conducted at the 0.1-megawatt (MW_e) scale, and then scaled to the 0.5-MW_e scale for testing at the National Carbon Capture Center (NCCC). Results will be used to evaluate the technical and economic feasibility of a full-scale implementation of this process.

technical goals

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

technical content

URS, in collaboration with the University of Texas (UT) and Trimeric Corporation, are investigating the use of concentrated PZ as a solvent for absorbing CO_2 from coal-fired power plant flue gas. Measured properties of PZ are shown in Table 1. Concentrated PZ has a faster CO_2 absorption rate, higher CO_2 capacity, lower volatility, and negligible thermal and oxidative degradation compared with conventional amine solvents. Evaluations of concentrated PZ for CO_2 removal have previously been performed through laboratory investigations, process modeling, and short-term testing in a 0.1-MW_e unit with synthetic flue gas. Results indicated greater than 90 percent CO_2 capture with significant progress towards DOE's goal of less than 35 percent increase in the cost of electricity (COE). This project continues the development of the PZ-based CO_2 absorption process with a field test at the NCCC to gain operational experience with the solvent in coal-fired flue gas, while employing a novel, high-temperature, advanced flash stripper configuration. The process parameters of the PZ solvent are listed in Table 1.

The project team is conducting this project in two phases. In the first phase, the PZ absorption process was combined with a novel regeneration scheme—a high-temperature two-stage flash (2SF), shown in Figure 1. This configuration was installed and tested at 0.1 MW_e in UT's Separations Research Program (SRP) plant with synthetic flue gas using PZ in the SRP plant absorption column. The results from the SRP test program and the techno-economic analysis demonstrated the benefits of using PZ as a solvent-of-choice for CO_2 capture. The results from the SRP test program demonstrated that 2SF regeneration is a viable

technology maturity:

Pilot-Scale (0.5 MW_e), Simulated Flue Gas and Actual Flue Gas Slipstream

project focus:

Piperazine Solvent with Flash Regeneration

participant:

URS Group

project number:

FE0005654

NETL project manager:

Bruce Lani
bruce.lani@netl.doe.gov

principal investigator:

Katherine Dombrowski
URS Group, Inc.
katherine_dombrowski@urscorp.com

partners:

University of Texas at Austin, Trimeric Corporation

start date:

10.01.2010

percent complete:

90%

alternative regeneration process to simple stripping; however, the techno-economic analysis showed only a marginal economic benefit of the 2SF process. Therefore, additional testing at the 0.1 MW scale was performed on the advanced flash stripper (Figure 2) to validate a significant reduction in energy requirement and capital cost. Testing at the SRP plant also determined that PZ with a 5 molal concentration is a superior solvent to PZ with an 8 molal concentration and was shown to improve cross exchanger performance and reduce heat duty. Combining the 5 molal PZ solvent with the advanced flash stripper, as shown in Figure 2, decreases the cost of CO_2 capture to less than $40/tonne.

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

The project team is proceeding to Phase II, in which the 5 molal PZ combined with the advanced flash stripper will be tested at the 0.5MW scale on coal-fired flue gas at NCCC.

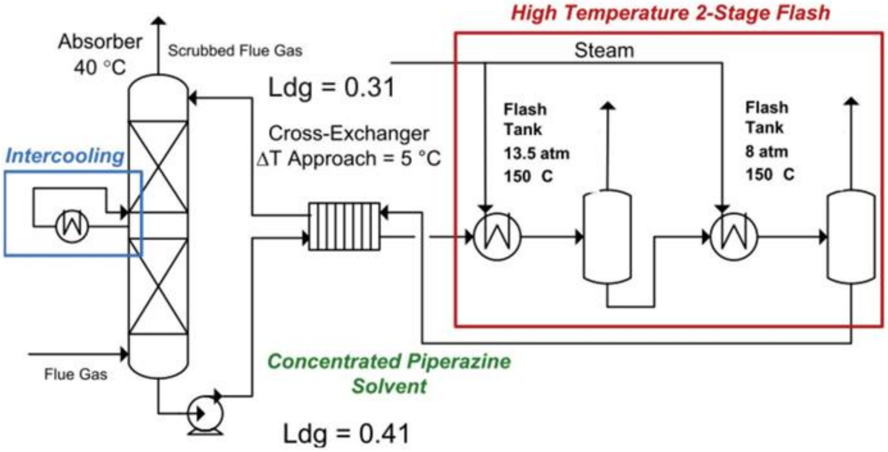

Figure 1: Diagram of PZ CO_2 absorption process with high-temperature two-stage flash

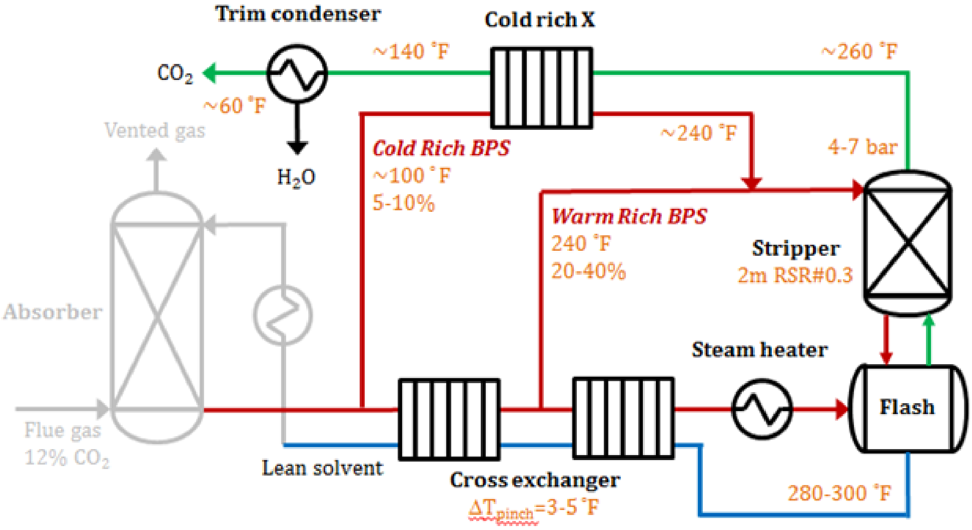

Figure 2: 5m PZ CO_2 absorption with the advanced flash stripper

TABLE 1: SOLVENT PROCESS PARAMETERS

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

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

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

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

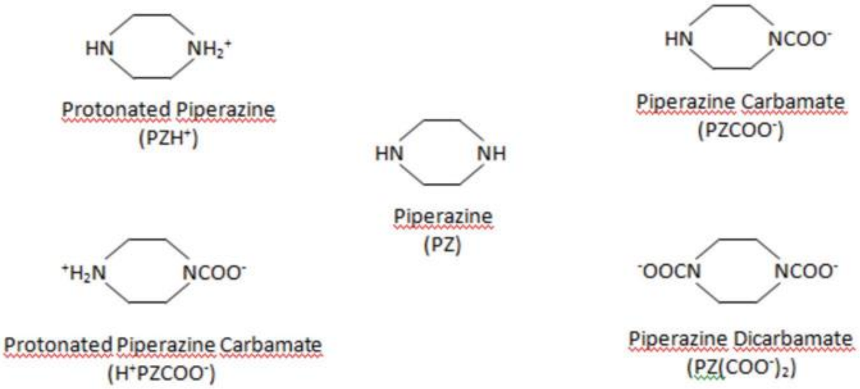

Figure 3: Molecular structure of piperazine species

These reactions are as follows:

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

TABLE 2: EQUILIBRIUM CONSTANTS FOR ABOVE REACTIONS

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

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

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

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

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

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

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

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

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

technology advantages

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

- Faster CO_2 absorption rate, higher working capacity, higher thermal stability, and less oxidative degradation—all of which point toward 10–20 percent less energy use.

- Lower capital costs due to reduced energy use, greater stripper pressure (reduced compressor size), and faster kinetics.
- Additional savings in COE may be achieved by optimization of absorber packing, flue gas pre-treating, compressors, heat exchangers, and design improvements realized as part of this project.

R&D challenges

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

status

Further testing of the 5 molal PZ solvent at larger scale is needed to demonstrate reliable operation on coal-fired flue gas and during longer term operation in which excursions of CO_2 loading, temperature, and water balance are encountered. A 3-month test will be conducted with the 0.5 MW_e absorption column at the NCCC in conjunction with the advanced flash stripper. Methods to reduce solvent degradation will also be evaluated during the NCCC tests.

available reports/technical papers/presentations

Rochelle, G., "Pilot Plant Testing of Piperazine with Advanced Flash Regeneration," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/G-Rochelle-UTA-Evaluation-of-Piperazine.pdf*

Rochelle, G., "Pilot Plant Testing of Piperazine with Advanced Flash Regeneration," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/G-Rochelle-UTAustin-Piperazine-with-Flash-Regeneration.pdf*

Dombrowski, K., "Pilot Plant Testing of Piperazine with High T Regeneration," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/K-Dombrowski-AECOM-Concentrated-Piperazine.pdf*

Rochelle, G., "Pilot Plant Testing of Piperazine with High T Regeneration," presented at the 2014 NETL CO2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/G-Rochelle-UTAustin-Evaluation-Of-Concentrated-Piperazine.pdf*

Nielsen, P. T.; Li, L.; Rochelle, G. T., "Piperazine Degradation in Pilot Plants." GHGT-11; Energy Proc. 2013.

Fulk, S. M.; Rochelle, G. T., "Modeling Aerosols in Amine-Based CO_2 Capture," GHGT-11, Energy Proc. 2013.

Fine, N. A.; Goldman, M. J.; Nielsen, P. T.; Rochelle, G. T., "Managing N-nitrosopiperazine and Dinitrosopiperazine," presented at GHGT-11 Kyoto, Japan. November 18–22, 2012. Energy Procedia, 2013.

Rochelle, G., "Pilot Plant Testing of Piperazine with High T Regeneration," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/G-Rochelle-UTA-Concentrated-Piperazine-for-CO2-Capture.pdf*

Madan, T.; “Stripper Configurations and Modeling for CO_2 Capture Using Piperazine.” M. S. Thesis. The University of Texas at Austin, May 2013.

Rochelle, G., “Pilot Plant Testing of Piperazine with High T Regeneration,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Events/2012/CO2%20Capture%20Meeting/G-Rochelle-UT-Austin-Piperazine.pdf*

Sexton, A., “Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *https://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/23Aug11-Sexton-Trimeric-Concentrated-Piperazine-for-CO2-Capt.pdf*

Freeman, S.A., “Thermal Degradation and Oxidation of Aqueous Piperazine for Carbon Dioxide Capture,” Ph.D. Thesis, University of Texas at Austin, May 2011.

Dombrowski, K., “Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *https://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/Katherine-Dombrowski---URS-Corporation.pdf*

Hybrid Encapsulated Ionic Liquids for Post-Combustion Carbon Dioxide Capture

primary project goals

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

technical goals

- Encapsulated ILs/PCILs structural integrity: microcapsules in fluidized beds able to contain the ILs without leaking.
- Uptake of CO_2 by encapsulated ILs/PCILs: greater than 50 percent CO_2 absorption from a humid N_2-CO_2 gas mixture in lab-scale testing.
- Durability/recyclability of the encapsulated ILs/PCILs: less than 20 percent decline in absorption capacity of CO_2 after 5 cycles in humid N_2-CO_2 gas mixture.
- Solvent regeneration: at least 80 percent of the absorbed CO_2 removed by hot vapor (steam) without significant damage to the particles.
- Substantial technology progress towards a capture system enabling 90 percent CO_2 capture with 95 percent CO_2 purity at a cost of electricity 30 percent less than baseline aqueous amine technologies.

technical content

Conventional solvent-based carbon capture methods typically employ amines such as monoethanolamine (MEA) as the capture solvent. However, amines are corrosive, degrade over time, and have relatively high vapor pressures making their leakage into the environment more likely. Ionic liquids (a class of ionic salts tending to have large nitrogen or phosphorous-bearing cations with alkyl chain substituents), are anhydrous, liquid at ambient temperatures, have low vapor pressures, are thermally stable and relatively non-corrosive, and certain of them have considerable affinity for absorption of CO_2 and selectivity towards CO_2 in gas mixtures. For example, the hexafluorophosphate (PF_6^-) and tetrafluoroborate (BF_4^-) anions have been shown to be amenable to CO_2 capture.

Ionic liquids might be used in a similar process to amine gas treating to effect carbon capture from flue gas, where the flue gas is contacted with the solvent in

technology maturity:

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

project focus:

Microencapsulated CO_2 Capture Materials

participant:

University of Notre Dame

project number:

FE0026465

predecessor projects:

N/A

NETL project manager:

David Lang
david.lang@netl.doe.gov

principal investigator:

Mark McCready
University of Notre Dame
mjm@nd.edu

partners:

Lawrence Livermore National Laboratory

start date:

10.01.2015

percent complete:

70%

an absorption column, and the rich solvent is regenerated in a stripper column at higher temperature affected by use of steam heating. Ionic liquids consistently show CO_2 absorption behavior of decreasing solubility with increasing temperature, enabling conventional temperature swing absorption cycling. Because they have increasing CO_2 solubility with increasing pressure, ionic liquids could also be stripped using pressure swing or sweep with inert gases, possibly reducing the process energy requirement.

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

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

Selection of Suitable ILs and PCILs

Strongly-performing ILs and PCILs would have several favorable properties/characteristics:

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

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

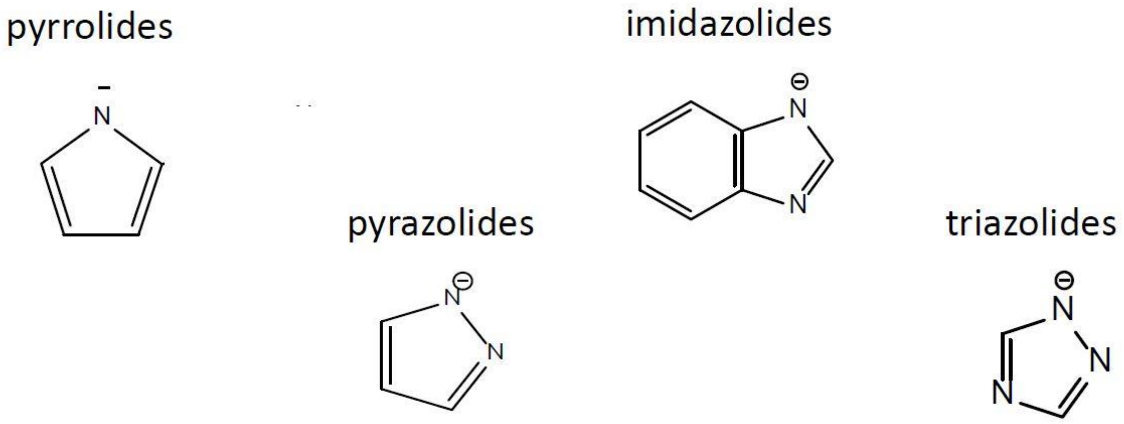

Figure 1: Several types of aprotic heterocyclic anions

The researchers have evaluated a number of possiblities for ILs and PCILs prepared by LLNL, and have settled on one IL and one PCIL for continued development in this technology:

- NDIL0230
- NDIL0309

One of these is a phase change ionic liquid, which will undergo phase change to and from liquid and solid at the varying temperatures it experiences during regeneration and absorption. This is expected to confer certain energy efficiency advantages as discussed below in process implementation.

Microencapsulation

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

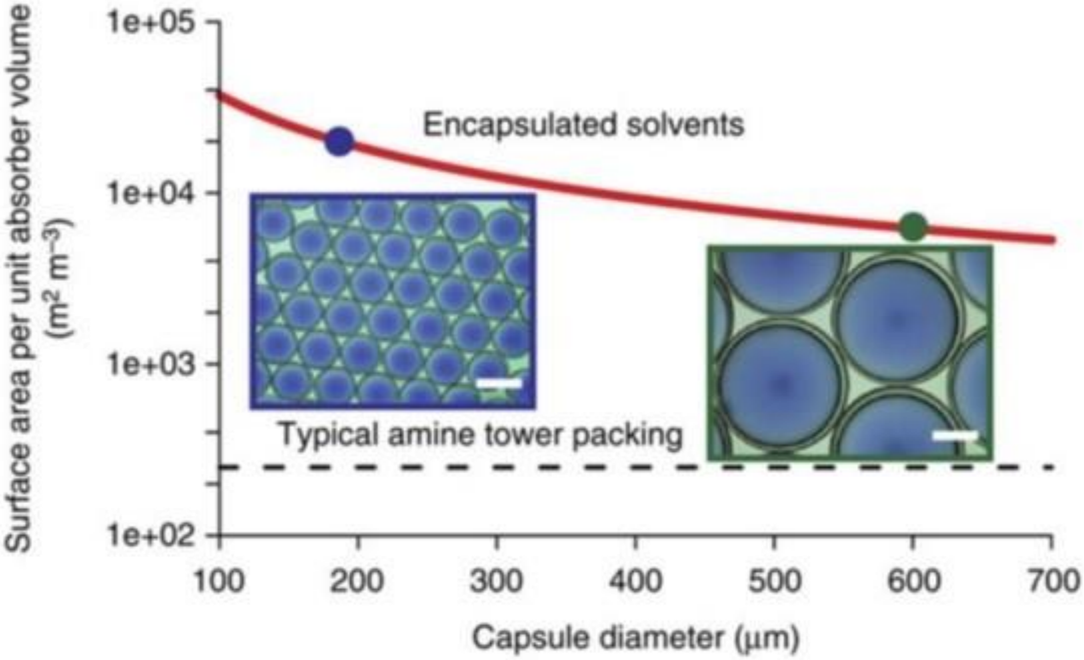

Figure 2: Surface area benefit of microencapsulation

The polymer shell must satisfy several conditions, including ability to reliably contain the IL contents and maintain general physical stability, provide negligible diffusion resistance to CO_2, and to not adversely affect the IL absorption reaction.

The technology for creating polymer-shell encased IL microcapsules is now well established by LLNL, as initial issues with incompatibility of the ILs with the polymer material resulting in the polymer deactivating the IL have since been overcome. Presently, LLNL has settled on their in-house developed and refined Thiolene-Q shell material formulation, which has chemical compatibility with NDIL0230 and NDIL0309, and for which they have found an alternative crosslinker for improved NDIL0230 microcapsule production and in-air production. Figure 3 depicts this formulation. Figure 4 is a magnified image of the microcapsules that have been successfully fabricated using this material, encapsulating the chosen IL.

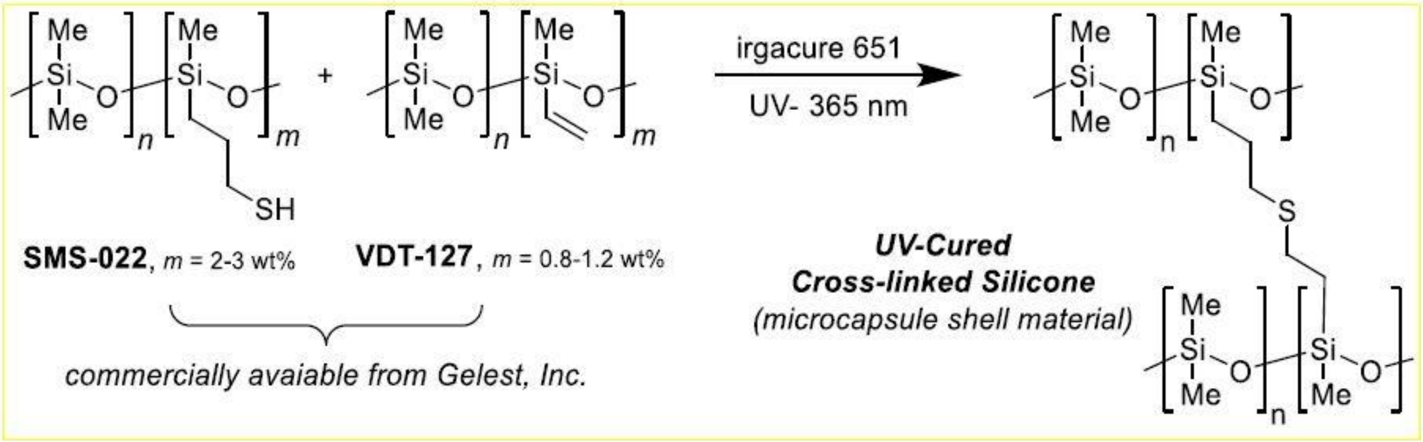

Figure 3: Thiolene-Q shell material

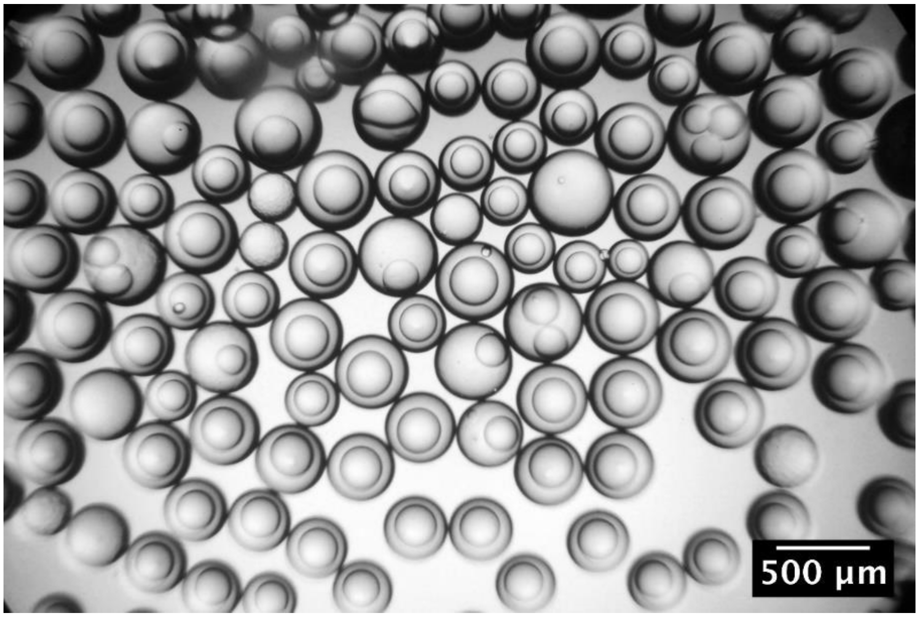

Figure 4: Thiolene-Q encased IL microcapsules

In testing that has been underway, some notable findings have been as follows:

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

PCIL Process Implementation

Process advantages result from the inherent characteristics of phase change ionic liquids in temperature swing absorption cycles, as depicted in Figure 5. In the absorption column on the left, a PCIL slurry containing encapsulated PCILs at low temperature (at which the PCILs are in the solid phase) is contacted countercurrently with CO_2-containing flue gas passing up the column. The PCIL reacts exothermically with CO_2, creating heat which is absorbed by the PCIL particles, causing them to melt. The PCIL-CO_2 liquid leaving the column is sprayed into a dryer shown on the right, which serves as the regenerator in this process cycle. The PCIL is heated in the dryer, causing it to release CO_2 in relativley pure gaseous form, which is withdrawn and compressed for transport or storage. The heat duty of the stripper is reduced somewhat by the heat of fusion of the PCIL as it goes from liquid to solid phase. Also, the cooling duty of the PCILs on the absorption side is reduced by the phase change from solid to liquid phase.

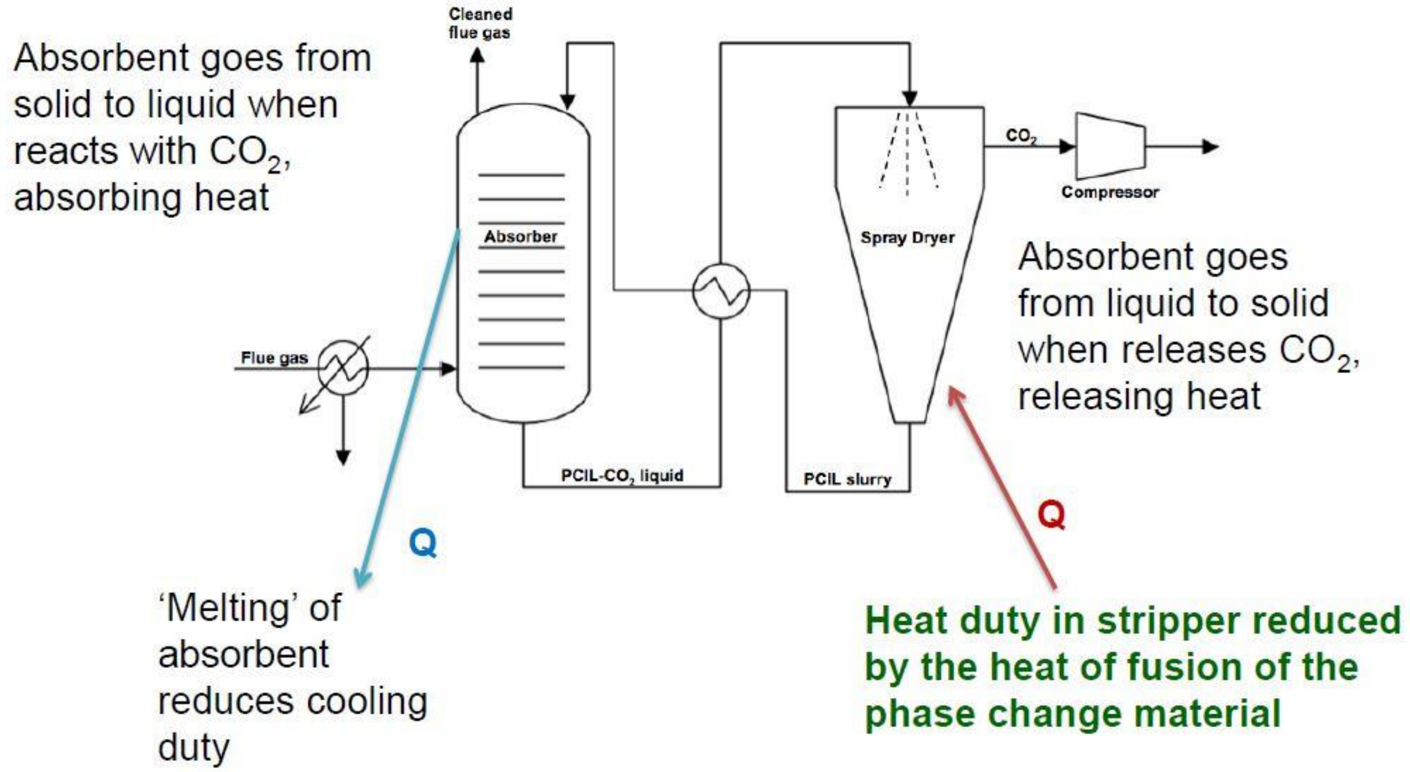

Figure 5: CO_2 capture cycling with phase change material

The result of this is that the overall heat duties on either side of the process cycle are moderated somewhat by the phase changes occuring. This is more clearly depicted in Figure 6, which accounts how the phase changes of the PCILs reduce the total molar heat duty on either side by 20 kJ/mol. Instead of needing to supply the entire 50 kJ/mol by external heating of the dryer/regenerator, only the net amount of 30 kJ/mol needs to be supplied, the other 20 kJ/mol being contributed by the PCIL phase changes. This should lessen the parastic energy demand for operating the process relative to a non-phase change scenario.

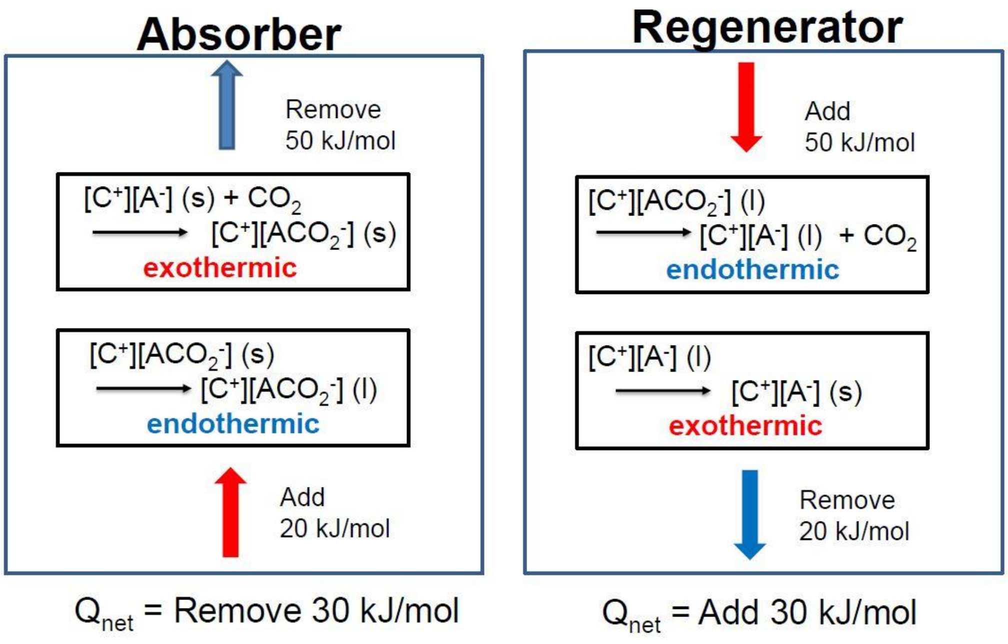

Figure 6: Heat duties for CO_2 capture with PCILs

TABLE 1: SOLVENT PROCESS PARAMETERS

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

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameters

Process Design Concept – See Figure 7 below.

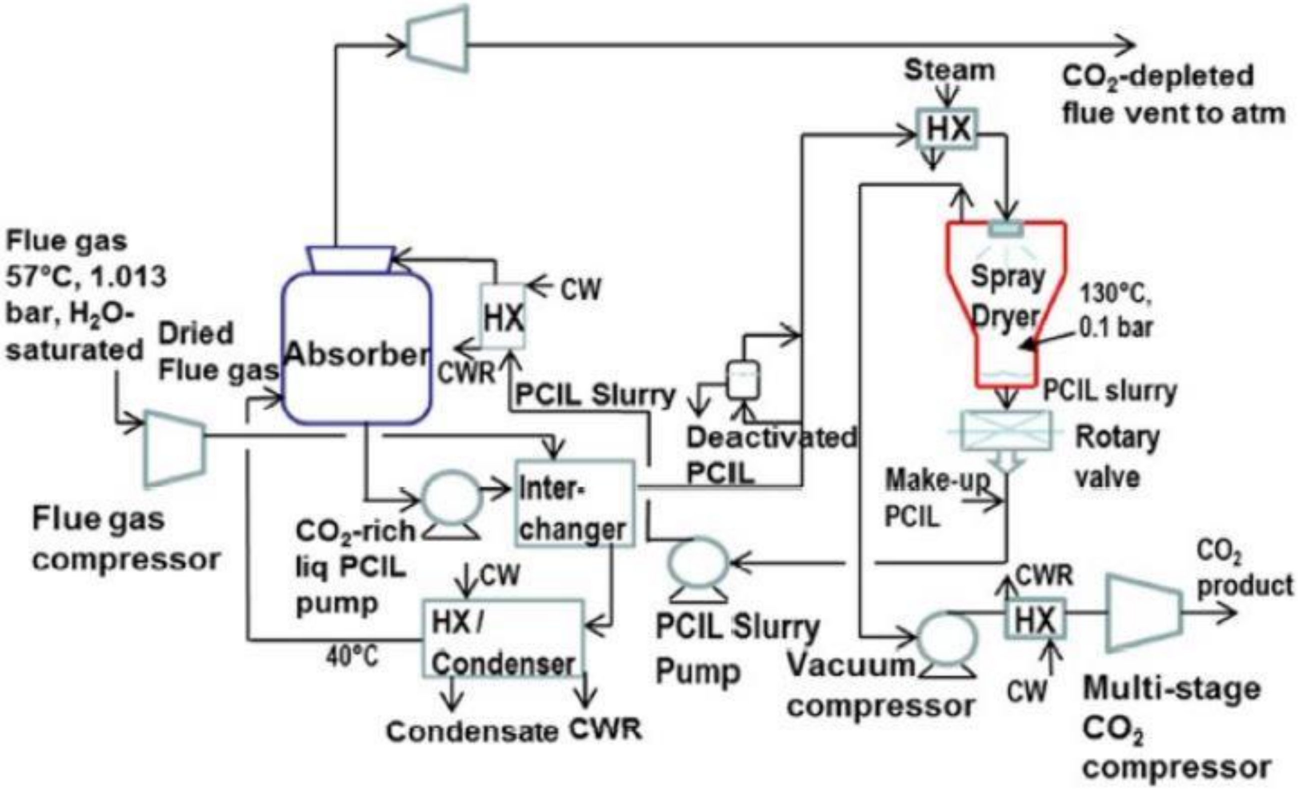

Figure 7: Process flow diagram for CO_2 capture in a full-scale plant using PCILs

technology advantages

- The encapsulation of ILs and PCILs in micrometer sized shells is projected to increase the mass transfer area by an order of magnitude or more.
- Significant reduction of the capital costs of the absorber and regenerator in CO_2 capture systems.

R&D challenges

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

status

Laboratory-scale testing of the successfully encapsulated IL and PCIL in fluidization and absorption/desorption cycling has been underway, and in ongoing work kilogram quantities of the microencapsulated IL and PCIL are to be produced and tested. Over five cycles of absorption and regeneration, the CO_2 capacity has been consistently measured at 0.64–0.68 moles CO_2/mol PCIL. Although a full techno-economic analysis is not in current scope, process modeling and economics will begin to quantify the potential of this technology for meeting DOE goals.

available reports/technical papers/presentations

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

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

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

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

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

primary project goals

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

technical goals

- Operate DAC pilot facility, complete sensitivity analysis and optimize components for the DAC applied to dilute CO_2 sources.
- Provide engineering input for scale-up and cost projections.
- Prepare technology cost projections and a technical assessment of applicability of DAC to coal stream.

technical content

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

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

technology maturity:

Pilot-Scale

project focus:

Direct Air Capture from Dilute CO_2 Sources

participant:

Carbon Engineering Ltd.

project number:

FE0026861

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Jenny McCahill
Carbon Engineering Ltd.
jmccahill@carbonengineering.com

partners:

N/A

start date:

09.19.2016

percent complete:

70%

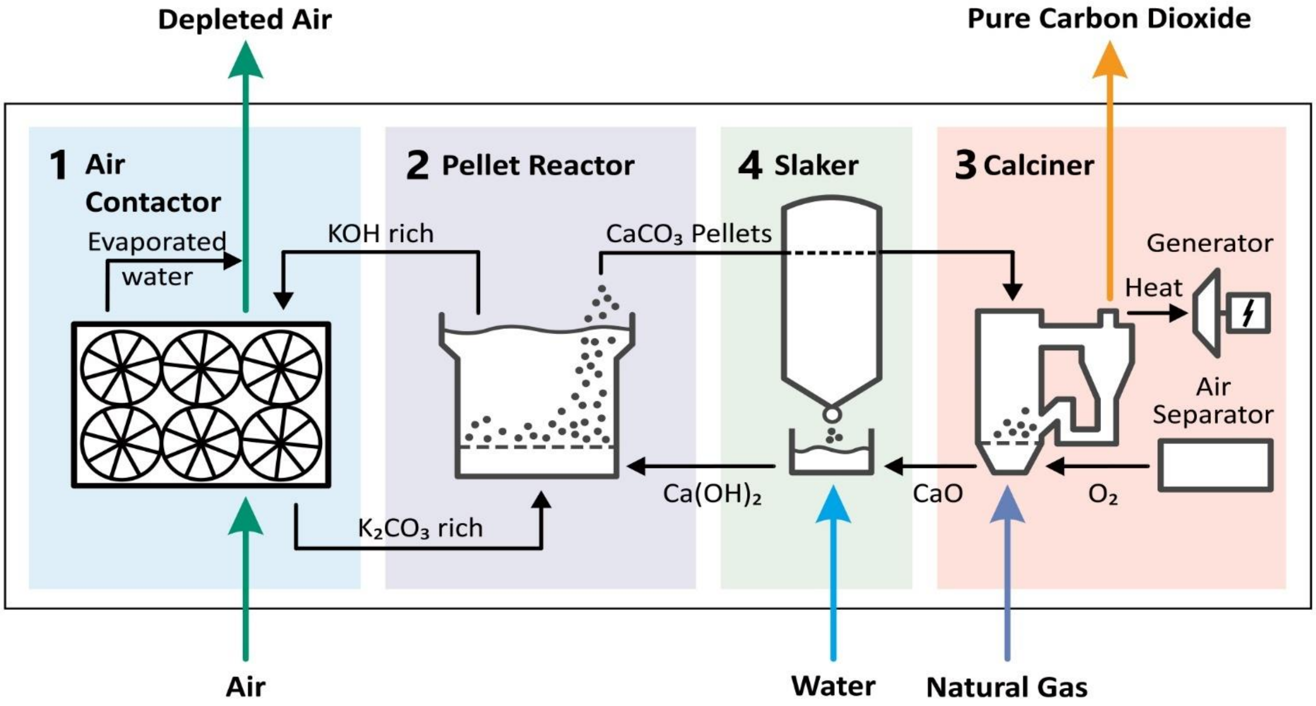

Figure 1: Schematic of the DAC process

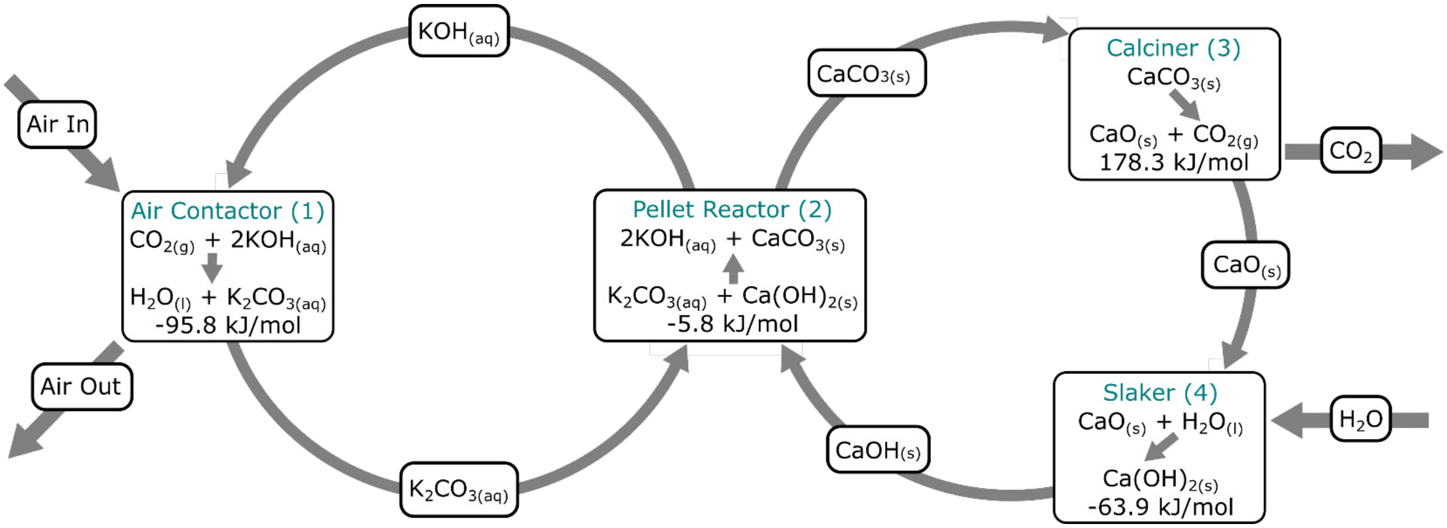

Figure 2: Chemistry of the DAC process

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

TABLE 1: PROCESS PARAMETERS

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

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

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

Gas Pretreatment Requirements – No treatment of atmospheric air required.

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

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

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

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

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

technology advantages

- Process system with air contactor, pellet reactor, slaker and calciner can be easily located anywhere.
- Negative emission technology.
- Technology can manage CO_2 emissions from any dilute source.
- Highly scalable technology.

R&D challenges

- Compared to standard CCS, there is a higher thermodynamic barrier for dilute source capture.
- Compared to standard CCS, a larger air volume must be processed for dilute source capture.

status

Testing is ongoing. A mass transfer coefficient (K_L) in the air contactor of greater than 1.0 was achieved. Testing in the pellet reactor confirmed that filtration improved retention >20 percent. Slaker tests achieved 98 percent conversion of CaO produced by the calciner to $Ca(OH)_2$.

available reports/technical papers/presentations

Ritchie, J., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," Project Continuation Application Review Meeting Presentation, September 2017.
https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026861-2017-09-18-CE-DOE-CA-Presentation-DOE.pdf

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

Ritchie, J., "Dilute Source Carbon Dioxide (CO_2) Capture: Management of Atmospheric Coal-Produced Legacy Emissions," Project Kick-Off Meeting Presentation, March 2017.
https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026861-Kick-off-mtg.pdf

Large Bench-Scale Development of Non-Aqueous Solvent Carbon Dioxide Capture Process for Coal-Fired Power Plants Utilizing Real Coal-Derived Flue Gas

primary project goals

Research Triangle Institute (RTI) is developing and testing at the large bench-scale the non-aqueous solvent (NAS) carbon dioxide (CO_2) capture process, with potential for reduction in parasitic energy penalty.

technical goals

- Evaluate NAS solvent degradation and material compatibility.
- Improve the physical properties of the NAS.
- Complete baseline testing of monoethanolamine (MEA) control and NAS in unmodified bench-scale test unit at the SINTEF Tiller plant.
- Design optimal NAS-based regenerator and absorber wash section.
- Design, procure and install NAS-specific components in Tiller plant.
- Complete 1200 hours cumulative bench-scale testing with NAS solvent on coal-derived flue gas at Tiller plant modified with NAS-specific components, showing 90 percent CO_2 capture and proper water balance.
- Show reduction in parasitic energy penalty to <2.0 GJ/tonne CO_2 captured.
- Complete techno-economic analysis to confirm RTI's NAS process can reduce CO_2 capture costs.

technical content

Research Triangle Institute is continuing development of a non-aqueous solvent-based CO_2 capture process that was previously developed and tested at a smaller scale with simulated flue gas under DOE-funded project FE0013865. Non-aqueous solvents have the potential to significantly reduce the cost of CO_2 capture from coal-fired flue gas when compared to aqueous amine-based solvent processes by reducing the energy required for solvent regeneration. RTI's NAS is a hydrophobic, sterically-hindered, carbamate-forming amine with low-water solubility solubilized in a diluent having low vapor pressure, low viscosity, and low-water solubility. It is characterized by low heats of absorption and generation of high CO_2 partial pressures at low temperatures and has the potential to reduce the regeneration energy to <2.0 GJ/tonne CO_2. The overall reboiler heat duty, or thermal regeneration energy, is made up of the sensible heat, heat of vaporization of water and heat of absorption. For NAS, the heat of vaporization is negligible due to the lack of water. Also, non-aqueous solvents overcome the foaming issues that are often associated with aqueous solvents, as shown in Figure 1. RTI's CO_2-rich non-aqueous solvent has a viscosity of less than 30 cP, and is non-foaming.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Non-Aqueous Solvent

participant:

Research Triangle Institute

project number:

FE0026466

predecessor projects:

FE0013865

NETL project manager:

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Research Triangle Institute
szhou@rti.org

partners:

Linde; SINTEF

start date:

10.01.2015

percent complete:

70%

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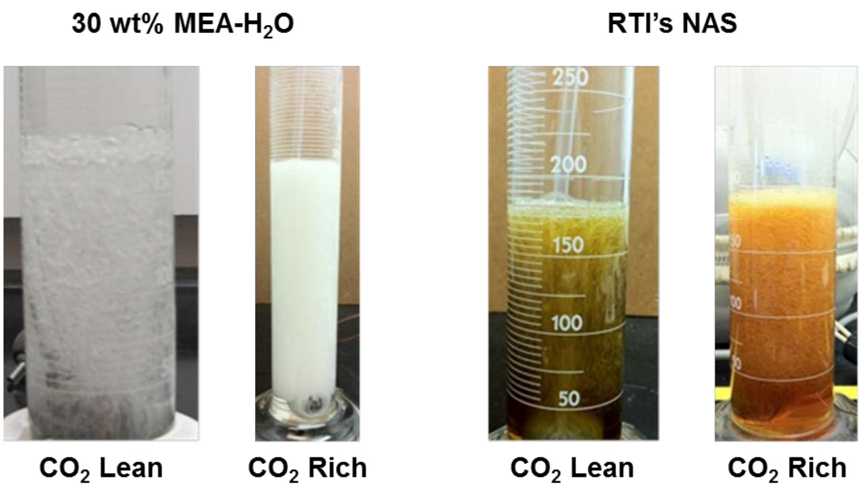

Figure 1: Comparison of foaming in aqueous and RTI's non-aqueous solvents

RTI's is using the bench-scale test unit (up to 60kW) at SINTEF's Tiller plant to experimentally show that its NAS is capable of achieving 90 percent CO_2 capture and generating a high-purity CO_2 product (>95 percent CO_2) as well as to evaluate the effectiveness of the developed NAS recovery/wash section and solvent regenerator design. The solvent chemistry is being refined to increase CO_2 loading, and multiple formulations have been screened for performance. Bench testing at SINTEF's Tiller plant will be done using the MEA control and the NAS in an unmodified configuration of the test unit. This will be followed by modification of the plant with NAS-specific components, including a new particulate filter, updated coal-burner control software, additional absorber intercoolers, additional water wash section, regenerative "inter-heaters", and one additional cross-flow heat exchanger, to allow optimal operating conditions to be identified and long-term testing to be completed.

The NAS CO_2 capture process, shown in Figure 2, is similar to conventional solvent scrubbing systems with key novel design features:

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

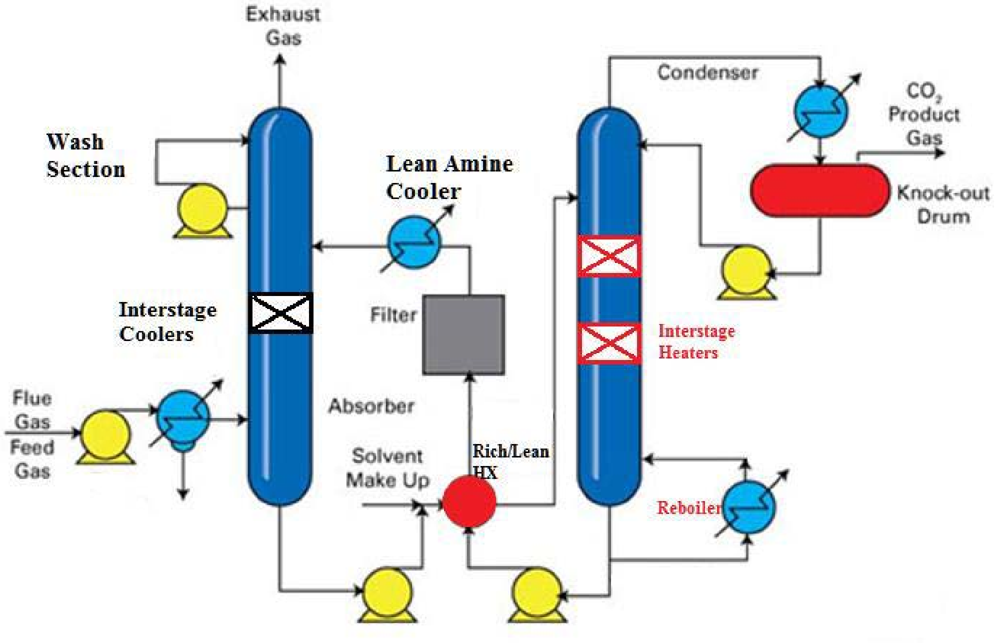

Figure 2: NAS CO_2 capture process diagram

TABLE 1: SOLVENT PROCESS PARAMETERS

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

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

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical

Solvent Contaminant Resistance – More resistant than MEA to SO_x and NO_x.

Solvent Foaming Tendency – Less foaming than aqueous amine solvent.

Flue Gas Pretreatment Requirements – Temperature adjustment and SO_x control.

Solvent Make-Up Requirements – 0.2 to 0.5 kg/tonne CO_2.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

technology advantages

- Low water solubility.
- Reduced regeneration energy.
- Favorable thermodynamics.
  - Low heat of absorption.
  - High working capacity based on vapor-liquid equilibrium (VLE).
- Low vapor pressure (<0.3 kPa (40 °C), <10 ppm emissions in treated flue gas).
- Low conductivity, low corrosion rates.
- Low oxygen solubility.

R&D challenges

- Implementation of NAS-specific regenerator.
- Minimize the rise in absorber temperature.
- Obtain sufficient heat exchange for optimal performance.
- Improve the working capacity of the solvent.

status

RTI has tested multiple NAS formulations and identified an improved formulation, NAS-5. Experimental testing of NAS-5 showed a specific reboiler duty of approximately 2.1 GJ/tonne CO_2. They have completed 405 hours of baseline testing with their NAS solvent at the SINTEF Tiller plant in an unmodified configuration, indicating a reboiler heat duty of 2.7 GJ/tonne CO_2. Modification of the Tiller plant with NAS-specific components has been completed. Parametric testing to determine optimal operating parameters and reduced reboiler duty has also been completed. Long-term testing is to start shortly.

available reports/technical papers/presentations

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Large Pilot-Scale Testing of Linde/BASF Post-Combustion CO_2 Capture Technology at the Abbott Coal-Fired Power Plant

primary project goals

The project was aimed at capturing ~300 tonnes per day (tpd) of carbon dioxide (CO_2) at a 90 percent capture rate from existing coal-fired boilers at the Abbott Power Plant on the campus of the University of Illinois at Urbana-Champaign (UIUC) using Linde/BASF's novel amine-based CO_2 capture technology. The project also established strategies for workforce development for the operation and maintenance of carbon capture systems based on the Linde-BASF technology that are retrofitted to existing power plants. Phase I of this project included completion of a preliminary plant design with engineering and cost estimates, a host site agreement, and a detailed techno-economic analysis, demonstrating that the implementation of Phase 2 (detailed design, construction, and operation) of the project was feasible.

technical goals

- Advance the development of Linde/BASF's amine-based CO_2 capture technology to large pilot-scale and integrate novel process options that reduce its specific energy consumption to 2.3 GJ/tonne CO_2.
- Design a pilot system of nominal 15 megawatt electric (MW_e) incorporating the Linde-BASF advanced CO_2 capture technology and integrate with the coal-fired boilers at the Abbott Power Plant.
- Optimize the process at large pilot scale and gather performance data to enable a robust design of commercial size plants.
- Provide a guideline for the retrofit of the CO_2 capture technology to other existing plants.
- Illustrate a path forward for the utilization of the captured CO_2.

technical content

A 15-MW_e pilot plant of the Linde-BASF advanced CO_2 capture technology was designed in order to be integrated with the University of Illinois' Abbott Power Plant. The goal was to demonstrate the viability of continuous operation under realistic conditions with high efficiency and capacity. The technology combines BASF's novel amine-based solvent, OASE® blue, with Linde's process and engineering innovations, allowing for a significant increase in energy efficiency and reduced cost for CO_2 recovery from coal-based power plants. BASF's OASE® blue technology has been developed to address the key drawbacks in the large-scale application of monoethanolamine (MEA) for flue gas carbon capture, including: (1) high specific energy for regeneration, (2) lack of stability toward thermal and oxidative degradation, (3) increased corrosiveness with increased CO_2 loading, and (4) lack of tolerance to impurities from coal combustion products. Testing of a 0.45-MW_e pilot plant incorporating the Linde-BASF technology and

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream (equivalent to 15 MW_e)

project focus:

Linde/BASF CO_2 Capture Process

participant:

University of Illinois at Urbana-Champaign

project number:

FE0026588

predecessor projects:

FE0007453

NETL project manager:

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partners:

The Linde Group; BASF Corporation; Affiliated Engineers, Inc.; Association of Illinois Electric Cooperatives

start date:

12.01.2011

percent complete:

99%

utilizing lignite-fired power plant flue gas has shown that the OASE® blue solvent is stable, with little degradation observed over 5,000 hours, whereas the reference MEA solvent started to degrade appreciably under the same conditions after 2,000 hours. The Linde-BASF CO_2 capture process was also previously tested at 1.5-MW_e-scale at the National Carbon Capture Center (NCCC) in project DE-FE0007453. This study validated solvent stability and demonstrated a cyclic capacity 20 percent higher than MEA and regenerator steam consumption 25 percent lower than MEA. These results confirmed the ability of this technology to be cost-effective, energy efficient, and compact. This 15-MW_e project aims to optimize the process at larger scale and gather performance data to enable a robust commercial design.

The key benefits of the process are:

- A flue gas blower downstream of the absorber aimed at both energy and cost reduction (due to the reduced volume of flue gas handled by the blower).
- An integrated pre-scrubber and direct contact cooler that reduces SO_x content below 5 ppm and simultaneously cools down the flue gas stream from ~93 °C to ~35–40 °C.
- A gravity-driven inter-stage cooler for the absorber that eliminates the capital and operating expenses of a solvent pump and related controls.
- A regenerator designed for operation at pressures up to 3.4 bara with the potential to significantly reduce CO_2 compression energy requirements.
- A solvent-solvent heat exchanger designed to operate over a wide range of temperatures to optimize the performance and capital cost trade-off.
- Innovative reboiler design that minimizes thermal degradation of the solvent and provides for faster dynamics to respond to load changes.
- High-capacity structured packing that reduces the diameter of the absorber.
- Innovative water wash section at the top of the columns to reduce amine emissions, even in the presence of aerosols.
- A stripper inter-stage heater used to enhance energy efficiency of CO_2 stripping from the solvent by recovering heat from the lean solvent to provide intermediate reboil, thereby reducing energy consumption of solvent regeneration.

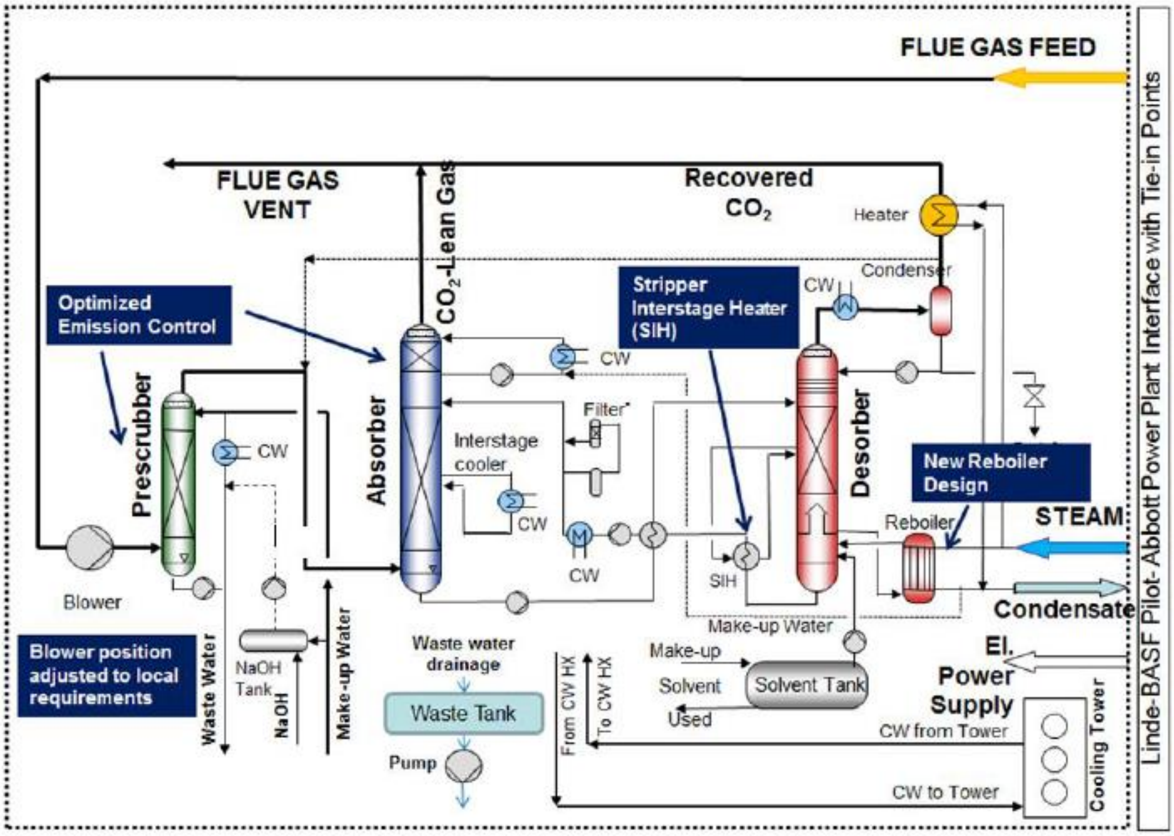

Figure 1: Process flow diagram of the Linde-BASF CO_2 capture process at Abbott Power Plant

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	proprietary
Normal Boiling Point	°C	proprietary	proprietary
Normal Freezing Point	°C	proprietary	proprietary
Vapor Pressure @ 15 °C	bar	proprietary	proprietary
Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	proprietary	proprietary
Specific Gravity (15 °C/15 °C)	—	proprietary	proprietary
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	proprietary
Viscosity @ STP	cP	proprietary	proprietary
Absorption			
Pressure	bar	1.0	0.9–1.1
Temperature	°C	30–70	30–60
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Absorption	kJ/mol CO_2	proprietary	proprietary
Solution Viscosity	cP	proprietary	proprietary
Desorption			
Pressure	bar	1.6–3.4	1.6–3.4
Temperature	°C	124–140	124–140
Equilibrium CO_2 Loading	mol/mol	proprietary	proprietary
Heat of Desorption	kJ/mol CO_2	proprietary	proprietary
Proposed Module Design for 550-MWe PCC Plant		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99.98% (dry), 3.4 bara	90%, 99.98% (dry), 3.4 bara
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	proprietary	

Definitions:

Bara – Absolute pressure (pressure relative to absolute vacuum).

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

Flue Gas Assumptions –Flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) (wet basis) are:

		Composition						
		mol%					ppmv	
Pressure psig	Temperature °F	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
0.2	200	5.70	14.40	68.80	10.30	0.80	68	211

Other Parameter Descriptions:

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

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

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

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

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

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

Process Design Concept – See Figure 1.

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

technology advantages

- Significant reduction in regeneration steam consumption (24 to 40 percent lower), electrical power (14–26 percent lower), and cooling water duty (26–43 percent lower) compared to a reference MEA plant.
- Increased higher heating value efficiency for power production (~31.7 percent efficiency) and lower thermal load compared to a reference MEA plant (28.4 percent efficiency) due to a combination of advanced solvent and process improvements, including integrated pre-scrubber and direct contact cooler, downstream gas blower, higher desorber pressure, and interstage gravity-flow cooler.
- The total plant costs are ~20 percent lower compared to a reference MEA plant, with significantly lower post-combustion capture plant capital costs.
- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is the producer of the OASE blue® solvent and the owner of the solvent technology A major global player in the chemical industry, BASF has the capabilities to reliably produce and supply the OASE blue® solvent in sufficient volumes needed for commercialization, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.

R&D challenges

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

status

A preliminary plant design was developed for a large pilot capable of capturing 300 tpd of CO_2 at a 90 percent capture efficiency. The site for the Linde-BASF capture plant (located near the Abbott Power Plant) was established and evaluated. An environmental, health, and safety analysis, techno-economic analysis, and technology gap analysis were also completed. The Phase I effort has shown that implementation of this project is feasible at the Abbott Power Plant.

available reports/technical papers/presentations

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ION Advanced Solvent CO_2 Capture Pilot Project

primary project goals

ION Engineering aims to advance their post combustion carbon capture process using a novel solvent through pilot-scale testing at the National Carbon Capture Center's (NCCC) Pilot Solvent Test Unit (PSTU) at 0.6-megawatt electric (MW_e) scale and at the Technology Centre Mongstad (TCM) at 12-MW_e scale. The low-aqueous solvent system offers higher CO_2 carrying capacity and reduced regeneration energy requirements resulting in lower cost of capture.

technical goals

- Scale-up of ION's solvent system to determine empirical values utilizing an existing test facility designed for aqueous mono-ethanolamine (aq-MEA).
  - Complete modifications of the 0.6-MW_e PSTU at the NCCC and perform testing on the PSTU using coal-fired flue gas.
  - Complete subsequent test campaign at the 12-MW_e TCM pilot plant with residue fluid catalytic cracker (RFCC) flue gas, a surrogate for coal-fired flue gas, to further scale-up.
- Additional objectives include, validation of ION's process simulation module in Optimized Gas Treating's ProTreat® software, complete solvent stability analyses, final techno-economic analysis (TEA), and environment, health, and safety (EH&S) analysis. Provide recommended design configuration for ION's solvent technology when integrated into a 550-MW power plant, and estimate carbon capture cost.

technical content

ION Engineering is testing their novel solvent based CO_2 capture process at the pilot-scale. The process is based on the use of a novel amine carbon capture solvent developed previously in Department of Energy (DOE) funded project DE-FE0005799. The project aim is to evaluate ION's solvent approach for amine-based CO_2 capture to remove CO_2 from coal-fired flue gas.

ION's solvent system is similar to well-understood aqueous amine solvent-based processes in that it utilizes proven amines as chemical solvents for CO_2 capture. However, it differs significantly as it is low-aqueous, replacing a significant amount of water with another component. This low-aqueous solvent exhibits significant reductions in regeneration energy requirements and significantly higher CO_2 loading capacities. Additionally, these properties will result in reduced parasitic loads, liquid solvent flow rates, corrosion, maintenance, and equipment sizes when scaled-up for commercial systems, thus leading to reductions in both capital and operating expenses. Figure 1 shows a power plant with an amine-based solvent carbon capture system.

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream (0.6 MW_e and 12 MW_e)

project focus:

Low-Aqueous Solvent

participant:

ION Engineering, LLC

project number:

FE0013303

predecessor projects:

FE0005799

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partners:

Nebraska Public Power District; University of Alabama; National Carbon Capture Center; CO_2 Technology Centre Mongstad; SINTEF; Optimized Gas Treating

start date:

10.01.2013

percent complete:

95%

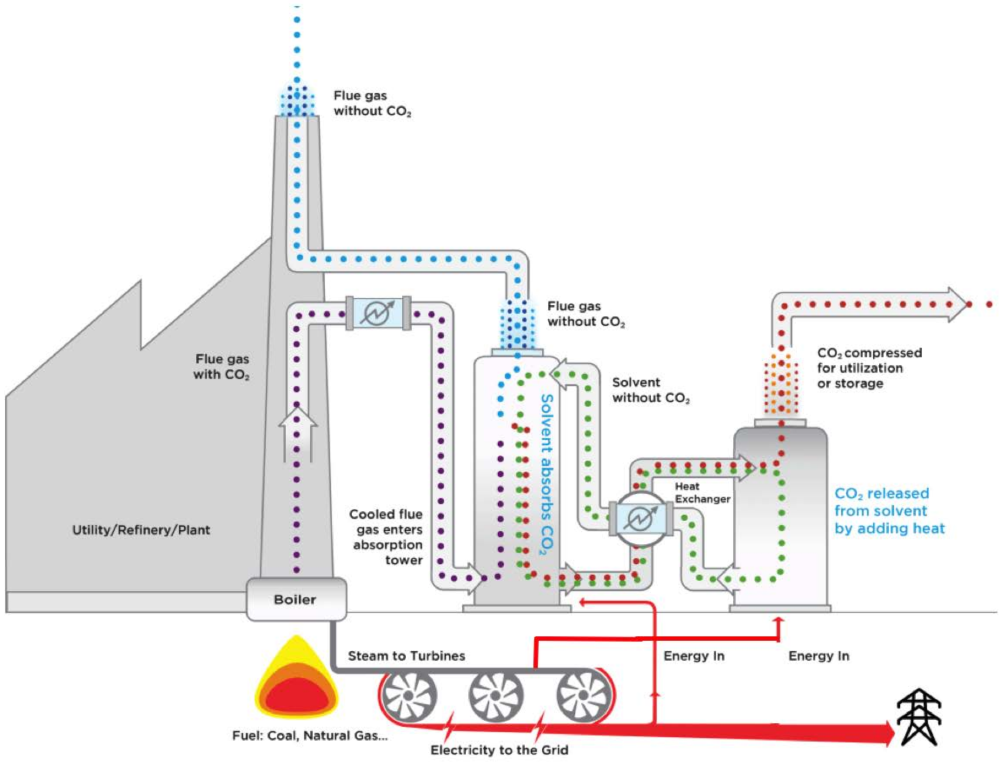

Figure 1: Power plant with carbon capture

ION's solvent-based process steps include pre-scrubbing to remove sulfur oxides (SO_x), several other gases and most of the particles; a direct contact cooling unit to control the inlet flue gas temperature and humidity; an absorber consisting of a packed column with counter-flow for removal of CO_2 into the proprietary solvent; and water wash to remove solvent droplets and vapors from the exhaust gas. Following the absorption step, the final unit operation is a regenerator to produce the CO_2, recover the solvent and recycle the solvent back to the absorber.

The operation of the slipstream pilot unit had been used to validate the process model for ION's solvent technology. The output of this model is an optimized process design, that capitalizes on the unique properties of ION's solvent, will be utilized for a techno-economic assessment of the technology.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	75–95	same
Normal Boiling Point	°C	150–210	same
Normal Freezing Point	°C	-15–2	same
Vapor Pressure @ 15 °C	bar	$1\text{-}2 \times 10^{-4}$	same
Manufacturing Cost for Solvent	$/kg	proprietary	proprietary
Working Solution			
Concentration	kg/kg	0.6–0.85	same
Specific Gravity (15 °C/15 °C)	-	0.9–1.2	same
Specific Heat Capacity @ STP	kJ/kg-K	2–3	same
Viscosity @ STP	cP	<5	same
Absorption			
Pressure	bar	1.0–1.15	same
Temperature	°C	20–50	same
Equilibrium CO_2 Loading	mol/mol	0.4–1.0	same
Heat of Absorption	kJ/mol CO_2	50–100	same
Solution Viscosity	cP	<20	same
Desorption			
Pressure	bar	1.1–1.8	same
Temperature	°C	80–150	same
Equilibrium CO_2 Loading	mol/mol	0.01–0.40	same
Heat of Desorption	kJ/mol CO_2	50–100	same
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A N/A N/A	
Absorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent

(e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The physico-chemical properties of ION's solvent system allow for a unique mechanism that combine fast kinetics with low energy consumption.

Solvent Contaminant Resistance – SO_x and nitrogen oxides (NO_x), other than NO, are absorbed into the solvent and lower the carrying capacity of CO_2. Oxidative degradation is manageable. To date, ION solvent system has not been limited by contaminant concentration.

Solvent Foaming Tendency – No foaming issues have been seen during either of ION's solvent pilot test campaigns.

Flue Gas Pretreatment Requirements – It is preferred that the flue gas be saturated with water vapor and can include any concentration of CO_2. Pretreatment to levels of SO_x <10–30ppm (spikes are manageable) and NO_x <100–200ppm is also favored.

Solvent Make-Up Requirements – Proprietary.

Waste Streams Generated – Proprietary.

Process Design Concept – Flowsheet/block flow diagram (Included above).

Proposed Module Design – N/A.

technology advantages

Relative to aq-MEA technology, ION's solvent technology offers the following benefits to lower operating and capital costs for CO_2 capture:

- Reduction in regeneration energy requirements.
- Higher CO_2 loading capacities.
- Reduced corrosion and solvent losses.
- Faster absorption kinetics.
- Less makeup water used by the process.

R&D challenges

- Determining solvent stability, degradation, and corrosion potential under coal-fired conditions.
- Prove energy consumption of under 2.5 MJ/kg CO_2 at pilot scale utilizing ION system design.

status

ION Engineering has successfully completed pilot-scale testing of their solvent-based capture system with multiple flue gas types at the NCCC PSTU (0.6-MW_e scale) and TCM (12-MW_e scale). ION completed over 1,100 hours testing at the NCCC, achieving over 98 percent CO_2 capture with an energy requirement of 3.7 MJ/kg CO_2 (1,600 BtU/lb CO_2) at steady state. A TEA using ProTreat® simulations validated at the NCCC test campaign indicated a capture cost of $39–45/tonne CO_2, along with a 38 percent reduction in capital costs and 28 percent reduction in operating costs compared to DOE baseline case 12. ION's advanced solvent system was evaluated at TCM using flue gas containing 3.5–14.5 percent CO_2, with over 14,000 tonnes CO_2 captured with greater than 98 percent purity achieved during greater than 2,750 hours testing in the campaign. Testing using flue gas containing 12.5 percent CO_2 indicated an energy requirement of 3.2–3.5 MJ/kg CO_2 (1,375–1,500 Btu/lb CO_2) while capturing 85–92 percent CO_2. A final update was made to the TEA after testing at TCM which indicates a capture of cost of $35–44/tonne CO_2, utilizing ION's optimized plant design with an energy consumption of 2.5 MJ/kg CO_2 (1,090 Btu/lb CO_2).

available reports/technical papers/presentations

Meuleman, E., et al., "ION Advanced Solvent CO_2 Capture Pilot Project," 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/1-Monday/E-Meuleman-Ion-Advanced-Solvent-Project.pdf*

Brown, N., et al., "Novel advanced solvent-based carbon capture pilot demonstration at the National Carbon Capture Center," 13th International Conference on Greenhouse Gas Control Technologies, GHGT-13. 2017.

Meuleman, E., et al., "ION Advanced Solvent CO_2 Capture Pilot Project," 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/E-Meuleman-ION-ION-Advanced-Solvent.pdf*

Brown, A., et al., "ION Novel Solvent System for CO_2 Capture," 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/A-Buz-Brown-ION-Advanced-Solvent-Pilot.pdf*

Brown, N., et al., "ION Advanced Solvent CO_2 Capture Pilot Project," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/N-Brown-ION-ION-Advanced-Slipstream-Pilot-Project.pdf*.

Brown, A., et al., "ION Advanced Solvent CO_2 Capture Pilot Project," Kick-Off Meeting Presentation, December 2013. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/fe0013303-Slipstream-Kickoff-Presentation.pdf.*

Bench-Scale Process for Low-Cost Carbon Dioxide Capture Using a Phase-Changing Absorbent

primary project goals

GE Global Research is designing and optimizing a bench-scale process using a novel phase-changing aminosilicone-based carbon dioxide (CO_2)-capture solvent (absorbent) to establish scalability and technical and economic feasibility of using a phase-changing CO_2-capture absorbent for post-combustion capture, with the ultimate goal of achieving an overall reduction in CO_2 capture cost.

technical goals

- Design and build a bench-scale system for post-combustion CO_2 capture using a phase-changing aminosilicone-based solvent.
- Develop preliminary process and cost models.
- Conduct bench-scale testing on unit operations to evaluate performance and define parameters for scale-up.
- Evaluate materials of construction, manufacturability of solvent, assemble continuous bench-scale system, and update the process model.
- Perform testing on continuous system to optimize process parameters.
- Perform EH&S and techno-economic assessments and devise a scale-up strategy.

technical content

GE Global Research is designing and optimizing a new process for a phase-changing CO_2 capture solvent for use in post-combustion capture in coal-fired power plants. The process is based on the use of the silicone-based phase change solvent (GAP-0), which was developed at the lab-scale in a previous ARPA-E project (DE-AR0000084). The liquid solvent rapidly absorbs CO_2 at low temperatures (40–50 °C) with high loading (>17 percent weight gain) to form a solid carbamate salt. The carbamate salt readily decarboxylates at high temperatures. The innovative process is designed to make use of the unique phase-change properties of the aminosilicone solvent.

The process as originally designed, shown in Figure 1, starts in the absorber, where the liquid phase-changing solvent is sprayed in fine droplets into the flue gas, reacting with the CO_2 to form solid particles. The solids are conveyed in an extruder, moving from the low-temperature, low-pressure absorber to the high-temperature, high-pressure desorber. The unique design of the extruder permits heating and compression of the solids, allowing for continuous delivery of the solids into the pressurized desorber. The solids are heated in the desorber, leading to decarboxylation. CO_2 is separated from the liquid phase-changing solvent in the desorber, allowing for recovery of the CO_2 and recycle of the solvent.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Phase-Changing Absorbent

participant:

GE Global Research

project number:

FE0013687

predecessor projects:

ARPA-E project DE-AR0000084

NETL project manager:

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principal investigator:

Tiffany Westendorf
GE Global Research
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partners:

Coperion Corporation

start date:

01.01.2014

percent complete:

100%

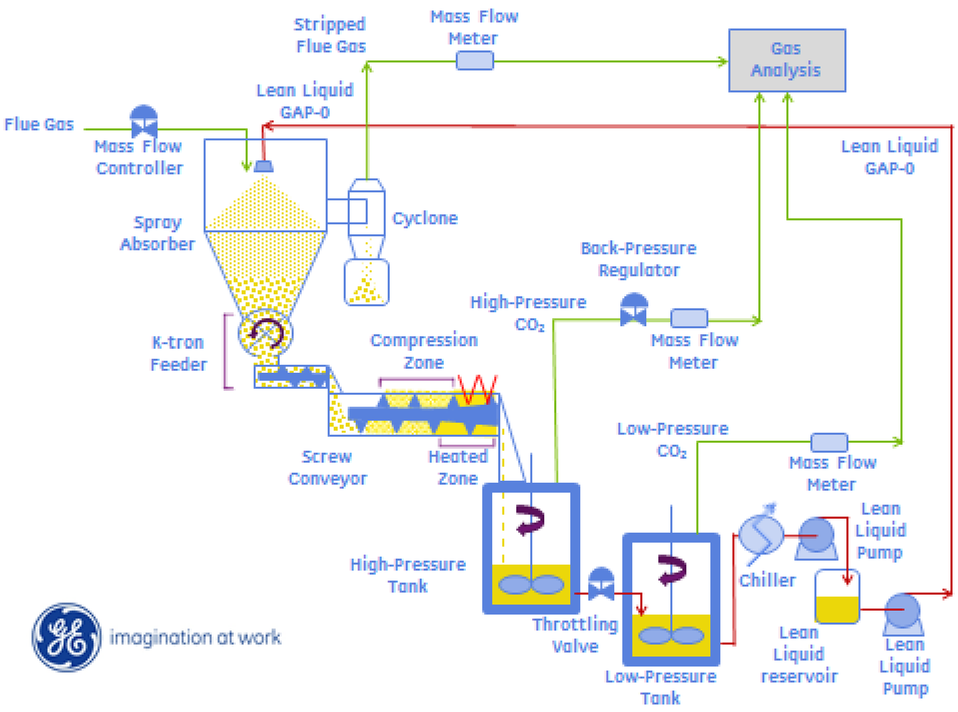

Figure 1: Phase-changing absorbent process

During the project, the process was modified based on understanding water effects on the carbamate and thermal stability of the carbamate. This revised process, as shown in Figure 2, produces a water-carbamate solids slurry in the spray absorber, which is transferred to the desorber inlet by a slurry pump. The single stage desorber operates at near-atmospheric pressure.

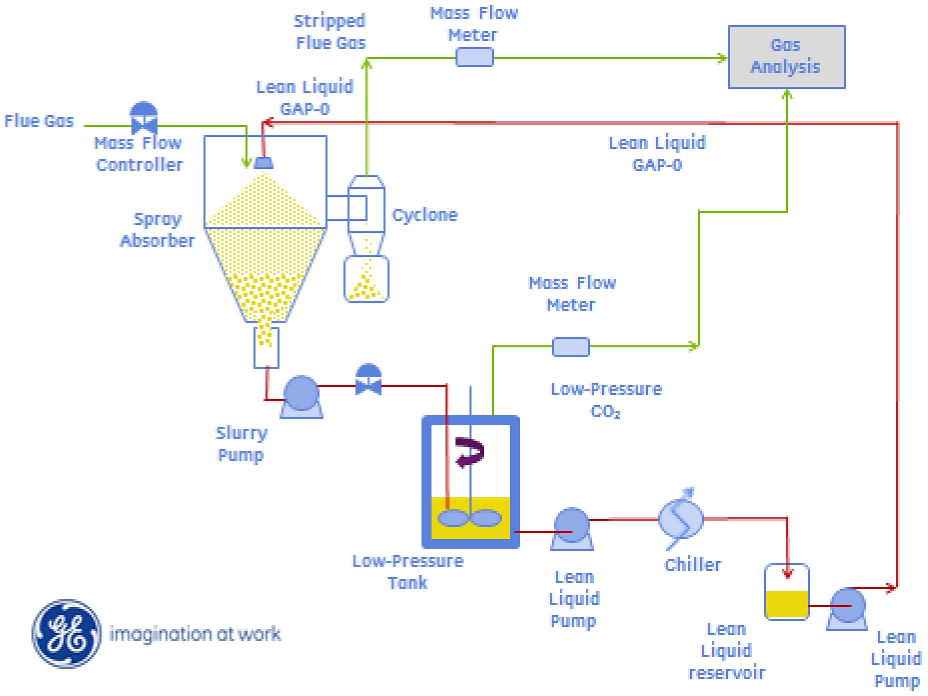

Figure 2: Updated process using a slurry rich phase

Testing of the bench-scale system provided data, including mass transfer parameters, kinetic parameters, heat transfer parameters, solvent stability, effects of flue gas contaminants, and recommended operating conditions, to perform a techno-economic assessment and develop a scale-up strategy. The project aimed to establish scalability and technical and economic feasibility of using a phase-changing CO_2-capture absorbent for post-combustion capture of CO_2 from coal-fired power plants.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value	
Molecular Weight	mol^{-1}	248.51	248.51	
Normal Boiling Point	°C	258.7	258.7	
Normal Freezing Point	°C	<0	<0	
Vapor Pressure @ 15 °C	bar	1.8×10^{-5}	1.8×10^{-5}	
Manufacturing Cost for Solvent	\$/kg	TBD	TBD	
Working Solution				
Concentration	kg/kg	1	0.9	
Specific Gravity (15 °C/15 °C)	-	0.891	0.891 (GAP-0)/1.0 (water)	
Specific Heat Capacity @ STP	kJ/kg-K	2.29	2.29 (GAP-0)/4.18 (water)	
Viscosity @ STP	cP	4.4	12.3 (10% water, 90% GAP-0)	
Absorption				
Pressure	bar	1	1	
Temperature	°C	30	40-60	
Equilibrium CO_2 Loading	mol/mol	0.9	0.65	
Heat of Absorption	kJ/mol CO_2	-113.4	-113.4	
Solution Viscosity	cP	N/A	N/A	
Desorption				
Pressure	bar	7	1	
Temperature	°C	160	130	
Equilibrium CO_2 Loading	mol/mol	0.34	0.23	
Heat of Desorption	kJ/mol CO_2	-113.4	-113.4	
Proposed Module Design		*(for equipment developers)*		
Flue Gas Flowrate	kg/hr	2,767,497		
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	150
Absorber Pressure Drop	bar	TBD		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—		

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical absorption

Solvent Contaminant Resistance – Solvent absorbs sulfur dioxide (SO_2), forming heat-stable salts.

Solvent Foaming Tendency – Limited.

Flue Gas Pretreatment Requirements – Flue gas desulfurization, cooling to <40 °C.

Solvent Make-Up Requirements – TBD.

Waste Streams Generated – In the commercial scale process, a small slipstream of the phase-changing absorbent may be purged from the process to limit accumulation of sulfur compounds in the solvent.

Process Design Concept – See Figure 2 above.

technology advantages

- Non-aqueous, pure solvent.
- Superior properties compared to reference case (MEA) results in potential for cost reduction.
  - Lower heat capacity.
  - Low corrosivity.
  - Low vapor pressure.
- High CO_2 loading and intensified mass transfer requires smaller equipment.

R&D challenges

- Cost and availability of the solvent.

- Thermal degradation of solvent.
- Development of an advanced low-temperature desorber.
- Development of correlations between the primary system variables and unit operations performance to determine scale-up effects, particularly on heat transfer in the absorber and desorber.

status

GE and NETL mutually agreed to terminate the project prior to completion of the final task due to internal changes within GE. GE had designed, built, and tested a bench-scale system to evaluate their phase-changing solvent system. A techno-economic assessment based on bench-scale testing data indicated a first-year CO_2 capture cost of \$52.1/tonne compared to \$66.4/tonne for an aqueous amine process, with cost improvement primarily due to higher working capacity, lower corrosivity, lower vapor pressure, and lower heat capacity of the phase changing solvent. However, as much as \$88/tonne could be added to the CO_2 capture cost for solvent make-up costs due to the thermal degradation of this solvent at the Continuous Stirred Tank Reactor (CSTR) desorber operating temperatures, confirming the need for development of a low-temperature desorber.

available reports/technical papers/presentations

"Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," Final Report, May 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/fe0013687-final-report.pdf*

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/T-Westendorf-GE-Phase-Changing-Absorbent.pdf*

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/T-Westendorf-GE-Phase-Changing-Absorbent.pdf*

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," Budget Period 1 Briefing Presentation, Pittsburgh, PA, February 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/2015-02-23-DE-FE0013687-BP1-briefing.pdf*

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/T-Westendorf-GE-Phase-Changing-Absorbent.pdf*.

Westendorf, T., "Bench-Scale Process for Low-Cost CO_2 Capture Using a Phase-Changing Absorbent," Project Kick-Off Meeting Presentation, Pittsburgh, PA, November 20, 2013. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/2013-11-20-Kickoff-Meeting-GE-FE0013687.pdf*.

Accelerating the Development of “Transformational” Solvents for CO_2 Separations

technology maturity:

Laboratory Scale

project focus:

CO_2-Binding Organic Liquid (CO2BOL) Solvents

participant:

Pacific Northwest National Laboratory

project number:

FWP-65872

predecessor projects:

FE0007466

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partners:

N/A

start date:

04.01.2014

percent complete:

100%

primary project goals

Pacific Northwest National Laboratory (PNNL) developed transformational carbon dioxide (CO_2) capture solvents based on their nonaqueous switchable organic solvents, known as CO_2-binding organic liquids (CO_2BOLs). The project focus used computation-aided molecular design to optimize, synthesize, and characterize CO_2BOLs with a CO_2-rich viscosity of less than 50 cP at a cost of less than $10/kg.

technical goals

- Develop a physical property model to predict the viscosity of CO_2BOL compounds.
- Develop a model to predict thermodynamic properties of CO_2BOL compounds.
- Design and synthesize promising CO_2BOL candidate compounds and compare solvent properties with predicted molecular simulations.
- Synthesize candidates meeting desired cost and viscosity targets for further evaluation to determine how molecular structure impacts solvent system viscosity.
- Update thermodynamic and process models using data from CO_2BOL testing to predict process performance and cost.

technical content

Solvent Platform

PNNL developed transformational CO_2 capture solvents based on their nonaqueous switchable organic solvents, known as CO_2BOLs. This project advanced the development efforts of the previously funded DOE project DE-FE0007466.

CO_2BOLs are a class of switchable ionic liquids (molecular liquids that become ionic in the presence of CO_2) that have lower specific heat and higher CO_2 working capacities compared to aqueous amines, resulting in potential savings in the sensible heat required to strip CO_2.

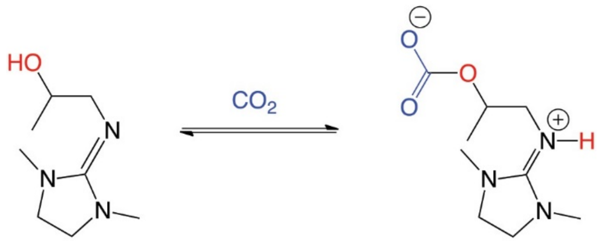

Figure 1: Uptake of CO_2 by Alkanolguanidine BOL (left), and formation of Zwitterionic CO_2BOL (right)

Like aqueous amines, CO_2BOLs are basic, but the base (e.g., guanidine, amidine) does not directly react with CO_2. Instead, the alcohol component reacts with CO_2, forming alkyl carbonic acid, and subsequently transfers a proton to the base, forming liquid alkylcarbonate. Current CO_2BOL generation combines the base and the alcohol moieties in a single molecule, lowering volatility (Figure 1).

The addition of a non-polar solvent (anti-solvent) to CO_2BOLs and other switchable solvents during the solvent regeneration destabilizes bound CO_2, thus potentially lowering the temperature at which the stripper can be operated; (this is referred to as the polarity-swing-assisted regeneration [PSAR] process). Preliminary results indicate that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C. This allows novel possibilities for heat integration, such as transferring heat from the absorber to the stripper using heat pumps, thereby lowering steam demand for solvent regeneration. The anti-solvent can be separated out from the CO_2BOL by cooling and liquid-liquid phase separation. A schematic of the CO_2BOL-PSAR process is shown in Figure 2.

Previous generations of single-component CO_2BOLs were highly viscous before CO_2 absorption. The current generation of alkanolguanidine CO_2BOLs has lower viscosity before CO_2 absorption.

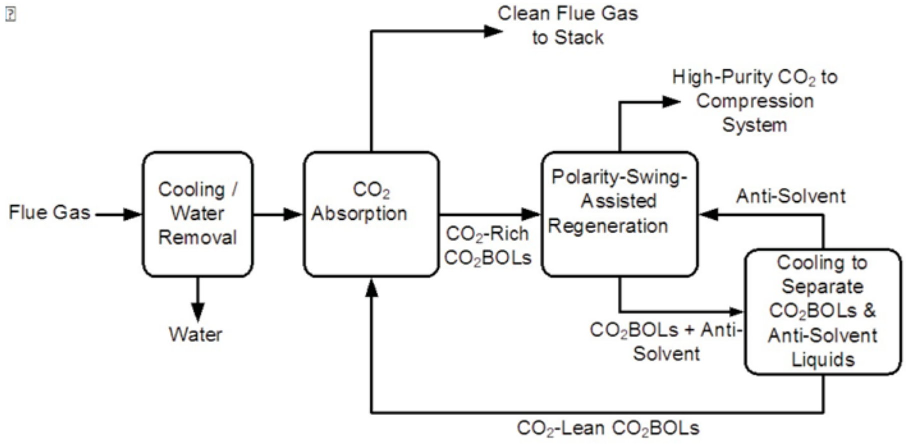

Figure 2: CO_2BOL absorption and PSAR process

The solvent and process parameters identified to date are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	171.14	171.14
Normal Boiling Point	°C	262 (decomposes >200)	262 (decomposes >200)
Normal Freezing Point	°C	<0	<0
Vapor Pressure @ 15 °C	bar	0.179 (37 °C) (DBU) 0.001 (100 °C)	0.001
Manufacturing Cost for Solvent	$/kg	$35	$10
Working Solution			
Concentration	kg/kg	1 (anhydrous) 0.91 (hydrated)	1 (anhydrous) 0.91 (hydrated)
Specific Gravity (15 °C/15 °C)	-	1.03	1.03
Specific Heat Capacity @ STP	kJ/kg-K	1.9	1.9
Viscosity @ STP	cP	1.9 (CO_2-free solvent) 50 (lean solvent)	1.9 (CO_2-free solvent) 11 (lean solvent)
Absorption			
Pressure	bar	1 (near atmospheric, 0.15 bar CO_2 partial pressure)	1 (near atmospheric, 0.15 bar CO_2 partial pressure)
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5 (at 0.15 bar CO_2 partial pressure)	0.5 (at 0.15 bar CO_2 partial pressure)
Heat of Absorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Solution Viscosity	cP	356	50
Desorption			
Pressure	bar	2	2
Temperature	°C	103.8	103.8
Equilibrium CO_2 Loading	mol/mol	0.25	0.25
Heat of Desorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Molecular Design and Optimization

The objective of this project was to expand DOE's Office of Fossil Energy's (FE) capabilities for molecular design and optimization of transformational solvent systems, starting with PNNL's CO_2BOLs solvent platform as a model for this activity. Key program metrics include identification of a viable candidate with a CO_2-loaded viscosity below 50 cP and at a cost no greater than $10/kg, and to learn why viscosity increases occur in water-lean solvents and how to minimize viscosity increases. To achieve this, PNNL has developed a novel physical property prediction model that can accurately reproduce laboratory-measured material properties. Previously synthesized and characterized CO_2BOL derivatives from PNNL's completed programs were used to establish the molecular model. A concurrent molecular design effort was started to produce libraries of new compounds with reduced viscosity by introducing design motifs based on organic chemistry principles. Once the molecular model was completed, molecules in the library were simulated to determine which compounds showed reduced viscosity, and, more importantly, why they were less viscous. Modeled compounds are compared against synthesized compounds for validation and refinement (Figure 3). Once design principles were discovered, these new structural motifs were introduced into subsequent molecular designs to achieve reductions in rich-solvent viscosity.

To date, the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The model has identified hydrogen bonding and electrostatic (specifically dipole-dipole between molecules) interactions as the most critical design elements for low-viscosity CO_2BOLs, and from this knowledge we have designed and simulated hundreds of molecules, with tens of candidate molecules that are projected to be less viscous than the previous derivative. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE's solvent portfolio.

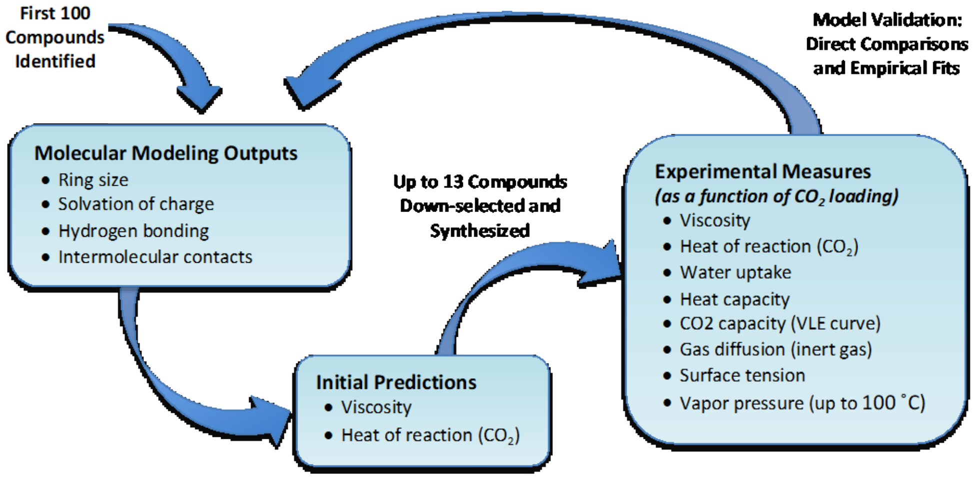

Figure 3: Molecular modeling prediction vs. experimental measures

Definitions:

***STP* –** Standard temperature and pressure (15 °C, 1 atm).

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

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

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

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

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

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

***Concentration* –** The mass fraction of pure solvent in working solution.

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

Other Parameter Descriptions:

***Chemical/Physical Solvent Mechanism* –** The chemical reaction for the CO_2 capture process with a representative CO_2BOL is shown in Figure 1.

***Solvent Contaminant Resistance* –** Tests of CO_2BOL reactivity with hydrogen chloride (HCl), sulfur oxide (SO_x) and nitrogen oxide (NO_x) will be conducted. In general, CO_2BOLs form heat-stable salts (HSS) with sulfur dioxide (SO_2), NO_x, and HCl. The solvent can be recovered from the HSS using caustic wash or with ion exchange resins. Levels of HSS formation are expected to be similar to that of MEA. Minimal adverse impacts due to arsenic and mercury in the flue gas are expected.

***Solvent Foaming Tendency* –** Foaming tendency has not been observed in prior formulations during bench-scale testing. Foaming of future derivatives remains unknown.

***Flue-Gas Pretreatment Requirements* –** Water management with any of the alkanolguanidine-based CO_2BOLs is different from that with MEA.CO_2BOL solvents are designed to minimize water uptake by the solvent, as the presence of water increases solution viscosity and increases the energy required to regenerate the CO_2BOL. As such, CO_2BOL formulations are favored energetically to run with a 5 wt% steady-state loading of water. To achieve this loading target, the process requires a small refrigeration unit upstream of the absorber to condense out water. Other flue-gas pretreatment requirements (for acid-gas contaminants) are expected to be similar to those with MEA.

***Solvent Makeup Requirements* –** Until a formal lifetime analysis can be made, the estimated makeup rate of CO_2BOLs will depend on the anticipated thermal and chemical degradations. Currently, evaporative losses are projected to be 40 kg per annum.

***Waste Streams Generated* –** CO_2BOLs have lower vapor pressure than MEA, and post-absorber CO_2BOL emissions would be at lower levels (estimated at 0.7 parts per billion [ppb]). Other major waste streams may include stripper wastes and reclaimer wastes.

***Proposed Module Design* –** Unless noted, the following should be assumed for flue gas leaving the flue gas desulfurization (FGD) (wet basis): feed pressure 1.014 bar, temperature 57 °C, and composition as shown in the table below.

Pressure	Temperature	Composition						
		vol%					ppmv	
bara	°C	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1.014	57	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

Solvent Platform

- The lower solvent specific heat and water content leads to smaller parasitic load than current solvents (MEA).
- The lower solvent evaporative losses and thermal degradation may lead to lower cost of CO_2 capture.
- The rates of liquid-phase mass-transfer kinetics with CO_2BOLs are comparable to those of current solvents (MEA and piperazine), albeit at higher solution viscosity.
- PSAR may enable low-temperature CO_2BOL regeneration, reducing the pressure of low-pressure steam used for regeneration, thereby increasing net power production and reducing parasitic loads.
- Heat integration possibilities with PSAR and CO_2BOLs may have minimal impact on steam plant cycles, facilitating retrofits for existing plants.

Molecular Design and Optimization

- The current PNNL-developed reduced molecular model can predict solvent thermodynamic and kinetic behavior, providing projections of solution viscosity and heats of reaction. This model enables rapid screening of advanced water-lean solvent platforms for development, as compared to conventional computationally intensive molecular dynamics simulations.
- The PNNL model has identified hydrogen bonding and electronic stacking as the two most critical contributors to viscosity in water-lean solvent platforms such as CO_2BOLs, enabling rapid optimization of solvent chemistry.
- The PNNL model is translatable to other solvent platforms across DOE's portfolio.

R&D challenges

Solvent Platform

- The estimated cost of manufacturing the current-generation CO_2BOL solvent is high, leading to high operation costs.
- Water absorption by the CO_2BOL requires the amount of water in the flue gas to be reduced significantly by refrigeration to avoid water buildup in the solvent recirculation loop. However, these nominal capital costs and auxiliary electric loads are recovered in the net power gains by the PSAR.

Molecular Design and Optimization

- The challenge is to make targets from molecular predictions at a cost of $10/kg.

status

The project was completed on September 30, 2017. PNNL results indicated that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C, allowing novel possibilities for heat integration thereby lowering steam demand for solvent regeneration. PNNL also determined that the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE’s solvent portfolio.

available reports/technical papers/presentations

Heldebrant, D., “Accelerating the Development of ‘Transformational’ Solvents for CO2 Separations,” 2017 NETL CO2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/2D-Heldebrant2-PNNL-Transformational-Solvents.pdf*

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Large Pilot-Scale Carbon Dioxide (CO_2) Capture Project Using Aminosilicone Solvent

primary project goals

GE Global Research developed a plan to define a 10-MW_e large pilot-scale project for post-combustion carbon dioxide (CO_2) capture using their novel aminosilicone-based solvent, minimizing and quantifying risks associated with technical success, cost, and schedule. The information from this Phase I project can be used to inform the experimental design, budget, and schedule for a Phase II pilot test project.

technical goals

- Evaluate and select a site for the 10-MW_e large pilot plant.
- Qualify a supplier for the aminosilicone solvent.
- Develop a technology gap analysis, a screening-level design and cost estimate.
- Prepare an environmental, health, and safety assessment.
- Complete a techno-economic analysis for the CO_2 capture system.

technical content

GE Global Research, in Phase I of this large-pilot project, developed a project plan for large-scale (10-MW_e) testing of their aminosilicone-based solvent CO_2 capture process. In prior project FE0013755, GE Global Research designed, constructed, and operated a 0.5-MW_e slipstream post-combustion CO_2 capture pilot-scale process using this solvent at the NCCC Pilot Solvent Test Unit (PSTU), as shown in Figure 1. The process is based on the use of the aminosilicone-based solvent which was developed on the bench-scale in previous US DOE funded projects (DE-FE0007502 and DE-NT0005310). Specifically, the solvent system is composed of a mixture of GAP-1m and triethylene glycol (TEG). The carbamate formed upon CO_2 absorption does not precipitate out in this solvent mixture. The solvent has a much lower volatility than monoethanolamine (MEA), which simplifies the desorption process and decreases the energy required for CO_2 desorption. The solvent can be regenerated at elevated pressures, resulting in lower compression costs. The solvent also shows higher CO_2 capacity, high thermal stability, and low corrosivity.

technology maturity:

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

project focus:

Aminosilicone Solvent

participant:

GE Global Research

project number:

FE0026498

predecessor projects:

FE0013755
FE0007502
NT0005310

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partners:

N/A

start date:

10.01.2015

percent complete:

100%

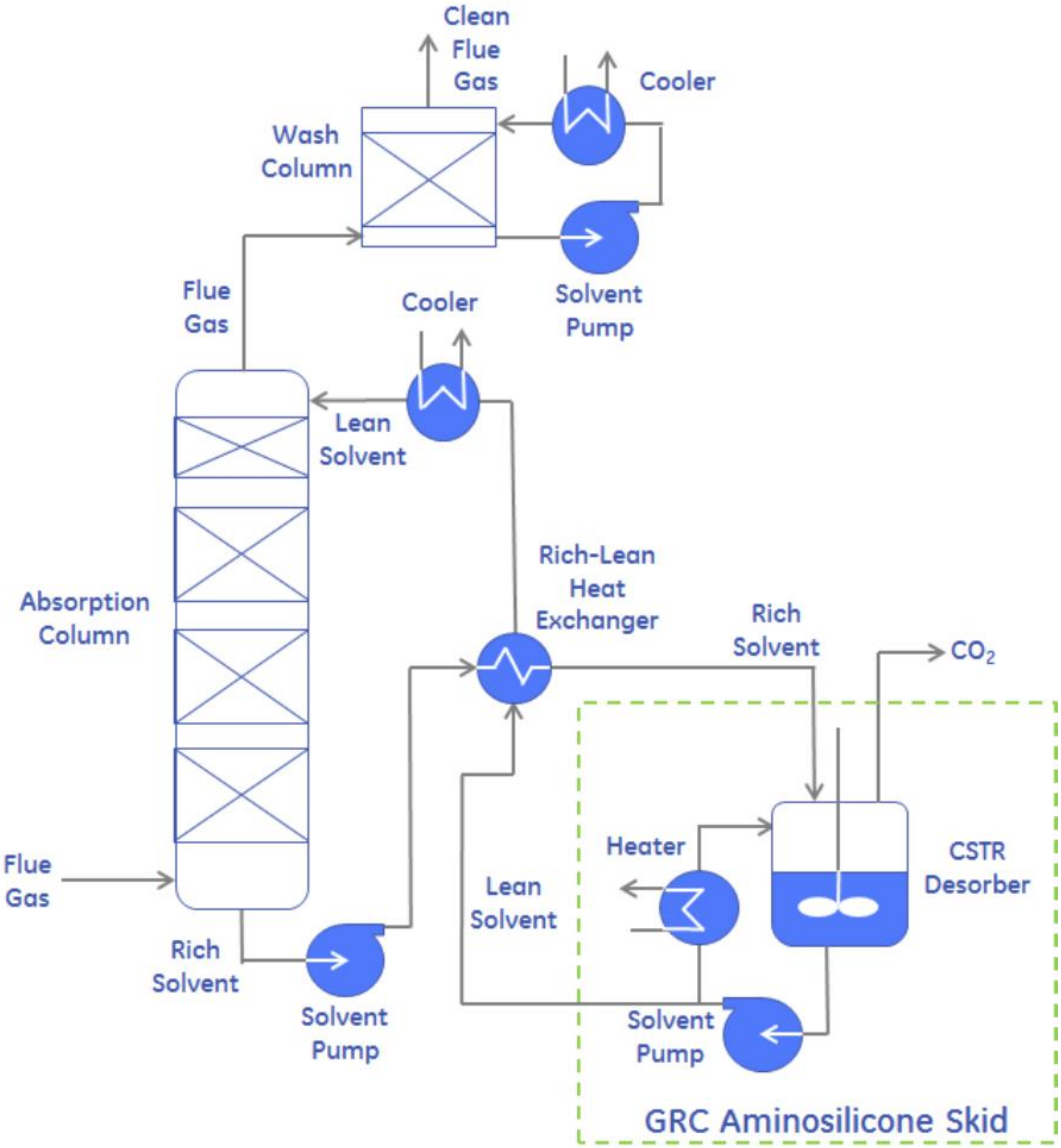

Figure 1: Pilot-scale system at NCCC

Testing on the 0.5-MW$_e$ pilot-scale system using coal-fired flue gas provided data, including mass transfer parameters, kinetic parameters, heat transfer parameters, solvent stability, effects of flue gas contaminants, and recommended operating conditions, to update process models and to perform a techno-economic assessment and determine a scale-up strategy.

Two different desorption concepts were evaluated. The first, as shown above in Figure 1, used a continuous stirred tank reactor (CSTR) for desorption. The benefits of this concept include lower capital cost, simple operation, single stage desorption, and a small footprint. Adding water recycle can lower thermal degradation, decrease wastewater, and reduce solvent loss.

The other concept evaluated, shown in Figure 2, used a steam stripper column (SSC). This is a multistage desorption process resulting in a lower desorption temperature.

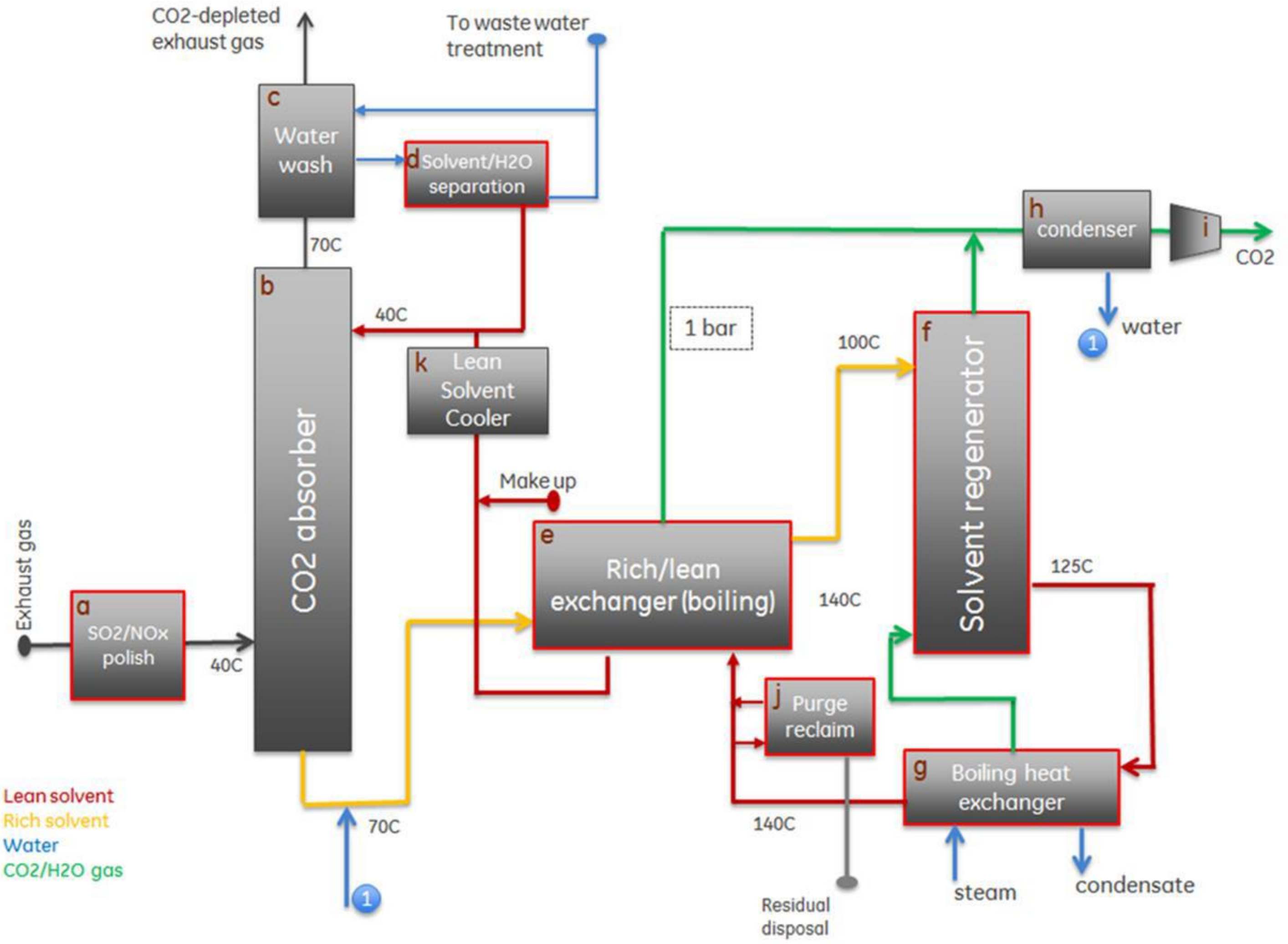

Figure 2: Process design with steam stripper

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	322.67 (GAP-1$_m$)/150.17 (TEG)	322.67 (GAP-1$_m$)/150.17 (TEG)
Normal Boiling Point	°C	310 (GAP-1$_m$)/287 (TEG)	310 (GAP-1$_m$)/287 (TEG)
Normal Freezing Point	°C	-85 (GAP-1$_m$)/-7 °C (TEG)	-85 (GAP-1$_m$)/-7 °C (TEG)
Vapor Pressure @ 15°C	bar	0.005 bar @ 140 °C (TEG) 0.037 bar @ 140 °C (GAP-1m)	0.005 bar @ 140 °C (TEG) 0.037 bar @ 140 °C (GAP-1m)
Manufacturing Cost for Solvent	\$/kg	—	—
Working Solution			
Concentration	kg/kg	60/40 GAP-1$_m$/TEG	60/40 GAP-1$_m$/TEG
Specific Gravity (15°C/15°C)	-	0.913 (GAP-1$_m$)/1.124 (TEG)	0.913 (GAP-1$_m$)/1.124 (TEG)
Specific Heat Capacity @ STP	kJ/kg-K	2.319 (60/40 GAP-1$_m$/TEG)	2.319 (60/40 GAP-1$_m$/TEG)
Viscosity @ STP	cP	4.37 (GAP-1$_m$)/49 (TEG)	4.37 (GAP-1$_m$)/49 (TEG)
Absorption			
Pressure	bar	0 (gauge)	0 (gauge)
Temperature	°C	40-60 °C	40-60 °C
Equilibrium CO$_2$ Loading	mol/mol	0.78 (CO$_2$)/1 (GAP-1$_m$)	0.78 (CO$_2$)/1 (GAP-1$_m$)
Heat of Absorption	kJ/mol CO$_2$	99.7 (60/40 GAP-1$_m$ in TEG)	99.7 (60/40 GAP-1$_m$ in TEG)
Solution Viscosity	cP	431 (60/40 GAP-1$_m$ in TEG)	431 (60/40 GAP-1$_m$ in TEG)
Desorption			
Pressure	bar	2 (gauge)	2 (gauge)
Temperature	°C	140 °C	140 °C
Equilibrium CO$_2$ Loading	mol/mol	0.25 (CO$_2$)/1 (GAP-1)	0.25 (CO$_2$)/1 (GAP-1)
Heat of Desorption	kJ/mol CO$_2$	99.7 (60/40 GAP-1$_m$ in TEG)	99.7 (60/40 GAP-1$_m$ in TEG)
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	99.7 (60/40 GAP-1$_m$ in TEG)	
CO$_2$ Recovery, Purity, and Pressure	% / % / bar	90 95 3	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Chemical/Physical Solvent Mechanism – The reaction of the GAP class of aminosilicones with CO_2 is shown in Figure 2. The aminosilicone in this study is a mixture of GAP molecules where the average value of the subscript (x) shown in Figure 2 is one. This solvent is designated GAP-1. GAP-1 is combined with TEG in a 60/40 (by weight) mixture to inhibit the solidification that occurs when the neat solvent (GAP-1) reacts with CO_2.

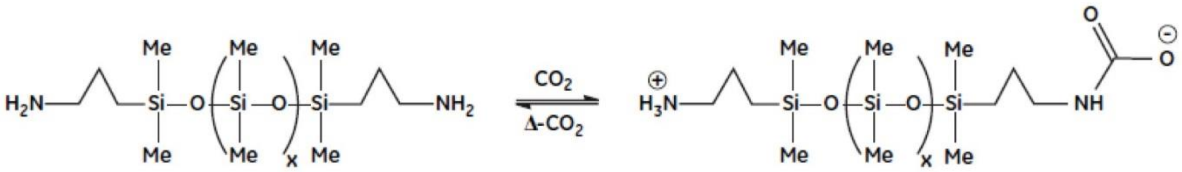

Figure 2: Reaction of GAP class of aminosilicones with CO_2 to form GAP carbamate

Solvent Contaminant Resistance – As with MEA, aminosilicones will react irreversibly with sulfur dioxide (SO_2) to form heat- stable salts (HSS). Solvent makeup will be required to replace aminosilicone lost to reaction with SO_2.

Solvent Foaming Tendency – None observed.

Flue Gas Pretreatment Requirements – In a full-scale system, the flue gas pretreatment requirements are identical to those of an MEA-based process, including a selective catalytic reduction reactor, particulate removal, and flue gas desulfurizer (FGD).

Solvent Make-Up Requirements – In addition to the solvent makeup required due to reaction of aminosilicone with SO_2, additional solvent makeup will be required due to thermal decomposition. However, it has been demonstrated that GAP-1 is significantly more thermally stable than MEA, as discussed below.

Waste Streams Generated – A waste stream of HSS from the reaction of SO_2 with aminosilicone will be generated.

Process Design Concept – The process flow diagram for the aminosilicone-based, bench-scale CO_2-capture system is shown in Figure 3.

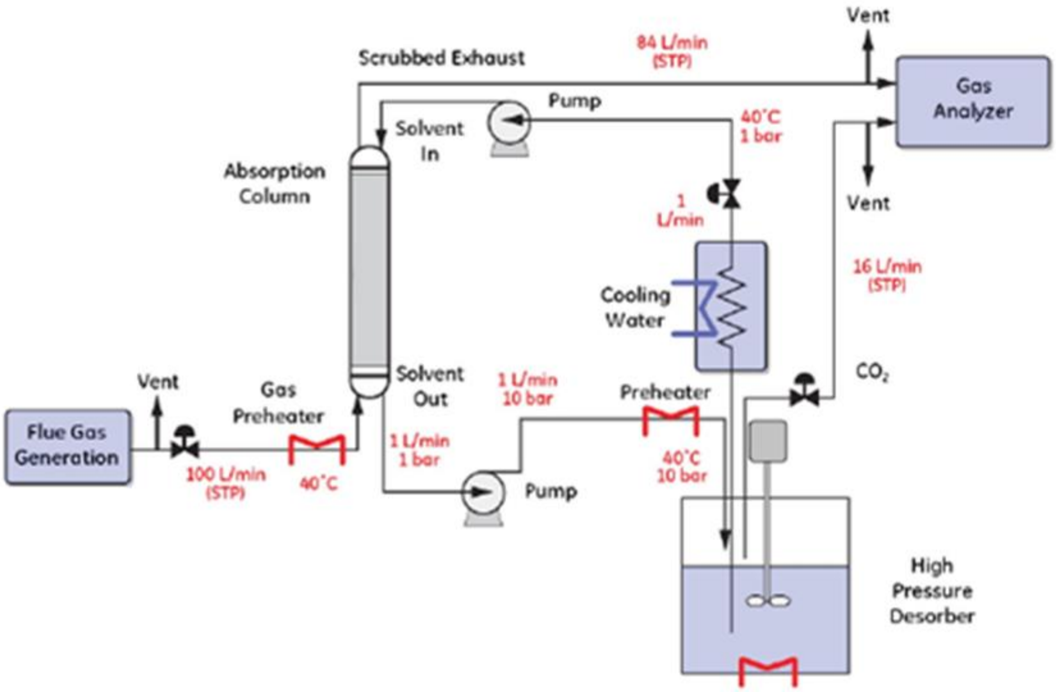

Figure 3: The process flow diagram for the bench-scale system

technology advantages

- Lower volatility.
  - Simplified separations.
  - Less energy wasted vaporizing solvent and/or water.
  - Lower airborne release rates.
- Lower heat capacity.
- Reduced corrosion.
- Potential for decreased issues with aerosol formation.

R&D challenges

- Completing design to integrate the process into the host site.

status

This project was completed. GE qualified a major chemical manufacturer as the GAP-1 solvent supplier. A 100-kg solvent sample was received and tested on the bench-scale, meeting purity and performance specifications. The phase I project effort identified Technology Centre Mongstad as a host site, and designed and estimated the cost for retrofit to accommodate the GE solvent at the TCM plant. The techno-economic analysis indicated a CO_2 removal cost using the steam stripper for desorption as \$42/tCO_2 (entitlement) and \$48/tCO_2 (with degradation, at ~15 percent/year solvent makeup). The CO_2 removal cost using the CSTR desorber was higher, with the cost dominated by the solvent make-up costs. Due to a schedule slip in the testing at NCCC (predecessor project FE0013755), GE decided not to submit a Phase II application.

available reports/technical papers/presentations

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DiPietro, P., “Large Pilot-Scale CO_2 Capture Project Using Aminosilicone Solvent,” Project Kick-Off Meeting Presentation, Pittsburgh, PA, November 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026498-Kickoff-Presentation.pdf*

Wood, B., “Pilot-Scale Silicone Process for Low-Cost CO_2 Capture,” 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *http://netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/1-Monday/B-Wood-GE-Silicone-Process-for-CO2-Capture.pdf*

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Development of Mixed-Salt Technology for Carbon Dioxide Capture From Coal Power Plants

primary project goals

SRI International is developing a novel ammonia and potassium carbonate-based mixed-salt solvent carbon dioxide (CO_2) capture process and testing it at large bench scale to demonstrate the enhanced CO_2 capture efficiency, high loading capacity, and reduced energy consumption.

technical goals

- Demonstrate the individual absorber and regenerator processes for ammonia (NH_3) and potassium carbonate (K_2CO_3) solvent systems with high efficiency and low NH_3 emission and reduced water use compared to the state-of-the-art ammonia-based technologies.
- Develop a comprehensive thermodynamic modeling package.
- Demonstrate the completely integrated absorber-regenerator CO_2 capture system at the bench-scale and optimize the system operation.
- Collect data to perform the detailed techno-economic analysis (TEA) of CO_2 capture process integration to a full-scale power plant.
- Test two alternative flowsheets for process optimization, test system at highest possible CO_2 loadings, and determine steam usage for regeneration.
- Test the continuous operation of the process in an integrated absorber-regenerator system.

technical content

SRI International is developing a novel mixed-salt solvent process (MSP) for post-combustion CO_2 capture and testing it in a large bench scale, integrated absorber-regenerator system. To enhance the desired properties of the CO_2 capture solution, the MSP uses a mixture of ammonia and potassium carbonate, which are widely used individually in well-established technologies. A singular ammonia-based process such as chilled ammonia has several advantages: very high CO_2 loading capacity, reduced reboiler duty due to high pressure regeneration, and fast absorption kinetics. Challenges of this process include the need for large water wash to reduce ammonia emissions, requirement to chill the solvent, and energy usage for solid dissolution. A singular potassium carbonate-based process offers several advantages: no emissions, long-term industrial use, and simple permitting. However, this process has lower efficiency and CO_2 loading, as well as energy requirements for solid dissolution and vacuum water stripping. By combining these two solvent technologies, SRI capitalizes on the advantages of each while minimizing the drawbacks. The MSP maintains the high CO_2 loading and enhanced absorption kinetics, delivering high pressure CO_2 in a solids-free system. Furthermore, by combining the salts, the capture system experiences reduced reboiler and auxiliary electricity loads, reduced ammonia emission, reduced water usage, and a reduced system footprint.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Ammonia and Potassium Carbonate-Based Mixed Salt Solvent

participant:

SRI International

project number:

FE0012959

predecessor projects:

N/A

NETL project manager:

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partners:

Aqueous Systems Aps; POLIMI; Stanford University; OLI Systems Inc.; IHI Corporation

start date:

10.01.2013

percent complete:

95%

The MSP System, shown in Figure 1 comprises two isothermal absorbers, a selective regenerator and auxiliary equipment. The absorbers operate with different ammonia to potassium ratio (NH_3/K) solutions formulated to maximize the absorption and minimize the ammonia loss. The absorber system is designed to integrate downstream of a flue-gas desulfurization (FGD) unit in a PC power plant. The CO_2 in the flue gas stream is absorbed in the absorber columns, which are operated with liquid recycle and heat exchangers to remove the heat of reaction and keep the solution at the optimum temperature for efficient absorption and minimum ammonia slip. The CO_2-rich solutions from the absorbers are sent to the regenerator for CO_2 stripping and solvent regeneration. The MSP uses a selective regenerator to regenerate two CO_2-lean salt streams with different NH_3/K ratios. These streams are drawn from a lower-middle stage and the bottom stage of the regenerator. The regenerator is operated at high-pressure, isobaric conditions and has a temperature gradient along the height of the column. The key advantage of the MSP regenerator design is to capture the latent heat within the regenerator before the stream exits the vessel, thus generating almost dry CO_2 stream (H_2Ovap/CO_2 <0.2) at high pressure reducing both operational and capital CO_2 compression costs. The overall benefit of MSP is a significant reduction in the cost of the CO_2 capture.

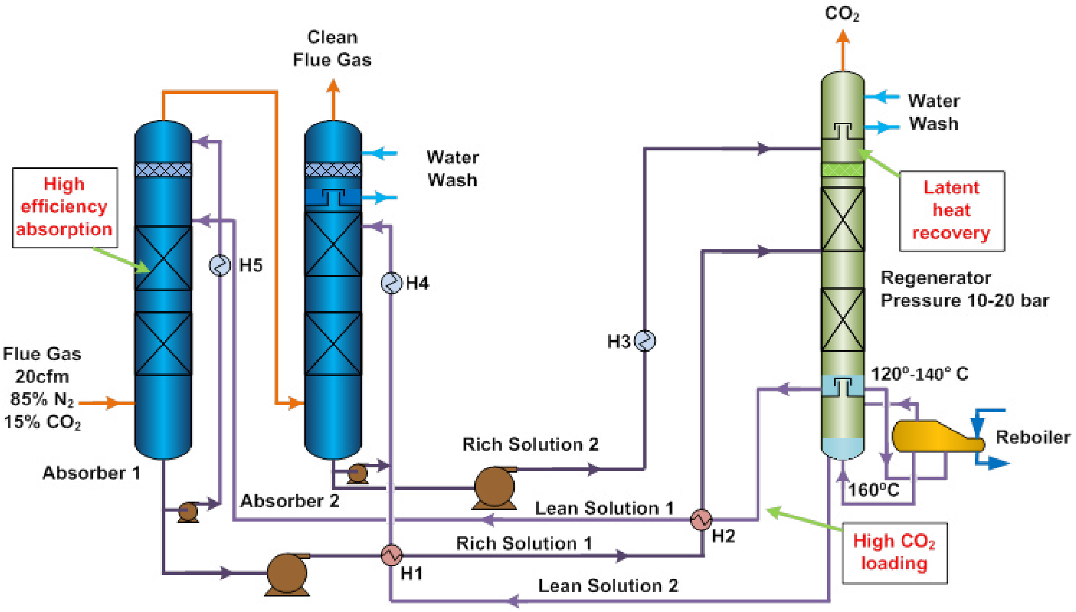

Figure 1: SRI mixed-salt simplified process diagram

Bench-scale operation of the individual absorber and regenerator units provided optimized process parameters prior to the design and testing of the large bench-scale integrated absorber-regenerator system. The absorbers at the bench-scale test unit are shown in Figure 2. Testing on the integrated system along with process modeling provided parametric optimization to go along with the techno-economic assessment to determine costs associated with use of this system in a 550-megawatt electric (MW_e) power plant.

The solvent and process parameters are provided in Table 1.


Absorbers
Regenerator

Figure 2: SRI's large bench-scale integrated mixed-salt system

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	18	18
Normal Boiling Point	°C	100	100
Normal Freezing Point	°C	0	0
Vapor Pressure @ 15 °C	bar	0.17	0.17
Manufacturing Cost for Solvent	\$/kg	-	-
Working Solution			
Concentration	kg/kg	0.35	0.35
Specific Gravity (15 °C/15 °C)	-	1.1-1.3	1.1-1.3
Specific Heat Capacity @ STP	kJ/kg-K	3.0–4.0	3.0–4.0
Viscosity @ 15°C	cP	1.5-1.6	1.5-1.6
Absorption			
Pressure	bar	1	1
Temperature	°C	20–30	25–30
Equilibrium CO_2 Loading	mol/mol	0.6 (rich)	0.6 (rich)
Heat of Absorption	kJ/mol CO_2	1,000–1,200	<1,200
Solution Viscosity	cP	1.5-1.8	1.5-1.8
Desorption			
Pressure	bar	>10	>10
Temperature	°C	120–160	120–160
Equilibrium CO_2 Loading	mol/mol	0.2 (lean)	<0.2 (lean)
Heat of Desorption	kJ/mol CO_2	1,000-1,200	<1,200
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	-	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 ~20	
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

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

$$K_2CO_3 - NH_3\text{-}xCO_2\text{-}H_2O \leftrightarrow K_2CO_3 - NH_3\text{-}yCO_2\text{-}H2O$$

Where y>x

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

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

Flue Gas Pretreatment Requirements – Unlike in MEA system, mixed-salt system does not require deep FGD; 200 parts per million (ppm) level SO_2 is acceptable.

Solvent Make-Up Requirements – Mixed-salt is a mixture of ammonia and potassium carbonate (K_2CO_3) and it is inexpensive and readily available. The loss of solvent is expected to be <0.2 kg/ tonne of CO_2 captured.

Waste Streams Generated – Ammonium sulfate from the SO_2 and trace capture in the DCC.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

technology advantages

- Solvent uses inexpensive, industrially available materials.
- Requires no feed stream polishing.
- No hazardous waste generation.
- Uses known process engineering.

- No solids.
- High CO_2 loading capacity.
- Produces clean CO_2 stream at high pressure with reduced compression costs.
- Reduced energy consumption compared to MEA.
- Reduced auxiliary electricity loads.

R&D challenges

- Reduction of ammonia evaporation at higher reaction rates.

status

SRI has completed bench-scale testing of the integrated two-stage absorber system with the regenerator using simulated flue gas, indicating cyclic operation with greater than 90 percent CO_2 capture (at ~0.3 ton/day) with cyclic CO_2 lean and rich loading between 0.2 and 0.59 mol/mol (maximum cyclic CO_2 loading achieved is ~10 wt%.). Lean solutions with two compositions, ammonia rich and potassium rich, were generated using a two-stage regenerator. The two-stage absorber approach showed a reduction in ammonia emissions. Overall, long-term operability of the integrated system was shown over 1.5 years. The TEA for the mixed-salt technology showed a reduction in heat duty (compared to the Econamine baseline) from 3.56 to 2.0 MJ/kg CO_2 and a cost of CO_2 captured of approximately \$38/tonne CO_2.

available reports/technical papers/presentations

Jayaweera, I., "Development of Mixed-Salt Technology for Carbon Dioxide Capture from Coal Power Plants," 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/1I-Jayaweera1-SRI-Mixed-Salt-Technology.pdf*

Kang, C.A., Brandt, A.R., Durlofsky, L.J., and Jayaweera, I, "Assessment of advanced solvent-based post-combustionCO_2 capture process using bi-objective optimization technique", Applied Energy, 179 (2016), 1209-1219.

Jayaweera, I., Jayaweera, Palitha, Krishnan, Gopala N., Sanjurjo, Angel, "Rate enhancement of CO_2 absorption in aqueous potassium carbonate solutions by an ammonia-based catalyst," US Patent 9,339,757, issued May 17, 2016

Jayaweera, I., Jayaweera, Palitha, Yamasaki, Yuki, and Elmore, R, "Mixed-Salt Solutions for CO_2 Capture," Book Chapter 8 in Absorption-Based Post-Combustion Capture of Carbon Dioxide; Elsevier, 2016 (pp 167-200)

Jayaweera, I., "Development of Mixed-Salt Technology for Carbon Dioxide Capture from Coal Power Plants," 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/I-Jayaweera-SRI-Mixed-Salt-Technology-for-CO2-Capture.pdf*

Jayaweera, I., "Development of Mixed-Salt Technology for Carbon Dioxide Capture from Coal Power Plants," 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/I-Jayaweera-SRI-Mixed-Salt.pdf*

Jayaweera, I., P. Jayaweera, R. Elmore, J. Bao, S. Bhamidi, "Update on mixed-salt technology development for CO_2 capture from post-combustion power stations," Energy Procedia 63, 2014, 640-650.

Jayaweera, I., "Development of Mixed-Salt Technology for Carbon Dioxide Capture from Coal Power Plants," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/I-Jayaweera-SRI-Development-Of-Mixed-Salt-Technology.pdf*.

Jayaweera, I., P. Jayaweera, R. Elmore, J. Bao, S. Bhamidi, "Update on mixed-salt technology development for CO_2 capture from post-combustion power stations," Energy Procedia 63 (2014) 640-650.

Jayaweera, I., "Development of Mixed-Salt Technology for Carbon Dioxide Capture from Coal Power Plants," Project Kick-Off Meeting Presentation, Morgantown, WV, December 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/SRI-Mixed-Salt-Presentation-121113.pdf*.

Jayaweera, I. S., P. Jayaweera, G. Krishnan, and A. Sanjurjo, "The race for developing promising CO2 capture technologies ready for 2020 deployment: Novel mixed-salt based solvent technology." Pap.-Am. Chem. Soc., Div. Energy Fuels 2013, (1):58.

Advanced Solvent-Based Carbon Capture Technology Development

primary project goals

Southern Company Services evaluated the technical and economic feasibility of adding an integrated stripper/reboiler, particulate matter management, and a new solvent to the existing 25-megawatt electric (MW_e)-scale, amine-based Kansai Mitsubishi Carbon Dioxide Recovery Process (KM CDR Process™) at Southern Company's Plant Barry.

technical goals

- Perform preliminary techno-economic analysis, preliminary design, and technical gap analysis for a large-scale pilot plant project.
- Define a project plan to include baseline, parametric, and long-term testing.
- Evaluate technical and economic feasibility of full-scale installation of further improvements to the KM CDR Process™, including a built-in reboiler, particulate matter management, and a new solvent.

technical content

The KM CDR Process™ at Plant Barry (Figure 1) is a fully-integrated carbon capture and storage (CCS) plant and has achieved 90 percent CO_2 capture at a production rate of 500 metric tons per day. The large-scale pilot plant uses the proprietary KS-1™ solvent, which shows several benefits relative to monoethanolamine (MEA)-based processes. In this project, the key technical challenges of high-steam consumption, solvent performance degradation, and process equipment footprint were investigated by Southern Company Services by: (1) evaluating a built-in reboiler, (2) evaluating the reduced operating and capital costs associated with reduction or elimination of mechanical filtration of particulate matter, and (3) conducting a new solvent test plan (referred to as NSL) to demonstrate a new solvent (termed New Solvent A), which is expected to reduce regeneration steam as well as raw material costs. This Phase I of the project was to evaluate the technical and economic feasibility of full-scale installation of these improvements to the KM CDR Process™. Phase II, which was not awarded, would have covered the engineering, construction, and testing at the pilot plant.

The built-in reboiler would replace the regenerator reboiler and stripper with an integrated unit as shown in Figure 2. It would use a welded-plate heat exchanger, designed for high condensation or evaporation duty, installed in the column, reducing capital and operating cost and footprint.

Particulate matter management would determine if solvent purification can be eliminated. By turning off the solvent purification system to mimic removal of the flue gas filtering process, allowing particulate matter levels in the solvent to build, the maximum allowable particulate matter concentration at which the solvent performance degrades can be determined.

A new improved amine solvent, Advanced Solvent A developed by Mitsubishi Heavy Industries America (MHIA), was proposed to replace their KS-1™ amine solvent. This solvent offers reduced steam consumption compared to both the KS-1™ and MEA solvents.

technology maturity:

Large-Pilot, Actual Flue Gas (equivalent to 25 MW_e)

project focus:

Amine-Based Solvent and Process Improvements

participant:

Southern Company Services

project number:

FE0026590

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
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principal investigator:

John Carroll
Southern Company Services
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partners:

Mitsubishi Heavy Industries America; AECOM

start date:

10.01.2015

percent complete:

100%

Figure 1: KM CDR Process™ at Plant Barry

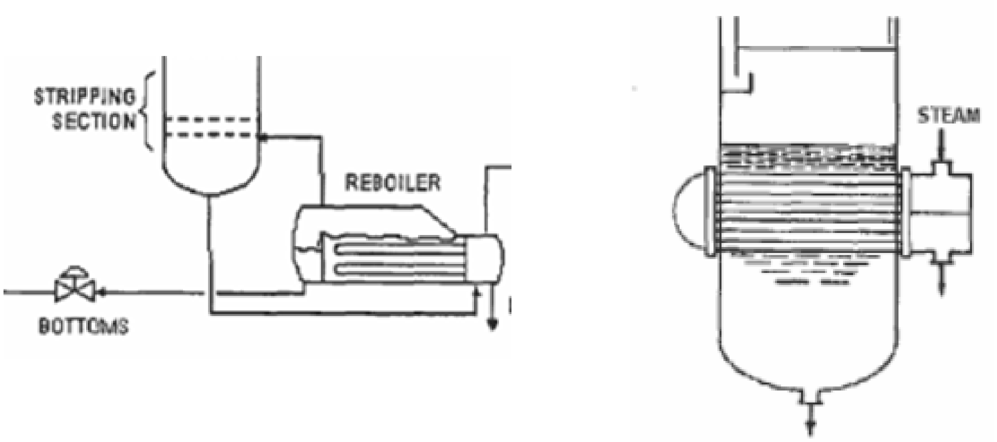

Figure 2: (L) Conventional reboiler and stripper; (R) proposed integrated built-in reboiler

TABLE 1: SOLVENT PROCESS PARAMETERS

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

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent

(e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

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

Solvent Contaminant Resistance – New Solvent A is highly resistant to contaminant compared to conventional solvent MEA.

Solvent Foaming Tendency – New Solvent A has low foaming tendency compared to conventional solvent MEA.

Flue Gas Pretreatment Requirements – Flue gas cooling and SO_x removal unit may be required depending on flue gas conditions.

Solvent Make-Up Requirements – Solvent makeup rate depends on the impurities level in the flue gas but is generally lower than conventional solvent MEA.

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

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

Proposed Module Design –Not applied.

technology advantages

- New Solvent A has potential to reduce steam regeneration requirements by 5 percent from their KS-1^{TM} amine solvent and by 37 percent from MEA.
- Reduced capital and operating cost and footprint for the built-in reboiler.

R&D challenges

- Determining maximum allowable particulate matter concentration at which solvent performance degrades.
- Matching or reducing heat transfer efficiency and steam consumption for the built-in reboiler compared to non-integrated reboiler.
- Minimizing corrosion, scaling, and impurity buildup from testing.
- Integration of process updates with operations at Plant Barry.

status

Phase I has been completed. A preliminary techno-economic analysis of the KM CDR Process™ indicated a cost of CO_2 capture of \$58.8/tonne and cost of electricity (COE) of 133.7mils/kW. Adding the built-in reboiler, particulate matter management, and new solvent further improved costs to \$56.0/tonne CO_2 captured and COE of 130.6 mils/kW. The project was not awarded a Phase II.

available reports/technical papers/presentations

Thomas, J., "Advanced Solvent-Based Carbon Capture Technology Development," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/J-Thomas-SouthernCo26590-Advanced-Solvent-Based-Capture.pdf*

Thomas, J., "Demonstration of Advanced CO_2 Capture Process Improvements for Coal-Fired Flue Gas," Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026590-Kickoff-Presentation.pdf*

Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas

primary project goals

Southern Company Services developed viable heat integration methods for the capture of carbon dioxide (CO_2) produced from pulverized coal (PC) combustion. The project quantified energy efficiency improvements to an existing amine-based CO_2 capture process by utilizing a waste heat recovery, high-efficiency system (HES) and evaluated the technical and economic feasibility of full-scale implementation of this technology.

technical goals

- Reduction of the amount of extraction steam required for sensible heat load in the solvent regeneration system by providing process stream heating through waste heat streams.
- Heating of boiler feed water through waste heat to reduce extraction steam demands on the low-pressure (LP) turbine.
- Increasing LP steam available for power generation or CO_2 regeneration.

technical content

Southern Company Services developed viable heat integration methods for the capture and sequestration of CO_2 produced from PC combustion. A waste heat recovery technology, HES, was integrated with an existing 25-megawatt electric (MW_e) amine-based CO_2 capture process, (MHI's Kansai Mitsubishi Carbon Dioxide Recovery (KM-CDR™) process), at Plant Barry to evaluate improvements in the energy efficiency of the CO_2 capture process. Pilot-scale testing also provided operational experience to determine the stability of the integrated HES/CO_2 capture process, particularly with use of a high-sulfur flue gas. An advanced level of heat integration between the power plant and the CO_2 capture facility is demonstrated by using waste heat to provide process heating to the CO_2 absorber process condensate and boiler feed-water, reducing the extraction steam requirements, making more low pressure steam available for CO_2 regeneration or power generation. The heat integration approach involves the incorporation of a CO_2 cooler within the carbon capture and storage (CCS) plant and a low temperature flue gas cooler (HES) installed downstream of the power plant's air-preheater. The CO_2 cooler is a standard heat exchanger that recovers waste heat from the outlet of the stripper in the CO_2 capture facility and the HES is a form of regenerative heat exchange that extracts waste heat from the flue gas exiting the plant's air-preheater. The HES technology provides other benefits to the host plant, including reduced water usage in the flue gas desulfurization (FGD) due to lower flue gas temperatures, better electrostatic precipitator (ESP) performance due to lower ash

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

Waste Heat Integration

participant:

Southern Company Services

project number:

FE0007525

predecessor projects:

N/A

NETL project manager:

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principal investigator:

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partners:

Mitsubishi Heavy Industries, America, Inc., AECOM

start date:

10.01.2011

percent complete:

100%

resistivity, and enhanced removal of sulfur trioxide (SO_3) and trace metals from the flue gas in existing systems. These improvements have the added benefit of reducing both amine solvent loss and accumulation of metals, thereby reducing operating costs of the solvent capture process.

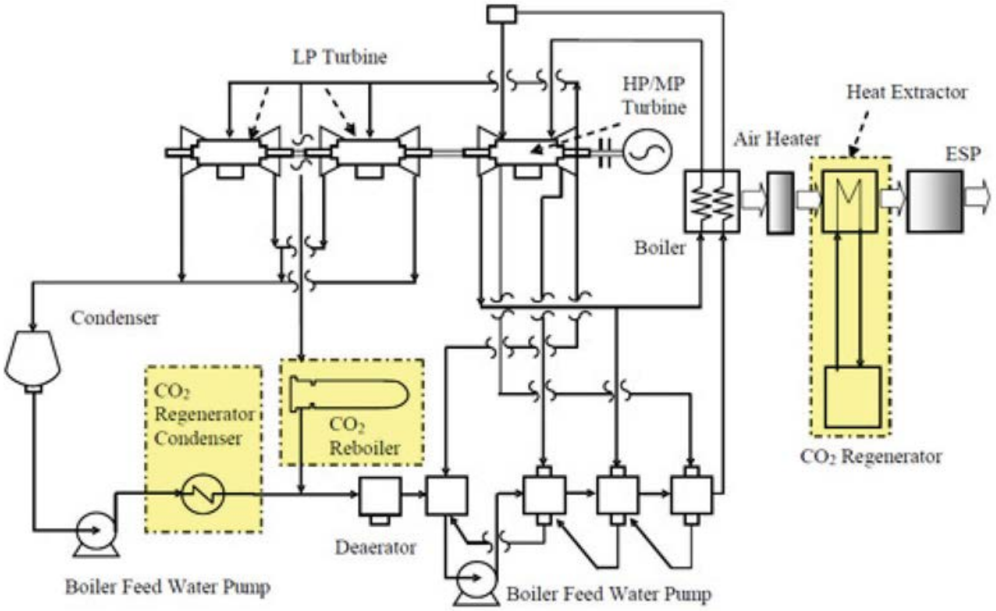

Figure 1: Heat integration of power plant and CCS, including HES

technology advantages

- Costs driven by flue gas compression. The HES provides the efficient use of traditionally wasted heat in coal-fired flue gas and captured CO_2.
- Water usage and parasitic energy loss in carbon capture and storage (CCS) is reduced by the technology.
- The HES accommodates more efficient removal of SO_3 and heavy metals in the ESP by reducing the flue gas temperature and resistivity of fly ash.
- This technology could prove to be a vital method of controlling water usage in FGD due to lower flue gas inlet temperature.
- Potential to simplify the boiler/steam turbine cycles and reduce the number of heat exchange systems in base plant, leading to reduced capital cost.

R&D challenges

- Developing and demonstrating control schemes that maintain proper heat balance in the steam cycle and carbon capture plant.
- Lowering flue gas temperature after the air-preheater can be problematic due to metal corrosion potential as a result of acid gas condensation; developing specific operating parameters and controls to manage the threat is a specific challenge.
- Uncertainty on the reliability of the system with higher sulfur fuels (>1 percent).

status

Operation and testing of the KM-CDR™ CO_2 capture process was completed at the host PC power plant, Plant Barry, with heat integration, confirming an improvement in energy efficiency and cost of electricity. Testing also showed removal of SO_3 to less than 0.05 ppm and removal of other trace metal impurities, confirming an improvement in ESP performance, as well as a reduction in water consumption. The HES was operated for 913 hours for the long-term durability test and showed no damage to tubes or soot blowers and no ash deposition on tube walls.

available reports/technical papers/presentations

Honjo, S., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/S-Honjo-MHIA-Waste-Heat-Integration.pdf*

"Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," Project Closeout Meeting presentation, May 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/DE--FE0007525-Southern-Company-HES-Closeout-Meeting.pdf*

Thomas, J., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/J-Thomas-SouthernCo-Waste-Heat-Integration.pdf*

Thomas, J., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Thomas-Southern-Waste-Heat-Integration-with-Solvent.pdf*

Wall. T., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *https://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/T-Wall-Southern-Waste-Heat-Integration-With-Solvent-Process.pdf*

Wall, T., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *https://www.netl.doe.gov/File%20Library/Events/2013/Co2%20Capture/T-Wall-SouthernCo-Waste-Heat-Integration.pdf*

Dombrowski, K. and Wu, T., "Development and Demonstration of Waste Heat Integration with Solvent Process for More Efficient CO_2 Removal from Coal-Fired Flue Gas," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Events/2012/CO2%20Capture%20Meeting/K-Dombrowski-URS-Waste-Heat-Integration.pdf*

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION SORBENT TECHNOLOGIES

Novel Process that Achieves 10 mol/kg Sorbent Swing Capacity in a Rapidly Cycled Pressure Swing Adsorption Process

primary project goals

Georgia Tech Research Corporation is developing polymeric fibers embedded with metal organic framework (MOF) sorbent in a prototype fiber sorbent module in a sub-ambient rapidly cycled pressure swing adsorption (RCPSA) process. Lab-scale testing on the system will be done with simulated flue gas, followed by modeling and optimization of fiber and hollow fiber module operation, and techno-economic analysis of a full-scale system.

technical goals

- Synthesize the metal organic framework (MOF) sorbent.
- Perform testing for sub-ambient sorption isotherms.
- Complete spinning of hollow fibers containing the MOF.
- Construct the rapid cycle pressure swing adsorption system and complete testing of hollow fiber sorbent modules and hollow fiber sorbent modules with phase change materials.
- Model and optimize fiber and hollow fiber module operation as well as flue gas conditioning optimization.
- Prepare an overall system techno-economic analysis.

technical content

Georgia Tech is developing a process to achieve 10 mole per kg sorbent swing capacity using a rapidly cycled pressure swing adsorption process. The sorbent system includes novel polymeric hollow fibers embedded with MOF. An example of the hollow fibers is shown in Figure 1. MOF are known to have good carbon dioxide (CO_2) capacity and rapid adsorption/desorption kinetics if kept isothermal. The team is developing a scalable, modular contactor for the sorbents with high surface area, low pressure drop and low mass transfer resistance. A stationary phase-change material is incorporated in the hollow fiber sorbents (Figure 2) to maintain isothermal adsorption/desorption. This material, which has a melting/freezing point equivalent to the system operating temperature, will melt as heat is released as CO_2 is adsorbed and freeze as CO_2 is desorbed, therefore no steam or cooling water is needed. The system consists of modules containing the hollow fibers.

technology maturity:

Lab-Scale, Simulated Flue Gas

project focus:

Pressure Swing Adsorption Process with Novel Sorbent

participant:

Georgia Tech Research Corporation

project number:

FE0026433

predecessor projects:

N/A

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partners:

Inmondo Tech, Inc.

start date:

10.01.2015

percent complete:

70%

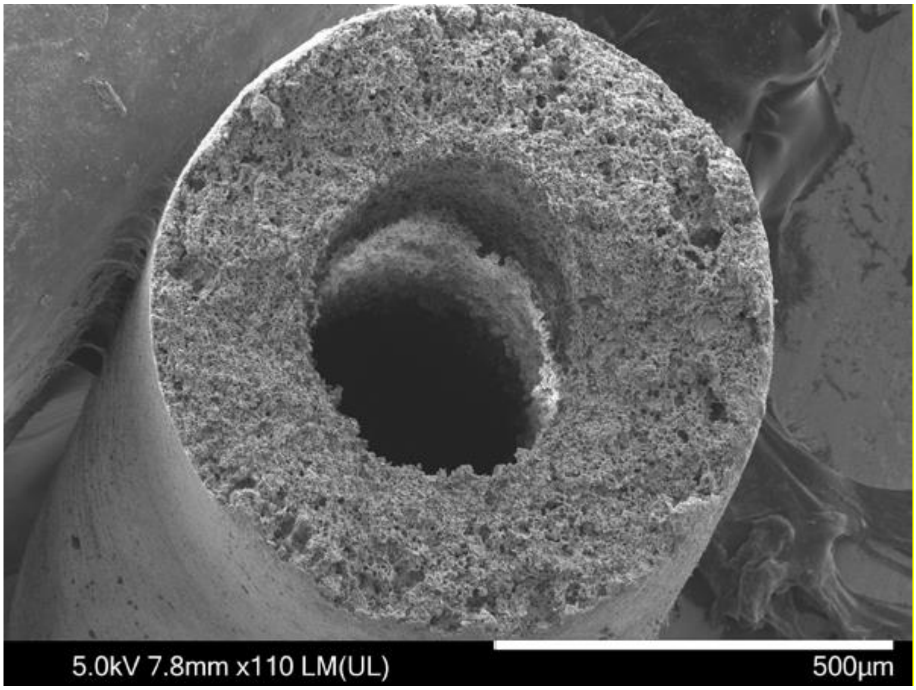

Figure 1: UiO-66/cellulose acetate fiber sorbents: ~55 wt% UiO-66.

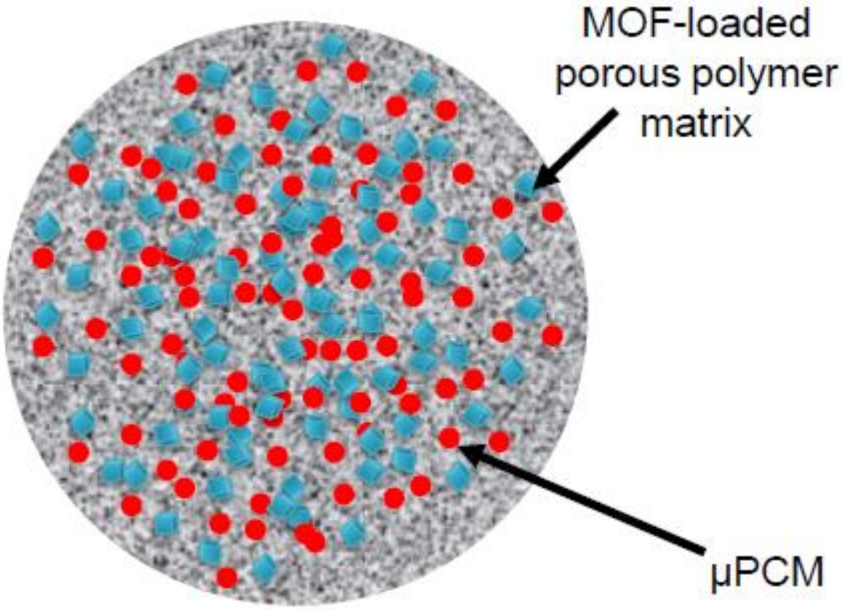

Figure 2: Phase-change material in hollow fiber sorbents

The overall CO_2 capture process is shown in Figure 3. The conditioned flue gas is passed through a sub-ambient heat exchanger before entering the PSA unit containing the hollow fiber sorbent modules. The steps of the RCPSA process—pressurization, adsorption, depressurization, desorption—are shown in Figure 4. Sub-ambient conditions increase adsorption selectivity and working capacity.

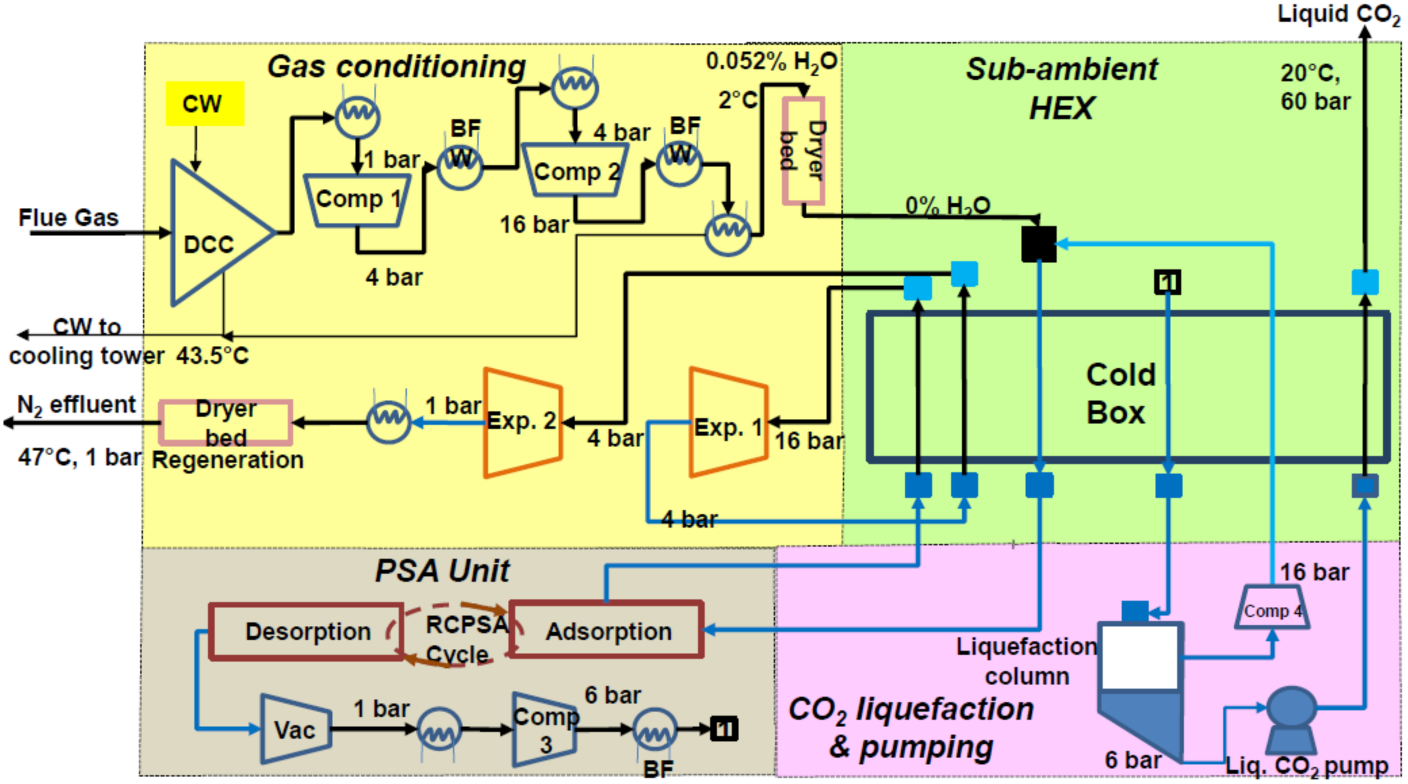

Figure 3: Process flow diagram

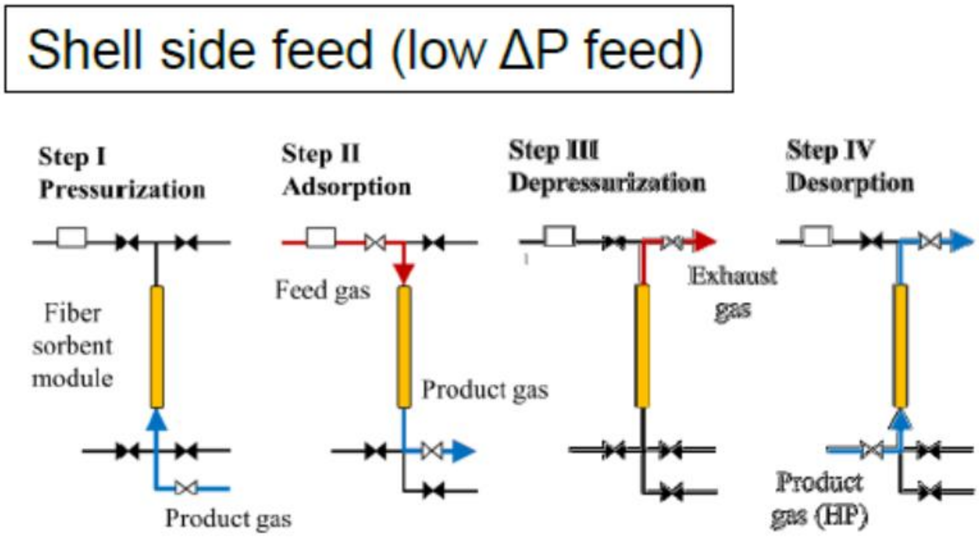

Figure 4: Pressure swing adsorption process

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	1,200	1,200
Average Particle Diameter (diameter of fiber)	mm	1.2	0.8
Particle Void Fraction (void fraction of the fiber bed)	m^3/m^3	0.4	0.35
Packing Density	m^2/m^3	1,000	2,000
Solid Heat Capacity @ STP	kJ/kg-K	1,600	1,600
Crush Strength	kg$_f$	unknown	not specified
Manufacturing Cost for Sorbent	$/kg	unknown	30
Adsorption			
Pressure	bar	2	2
Temperature	°C	-30	-30
Equilibrium Loading	g mol CO_2/kg	10.2	delta (ads-des) =10
Heat of Desorption	kJ/mol CO_2	21.5	< 35
Desorption			
Pressure	bar	0.1	0.3
Temperature	°C	-30	-30
Equilibrium CO_2 Loading	g mol CO_2/kg	1.6	Delta (ads-des) =10
Heat of Adsorption	kJ/mol CO_2	21.5	< 35
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed fiber/parallel flow/cyclic	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	92/80/1	92/95/1
Adsorber Pressure Drop	bar	0.1	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	485	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Physisorption.

Sorbent Contaminant Resistance – High, resistant to humid SO_2 at 50 ppm.

Sorbent Attrition and Thermal/Hydrothermal Stability – N/A.

Flue Gas Pretreatment Requirements – Pressurization, dehydration, cooling.

Sorbent Make-Up Requirements – None.

Waste Streams Generated – Clean (100%RH) N_2.

Process Design Concept – Discussed above.

technology advantages

- High working capacity of MOF sorbents.
- High contact area, low pressure drop and low mass transfer resistance for the modules.
- Sub-ambient conditions increase adsorption selectivity and working capacity.

- The efficiency of the pressure swing cycle is boosted by installing a stationary phase-change material in the fiber sorbents that will isothermally melt upon release of sorption enthalpy and conversely isothermally freeze upon CO_2 desorption, requiring no steam or cooling water.
- Improved sulfur oxide (SO_x) removal from cold water.
- CO_2 liquefaction and pumping can be used instead of CO_2 compression.
- Sub-ambient heat exchange and CO_2 liquefaction are commercially demonstrated.

R&D challenges

- Integrating MOF into the fiber to maintain CO_2 capacity.
- Effective seals for fiber modules.

status

The UiO-66 MOF has been synthesized and fibers were spun containing the MOF. Breakthrough experiments were performed in the RCPSA system. Phase change material was successfully incorporated into the MOF fiber sorbents and into the sorbent modules.

available reports/technical papers/presentations

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/R-Lively-GIT-10-MOLKG-Sorbent-Swing-Capacity.pdf*

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/R-Lively-GeorgiaIT-Sub-ambient-Pressure-Swing-Adsorption.pdf*

Lively, R., et al. "Enabling 10 mol/kg Swing Capacity via Heat Integrated Sub-ambient Pressure Swing Adsorption," Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026433-Kickoff-Meeting.pdf*

Park, J,. et al. "Establishing upper bounds on CO2 swing capacity in sub-ambient pressure swing adsorption via molecular simulation of metal–organic frameworks" J. Mater. Chem. A, 2017, 5, 12258-12265 *http://pubs.rsc.org/-/content/articlehtml/2017/ta/c7ta02916k*

Park, J., et al. "How Reproducible Are Isotherm Measurements in Metal–Organic Frameworks?" Chem. Mater., 2017, 29 (24), pp 10487–10495
http://pubs.acs.org/doi/abs/10.1021/acs.chemmater.7b04287

Evaluation of Amine-Incorporated Porous Polymer Networks as Sorbents for Post-Combustion CO_2 Capture

primary project goals

Texas A&M University is developing amine-incorporated porous polymer networks (aPPN) for use as sorbents for post-combustion carbon dioxide (CO_2) capture. The project includes lab-scale fixed-bed testing of sorbent performance and the scale-up of sorbent synthesis.

technical goals

- Complete initial CO_2 adsorption testing with multiple aPPN formulations.
- Identify synthesis conditions that result in optimal sorbent performance and cost.
- Produce approximately 200 grams of at least the two top-performing sorbent formulations.
- Determine CO_2 working capacity of top-performing sorbent formulation after 30 cycles in automated fixed-bed testing.
- Scale-up to synthesis of at least 1 kg of top performing aPPN.
- Complete fixed-bed cycling tests with top performing aPPN in presence of moisture and sulfur dioxide (SO_2).
- Perform initial technical and economic feasibility study.

technical content

Porous polymer networks are crosslinked polymers with high surface area, low density, and high thermal and chemical stability. These properties can be advantageous for CO_2 capture sorbents. The incorporation of amine groups also provides the capability to fine tune CO_2 selectivity. Texas A&M is developing novel amine-incorporated porous polymer networks with high CO_2 uptake capacities and working capacities. Multiple aPPN formulations, specifically sorbents PPN-150 and PPN-151 series, are being synthesized and tested. Sorbent synthesis parameters, including reaction time, reaction headspace, solvent systems, and amine loading times and conditions, are being optimized. The PPN-150 series molecule is shown in Figure 1.

technology maturity:

Lab-Scale, Simulated Flue Gas

project focus:

Porous Polymer Networks

participant:

Texas A&M University

project number:

FE0026472

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Hong Cai "Joe" Zhou
Texas A&M
zhou@chem.tamu.edu

partners:

framergy™, Inc.

start date:

10.01.2015

percent complete:

70%

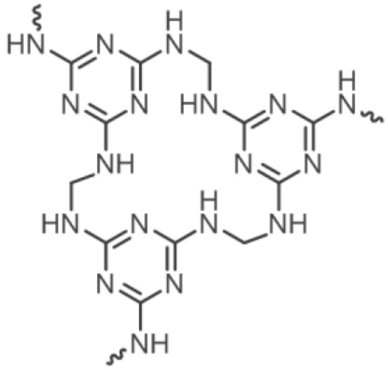

Figure 1: PPN-150 series

technology advantages

- PPNs have high surface area, extremely low density, and high thermal and chemical stability.
- Amine-tethered PPNs show large increase in CO_2 uptake capacities at low pressures and high CO_2/nitrogen (N_2) selectivity.

R&D challenges

- Reducing the cost of sorbent production.
- Scaling up sorbent production while maintaining sorbent performance.

status

Texas A&M has synthesized and screened multiple PPN candidates and demonstrated that their PPN-150 series amine-incorporated porous polymer network sorbents can achieve greater than 0.1 kg/kg CO_2 working capacity. Sorbent synthesis parameters, including reaction time, reactor headspace, solvent systems, and amine loading times and conditions, have been optimized. Synthesis of PPN-150 series sorbent has been successfully scaled to a 200-gram batch size. Fixed bed regeneration testing indicated a regenerative energy demand at 85 °C of 1.0 MJ/kg CO_2 for PPN-150-DETA and 1.8 MJ/kg CO_2 for PPN-151-DETA.

available reports/technical papers/presentations

Zhou, H. "Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture," presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/H-C-J-Zhou-Texas-A-M-Porous-Polymer-Networks.pdf*

Zhou, H. "Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture," presented at the Budget Period 2 Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026472-BP2-Review-Presentation-08-15-17.pdf*

Zhou, H. and Perry, Z. "Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/J-Zhou-TAMU-Amine-Incorporated-Porous-Polymer-Networks.pdf*

Zhou, H. "Evaluation of Amine-Incorporated Porous Polymer Networks (aPPNs) as Sorbents for Post-Combustion CO_2 Capture," presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026472-Kick-off-Presentation.pdf*

Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture

primary project goals

SRI International operated a bench-scale test unit for post-combustion carbon dioxide (CO_2) capture to demonstrate their process using a novel low-cost, low-energy, and high-capacity carbon sorbent in a single column integrating both the absorber and desorber. SRI also designed a 0.5-megawatt electric (MW_e) pilot-scale test unit.

technical goals

- Operate SRI's 40-kilowatt electric (kW_e) sorbent test unit on actual flue gas at the National Carbon Capture Center (NCCC) to provide data for initial techno-economic assessment and for pilot plant design.
- Design 0.5-MW_e slipstream pilot plant for post-combustion CO_2 capture using the novel sorbent.
    - Complete preliminary techno-economic assessment and environment, health, and safety (EH&S) assessment based on data from testing.
- Develop sorbent formulation and method of manufacture.

technical content

SRI International tested their process for post combustion CO_2 capture on the bench-scale using their novel carbon sorbent. The technology is based on the sorbent developed in a previously funded DOE project NT0005578. This novel sorbent, manufactured by ATMI, Inc., is composed of carbon microbeads, as shown in Figure 1. These microbeads show excellent CO_2 capacity and selectivity, fast adsorption/desorption kinetics, and good resistance to agglomeration and attrition, allowing for reductions in both capital and operating expenses. Reduced steam regeneration requirements in the process can reduce the parasitic power load.

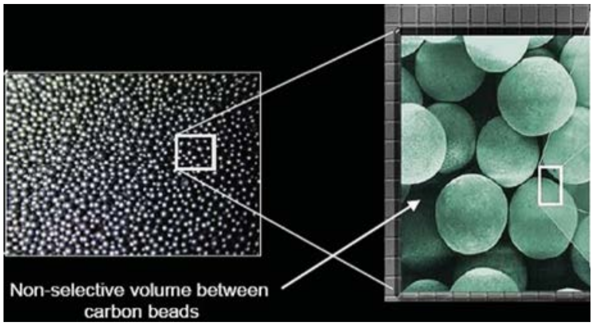

Figure 1: Graphic displays of novel carbon pellets sorbent

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Novel Solid Sorbent

participant:

SRI International

project number:

FE0013123

predecessor projects:

NT0005578

NETL project manager:

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principal investigator:

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partners:

ATMI, Inc.; Linde, LLC;
Electric Power Research Institute

start date:

10.01.2013

percent complete:

100%

Figure 2 depicts the proposed sorbent system for an existing coal-fired power plant. Flue gas first enters an existing flue gas desulfurization (FGD) system where most of the sulfur content is removed. The gas is then cooled before entering the continuous falling-bead sorbent reactor which integrates the adsorber and stripper in a single vertical column, providing a low pressure drop for gas flow and minimizing physical handling of the high capacity carbon sorbent (0.05–0.08 kg of CO_2 per kg of sorbent). As the gas stream passes over the lean sorbent, CO_2 is removed from the gas and adsorbed by the sorbent. The loaded sorbent cascades down the separation column and is heated by low-pressure steam, causing the sorbent to release the adsorbed CO_2. The CO_2 is siphoned off to a compressor where it can be prepared for sequestration. The sorbent is then dried, cooled, and sent back into the separation column for reuse and the cycle begins again.

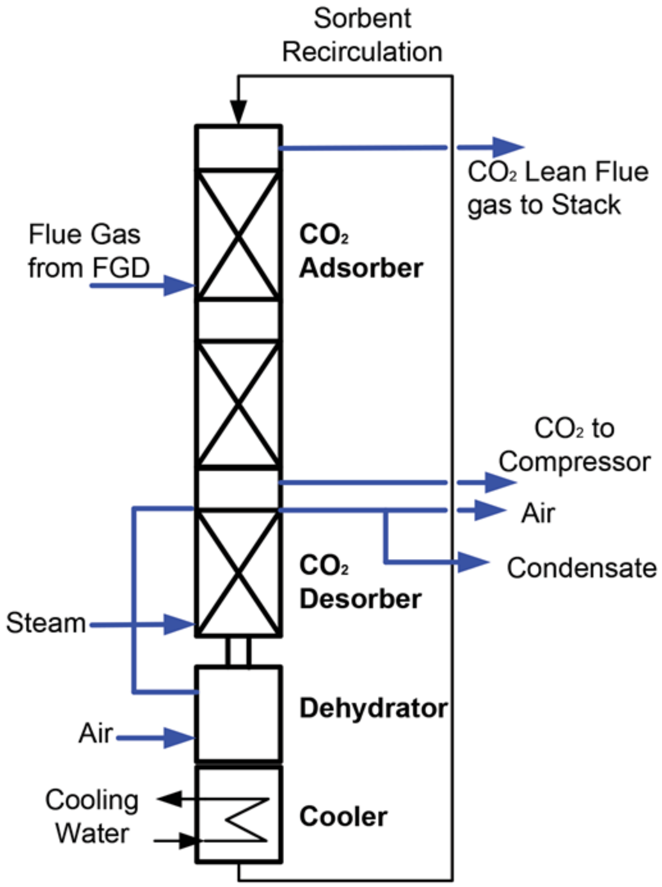

Figure 2: Sorbent system

SRI also designed a 0.5-MW_e pilot-scale system based on this technology. The system includes a heat exchanger for recovering sensible heat from the hot, regenerated sorbent for use to preheat the sorbent from the adsorber. The system is designed for a nominal flue gas flow of 70 cubic feet per minute (cfm) and a CO_2 capture capacity of approximately 1 ton/day.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,100	1,100
Bulk Density	kg/m^3	700	700
Average Particle Diameter	mm	0.2	0.2
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.1×10^9	1.1×10^9
Solid Heat Capacity @ STP	kJ/kg-K	1.0	1.0
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	proprietary	proprietary
Adsorption			
Pressure	bar	1	1
Temperature	°C	20	20
Equilibrium Loading	g mol CO_2/kg	4	4
Heat of Adsorption	kJ/mol CO_2	27	27
Desorption			
Pressure	bar	1	1
Temperature	°C	100	100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.96	0.96
Heat of Desorption	kJ/mol CO_2	27	27
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	continuous, moving bed	
Flue Gas Flowrate	kg/hr	1,860	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 1	
Adsorber Pressure Drop	bar	0.005	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Rapid physical adsorption and desorption rates: The adsorption of CO_2 occurs on the micropores of the sorbent with low activation energy (<5 kJ/mole), allowing rapid equilibrium. Similarly, the adsorbed CO_2 is desorbed rapidly at the regeneration temperature (≈100 °C), and the sorbent performance can be predicted by equilibrium models.

Sorbent Contaminant Resistance – The sorbent is pure carbon and generally resistant to many contaminants. The sulfur dioxide (SO_2) needs to be reduced to <10 parts per million (ppm) levels, preferably to 1 ppm level. Nitrogen oxides (NO_x) can be present at ≈50 ppm levels. Fly-ash particles in flue gas downstream of an electrostatic precipitator do not appear to interfere with CO_2 adsorption.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent granules are hard and attrition-resistant. No observable attrition was noticed in a recent field test conducted over 7,000 cycles of adsorption and regeneration. The sorbent has a high hydro-thermal stability and direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.

Flue Gas Pretreatment Requirements – Reduce SO_2 levels to <5 ppm. The flue gas needs to be cooled to ≈25 °C.

Sorbent Makeup Requirements – Preliminary data suggest multi-year lifetime for sorbent makeup.

Waste Streams Generated – The sorbent particles are hard and attrition-resistant, and no fine sorbent particles are generated during operation. Steam condensate from the dehydrator may need to be treated before cycling back to the steam boiler.

Process Design Concept – The module will be located between FGD and flue gas chimney.

technology advantages

- Low cost carbon sorbent.
- Low activation energy and rapid cycling for adsorption/desorption.
- Reduced capital and operating costs.
- The sorbent has a high capacity for CO_2 adsorption (20 wt% at 1 atm CO_2) and good selectivity for CO_2 over other flue gas components (CO_2-N_2 separation factor >20).
- Low heat capacity minimizes thermal energy required to heat the sorbent to regeneration temperature.
- Carbon sorbent particles have excellent attrition resistance, minimal dust generation, and high resistance to agglomeration.
- High hydrothermal stability: Direct heating with steam can be used for CO_2 desorption. The sorbent regenerated at the elevated temperature can be cooled by evaporative cooling of moisture adsorbed on the sorbent.
- High thermal conductivity: The thermal conductivity of 0.8 W/m-K enables rapid thermal equilibrium between the surface and interior of the microbeads.

- The sorbent is essentially hydrophobic, indicating little interaction between the condensed water and the sorbent. The thermal energy required to desorb the condensed water is significantly less than that required to evaporate water from oxide surfaces such as those found in molecular sieves (zeolites), alumina, and silica.
- Continuous, falling microbead sorbent reactor geometry integrates the adsorber and stripper in a single vertical column.
    - Low pressure drop for gas flow.
    - Minimal physical handling of solvent.

R&D challenges

- Other elements of the flue gas, such as sulfur oxides (SO_x), may compete with CO_2 in being adsorbed by the sorbent, reducing the amount of CO_2 that is adsorbed as the gas passes through the reactor.

status

The project was completed on June 30, 2016. SRI completed approximately 250 hours of testing on their 40-kW_e bench-scale unit using actual flue gas at the NCCC. The project achieved CO_2 purity of 93 percent and CO_2 capture efficiency of 67 percent. SRI indicated that 90 percent capture is achievable by decreasing the sorbent temperature and increasing the adsorber height. A basic engineering design package was completed for the 0.5-MW_e pilot unit.

available reports/technical papers/presentations

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," presented at Project Review Meeting, Pittsburgh, PA, June 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0013123-Project-Review-Presentation-06-21-2016.pdf*

Hornbostel, M. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," presented at 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/M-Hornbostel-SRI-Pilot-Advanced-Sorbent-Process.pdf*

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture," Project Review Meeting, Pittsburgh, PA, October 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0013123-Project-Review-Presentation-10-28-2014.pdf*

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Krishnan, G., "Development of Novel Carbon Sorbents for CO_2 Capture," Final Technical Report, March 2014. *http://www.osti.gov/scitech/servlets/purl/1132602*.

Krishnan, G. "Pilot-Scale Evaluation of an Advanced Carbon Sorbent-Based Process for Post-Combustion Carbon Capture", presented at Project Kickoff Meeting, Pittsburgh, PA, December 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/FE0013123-Kickoff-Presentation-12-04-2013.pdf*

Krishnan, G. "Development of Advanced Carbon Sorbents for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO_2%20Capture/G-Krishnan-SRI-Advanced-Carbon-Sorbents.pdf*.

Krishnan, G. "Development of Advanced Carbon Sorbents for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO_2/development-of-advanced-carbon-sorbents-july2012.pdf*.

Hornbostel, M. "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.
http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/22Aug11-Hornbostel-SRI-Novel-Carbon-Sorbents.pdf.

Krishnan, G. "Development of Novel Carbon Sorbents for CO_2 Capture," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.
http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/monday/Gopala%20Krishnan-NT0005578.pdf.

Krishnan, G, "Development of Novel Carbon Sorbents for CO_2 Capture – Project Overview," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.
http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5578%20SRI%20carbon%20sorbent%20%28Hornbostel%29%20mar09.pdf.

Sorbent Based Post-Combustion CO_2 Slipstream Testing

primary project goals

TDA Research is designing, constructing, and operating a slipstream 0.5-MW_e pilot-scale process for post-combustion carbon dioxide (CO_2) capture using their low-cost alkalized alumina sorbent to conduct parametric and long-term, steady-state testing to demonstrate the effectiveness of the technology to reduce the cost of CO_2 capture and to develop scale-up conditions for the process.

technical goals

- Modify bench-scale unit to mimic proposed pilot-plant configuration and conduct testing in bench unit to optimize process and collect data for pilot-plant design.
- Characterize breakthrough performance and pressure drop for different sorbent pellet sizes.
- Design pilot-plant unit based on developed low-cost alkalized alumina sorbent technology.
- Scale-up production of sorbent.
- Fabricate and install pilot-plant unit at the National Carbon Capture Center (NCCC).
- Perform parametric and steady-state testing on pilot plant using actual flue gas.
- Update EH&S study and techno-economic analysis based on pilot-plant testing results.

technical content

TDA Research is designing, constructing, and operating a slipstream 0.5-MW_e pilot-scale process for post-combustion CO_2 capture. This technology is based on their novel sorbent developed previously in a Department of Energy (DOE)-funded project DE-NT0005497. TDA's CO_2 capture system uses a dry alkalized alumina sorbent. The regenerable sorbent acts as a physical adsorbent for CO_2. The CO_2 capture process runs near isothermally at around 140–150 °C in both adsorption and regeneration, requiring no heating or cooling between adsorption and regeneration steps. The sorbent is regenerated with low pressure (15.5 pounds per square inch absolute [psia]) steam. The sorbent shows excellent tolerance to contaminants, including sulfur dioxide (SO_2) and nitrogen oxides (NO_x).

An overall schematic of TDA's system is shown in Figure 1, consisting of two primary components: (1) the adsorber/regenerator unit and (2) the CO_2 compression and purification unit. The process is designed for the sorbent to remove the CO_2 from the flue gas at intermediate temperature and near ambient pressure, and then be regenerated with low-pressure superheated steam.

technology maturity

Pilot-Scale, Actual Flue Gas Slipstream (0.5 MW_e)

project focus:

Alkalized Alumina Solid Sorbent

participant:

TDA Research, Inc.

project number:

FE0012870

predecessor projects:

NT0005497

NETL project manager:

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principal investigator:

Jeannine Elliott
TDA Research, Inc.
jelliott@tda.com

partners:

University of California at Irvine, Porocel, Babcock and Wilcox, Louisiana State University, Western Research Institute

start date:

02.03.2014

percent complete:

70%

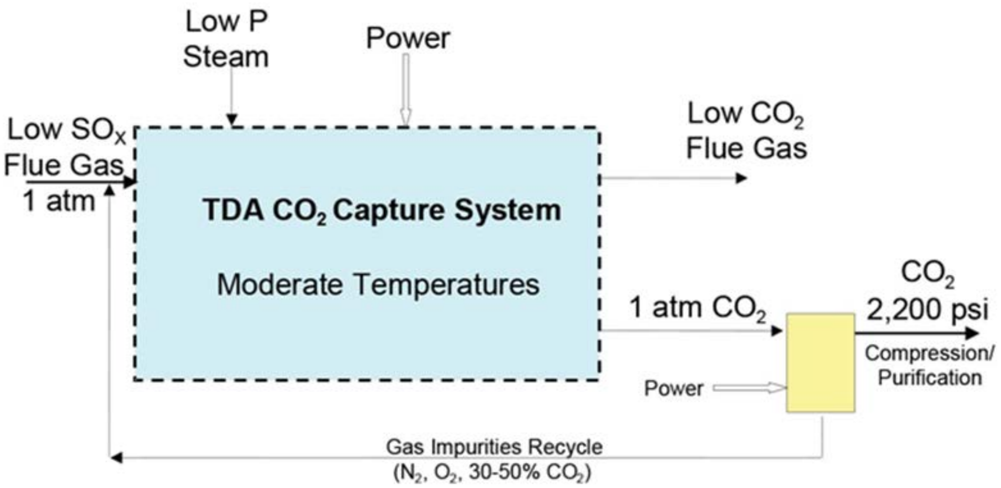


Figure 1: Schematic of TDA's CO$_2$ capture system

The slipstream pilot plant is a 0.5-MW$_e$ skid mounted system, to be installed at the NCCC. The adsorber/regeneration system is made up of multiple fixed beds containing the alumina sorbent that switch between adsorption, regeneration, and purge operations. The complete slipstream pilot unit includes adsorber/regeneration beds, heat exchangers, blowers, valving, and instrumentation.

Slipstream pilot-unit testing under both parametric and steady-state conditions using actual coal-fired flue gas provides data and recommended operating conditions to update the techno-economic analysis and EH&S assessment as well as for definition of recommended scale-up conditions. The project aims to demonstrate the novel system for reduction in carbon capture cost.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

<table>
<tr><th>Sorbent</th><th>Units</th><th colspan="3">Current R&D Value</th><th colspan="3">Target R&D Value</th></tr>
<tr><td>True Density @ STP</td><td>kg/m³</td><td colspan="3">750</td><td colspan="3">750</td></tr>
<tr><td>Bulk Density</td><td>kg/m³</td><td colspan="3">520</td><td colspan="3">520</td></tr>
<tr><td>Average Particle Diameter</td><td>mm</td><td colspan="3">1.5</td><td colspan="3">3.175</td></tr>
<tr><td>Particle Void Fraction</td><td>m³/m³</td><td colspan="3">0.55</td><td colspan="3">0.55</td></tr>
<tr><td>Packing Density</td><td>m²/m³</td><td colspan="3">9.4E+07</td><td colspan="3">9.4E+07</td></tr>
<tr><td>Solid Heat Capacity @ STP</td><td>kJ/kg-K</td><td colspan="3">0.72</td><td colspan="3">0.72</td></tr>
<tr><td>Crush Strength</td><td>kgf</td><td colspan="3">8</td><td colspan="3">8</td></tr>
<tr><td>Manufacturing Cost for Sorbent</td><td>$/kg</td><td colspan="3">6.5</td><td colspan="3">3</td></tr>
<tr><th>Adsorption</th><td></td><td colspan="3"></td><td colspan="3"></td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="3">1.12</td><td colspan="3">1.12</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">140</td><td colspan="3">140</td></tr>
<tr><td>Equilibrium Loading</td><td>g mol CO₂/kg</td><td colspan="3">1.0</td><td colspan="3">1.5</td></tr>
<tr><td>Heat of Adsorption</td><td>kJ/mol CO₂</td><td colspan="3">-12.5 to -41.9</td><td colspan="3">-12.5 to -41.9</td></tr>
<tr><th>Desorption</th><td></td><td colspan="3"></td><td colspan="3"></td></tr>
<tr><td>Pressure</td><td>bar</td><td colspan="3">1.17</td><td colspan="3">1.17</td></tr>
<tr><td>Temperature</td><td>°C</td><td colspan="3">150</td><td colspan="3">150</td></tr>
<tr><td>Equilibrium CO₂ Loading</td><td>g mol CO₂/kg</td><td colspan="3">0.93</td><td colspan="3">1.0</td></tr>
<tr><td>Heat of Desorption</td><td>kJ/mol CO₂</td><td colspan="3">12.5 to 41.9</td><td colspan="3">12.5 to 41.9</td></tr>
<tr><th>Proposed Module Design</th><td></td><td colspan="6">(for equipment developers)</td></tr>
<tr><td>Flow Arrangement/Operation</td><td>—</td><td colspan="6">Multiple fixed bed</td></tr>
<tr><td>Flue Gas Flowrate</td><td>kg/hr</td><td colspan="6">2,273</td></tr>
<tr><td>CO₂ Recovery, Purity, and Pressure</td><td>% / % / bar</td><td colspan="2">90</td><td colspan="2">95</td><td colspan="2">1.013</td></tr>
<tr><td>Adsorber Pressure Drop</td><td>bar</td><td colspan="6">0.02</td></tr>
<tr><td>Estimated Adsorber/Stripper Cost of Manufacturing and Installation</td><td>$\frac{\$}{kg/hr}$</td><td colspan="6">—</td></tr>
</table>

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The sorbent is an adsorbent and is regenerated with steam.

Sorbent Contaminant Resistance – Based on extended cycling 1,500 hours with simulated flue gas with 13.8 percent CO_2, 104 parts per million (ppm) SO_2, 3 percent oxygen (O_2), and 9 percent water (H_2O), sorbent life was calculated to be 1 year with 5ppm of SO_2. No effect of NO_x on capacity was seen after 200 cycles with 739 ppm nitric oxide (NO) and 84 ppm nitrogen dioxide (NO_2).

Sorbent Attrition and Thermal/Hydrothermal Stability – None provided.

Flue Gas Pretreatment Requirements – Flue gas should have <5 ppm sulfur oxides (SO_x).

Sorbent Makeup Requirements – 15 percent per year.

Waste Streams Generated – None known.

Process Design Concept – See Figure 1 above.

Proposed Module Design – Note the module location, as well as the pressure, temperature and composition of the gas entering the module. TDA's CO_2 capture system is located downstream of the FGD unit. The adsorbent removes dilute CO_2 from the flue gas (10–14 percent CO_2, 8–10 percent H_2O, <5 ppm SO_2) at intermediate temperature (140 °C) and near ambient pressure.

technology advantages

- Inexpensive, durable sorbent.
- Low pressure (17 psi) steam for sorbent regeneration, low regeneration energy.
- Near isothermal operation.
- No heat recovery from solids required.
- Rapid adsorption/regeneration kinetics due to surface-only adsorption.
- Low heat of adsorption.
- Counter-current operation maximizes capture efficiency and sorbent loading.

R&D challenges

- Minimize the parasitic demands from the sorbent system.
- Effectively produce a sorbent from low-cost raw materials with extensive regenerative life.

status

TDA Research has completed design of the 0.5-MW_e scale pilot plant test unit and fabrication is underway. The skid will be installed at NCCC followed by parametric and steady state testing using an actual flue gas slipstream.

available reports/technical papers/presentations

Elliott, J. and Yi, F. "Sorbent Based Post-Combustion CO_2 Slipstream Testing," Presented at 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/J-Elliott-TDA-Post-Combustion-CO2-Slipstream-Testing.pdf*

Elliott, J., "Post-Combustion CO_2 Capture with Low Cost Solid Sorbent Slipstream Testing," Presented at 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/J-Elliott-TDA-Slipstream-Test-of-Sorbent-Based-Capture.pdf*

Elliott, J. and Copeland, B. "Sorbent Based Post-Combustion CO_2 Slipstream Testing," Presented at 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Elliot-TDA-Sorbent-Slipstream-Testing.pdf*

Elliott, J., et al. "Sorbent Based Post-Combustion CO_2 Slipstream Testing," Presented at 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/J-Elliot-TDA-Sorbent-Based-Post-Combustion-CO2-Slip-Stream.pdf*.

Elliott, J., et al. "Sorbent Based Post-Combustion CO_2 Slipstream Testing," Project Kick-Off Meeting Presentation, Pittsburgh, PA, May 20, 2014. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/FE0012870-Kickoff-Mtg-05-2014.pdf*.

Elliot, J.; and Copeland, R. "Low-Cost Solid Sorbent for CO_2 Capture on Existing Coal-Fired Power Plants," Final Report, November 15, 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/05497-Final-Report-083113.pdf*.

Elliot, J., and Srinivas, G. "Low-Cost Sorbent for CO_2 Capture on Existing Plants," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/low-cost-sorbent-july2012.pdf*

Elliot, J., and Srinivas, G. "Post-Combustion CO_2 Capture with Alkalized Alumina," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/5497%20TDA%20sorbent%20%28Elliott%29%20mar09.pdf*.

Elliot, J., Srinivas, G., and Copeland, R. "Low-Cost Sorbent for Capturing CO_2 Emissions Generated by Existing Coal-Fired Power Plants," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/cO2capture/presentations/monday/Jeannine%20Elliott-NT0005497.pdf*.

Elliot, J., Srinivas, G., and Copeland, R. "Low-Cost Solid Sorbent for CO_2 Capture on Existing Coal-Fired Power Plants," presented at the 26th Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 2009. *http://www.tda.com/Library/docs/PCC%20Sept%202009%20v3.pdf*.

Elliot, J., and Srinivas, G. "Low-Cost Sorbent for Capturing CO_2 Emissions Generated by Existing Coal-Fired Power Plants–Project Overview," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/low-cost-sorbent-mar2009.pdf*

Lab- and Bench-Scale Applications for Research and Development of Tranformational Carbon Dioxide Capture

primary project goals

Research Triangle Institute (RTI) is developing novel third generation fluidizable solid sorbents for their sorbent-based carbon dioxide (CO_2) capture process. Two different types of sorbents are being developed, based on hybrid metal organic frameworks (MOF) and hybrid phosphorus dendrimers (*P*-dendrimers), with long-term performance testing of the most promising sorbents in a fluidized bed reactor.

technical goals

- Design, synthesize, and optimize two novel fluidizable CO_2 adsorbents based on hybrid MOFs and hybrid phosphorus dendrimers.
- Demonstrate superior performance of these solid sorbents at lab-scale in a packed bed reactor.
- Evaluate impact of flue gas contaminants such as sulfur oxides (SO_x), nitrogen oxides (NO_x), oxygen (O_2), water (H_2O).
- Scale up production of selected sorbents in fluidizable form.
- Complete performance testing in lab-scale fluidized bed reactor.
- Conduct a high-level techno-economic analysis.

technical content

RTI is developing novel hybrid fluidizable sorbents for CO_2 capture based on hybrid MOFs and hybrid *P*-dendrimers.

The hybrid MOF-based sorbents are based on impregnating polyethylenimine (PEI) on a MOF-silica support. For this sorbent, the silica provides attrition resistance, fluidizability, low cost and acceptable density. The MOF has very high surface area and tunable pore sizes. The PEI is a polymer with a repeating amine unit, providing high amine content, high CO_2 affinity, and a relatively low cost. RTI has developed a new approach for MOF-silica hybrid preparation using solid state synthesis. Hybrid MOF-silica prepared from this method exhibited high MOF loading, excellent MOF dispersion and homogeneity, and enhanced attrition resistance and fluidizability. Figure 1 shows the high MOF loading in the silica using a confocal microscope.

technology maturity:

Lab-Scale, Simulated Flue Gas

project focus:

Fluidizable Solid Sorbents

participant:

Research Triangle Institute (RTI)

project number:

FE0026432

predecessor projects:

N/A

NETL project manager:

Steve Mascaro
steve.mascaro@netl.doe.gov

principal investigator:

Dr. Mustapha Soukri
RTI
msoukri@rti.org

partners:

N/A

start date:

10.01.2015

percent complete:

85%

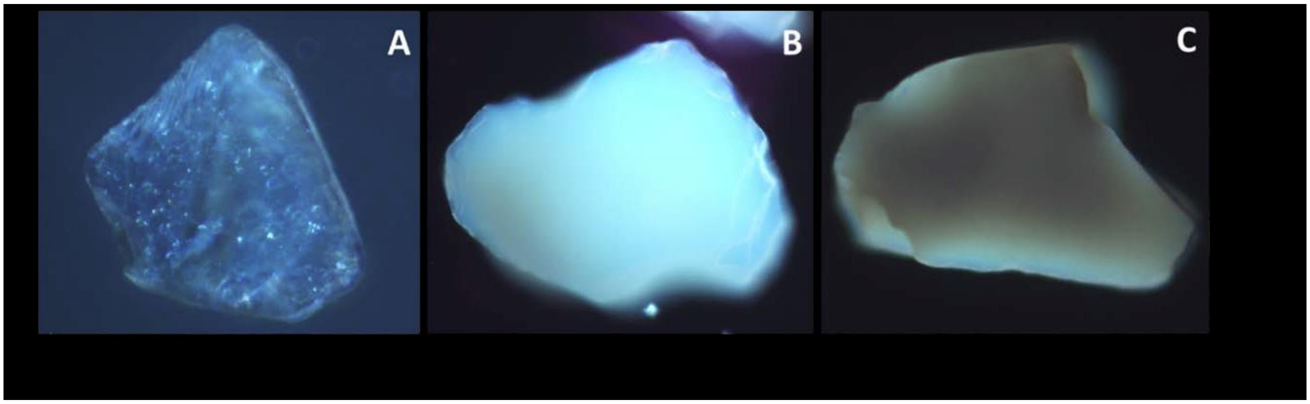


Figure 1: MOF loading in silica: (A) transparent amorphous silica; (B) 20% MOF; (C) 35% MOF

Dendrimers are repeatedly branched, large spherical molecules. *P*-dendrimers provide a rigid scaffold, hydrophobic interior and well defined spatial location of the functional groups, along with high thermal stability. An example of a dendrimer structure is shown in Figure 2. RTI is developing an approach to produce sorbents by covalently grafting amine-functionalized *P*-dendrimers on solid supports such as silica, to improve stability and fluidizability.

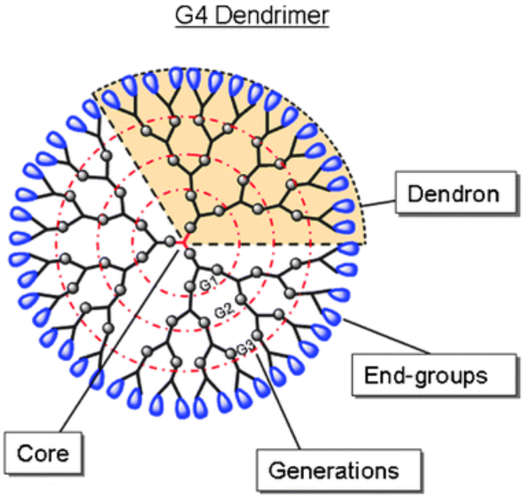


Figure 2: Dendrimer structure

A packed bed reactor is used to screen the novel hybrid sorbents with multi-cycle adsorption-regeneration, measuring CO_2 loading and rate along with contaminant effects. A visual fluidized-bed reactor, shown in Figure 3, is utilized to verify the fluidizability of the sorbents under realistic process conditions and to test optimal fluidization conditions.

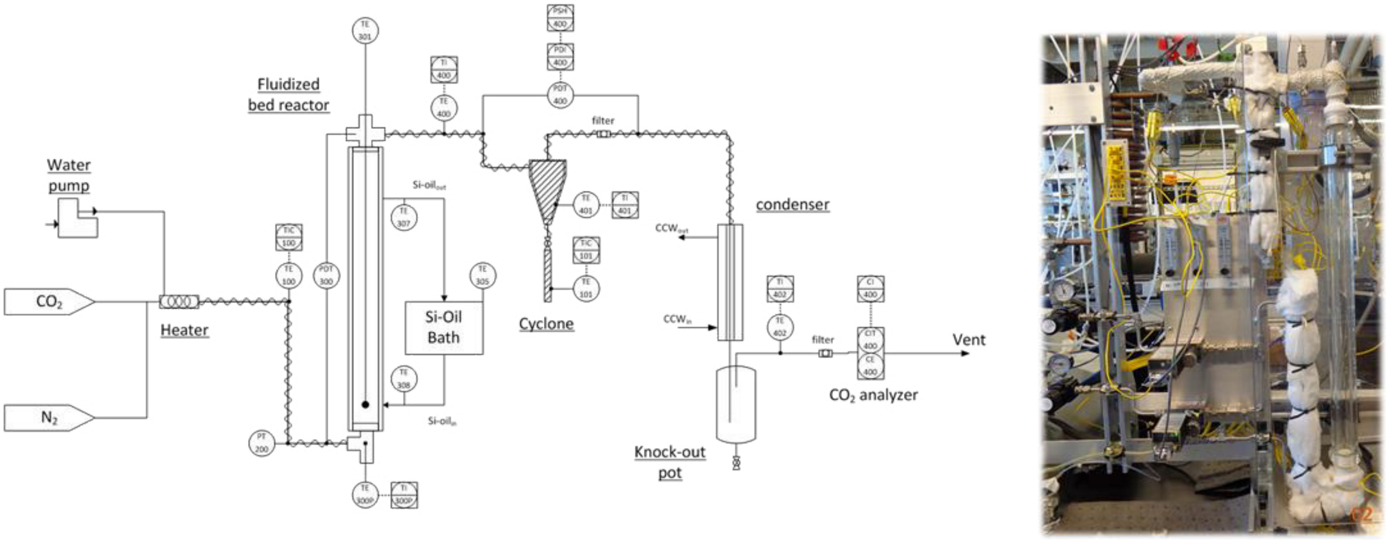


Figure 3: RTI visual fluidized-bed reactor

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	650–750	—
Average Particle Diameter	mm	165	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	1.5	—
Crush Strength	kg_f	10%	—
Manufacturing Cost for Sorbent	$/kg	20	—
Adsorption			
Pressure	bar	1–1.2	—
Temperature	°C	60–70	—
Equilibrium Loading	g mol CO_2/kg	12.5	—
Heat of Adsorption	kJ/mol CO_2	95–100	—
Desorption			
Pressure	bar	1.3–1.4	—
Temperature	°C	120	—
Equilibrium CO_2 Loading	g mol CO_2/kg	0.5–1	—
Heat of Desorption	kJ/mol CO_2	95–100	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— —	—
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

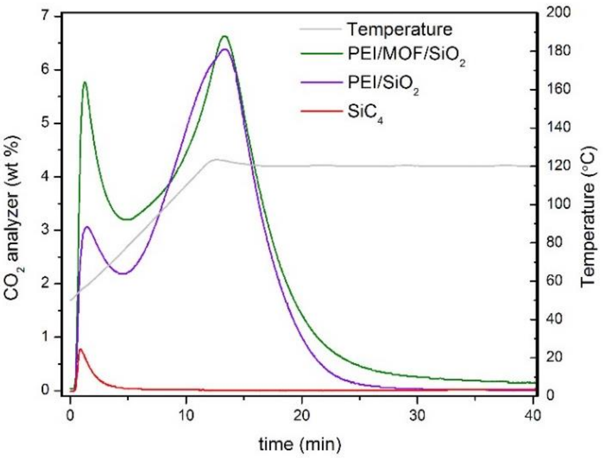
Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption breakthrough profile for the MOF-based solid sorbent shows a superior CO_2 adsorption compared to PEI/SiO_2. The regeneration profiles show an interesting profile in terms of CO_2 desorption for the hybrid sorbent containing MOF nanocrystals. Larger concentration of early released adsorbate is measured for the PEI/MOF/SiO_2 hybrid sorbent, which is attributed to weakly adsorbed CO_2 via physisorption, since the temperature required to release them is lower than 80 °C. In addition, PEI/MOF/SiO_2 exhibits higher CO_2 desorption between 80 and 100 °C that suggests a slightly better use of the PEI amines for CO_2 chemisorption as well. This result highlights the unusual dual adsorption performance of our hybrid sorbents containing MOF nanocrystals compared to the pure silica counterpart.



Regeneration profiles for PEI/MOF/SiO_2 (green) compared to conventional PEI/SiO_2 (purple)

Sorbent Contaminant Resistance – Fluidized MOF/SiO_2 hybrid sorbents have demonstrated good CO_2 adsorption capacity under simulated flue gas conditions, since they exhibit 140 percent higher CO_2 capacity and similar deactivation (*ca* 10 percent after 250 cycles) than the reference PEI impregnated on bare mesoporous silica. As flue gas from coal-fired power plants typically contains other acid-gas impurities such as SO_2 and NO_x that can dramatically influence the CO_2 capture efficiency. The results show a clear deactivation of the CO_2 adsorption capacity of the sorbents under the presence of SO_2. This deactivation is due to the irreversible reaction occurring during the adsorption step between SO_2 and PEI amines, which are not further active for the CO_2 capture. On the other hand, excellent stability has been observed under elevated concentration of NO_x. Therefore, the presence of MOF nanocrystals within the hybrid solid sorbent does not reduce the tendency of PEI amines to be deactivated by irreversible binding with SO_2, as similar deactivation has been measured for PEI/SiO_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – This work is the first example of CO_2 capture from simulated flue gas in a fluidized bed configuration using a MOF based CO_2 solid sorbent. The application of MOFs on this configuration have never been proposed due to the poor attrition, handling and lack of fluidizability of bulk MOFs. By engineering MOFs within mesoporous silica, the final sorbent is demonstrating excellent fluidizability, handling and improved attrition resistance (up to 2–3 times compared to SiO_2, and 6-7 times compared to MOF). Very aggressive regeneration conditions (stream containing 80 v/v percent H_2O balanced with N_2 at 100 °C for 1 hr) were used to check the stability of this sorbent, the CO_2 adsorption capacity was practically maintained for PEI/MOF/SiO_2 whereas a significant drop was observed for the MOF-free sorbent.

Flue Gas Pretreatment Requirements – An additional unit should be included up-stream for scrubbing the SO_2 levels in the flue gas down to a single digit ppm level prior to reach the fluidized bed reactor to elongate the life of the hybrid solid sorbents and reduce the make-up rate.

Sorbent Make-Up Requirements – Fluidized MOF/SiO_2 hybrid sorbents demonstrate an excellent attrition resistance and therefore reduced significantly the make-up rate.

Waste Streams Generated – Two waste streams could be generated:

- Sorbent attrition fines could be reprocessed and used as sulfur guard-bed.
- Steam condense from regenerator CO2 capture steam usually has leached PEI. However, water-wash experiments of our sorbent showed very little PEI leaching. This suggests that the condensed water will be easily processed and reused.

Process Design Concept – RTI proposes the use of multi-stage fluidized bed absorber-regenerator process for the capture and recovery of CO_2. By employing fluidized bed reactors with heat transfer internals, the process temperature in each stage will be controlled precisely by removing heat during adsorption and adding heat in the regenerator. Multi-stage reactors are essential in maximizing sorbent rich loading in the absorber and lean loading in the regenerator, thereby maximizing working capacity.

technology advantages

- High theoretical CO_2 loading for *P*-dendrimers.
- MOF/silica fluidized hybrid materials offer several advantages.
    - High MOF loading (up to 40 percent)
    - Excellent MOF dispersion and homogeneity
    - Good water and air stability
    - Good chemical and thermal stability
    - Tunable pore size distribution
    - Elevated surface area (up to 900 m^2/g) and density (0.65 g/cm^3)
    - Enhanced attrition resistance
    - Good fluidizability
- High CO_2 capacity (≥12 wt%) and good stability of hybrid MOF-based adsorbents.

R&D challenges

- Reducing sorbent production costs, particularly for the *P*-dendrimer based adsorbents.

status

RTI has developed a novel technique to grow MOF inside the pores of silica supports. Testing of the three most promising PEI-impregnated silica-MOF sorbents has shown high (>12 percent) CO_2 capacity with good MOF dispersion and homogeneity, good water and air stability, good chemical and thermal stability, enhanced attrition resistance, and excellent fluidizability. The sorbents exhibit better performance and long-term stability in a fluidized configuration. Production of the hybrid MOF-based sorbent has been scaled from 20-mg to 4-kg scale. Three *P*-dendrimer sorbents were evaluated and showed high (>13.0 wt%) CO_2 capacities over at least 250 cycles.

available reports/technical papers/presentations

Soukri, M., et al. “Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants,” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/M-Soukri-RTI-Solid-Sorbent.pdf*

Soukri, M., et al. “Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants,” Budget Period 1 Review Meeting, Pittsburgh, PA, April 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026432-BP1-Review.pdf*

Soukri, M., et al. “Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/M-Soukri-RTI-Lab-scale-Sorbent.pdf*

Soukri, M. “Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants,” Project Kickoff Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026432--Kick-off-Presentation.pdf*

CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION MEMBRANE TECHNOLOGIES

Novel Carbon Dioxide-Selective Membranes for CO_2 Capture from Less than 1% CO_2 Sources

primary project goals

Ohio State University (OSU) is developing a cost-effective design and manufacturing process for new membranes and membrane modules that capture carbon dioxide (CO_2) from sources with less than 1 percent CO_2.

technical goals

- Synthesize and characterize laboratory-scale membranes and conduct performance studies.
- Fabricate pilot-size membrane (~14" by >20').
- Fabricate, evaluate, and down-select from plate-and-frame and spiral-wound membrane modules.
- Fabricate 3 laboratory membrane modules and test with less than 1 percent CO_2 simulated gas mixture.

technical content

Ohio State University is continuing their work on developing novel CO_2-selective membranes that capture CO_2 from less than 1 percent CO_2 concentration sources. The membrane is inexpensive, consisting of a cost-effective nanoporous polymer support (polyethersulfone [PES]) and a top layer coating of thin, highly-selective, permeable, amine-containing polymer membrane as shown in Figure 1. The membrane modules are incorporated in a two-stage membrane process that would be implemented after the primary CO_2 capture system in a power plant, which has already captured >90 percent CO_2 from flue gas. In the first membrane module, CO_2 is removed from the feed gas by using vacuum and the permeate stream is used as the feed for the second membrane module, where additional CO_2 is removed by vacuum such that the 90 percent capture and 95 percent purity targets are met.

technology maturity:

Lab-Scale, Simulated Flue Gas

project focus:

Selective Membranes for <1% CO_2 Sources

participant:

Ohio State University

project number:

FE0026919

predecessor projects:

N/A

NETL project manager:

José Figueroa
jose.figueroa@netl.doe.gov

principal investigator:

W.S. Winston Ho
Ohio State University
ho.192@osu.edu

partners:

TriSep Corporation; Gradient Technology; American Electric Power

start date:

03.01.2016

percent complete:

60%

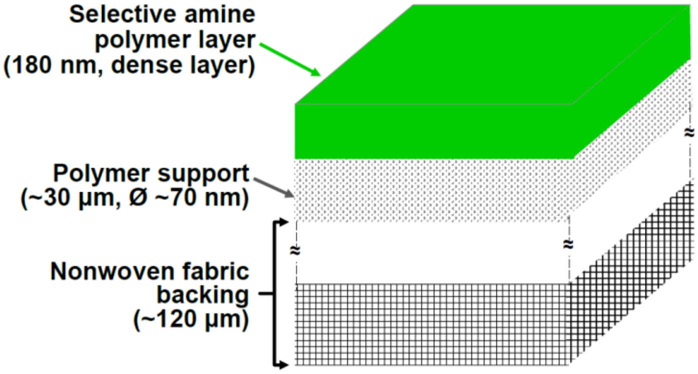


Figure 1: Selective amine polymer layer/polymer support

CO_2 permeates through the membrane via a facilitated transport mechanism where CO_2 reacts with amines reversibly to facilitate CO_2 transport whereas nitrogen (N_2) cannot react with amines, resulting in very high CO_2/N_2 selectivity. The amine polymer layer contains mobile carriers that react with CO_2 to facilitate transport (Figure 2). The CO_2 flux increases as pressure increases until it reaches a saturation point in which CO_2 reacts with all carriers in the membrane. At low pressure (or low CO_2 concentration), more free carriers are available, and, therefore, CO_2 permeance is higher due to greater CO_2 facilitation. Since sulfur dioxide (SO_2) permeates through the membrane, OSU proposes to add an SO_2 polishing step before the membrane process to remove SO_2 to less than 1–3 parts per million (ppm). A CO_2 permeance of 1,800 gas permeation unit (GPU) and a CO_2/N_2 selectivity of greater than 140 using a simulated gas mixture containing less than 1 percent CO_2 are the target performance criteria for these membranes. New and improved membranes are synthesized in which the polyamine layer is modified to achieve a higher CO_2 permeance and a hydrophilic agent is incorporated into the substrate to improve porosity, permeance, and adhesion.

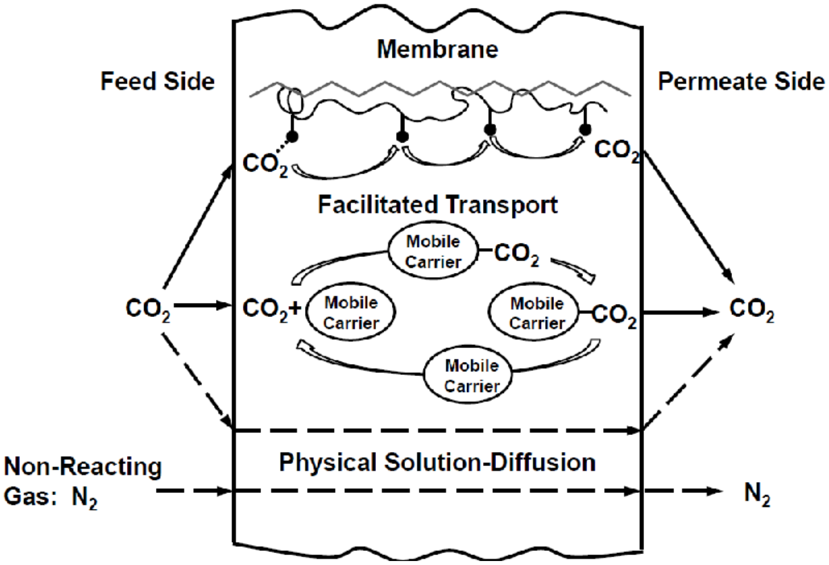


Figure 2: Facilitated transport on amine polymer layer

A continuous membrane fabrication machine with roll-to-roll operations was developed at OSU in a previous project to enable scale up of the PES support. OSU is using this low-cost manufacturing method to produce prototype membranes of 14 inches in width for >50 feet. Two types of membrane modules are being fabricated and evaluated. Plate-and-frame modules are shown in Figure 3 and spiral-wound modules are shown in Figure 4.

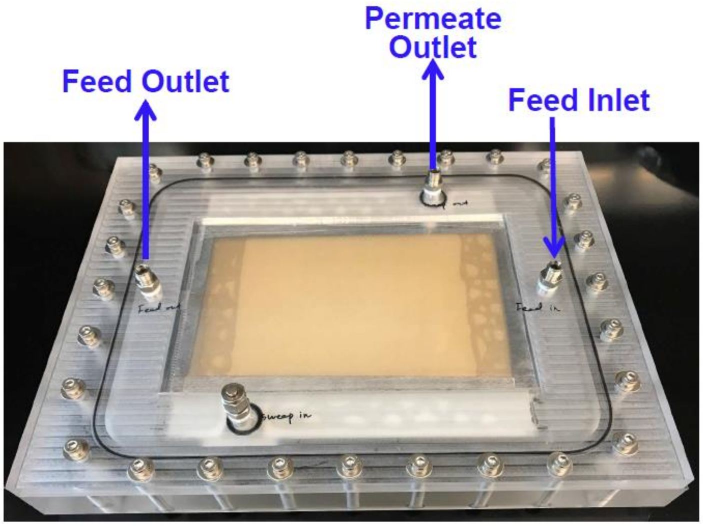


Figure 3: Plate-and-frame membrane module

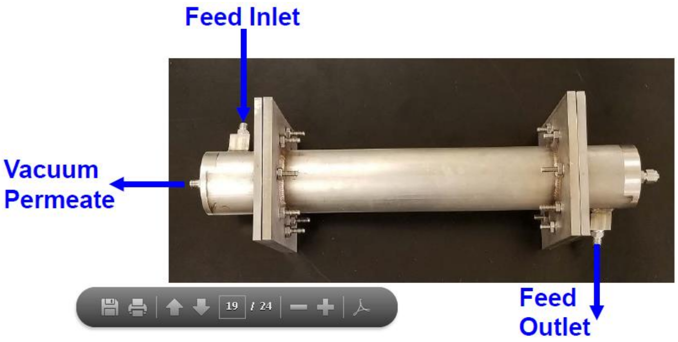


Figure 4: Spiral-wound membrane module

A preliminary techno-economic analysis has indicated a capture cost of about \$268/tonne CO_2 captured. However, through membrane improvement and process optimization during this project, the cost will be reduced.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	Fixed and mobile amine carriers as the membrane matrix	
Materials of Fabrication for Support Layer	—	Nanoporous polyethersulfone	
Nominal Thickness of Selective Layer	nm	100–200	100–170
Membrane Geometry	—	Flat sheet	Flat sheet
Max Trans-Membrane Pressure	bar	10	10
Hours Tested without Significant Degradation	—	450	1,200
Manufacturing Cost for Membrane Material	\$/m^2	10	<10
Membrane Performance			
Temperature	°C	57–67	57–87
CO_2 Pressure Normalized Flux	GPU or equivalent	1,800	2,200
CO_2/H_2O Selectivity	—	About 1	About 1
CO_2/N_2 Selectivity	—	140–200	150–225
CO_2/SO_2 Selectivity	—	About 1	About 1
CO_2/H_2 Selectivity	—	About 100	About 100
Type of Measurement	—	Mixed gas	Simulated gas mixture

Proposed Module Design		(for equipment developers)
Flow Arrangement	—	Countercurrent
Packing Density	m^2/m^3	1,800
Shell-Side Fluid	—	Permeate containing CO_2 (vacuum is used on the permeate side)
Flue Gas Flowrate	kg/hr	4,346
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >95%, 0.2 – 4 bar
Pressure Drops Shell/Tube Side	bar	0.007 bar/m permeate/0.07 bar/m feed
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	\$500/(kg/hr), \$32/m^2 or \$268/tonne CO_2 capture cost

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.35×10^{-10} mol/(m^2-s-Pa) [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (flue gas) stream.

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

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

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
14.7 psia	135°F	0.99	17.25	78.62	2.34	0.80	42	74

Other Parameter Descriptions:

Membrane Permeation Mechanism – Facilitated transport using chemical reaction to enhance separation.

Contaminant Resistance – 3 ppm SO_2 and 3–7 percent O_2.

Flue Gas Pretreatment Requirements – SO_2 polishing step (with 20 percent NaOH) to have 1–3 ppm SO_2.

Membrane Replacement Requirements – About once every 4 years.

Waste Streams Generated – No additional waste streams generated.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

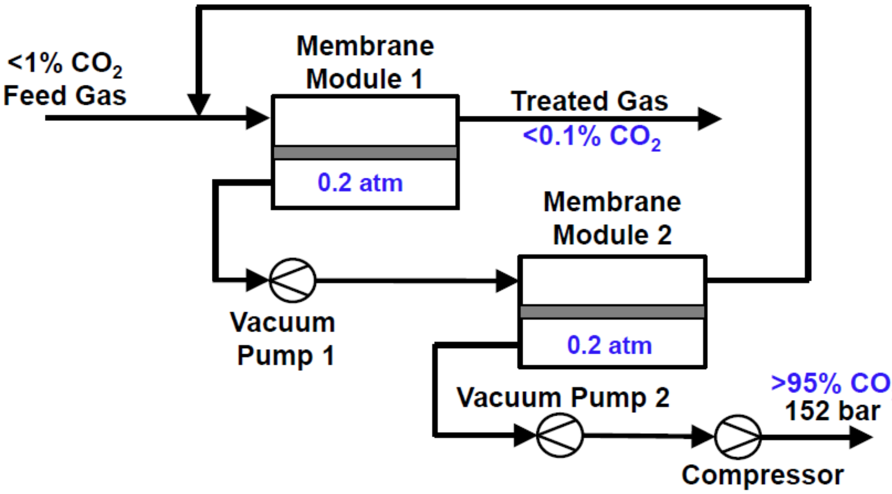


Figure 5: Two-stage membrane process

technology advantages

- Energy-efficient technology.
- Modular and simple operation with low capital and operating costs.
- Low-cost membrane (<\$2.00/ft^2).

R&D challenges

- Achieving very high membrane performance (CO_2 permeance of 1,800 GPU and CO_2/N_2 selectivity of >140).
- Membrane stability in presence of contaminants.

status

A CO_2 permeance of 1,800 GPU and a CO_2/N_2 selectivity of 220 was achieved in lab-scale testing of the 14”-wide membranes at 67 °C using a 1 percent concentration feed gas. Both membrane modules were fabricated and showed good stability with 3 ppm SO_2 and a CO_2 permeance of ~1,800 GPU at 67 °C. The preliminary techno-economic analysis showed a CO_2 capture cost of \$268/tonne and a 19 percent increase in cost of electricity (COE).

available reports/technical papers/presentations

Ho, W., “Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources,” presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/W-Ho-OSU-Capture-from-less-than-1--CO2-Sources.pdf*

Ho, W., “Novel CO_2-Selective Membranes for CO_2 Capture from <1% CO_2 Sources,” Continuation Application Status Meeting, Pittsburgh, PA, February 2017. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/DE-FE0026919-Continuation-Application-Status-Mtg-2-27-17.pdf*

Bench Scale Testing of Next-Generation Hollow Fiber Membrane Modules

primary project goals

Air Liquide (AL) is developing a novel polyimide-based membrane material (PI-2) for application in their hybrid process that combines cold membrane operation with cryogenic separation to reduce the overall cost of capturing carbon dioxide (CO_2) from flue gas. The focus of the project is to advance the high CO_2 permeance PI-2 material to commercial-scale 6-inch bundles for testing with actual flue gas in a 0.3-MW_e test unit at the National Carbon Capture Center (NCCC).

technical goals

- Design and manufacture 4-inch PI-2 bundles reaching >90 Nm^3/h feed at 90 percent CO_2 recovery and >58 percent CO_2 purity.
- Identify other hybrid processes with possibility of economic feasibility.
- Design and manufacture 6-inch PI-2 bundles reaching >400 Nm^3/h feed at 90 percent CO_2 recovery and >58 percent CO_2 purity.
- Field-test 6-inch bundles at 0.3-MW_e scale with real flue gas at NCCC.
- Complete a techno-economic analysis to evaluate potential to meet carbon capture cost targets.

technical content

Air Liquide is developing a next-generation membrane material (PI-2) for application with their novel, sub-ambient temperature, membrane-based CO_2 capture technology. The process combines the use of commercial polyimide (PI) hollow-fiber membrane bundles with cryogenic operation to selectively remove the CO_2 from flue gas.

Figure 1 presents a simplified block diagram of the cold membrane process. A highly selective membrane provides pre-concentration of CO_2 prior to CO_2 partial condensation in a liquefaction unit. The membrane is operated at sub-ambient temperature, approximately -30 °C, for enhanced CO_2/N_2 selectivity. The cryogenic heat exchanger system provides energy integration between the membrane and the CO_2 liquefaction system.

technology maturity:

Bench-Scale, Simulated Flue Gas, Actual Flue Gas (0.3-MW_e)

project focus:

Subambient Temperature Membrane

participant:

American Air Liquide, Inc.

project number:

FE0026422

predecessor projects:

FE0013163
FE0004278

NETL project manager:

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principal investigator:

Alex Augustine
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alex.augustine@airliquide.com

partners:

Air Liquide Engineering; Air Liquide – ALAS; Parsons Government Services, Inc.

start date:

10.01.2010

percent complete:

75%

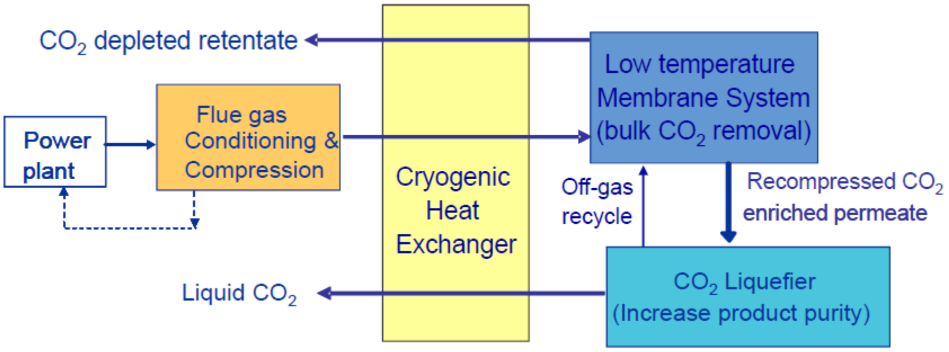

Figure 1: Block diagram of the cold membrane process

Figure 2 shows a schematic diagram of the hybrid cold membrane process. The process lines in Figure 2 are color-coded (black for ambient temperature; dark blue for approximately -30 °C; and light blue for approximately -50 °C). The pre-treated flue gas is compressed to approximately 230 psi (16 bar). The heat of compression is captured in boiler feed water, raising its temperature to approximately 147 °C. The compressed flue gas is then dried in a dehydration unit to prevent water condensation when the stream is cooled in the brazed aluminum heat exchanger to approximately -40 °C. The cooled, dried, compressed flue gas is then fed to the membrane to produce a residue stream with approximately 1.8 percent CO_2 at approximately 215 psi (15 bar) and a permeate stream with 60 to 70 percent CO_2 at approximately 17 psi (1.1 bar). After the residue is sent through the heat exchanger, further cooling and energy recovery is done via a series of turbo-expanders with the resulting stream at -57 °C. The cold stream is again sent through the heat exchanger to provide cold for the overall process. Finally, the excess pressure energy remaining in the warmed residue is partly recovered in a warm turbo-expander before venting. A fraction of the vent gas is used to regenerate the drier. The permeate stream is recompressed, cooled in the heat exchanger, and undergoes phase separation in the cryo-phase separator. Liquid CO_2 is pumped from the separator to provide a sequestration-ready product CO_2 at approximately 870 psi (60 bar), or greater, and 20 °C. The overhead from the cryo-phase separator is warmed through the heat exchanger and then undergoes energy recovery in a turbo-expander. This stream is mixed with the incoming dried flue gas, which raises the mixed feed concentration entering the membrane to 18 percent CO_2. The higher CO_2 content improves system recovery and efficiency of the membrane separation.

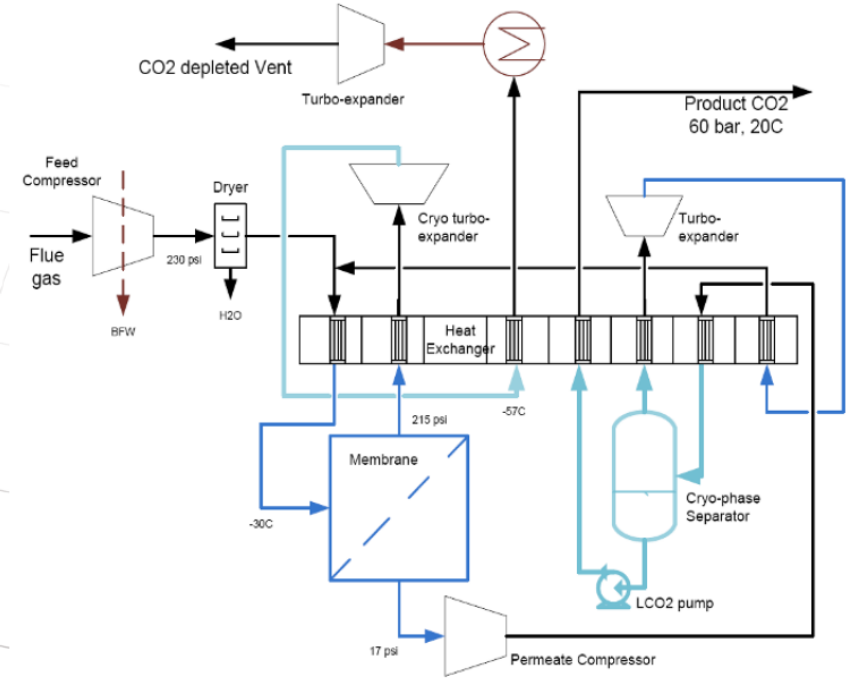

Figure 2: Schematic diagram of cold membrane process

For most membrane materials, permeability decreases and selectivity increases with a decrease in operating temperature. However, laboratory measurements of AL's commercial PI hollow-fiber membranes operated at temperatures below -20 °C show two to four times higher CO_2/nitrogen (N_2) selectivity with minimal loss of CO_2 permeance compared to ambient temperature values. Closed-loop, bench-scale (0.1 MW_e) testing of Air Liquide's existing low-cost commercial membranes (PI-1) was conducted at subambient temperatures in project FE0004278 using synthetic flue gas (CO_2 and N_2). The 6-inch bundles exhibited stable performance over 8 months of operation and 12-inch bundles showed excellent mechanical integrity for 2 months. Preliminary data indicated that 12-inch bundle performance was lower compared to the 6-inch bundles due to non-ideal flow conditions. By modifying bundle fabrication methods and incorporating a membrane sweep stream in the process, productivity of the 12-inch bundles was improved by approximately 30 percent. A novel membrane material (PI-2) has shown the potential to have similar high selectivity and greater than 5 times the fiber permeance of PI-1 in initial laboratory testing with simulated flue gas. PI-2 has the potential for a significant reduction in membrane system cost. Productivity increases as the membrane is scaled to 4-inch and 6-inch bundles. Testing of the PI-2 membranes at 0.1 to 0.3 MW_e-scale with actual flue gas allows for a direct comparison with the PI-1 material based on identical test equipment and conditions.

Fabrication and installation of the 0.3-MW_e field test unit (Figure 3) at the NCCC allows for parametric testing and long-term continuous runs on the optimized PI-1 membrane modules as well as the advanced high-permeance PI-2 membrane modules. Dynamic tests to quantify the performance of the carbon capture system provide data for a final techno-economic analysis for a 550-MW_e power plant with optimized membrane bundles to assess the system's ability to reach the targets of >90 percent CO_2 capture and >95 percent purity at a capture cost approaching $40/tonne.

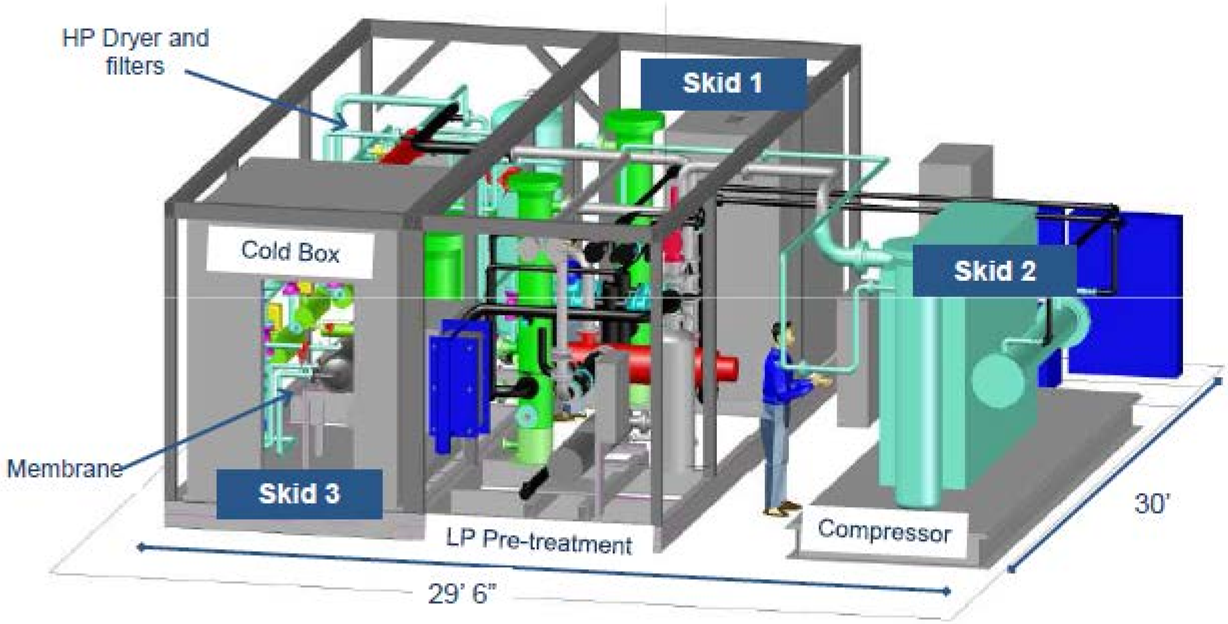

Figure 3: 0.3-MW_e test unit at NCCC, Pilot Bay 3

Hybrid process configurations such as membrane/absorption or membrane/sorbent processes have also been proposed incorporating PI-2 membrane material to reduce the compression energy penalty.

The membrane and process parameters identified to date are provided in Table 1.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polyimide	polyimide
Materials of Fabrication for Support Layer	—	polyimide	polyimide
Nominal Thickness of Selective Layer	µm	<0.1 µm	<0.1 µm
Membrane Geometry	—	hollow fiber	hollow fiber
Maximum Trans-Membrane Pressure	bar	20	20
Hours Tested without Significant Degradation	—	PI-2: 4-inch bundle 340 hrs (synthetic flue gas) PI-2: 6-inch bundle 325 hrs (actual flue gas)	500+ hours (actual flue gas)
Manufacturing Cost for Membrane Material	$\$/m^2$	-	Pending TEA
Membrane Performance			
Temperature	°C	-30 °C to -45 °C	-30 °C to -45 °C
CO_2 Pressure Normalized Flux	GPU or equivalent	PI-2 6-inch bundle: 657 Nm^3/hr of bundle productivity	400 Nm^3/h
CO_2/H_2O Selectivity	—	<0.2 (dry gas)	<0.2 (dry gas)
CO_2/N_2 Selectivity	—	>50	>70
CO_2/SO_2 Selectivity	—	0.3	0.3
Type of Measurement	—	6” bundle parametric and long-term testing with synthetic flue gas	6” bundle parametric and long-term testing with actual flue gas
Proposed Module Design		(for equipment developers)	
Flow Arrangement	—	hollow fiber	
Packing Density	m^2/m^3	approximately 1,500 m^2/m^3	
Shell-Side Fluid	—	CO_2-rich permeate	
Flue Gas Flowrate	kg/hr	>2,700 Nm^3/hr / 12-inch bundle	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >95% purity in hybrid process (>58% CO_2 purity from membrane), 60 bar	
Pressure Drops Shell/Tube Side	bar	0.1 bar shell side/1 bar tube side	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	pending TEA	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane’s permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units]. Bundle productivity in terms of feed flow rate in Nm^3/hr is reported.

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Nominally based on solution-diffusion.

Contaminant Resistance – Expected to be resistant to acidic components based on experience to date.

Flue Gas Pretreatment Requirements – Particulate removal and acid component removal to meet compressor specifications, dehydration to meet cold box specifications, mercury (Hg) removal to meet heat exchanger specification.

Membrane Replacement Requirements – Membrane productivity decline was too small to be quantified in bench-scale test with synthetic gases.

Waste Streams Generated – Acidic water.

Process Design Concept – See Figure 2.

technology advantages

- Novel high flux PI-2 material enables a significant reduction in membrane area and corresponding capital cost.
- Subambient operation improves membrane performance.
- Process design provides partial recovery of the flue gas compression energy.
- Process design provides an economic method of cooling the flue gas feed to the required sub-ambient temperature for optimal membrane operation without external refrigeration.
- The process design can be combined with a novel scheme for contaminant (SO_2, NO_x) removal.

R&D challenges

- Subambient membrane operation requires development of suitable membrane module materials with adequate permeance and selectivity in a commercial membrane module.
- Long-term membrane module performance stability.
- Integration of subambient membrane process, including energy integration with the CPU, as well as energy integration with the power plant, such as compression and turbo-expansion schemes, heat economizers, and energy conservation.
- Flue gas contaminant-specific challenges, including acid gas (NO_x, SO_2) separation, compressor materials of construction, particulate removal, Hg removal, and water management.
- Novel PI-2 material development must achieve tolerance to operating pressure/temperature, effective epoxy seals, long term stability, and manufacturing reproducibility.

status

The 1-inch PI-2 permeators and PI-1 commercial scale bundles completed over 500 hours of steady-state testing on the 0.3-MW_e test unit at the NCCC showing stable performance. Multiple 4-inch prototype PI-2 membrane modules have achieved greater than 90 Nm^3/hr productivity at 90 percent capture and greater than 58 percent CO_2 purity through testing on the 0.1-MW_e bench-scale skid with synthetic flue gas. Multiple 6-inch bundles have achieved greater than 400 Nm^3/hr productivity at 90 percent capture and 58 percent CO_2 purity through testing on the 0.3-MWe field-test unit with real flue gas.

available reports/technical papers/presentations

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Integrated Testing of a Membrane CO_2 Capture Process with a Coal-Fired Boiler

primary project goals

Membrane Technology and Research, Inc. (MTR) is advancing the development of a carbon dioxide (CO_2) capture process that incorporates their innovative Polaris™ membranes and a selective-recycle sweep module design through pilot-scale testing of the existing, 1-megawatt electric (MW_e) membrane system integrated with a Babcock & Wilcox (B&W) 0.6-MW_e coal-fired research boiler.

technical goals

- Integrate MTR's 1-MW_e membrane CO_2 capture system with B&W's 0.6-MW_e research boiler for operation of the integrated system with recycle of CO_2 to the boiler.
- Perform testing on the integrated system using two types of coal to analyze process parameters while monitoring boiler performance and CO_2 capture efficiency.

technical content

MTR is performing small pilot-scale operation of the 1-MW_e CO_2 capture system using Polaris™ membranes with B&W's 0.6-MW_e coal-fired research boiler to determine how various membrane parameters impact the performance of a boiler system. The small pilot membrane system was successfully tested in previous projects with real flue gas and the boiler was successfully tested with CO_2-laden air at B&W.

MTR's Polaris™ membranes, developed in a previous project, DE-NT43085, exhibit high CO_2 permeance and high CO_2/N_2 selectivity for post-combustion flue gas applications. This thin-film composite membrane utilizes hydrophilic polymers. Commercially available Polaris™ membranes have approximately 10 times the CO_2 permeance of conventional gas separation membranes and recent studies have improved membrane performance, demonstrating a permeance of 3,000 gas permeation unit (GPU) at lab-scale. The combination of these membranes with a novel sweep module design that utilizes incoming combustion air to generate a separation driving force greatly reduces the projected cost of CO_2 capture.

MTR's novel two-step membrane process design includes two types of membrane arrangements: a conventional crossflow module and a novel countercurrent sweep module. First, the combustion flue gas enters a crossflow module, which removes most of the CO_2. The retentate from the crossflow module is then fed into a countercurrent sweep module, from which the permeate is recycled back to the boiler via an air sweep. This increases the CO_2 concentration of the flue gas entering the initial crossflow module. The CO_2-rich permeate from the crossflow module is dehydrated and compressed. A second-stage crossflow module is used after compression to further enrich the CO_2 stream by recycle of the permeate back to the inlet of the compressor. Operation of the integrated membrane-boiler system involves the recycling of CO_2-laden air back to B&W's boiler via the sweep membrane.

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 1 MW_e)

project focus:

Polaris™ Membrane/Boiler Integration

participant:

Membrane Technology and Research, Inc.

project number:

FE0026414

predecessor projects:

DE-NT0005312
FC26-07NT43085
FE0005795
FE0007553
FE0013118

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partners:

Babcock & Wilcox, Southern Company/National Carbon Capture Center

start date:

04.01.2007

percent complete:

90%

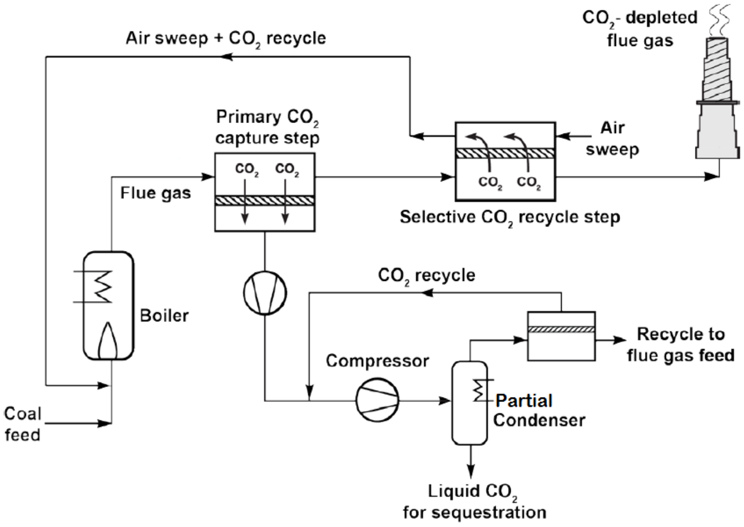

Figure 1: MTR CO_2 capture process

A membrane skid designed to capture 1-tonne of CO_2 per day from a 7,000 standard m^3/day (250,000 standard cubic feet per day [scfd]) flue gas slipstream was installed and tested at the National Carbon Capture Center (NCCC) (Figure 2). The skid can hold up to eight (four crossflow and four countercurrent sweep), 8-inch diameter Polaris™ membrane modules. The test demonstrated membrane operation in commercial-scale modules and determined typical membrane lifetimes under coal combustion flue gas operating conditions.

Figure 2: Membrane skid used for 1-tpd bench-scale slipstream testing at NCCC

Scale-up of the Polaris™ capture system from the 1-tonne per day (tpd) bench-scale unit to a 20-tpd small pilot system using commercial-scale membrane components was completed in a previous project (DE-FE0005795). The 20-tpd system is a two-level design with membrane modules located on the upper level and all rotating and associated equipment on the lower level. Like the 1-tpd unit, the 20-tpd unit was designed for slipstream operation (no CO_2 recycle) at the NCCC and is shown in Figure 3.

Figure 3: 20-tpd small pilot system installed at NCCC

Polaris™ membranes are packed into spiral-wound membrane modules, the most commonly used module design for commercial membrane installations today, and can meet low pressure-drop and high packing-density performance targets. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95 percent of the reverse osmosis (RO) desalination industry and more than 60 percent of the membrane market for CO_2 removal from natural gas. Figure 4 shows the general design features of a spiral-wound membrane module. The module consists of a permeate collection tube with a spiral formation of permeate spacers and feed spacers, which allow the flue gas and separated CO_2 to flow through the device. Each module contains 20 to 50 m^2 of membrane. A total membrane area of about 0.5 to 1 million m^2 is required to achieve 90 percent CO_2 capture for a 550-MW_e plant. Figure 5 shows a proposed design for efficient module packing in a full-scale membrane system that consists of 7 tubes nested in a single pressure vessel. Each set of modules is stacked on a skid and connected together to form a single "mega-module." About 130 mega-module skids would be required for a 550-MW_e power plant. The process parameters for the Polaris™ membranes in a spiral-wound module configuration are shown in Table 1.

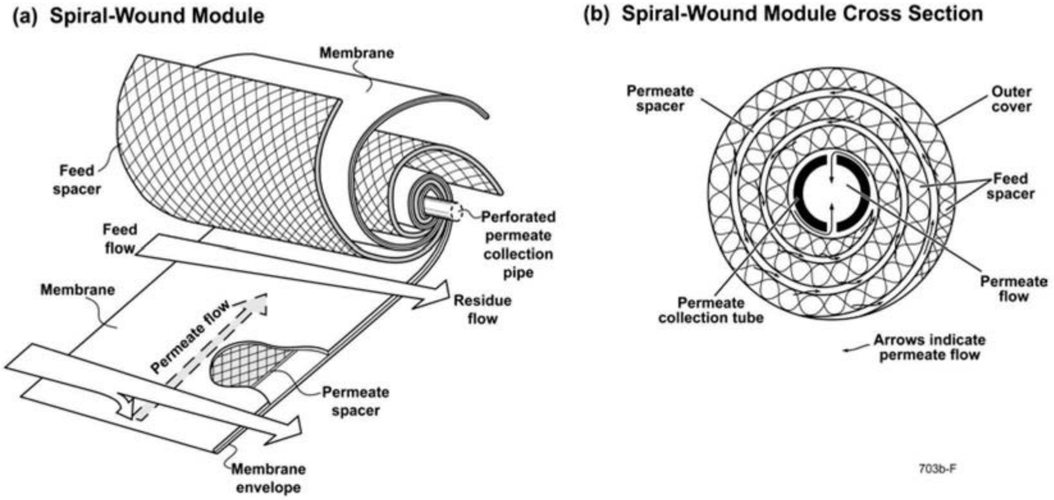

Figure 4: Schematic diagram of a spiral-wound membrane module

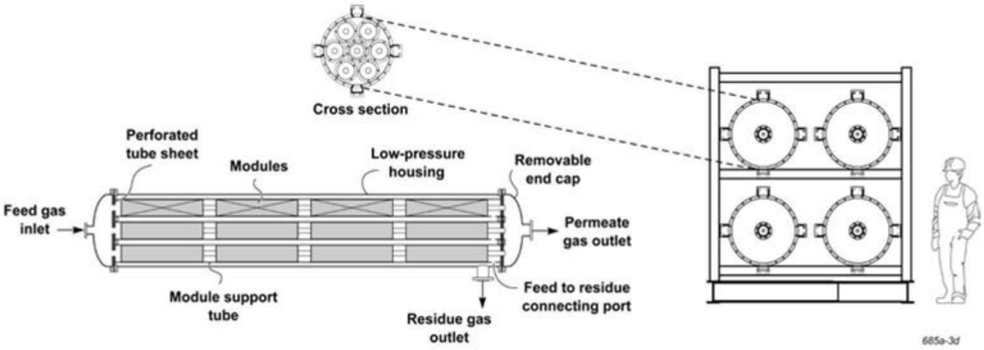

Figure 5: Full-scale membrane system design using spiral-wound modules

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry	—	spiral	spiral
Max Trans-Membrane Pressure	bar	70	70
Hours Tested without Significant Degradation	—	13,000 (coal)	25,000 (coal)
Manufacturing Cost for Membrane Material	$/m^2	50	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,700	>2,500
CO_2/H_2O Selectivity	—	0.3	0.3
CO_2/N_2 Selectivity	—	25	25
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow and countercurrent	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	500	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: <0.05/sweep: 0.1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	<50	

MTR applied an alternative approach to membrane packing to develop plate-and-frame modules optimized for low-pressure, countercurrent sweep operation. Testing of the small pilot-scale 20-tpd system incorporated this novel large-area membrane contactor module designed by MTR in project DE-FE0007553. A single 100 m^2 membrane module element has the equivalent membrane area of five 8-inch spiral-wound membrane modules. Figure 6 shows the plate-and-frame module design and Figure 7 shows a full-scale 500 m^2 mega-module which consists of a pressure vessel with 5 module elements. These mega-modules reduce the footprint of the plant and have a lower air sweep pressure drop compared with the spiral-wound modules, resulting in energy and cost savings. The plate-and-frame module skids are projected to cost \$30/m^2 of membrane at full commercialization stage.

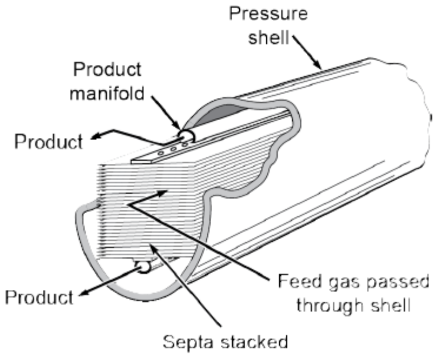

Figure 6: Plate-and-frame module

Figure 7: 500-m^2 plate-and-frame module skid

The integrated membrane-boiler testing also utilized the plate-and-frame module for the sweep stage in lieu of the spiral-wound modules. Figure 8 shows the main two-floor skid and the smaller low-pressure drop sweep module anchored to B&W's research facility.

Figure 8: MTR skids installed at B&W's SBS-II research facility

MTR is also evaluating a hybrid membrane-absorption process system combining Polaris™ membranes and an amine solvent-based capture system. A hybrid membrane-absorption process system is being designed that combines MTR's plate-and-frame sweep module with an amine solvent-based capture system developed by The University of Texas at Austin (UT-Austin) that uses a piperazine (PZ) solvent and advanced high-temperature/high-pressure regeneration. This hybrid design requires significantly less membrane area for a two-step CO_2 capture process compared to MTR's all-membrane process. In the hybrid design, MTR's Polaris™ membrane recycle stage enriches flue gas from ~13 to ~20 percent CO_2 and a 5 molal PZ advanced flash stripper with cold-rich bypass is optimized to take advantage of the higher CO_2 concentration. Both series and parallel configurations were considered with the hybrid design, as shown in Figure 9. Process modeling of MTR's plate-and-frame skid integrated with UT-Austin's Separations Research Program (SRP) 0.1-MW_e Pilot Plant shows that a hybrid-parallel configuration offers a lower cost of capture than the series configuration. Process parameters for the Polaris™ membranes in a plate-and-frame module configuration are shown in Table 2.

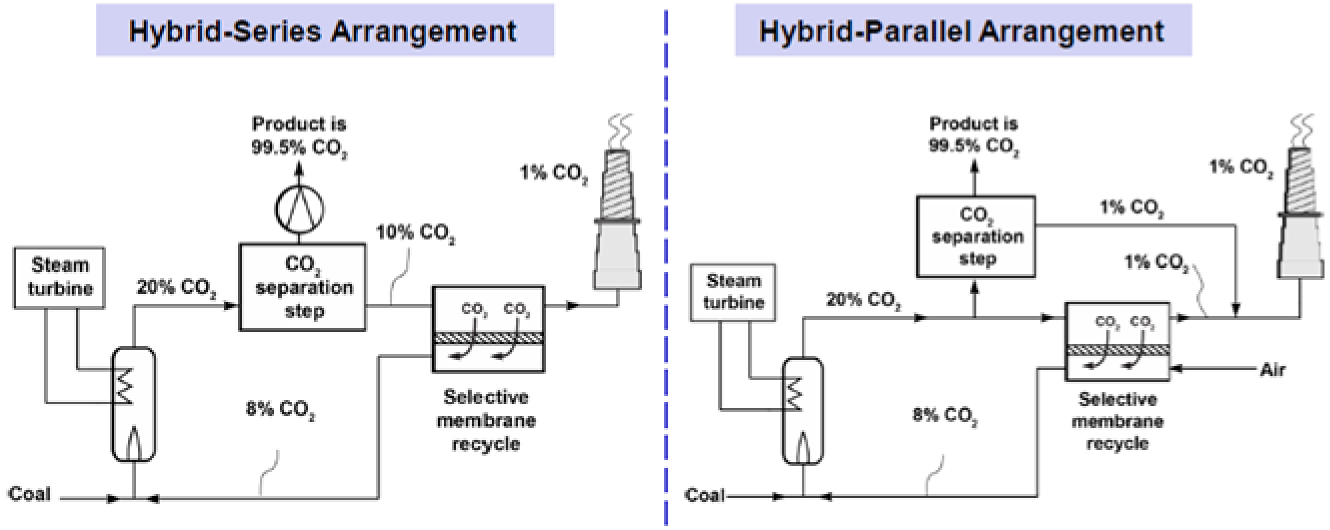

Figure 9: Two hybrid configurations for membrane-absorption CO_2 capture process

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	proprietary polymer	
Materials of Fabrication for Support Layer	—	proprietary polymer	
Nominal Thickness of Selective Layer	μm	<1	<1
Membrane Geometry	—	plate-and-frame	plate-and-frame
Max Trans-Membrane Pressure	bar	2	2
Hours Tested without Significant Degradation	—	600	600
Manufacturing Cost for Membrane Material	$/m²	100	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,500	>2,500
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	pure gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	Crossflow, partial countercurrent	
Packing Density	m²/m³	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	5,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.1/sweep: 0.2	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	<50	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Permeation through the Polaris™ membrane occurs by the passive solution-diffusion mechanism.

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as mercury, arsenic, etc., was examined in the field tests at NCCC and no major issues were found.

Flue Gas Pretreatment Requirements –The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. The field tests at NCCC treated post-FGD flue gas, and. in extended testing (>13,000 hours), fouling was not a significant issue.

Membrane Replacement Requirements – The target membrane module lifetime is 3 years, which is at the conservative end of the typical industrial gas separation module lifetime of 3–5 years.

Waste Streams Generated – The membrane process will recover >95 percent of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

Process Design Concept – See Figure 1.

technology advantages

- The Polaris™ membranes developed are more than 10 times more permeable to CO_2 than conventional membranes, which reduce the required membrane area and capital costs.
- A membrane system does not contain any chemical reactions or moving parts, making it simple to operate and maintain.
- The membrane material has a high tolerance to wet acid gases and is inert to O_2.
- The membrane system has a compact footprint and low energy cost.
- The membrane capture system can recover water from flue gas.
- The use of an existing air stream to generate a CO_2 partial-pressure gradient in the countercurrent sweep membrane stage reduces the need for compressors or vacuum pumps, thus reducing the overall energy cost.
- The recycled CO_2 from the air sweep to the boiler increases the CO_2 partial-pressure driving force for separation in the initial CO_2 separation step (either membrane or absorption/stripper unit), reducing total system cost.
- The hybrid membrane/absorption process can be used with different capture technologies.

R&D challenges

- Scale up of advanced Polaris™ membranes that exhibit a CO_2 permeance of 3,000 GPU to reduce the capital cost of the membrane system.
- Minimizing the impact of the sweep stream CO_2 recycle on boiler performance.

status

MTR's existing 20-tpd small pilot membrane system incorporating the optimized plate-and-frame sweep modules completed a 1,400-hour field test at the NCCC, consistently capturing >85 percent of the CO_2 in a flue gas slipstream. Parametric tests of the 20-tpd membrane system recycling CO_2 to B&W's research boiler were conducted over a five-week period with Powder River Basin and eastern bituminous coals, achieving 90 percent CO_2 capture and a variety of partial capture conditions. Process modeling of MTR's plate-and-frame skid integrated with UT-Austin's SRP Pilot Plant demonstrated that a hybrid-parallel configuration is superior to a hybrid-series design. The SRP Pilot Plant has been modified and is prepared for hybrid testing with MTR's skid under parallel conditions.

available reports/technical papers/presentations

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CARBON CAPTURE TECHNOLOGY SHEETS

POST-COMBUSTION NOVEL CONCEPTS

Additively Manufactured Intensified Device for Enhanced Carbon Capture

primary project goals

In this project, Oak Ridge National Laboratory (ORNL) is focused on developing intensified devices for enhanced carbon dioxide (CO_2) capture. The main objective is to enable the Department of Energy (DOE) to accomplish its goal for transformational carbon capture technologies by reducing equipment sizes and costs, and optimizing operating conditions for each piece of equipment.

technical goals

Several incremental goals over the course of this project are:

- Design realization of intensified device geometries.
- Demonstration of the manufacturability of an equivalent geometry of a widely used packing structure (MellaPak 250) and intensified device design with additive manufacturing techniques.
- Measurement of core metrics of the additively manufactured MellaPak 250-equivalent to compare to its commercial counterpart.
- Printing of the device-scale prototype of MellaPak 250-equivalent.
- Measurement of the core metrics of the printed intensified device design.
- Printing of the device-scale prototype of intensified device design.
- Conduct prototypical device-scale validation experiments with printed MellaPak 250-equivalent and the intensified device design.

technical content

This project focuses on the development of enhanced CO_2 capture with intensified devices, which can combine multiple thermodynamic operations into one unit. Improvements in solvent-based CO_2 capture devices are targeted through analysis of monoethanolamine absorption and desorption of CO_2. For example, the multi-functionality of these intensified devices is envisioned to be achieved through graded packing structures with built-in heat exchanging channels made by additive manufacturing technologies, namely three-dimensional (3D) printing.

To execute this project, an integrated team from ONRL's Energy and Transportation Science Division is tasked with applying capabilities in computational fluid dynamics, additive manufacturing and absorber-scale demonstration/validation experiments.

Conventional carbon capture systems are configured with multiple unit operations which use sequentially coupled stages for mass transfer and heat transfer. Since solvent- and sorbent-based capture intrinsically couples mass transfer and heat transfer at the fundamental length scales, multiple stages of single-purpose unit operations would result in larger equipment size, higher equipment costs, and potentially less than optimal operating conditional for the equipment. This project aims to use additive manufacturing technologies to develop a graded packing structure to allow for the integration of heat exchange, reaction and potentially

technology maturity:

Bench Scale

project focus:

Additive Manufacturing for CO_2 Capture

participant:

Oak Ridge National Laboratory

project number:

FWP-FEAA130

predecessor projects:

N/A

NETL project manager:

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partners:

N/A

start date:

07.01.2017

percent complete:

20%

mass exchange in one multi-functional structure, and then to optimize the geometry to maximize the capture performance.

Figure 1: ORNL will fabricate an equivalent structure to this Mellapak Structured Packing

technology advantages

Improvement of device scale capture efficiency by simultaneously increasing reactive surface area and enhancing heat exchange efficiency in order to maintain the forward absorption reaction in the absorber column.

R&D challenges

Fabrication of a benchmark geometry for a conventional packing structure, interpreting the computationally-derived intensified device requirements, and demonstrating the manufacturability of the intensified device design via large scale direct deposition techniques.

status

Project is in its initial stages and no updates are available.

available reports/technical papers/presentations

N/A

Pilot Test of Novel Electrochemical Membrane System for Carbon Dioxide Capture and Power Generation

primary project goals

FuelCell Energy, Inc. (FCE) is developing an electrochemical membrane (ECM)-based Combined Electric Power and Carbon-Dioxide Separation (CEPACS) system for carbon dioxide (CO_2) capture that also provides additional electric power generation. The focus of the current project includes pilot-scale testing of a 3-megawatt (MW) system to capture CO_2 from a flue gas slipstream of an operating pulverized coal (PC) plant.

technical goals

- Design, fabricate, and install a small pilot-scale plant, prototypical of a commercial unit, for capturing 60 tonnes per day (tpd) of CO_2 from the flue gas slipstream of a PC plant.
- Configure the design of the flue gas pretreatment subsystem appropriate for removal of the contaminants from the flue gas slipstream.
- Conduct at least 2 months of testing of the pilot-scale plant for >90 percent of carbon capture from the flue gas slipstream.
- Perform a techno-economic analysis (TEA) of ECM carbon capture applied to a 550-MW baseline supercritical PC plant, achieving 30 percent less cost-of-electricity (COE) as compared to amine scrubbers.

technical content

FCE, in collaboration with AECOM Technical Services and Southern Company Services, is engaged in development of a CEPACS pilot plant to be demonstrated in a PC plant operated by Alabama Power. The CEPACS system is based on FCE's ECM technology derived from their internal reforming carbonate fuel cell products carrying the trade name of Direct FuelCell® (DFC®). The prominent feature of the ECM is its capability to produce electric power while capturing CO_2 from the flue gas of a PC power plant, resulting in a net efficiency gain. The ECM does not require flue gas compression as it operates on the principle of electrochemistry. The membrane utilizes a supplemental fuel (such as coal-derived synthesis gas [syngas], natural gas, or a renewable resource) as the driver for the combined CO_2 capture and electric power generation. The ECM consists of ceramic-based layers filled with carbonate salts that separate CO_2 from the flue gas with a selectivity of 100 percent over the nitrogen present. Because of the electrode's fast reaction rates, the membrane does not require a high CO_2 concentration in its feed gas. The ECM technology development and verification

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 3 MW_e)

project focus:

Electrochemical Membranes

participant:

FuelCell Energy, Inc.

project number:

FE0026580

predecessor project:

FE0007634

NETL project manager:

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partners:

Southern Company, AECOM, Pacific Northwest National Laboratory

start date:

10.01.2015

percent complete:

20%

roadmap has been consisting of small-scale component fabrication and testing, contaminant pretreatment evaluation, bench-scale testing of a 12-m^2 ECM separation unit with CO_2 compression and chilling, and the design, fabrication, and testing of an ECM-based pilot plant capable of capturing 60 tpd of CO_2.

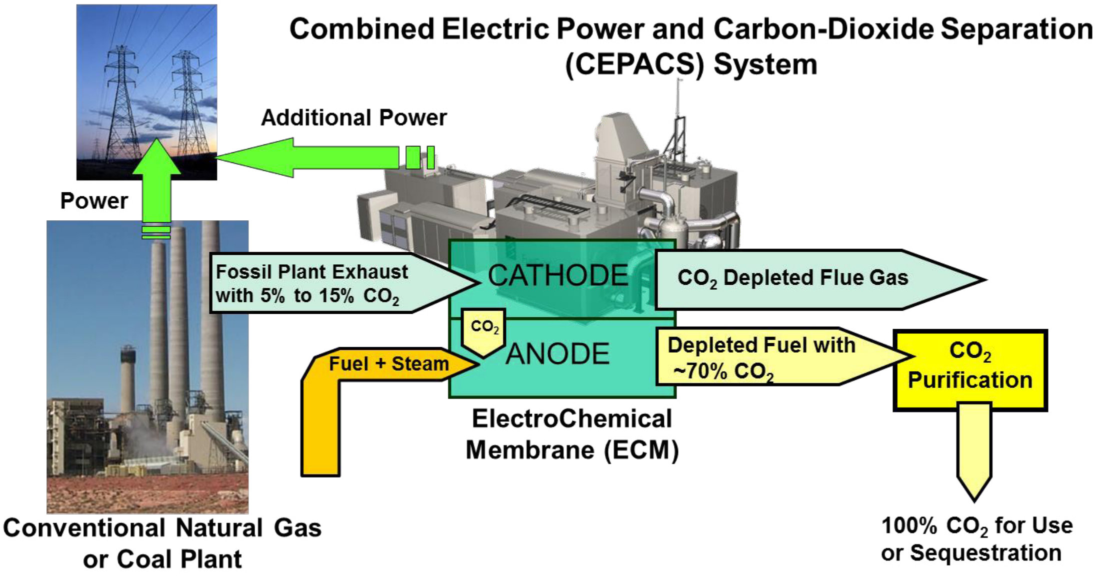

Figure 1: CEPACS system

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	alkali carbonate/$LiAlO_2$	
Materials of Fabrication for Support Layer	—	stainless steel	
Nominal Thickness of Selective Layer	µm	600	600
Membrane Geometry	—	planar (flat sheets)	planar (flat sheets)
Max Trans-Membrane Pressure	bar	<0.1	<0.1
Hours Tested without Significant Degradation	—	6,500	8,000
Manufacturing Cost for Membrane Material	\$/m^2	100	100
Membrane Performance			
Temperature	°C	650	650
Volumetric Flux*	GPU or equivalent	0.0116 cc/s/cm^2	≥0.01 cc/s/cm^2
CO_2/H_2O Selectivity	—	infinity	infinity
CO_2/N_2 Selectivity	—	infinity	infinity
CO_2/SO_2 Selectivity	—	59.9×10^{61}	59.9×10^6
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	crossflow	
Packing Density	m^2/m^3	16	
Shell-Side Fluid	—	CO_2-containing flue gas (permeate stream)	
Flue Gas Flowrate	kg/hr	6300	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99.7%, 1 bar	
Pressure Drops Shell/Tube Side	bar	0.025/0.01	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	350	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Volumetric flux, rather than permeance, is considered a major performance parameter for the ECM. Permeance generally applies to membranes that use pressure or partial pressure as the driving force. In the case of ECM, the driving force is the electrochemical potential.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.

Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

Steam Reforming – Method that converts steam and hydrocarbon fuel (such as natural gas, syngas, or biogas) into hydrogen.

Other Parameter Descriptions:

Membrane Permeation Mechanism – The operating principle of ECM is shown in Figure 2, along with the electrochemical reactions involved. The ECM is composed of a thin matrix layer of ceramic material (lithium aluminate), sandwiched between two electrodes (anode and cathode). The membrane is impregnated with a mixture of alkali metal (Li/Na/K) carbonate electrolyte, which constitutes a molten phase immobilized in the ECM pores at the operating temperature of 550–650 °C. The anode and cathode are porous to allow gas diffusion. The inner matrix layer is filled with electrolyte and is impervious to gas transport, while providing a path for ionic transfer across the membrane. Carbon dioxide and oxygen present in the flue gas of a coal power plant are used as reactants at the cathode. The ECM utilizes hydrogen (H_2) at the anode. The hydrogen is made available to the anode by a mixture of a fuel (such as natural gas, syngas, or biogas) and steam. The hydrocarbon content of the fuel is internally steam reformed to produce hydrogen in the anode chamber.

The electrochemical reactions (Figure 2) involve the formation of carbonate ions (CO_3^{2-}) at the cathode by the combination of oxygen (O_2), CO_2, and two electrons; transportation of the carbonate ions to the anode through electrolyte; and finally, reaction of the carbonate ion with H_2 at the anode, producing water (H_2O), CO_2, and two electrons. The internal transport of carbonate ions in an ECM assembly (or cell) and the flow of electrons in the external circuit results in electric power generation as a consequence of the electrochemical CO_2 separation process. The direct current (DC) power produced is converted to alternating current (AC) power using an inverter.

Overall, the operating mechanism of the ECM cell results in the separation (from flue gas) and transfer of CO_2 into the anode exhaust stream (resulting in a CO_2-rich stream), and a much reduced volumetric flow rate in the flue gas, compared to the original flue gas stream.

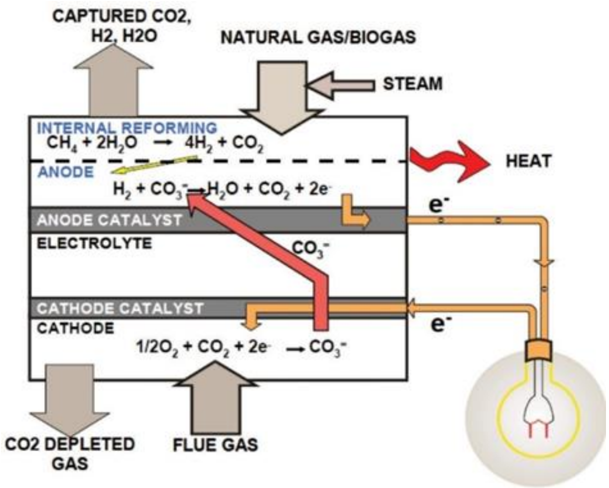

Figure 2: Separation of CO_2 in the electrochemical membrane cell

Contaminant Resistance – A comprehensive contaminant evaluation study was performed to address possible interactions of the impurities that may be present in flue gas with ECM cell. Pacific Northwest National Laboratory (PNNL) performed the analysis and testing using ECM cells provided by FCE. Four main flue gas impurities were considered—sulfur, chlorine, mercury and selenium. The study included thermochemical modeling to predict the possible impurity-membrane interactions, and experimental work to assess the extent of the interactions, if any. Prevalent forms of S, Cl, Hg, and Se which can be present in flue gas were identified and included in the evaluation tests. Effect of these contaminants on ECM cell performance and endurance was studied. Based on the experimental results, contaminant tolerance levels for the ECM were identified. The contaminant levels expected from the flue gas clean-up (polishing flue gas desulfurization [FGD]) subsystem were estimated by URS and compared with the ECM tolerance levels. The contaminant (effect) evaluation showed that the ECM tolerance levels are well above the contaminant levels expected in treated flue gas. While the power output decreased during operation with an SO_2 concentration of 10 parts per million (ppm) and higher, the voltage loss was found to be nearly fully reversible on return to a lower concentration level (1 ppm) and did not impact CO_2 flux. Laboratory tests have indicated that ECM has the potential to eliminate 60–70 percent of the NO_x species present in the flue gas of a coal power plant.

Flue Gas Pretreatment Requirements – After the existing PC plant's FGD step removes SO_2 in the flue gas to less than 5 ppm, flue gas entering the CEPACS plant is routed through a secondary polishing FGD system, to further reduce the inlet SO_2 concentration to less than 0.4 ppm. The cleaned flue gas is then mixed with supplemental air. This serves to raise the oxygen partial pressure in the stream for proper operation of ECM modules. The mixed stream is preheated to the ECM operating temperature of ≈650 °C using waste heat available in the system.

Membrane Replacement Requirements – The CEPACS is designed with the ECM modules replacement after 10 years of operation. Therefore, ECM modules are required for the initial start-up and then to be replaced twice during the 30-year lifetime of the CEPACS plant.

Waste Streams Generated – The CEPACS plant produces minimal waste streams. Since water is generated by the electrochemical reactions within the ECM module, the system generates excess clean process water. This excess process water can be utilized in the existing PC plant to reduce raw water consumption. The polishing FGD generates a waste stream that is treated in the existing PC plant dewatering and water treatment equipment.

Process Design Concept – See Figure 1.

technology advantages

- Unlike other scrubber and membrane-based CO_2 capture technologies, the ECM-based CEPACS system produces additional electric power with use of a supplemental fuel, rather than reducing the net power plant output.

- The net efficiency of a CEPACS-equipped PC plant with >90 percent CO_2 capture is estimated to be ≈6 percent higher than the net efficiency of a baseline PC plant without CO_2 capture.
- The ECM technology exhibits complete selectivity toward CO_2 as compared to nitrogen (N_2).
- The ECM technology is anticipated to reduce flue gas NO_x emissions by 60–70 percent.
- The ECM is a modular technology, allowing for phased addition of CO_2 capture capacity over time.
- The ECM-based CEPACS system has the potential to significantly reduce the cost of CO_2 capture.
- The CEPACS system generates excess clean water as part of the electrochemical separation process, reducing the total plant water usage.

R&D challenges

- The CEPACS process design needs to be demonstrated at large scale.
- Membrane operational characteristics need to be investigated with consideration for minimization of the system cost.

status

A pilot-scale (3-MW_e equivalent) CEPACS system is being designed to capture up to 60 tpd of CO_2 and will be installed at the James M. Barry Electric Generating Station in Alabama and tested for at least 2 months.

A bench-scale CEPACS system utilizing an 11.7 m^2 (10 kW_e) ECM stack completed 9 months of steady-state testing and over 15,000 hours, including follow-on parametric testing, while exhibiting stable performance and separating more than 90 percent of CO_2 from a simulated PC plant flue gas stream at constant CO_2 flux. A polishing wet-FGD scrubber was designed to sufficiently clean flue gas for ECM operation.

available reports/technical papers/presentations

Ghezel-Ayagh, H., "Pilot Test of Novel Electrochemical Membrane System for Carbon Dioxide Capture and Power Generation," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/H-Ghezel-Ayagh-FCE-Novel-Electrochemical-Membrane.pdf.*

Ghezel-Ayagh, H., "Pilot Test of Novel Electrochemical Membrane System for Carbon Dioxide Capture and Power Generation," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/1-Monday/H-Ghezel-Ayagh-FCE-Electrochemical-Membrane-System.pdf.*

"Electrochemical Membranes for CO_2 Capture and Power Generation," Project close-out meeting presentation, June 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/DE-FE-0007634-CloseOut-june-10-2016-Public.pdf.*

Ghezel-Ayagh, H., "Electrochemical Membranes for CO_2 Capture and Power Generation," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/H-Ghezel-Ayagh-FCE-Electrochemical-Membranes.pdf.*

M. Spinelli, S. Campanari, M.C. Romano, S. Consonni, T. G. Kreutz, H. Ghezel-Ayagh, S. Jolly, M. Di Nitto, "Molten Carbonate Fuel Cells as Means for Post-Combustion CO_2 Capture: Retrofitting Coal-Fired Steam Plants and Natural Gas-Fired Combined Cycles," Proceedings of the ASME 2015 Power and Energy Conversion Conference, Paper 2015-49454, June 28–July 2, 2015, San Diego, CA.

Cryogenic Carbon Capture Development

primary project goals

The objective of this project is to increase the reliability, efficiency, and scalability of the Cryogenic Carbon Capture™ (CCC) process and prepare it for a pilot demonstration.

technical goals

- Improving key areas of the process through iterative design and experimentation, culminating with improvements integrated into the existing skid-scale system developed under previous funding called the CCC External Cooling Loop (CCC-ECL™) system.
- Integrating the recommended improvements into the CCC-ECL™ system and confirming their contributions through experimental process testing.
- Making modeling and estimation improvements to improve the techno-economic analyses.

technical content

Sustainable Energy Solutions (SES), with their partners Brigham Young University, Electric Power Research Institute, and Tri-State Generation & Transmission Association, Inc., will further advance the external cooling loop (ECL) version of their Cryogenic Carbon Capture™ (CCC) technology. SES developed the CCC-ECL™ technology under previous research funded by the Advanced Research Projects Agency-Energy (ARPA-E) project titled "Cryogenic Carbon Capture" (DE-AR0000101), the state of Wyoming, and others. Process improvements implemented in this work address issues discovered during the previous field tests at power plants, cement kilns, and heating plants. The CCC technology separates carbon dioxide (CO_2) and other pollutants from coal-derived flue gas by cooling the flue gas to approximately -130 °C, at which temperatures CO_2 forms a solid (desublimates); the solid separates from the remaining gas, after which the process pressurizes and melts the CO_2 stream. The CCC process is minimally invasive and represents a bolt-on carbon capture retrofit technology. It also requires 50 percent less parasitic energy and costs about 50 percent less than an amine absorption process. In this project, the team improves process unit operations' reliability and performance through iterative design and experiment, culminating with improvements integrated into the existing skid-scale CCC-ECL™ system. Sustainable Energy Solutions will demonstrate the modified skid on a power plant slipstream for a minimum of 500 continuous hours during a several-month series of tests. Reconciliation of test results and process modeling update the techno-economic analyses of the CCC technology.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Novel Concepts/Cryogenic Carbon Capture Process

participant:

Sustainable Energy Solutions

project number:

FE0028697

predecessor projects:

DE-AR0000101 (ARPA-E)

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partners:

Brigham Young University, Electric Power Research Institute, and Tri-State Generation & Transmission Association, Inc.

start date:

10.01.2016

percent complete:

33%

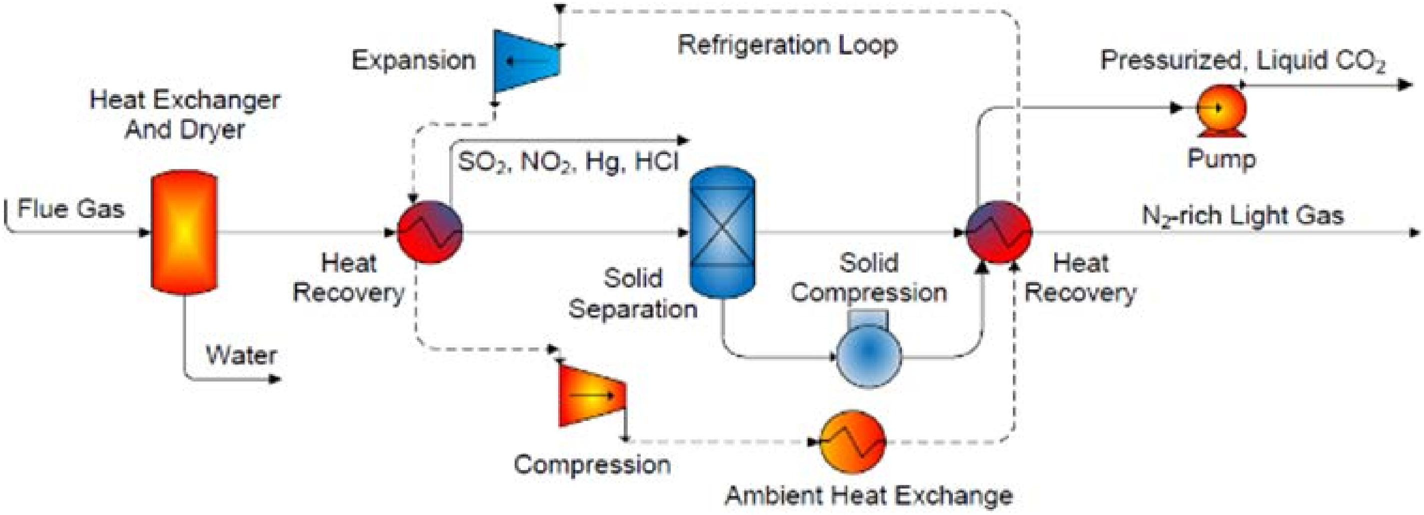

Figure 1: Cryogenic Carbon Capture™ process implemented using an ECL™ system

technology advantages

- The CCC process retrofits existing plants or provides a greenfield solution to any continuous CO_2 source (coal-based power, natural gas, cement, integrated gasification combined cycle, refineries, etc.).
- The CCC process captures 90–99+ percent of the CO_2, and most pollutants (sulfur oxides, nitrogen oxides, mercury), at half the cost and energy of alternative carbon capture technologies and recovers more water from flue gas than it requires for operation (reduces overall water demand).
- An increase in reliability, efficiency, and scalability of the CCC process can make significant progress toward the U.S. Department of Energy's (DOE) goal of $40/tonne of CO_2 captured by 2025.

R&D challenges

- Innovative desublimating heat exchangers can be further optimized. Solids handling process equipment must avoid fouling, plugging, and level upsets. Innovative, scalable flue gas dryer requires demonstration.
- Effectiveness of solid-liquid separation is critical for pilot-scale implementation.

status

SES is refining the CCC process in several areas, including gas drying, reducing the dissolved CO_2 in solid-liquid separations, improving the heat exchanger and light gas dispersal, while working toward operation of a demonstration unit.

available reports/technical papers/presentations

Baxter, L., "Cryogenic Carbon Capture Development," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/L-Baxter-SES-Cryogenic-Carbon-Capture.pdf.*

"Cryogenic Carbon Capture Development," presented at the Project Kickoff Meeting, December 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/SES-FE0028697-kick-off.pdf.*

Jensen, M. J., C. S. Russell, D. Bergeson, C. D. Hoeger, D. J. Frankman, C. S. Bence and L. L. Baxter (2015). "Prediction and validation of external cooling loop cryogenic carbon capture (CCC-ECL) for full-scale coal-fired power plant retrofit." International Journal of Greenhouse Gas Control, Vol. 42: 200-212.

Energy Efficient GO-PEEK Hybrid Membrane Process for Post-Combustion Carbon Dioxide Capture

primary project goals

Gas Technology Institute (GTI) is developing a hybrid process for post-combustion carbon dioxide (CO_2) capture that combines a graphene oxide (GO)-based separation membrane unit with their polyether ether ketone (PEEK) hollow fiber membrane contactor (HFMC) unit to achieve a reduction in carbon capture cost. This effort includes laboratory development of GO-based and PEEK membranes and laboratory testing of the integrated GO-PEEK process.

technical goals

- Prepare GO-based membranes on porous hollow fiber supports.
- Optimize GO-based membranes to achieve CO_2 permeance of ≥1,000 gas permeation unit (GPU) and CO_2/nitrogen (N_2) selectivity of ≥90.
- Perform stability testing of optimized GO-based membranes using simulated flue gas.
- Optimize and fabricate PEEK hollow fiber membrane modules with a permeance of at least 3,000 GPU and perform quality control and membrane contactor testing.
- Modify existing HFMC apparatus to incorporate the GO-PEEK integrated system.
- Perform testing of the laboratory-scale GO-PEEK hybrid system with simulated flue gas.

technical content

GTI, in collaboration with University of South Carolina, Air Liquide Advanced Separations, and Trimeric Corporation, is integrating the GO-based membrane process with the PEEK HFMC process. The singular HFMC technology using PEEK hollow fiber membrane modules with a CO_2 permeance of 2,000 GPU is currently at pilot-scale (0.5 MWe) development using coal-fired flue gas at the National Carbon Capture Center (NCCC) in project DE-FE0012829. Laboratory-scale testing of the hybrid GO-PEEK membrane process and optimization of both the GO-based and PEEK membranes are the overall scope of this project. The GO-PEEK membrane process, as shown in Figure 1, is designed to capture 45 percent of the CO_2 from flue gas using the conventional GO-based membrane process and then capture another 45 percent of CO_2 using the PEEK membranes.

The GO-based membrane consists of a GO-based layer supported on polyethersulfone (PES) hollow fibers and has been optimized to obtain improved selectivity and CO_2 permeance compared to other separation membranes. Table 1 provides a summary of the GO membrane process parameters.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Hybrid GO-PEEK Membrane Process

participant:

Gas Technology Institute

project number:

FE0026383

predecessor projects:

FE0012829
FE0004787

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partners:

Air Liquide Advanced Separations, Trimeric Corporation, University of South Carolina

start date:

10.01.2010

percent complete:

30%

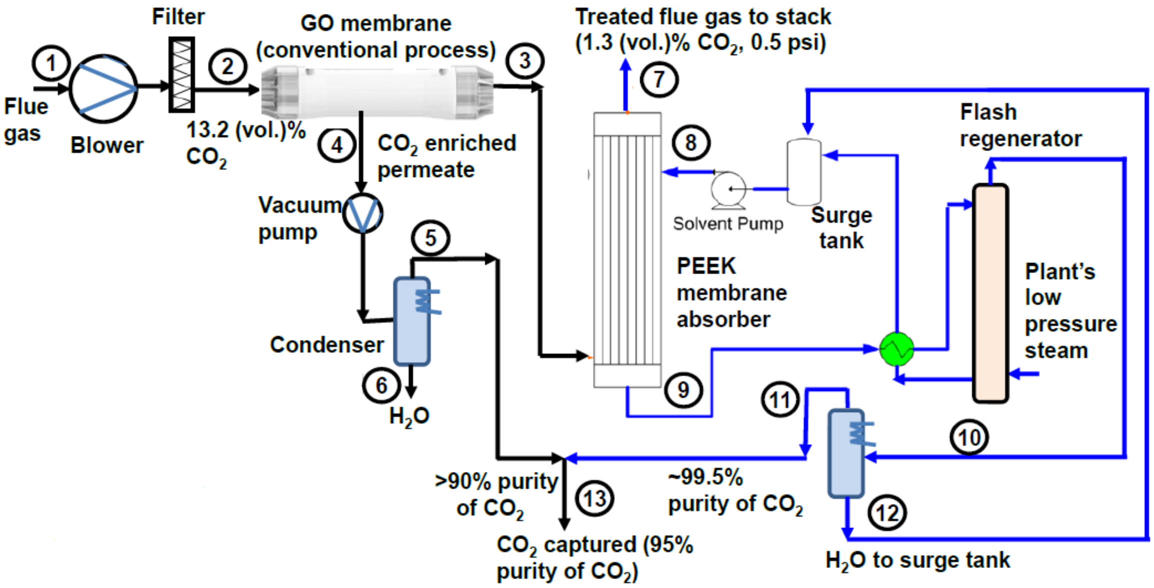

Figure 1: GO-PEEK hybrid process

The PEEK HFMC process is based on a combination of solvent absorption and hollow fiber membrane technologies, applying the advantageous features of both and enabling economical utilization of advanced absorption solvents. The HFMC is a high surface area membrane device that uses nano-porous PEEK fibers to facilitate mass transfer of CO_2 to a solvent for absorption. In this process, CO_2-containing flue gas passes through one side of the PEEK HFMC, while a CO_2 selective solvent (for example, activated methyldiethanolamine [MDEA]) flows on the other side. Carbon dioxide permeates through the hollow-fiber-membrane pores and is chemically absorbed into the solvent, while nitrogen has low solubility in the solvent. The membrane surface is modified to be super hydrophobic to ensure independent gas and liquid flow under flue gas conditions. The CO_2-rich solvent is regenerated in a PEEK membrane desorber operated in a reverse process. Figure 2 shows the basic mass transfer principle using the porous, hollow-fiber PEEK membrane contactor. The membrane matrix is filled with gas and mass transfer occurs via a diffusion reaction mechanism. The driving force is the difference in chemical potential of the CO_2 in the gas side versus the liquid side of the membrane. Optimization of the PEEK fiber structure and the hydrophobic coating layer increases CO_2 permeance. The main process features of the PEEK membrane/solvent technology include: a higher CO_2 loading differential between rich and lean solvent is possible; increased mass transfer reduces system size; high specific surface area available for mass transfer; independent gas and liquid flow; linear scale up; and concentrated solvents or specialty absorbents can be used. Table 2 provides a summary of the PEEK membrane process parameters.

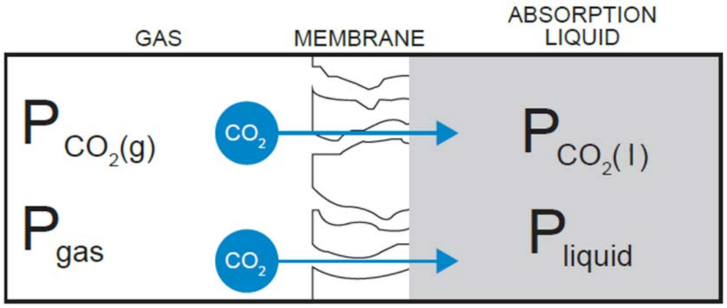

Figure 2: Mass transfer principle for hybrid membrane/solvent contactor

TABLE 1: GO MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	GO flakes	
Materials of Fabrication for Support Layer	—	polyether sulfone	
Nominal Thickness of Selective Layer	µm	0.002–0.05	0.002–0.02
Membrane Geometry	—	Hollow fiber or flat sheet	Hollow fiber or flat sheet
Max Trans-Membrane Pressure	bar	<5	1
Hours Tested without Significant Degradation	—	20	>50
Manufacturing Cost for Membrane Material	$/m²	100	30
Membrane Performance			
Temperature	°C	80	65
CO_2 Pressure Normalized Flux	GPU or equivalent	1,020	1,000
CO_2/H_2O Selectivity	—	—	—
CO_2/N_2 Selectivity	—	680	>90
CO_2/SO_2 Selectivity	—	—	—
Type of Measurement	—	Mixed gas	Mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	hollow fiber bundles	
Packing Density	m²/m³	>1,000	
Shell-Side Fluid	—	permeate (CO_2-rich)	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	—	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

TABLE 2: PEEK MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	not applicable for membrane contactor	
Materials of Fabrication for Support Layer	—	PEEK	
Nominal Thickness of Selective Layer	µm	not applicable for membrane contactor	
Membrane Geometry	—	hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	4	4
Hours Tested without Significant Degradation	—	200 hours	≥60 days
Manufacturing Cost for Membrane Material	$\$/m^2$	80	30
Membrane Performance			
Temperature	°C	40 °C	40 °C
CO_2 Pressure Normalized Flux	GPU or equivalent	2,000	3,000
CO_2/H_2O Selectivity	—	not applicable	not applicable
CO_2/N_2 Selectivity	—	>1,000	>1,000
CO_2/SO_2 Selectivity	—	0.64	0.64
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent hollow-fiber	
Packing Density	m^2/m^3	1,000–2,000	
Shell-Side Fluid	—	liquid solvent	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	—	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – The PEEK HFMC process is driven by the chemical potential difference of CO_2 between the gas phase and the solvent phase and high purity of CO_2 product can be generated in a single stage. The process selectivity for the hybrid membrane/absorption process approaches thousands and is determined by the chemical affinity of the absorption solvent to CO_2. As compared with the conventional membrane process, the permeate side partial pressure of CO_2 can be considered to be close to zero due to the chemical interaction of CO_2 with the absorption solvent. Therefore, the pressure ratio in the hybrid membrane/absorption process approaches infinity. Note that membrane selectivity is not required in a hybrid membrane/absorption process, although the porous super-hydrophobic membranes used in this project showed some selectivity for CO_2 over N_2.

Contaminant Resistance – Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column. Membrane will provide a measure of protection for the solvents from degradation by contaminants (a barrier).

Flue Gas Pretreatment Requirements – Particle removal.

Membrane Replacement Requirements – To be determined with actual coal-fired flue gas, however a 5-year life is estimated based on field data of PEEK commercial membrane used in natural gas industry.

Waste Streams Generated – None.

Process Design Concept – See Figure 1.

technology advantages

- The GO-PEEK process for a 45 percent/45 percent capture case has a projected cost that can be 31 percent lower than DOE’s benchmark amine technology.
- The system size of the GO-PEEK process can be reduced by up to 70 percent compared to a conventional solvent-based process.
- The GO-PEEK hybrid process combines the simply equipped nature of the conventional gas separation membrane process and the high selectivity of the membrane contactor process.
- The PEEK hollow fiber membrane has an interfacial gas/liquid area that is 10 times higher than conventional packed or tray absorption columns, thus increasing mass transfer.

R&D challenges

- Long-term stability of both GO and PEEK membranes.
- Improve CO_2 permeance in GO membranes.
- Develop larger diameter modules and an advanced manufacturing process to lower membrane costs.

status

The singular PEEK HFMC technology using commercial-sized 8-inch modules with a CO_2 permeance of 2,000 GPU is being tested at the NCCC and preliminary results indicate that DOE’s performance targets can be achieved. The PEEK fibers were optimized to obtain an intrinsic CO_2 permeance of >3,000 GPU and 2-inch PEEK membrane modules with a CO_2 permeance of 2,440 GPU were effective in capturing CO_2 from low CO_2-concentration feeds with an activated MDEA solvent. GO membranes were optimized to obtain a CO_2 permeance of >1,000 GPU and a CO_2/N_2 selectivity of >600 in a hollow fiber configuration. Testing of the integrated laboratory-scale GO-PEEK hybrid system will be performed with simulated flue gas after further optimization and stability testing of the GO membranes.

available reports/technical papers/presentations

Li, S., et al., "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-combustion CO_2 Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/S-Li-GTI-Hybrid-Membrane-Process.pdf.*

Li, S., et al., "Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/1-Monday/S-Li-GTI-Super-Hydrophobic-Membrane.pdf.*

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Li, S., et al., "Pilot-Scale Development of a PEEK Hollow Fiber Membrane Contactor Process for Post-Combustion CO_2 Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/1-Monday/S-Li-GTI-Membrane-Contractor-Process.pdf.*

Li, S., et al., "Energy Efficient GO-PEEK Hybrid Membrane Process for Post-combustion CO_2 Capture," Project kick-off meeting presentation, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026383-Kickoff-Presentation.pdf.*

Zhou, J., et al., "Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/SJ-Zhou-GTI-Pilot-Nanoporous-Membrane-Contactor.pdf.*

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Li, S., et al., "Post-combustion CO_2 Capture Using PEEK Hollow Fiber Membrane Contactors," Suzhou, China, July 2014.

Zhou, J., et al., "Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-James-Zhou-GTI-Nanoporous-Super-Hydrophobic-Membrane.pdf.*

Meyer, H., "Hollow Fiber Membrane Contactors for CCS on Natural Gas Power Systems," Workshop on Technology Pathways Forward for Carbon Capture and Storage on Natural Gas Power Systems, Washington, DC, April 2014.

"Pilot Test of a Nanoporous, Super-hydrophobic Membrane Contactor Process for Post-Combustion Carbon Dioxide Capture," Factsheet, February 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0012829.pdf.*

Leppin, D., "Development of Porous PEEK® Hollow Fiber-based Gas/Liquid Membrane Contactors for Sour Gas Treating," Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, February 2014.

Zhou, J., et al., "Pilot Test of a Nanoporous, Super-Hydrophobic Membrane Contactor Process for Post-combustion CO_2 Capture," Project Kick-Off Presentation, November 2013. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Kickoff-Meeting-DE-FE0012829.pdf.*

Zhou, J., et al., "Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/SJ-Zhou-GTI-Membrane-Absorption-Process.pdf.*

Zhou, J., et al., "Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/J-Zhou-GTI-Hybrid-Membrane-Process.pdf*.

"Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture," Factsheet, November 2011. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/FE0004787.pdf.*

Li, S., et al., "Hybrid Membrane/Absorption Process for Post-combustion CO_2 Capture," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Li-GTI-Hybrid-Membrane-Absorption-Process.pdf.*

Zhou, J., et al., "Hybrid Membrane/Absorption Process for Post-Combustion CO_2 Capture (Membrane Contactor)," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Shaojun-Zhou---Gas-Technology-Institute.pdf.*

Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System, and Process Integration

primary project goals

Liquid Ion Solutions, in collaboration with Pennsylvania State University and Carbon Capture Scientific, is developing and evaluating a hybrid membrane/solvent system that employs a novel interfacially-controlled envelope (ICE) membrane for post-combustion carbon dioxide (CO_2) capture. The goal of the project is to complete lab-scale testing of Liquid Ion Solutions LLC's hybrid membrane/solvent system for post-combustion CO_2 capture while demonstrating significant progress toward achievement of the overall fossil energy performance goals of 90 percent CO_2 capture rate with 95 percent CO_2 purity at a cost of electricity 30 percent less than baseline capture approaches.

technical goals

- An optimized project flow diagram is being developed, and basic performance calculations are being conducted. Parallel to this effort, ICE membranes are being developed by synthesizing polyphosphazene polymers using advanced fabrication techniques.
- An isochoric membrane test system is being designed and built.
- The absorber portion of the advanced solvent system is being tested using an existing packed-bed column.
- ICE membranes are being tested and optimized, the air stripper for the advanced solvent system is also being tested, and an isobaric membrane test system is being constructed for simulated flue gas testing.
- Simulated flue gas testing and an initial technical and economic feasibility study are being conducted, demonstrating significant progress toward achieving a cost of electricity 30% less than baseline carbon capture approaches.

technical content

Liquid Ion Solutions LLC, in partnership with Pennsylvania State University and Carbon Capture Scientific, is developing and validating a transformational hybrid membrane/solvent system for post-combustion CO_2 capture from flue gas. The project is building upon work previously conducted by Liquid Ion Solutions in mixed-matrix membrane (MMM) development, Penn State in polymer synthesis and property optimization, and Carbon Capture Scientific in solvent systems. The hybrid technology is a two-stage CO_2 capture system combining a membrane separation process and an absorption/stripping process with heat integration between the absorption column and stripping column using a heat pump cycle. Process air is used to sweep the stripper, resulting in much lower regeneration temperatures and enabling heat integration to the point that no process steam is required. To reduce capital cost, a next-generation membrane technology with higher permeance is being developed. The ICE membrane

technology maturity:
Laboratory Scale

project focus:
Novel Concepts/ICE Membrane for Post-Combustion CO_2 Capture

participant:
Liquid Ion Solutions LLC

project number:
FE0026464

predecessor projects:
N/A

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partners:
Pennsylvania State University, Carbon Capture Scientific

start date:
10.01.2015

percent complete:
62%

is making use of a transport zone neglected in conventional MMMs. By carefully controlling the interface between the polymer and inorganic particles within the MMM, CO_2 transport is encouraged and nitrogen transport diminished in the gap between the two phases. Permeance is directly tied to membrane area. The development of the ICE membranes can reduce the capital cost of the hybrid process below that of the baseline technologies. The research team is combining computer simulation with lab-scale experimentation (using simulated flue gas), to develop, optimize, and test ICE membranes. The team will also test the absorption column and air stripper, and complete a techno-economic analysis of the hybrid technology.

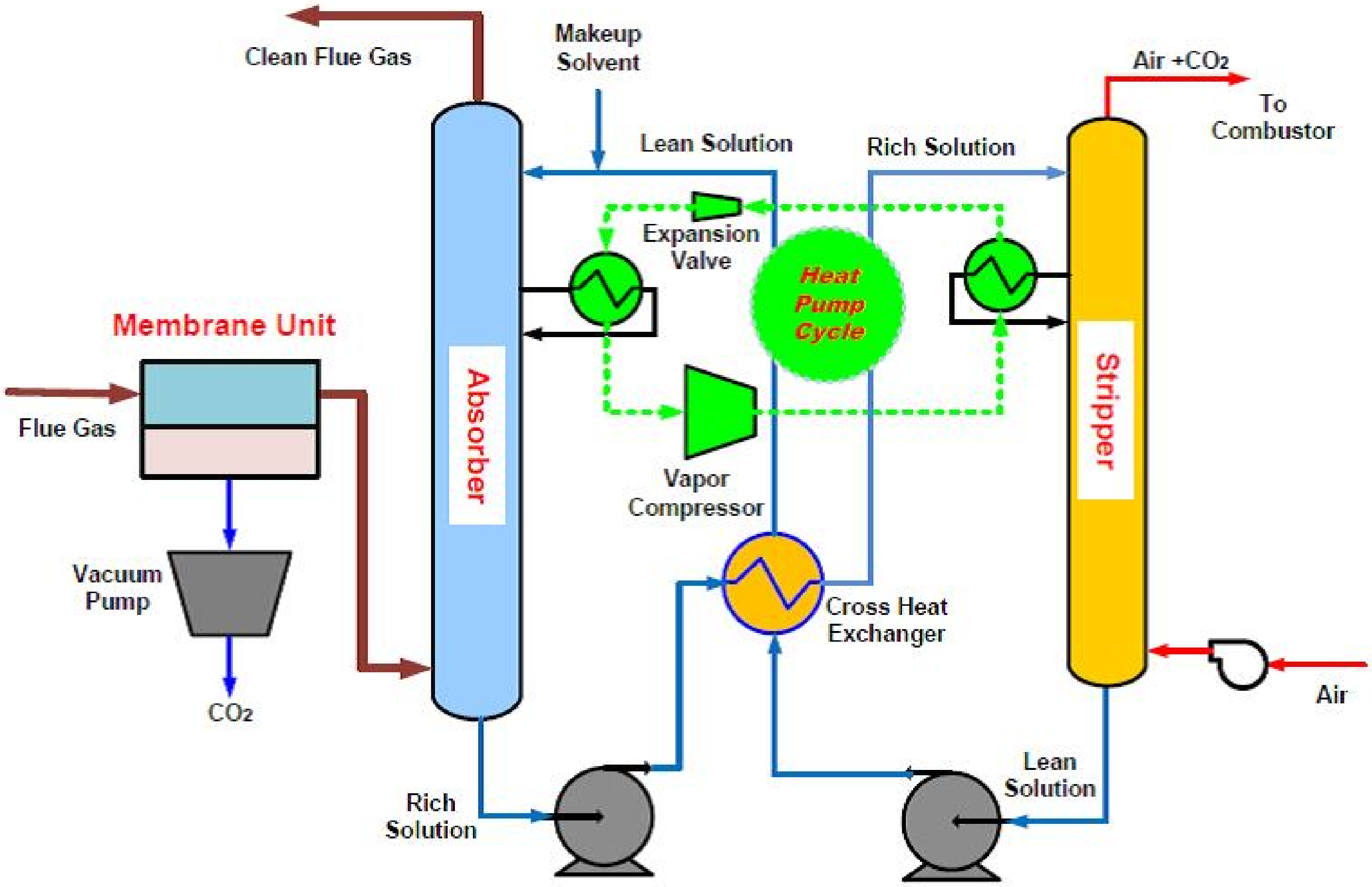

Figure 1: Hybrid membrane solvent system

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polyphosphazenes/panoparticle composites	
Materials of Fabrication for Support Layer	—	porous hydrophilic PVDF	
Nominal Thickness of Selective Layer	µm	10	0.5
Membrane Geometry	—	flat discs	flat discs
Max Trans-Membrane Pressure	bar	1.0	1.0
Hours Tested without Significant Degradation	—	60	100
Manufacturing Cost for Membrane Material	$\$/m^2$	30	2–5
Membrane Performance			
Temperature	°C	40	40
CO_2 Pressure Normalized Flux	GPU or equivalent	140	5,000
CO_2/H_2O Selectivity	—	—	—
CO_2/N_2 Selectivity	—	42	50
CO_2/SO_2 Selectivity	—	—	—
Type of Measurement	—	mixed gas	mix gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	spiral wound/crossflow	
Packing Density	m^2/m^3	600	
Shell-Side Fluid	—	Low-pressure CO_2	
Flue Gas Flowrate	kg/hr	2,716, 229	
CO_2 Recovery, Purity, and Pressure	%/%/bar	85/95/0.2	
Pressure Drops Shell/Tube Side	bar	0.1	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	240	

Definitions:

***Membrane Geometry* –** Flat discs or sheets, hollow fibers, tubes, etc.

***Pressure Normalized Flux* –** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

***GPU* –** Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

***Type of Measurement* –** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

***Flow Arrangement* –** Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

***Packing Density* –** Ratio of the active surface area of the membrane to the volume of the module.

***Shell-Side Fluid* –** Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Surface diffusion.

Contaminant Resistance – Polyphosphazenes are highly chemically and thermally stable. Resistance to contaminants is expected to be high.

Flue Gas Pretreatment Requirements – High-efficiency particulate removal is necessary for the membrane and SO_x needs to be reduced to less than 10ppm as required with most of amine-based solvents.

Membrane Replacement Requirements – The goal is to develop membrane models that will last at least two years.

Waste Streams Generated – A stream consisting of 95 percent CO_2 and a flue gas stream containing less than 1.5 percent CO_2 will be generated.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	112.4	112.4
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15 °C	bar	<0.01	<0.01
Manufacturing Cost for Solvent	$/kg	2	2
Working Solution			
Concentration	kg/kg	50/100	50/100
Specific Gravity (15 °C/15 °C)	-	1.05	1.05
Specific Heat Capacity @ STP	kJ/kg-K	3.3	3.3
Viscosity @ STP	cP	12.5	12.5
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	30	30
Equilibrium CO_2 Loading	mol/mol	0.48	0.48
Heat of Absorption	kJ/mol CO_2	57	57
Solution Viscosity	cP	5.3	5.3
Desorption			
Pressure	bar	1	1
Temperature	°C	60	60
Equilibrium CO_2 Loading	mol/mol	0.33	0.33
Heat of Desorption	kJ/mol CO_2	57.0	57.0
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,716,229	
CO_2 Recovery, Purity, and Pressure	% / % / bar	80/10/0.10	
Absorber Pressure Drop	bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	160	

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent

(e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

Chemical/Physical Solvent Mechanism – MDEA (methyl diethanolamine) in aqueous solution is a base and reacts reversibly with CO_2 dissolved in water as acid via a temperature-swing mechanism.

Solvent Contaminant Resistance – MDEA is more stable compared to MEA, but is the same as MEA and will react with sulfur dioxide (SO_2) and sulfur trioxide (SO_3) to form stable salts.

Solvent Foaming Tendency – Aqueous MDEA has little tendency for foaming.

Flue Gas Pretreatment Requirements – SO_2 or SO_3 needs to be reduced to less than 10ppm to avoid stable salt accumulation.

Solvent Make-Up Requirements – Solvent make-up is required due to solvent degradation and some vapor loss with flue gas, but the make-up requirements are manageable. It is expected that the loss will be less than $1/tonne CO_2 captured.

Waste Streams Generated – The degradation products of the solvent and the products from interaction between solvent and contaminants will generate some waste materials. The amount should be minimal.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

technology advantages

By combining the polyphosphazene membranes that have greater permeance and selectivity, with the hybrid process scheme which uses a solvent technology to address the low CO_2 concentration portion of the separation, the technology will make progress toward achieving the DOE performance goals. The combination of lab-scale experimentation on simulated flue gas with modeling and systems analysis shows the increase in energy and cost advantages of the hybrid technology with further scale-up.

R&D challenges

- Modify the surface of the polymer to tune optimal interaction between CO_2 and the polymer.
- Develop a first-generation ICE membrane with 2,500 GPU permeance and 25 CO_2/N_2 selectivity and progress to 5,000 GPU permeance and 30 CO_2/nitrogen (N_2) selectivity.
- Successfully fabricate the selected ICE membrane with reproducible results.

status

Statistical tools are being used to optimize membrane composition, including concentration and surface modification of the nanoparticles, and their degree of crosslinking. Over 30 compositions are being examined, and selection will be tested in simulated flue gas.

available reports/technical papers/presentations

Luebke, D., "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System, and Process Integration," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/2-Tuesday/D-Luebke-Liquid-Ion-Hybrid-Capture-System.pdf.*

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Luebke, D., "Lab-Scale Development of a Hybrid Capture System with Advanced Membrane, Solvent System, and Process Integration," presented at the 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/D-Luebke-LIS-Hybrid-Capture-System.pdf.*

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Process Intensification for Carbon Capture

primary project goals

Altex Technologies Corporation, in partnership with Pennsylvania State University, is developing an integrated temperature and pressure swing (ITAPS) carbon capture system. By enabling the production of ITAPS reactors at low cost and integrating an ITAPS carbon capture system with existing unit operations, capital and operating costs for carbon dioxide (CO_2) capture from coal-fired power plants will be reduced.

technical goals

- Previously developed sorbents are being tested in a laboratory-scale contactor. Results will be used to develop a full-scale system.
- A technical and economic analysis of the technology is being conducted.

technical content

Altex Technologies Corporation, in partnership with Pennsylvania State University, is developing an ITAPS carbon capture system to lower the cost of carbon capture from flue gas streams of coal-fired power plants. The system provides a combustion-air preheat for the gas turbine during the absorption phase of the cycle and cooling of the steam condenser during the regeneration phase of the cycle. This approach reduces the capital cost of the carbon capture system and reduces water usage by providing an effective means of dry cooling the steam-turbine exhaust. The ITAPS system is designed to function with the steam condenser in an integrated gasification combined cycle power plant, in which steam turbine exhaust is used to regenerate and produce CO_2 from one ITAPS reactor, while a second ITAPS reactor captures CO_2. In this project, a bench-scale ITAPS unit is being constructed utilizing Altex's highly effective, low-cost microchannel heat exchangers coated with molecular-basket sorbents. These sorbents were previously developed and optimized by Penn State University. The performance of CO_2 sorption and desorption is being measured in this unit and will be used to design a full-scale system. The test results and analysis are being used to validate the technical and economic feasibility of the system process and components, and compared with alternative carbon capture technologies.

technology maturity:

Laboratory Scale

project focus:

Novel Concepts/Integrated Temperature and Pressure Swing Carbon Capture System

participant:

Altex Technologies Corporation

project number:

SC0013823

predecessor projects:

N/A

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principal investigator:

Ken Lux
Altex Technology Corporation
ken@altextech.com

partners:

Pennsylvania State University

start date:

06.08.2015

percent complete:

76%

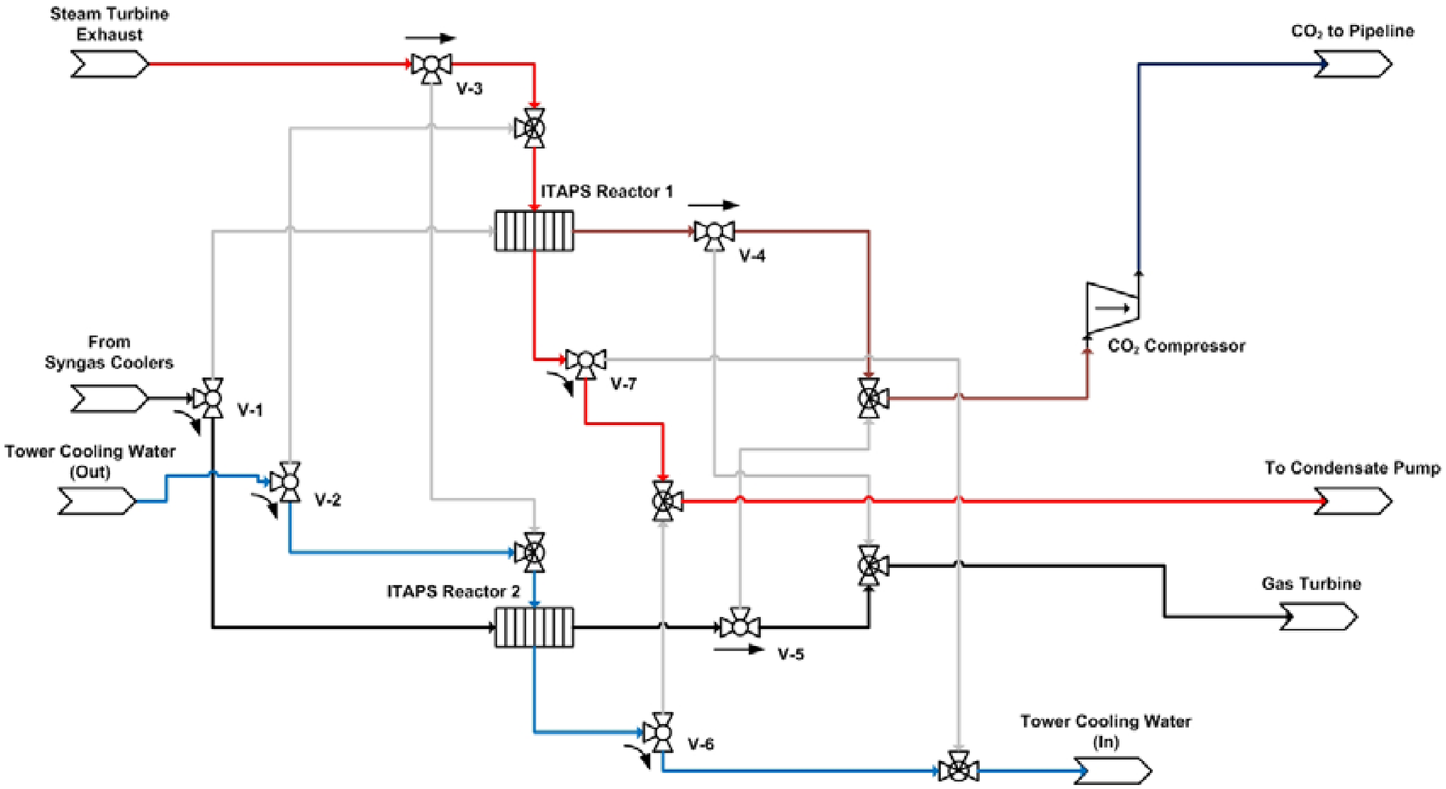

Figure 1: Simplified process flow diagram for Altex's integrated temperature and pressure swing carbon capture process

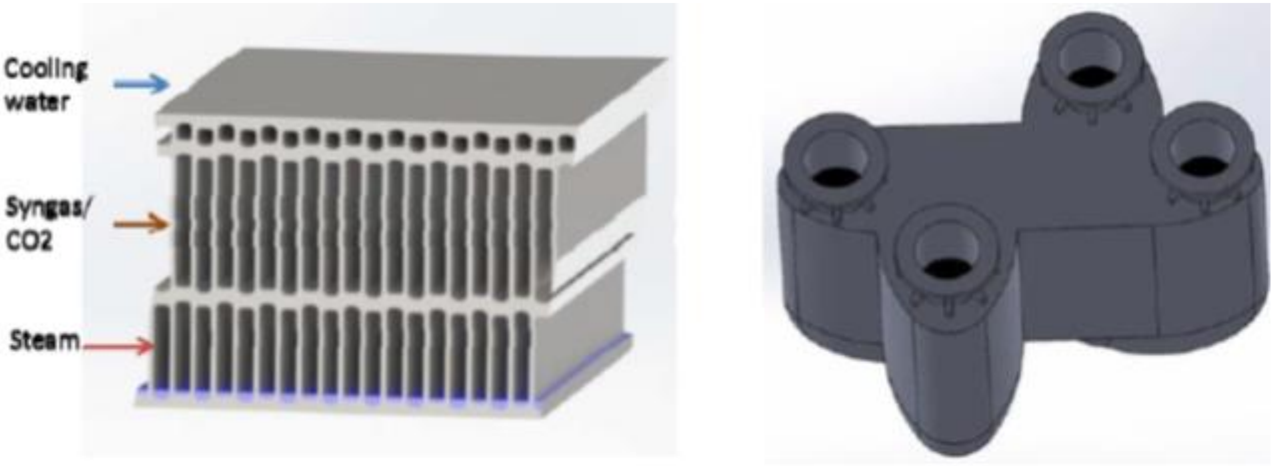

Figure 2: Illustration of ITAPS minichannel HELC-based indirectly heated and cooled reactors

technology advantages

A key to the ITAPS approach is the sorbent that is applied to the high surface area wash coated minichannel reactor and the indirect heating and cooling of that sorbent. The reactors are being developed to be capable of high mass-transfer rate of CO_2 to the sorbent coated on the walls of the reactors. Pennsylvania State University has previously developed CO_2 sorbents that exhibit high capacity and low desorption temperatures, providing an advantage over other CO_2 sorbents. This results in lower round-trip energy costs for a complete sorption-desorption cycle, compared to other sorbents.

R&D challenges

By utilizing Pennsylvania State University's novel molecular-basket sorbents (MBSs) in the ITAPS minichannel reactors, several technical challenges can be overcome. Specifically:

- The pressure drop through the reactor can be reduced relative to a packed bed absorber, much in the same way that the monolith-supported catalysts reduce the pressure drop in selective catalytic reactors (SCRs) and, more commonly, in automobile catalytic converters. This will enable ITAPS to handle high gas-flow rates.
- By operating at lower temperature and with lower heat of sorption, less parasitic energy draw is needed, thereby boosting plant net efficiency.
- By coating the sorbent on the high surface area of an Altex minichannel reactor, the catalyst remains fixed and is not subject to particle attrition resulting from particle-particle contact, as would occur in a fluidized bed.
- The MBS sorbents are engineered with specific chemical surface functionality, which allows for high CO_2 sorption capacities in high-humidity conditions.

status

Project was started but no updates are available.

available reports/technical papers/presentations

N/A

Advanced Carbon Dioxide Compression with Supersonic Technology

primary project goals

Continuing the prior efforts of Ramgen Power Systems, Dresser-Rand, A Siemens Business is developing a unique compressor technology based upon flight-based supersonic/shockwave compression principles for use as a carbon dioxide (CO_2) compressor. Advancing supersonic compressor technology will help meet overall goals of lower capital costs, smaller footprints, and improved energy efficiencies of carbon capture systems (CCS).

technical goals

- Increase the performance of CO_2 supersonic compression from a previously demonstrated single-stage pressure ratio of 11.5:1 to the goal of efficient 100:1 total pressure ratio CO_2 compression across two stages.
- Operate at a compressor CO_2 flow rate of 100 pounds per second, suitable for CCS applications in 125-MW_e coal-fired power plants.
- Validate compressor performance of pilot-scale compressors, testing on gas representative of a CO_2 capture system in a CCS process.
- Perform techno-economic analysis of the integration of supersonic CO_2 compression in a 550-MW_e power plant to quantify economic benefits of the technology for scenarios of large-scale power generation with CCS.

technical content

Supersonic CO_2 Compression

Dresser-Rand (which acquired the assets of Ramgen Power Systems in 2014) is developing supersonic shockwave compression technology, similar in concept to an aircraft supersonic engine inlet, for use in a stationary compressor. This compressor design features a rapidly rotating, enclosed disk that generates supersonic speeds at its rim, generating shockwaves in and thereby compressing gases introduced into a channel surrounding the rim. Compared to conventional compressor technologies, supersonic compression offers several potential advantages: high compression efficiency, high single-stage compression ratios, opportunity for waste heat recovery, and low capital cost. For example, Dresser-Rand's shock compression has the potential to develop compression ratios from 2.0 to 15.0 per stage with an associated adiabatic efficiency of 80–85 percent. For CO_2 compression applications, a nominal two-stage 100:1 compression ratio is envisioned, featuring a pair of 10:1 compression stages with an intercooler located between the stages.

Figure 1 provides a cross-sectional view of a single-stage supersonic compressor, which gives some idea of the engineering embodied in a compressor of this type.

technology maturity

Pilot-Scale, 1.5 MTPA (million tons per annum) of CO_2

project focus:

Supersonic Compression

participant:

Dresser-Rand, A Siemens Business

project number:

FE0026727

predecessor projects:

FE0000493
FC26-06NT42651

NETL project manager:

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partners:

Ramgen Power Systems

start date:

05.10.2006

percent complete:

70%

Figure 1: Cross-sectional model of a single-stage supersonic compressor

Principles of Supersonic Compression

When shockwaves pass through a gas, they cause a localized compression. Figure 2 shows that the rotating rotor rim has small, shallow angles that, when rotating at supersonic speed, will produce a series of oblique shocks terminating in a final normal shock. These shockwaves can be seen in the 3-D Euler computational fluid dynamics (CFD) image shown.

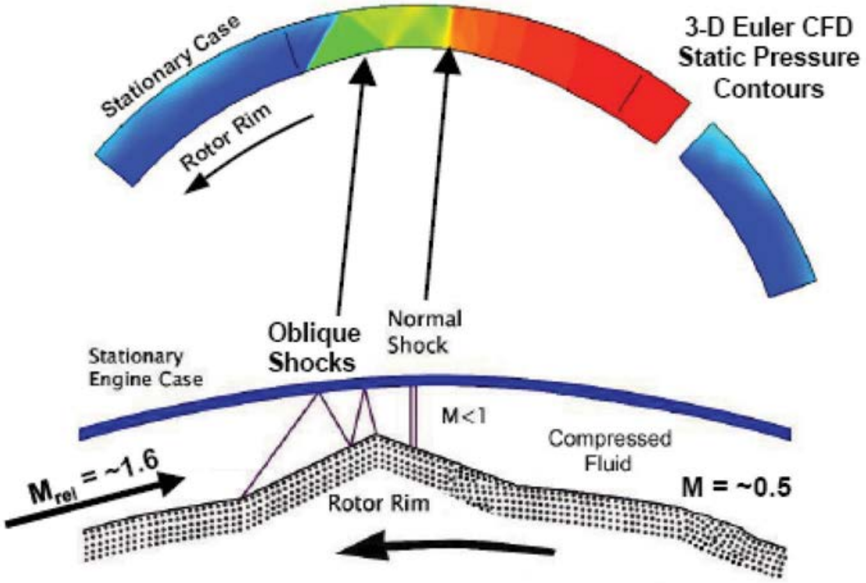

Figure 2: Schematic of rotor rim and engine case and 3-D Euler CFD image depicting shockwave behavior

Additionally, strakes (ridges) are incorporated into the design of the rotor to form sidewalls. The strakes are utilized to segregate individual shock compression ducts, as well as to separate high-pressure discharge gas from low-pressure suction. The combination of shocks and strakes result in a compressed fluid delivered from a stationary discharge duct with compression efficiencies comparable to conventional industrial turbo-compressors but with much higher single-stage pressure ratios. The heat generated during this single stage of shockwave compression is higher than that generated during conventional compression, yielding gas discharge temperatures exceeding 290 °C (550 °F). This is a relatively high-quality source of waste heat that can be recovered and utilized gainfully in optimizing overall system thermal efficiency. The high mechanical efficiency and waste heat recovery opportunity combine to deliver significant installed and operational cost savings versus existing turbo-compressors.

To better illustrate this concept, consider two stages of compression used with an intercooler located between the stages to optimize the efficiency of the compression process. Figure 3 shows the energy required as shaft work and the waste thermal energy recovery potential for a 200-MW coal plant with 90 percent CO_2 capture.

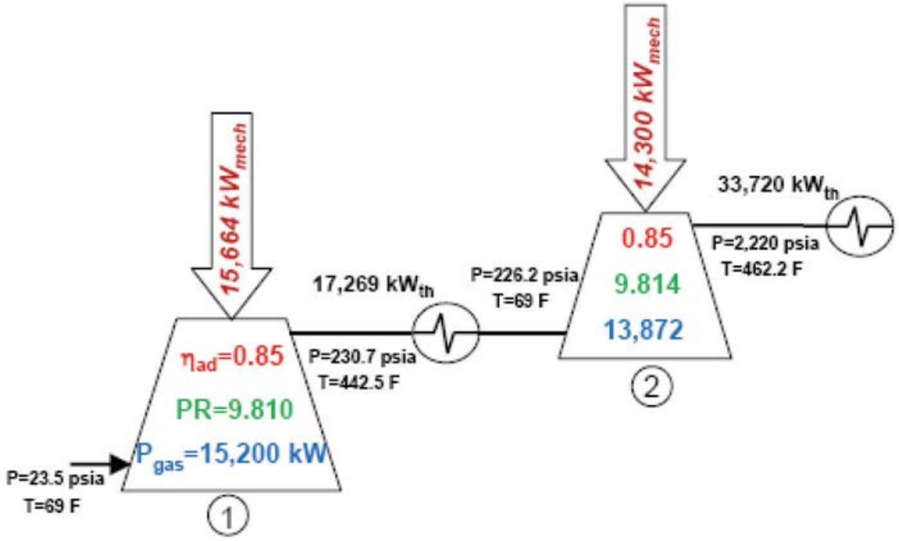

Figure 3: Schematic diagram of a two stage ~100:1 compression system with waste heat recovery

As seen in Figure 3, the total shaft power is 29,964 kW_{mech}, which corresponds to a heat of compression of 50,989 kW_{th}. Approximately 28,986 kW_{th} of the heat of compression lost is recoverable down to 93 °C (200 °F).

technology advantages

- Competitive operating efficiency and reduced installed capital cost (approximately 50 percent) over multistage bladed turbo-compressors.
- Lowered footprint of the CO_2 compression island in the plant, less piping and fewer intercoolers
- High-stage discharge temperature enables cost-effective recovery of heat of compression:
    - Improves CCS efficiency.
    - Reduces power plant de-rate.

R&D challenges

- Complicated shockwave aerodynamics in the gas flow path requires intensive computing capabilities and model development.
- High rotational speeds and the resulting stresses can result in expensive rotor manufacturing techniques.
- High-pressure ratio compressors yield high rotor thrust loads on bearings and structure.

status

Testing for the high-pressure CO_2 compressor was concluded in 2015, with the final test phase achieving a 11.5:1 compression ratio, better than the required 10:1 ratio. Assembly of a high-flow low-pressure compressor to be used in future testing is currently underway. Conclusion of successful demonstration of both the high-pressure and low-pressure compressors will complete the demonstration of the two 10:1 stages required to provide a 100:1 total pressure ratio system.

available reports/technical papers/presentations

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Koopman, A., "*Design and Testing of CO_2 Compression Using Supersonic Shock Wave Technology*," Final Report, August 2009 through March 2015, DOE Award Number: DE-FE0000493, Seattle Technology Center, Dresser-Rand Company, Bellevue, WA, June 2015.

Lupkes, K., "*Ramgen Supersonic Shock Wave Compression and Engine Technology*," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

Grosvenor, A.D.; Zheltovodov, A.A.; Derunov, E.K.; 2012; "Numerical Prediction of 3-D Shock-Induced Turbulent Flow Separation Surrounding Bodies of Revolution Adjacent to a Flat Surface," EUCASS Book Series on Advances in Aerospace Sciences, Progress in Flight Physics, Eds. Ph. Reijasse, D. Knight, M. Ivanov, and I. Lipatov, Torus Press, ISBN/ISSN: 978-2-7598-0674-4, pp. 119-140.

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Grosvenor, A.D.; Zheltovodov, A.A.; Matheson, M.A.; Sailer, L.M.; Krzysztopik, M.; Gutzwiller, D. P.; 2011; "Verification for a Series of Calculated 3-D Shock Wave/Turbulent Boundary Layer Interaction Flows," Proceedings 4th European Conference for Aerospace Sciences (EUCASS 2011). July 4–8, 2011, Saint Petersburg, Russia. Paper 578.

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Grosvenor, A.D.; Zheltovodov, A.A.; Derunov, E.K.; 2010; "SWBLI Calculations in Conditions of Aerodynamic Interference of Two Bodies of Revolution with a Flat Surface," ICMAR, Novosibirsk, Russia.

Lawlor, S., "*CO_2 Compression Using Supersonic Shock Wave Technology*," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, May 2009.

Grosvenor, A.D.; Zheltovodov, A.A.; Derunov, E.K.; 2009; "Numerical Prediction of 3-D Shock-Induced Turbulent Flow Separation Surrounding Bodies of Revolution Adjacent to a Flat Surface," Proceedings of the European Conference for Aero-Space Sciences (EUCASS), Versailles, France.

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Grosvenor, A.D., 2008, "Numerical Studies Toward Prediction, Analysis and Treatment of SWBLI in Transonic Compressors," Proceedings of the International Conference on the Methods of Aerophysical Research (ICMAR), Novosibirsk, Russia.

Grosvenor, A.D.; Taylor, D.A.; Bucher, J.R.; Aarnio, M.J.; Brown, P.M.; Draper, R.D.; Lawlor, S.P., 2008; "Measured and Predicted Performance of a High Pressure Ratio Supersonic Compressor Rotor," Turbo Expo 2008 Berlin, GT2008-50150.

Grosvenor, A.D., 2007, "RANS Prediction of Transonic Compressive Rotor Performance Near Stall," Turbo Expo 2007 Montreal, GT2007-27691.

Grosvenor, A.D.; Brown, P.M.; Lawlor, S.P.; 2006; "Design Methodology and Predicted Performance for a Supersonic Compressor Stage," Turbo Expo 2006 Barcelona, GT2006-90409.

Advanced Manufacturing to Enable Enhanced Processess and New Solvents for Carbon Capture

primary project goals

Lawrence Livermore National Laboratory (LLNL), Harvard University, and Carnegie Mellon University (CMU) have teamed to develop processes that enhance and enable the use of new solvents to capture carbon dioxide (CO_2). The technology uses advanced manufacturing techniques to reduce the cost of carbon capture for coal-fired power plants, and support the Carbon Capture Program's goal of advancing the technical, economic, and environmental performance of second-generation and transformational systems and technologies for future deployment.

technical goals

- LLNL and its partners will investigate encapsulation of new solvents that pose challenges to conventional process, explore enhanced CO_2 absorber designs based on advanced manufacturing, identify the best process configuration for encapsulated solvents, and develop and apply techniques for rapid determination of solvent properties using microfluidics.

technical content

LLNL, Harvard University, and CMU are developing processes that enhance and enable the use of advanced solvents to capture carbon dioxide (CO_2) from power plants using advanced manufacturing techniques. New solvents for the capture of CO_2 from coal-fired power plant flue gas pose challenges for conventional equipment due to slow kinetics, high viscosity, phase changes, corrosivity, or other issues. The team will develop processes to enhance and enable the use of these otherwise thermodynamically favorable solvents to capture CO_2 using advanced manufacturing techniques to encapsulate the solvents in a permeable membrane to overcome these challenges. Candidate solvents include CO_2-binding organic liquids developed by Pacific Northwest National Laboratory, ionic liquids, and nano-metal-organic hybrids. Using a combination of first-principles calculations, computational fluid dynamics models, and bench-scale experiments, the team will identify and assess improvements to the design of industrial CO_2 absorbers made possible by advanced manufacturing. A range of novel concepts for improving the efficiency of gas-liquid exchange in industrial reactors will be explored. Process configurations for the microencapsulated CO_2 sorbents (MECS) will be identified by evaluating fluidized bed and fixed bed configurations using a combination of bench-scale experiments, analytical models, and numerical models. The most promising basic configuration (fluidized bed, fixed bed, or other) will be selected for further refinement. The properties of potential solvents will be measured using LLNL's microfluidic technique for rapid characterization of solvent properties. The custom apparatus, developed previously with National Energy Technology Laboratory support, will be used to measure the CO_2 absorption rate and capacity of candidate solvents.

technology maturity:

Laboratory Scale

project focus:

Novel Concepts/ Encapsulation of Solvents in Permeable Membrane for CO_2 Capture

participant:

Lawrence Livermore National Laboratory

project number:

FWP-FEW0194

predecessor projects:

N/A

NETL project manager:

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partners:

Harvard University
Carnegie Mellon University

start date:

03.01.2015

percent complete:

89%

Figure 1: Microcapsule production scaled up by parallelization

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	980–1,050	—
Bulk Density	kg/m^3	~650	—
Average Particle Diameter	mm	0.5	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	3–10	—
Adsorption			
Pressure	bar	0.05–10	—
Temperature	°C	20–60	—
Equilibrium Loading	mol CO_2/kg	0.8–2	2–3
Heat of Adsorption	kJ/mol CO_2	~44–90	—
Desorption			
Pressure	bar	1	1–80
Temperature	°C	80–100	80–160
Equilibrium CO_2 Loading	g mol CO_2/kg	—	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	packed bed or fluidized bed	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 95 1--140	
Adsorber Pressure Drop	bar	<0.5	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Chemical.

Sorbent Contaminant Resistance –Water tolerant, absorbs SO_x and NO_x but potentially regenerable by ion exchange.

Sorbent Attrition and Thermal/Hydrothermal Stability – Attrition resistant compared to brittle solids.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

technology advantages

Microcapsules are high surface area, permeable microreactors that enable advanced solvents to achieve transformational carbon capture.

MECS may overcome all or many of the characteristics inherent in some new CO_2 capture sorbents, which include slow kinetics, high viscosity, phase changes, corrosivity, or other issues.

R&D challenges

Encapsulating advanced solvents takes research and development, including choosing shell materials, developing scale up methods, and testing packing methods.

status

Top-level process design and cost estimates for MECS are underway, as are design of a small pilot with MECS. Proof-of-concept validation with advanced packing motif is planned.

available reports/technical papers/presentations

Stolaroff, J. K.; Ye, C.; Oakdale, J. S.; Baker, S. E.; Smith, W. L.; Nguyen, D. T.; Spadaccini, C. M. & Aines, R. D. (2016). Microencapsulation of advanced solvents for carbon capture. *Faraday Discuss.*, *The Royal Society of Chemistry*, 192, 271-281

Stolaroff, J.K., Bourcier, W.L., "Thermodynamic assessment of microencapsulated sodium carbonate slurry for carbon capture." *Energy Procedia* 63 (2014) 2331 – 2335.

Stolaroff, J., "Advanced Manufacturing to Enable New Solvents and Processes for Carbon Capture," presented at the 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/2J-Stolaroff2-LLNL-Microencapsulation.pdf*

Vericella, J. J.; Duoss, E. B.; Stolaroff, J. K.; Baker, S. E.; Hardin, J. O.; Lewicki, J.; Glogowski, E.; Floyd, W. C.; Valdez, C. A.; Smith, W. L.; Jr., J. H. S.; Bourcier, W. L.; Spadaccini, C. M.; Lewis, J. A. & Aines, R. D. "Encapsulated liquid sorbents for carbon dioxide capture." *Nature Communications,* 2015, 6, 1-7.

Supersonic Post-Combustion Inertial CO_2 Extraction System

primary project goals

Orbital ATK, Inc. (OA) developed an inertial carbon dioxide (CO_2) extraction system (ICES) that converts CO_2 from flue gas to solid CO_2 (dry ice) using supersonic expansion followed by inertial separation. The project included bench-scale testing of the system with simulated flue gas.

technical goals

- Demonstrate ICES at bench-scale including condensation, migration, CO_2 removal, and diffusion of the CO_2-depleted flue gas to atmospheric pressure.
- Develop approach to obtain condensed CO_2 particle size required for effective migration and separation.
- Demonstrate pressure recovery efficiency of system consistent with economic goals.
- Demonstrate CO_2 capture efficiency.

technical content

Orbital ATK, Inc. designed an inertial CO_2 extraction system (ICES) that aims to achieve an overall reduction in total carbon capture cost for post-combustion CO_2 capture. The ICES system, shown in Figure 1, is derived from aerospace applications and is based on supersonic inertial separation technology. Compressed flue gas is directed to a converging-diverging nozzle and undergoes supersonic expansion (high velocity, low pressure and temperature), which results in CO_2 desublimation. Turning the supersonic flow in the curved flow path causes inertial separation of the dense, solid CO_2 particles, which are collected in a CO_2-rich stream through a duct in the wall into a cyclone separator where the CO_2 solids are collected. The CO_2-depleted stream is diffused and sent to the stack.

Factors for improved performance of the ICES system included controlling and increasing CO_2 particle size to increase migration and capture, pre-cooling of the flue gas to enable subsonic condensation and promote heterogeneous nucleation for larger particles, and efficient pressure recovery. The compact design, along with efficiencies in CO_2 capture, reduces costs of the carbon capture system. An initial techno-economic assessment by Worley Parsons estimated a $41.80/tonne CO_2 captured for an ICES plant, with cost savings coming from lower capital costs (smaller equipment), lower operating costs (no moving parts, chemicals or media), and improved capture efficiency compared to a typical amine solvent-based plant. However, further studies found that more compression is required due to lower pressure recovery than predicted and, therefore, a cost of >$50/tonne CO_2 captured is anticipated. ICES is expected to have comparatively favorable economics for applications requiring less capture and/or applications with lower CO_2 concentration since compression costs scale with these parameters.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Supersonic Inertial CO_2 Extraction System

participant:

Orbital ATK, Inc.

project number:

FE0013122

predecessor projects:

N/A

NETL project manager:

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principal investigator:

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partners:

ACENT Laboratories LLC; Electric Power Research Institute; Ohio State University, New York State Energy Research and Development Authority, WorleyParsons Group, Inc.

start date:

10.01.2013

percent complete:

100%

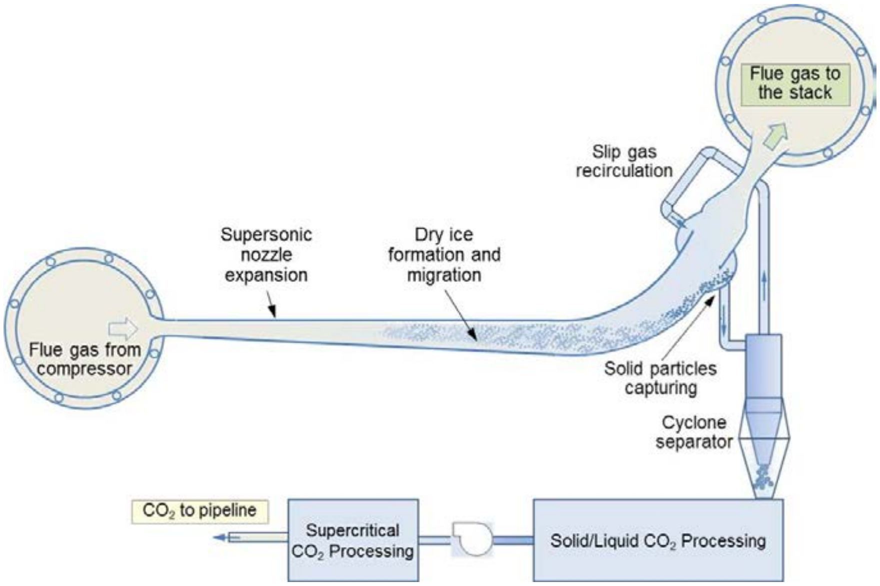

Figure 1: ICES system

Lab-scale testing of the system in a previous project has shown that CO_2 particles of >2.5 μm is required to ensure efficient inertial migration. Initial test results also proved that CO_2 only condenses on solid or liquid media in the flow (heterogeneous condensation). This led to the conclusion that solid CO_2 seeding is the most viable path to 90 percent CO_2 capture by causing flue gas CO_2 to condense on particles that are already >2.5 μm. Preliminary testing on a bench-scale apparatus (Figure 2) using a liquid throttle to inject CO_2 of a controlled particle size in the duct demonstrated >50 percent capture of solid CO_2 and indicated a higher amount of CO_2 captured with a lower inlet temperature. An approach was developed to recirculate a fraction of the collected liquid CO_2 back to the inlet to achieve additional cooling at the inlet along with the creation of large "seeded" particles to promote heterogeneous nucleation capable of migration. However, compression requirements would further increase with this method since more energy would be needed to accelerate the added mass of the recycled CO_2 to high speed. Based on thermodynamic analyses, a method for pre-cooling of the flue gas using captured CO_2 as a "cold sink" was determined to be the best approach. This pre-cooling enables subsonic condensation of a small quantity of CO_2 (and trace water) resulting in "in situ" seeding without the need to recirculate solid CO_2. Testing of a subsonic ICES system with pre-cooling by liquid nitrogen showed that a significant amount of CO_2 condensed into large CO_2 particles with an average size of 30–40 μm.

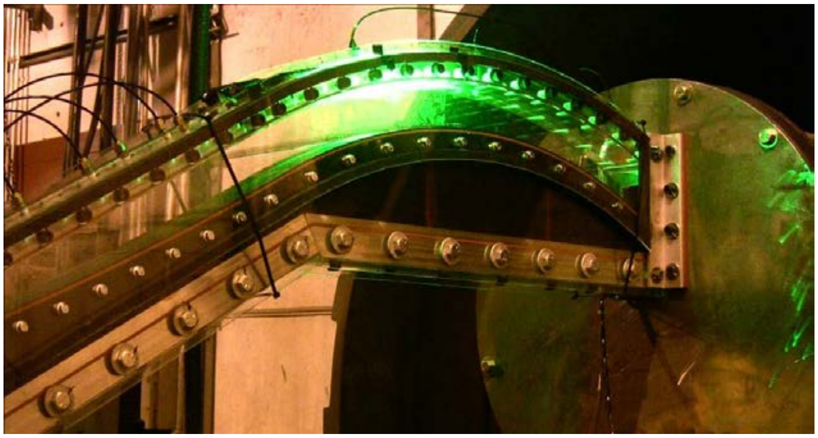

Figure 2: Bench-scale ICES test apparatus illuminated with laser sheet

Scaling the technology for use in a full-scale power plant involves combining multiple ICES units for increased capacity. The compactness of the group of ICES units, as shown in the proposed plant configuration in Figure 3, leads to substantial reductions in the footprint capture plant compared to a similar capacity capture plant using amine solvent capture technology (8,000 m^2 vs. 20–30,000 m^2). Stacking the ICES nozzles and compressors further reduces the footprint.

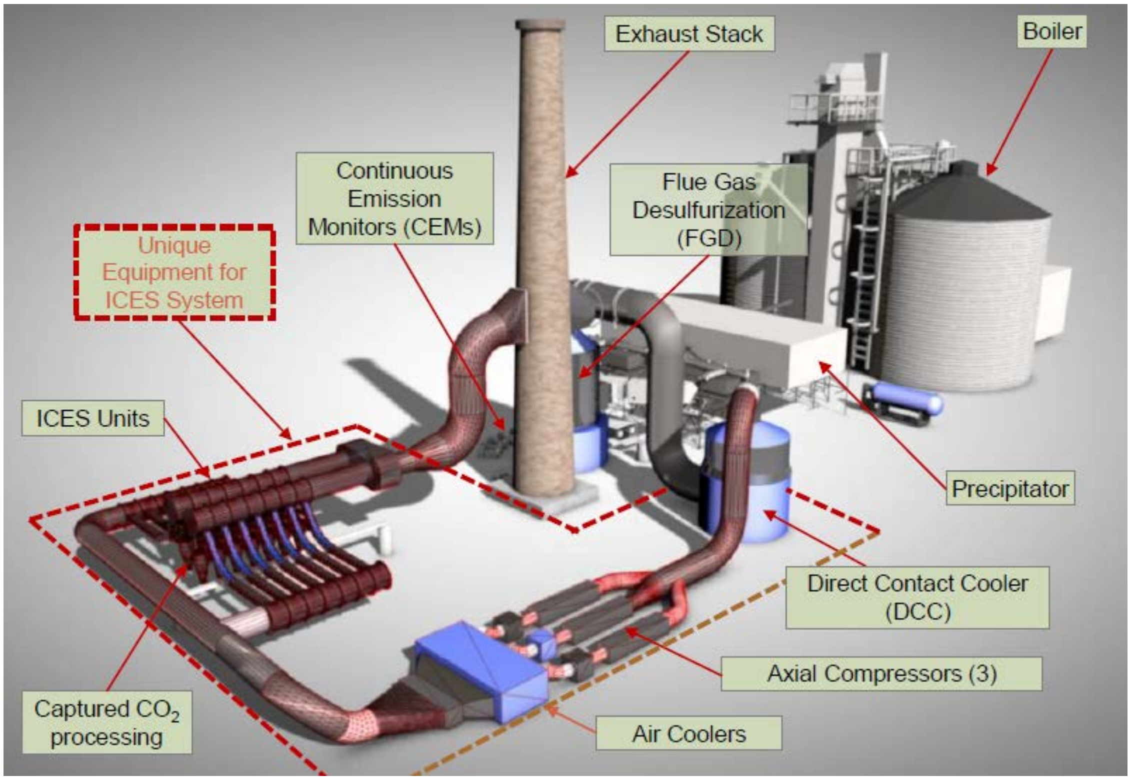

Figure 3: ICES plant layout and footprint

Definitions:

Inertial Separation – Method that uses a rapid change in air direction and principles of inertia to separate particulate from an air stream.

Heterogeneous nucleation **–** Process that occurs in the formation of a crystal from a solution, liquid, or vapor, in which particles become arranged in a pattern characteristic of a crystalline solid, forming a site upon which additional particles are deposited as the crystal grows.

technology advantages

- No moving parts, chemicals/additives, or consumable media.
- No refrigeration expense—low temperatures from supersonic expansion.
- Inexpensive construction based on sheet metal and concrete.
- Small equipment footprint.
- “Cold sink” available from accumulated solid CO_2.
- Costs driven by flue gas compression.

R&D challenges

- Development of optimized supersonic contour to maximize particle size and migration and minimize pressure losses.
- Minimization of slip gas that is removed with solid CO_2.
- CO_2 purity—condensable flue gas impurities removed along with CO_2.
- Solid CO_2 processing.
- Optimization of flow path pressure recovery.

status

Testing of a bench-scale capture duct/diffuser system achieved ≥50 percent CO_2 capture. Testing of a subsonic ICES test article demonstrated large CO_2 particle formation through partial subsonic condensation enabled by pre-cooling of the flue gas. The pre-cooling approach addresses the increase in compression requirements that evolved from thermodynamic modeling efforts. Future work will continue optimization of the ICES for a range of CO_2 concentrations and/or CO_2 capture levels to identify the most favorable operating conditions.

available reports/technical papers/presentations

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https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/Final-Report-ATK-FE0013122-April-2017.pdf

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https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/T-Castrogiovanni-ACENT-Supersonic-Inertial-CO2-Extraction.pdf

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http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/A-Castrogiovanni-ATK-Supersonic-Post-Combustion.pdf

“Supersonic Post-Combustion Inertial CO_2 Extraction System,” Kickoff Presentation, November 2013.
http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/11-14-2013-NETL-ICES-Kickoff-Nonproprietary.pdf

CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION SORBENT TECHNOLOGIES

Pilot Testing of a Highly Effective Pre-Combustion Sorbent-Based Carbon Capture System

primary project goals

TDA Research, Inc., is continuing development of a new sorbent-based pre-combustion carbon capture technology for integrated gasification combined cycle (IGCC) power plants. The process uses an advanced physical adsorbent that selectively removes carbon dioxide (CO_2) from coal derived synthesis gas (syngas) above the dew point of the gas. The project aims to prove the viability of the new technology by using data collected from the pilot plant tests to complete high fidelity engineering and cost analyses to calculate the impact of the carbon capture system on the cost of electricity generation at a coal-fired IGCC power plant and the potential of the technology to meet the DOE goals of 90 percent CO_2 capture and 95 percent purity at a cost of less than \$40/tonne CO_2 captured.

Having shown promise under a previously-funded DOE project (FE0000469), this sorbent is being evaluated at a larger scale, for longer durations, and under conditions that are more representative of a coal gasification-based application. Current research objectives are to collect performance data for this advanced sorbent including: two 0.1-MW_e tests with a fully-equipped prototype unit using actual synthesis gas to prove the viability of the new technology; long-term sorbent life evaluation in a bench-scale setup; the fabrication of a pilot-scale testing unit that will contain eight sorbent reactors; and the design of a CO_2 purification subsystem.

technical goals

- Enable pre-combustion CO_2 capture from syngas at 200 to 250 °C and pressures up to 60 bar, with >90 percent recovery and CO_2 purity of at least 95 percent using a functionalized carbon sorbent in a pressure swing adsorption (PSA)-based cycle.
- Improve adsorber reactor design including the optimized reactor internals and bed geometry through computational fluid dynamics (CFD) analysis and PSA cycle optimization with adsorption modeling.
- Complete two pilot-scale field tests at the National Carbon Capture Center (NCCC) and at Sinopec's IGCC plant on syngas slipstream at 0.1 MW_e equivalent, at design conditions and for extended durations (e.g. >3,000 hours at NCCC) to demonstrate capability to meet all performance objectives (e.g. CO_2 removal efficiency, hydrogen [H_2] recovery, sorbent life and performance).
- Validate long-term performance, durability and lifetime of the sorbent through 60,000 cycles with no more than 2 percent percent decrease in adsorption capacity over fresh sorbent (enabling projected lifetime of 5 years for the sorbent).
- Enable improved IGCC plant efficiency (3–4 percentage points) over conventional IGCC, improving cost of electricity in coal-based power production.

technology maturity:

Pilot-Scale, Actual Syngas Slipstream (equivalent to 0.1 MW_e)

project focus:

High-Capacity Regenerable Sorbent

participant:

TDA Research, Inc.

project number:

FE0013105

predecessor projects:

FE0000469

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partners:

Gas Technology Institute, University of California at Irvine (UCI), University of Alberta, Sinopec

start date:

10.01.2013

percent complete:

80%

technical content

TDA Research is designing, constructing, and operating a slipstream 0.1-MW$_e$ pilot-scale process for pre-combustion CO_2 capture to assess their novel adsorbent for the selective removal of CO_2 from syngas. The adsorbent consists of a mesoporous carbon grafted with surface functional groups that remove CO_2 via an acid-base interaction. The novel process is based on TDA's high-temperature PSA technology using the new adsorbent to selectively remove CO_2 from syngas in an IGCC power plant. The integration of the CO_2 separation unit into the IGCC plant is shown in Figure 1.

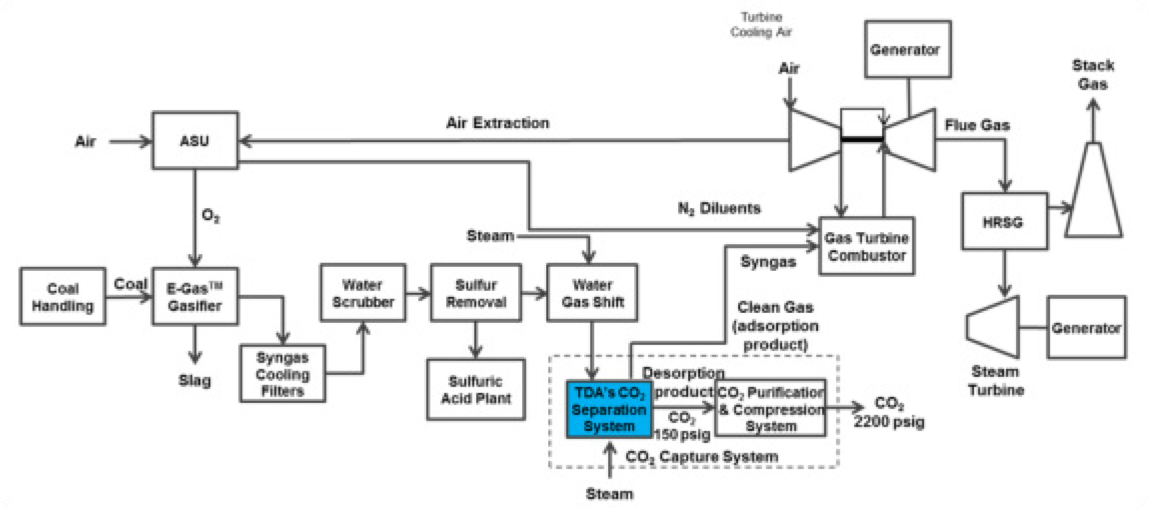


Figure 1: TDA's CO_2 capture system integration in IGCC power plant

The CO_2 capture system uses multiple sorbent beds that switch operating modes between adsorption and regeneration. In addition to the conventional pressure and temperature swing operation, the sorbent can be regenerated under near isothermal and isobaric conditions, with the driving force for separation provided by a swing in CO_2 concentration.

The sorbent removes CO_2 via strong physical adsorption. The CO_2 surface interaction is strong enough to allow operation at elevated temperatures. Because the CO_2 is not bonded via a covalent bond, the energy input to the regeneration is low—only 3.8 to 4.9 kcal/mole of CO_2 removed (comparable to Selexol™). This energy requirement is much lower than that of the chemical absorbents (e.g., sodium carbonate [Na_2CO_3] requires 29.9 kcal/mol) and amine solvents (≈14 kcal/mol). The energy output loss of the IGCC plant is expected to be similar to that of Selexol's; however, a higher overall IGCC efficiency can be achieved due to higher temperature CO_2 capture.

The pilot plant design includes a gas conditioning unit and a high temperature pressure swing adsorption based CO_2 separation unit, as shown in Figure 2. The gas conditioning unit allows for adjustment of the concentration and purity of the synthesis gas. The CO_2 separation unit consists of eight high-temperature sorbent beds. The design of the CO_2 capture skid for the 0.1 MW pilot unit is shown in Figure 3.

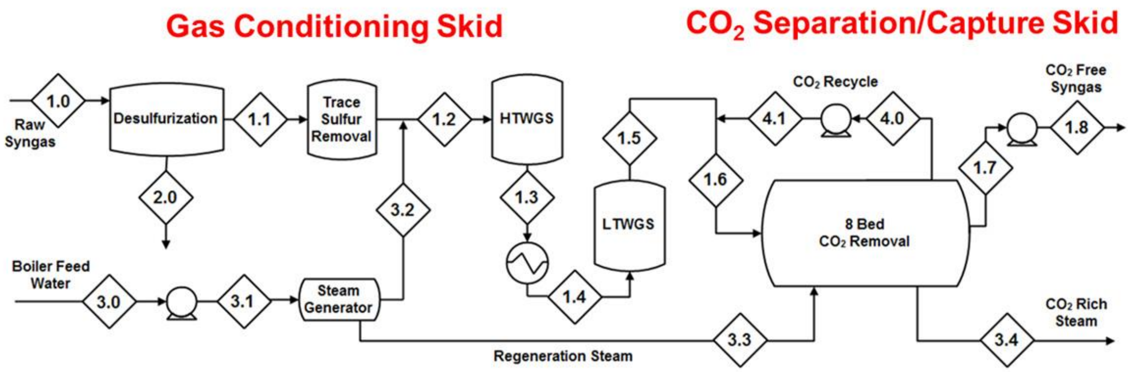


Figure 2: Flow diagram for TDA's pilot test unit

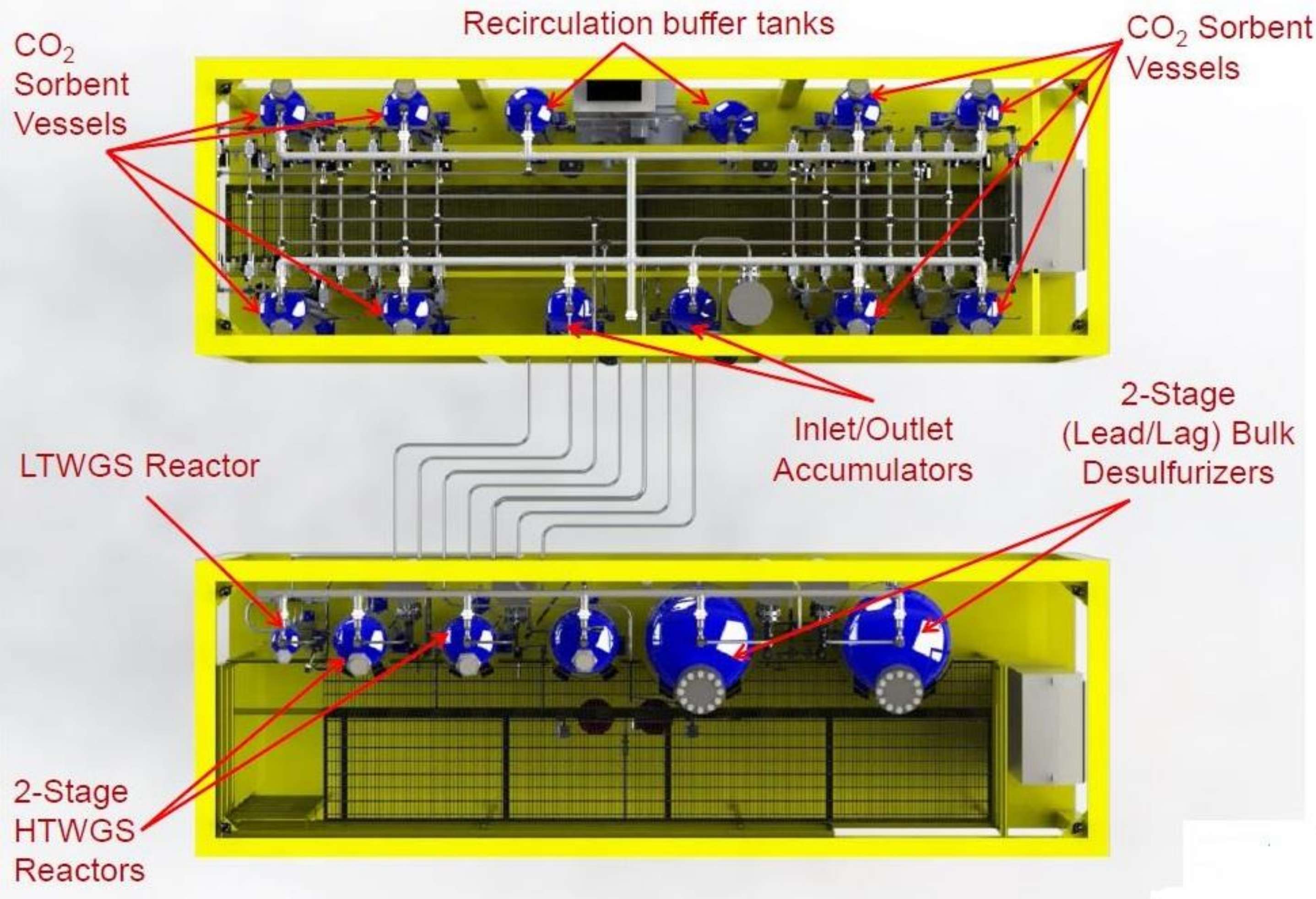
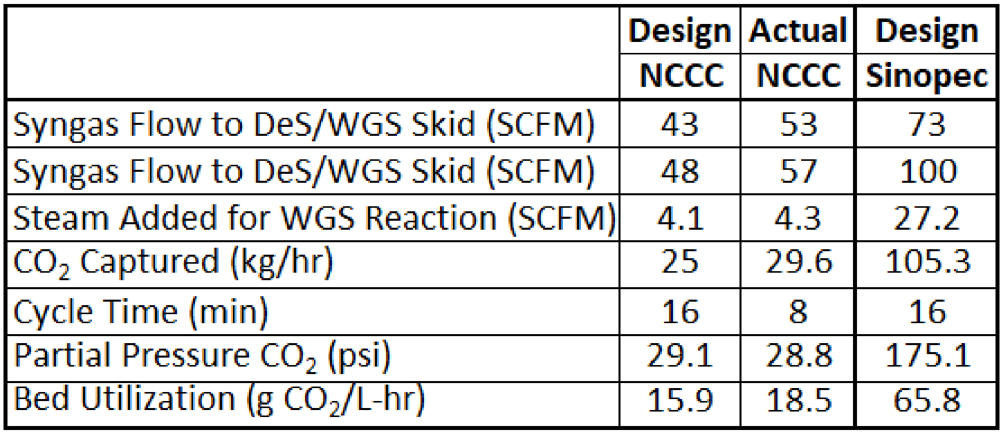


Figure 3: Overhead view of carbon capture skid

In 2017 TDA's 0.1 MW_e pilot-scale eight-bed PSA unit was installed at the NCCC (Figure 4) and tested in real coal derived synthesis gas. The pilot unit ran for 707 hours of continuous operation at over 90 percent carbon capture, with 17 percent higher capture than the design specification of 48 standard cubic feet per minute (SCFM) of syngas flow. The summary results are given in Figure 5. This table also shows the upcoming design performance parameters for the Sinopec oxygen-based gasifier testing at considerably increased throughput.

Figure 4: TDA's 0.1-MW_e pilot unit installed in the test pad at NCCC (Wilsonville, AL)



	Design NCCC	Actual NCCC	Design Sinopec
Syngas Flow to DeS/WGS Skid (SCFM)	43	53	73
Syngas Flow to DeS/WGS Skid (SCFM)	48	57	100
Steam Added for WGS Reaction (SCFM)	4.1	4.3	27.2
CO_2 Captured (kg/hr)	25	29.6	105.3
Cycle Time (min)	16	8	16
Partial Pressure CO_2 (psi)	29.1	28.8	175.1
Bed Utilization (g CO_2/L-hr)	15.9	18.5	65.8

Figure 5: Summary performance results of pilot-scale testing

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,314	1,314
Bulk Density	kg/m^3	620	620
Average Particle Diameter	mm	0.42–1.68	0.42–1.68
Particle Void Fraction	m^3/m^3	0.368	0.368
Packing Density	m^2/m^3	4.59E+08	4.59E+08
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg_f	3	3
Manufacturing Cost for Sorbent	$/kg	3.88	3.88
Adsorption			
Pressure	bar	33.8	33.8
Temperature	°C	198	198
Equilibrium Loading	g mol CO_2/kg	1.04	1.04
	g mol CO_2/m^3	645	645
Heat of Desorption	kJ/mol CO_2	-28.5	-28.5
Desorption			
Pressure	bar	10	10
Temperature	°C	195.5	195.5
Equilibrium CO_2 Loading	g mol CO_2/kg	0.005	0.005
	g mol CO_2/m^3	3.22	3.22
Heat of Desorption	kJ/mol CO_2	28.5	28.5
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	radial-flow fixed bed/cyclic	
Flue Gas Flowrate	kg/hr	668,083	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90.0% 90.0% 90.0%	
Adsorber Pressure Drop	bar	1.41	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	212.8	

[+] CO_2 is recovered at 10 bar from TDA's CO_2 capture and purification system, which is further compressed to 152.7 bar with a final CO_2 purity of 99.96%

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading, which typically occurs at the bottom of the adsorption column.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – Surface functionalized mesoporous carbon removing CO_2 via weak interactions similar to physical adsorption at temperatures above the dew point of the synthesis gas.

Sorbent Contaminant Resistance – The sorbent is highly resistant to contaminants such as H_2S, COS, NH_3 and trace metals such as Hg, As etc. If needed, additional functionalities can be incorporated into the sorbent to remove these contaminants simultaneously with CO_2. Results of the 707-hour-long testing with coal derived synthesis gas with the 0.1 MW_e pilot unit at NCCC in Wilsonville, Alabama, showed excellent resistance to contaminants that could be present in synthesis gas.

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent has good thermal/hydrothermal stability; it is stable in nitrogen up to 900 °C and in steam stable up to 400 °C. The attrition index for the sorbent is estimated to be 0.1% loss per 1,000 h operation.

Syngas Pretreatment Requirements – Syngas needs to be shifted to convert CO present into CO_2 and H_2 via water gas shift reaction and sulfur content needs to be reduced to less than 100 ppm before CO_2 removal.

Sorbent Make-Up Requirements – The expected life of the sorbent is 5 years. The annualized sorbent make-up requirement is expected to be 261.5 tonnes on the 550 MW_e process plant basis.

Waste Streams Generated – Condensate from cooling the raw CO_2 stream.

Process Design Concept – See Figure 1.

Proposed Module Integration – TDA's CO_2 separation, purification and compression system is located downstream of the warm gas sulfur removal and the water-gas-shift processes as shown in Figure 1.

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
497.5	388.4	30.28	0.73	2.04	0.45	39.11	26.59	<10

technology advantages

- Warm gas CO_2 capture above dew point of syngas leads to more steam in the hydrogen rich gas entering the turbine.
    - Improved efficiency.
    - Higher mass throughput to gas turbine.
    - Lower gas turbine temperature lowers need for high pressure nitrogen (N_2) dilution and lowers nitrogen oxide (NO_x) formation.
- High steam content feed more suited for next generation hydrogen turbines under development.
- High working capacity and cycle life of sorbent.
- Carbon dioxide recovered at pressure reduces compression costs for sequestration.
- A weak CO_2 surface interaction allows fast regenerations at low temperature with the minimal or no heat input.
- Short adsorption/regeneration cycles reduce bed size and weight.

R&D challenges

- Assuring consistency in sorbent material and minimizing batch-to-batch variation for large scale manufacture.
- Reducing the use of purge gas during regeneration.
- Confirming resistance to syngas contaminants.

status

Pilot-scale testing at the NCCC has been completed in mid-2017 with successful attainment of 90+ percent carbon capture at greater than design flows of syngas, and with the sorbent maintaining high CO_2 capacities in operational cycling.

available reports/technical papers/presentations

"*PSA Based CO_2 Capture Above the Dew Point of Synthesis Gas for IGCC Power Plants*," presented at the 2017 AIChE Annual Meeting, Minneapolis, MN, November 2017.

"*Highly Efficient Warm Gas Carbon Capture System for IGCC Power Plants*," presented at the 2017 AIChE Annual Meeting, Minneapolis, MN, October 2017.

"*Pilot Scale Evaluation of Pre-Combustion Carbon Capture Process*," presented by Gökhan Alptekin, TDA Research, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," presented by Gökhan Alptekin, TDA Research Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Pilot Scale Evaluation of Pre-Combustion Carbon Capture Process*," presented by Gökhan Alptekin, TDA Research Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

Alptekin, G., et. al. "*A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture*," Final Report, September 30, 2012.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," presented by Gökhan Alptekin, TDA Research Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Pilot Testing of a Highly Efficient Pre-Combustion Sorbent-Based Carbon Capture System*," Project Kick-Off Meeting, January 2013.

Alptekin, G., Jayaraman, A., and Copeland, R., *"Low Cost, High Capacity Regenerable Sorbent for Precombustion CO_2 Capture*," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

Alptekin, G., “A Low Cost, High Capacity Regenerable Sorbent for CO_2 Capture,” presented at the International Colloquium on Environmentally Preferred Advanced Power Generation (ICEPAG), Costa Mesa, CA, February 2012.

Alptekin, G., Jayaraman, A., Dietz, S., and Schaefer, M., “High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture,” presented at the 28th Annual International Pittsburgh Coal Conference (IPCC), Pittsburgh, PA, September 2011.

Alptekin, G., Jayaraman, A., and Copeland, R., “Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION MEMBRANE TECHNOLOGIES

Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture

primary project goals

Arizona State University's project objectives are to develop tools and methods for scaling-up zeolite membrane fabrication and water gas shift (WGS) zeolite membrane reactors, and to construct bench-scale zeolite membrane modules and test their performance for WGS with carbon dioxide (CO_2) capture on coal-derived syngas.

This will be the first effort to study zeolite membrane reactors for high-temperature chemical reaction and gas separation at this scale. The process design and techno-economic analysis, with the input of the experimental findings, will validate the effectiveness of the zeolite membrane reactor (ZMR) for WGS reaction and CO_2/hydrogen (H_2) separation. The results of this project will provide a foundation and guide for further scaling up of the membrane reactor technology for pre-combustion CO_2 capture at pilot-scale.

technical goals

- Identify structure and operation conditions for a bench-scale membrane reactor through modeling and experimental study of the WGS reaction in a single-tube zeolite membrane reactor.
- Fabricate chemically and thermally stable alumina tubule supports and zeolite membranes of suitable quantity in consistent quality.
- Design and fabricate multiple-tube zeolite membrane modules with adequate seals for hydrogen separation and WGS reaction at high temperature and pressures.
- Assemble and test the bench-scale zeolite membrane modules with desired catalyst for WGS reaction.
- Demonstrate effective production of H_2 and CO_2 capture by the bench-scale zeolite membrane reactor from a coal gasification syngas at temperatures of 400–550 °C and pressures of 20–30 atm, to produce 2 kg H_2/day (equivalent to 2 kW_{th} integrated gasification combined cycle [IGCC] power plant).
- Perform process design and techno-economic and environmental, health, and safety (EH&S) risk analyses to evaluate performance and cost-effectiveness of the zeolite membrane reactor integrated in a 550-MW_e IGCC plant with CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily H_2 and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas, could be replaced, in whole, by a novel WGS shift reactor that integrates zeolite-based H_2 separation membranes. Within the zeolite membrane WGS reactor, H_2 would be withdrawn directly from the reaction chamber, efficiently increasing the driving force for the WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are

technology maturity:

Bench-Scale, Actual Syngas (2 kg per day equivalent to 2 kW_{th})

project focus:

Zeolite Membrane Reactor

participant:

Arizona State University

project number:

FE0026435

predecessor projects:

N/A

NETL project manager:

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principal investigator:

Jerry Lin
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partners:

Media and Processes Technology Inc., University of Cincinnati, Nexant Inc. University of Kentucky

start date:

10.01.2015

percent complete:

60%

replaced by a single, elegantly performing reactor. This process concept, with the zeolite membrane reactor replacing the conventional WGS process stages and amine absorption unit, is depicted in Figure 1.

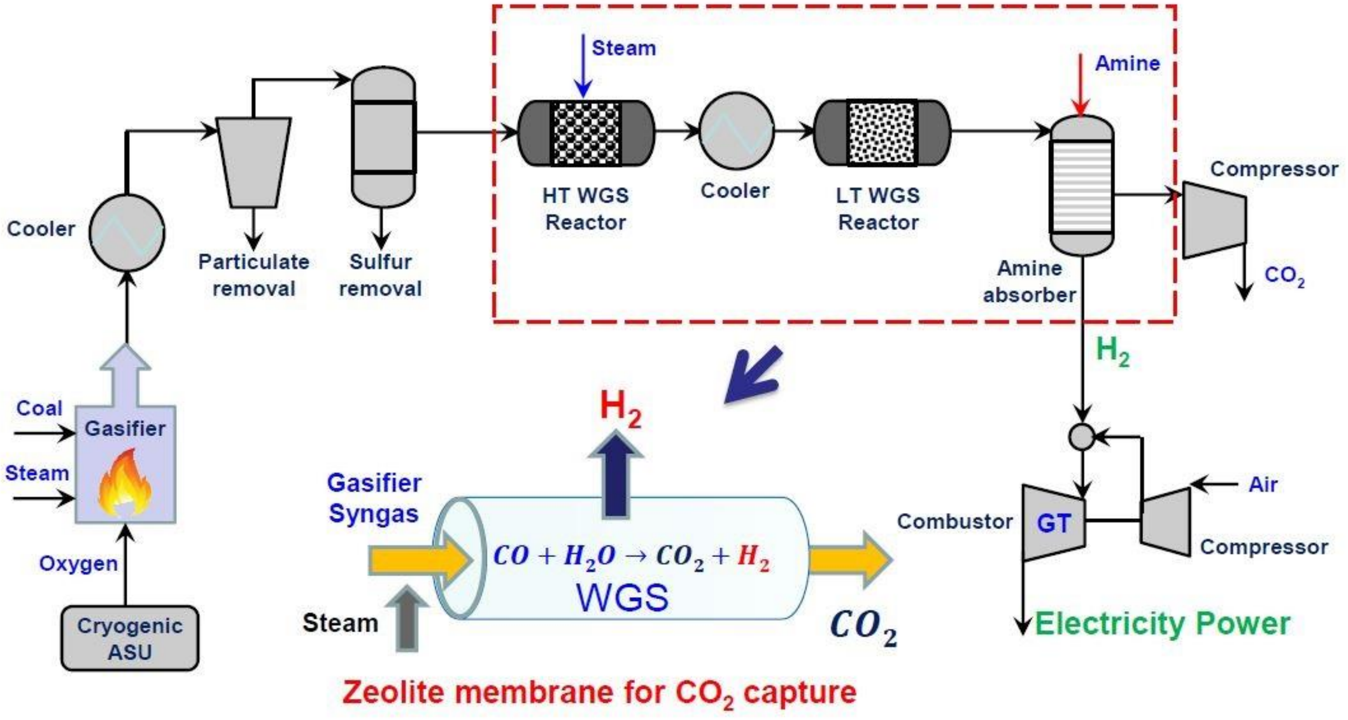

Figure 1: Zeolite membrane reactor for WGS reaction and CO_2 capture in context of coal gasification plant cycle

However, the operating environment in the reactor is challenging. Past findings have suggested that zeolite membranes, which are inorganic and can be tailored or selected for specific gas separation applications, can meet the functional requirements and operational conditions as follows:

- Operation at 350–550 °C
- Chemically stable in hydrogen sulfide (H_2S), thermally stable at ≈400 °C
- Hydrogen permeance = 2×10^{-7} mol/m^2.s.Pa (600 GPU)
- Hydrogen/CO_2 selectivity = 20-40

In Arizona State's previous work, MFI type zeolite (an aluminosilicate zeolite belonging to the pentasil family of zeolites) was used in a laboratory-scale zeolite membrane WGS reactor, and continues as the basis in current work. See Figure 2 for the zeolite structure, and a highly magnified view of the zeolite layer deposited on an alumina substrate. Although this zeolite has been traditionally used as a catalyst for hydrocarbon isomerization and the alkylation of hydrocarbons, it serves in the current work as a hydrogen-permeable membrane layer suitable for deposition on alumina, which can be formed into the desired tubes for fitting into WGS reactor modules.

The MFI zeolite pores have an effective diameter of ~ 0.56 nm, which is large enough for the small gas molecules involved in the WGS reaction to permeate through by gaseous diffusion mechanism. Therefore, pristine MFI-type zeolite membranes offer high H_2 permeance but with limited H_2/CO_2 selectivity defined by the Knudsen factor (~ 4.75) at high temperatures where the permeating gases become non-adsorbing to the zeolite. The MFI type zeolite membranes can be modified by in situ deposition of mono silica species to the internal pore wall that narrows down the effective zeolite pore diameter from ~ 0.56 nm to < 0.36 nm. Such a reduced pore size enables the highly selective size-exclusion effect between the small H_2 molecule (kinetic diameter d_k = 0.289 nm) and other slightly larger molecules like CO_2 (d_k = 0.330 nm), CO (d_k = 0.376 nm), and CH_4 (d_k = 0.380 nm).

Arizona State University and University of Cincinnati have developed an on-stream catalytic cracking deposition (CCD) method for modification of the MFI-type zeolite membrane that effectively controls the silica deposition within a small portion of the zeolitic channels near the membrane surface. This well-controlled modification avoids excessive loss in H_2 permeance while achieving substantially improved H_2 selectivity over CO_2, CO and H_2O.

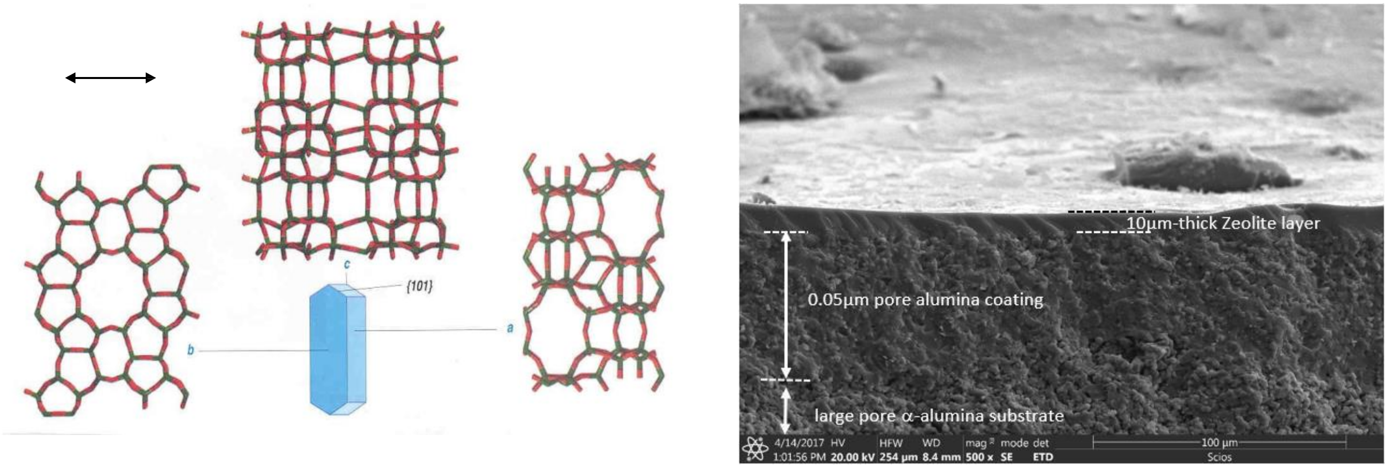

Figure 2: MFI-type zeolite (ZSM-5 or silicalite) (on left); magnified view of zeolite membrane (on right)

Figure 3 depicts the laboratory-scale tubular membrane reactor for testing separation performance and water gas shift reaction of a zeolite membrane tube containing WGS catalyst. Feed gas is passed to the bore side of the tube, and as the gas passes over the catalyst, increasing amounts of H_2 are generated. The zeolite allows H_2 to readily pass through the membrane tube, while keeping the larger carbon monoxide (CO), water (H_2O), and CO_2 molecules inside. Retentate is enriched in CO_2 after the WGS reaction.

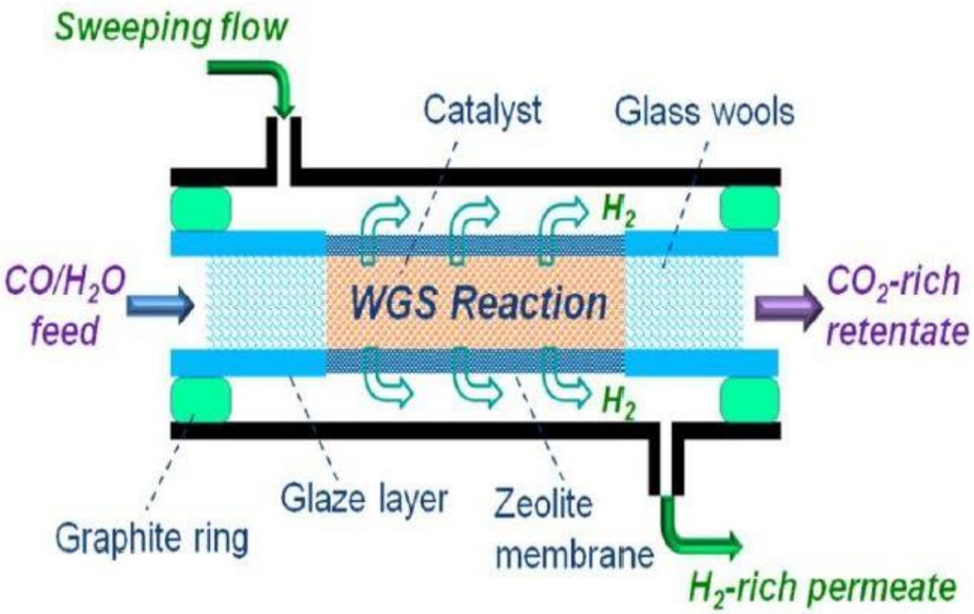

Figure 3: Zeolite membrane tubular WGS reactor

Previously, CCD modified MFI zeolite membranes showed long-term stability in WGS reaction at 400–550 °C with a high H_2S content of ~400 ppm in feed. Modified MFI zeolite membranes with a H_2/CO_2 selectivity higher than 10 showed the ability to achieve CO-conversion well exceeding the equilibrium conversion in WGS reaction.

In this project, we reported the first experimental demonstration of near-complete CO conversion (~ 99.9%) in a single high-temperature and high-pressure WGS-ZMR that uses a CCD-modified MFI zeolite membrane supported on a commercially available low-cost small diameter alumina tube (outer diameter: 5.7 mm, provided by Media and Processes Technology Inc.).

This basic arrangement persists in the multi-tube reactors intended for bench-scale testing; these modules are depicted in Figure 4. The housing accommodates a full-length 21-tube bundle, and the main feed port can be completely removed to permit catalyst packing/removal.

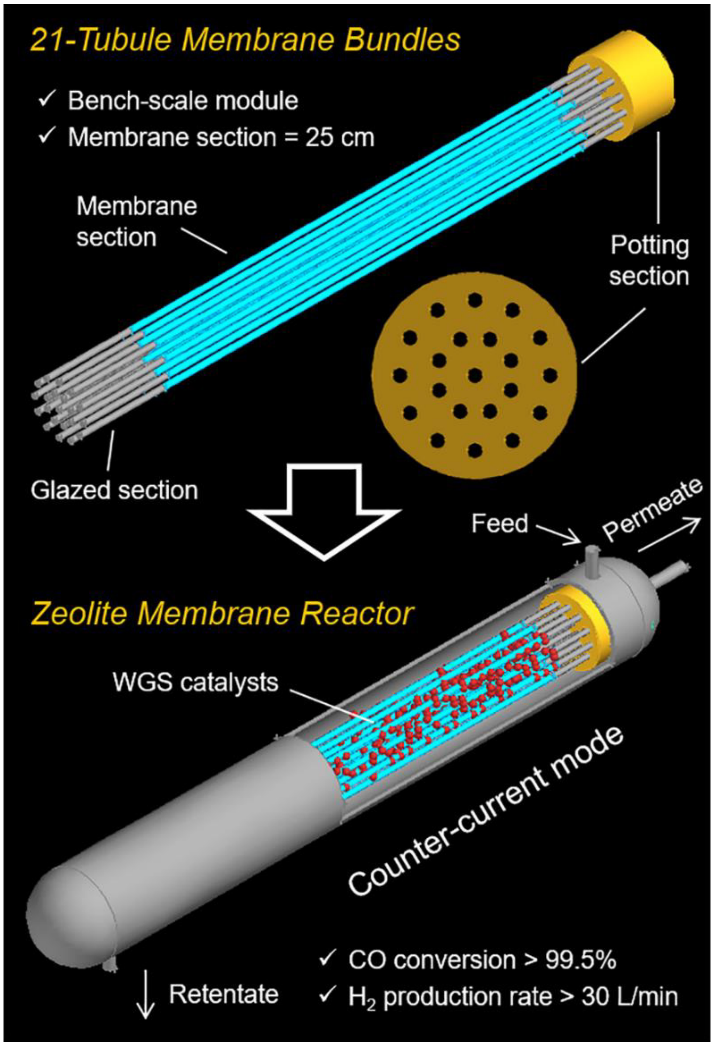

Figure 4: Zeolite membrane bundles and modules

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value *	Target R&D Value
Materials of Fabrication for Selective Layer	—	modified MFI zeolite	modified MFI zeolite
Materials of Fabrication for Support Layer	—	α-alumina	α-alumina
Nominal Thickness of Selective Layer	µm	~10	~5
Membrane Geometry	—	discs	tubes
Maximum Trans-Membrane Pressure	bar	~20	~30
Hours Tested without Significant Degradation	—	~100	>200
Manufacturing Cost for Membrane Material	$\$/m^2$	~800	~600
Membrane Performance			
Temperature	°C	400–500	400–500
H_2 Pressure Normalized Flux	GPU or equivalent	~300	300–600
H_2/H_2O Selectivity	—	>100	>100
H_2/CO_2 Selectivity	—	10–30	20–45
H_2/H_2S Selectivity	—	>60	>60
Sulfur Tolerance	ppm	1,000	10,000
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	Counter-current	
Packing Density	m^2/m^3	50-200	
Shell-Side Fluid	—	Retentate, CO_2-rich flow	
Syngas Gas Flowrate	kg/hr	5-20	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 95 ** ~30	
H_2 Recovery, Purity, and Pressure	%/%/bar	92 95 ~20	
Pressure Drops Shell/Tube Side	bar	10-30	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	~1,000	

* For the Current R&D Value, the calculation is based on lab-scale zeolite membranes reported in literature. Palladium based membranes have high hydrogen selectivity but low sulfur tolerance, which is not presented here.

** Gasifier, coal feedstock, and upstream unit operation (e.g., syngas pretreatment) specifications dependent.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivity should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – At temperatures above 400 ºC, the separation of H_2 and CO_2 through modified zeolite membranes is governed by translational gas diffusion in micropores.

Contaminant Resistance – Zeolite membranes and catalysts have excellent resistance to syngas contaminants.

Syngas Pretreatment Requirements – Particulate removal is required.

Membrane Replacement Requirements – The multiple-tube membrane bundle will be applied in the zeolite membrane reactor continuously over 200 hours without replacement.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensed water at the outlet of retentate side is recycled back as makeup water for the water-gas shift reaction.

Process Design Concept – As presented in Figure 1. A skid for bench-scale zeolite membrane reactors consisting primarily of a flow control system and a high temperature oven is connected into a coal-to-liquids facility by replacing the water gas shift unit.

Proposed Module Integration – The proposed bench-scale study of zeolite membrane reactor will be conducted at University of Kentucky, Center for Applied Energy Research. The multiple-tube membrane bundle will be located downstream of a Coal/Biomass-to-Liquids (CBTL) pilot facility which produces syngas with a rated feed capacity of 1 ton/day. The pressure and temperature of syngas entering the membrane module are 435 psia and 845 °F, respectively. The composition of the gas mixture is assumed:

		Composition						
Pressure	**Temperature**	vol%						ppmv
psia	°F	**CO_2**	**CO**	**CH_4**	**N_2**	**H_2**	**H_2O**	**H_2S**
435	845	32.3	34.1	0	2.8	25.7	3.4	>400

technology advantages

- The membrane reactor process could replace a conventional two-stage WGS reactor system requiring intercooling and a separate CO_2 capture unit, with a single WGS membrane reactor unit with potential for energy efficiency increase and equipment cost savings.
- Modified MFI zeolite membranes have remarkable resistance to sulfur species in the syngas feed and good thermal and hydrothermal stability, and show superior hydrogen permeance and high H_2/CO_2 selectivity.
- These tubular membranes can be fabricated into robust and stable multiple-tube modules at a high packing density.
- The zeolite membrane reactor based process will create a high-pressure CO_2 stream, capturing greater than 90 percent of CO_2 in post-shift syngas.

R&D challenges

- Low reproducibility of laboratory fabrication of long tube zeolite membranes in large quantity with hydrogen separation performance the same as a single short tube membrane.
- High-temperature hydrothermal stability of membrane bundle components and seals.
- Deterioration of strength of membrane tubes in use.
- WGS catalysts' thermal stability, poison resistance, and product selectivity maintained at high pressures (>15 atm) and temperatures (up to 550 °C).
- Removal of particulate matter from the syngas to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials if the technology is to become economically viable.

status

Zeolite membranes have been fabricated on cost-effective industrial tubular alumina substrates, and high pressure and temperature intermediate-scale zeolite membrane modules have been built and tested. WGS on zeolite membrane reactor was studied by experiments and modeling. Also, a process concept for the zeolite membrane reactor integration into a IGCC power plant system has been identified and will serve as the basis for eventual cost and performance estimates for this technology.

available reports/technical papers/presentations

A. Arvanitis, X. Sun, S. Yang, D. Damma, P. Smirniotis, J. Dong, "*Approaching complete CO conversion and total H_2 recovery for water gas shift reaction in a high-temperature and high-pressure zeolite membrane reactor*", Journal of Membrane Science, 549 (2018) 575–580.

"*Zeolite Membrane Reactor for Pre-Combustion Carbon Dioxide Capture*," presented by Jerry Lin, Arizona State University, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," Budget period 1 review meeting presentation, May 2017.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," presented by Jerry Lin, Arizona State University, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Zeolite Membrane Reactor for Pre-Combustion CO_2 Capture*," Project kickoff meeting presentation, January 2016.

Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and Carbon Dioxide Capture

primary project goals

The overall objective is to combine crosslinked polymers having size-sieving ability, and palladium (Pd)-based nanomaterials with very high hydrogen (H_2)/carbon dioxide (CO_2) solubility selectivity, to achieve membranes with superior performance relative to stand alone polymeric membranes. This project may lead to a new generation of membrane materials that combine robust performance with good processability to significantly decrease the cost of CO_2 capture, utilization, and sequestration, enabling environmentally-responsible energy production from abundant domestic coal.

technical goals

- Identify mixed matrix materials with H_2 permeability of 50 Barrers and H_2/CO_2 selectivity of 30 at 150–200 °C with simulated syngas.
- Prepare thin-film mixed matrix composite membranes with H_2 permeance of 500 gas permeation unit (GPU) and H_2/CO_2 selectivity of 30 at 150–200 °C, and perform parametric testing of these membranes using simulated syngas in the laboratory
- Conduct a 6-week field test of membrane stamps with real syngas from a gasifier, providing duration testing as well as assessing effects of exposure to syngas contaminants.

technical content

The State University of New York (SUNY) at Buffalo is developing a membrane-based process to capture carbon dioxide (CO_2) from coal-derived syngas. The key advancement of this technology is a series of novel sorption-enhanced mixed matrix membranes (MMMs) with high H_2 permeance (500 GPU) and high H_2/CO_2 selectivity (30) at temperatures up to 200 °C. The approach combines highly crosslinked polymers with strong size-sieving ability and palladium-based nanomaterials with high H_2/CO_2 selectivity to achieve membranes with performance superior to stand-alone polymeric membranes.

The working hypothesis explored in this technology development is that Pd nanoparticles exhibit extraordinary H_2 sorption, and therefore would confer favorable H_2/CO_2 solubility selectivity to thin-film composite (TFC) membranes into which they are incorporated (allowing H_2 to "hop" along the particle array). Such membranes, consisting of metallic Pd particles dispersed in a polymer matrix, are termed mixed matrix membranes. Figure 1 depicts this approach, in which a mixed matrix membrane should improve both permeance and selectivity for H_2 separation above those typical of base polymer membranes.

technology maturity:

Bench-Scale, Actual Syngas (10 PPH equivalent to 0.0066 MW_e)

project focus:

Mixed Matrix Membranes

participant:

State University of New York (SUNY)–Buffalo

project number:

FE0026463

predecessor projects:

N/A

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partners:

Membrane Technology and Research Inc.

start date:

10.01.2015

percent complete:

67%

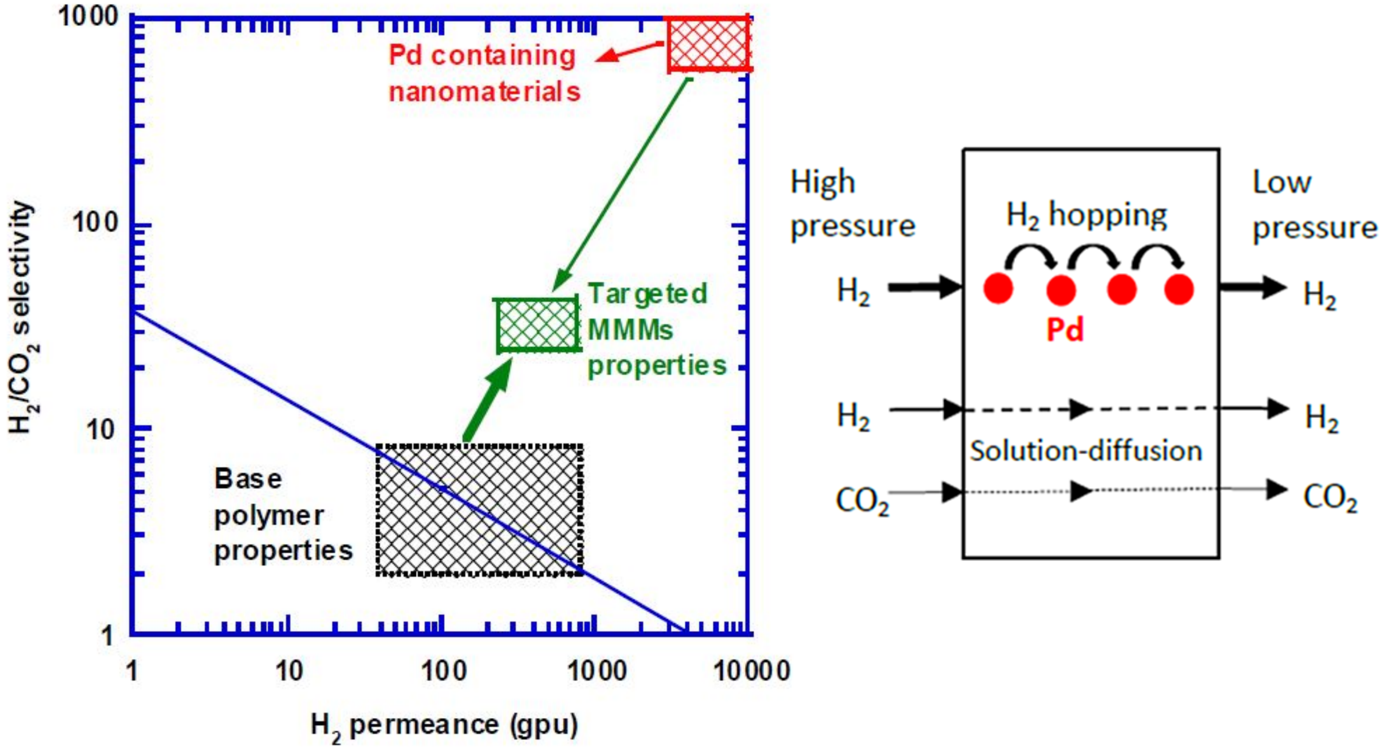

Figure 1: Mixed matrix materials approach

One of the most suitable choices of polymeric material for membranes intended for H_2 separation from hot syngas is poly[2,2′-(m-phenylene)-5,5′-bisbenzimidazole] (m-PBI) which has been widely investigated for elevated temperature H_2/CO_2 separation. One of the strategies to enhance the size-sieving ability in m-PBI is to crosslink the polymer chains to increase chain rigidity and/or decrease free volume, and in this work, the m-PBI is crosslinked using terephthaloyl chloride. SUNY also discovered that by doping with phosphoric acid (H_3PO_4), the PBI is favorably modified toward greater H_2/CO_2 selectivity while decreasing H_2 permeability. The H_3PO_4 tightens the polymer structure and increases size sieving ability while exhibiting stability up to 200 °C. The improvement in PBI polymer properties thus demonstrated is depicted in Figure 2.

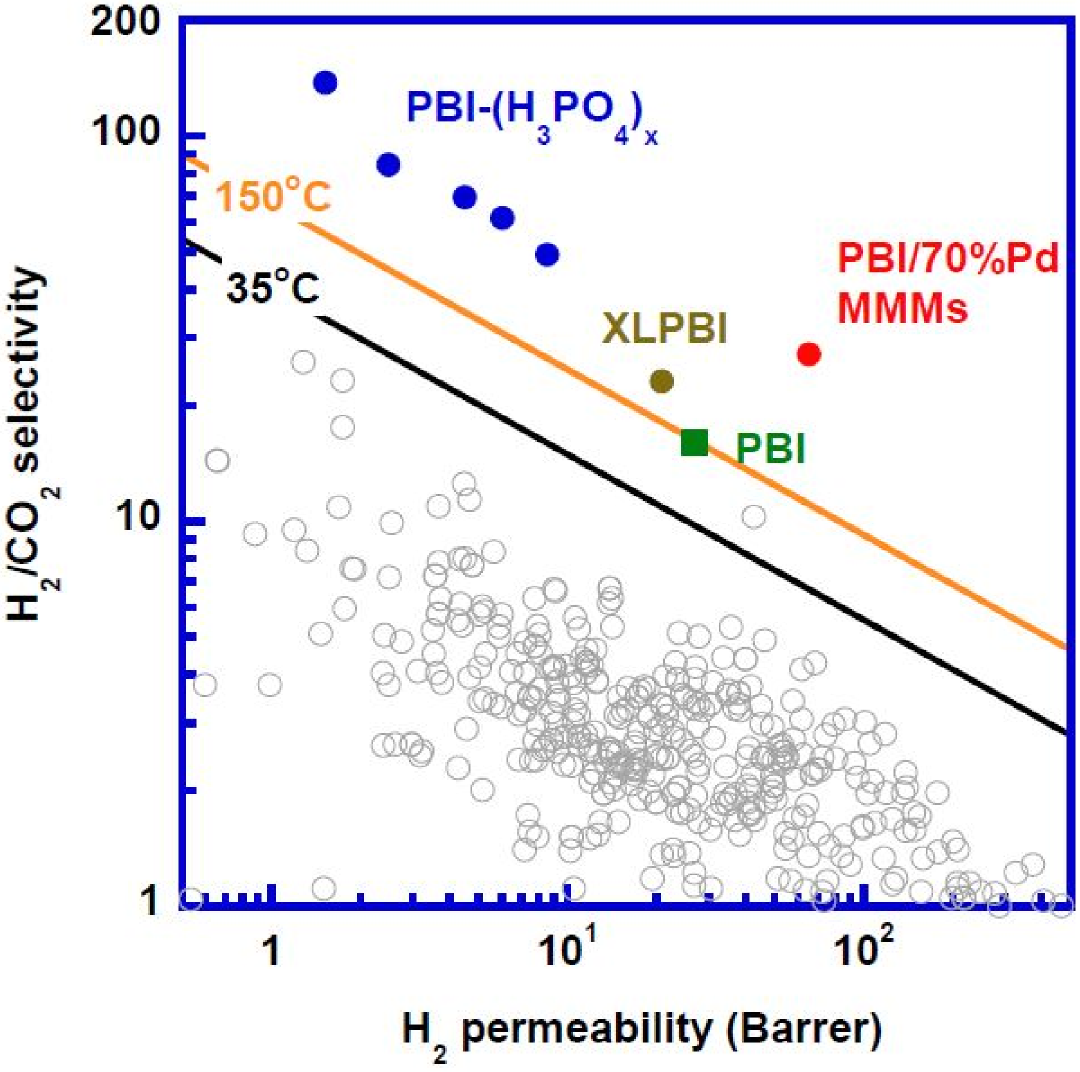

Figure 2: Polymer development and scale-up

An important aspect of development of this technology is synthesis of the Pd nanoparticles for incorporation in the MMMs. Both solution phase (colloidal) synthesis and gas phase (aerosol) synthesis using a high-temperature reducing jet (HTRJ) reactor developed by SUNY were investigated. The solution phase synthesis directly provides nanoparticles that are dispersible in common organic solvents, including those from which the polymer membranes are cast. However, the HTRJ process can more readily produce alloy nanoparticles and is likely to be a more scalable and cost-effective process at larger scale. Pd-Cu (60/40) alloy nanoparticles with typical size of 4–8 nm were successfully prepared using the HTRJ reactor; when tested, these evidenced extremely high H_2/CO_2 solubility selectivity (≈840), and H_2 chemisorption independent of gas pressure.

Particles prepared in the gas phase are collected as dry powders, and for incorporation into polymer membranes these nanoparticles must be stably dispersed in solvents that are also capable of dissolving the polymers of interest. The Pd alloy nanoparticles are suspended in toluene solvent, and mixed with 5.0 wt% PBI in dimethylacetamide (DMAc) solvent. The combined dual solvent system incorporating both the dissolved PBI and nanoparticles is sonicated, then placed on a plate or support and allowed to dry at elevated temperature and under vacuum. Currently, the mixed matrix PBI/Pd layer is created directly on a support structure of polydimethyl siloxane (PDMS) on pure PBI support, all of which is underlain by stainless steel mesh, as depicted in Figure 3. These images show PBI with 50 wt.% Pd, but latest syntheses have increased Pd nanoparticle content to 70 wt.%; the point depicted in red in Figure 2 shows the performance properties of the 70 wt.% Pd/PBI MMM.

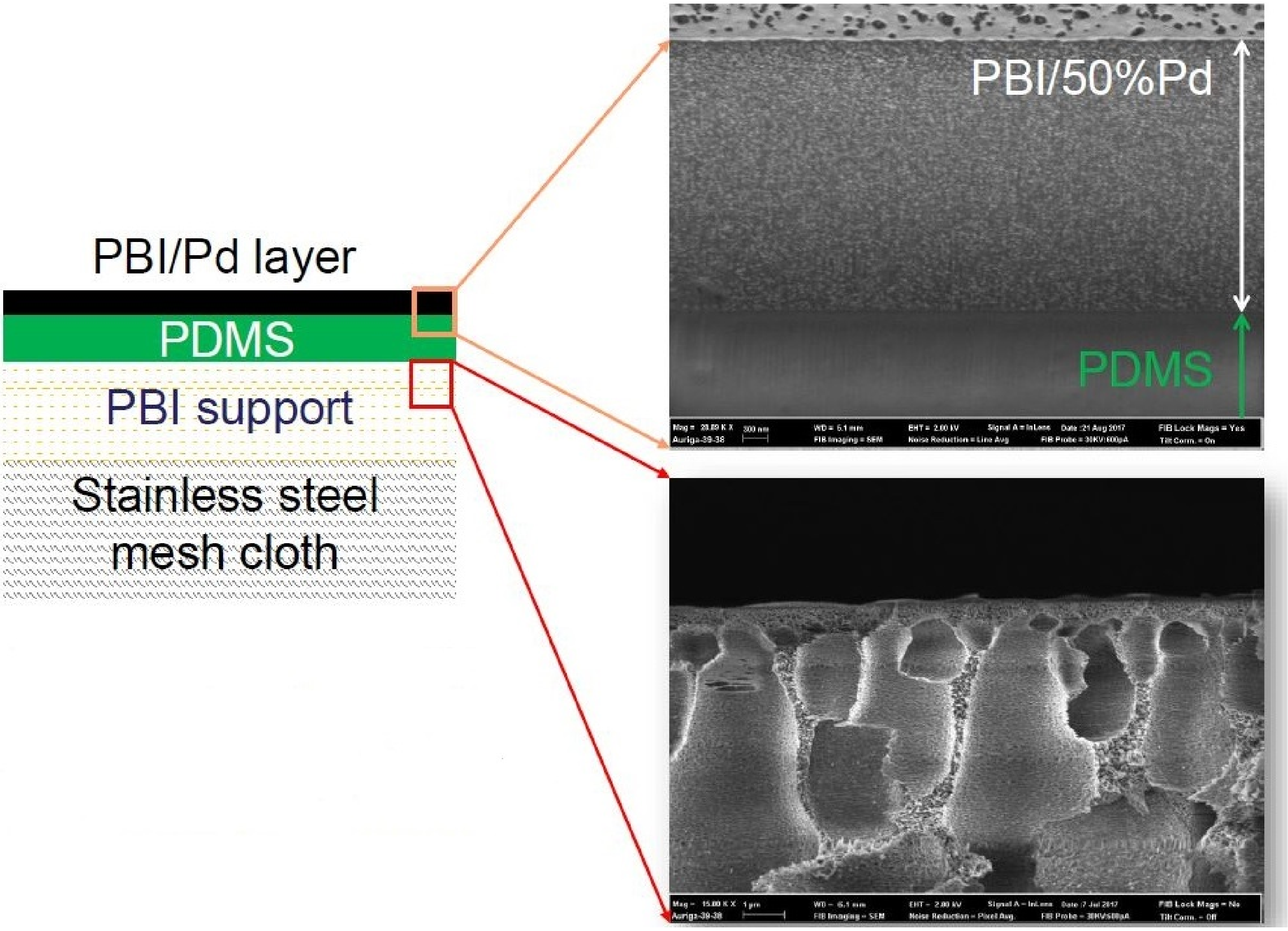

Figure 3: Cross-sectional SEM of TFC membranes

Figure 4 shows the effect of increasing H_2 permeability and selectivity in the MMMs with increasing amounts of Pd nanoparticles. From base case PBI, the 70 wt% Pd MMM more than doubles the permeability, and selectivity increases from 15 to 25 (near the target of 30).

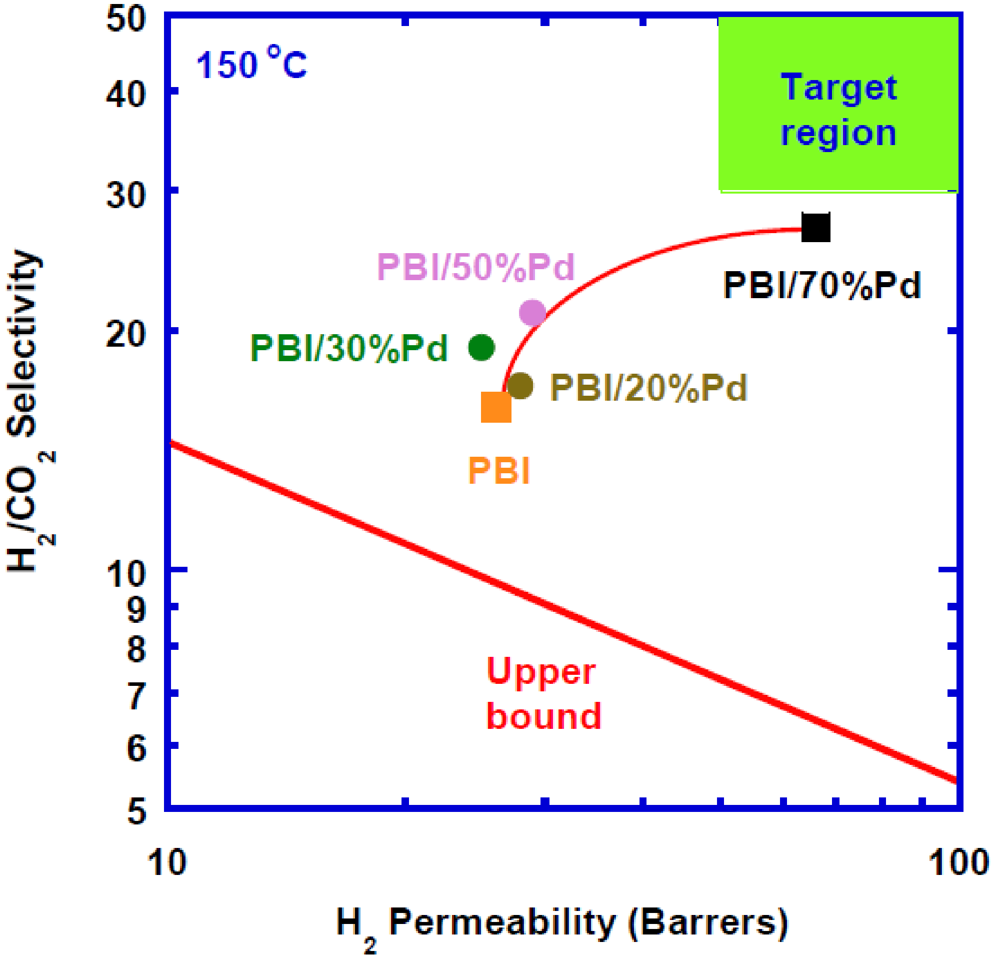

Figure 4: Effect of increasing Pd nanoparticle content on H_2/CO_2 separation properties in MMMs

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	polymers	
Materials of Fabrication for Support Layer	—	polysulfone, polyethersulphone, etc.	
Nominal Thickness of Selective Layer	µm	0.1–0.2	0.1
Membrane Geometry	—	Flat sheet or hollow fiber	Flat sheet
Maximum Trans-Membrane Pressure	bar	50	50
Hours Tested without Significant Degradation	—	1 month	3 weeks
Manufacturing Cost for Membrane Material	\$/m^2	10–50	20–50
Membrane Performance			
Temperature	°C	100–300	250
H_2 Pressure Normalized Flux	GPU	200	500
H_2/H_2O Selectivity	—	0.1–0.5	—
H_2/CO_2 Selectivity	—	20	30
H_2/H_2S Selectivity	—	10–20	20
Sulfur Tolerance	ppm	50	10
Type of Measurement	—	mixed-gas	mixed-gas
Proposed Module Design			
Flow Arrangement	—	spiral-wound modules	
Packing Density	m^2/m^3	1,000–5,000	
Shell-Side Fluid	—	syngas	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
H_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Barrer – gas permeability unit of membrane selective materials, 10^{-10} cm^3 (STP)/(cm^2 s cmHg)

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Resistant to water, high pressure CO_2. However, the effects of sulfur and CO on gas separation properties are to be determined.

Syngas Pretreatment Requirements – Sulfur removal and temperature adjustment.

Membrane Replacement Requirements – None.

Waste Streams Generated – None.

Process Design Concept – Flowsheet/block flow diagrams are being devised by Membrane Technology and Research, Inc.

Proposed Module Integration – The membrane system is after the low temperature shift reactor.

Pressure	Temperature	Composition						
psia	°F	vol%						ppmv
		CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
750	480-750	35-45	1-2	1-2	1-2	50-60	2-5	5-100

technology advantages

- Synergism created by incorporating Pd in a polymer membrane, taking advantage of the well-understood properties and performance of PBI in membrane gas separations with the extremely high H_2 selectivity and permeability of Pd.
- Cost savings over pure Pd membranes, using relatively little expensive Pd metal but still taking advantage of its hydrogen sorption properties and stability against sulfur compounds.
- Good processability derived from polymer based materials for the fabrication of the industrial thin film composite membranes.

R&D challenges

- Membrane stability at operating conditions (elevated pressure and temperature).
- Fabrication of thin-film composite membranes consistently to specification and without defects.
- Scaled-up production of high-purity Pd nanoparticles, and improving process yield.
- Attaining target region of selectivity vs. permeability in MMMs.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Cost reductions for the membrane module materials will be needed if the technology is to become economically viable.
- Scale-up and integration issues are a possibility given the large number of membranes needed to service a 550-MW_e plant.

status

In the first year of the project, mixed matrix materials with superior H_2/CO_2 separation properties, and polymers and nanomaterials with promising H_2/CO_2 separation properties were identified and prepared. Current work is concentrating on mixed matrix membrane fabrication, and on development of the field test unit.

available reports/technical papers/presentations

"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," presented by Haiqing Lin, University of Buffalo, The State University of New York, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Sorption Enhanced Mixed Matrix Membranes for Hydrogen Purification and CO_2 Capture*," project kickoff meeting presentation, Pittsburgh, PA, October 5, 2015.

L. Zhu, M. Swihart and H. Lin, Unprecedented size-sieving ability in polybenzimidazole doped with polyprotic acids for membrane H_2/CO_2 separation, *Energy & Environmental Science*, 2018, DOI: 10.1039/c7ee02865b

L. Zhu, M. Swihart and H. Lin, Tightening nanostructure of PBI for membrane H_2/CO_2 separation, *Journal of Materials Chemistry A*, 5, 19914-19923, 2017, DOI: 10.1039/C7TA03874G

Lingxiang Zhu, Maryam Omidvar and Haiqing Lin. "Manipulating Polyimide Nanostructures via Crosslinking for Membrane Gas Separation," Chapter 6 in *Membranes for Gas Separation*, pp. 243-270, World Scientific, Aug 11, 2017.

H. Lin, "Molecularly Engineering Membrane Materials for Separations through Enhanced Interactions: A Road Less Traveled," Department of Chemical and Materials Engineering and Center of Membrane Science, University of Kentucky, Lexington, KY, March 1, 2017.

Adams and Chen, *Materials Today*, **14** (2011) 282-289.

H. Lin et al., *J. Membr. Sci.* **457**, 149-161 (2014).

Merkel, Zhou and Baker, *J. Membr. Sci.*, **389**, 442 (2012).

Wijmans and Baker, *J. Membr. Sci.*, **107**, 1 (1995).

Development of a Pre-Combustion Carbon Dioxide Capture Process Using High-Temperature PBI Hollow-Fiber Membranes

primary project goals

SRI is developing a technically and economically viable carbon dioxide (CO_2) capture system at a bench-scale size based on a high-temperature polybenzimidazole (PBI) polymer membrane separation system, and optimizing the process for integration of that system into an integrated gasification combined cycle (IGCC) plant.

technical goals

- Reach PBI membrane-based performance targets of 100–125 gas permeation unit (GPU) for gas permeance and 20–25 selectivity for hydrogen (H_2) over CO_2.
- Evaluate the best operating conditions to achieve 90 percent CO_2 capture with high H_2 recovery in the context of an operating coal gasification-based combined cycle power plant.
- Fabricate membrane modules of sufficient capacity to process a syngas stream (50-kW_{th} equivalent of a shifted gas from an oxygen-blown gasifier) using equipment of industrial relevance.
- Perform bench-scale testing at temperatures ≈225 °C and up to a pressure of 30 bar under various operating conditions, including long-term steady-state conditions.
- Engage an industrial firm that specializes in the manufacture of hollow-fiber membranes for making membrane modules to transfer the membrane fabrication technology.

technical content

SRI is developing a bench-scale system to advance their PBI membrane-based CO_2 capture system previously developed under DOE-funded project FC26-07NT43090. The membrane is used for high-temperature pre-combustion separation of H_2 from shifted syngas, leaving a high concentration, high pressure CO_2-rich stream in the retentate. SRI's membranes are asymmetric hollow-fiber PBI, which is chemically and thermally stable at temperatures up to 450 °C and pressures up to 55 atm (800 psig). This characteristic permits the use of PBI membrane for CO_2 capture downstream of a water gas shift (WGS) reactor, without requiring further gas cooling before the PBI membrane, significantly increasing plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.

PBI-based hollow fibers, as seen in magnified view in Figure 1, offer a considerable advantage over coated stainless-steel tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1–0.5 micrometer separation layer (the dense layer). Ease of large scale manufacturability, high packing density, and the cost are notable advantages of hollow-fiber membrane systems.

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 50 kW_{th})

project focus:

PBI Polymer Membrane

participant:

SRI International

project number:

FE0012965

predecessor projects:

FC26-07NT43090

NETL project manager:

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partners:

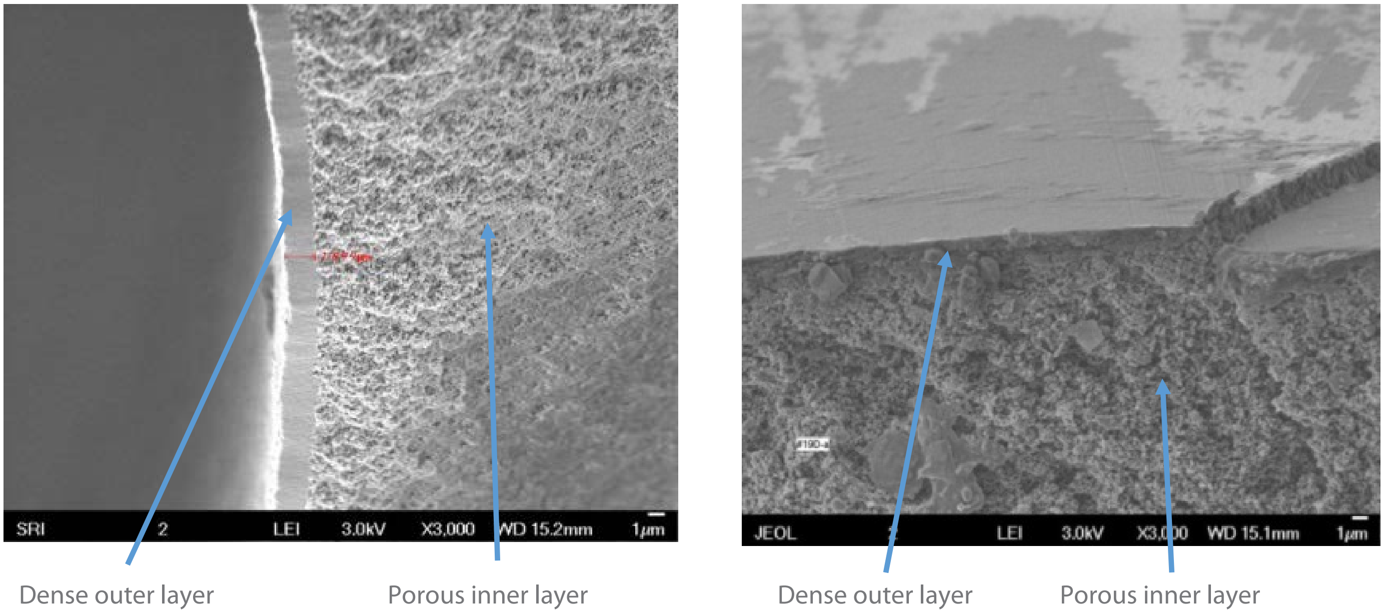
Enerfex, Inc., PBI Performance Products, Generon IGS

start date:

10.01.2013

percent complete:

95%



Dense layer ≈2 µm
H_2/CO_2 selectivity ≈40
H_2 permeance = 70 GPU

Dense layer ≤0.3 µm
H_2/CO_2 selectivity = 25 ± 2
H_2 permeance = 120 GPU

Figure 1: Cross-section of PBI hollow-fiber membranes showing layers

Single-bore, PBI-based hollow fibers have been shown to be highly durable, with near-constant levels of permeability and selectivity over the course of 330 days while in the presence of H_2, carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250 °C. Therefore, PBI fiber modules can be successfully used in pre-combustion CO_2 capture applications. Figure 2 shows the prototype membrane test system at SRI, which was used extensively at the development stage to evaluate fiber stability and gas separation properties with 0.5-in fiber modules. Figure 3 shows actual 2-in and 4-in fiber modules as fabricated at SRI. Figure 4 depicts the PBI skid which was designed for testing 4-in fiber modules. This skid was transported to the National Carbon Capture Center (NCCC) and installed for testing with a syngas slip stream. Figure 5 shows the installed PBI fiber test skid at NCCC.

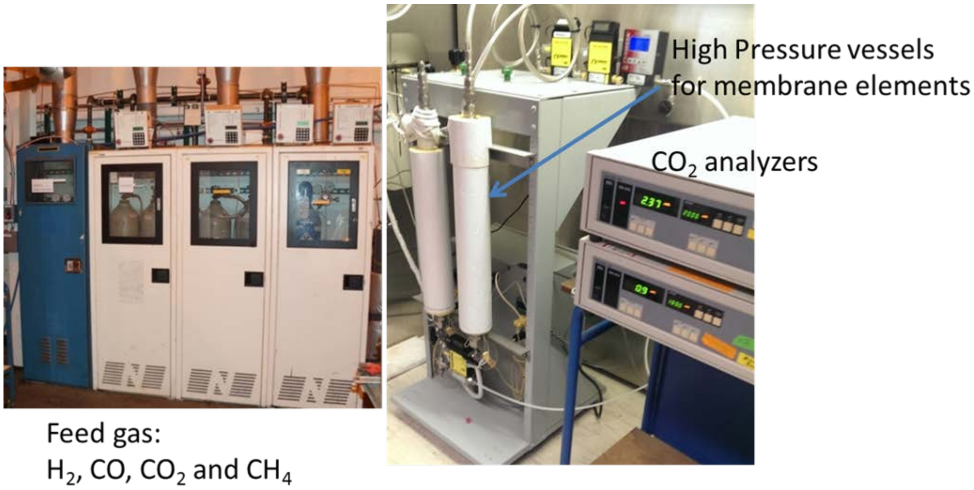


Figure 2: Photograph of the prototype membrane test system at SRI

Figure 3: Photographs of PBI asymmetric hollow-fiber modules, actual 2" module (left) and 4" potted module cross-section (right)

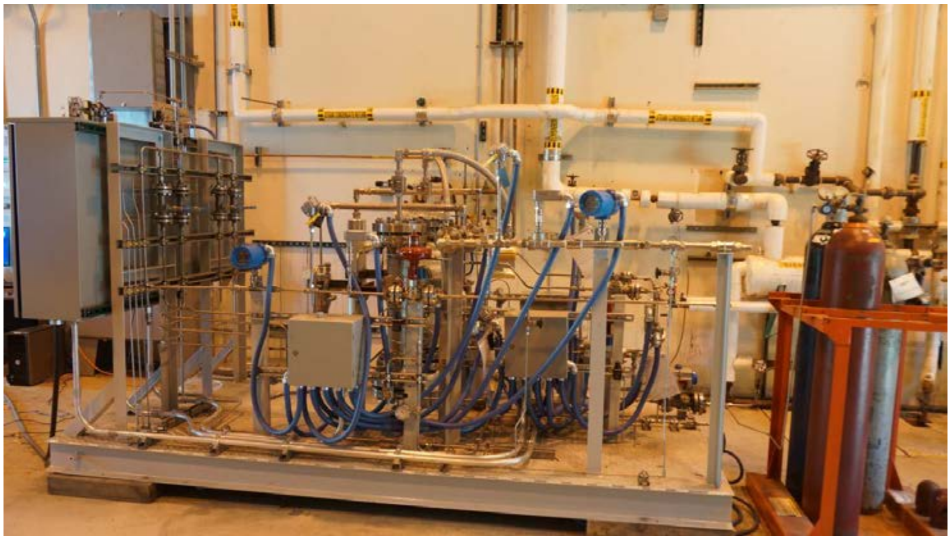


Figure 4: Photograph of the PBI skid in October 2016

Figure 5: Photograph of the PBI skid installed at NCCC in March 2017

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	PBI	PBI
Materials of Fabrication for Support Layer	—	PBI	PBI
Nominal Thickness of Selective Layer	µm	0.3–2	<0.5
Membrane Geometry	—	hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	≈14	>27
Hours Tested without Significant Degradation	—		
Manufacturing Cost for Membrane Material	$\$/m^2$	30–80	TBD
Membrane Performance			
Temperature	°C	200–250	225
H_2 Pressure Normalized Flux	GPU or equivalent	80–120	>120
H_2/H_2O Selectivity	—	<1	<1
H_2/CO_2 Selectivity (Dense layer thickness)	—	40 (>1 µm) and 22 (<0.3 µm)	40 (<0.3 µm)
H_2/H_2S Selectivity (Dense layer thickness)	—	>200 (>1 µm)	>200 (<0.3 µm)
Sulfur Tolerance	ppm	TBD	TBD
Type of Measurement	—	pure and mixed	mixed gases
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	>3,000	
Shell-Side Fluid	—	retentate or permeate	
Syngas Flowrate	kg/hr	22	
CO_2 Recovery, Purity, and Pressure	%/%/bar	TBD	
H_2 Recovery, Purity, and Pressure	%/%/bar	>98%, >49%, 30 bar	
Pressure Drops Shell/Tube Side*	bar	<0.007/0.03	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*Generon 4-inch module design with 200 µm bore diameter and 28–48 bar feed pressure was assumed.

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving and activated diffusion.

Contaminant Resistance – PBI is resistant to acidic contaminants.

Syngas Pretreatment Requirements – Tar removed.

Membrane Replacement Requirements – TBD.

Waste Streams Generated – Gaseous waste stream generated includes CO_2 and H_2S separated from the syngas. This stream will be further treated to remove H_2S.

Process Design Concept – Flowsheet/block flow diagram is shown in Figure 6.

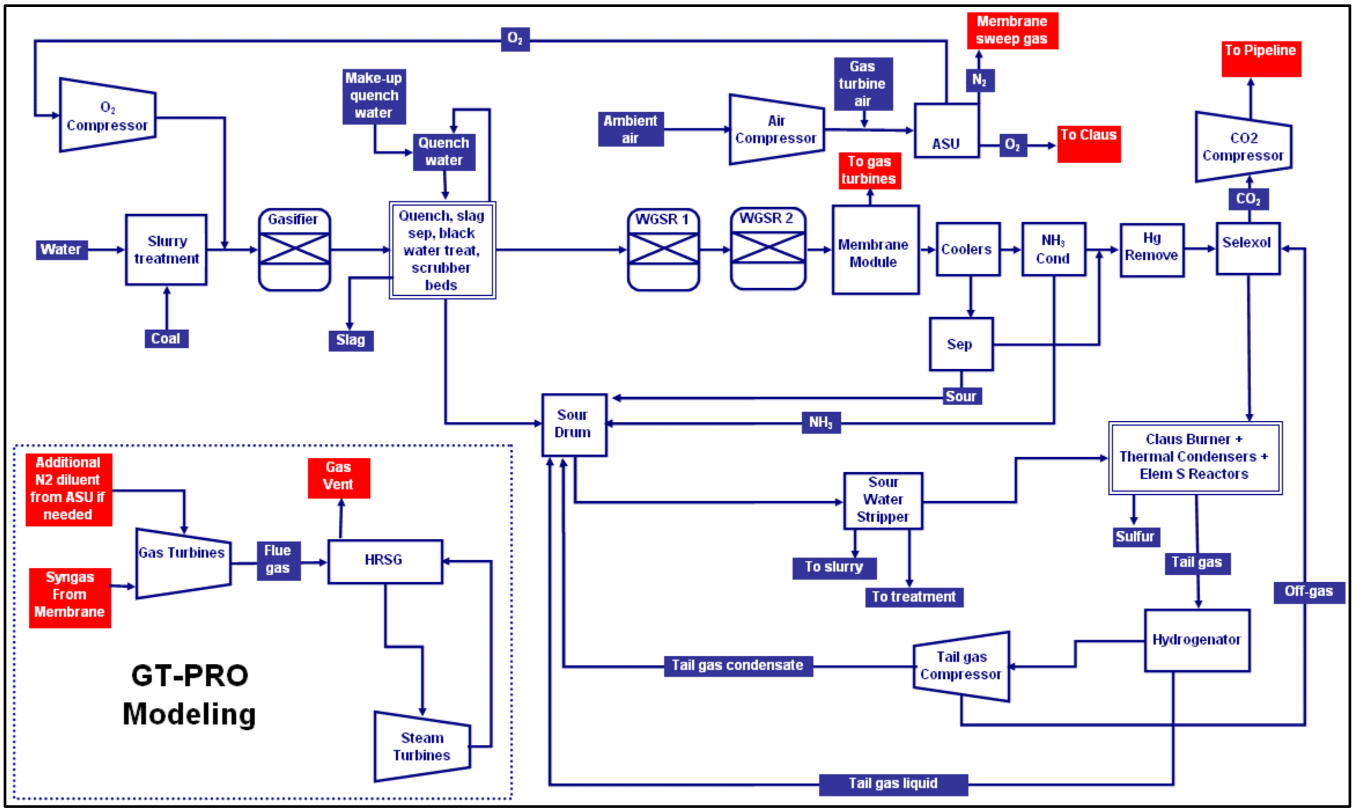
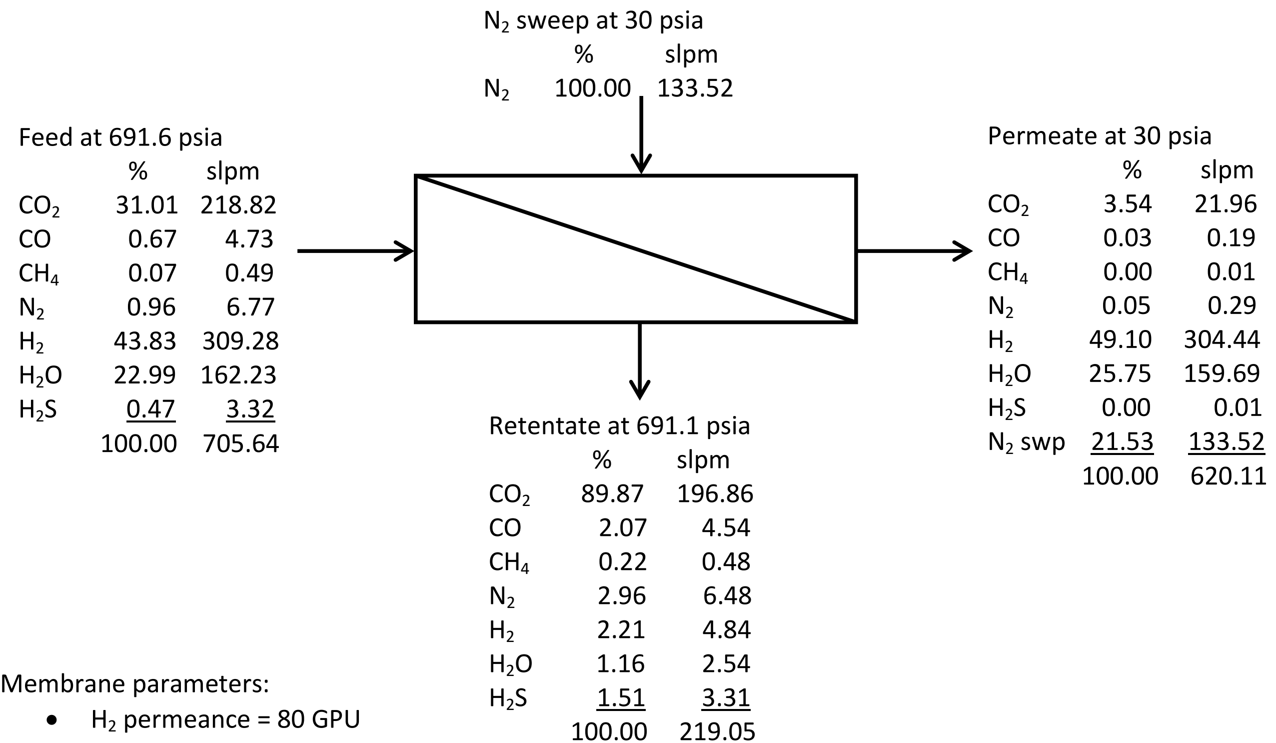


Figure 6: Flowsheet/block flow diagram showing PBI membrane integration in the overall system process

Proposed Module Integration – Module design is tubular with 4-in diameter and 36-in length. Figure 7 shows the simulated module performance, the pressure, temperature and composition of the gas entering the module, assuming H_2/CO_2 selectivity of 40. Note that the module feed gas is from an oxygen blown gasifier with a shifted syngas feed to the membrane. In an oxygen-blown gasifier (assumed in techno-economic analysis), the permeate recovers 98.4 percent of the feed H_2 and the retentate captures 90 percent of the feed CO_2. The retentate stream is further processed in a Claus plant to remove H_2S and a catalytic oxidizer to convert CO and CH_4 to CO_2 and H_2 to H_2O. The final retentate dry basis CO_2 purity is 96.88 percent.

The composition of the gas entering the module:

Pressure	Temperature	Composition vol%						
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
691.1	437	31.01	0.67	0.07	0.96	43.83	22.99	0.47



N_2 sweep at 30 psia

	%	slpm
N_2	100.00	133.52

Feed at 691.6 psia

	%	slpm
CO_2	31.01	218.82
CO	0.67	4.73
CH_4	0.07	0.49
N_2	0.96	6.77
H_2	43.83	309.28
H_2O	22.99	162.23
H_2S	0.47	3.32
	100.00	705.64

Permeate at 30 psia

	%	slpm
CO_2	3.54	21.96
CO	0.03	0.19
CH_4	0.00	0.01
N_2	0.05	0.29
H_2	49.10	304.44
H_2O	25.75	159.69
H_2S	0.00	0.01
N_2 swp	21.53	133.52
	100.00	620.11

Retentate at 691.1 psia

	%	slpm
CO_2	89.87	196.86
CO	2.07	4.54
CH_4	0.22	0.48
N_2	2.96	6.48
H_2	2.21	4.84
H_2O	1.16	2.54
H_2S	1.51	3.31
	100.00	219.05

Membrane parameters:

- H_2 permeance = 80 GPU
- H_2/CO_2 Selectivity = 40
- Dense layer thickness = 1.0 µm
- Membrane area = 8.5 m^2

Operating parameters:

- Feed temperature = 437°F
- 50 kWth Shifted Syngas Feed
- Permeate H_2 recovery = 98.4%
- Retentate CO_2 capture* = 90.0%

* Retentate CO_2 dry basis purity = 96.88% after H_2S removal and catalytic oxidation of CO, H_2 and CH_4

Figure 7: Simulation of a PBI module performance with an oxygen blown gasifier and a 50-kW_{th} shifted syngas feed

technology advantages

- PBI combines both useful throughput (permeability) and degree of separation (selectivity).
- PBI is thermally stable up to 450 °C, and sulfur tolerant.
- PBI asymmetric hollow fibers can be fabricated at increasingly small diameters, allowing increased fiber packing densities in modules realistically consistent with 7,000 m^2 of membrane surface area per m^3 of module volume.

R&D challenges

- Maintaining fiber and module fabrication quality/performance (avoiding membrane pinholes, macrovoids; module seal integrity) in scale up/transfer of technology to larger-scale manufacturing.
- Designing and synthesizing materials structure and configurations.
- Integration and optimization of membrane-based CO_2 separation systems in coal gasification-based plants.

status

SRI's PBI skid (capable of accommodating 6–8 4″ fiber modules, each with 0.6 t-CO_2 per day capacity) was fabricated in 2016, and installed at NCCC and tested there in 2017 with 2″ and 4″ modules. Overall, testing showed that the upper limit for H_2/CO_2 selectivity is ≈40, and confirmed that >90 percent recovery of CO_2 is possible at operating temperatures >190 °C. Techno-economic analysis shows that CO_2 capture cost for a combined cycle process would be <\$40/tonne of CO_2 captured, compared to \$52/tonne of CO_2 captured assuming the baseline technology (Selexol).

Next steps in further technology scale-up would involve long-term testing of the latest generation modules, and increasing module size to 8″ and testing in a large slip stream.

available reports/technical papers/presentations

"*Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow Fiber Membranes*," presented by Indira S. Jayaweera, SRI International, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes (HFMs)*," presented by Indira S. Jayaweera, SRI International, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Development of Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes*," presented by Indira S. Jayaweera, SRI International, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

"*Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane*," presented by Gopala Krishnan, SRI International, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Development of a Pre-Combustion Carbon Dioxide Capture Process Using High Temperature Polybenzimidazole Hollow-Fiber Membrane Fact Sheet*," July 2014.

"*Development of a Pre-Combustion CO_2 Capture Process Using High-Temperature PBI Hollow-Fiber Membranes*," Project Kick-Off Meeting Presentation, Pittsburgh, PA, June 9, 2014.

Krishnan, G., "*Fabrication and Scale-Up of Polybenzimidazole (PBI) Membrane Based System for Pre-Combustion Based Capture of Carbon Dioxide*," presented at 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

Krishnan, G.; Steele, D.; O'Brien, K.; Callahan, R.; Berchtold, K.; and Figueroa, J., "Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane," Energy Procedia, Volume 1, Issue 1, February 2009, pp. 4079-4088.

Gopala Krishnan; Indira Jayaweera; Angel Sanjurjo; Kevin O'Brien; Richard Callahan; Kathryn Berchtold; Daryl-Lynn Roberts; and Will Johnson," *Fabrication and Scale-up of Polybenzimidazole (PBI) Membrane Based System for Precombustion-Based Capture of Carbon Dioxide*", DOE Contract Number: FC26-07NT43090, 2012-March 31.

Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery

primary project goals

The Media and Process Technology Inc. (MPT) project objective has been to develop a dual-stage membrane-based process (DSMP) for pre-combustion carbon dioxide (CO_2) capture in an Integrated Gasification Combined Cycle (IGCC) power plant. The process utilizes MPT hydrogen (H_2)-selective carbon molecular sieve (CMS) membranes, in conjunction with conventional water gas shift (WGS) reactors, in the first stage for enhanced production and bulk recovery of H_2. Following cold gas clean-up, a palladium alloy-based membrane is used in the second stage for efficient residual hydrogen recovery from the high-pressure CO_2 gas stream just prior to sequestration.

technical goals

- Characterize the performance of the proposed CMS and Pd-alloy membrane technologies for H_2-CO_2 separations from simulated coal and biomass derived syngas in laboratory scale testing.
- Verify the membrane performance under extreme pressure conditions to qualify the technology for pre-combustion capture.
- Demonstrate the performance stability of the CMS and Pd-alloy multiple tube membrane bundles in actual gasifier syngas in bench-scale testing at the National Carbon Capture Center (NCCC).
- Develop the mathematical model from the performance database obtained in lab and bench-scale work.
- Perform techno-economic assessment (TEA) and environment, health, and safety (EH&S) analysis for the process using the performance database and models developed under this project.

technical content

The technological approach utilizes MPT's commercial ceramic tubular ultrafilter shown in Figure 1 as a support for the high performance H_2 selective membranes. Ultrathin CMS and Pd-alloy layers are deposited to form composite membranes and then packaged into high packing density multiple tube membrane elements as illustrated. In this bundle configuration, the membranes can be operated at high temperatures (up to 500 °C) and pressures (up to at least 1,200 pounds per square inch gauge [psig]) to support warm syngas cleanup in pre-combustion CO_2 capture.

technology maturity:

Bench-Scale, Actual Syngas (equivalent to 0.01 MW_e)

project focus:

Two-Stage Membrane Separation: Carbon Molecular Sieve Membrane Reactor followed by Pd-Based Membrane

participant:

Media and Process Technology, Inc.

project number:

FE0013064

predecessor projects:

FC26-07NT43057

NETL project manager:

Andrew Jones
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principal investigator:

Paul Liu
Media and Process Technology, Inc.
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partners:

Technip USA Corporation, University of Southern California

start date:

10.01.2013

percent complete:

100%

Figure 1: MPT ceramic ultrafiltration membranes as supports for high performance H_2 selective CMS and Pd-alloy membranes shown packaged into multiple tube membrane elements

MPT's Dual Stage Membrane Process (DSMP) is illustrated in Figure 2. In the process, the CMS and Pd-alloy membranes are used in distinctly different roles, taking advantage of their specific performance capabilities, to deliver high H_2 and CO_2 recovery from IGCC gasifier syngas. In the DSMP, the CMS membrane is deployed in a multiple step serial arrangement with the WGS reactors in two roles, specifically, (i) to recover the bulk H_2 from the gasifier off-gas and (ii) to enhance the equilibrium conversion in WGS reactors to improve net power output. The CMS membrane is operated at temperatures in the range of 250–300 °C and no syngas pretreatment is necessary, making them complementary to the WGS reactors in terms of operating conditions window and reactor performance enhancement.

In the 1st Stage CMS membrane section, only about 85 percent of the H_2 is recovered due to the "low" pressure (~800 psig) of the syngas and excessive carbon losses to the permeate at higher H_2 recovery levels. Hence, considerable H_2 remains that must be recovered to deliver adequate power output and to meet the cost of capture targets. For this purpose, a Pd-Ag alloy membrane is used in the 2nd stage of the process. Due to the well-known deficiencies of the Pd-based membrane, most specifically its vulnerability to sulfur poisoning and the resultant irreversible damage, it is deployed downstream of the CO_2 compressors. At this location in the process, the syngas has been processed through the Cold Gas Cleanup Unit (CGCU) to remove various contaminants (Hg, sulfur, tar, water, etc.) as required for storage; thus, potential membrane poisons are eliminated. Hence, the major limitation of the Pd membrane technology is avoided while the major benefit, specifically its ultra-high (potentially infinite) selectivity of H_2-to-CO_2, is brought to bear. With the addition of this 2nd stage, >99 percent of the produced H_2 is ultimately recovered.

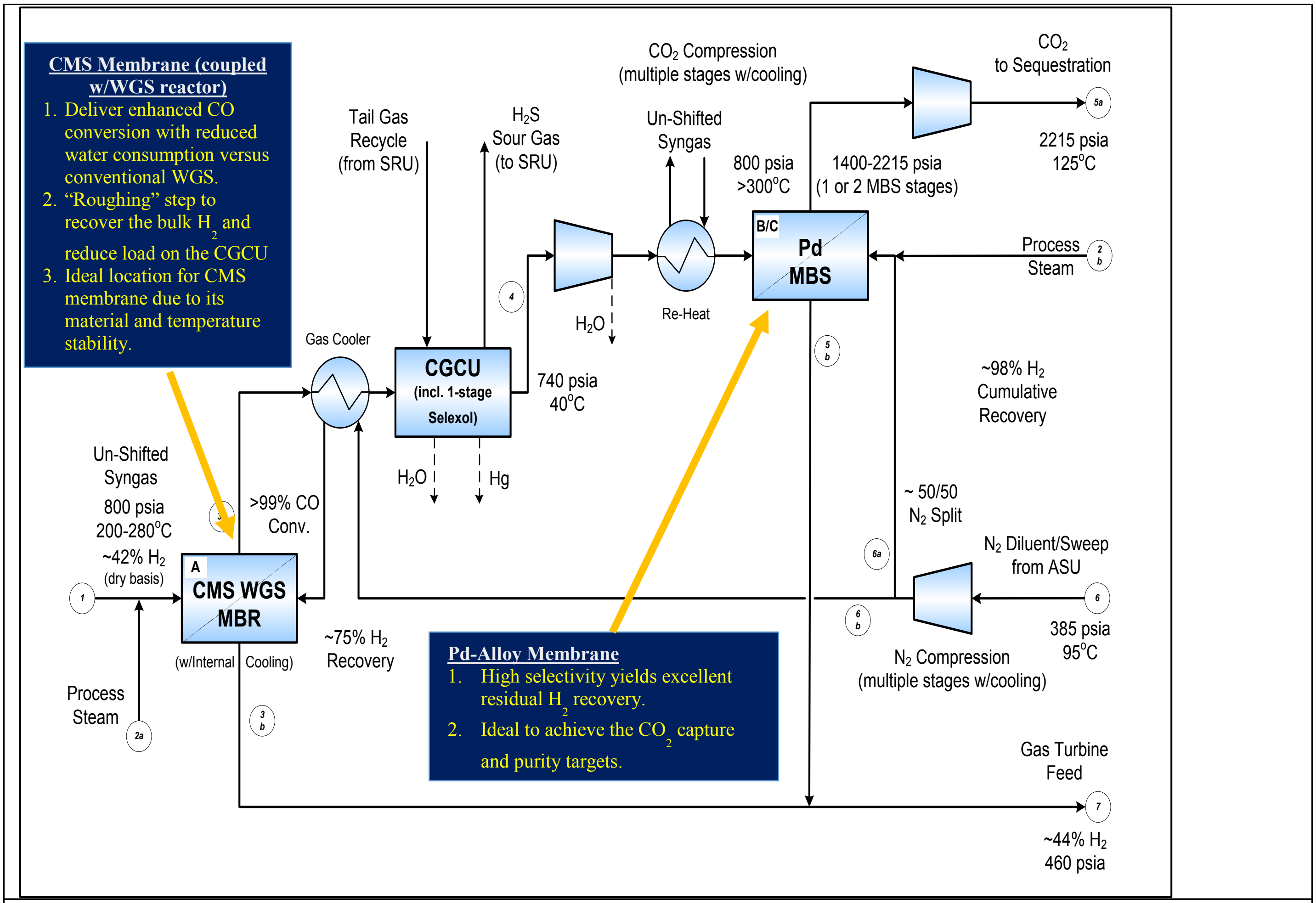

Figure 2: MPT Dual Stage Membrane Process for pre-combustion CO_2 capture

By replacing the dual-stage Selexol unit of the DOE baseline design with the proposed highly efficient and robust membrane technology, the DSMP achieves the DOE carbon capture targets, delivering 90 percent CO_2 capture at 94.5 percent purity, while producing higher net power output (+3 percent, 559 MW) at reduced cost of CO_2 captured (-14 percent, $33.2/tonne) in comparison with the base case.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$/m^2	<1,200	<750
Membrane Performance			
Temperature	°C	250–300	250–300
H_2 Pressure Normalized Flux	GPU or equivalent	500	900
H_2/H_2O Selectivity	—	2–4	>3
H_2/CO_2 Selectivity	—	35	>50
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>10,000	>10,000
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design			
Flow Arrangement	—	co/counter-current or cross-flow	
Packing Density	m^2/m^3	>450	
Shell-Side Fluid	—	permeate	
Syngas Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 95 >60	
H_2 Recovery, Purity, and Pressure	%/%/bar	.>80 >90 Up to 20	
Pressure Drops Shell/Tube Side	bar	—	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	1,500	

TABLE 2: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	palladium-alloy	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2 to 5	2 to 5
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82	>82
Hours Tested without Significant Degradation	—	>35,000 hours lab 150 hours at NCCC	—
Manufacturing Cost for Membrane Material	$\$/m^2$	1,800	<1,000
Membrane Performance			
Temperature	°C	250 to 400	250 to 400
H_2 Pressure Normalized Flux	GPU or equivalent	2,000 to >5,000	1,000 to >5,000
H_2/H_2O Selectivity	—	1,000 to >5,000	1,000 to >5,000
H_2/CO_2 Selectivity	—	1,000 to >5,000	1,000 to >5,000
H_2/H_2S Selectivity	—	N/A	N/A
Sulfur Tolerance	ppm	<10	<10
Type of Measurement	—	mixed gas.	mixed gas
Proposed Module Design			
Flow Arrangement	—	co- or counter-current	
Packing Density	m^2/m^3	450	
Shell-Side Fluid	—	feed/retentate	
Syngas Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	>99 93 to 94 >1,000	
H_2 Recovery, Purity, and Pressure	%/%/bar	>99 >99 1.2	
Pressure Drops Shell/Tube Side	bar	N/A	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	260	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – CMS: molecular sieving. Pd-alloy: H_2 dissolution and permeation.

Contaminant Resistance –.CMS: stable in gasifier raw syngas testing conducted at NCCC. Pd-alloy: stable in gasifier syngas with the removal of sulfur and tar species.

Syngas Pretreatment Requirements – CMS: No syngas pretreatment required. Pd-alloy: sulfur and tar-like species removal required.

Membrane Replacement Requirements – Unknown but lifetimes of >16,000 hours for the CMS and >35,000 hours for the Pd-alloy membranes have been demonstrated with no apparent loss in performance.

Waste Streams Generated – None.

Process Design Concept – See Figure 2.

Proposed Module Integration –

			Composition						
Membrane Material	Pressure psia	Temperature °F	vol%						ppmv
			CO_2	CO	CH_4	N_2, Ar	H_2	H_2O	H_2S
CMS	800	440–540	27.4	5.5	<1	~1	40.8	24.5	>5,000
Pd-alloy	>1,000	480–570	87.8	0.5	<1	~3	8.4	0.17	<10

technology advantages

- The proposed DSMP matches specific capabilities and properties of the CMS (high material stability) and Pd-alloy (high H_2 selectivity) membranes to different separation requirements at separate stages in the process, enabling efficient gas separations performance.
- The proposed DSMP delivers significant cost savings in cost of CO_2 captured due to reduced capital and parasitic compression costs relative to conventional technology. Further, since significant H_2 recovery is achieved in the first stage, the required size and cost of the cold gas cleanup unit is significantly reduced due to the nearly 50 percent reduction in gas volume processed.
- The CMS membranes exhibited excellent performance stability in the presence of untreated gasifier syngas in testing conducted at the NCCC. This makes them highly suitable for first-stage service in pre-combustion H_2 and CO_2 gas production and separations.
- The Pd-alloy membranes were also demonstrated to be highly stable in second stage residual H_2 recovery following cold gas clean-up prior to CO_2 sequestration. The high selectivity of the Pd-alloy permitted excellent residual H_2 recovery to achieve CO_2 capture and purity targets at higher power output and lower cost of CO_2 captured.
- By limiting the Pd-alloy membrane to residual H_2 recovery and fabricating it as an ultra-thin film on a ceramic support, the Pd metal demand/consumption is significantly reduced over CO_2 capture schemes that rely solely on Pd membrane use in flat sheet geometry, thereby addressing both issues of the very high cost and limited availability of Pd metal.

R&D challenges

- Develop the multiple tube membrane bundle suitable for the high-pressure gas processing.
- Fabricate CMS and Pd-alloy membrane bundles for bench-scale testing at the NCCC.
- Demonstrate performance stability of the multiple tube membrane bundles in actual gasifier syngas at the NCCC.
- Develop the mathematical model and confirm applicability to the proposed process in live gas testing.

status

Multiple tube CMS and Pd-alloy membrane bundles were tested at NCCC, exposed to synthetic and actual coal gasifier syngas for hundreds of hours, and found to be stable in this environment. Given this and their stability at elevated temperature and pressure, the technology is expected to be viable for CO_2 capture in IGCC process scenarios. Techno-economic analysis of proposed DSMP in pre-combustion CO_2 capture for an IGCC power has been completed. The TEA shows that net power production is improved by 3 percent and the cost of CO_2 captured is reduced by 14 percent over the NETL base plant case (IGCC with dual stage Selexol CO_2 capture). An EH&S assessment has been completed for the proposed process, and based upon this assessment, there is no reason to believe that a production process and operation meeting the EH&S satisfaction cannot be established to commercialize the proposed technology and process.

available reports/technical papers/presentations

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2015 NETL CO_2 Capture Technology, Pittsburgh, PA, June 2015.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Recovery*," presented by Richard Ciora, Media and Process Technology, Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*Robust and Energy Efficient Dual-Stage Membrane-Based Process for Enhanced CO_2 Capture*," NETL Fact Sheet, February 2014.

"*Robust & Energy Efficient Dual-Stage Membrane-Based Process for Enhanced Carbon Dioxide Recovery*," Project Kickoff Meeting Presentation.

Doug Parsley, Richard J. Ciora, Jr., Diane L. Flowers, John Laukaitaus, Amy Chen, Paul K.T. Liu, Jiang Yu, Muhammad Sahimi, Alex Bonsu, Theodore T. Tsotsis, "Field evaluation of carbon molecular sieve membranes for the separation and purification of hydrogen from coal-and biomass-derived syngas", *J. Membrane Science*, *450, 81* (2014)

M. Abdollah, J. Yu, H.T. Hwang, P.K.T. Liu, R.J. Ciora Jr., M. Sahimi, T. Tsotsis, "Process Intensification in Hydrogen Production from Biomass Derived Syngas", Ind. Eng. Chem. Res., **49**, 10986, (2010).

Abdollahi, M., et al., "Hydrogen Production from Syngas, using a Catalytic Membrane Reactor," presented at the North American Membrane Society, Charleston, SC, June 2009.

Abdollahi, M., et al., "Integrated One-Box Process for Hydrogen Production from Syngas," presented at the 2009 Annual Meeting, American Institute of Chemical Engineers (AIChE), November 2009.

CARBON CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION NOVEL CONCEPTS

Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems

primary project goals

Southern Research Institute is developing a combined magnesium oxide (MgO)-based carbon dioxide (CO_2) sorbent/water gas shift (WGS) reactor that offers high levels of durability, simplicity, flexibility and heat management ability. The primary project goal is to develop a combined CO_2 sorbent/WGS reactor-based process with advanced integrated heat management to capture 90 percent of the CO_2 from the Transport Reactor Integrated Gasifier (TRIG™) syngas for integrated gasification combined cycle (IGCC) applications.

technical goals

- Identify sorbent and operation conditions for a combined CO_2 sorbent/WGS reactor through modeling and experimental study of the WGS reaction at bench-scale.
- WGS reaction conversion extent of 90–95 percent of equilibrium CO conversion.
- CO_2 capture from coal gasification syngas at a temperature of 350 °C and pressure of 40 atm, space velocity 500–2,000 standard cubic cemtimeter (scc)/g/hr (for sorbent), 1,000–4,000 scc/cc/hr (for catalyst).
- CO_2 capacity of sorbent 3–5 mol/kg, 500 cycles with no degradation.
- Progress toward enabling combined MgO-based CO_2 sorbent/WGS reactor technology in a 550 MW_e IGCC plant, capable of 90 percent capture of CO_2 at 95+ percent purity while reducing the cost of electricity by 30 percent over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily hydrogen [H_2] and CO_2) and downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas, could be replaced in whole by a combined MgO-based CO_2 sorbent/WGS reactor unit. Within the WGS reactor, CO_2 would be withdrawn directly by the sorbent, efficiently increasing the driving force for the equilibrium WGS reaction to completion. As such, the multiple stages of the conventional WGS unit are replaced by a single, elegantly performing reactor (or banks of reactors in parallel as syngas throughput requires).

The CO_2 sorbent is MgO, which captures CO_2 according to reactions 1–3. CO_2 is present in the syngas from the original gasification reactions, and is additionally formed as a product of the WGS reaction (reaction 4):

technology maturity:

Laboratory-Scale, Simulated Coal-Derived Syngas

project focus:

Combined CO_2 Sorbent/WGS Reactor

participant:

Southern Research Institute

project number:

FE0026388

predecessor projects:

N/A

NETL project manager:

Isaac Aurelio
isaac.aurelio@netl.doe.gov

principal investigator:

Santosh Gangwal
sgangwal@southernresearch.org

partners:

IntraMicron Inc., Nexant Inc.

start date:

10.01.2015

percent complete:

67%

$$MgO(s) + CO_2(g) \leftrightarrow MgCO_3(s);\ \Delta H = -100.7\ KJ/mol \quad (1)$$

$$MgO(s) + H_2O(g) \leftrightarrow Mg(OH)_2(s);\ \Delta H = -81.1\ KJ/mol \quad (2)$$

$$Mg(OH)_2(s) + CO_2(g) \leftrightarrow MgCO_3(s) + H_2O(g);\ \Delta H = -19.5\ KJ/mol \quad (3)$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g);\ \Delta H = -41.2\ KJ/mol \quad (4)$$

The MgO sorbent gradually transforms to carbonate in the forward reactions, and must be regenerated to MgO in the reverse reactions to enable ongoing operation. Accordingly, the reactor must be operated in cyclic mode, with combined WGS reaction/CO_2 capture interval followed by a regeneration interval, with multiple reactors needed to maintain continual process operation. The regeneration is accomplished by reverse gas flow through the reactor at decreased pressure (atmospheric). Therefore, this can be regarded as a pressure swing adsorption system for CO_2 capture.

This technology takes advantage of IntraMicron's technology of Microfibrous Entrapped Catalysts (MFECs). These are based on microfibrous media (MFM), a highly porous structure (≈94 percent) that consists of randomly oriented microfibers. The random orientation of the microfibers provides a uniform flow profile throughout the bed, which minimizes channeling and assists with mixing. MFECs are prepared using a proprietary method that locks small catalyst particles (0–35 vol. %, and with size 40–300 microns) within the microfibrous media, as depicted in Figure 1(a). The microfibrous structure can be formed from a variety of materials including metals (Cu, Ni, etc.), alloys (stainless steel, brass), polymers, and glass, allowing the support structure to be tailored to a given reaction system. Metals are typically used when enhanced heat transfer is needed. This technology is very helpful in intensifying catalytic processes where catalyst performance is limited by transport-based inefficiencies, and improving heterogeneous contacting and/or heat transfer. Conventional WGS reactors have the catalyst in traditional packed beds, and it is believed that significant advantages can be realized by performing the WGS reaction using MFECs in the frozen-fluidized-bed configuration (Figure 1(c), which would reduce or eliminate intra-particle heat and mass transfer limitations experienced conventionally. For example, Figure 1(b) shows the better heat transfer in MFM as compared to a conventional packed bed of alumina.

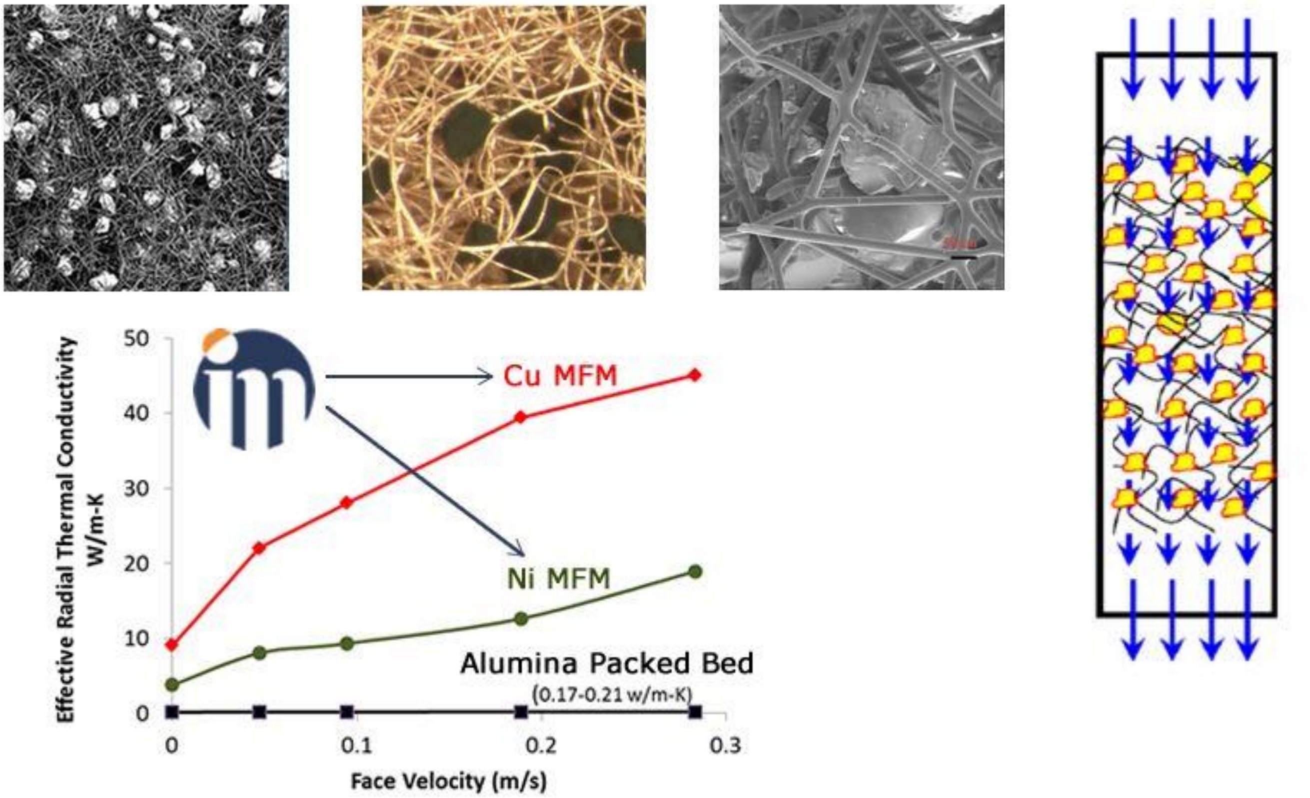

Figure 1: (a) Images of catalyst and sorbent particles entrapped in sintered microfibrous media (top left); (b) comparison of thermal conductivities of metal MFEC with alumina packed bed (bottom left); (c) improved gas flow through frozen fluidized bed configuration of MFECs (on right)

In the SR application, commercial WGS catalyst is used as the source material for the catalyst particles in the MFECs. Additionally, promoted MgO sorbent particles are also introduced into the MFM. The result consists of finely divided sorbent and catalyst particles in close proximity, and with good heat transfer characteristics and gas flow through the mesh holding them.

Although combining the WGS reaction and CO_2 capture in the same media provides intrinsic process intensification, it does create challenges in terms of the inevitable regeneration cycle demanded by the sorbent. The WGS catalyst is present in the reactor as the sorbent undergoes regeneration; the WGS catalyst obviously experiences no benefit from the regeneration cycle, and could experience degradation due to some conditions applied for regeneration.

Figure 2: SR's bench-scale CO_2 capture skid

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
Particle Density	kg/m^3	1,600	1,600
Bulk Density	kg/m^3	1,050	1,050
Average Particle Diameter	µm	1,50	150
Packing Density	kg/m^3	730	730
Sorbent Heat Capacity	kJ/kg-K	0.93	0.93
Manufacturing Cost for Sorbent	$/kg	TBD	TBD
Adsorption			
Total pressure	bar	40	40
Temperature	°C	350	350
Equilibrium Loading	g mol CO_2/kg	5.6	5.6
Heat of Adsorption	kJ/mol CO_2	-130	-130
Desorption			
Total pressure	bar	1	1
Temperature	°C	390	350
Heat of Desorption	kJ/mol CO_2	130	130

Definitions:

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Packing Density – Ratio of the active sorbent mass to the total adsorber volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figure 3 below.

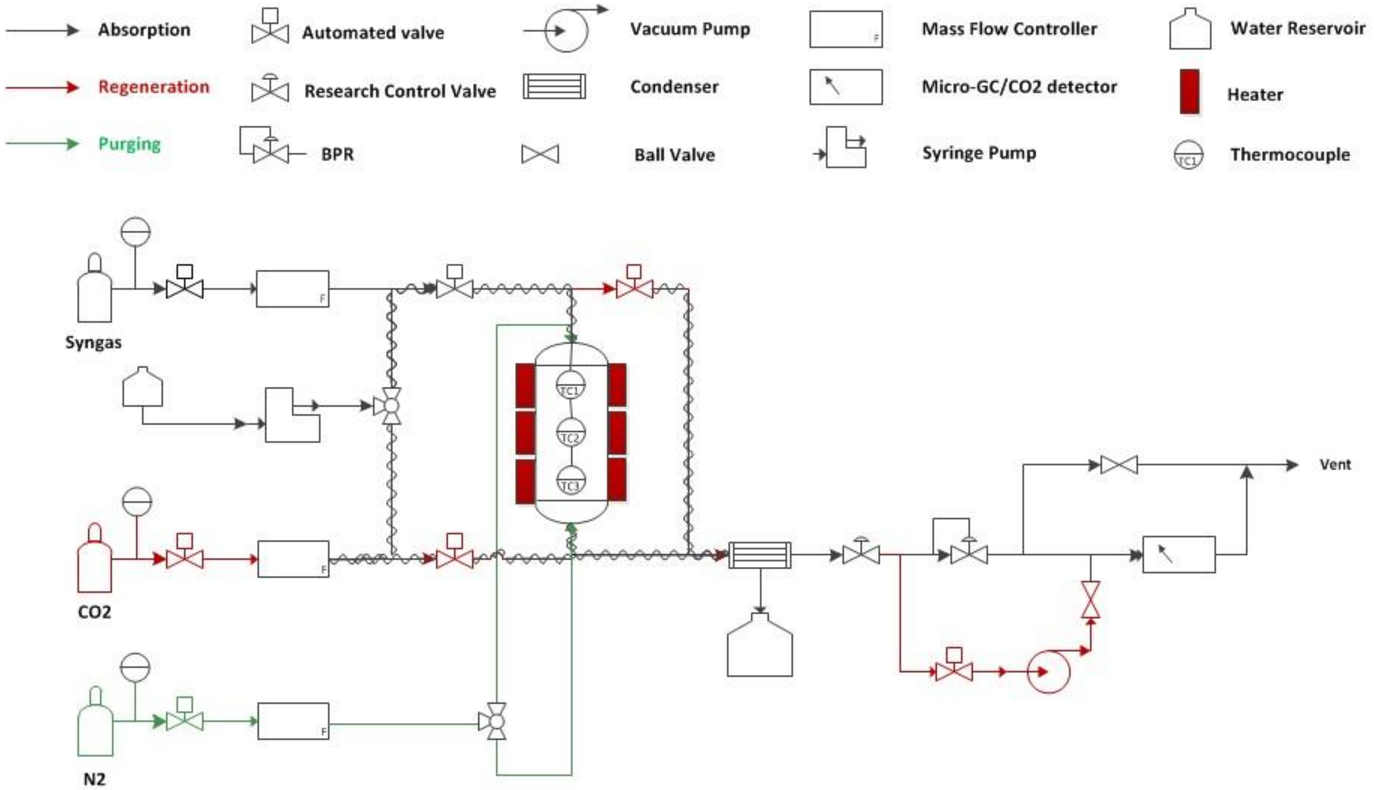

Figure 3: CO_2 capture reactor design (bench-scale)

Syngas Conditions – Pressure, temperature and composition of the gas entering the reactor, TRIG (air-blown) case:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	8.5	17.5	2.6	50.5	11.7	9.2	500

Pressure, temperature and composition of the gas entering the reactor, GE (oxygen-blown) case:

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
615	662	13.7	35.8	0.12	0.8	34.2	15.4	500

technology advantages

- Could replace conventional two-stage WGS reactor system with intercooling plus a separate CO_2 capture unit with a single WGS reactor unit, with potential for energy efficiency increase and equipment cost savings.
- CO_2 capture drives equilibrium-limited WGS toward CO_2 and H_2.
- Integrated heat management maintains thermodynamically favorable reaction temperatures for both exothermic CO_2 capture/WGS and endothermic regeneration.
- The current state-of-the-art CO_2 capture process involves scrubbing the gas stream at low temperature. SR's elevated temperature CO_2 capture technique eliminates the need to cool the gas stream coming from WGS reactor
- SR's high capacity and highly regenerable CO_2 sorbent provides fast adsorption/desorption kinetics, that can be applied in a pressure swing process under minimum temperature swing condition.

R&D challenges

- High levels of CO and CO_2 in syngas.
- Effect of contaminants in coal syngas on MFECs, MFECs' thermal stability, and product selectivity maintained at high pressures and temperatures.
- Heat management in reactor.
- Process integration with IGCC.
- Sorbent capacity, kinetics, and durability.
- WGS catalyst degradation during cycling.
- Scale-up and integration given the large number of reactor modules needed to service a 550-MW_e plant.

status

The hybrid CO_2 capture/WGS reactor has been run for hundreds of cycles at bench scale and testing so far has shown the sorbent to meet both CO_2 capture capacity and durability targets. Also, the WGS performance has been close to target. Reactor modeling and techno-economic evaluation is in process, and a 1,000 cycle test is planned at optimum conditions to demonstrate long-term durability.

available reports/technical papers/presentations

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*Combined Sorbent/WGS-Based CO_2 Capture Process with Integrated Heat Management for IGCC Systems*," presented by Andrew Lucero, Southern Research Institute, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*Combined Magnesium Oxide/Water Gas Shift-Based CO2 Capture Process,*" poster presentation at CO_2 Summit II: Technologies and Opportunities Conference, Santa Ana Pueblo, New Mexico, April 2016.

"*Combined Sorbent/WGS-Based CO2 Capture Process with Integrated Heat Management for IGCC Systems*," project kick off meeting presentation, October 2015.

A High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture

primary project goals

The University of Southern California (USC) is evaluating the technical feasibility of a membrane- and adsorption-enhanced water gas shift (WGS) process, employing a carbon molecular sieve (CMS) membrane reactor (MR) followed by an adsorption reactor (AR) for pre-combustion carbon dioxide (CO_2) capture. This process would replace the conventional two-stage WGS process and downstream conventional amine CO_2 absorption unit in an integrated gasification combined cycle (IGCC) cycle while delivering a 90% capture of CO_2 at 95%+ purity, and reducing the cost of electricity by 30% over plants employing conventional methods of CO_2 capture.

technical goals

- Validate WGS catalyst stability in this process context.
- Demonstrate in the laboratory CO_2 capture from simulated coal gasification syngas at temperatures up to 300 °C and pressure of up to 25 atm.
- Demonstrate in the laboratory CO_2 capacity of hydrotalcite sorbent of >3 wt%, >10 cycles with no degradation.
- Demonstrate progress toward enabling a MR/AR system in a 550 MW_e IGCC plant, capable of 90 percent capture of CO_2 at 95+ percent purity, while reducing the cost of electricity by 30 percent over IGCC plants employing conventional methods of CO_2 capture.

technical content

The working hypothesis of this project is that the conventional WGS unit found in a coal gasification process plant (for shifting the syngas toward primarily hydrogen [H_2] and CO_2) and the downstream conventional amine absorption unit for capturing the CO_2 from the shifted syngas, could be replaced in whole by a unique membrane- and adsorption-enhanced WGS reactor system (previously developed for H_2 production via methane steam reforming) that allows for in situ preferential H_2 permeation and simultaneous CO_2 adsorption. The reactor system is depicted, in the context of a typical IGCC power plant cycle, within the blue border-surrounded process block in Figure 1.

technology maturity:

Laboratory-Scale, Simulated Coal-Derived Syngas

project focus:

Combined CMS Membrane/WGS Reactor and Adsorption Reactor

participant:

University of Southern California

project number:

FE0026423

predecessor projects:

N/A

NETL project manager:

Andrew Jones
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principal investigator:

Theodore Tsotsis
tsotsis@usc.edu

partners:

Media and Process Technology Inc., University of California Los Angeles

start date:

10.01.2015

percent complete:

67%

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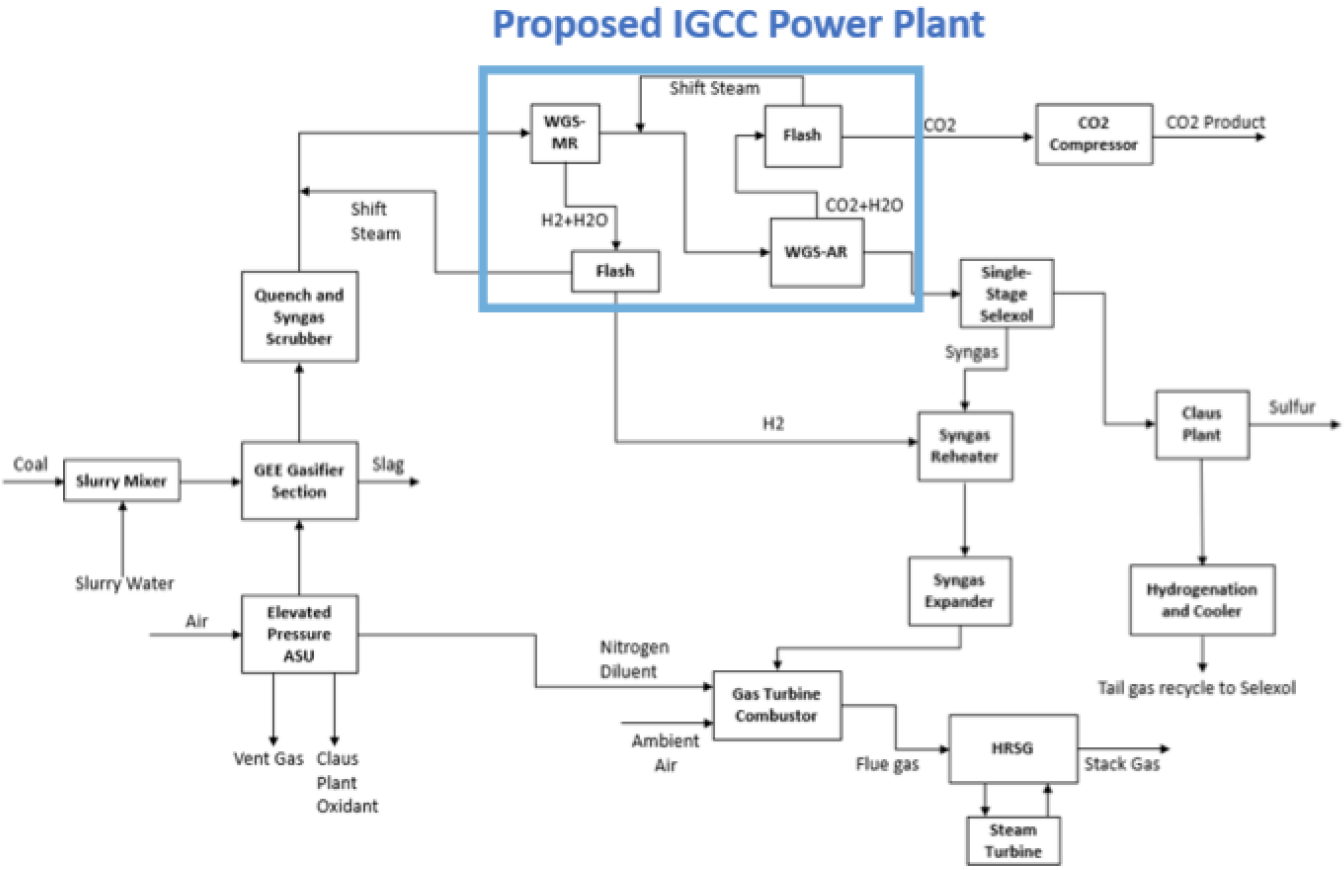

Figure 1: Proposed MR and AR system in the context of IGCC plant process

The system combines a MR and an AR in tandem to produce continuously a pure H_2 product (while attaining a 99+ percent CO conversion), until the adsorbent (in the AR unit) is saturated. The AR unit must then be taken off-stream and regenerated via steam-enhanced temperature swing adsorption (TSA). This unique reactor configuration can, therefore, be viewed as a hybrid MR-AR system with TSA cycling. Compared to conventional WGS followed by CO_2 capture using a conventional amine process, the MR-AR system is more efficient and compact. Furthermore, the use of a TSA rather than a pressure-swing CO_2 recovery step (as commonly practiced in AR systems) allows the recovery of CO_2 at high pressures, thus requiring no additional re-compression step for CO_2 storage. The combined MR-AR process is shown in more detail in Figure 2. Here, the syngas first passes into the MR vessel, consisting of WGS catalyst packed around an array of membrane tubes. The tubes are carbon molecular-sieve-based membranes on ceramic support, which are highly selective to H_2. The permeate consists of high-purity hydrogen. As the hydrogen is withdrawn from the MR vessel, the WGS reaction equilibrium is pushed toward further H_2 production. Retentate/rejected gases are passed to an array of ARs operating in a periodic manner, whereby at any given time some ARs are fed retentate gases and operate in reaction/adsorption mode, while the remaining ARs are fed steam and operate in a TSA regeneration mode. The ARs contain WGS catalyst, in addition to CO_2 sorbent. In this technology, hydrotalcite sorbents are utilized. This collocation of the WGS reaction and CO_2 separation functions in the AR allows traditional WGS reaction equilibrium limitations to be overcome, thus enabling enhanced shifting of the syngas to occur, until most of the carbon as CO is converted into CO_2 and adsorbed. Thus, relatively pure hydrogen gas exits the ARs at high pressure, when the ARs operate in reaction/adsorption mode, while a high-pressure steam/CO_2 mixture exits the ARs, when they operate in regeneration mode. In summary, the proposed process configuration, combining the MR and AR in tandem, provides significant process flexibility, and efficient high-pressure and high-purity hydrogen production, and CO_2 recovery.

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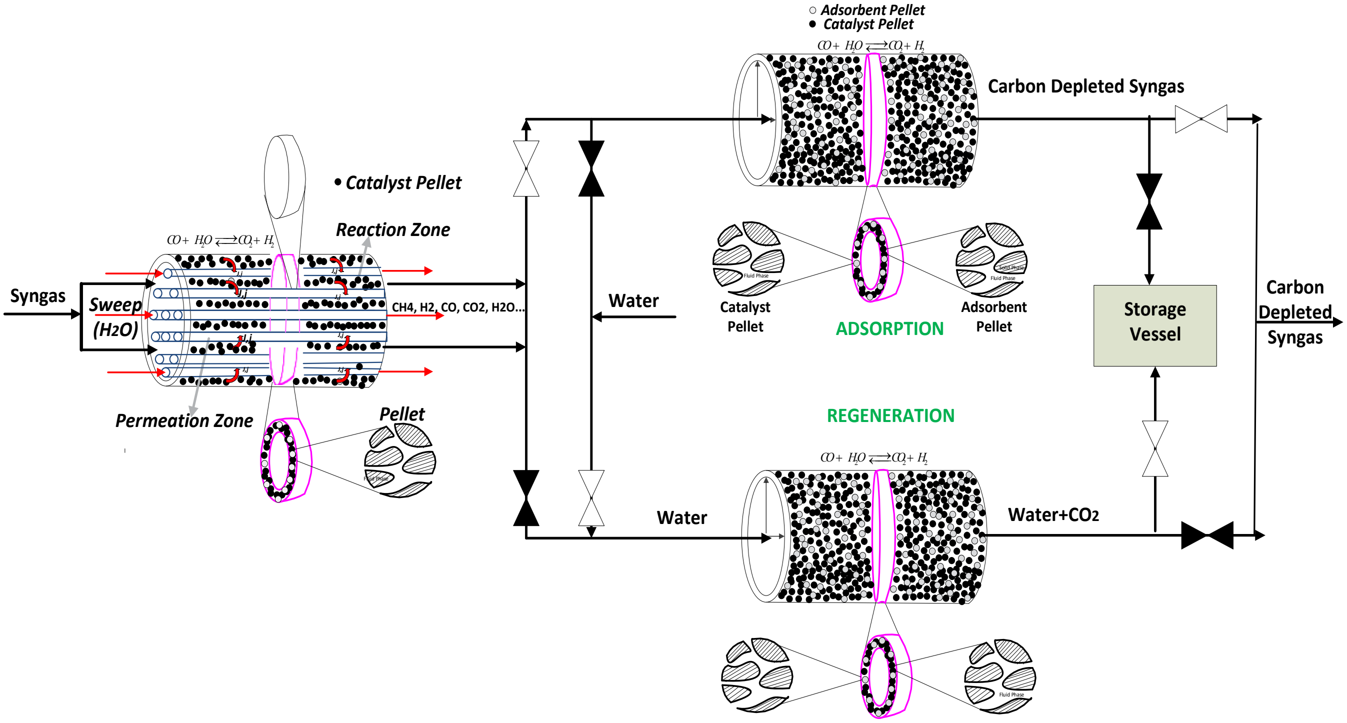

Figure 2: Proposed MR-AR process

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	carbon molecular sieve (CMS)	
Materials of Fabrication for Support Layer	—	alumina	
Nominal Thickness of Selective Layer	µm	2–3	2–3
Membrane Geometry	—	tubular	tubular
Maximum Trans-Membrane Pressure	bar	>82 bar	>82 bar
Hours Tested without Significant Degradation	—	>16,000 hours in lab, >1,000 hours at NCCC	—
Manufacturing Cost for Membrane Material	$/m^2	<1,500	<750
Membrane Performance			
Temperature	°C	250–300	250–300
H_2 Pressure Normalized Flux	GPU or equivalent	500	900
H_2/H_2O Selectivity	—	2–4	>3
H_2/CO_2 Selectivity	—	35	>50
H_2/H_2S Selectivity	—	>100	>100
Sulfur Tolerance	ppm	>10,000	>10,000
Type of Measurement	—	mixed gas	mixed gas

Proposed Module Design				
Flow Arrangement	—	co/counter-current or cross-flow		
Packing Density	m^2/m^3	>450		
Shell-Side Fluid	—	Permeate		
Syngas Gas Flowrate	kg/hr	—		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90	95	>60
H_2 Recovery, Purity, and Pressure	%/%/bar	>80	>90	Up to 20
Pressure Drops Shell/Tube Side	bar	—		
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	1,500		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Molecular sieving.

Contaminant Resistance – Resists all chemical contaminants in gasifier off-gas including H_2S, NH_3, heavy metals, organic vapors, tars, etc., based on bench-scale testing conducted at the National Carbon Capture Center (NCCC)

Syngas Pretreatment Requirements – Particulate removal should be practiced.

Membrane Replacement Requirements – Not known presently, but assumed to be 5 to 10 years. Over 16,000 hours of laboratory thermal stability testing has been demonstrated with no failure. Over 1,000 hours of live syngas testing at the NCCC has been conducted with no failure.

Waste Streams Generated – None

Process Design Concept – See Figure 1.

Proposed Module Integration – See below.

Entering Module	Pressure psia.	Temperature °F	Composition vol%						ppmv
			CO_2	CO	CH_4	N_2	H_2	H_2O	H_2S
MR	800	440-540	0.1089	0.2823	0.0010	0.0055	0.2689	0.3190	5700
AR	800**	440-540*	0.2480	0.1466	0.0009	0.0055	0.2590	0.3253	5700

* Species compositions shown for inlet temperature of 440 °F; **To match the exit gasifier conditions

TABLE 2: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	2849—3066	2849—3066
Bulk Density	kg/m^3	1322—1423	1322—1423
Average Particle Diameter	mm	0.6—0.85	0.6—0.85
Particle Void Fraction	m^3/m^3	0.536	0.536
Packing Density	m^3/m^3	0.4057	0.4057
Solid Heat Capacity @ STP	kJ/kg-K	—	—
Crush Strength	kg_f	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	25	>25
Temperature	°C	250-300	250-300
Equilibrium Loading	g mol CO_2/kg	~1	>2.5
Heat of Adsorption	kJ/mol CO_2	~10 kJ/mol	~10 kJ/mol
Desorption			
Pressure	bar	25	>25
Temperature	°C	400-450	<400
Equilibrium CO_2 Loading	g mol CO_2/kg	0.1-0.2	<0.1
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	See Figure 2	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90 / 95 / 25	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

Adsorption – The conditions of interest for adsorption are those that prevail at maximum sorbent loading.

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the sorbent. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Packing Density – Ratio of the active sorbent volume to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – See Figure 1.

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

technology advantages

- Hybrid concept process allows the simultaneous recovery of both H_2 and CO_2 at the low-temperature range of the WGS reaction.
- Improved WGS efficiency relative to conventional WGS system: enhanced reactor yield and selectivity via removal of both H_2 and CO_2 from the reacting phase.
- Significantly reduced catalyst weight usage requirements: reaction rate enhancement (over conventional WGS), due to the removal of both products, permits operation at lower W/F_{CO} (weight of catalyst/inlet molar flow rate of CO, kg-cat/(mol/hr)) thus resulting in significant catalyst savings.
- No syngas pretreatment required, given use of sour shift catalyst, and use of CMS membranes, which have proven to be stable in past/ongoing studies to all gas contaminants present in coal-derived syngas.
- Efficient H_2 production, and superior CO_2 recovery and purity: the synergy of the MR and AR units satisfies the CO_2 recovery/purity, carbon utilization (CO conversion), and hydrogen recovery/purity goals.

R&D challenges

- Heat management in reactors.
- Process integration with IGCC.
- Particulate matter needs to be controlled to reduce its potential impact on the reactor units.
- Scale-up and integration issues are a possibility given the large number of reactor modules needed to service a 550-MW_e plant.

status

To date, USC has completed the construction of a lab-scale MR-AR experimental system, prepared and characterized CMS membranes at anticipated process conditions, and prepared and characterized adsorbents at anticipated process conditions. These accomplishments have enabled testing on the individual MR and AR systems to begin, which is providing experimental data to be used in developing performance models for the reactor units and to conduct a preliminary technoeconomic analysis (TEA).

available reports/technical papers/presentations

Garshasbi, A., Chen, H., Cao, M., Karagöz, S., Ciora, R.J., Liu, P.K.T, Manousiouthakis, V.I., and Tsotsis, T.T., "*Membrane-based reactive separations for process intensification during power generation*", **Catalysis Today**, 2017, https://doi.org/10.1016/j.cattod.2017.10.039

"*A High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture*," presented by Vasilios Manousiouthakis, University of Southern California, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2017.

"*A High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture*," Theodore Tsotsis, University of Southern California, BP1 Review Presentation, August 2016.

"*A High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture*," presented by Theodore Tsotsis, University of Southern California, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

"*A High Efficiency, Ultra-Compact Process for Pre-Combustion CO_2 Capture*," project kick off meeting presentation, November 2015.

CARBON CAPTURE TECHNOLOGY SHEETS

R&D COLLABORATIONS

National Carbon Capture Center

primary project goals

The U.S. Department of Energy (DOE)/National Energy Technology Laboratory (NETL) and Southern Company operate the National Carbon Capture Center, a neutral research facility working to advance technologies to reduce greenhouse gas emissions from natural gas- and coal-based power plants. Located in Wilsonville, Alabama, the center offers a unique test bed for third-party technology evaluations of cost-effective carbon dioxide (CO_2) capture technologies—bridging the gap between laboratory research and large-scale demonstrations.

The National Carbon Capture Center offers exceptional benefit by providing technology developers with unique testing opportunities, and thereby accelerating the commercialization of low-cost, carbon capture processes. The center has surpassed 100,000 hours of technology testing for carbon capture innovators from the United States and six other countries. Through the testing of approximately 60 technologies, the center has directly participated in the reduction of carbon capture costs by one-third since 2011.

The National Carbon Capture Center will continue to meet its objective of evaluating advanced technologies, both domestic and international, to identify and resolve environmental, health and safety, operational, component, and system development issues, as well as to achieve scale-up and process enhancements in collaboration with the technology developers. Evaluations of DOE-sponsored projects, as well as projects from industry, universities, and other collaborative institutions, will provide a full spectrum of technologies for testing at the center.

technical content

The DOE Office of Fossil Energy's NETL, in cooperation with Southern Company, established the National Carbon Capture Center in 2009 to provide an independent, flexible and cost-efficient carbon capture technology testing facility with real industrial operating conditions as an alternative to onsite testing at power plants. In undertaking its mission, the center and its staff have been involved in a range of activities to develop the most promising technologies for future commercial deployment.

The National Carbon Capture Center provides test bays for simultaneous bench- and pilot-scale operation of advanced carbon capture technologies at commercially relevant process conditions. The site also houses two fully integrated processes for solvent evaluations: the Pilot-Scale Test Unit (PSTU) and bench-scale Slipstream Solvent Test Unit (SSTU). In addition to the flexible test site, the facility provides support for design, procurement, construction, installation, operation, data collection and analysis, and reporting in compliance with environmental and government regulations.

The types of technologies tested at the National Carbon Capture Center include enzymes, membranes, sorbents, solvents, hybrids, and associated systems. Testing with the PSTU and SSTU are conducted to provide extensive data on physical properties of solvents and perform solvent emission and degradation studies.

technology maturity:

Lab Scale/Bench Scale/Pilot Scale, Actual Flue Gas/Syngas

project focus:

Carbon Capture Testing Center

participant:

Southern Company

project number:

FE0022596

predecessor projects:

NT0000749

NETL Project Manager:

Andrew O'Palko
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principal investigator:

John Northington
Southern Company
jnorthin@southernco.com

partners:

American Electric Power, Duke Energy, Cloud Peak Energy, ClearPath, and EPRI

start date:

06.06.2014

percent complete:

80%

Center researchers have conducted numerous tests for the advancement of post-combustion carbon capture for pulverized coal or natural gas power plants, as well as gasification technologies and pre-combustion carbon capture. In mid-2017, after completing more than 30 projects in the gasification and pre-combustion carbon capture areas, the center concluded that work in response to changes in the scope of DOE-sponsored fossil energy research and development programs.

While the demand for post-combustion carbon capture options grows, new projects are planned as the National Carbon Capture Center continues to bring advanced technologies closer to the marketplace. In addition, the center has begun preparations for significant infrastructure additions to support carbon capture testing under natural gas-fired conditions.

Figure 1: Post-combustion test facilities at the National Carbon Capture Center

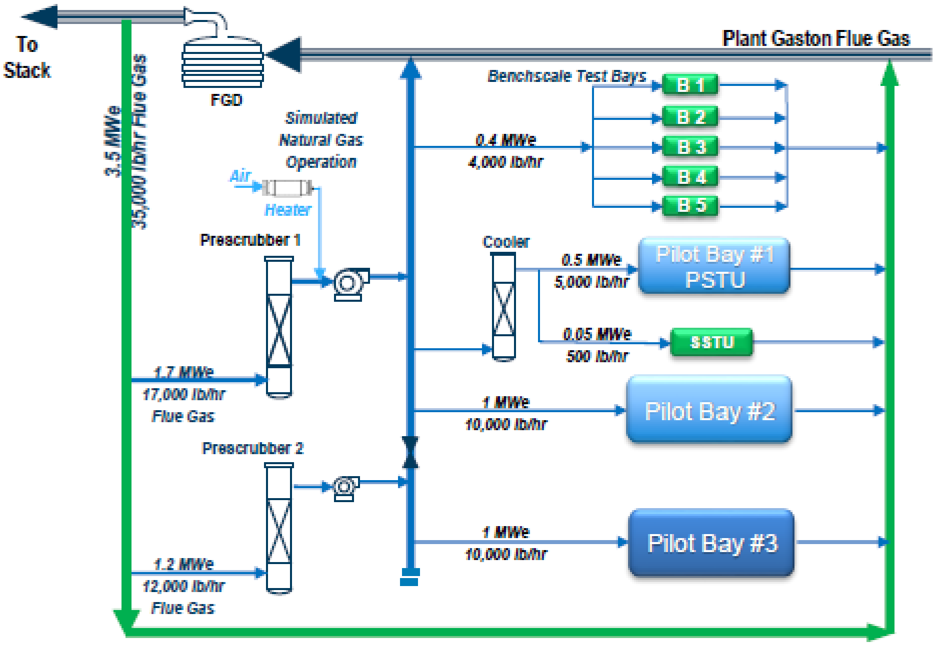

Figure 2: Diagram of post-combustion test facilities at the National Carbon Capture Center

technology advantages

The ability of the center's test facilities to support multiple tests simultaneously at various scales and to offer flexibility in capacity and process conditions will provide DOE with a wide range of data and information to accelerate the commercialization of carbon capture technologies and enable coal-based power plants to achieve near-zero emissions at a low cost. This project supports the DOE objective of 90 percent capture with 95 percent CO_2 purity at a cost of \$40/tonne of CO_2 captured in advanced coal-fired power plants by 2025, and a cost of less than \$40/tonne CO_2 captured by 2035.

In addition, planned expansion to increase carbon capture testing with flue gas from natural gas power plants will further identify breakthrough post-combustion carbon capture technologies, while supporting the nation's growing reliance on natural gas as a power generation resource.

R&D challenges

While pressure to reduce carbon emissions from fossil-fueled power generation continues to increase, adding carbon capture using conventional technologies would significantly increase the cost of electricity. To utilize the nation's abundant natural gas and coal resources in a carbon-constrained future, power generation must be equipped with advanced, cost-effective carbon capture technology. To address this challenge, the National Carbon Capture Center provides a highly skilled team, along with the infrastructure, real-world operating conditions and flexible testing needed for commercial application of carbon capture for natural gas- and coal-based power generation.

status

The post-combustion test facilities (Figure 1) utilize flue gas from Southern Company subsidiary Alabama Power's Plant Gaston Unit 5, a base-loaded, 880-megawatt supercritical pulverized coal boiler. The unit meets all environmental requirements utilizing state-of-the-art controls; thus, the flue gas extracted for testing is fully representative of commercial conditions. As shown in Figure 2 the site houses up to five bench-scale and two pilot-scale technology developer units, as well as the PSTU and SSTU for comprehensive solvent characterization. An air dilution system is also available for carbon capture testing under simulated natural gas flue gas conditions. Construction of a new system for generating natural gas flue gas for carbon capture testing is expected to begin in late 2018.

Post-combustion operation has consisted of more than 50,000 hours of testing enzymes, membranes, sorbents, solvents, hybrids and associated systems, which have included 31 developer projects and 56 test campaigns. More than 7,000 hours of testing have been conducted under simulated natural gas conditions. The PSTU has operated for over 15,000 hours in support of commercial developers and the DOE's Carbon Capture Simulation Initiative, with several solvents progressing to larger-scale testing at other facilities and commercial demonstration. The PSTU has demonstrated a near-100 percent mass and energy balance closure for many projects. The site has more than doubled its plant capacity from 12,000 to 30,000 lb/hr flue gas and has added systems (SSTU, air dilution, etc.), and enhanced instrumentation, sampling methods and analysis systems.

Accomplishments in the gasification and pre-combustion areas include over 50,000 hours of testing by technology developers. Scale-up and process intensification was achieved for several technologies. Gasification testing was conducted in both air -and oxygen-blown operation. Sensor testing has involved tunable diode laser sensors, particulate monitors, thermowells, and coal feeder instrumentation. Water-gas shift (WGS) catalyst tests showed that steam-to-carbon monoxide ratios can be reduced, relative to traditional recommendations, which in turn increases the net power output of an integrated gasification combined-cycle plant and reduces the cost of electricity with carbon capture. A number of advanced CO_2-absorbing chemical and physical solvents, various hydrogen- and CO_2-selective membranes, WGS catalysts, high-temperature mercury capture sorbents, and solid oxide fuel cells were tested. Performance data generated have been used to validate laboratory data under ideal conditions and allow for engineering design for scale-up.

available reports/technical papers/presentations

Advanced Technology Testing at the National Carbon Capture Center, Presented by John Carroll, Southern Company, 2017 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, Aug 2017.

2017 Update on Technology Testing at the National Carbon Capture Center, Presented by Barry Shirley, Southern Company, 42nd International Technical Conference on Clean Energy, Clearwater, FL, June 2017.

Advanced Technology Testing at the National Carbon Capture Center, Presented by Justin Anthony and John Carroll, Southern Company, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, Aug 2016.

Pre-Combustion Carbon Capture at the National Carbon Capture Center, Presented by John Socha, Southern Company, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

National Carbon Capture Center: Post-Combustion, Presented by Patrick Crossley, Southern Company, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

National Carbon Capture Center: Pre-Combustion CO_2 Capture, Presented by Tony Wu, Southern Company, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. (July 2014)

National Carbon Capture Center: Post-Combustion, Presented by John Wheeldon, National Carbon Capture Center, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Website: *https://www.nationalcarboncapturecenter.com/*

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COMPENDIUM OF CARBON CAPTURE TECHNOLOGY

APPENDIX:
Completed Projects

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX: POST-COMBUSTION SOLVENT TECHNOLOGIES

Slipstream Pilot-Scale Demonstration of a Novel Amine Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas

primary project goals

Linde is refining a post-combustion carbon dioxide (CO_2) capture technology incorporating BASF's novel amine-based solvent, with the main technical goal of significantly reducing solvent regeneration energy requirements over conventional monoethanolamine (MEA)-based amine capture. Technology development has been fostered by designing, building, and operating a 1-megawatt electric (MW_e) equivalent slipstream pilot plant at the National Carbon Capture Center (NCCC) to evaluate and optimize performance.

technical goals

- Capture at least 90 percent of CO_2 from coal-derived flue gas while demonstrating significant progress toward achievement of the DOE target of less than 35 percent increase in levelized cost of electricity (LCOE) (<$40/tonne CO_2).
- Produce a CO_2 product with a purity of at least 99.9 percent (dry basis) with low O_2 impurity levels that can meet the requirements for CO_2 utilization applications such as enhanced oil recovery (EOR).
- Successfully test the CO_2 capture technology at a capacity of >1.5 MW_e (>15,500 lb/hr flue gas).
- Validate amine emissions control methods.
- Successfully test regenerator at an operating pressure of 3.4 bar absolute (bara).
- Validate unique design features that lower overall capital and operating costs: (1) high-capacity packing, (2) gravity-driven interstage cooler, (3) blower positioned downstream of absorber, and (4) unique reboiler design providing low solvent holdup and fast dynamics.
- Reduce energy requirements ~27 percent relative to that of baseline MEA capture (2.65 GJ/tonne CO_2 vs. 3.61 GJ/tonne CO_2). Achieve specific regeneration energy of 2.65 GJ/tonne CO_2 (with additional heat integration concepts to further reduction to 2.3 GJ/tonne CO_2).
- Demonstrate solvent stability by showing a very low accumulation of heat stable salts (HSS) over the entire duration of parametric and long-term continuous testing (4,109 hours of testing with flue gas).
- Complete techno-economic assessment of a 550-MW_e power plant integrated with the Linde-BASF post-combustion capture plant incorporating BASF's OASE® blue aqueous amine-based solvent, and leveraging Linde's innovative process features to increase energy efficiency, improve emissions performance, and reduce plant footprint.

technology maturity:

Pilot-Scale, Actual Flue Gas (equivalent to 1 MW_e)

project focus:

Slipstream Novel Amine-Based Post-Combustion Process

participant:

Linde, LLC

project number:

FE0007453

predecessor projects:

N/A

NETL project manager:

Andrew Jones
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principal investigator:

Krish Krishnamurthy
Linde
krish.krishnamurthy@linde.com

partners:

BASF, Linde Engineering Dresden GmbH, Selas Fluid Processing Corporation, EPRI

start date:

12.01.2011

percent complete:

100%

technical content

Linde's technology uses BASF's OASE® blue solvent, which has been developed to address the key drawbacks in the large-scale application of MEA for flue gas carbon capture, including: (1) high specific energy for rich solvent regeneration/CO_2 recovery, (2) lack of solvent stability toward thermal and oxidative degradation, (3) increased solvent corrosiveness with increased CO_2 loading, and (4) lack of solvent tolerance to impurities from coal combustion products. The specific proprietary solvent was selected by: (1) screening approximately 400 chemical substances using vapor-liquid equilibrium measurements to determine approximate cyclic capacities, (2) laboratory measurements of the key thermodynamic and kinetic properties of the 70 screened candidates and their mixtures to identify approximately 15 targets, (3) testing of the targets to determine optimum circulation rate and specific energy consumption in a laboratory-scale mini-plant to identify the leading candidates, and (4) pilot testing of three candidates with real power plant flue gas to identify the optimum solvent for the flue gas application. CO_2 recovery from the solvent is carried out by using low-pressure steam, typically from the power plant steam cycle. Testing using a 0.45-MW_e pilot plant utilizing lignite-fired power plant flue gas has shown that the OASE® blue solvent is stable and little degradation was observed over 5,000 hours, whereas the reference MEA solvent started to degrade appreciably under same conditions after 2,000 hours.

Linde's post-combustion CO_2 capture process using BASF OASE® blue solvent technology has several distinct characteristics. Firstly, the direct-contact cooler, CO_2 absorber, and water wash are integrated into a single column with high-performance structured packing for increased capacity (smaller absorber diameter) and an advanced material of construction to minimize capital costs. Secondly, the absorber also has an inter-stage solvent cooler operating on gravity flow, eliminating the capital and operating expenses of a solvent pump. The flue gas blower is located downstream of the absorber to minimize its size (due to the reduced volume of flue gas handled by the blower). Further, the stripping column can be operated at higher pressures (up to 3.4 bara) than that of a MEA stripper, lowering compression costs. Finally, optional process heat integration allows steam, which is raised by heat exchange with flue gas upstream of the flue gas desulfurization (FGD) unit, to be used at an intermediate point in the desorber, and the use of back-pressure steam turbines allows the recovery of part of the energy of the intermediate-pressure (IP), low-pressure (LP) crossover steam.

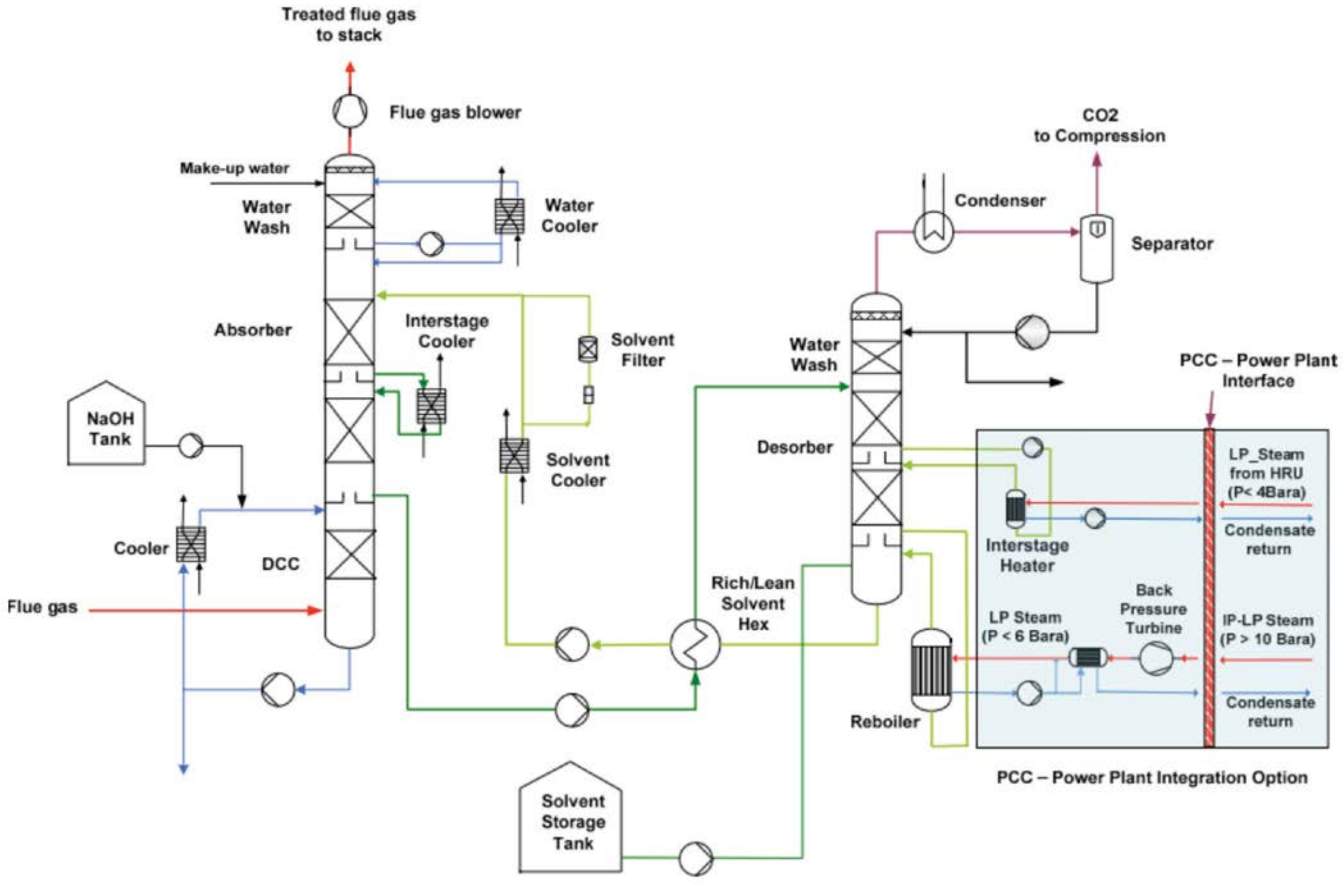


Figure 1: Linde-BASF post-combustion capture plant process concept

Techno-Economic Study Cases and Results

Three conceptual cases of pulverized coal combustion power plants with 90 percent CO_2 capture accomplished using the Linde-BASF technology were modeled to quantify expected costs and process efficiencies resulting from the improved solvent and the energy-saving process features noted above.

Linde-BASF LB1

The LB1 design employs high-performance structured packing, gravity-drain absorber intercooler, emission control system in absorber wash sections, blower downstream of absorber, novel stripper reboiler design, and elevated regeneration pressure (3.33 bar absolute). Modeling suggests this combination of features would result in a specific regeneration energy of 2.61 GJ/MT CO_2. The Wilsonville NCCC pilot plant is based on the LB1 design.

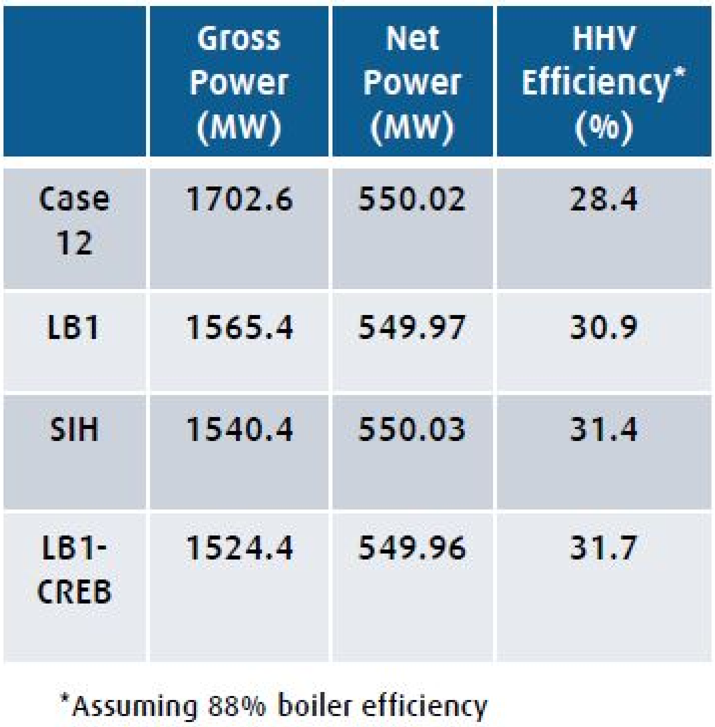
Linde-BASF SIH

The SIH design employs advanced stripper interstage heater design that improves heat recovery from CO_2-lean solution leaving stripper. Modeling suggests this combination of features would result in a specific regeneration energy of 2.30 GJ/MT CO_2.

Linde-BASF LB1-CREB

The LB1-CREB design employs novel cold CO_2-rich solution bypass exchanger and secondary CO_2-lean/CO_2-rich heat exchanger that optimizes heat recovery from hot CO_2 product vapor leaving stripper and hot CO_2-lean solution. Modeling suggests this combination of features would result in a specific regeneration energy of 2.10 GJ/MT CO_2.

Figure 2 show the overall power plant efficiencies for these cases, indicating incremental improvements over the baseline power plant case using the Linde technology, compared to conventional amine-based CO_2 capture (DOE NETL Bituminous Baseline Case 12).



	Gross Power (MW)	Net Power (MW)	HHV Efficiency* (%)
Case 12	1702.6	550.02	28.4
LB1	1565.4	549.97	30.9
SIH	1540.4	550.03	31.4
LB1-CREB	1524.4	549.96	31.7

*Assuming 88% boiler efficiency

Figure 2: Comparison of PCC plant case efficiencies from techno-economic analysis

The cost of CO_2 captured was estimated to be as follows:

DOE NETL Case 12 (baseline)	\$56.49/MT CO_2
Linde-BASF LB1	\$41.85/MT CO_2
Linde-BASF SIH	\$40.66/MT CO_2
Linde-BASF LB1-CREB	\$39.90/MT CO_2

One major reason the cost of CO_2 captured is significantly reduced in moving from Case 12 to LB1 is due to the higher inlet CO_2 gas pressure for CO_2 compression (48 psia for LB1 vs. 24 psia for Case 12) afforded by elevated regenerator pressure, which reduces downstream compression energy and capital costs. Additionally, as power plant efficiency increases, the flow rate of CO_2 produced decreases due to a reduced coal flow rate needed for the same power production. This leads to increasingly smaller incremental reductions in cost of CO_2 captured for each Linde-BASF process improvement.

Figure 3 shows the cost breakdowns for the cases relative to the baseline DOE NETL Case 12.

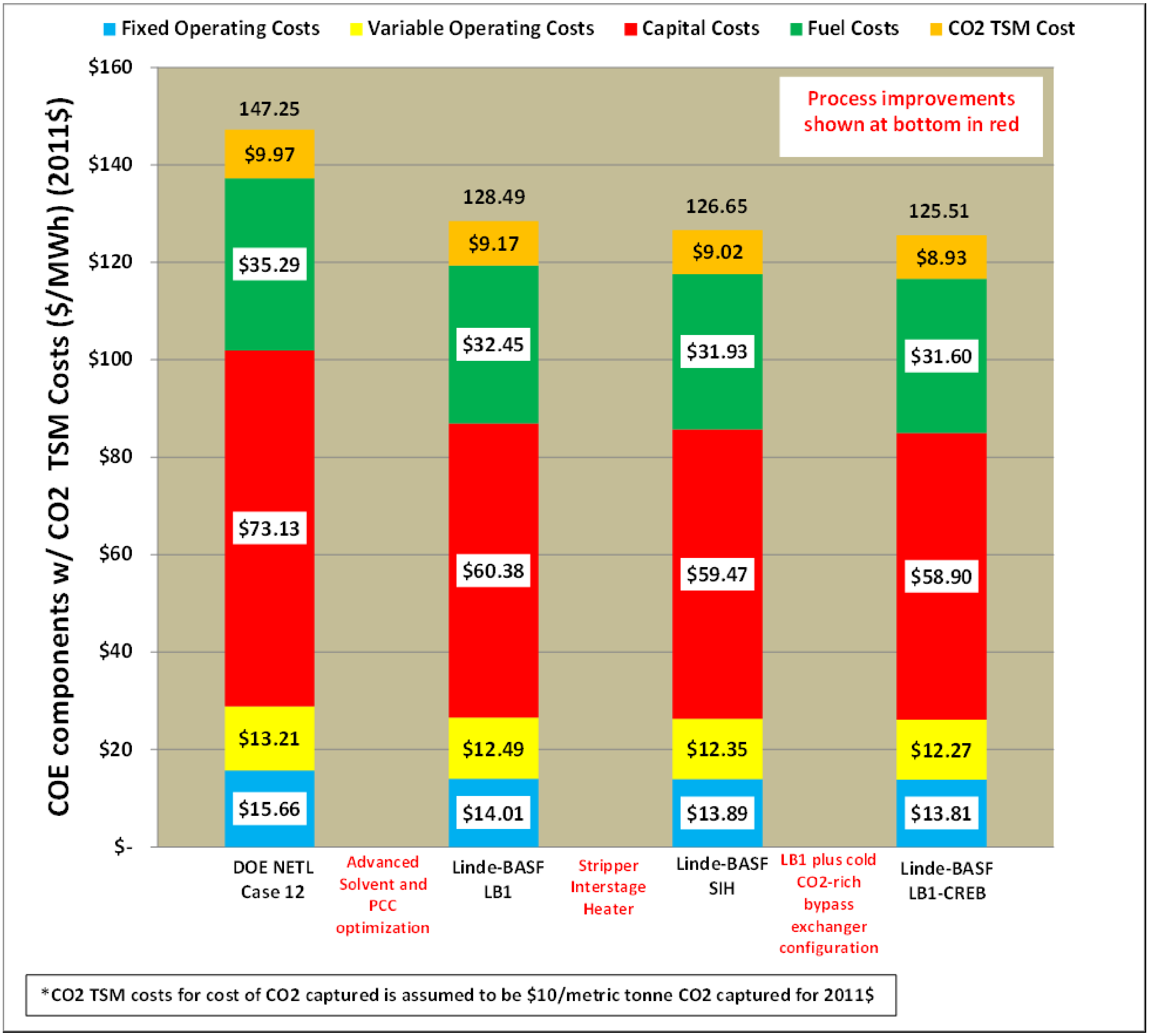


Figure 3: Cost of electricity comparisons from techno-economic analysis

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	proprietary	—
Normal Boiling Point	°C	proprietary	—
Normal Freezing Point	°C	proprietary	—
Vapor Pressure @ 15 °C	bar	proprietary	—
Manufacturing Cost for Solvent	$/kg	proprietary	—
Working Solution			
Concentration	kg/kg	proprietary	—
Specific Gravity (15 °C/15 °C)	-	proprietary	—
Specific Heat Capacity @ STP	kJ/kg-K	proprietary	—
Viscosity @ STP	cP	proprietary	—
Absorption			
Pressure	bar	≈1 atm	≈1 atm
Temperature	°C	30–70	30–60
Equilibrium CO_2 Loading	mol/mol	proprietary	—
Heat of Absorption	kJ/mol CO_2	proprietary	—
Solution Viscosity	cP	proprietary	—
Desorption			
Pressure	bar	1.6–2.5	1.6–3.4
Temperature	°C	124–132	124–140
Equilibrium CO_2 Loading	mol/mol	proprietary	—
Heat of Desorption	kJ/mol CO_2	proprietary	—
Proposed Module Design (for 550-MW_e PCC Plant)		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	LB1 Case: 2,718,270	SIH Case: 2,674,784
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99.98% (dry basis), 3.4 bara	90%, 99.98% (dry), 3.4 bara
Absorber Pressure Drop	bar	0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	proprietary	

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent

(e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

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

Solvent Contaminant Resistance – The OASE blue® solvent is highly resistant against many contaminants in the flue gas as shown in both parametric and long-term continuous tests (see EPRI report ["BASF-Linde Post Combustion Carbon Capture…"] for additional information).

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

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

Solvent Make-Up Requirements – The OASE blue® solvent make-up rate is determined by the sum of the amine losses in the treated gas leaving the absorber column and the rate of solvent degradation during operation over time. Low make-up rates were observed during long-term testing well below an operationally manageable threshold (see Final Testing Report ["Slipstream Pilot Plant Demonstration…"] on page 22). During the parametric testing, higher amine losses were observed and this was attributed to the lack of baghouse filter in the power plant resulting in a high density of fine aerosol particles in the flue gas that caused carryover of amine with the CO_2-depleted gas.

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

Process Design Concept – See Figure 1 above.

technology advantages

- Significant reduction in regeneration steam consumption (24–40 percent lower), electrical power (14–26 percent lower), and cooling water duty (26–43 percent lower) compared to a reference MEA plant.
- Higher plant efficiency due to a combination of advanced solvent and process improvements, including integrated absorber, down-stream gas blower, higher desorber pressure, and inter-stage gravity-flow cooler.
- Aggregate capital, O&M, fuel, and other cost reductions result in lower COE (15 percent less than the MEA-based DOE NETL reference case).
- The Linde-BASF technology is readily scalable to large capacities with a single-train system, offering the potential to further reduce costs by utilizing economies of scale.
- BASF is a producer of the solvent in addition to being the technology owner, thereby enabling application at scale by avoiding issues related to solvent manufacturing for large-scale commercial plants.

R&D challenges

- Proving the process enhancements at the 1-MW$_e$ plant and at larger scale.
- Validating the basis for scale up of the advanced process features and the large, single-train capability.

status

The Linde-BASF technology has been selected by DOE for Phase 1 of a large pilot plant demonstration opportunity. Linde has teamed with the University of Illinois in proposing Phase 2 work, identifying the Abbott coal fired power plant as the intended host site for the large pilot, which if selected and executed is expected to advance the technology to near-commercial readiness.

available reports/technical papers/presentations

“*Slipstream Pilot Plant Demonstration of an Amine-Based Post-Combustion Capture Technology for CO$_2$ Capture from Coal-Fired Power Plant Flue Gas*,” Final Report, February 2017.

Final Techno-Economic Analysis of 550 MW$_e$ Supercritical PC Power Plant CO$_2$ Capture with Linde-BASF Advanced PCC Technology,” January 2017.

“*Slipstream Pilot Plant Demonstration of a Amine-Based Post-Combustion Capture Technology for CO$_2$ Capture from Coal-Fired Power Plant Flue Gas*,” Final Project Review Meeting Presentation by Krish R. Krishnamurthy & Devin Bostick, Linde LLC, Pittsburgh, PA, January 2017.

“*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO$_2$ Capture from Coal-Fired Power Plant Flue Gas*,” presented by Krish R. Krishnamurthy, Linde LLC, 2016 NETL CO$_2$ Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

“*Development and Scale-Up of an Advanced Aqueous Amine-Based Post-Combustion CO$_2$ Capture Utilizing BASF's OASE® Blue Technology*,” presented by Krish R. Krishnamurthy, Linde LLC, 2016 Carbon Capture, Utilization & Storage Conference, Tysons, VA, June 2016.

“*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO$_2$ Capture from Coal-Fired Power Plant Flue Gas*, presented by Krish R. Krishnamurthy, Linde LLC, 2015 CO$_2$ Capture Technology Meeting, Pittsburgh, PA, June 2015.

“*Pilot plant demonstration of an advanced amine-based post-combustion capture technology for CO$_2$ capture from power plant flue gases*,” presentation at the 12th Greenhouse Gas Control Technologies (GHGT-12) Conference, October 2014.

Krishnamurthy, K., “*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO$_2$ Capture from Coal-Fired Power Plant Flue Gas*,” 2014 CO$_2$ Capture Technology Meeting, Pittsburgh, PA, July 2014.

Krishnamurthy, K., "*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," 2013 CO_2 Capture Technology Meeting, Pittsburgh, PA.

"*Techno-Economic Analysis of 550 MWe Subcritical PC Power Plant with CO_2 Capture*," Topical Report of initial techno-economic analysis, May 2012.

"*Techno-Economic Analysis of 550 MWe Subcritical PC Power Plant with CO_2 Capture*," presentation given at NETL by S. Jovanovic & K. Krishnamurthy, Pittsburgh, PA, May 2012.

"*Slipstream Pilot-Scale Demonstration of a Novel Amine-Based Post-Combustion Process Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," Project Kick-Off Meeting Presentation, November 2011.

"*Slipstream Pilot Plant Demo of an Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas*," presented by Krish R. Krishnamurthy, Linde LLC, 2011 Fall Technical Subcommittee Meeting, Pittsburgh, PA, October 31, 2011.

Krishnamurthy, K.R., "*Slipstream Pilot Plant Demo of an Amine-Based Post-Combustion Capture Technology for CO2 Capture from a Coal-Fired Power Plant Flue Gas*," presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA.

"BASF-Linde Post Combustion Carbon Capture Pilot Plant at the National Carbon Capture Center, 2016 Test Campaign Results, EPRI, February 2017.

"Slipstream Pilot Plant Demonstration of an Amine-Based Post-Combustion Capture Technology for CO_2 Capture from Coal-Fired Power Plant Flue Gas," Final Testing Report to NCCC, February 2017.

Improvement of GE Power's Chilled Ammonia Process Large Pilot with the Use of Membrane Technology

primary project goals

GE Power developed several concepts for improving their existing solvent-based Chilled Ammonia Process (CAP) for capturing carbon dioxide (CO_2) from coal-fired power plants by incorporating commercially available membrane technologies to reduce energy and capital costs. Three concepts were investigated at bench-scale to determine feasibility of testing with a large pilot CO_2 validation facility at Technology Centre Mongstad (TCM).

technical goals

- Implement several improvement concepts utilizing membrane technology at an existing CAP large-scale pilot plant to lower the overall cost of CAP CO_2 capture technology.
- Leverage CAP experience in collaboration with TCM, the host site, which operates an existing CAP large pilot facility (~15 MW_e equivalent) in Norway.
- Complete a techno-economic assessment (TEA) and technology gap analysis of membrane concepts for the CAP at a full-scale 550-MW power generation facility.
- Develop key project risks.

technical content

GE Power teamed with ElectroSep™, General Electric Power and Water, and Georgia Institute of Technology, to investigate concepts for improving an existing solvent-based CAP pilot plant using liquid-liquid bipolar and reverse osmosis membrane systems to reduce energy and capital costs. GE Power's CAP uses an ammonia-based solvent for the absorption of CO_2 from flue gas at low temperature. Ammonia is an energy-efficient reagent that is stable, not susceptible to contaminants in flue gas, and is replenished in low consumption rates. The CAP has been tested at large pilot scale (20 MW_e) and is prepared for large scale demonstration in 2020. The main features of the CAP technology are:

- The flue gas leaving the CAP has no solvent degradation byproducts and the solvent can tolerate higher amounts of residual acid gases (SO_x, NO_x, etc.) in the incoming flue gas.
- The CAP technology can utilize cooler ambient conditions to lower the energy consumption of the process.
- The reactions within the CO_2 absorption process are reversible with regeneration of the solvent at elevated pressure allowing for reduced CO_2 compression.
- The CAP reagent is anhydrous ammonia—a low cost, commodity chemical that is readily available.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Chilled Ammonia Process Improvements

participant:

GE Power

project number:

FE0026589

predecessor projects:

N/A

NETL project manager:

Steven Mascaro
steven.mascaro@netl.doe.gov

principal investigator:

David Muraskin
GE Power
david.j.muraskin@power.alstom.com

partners:

ElectroSep™; General Electric Power and Water; Georgia Institute of Technology; Technology Centre Mongstad

start date:

10.01.2015

percent complete:

100%

- The byproduct is an aqueous ammonium sulfate stream that can be used commercially as fertilizer.

Three concepts for improving the CAP CO_2 capture technology using commercially available membrane systems were previously investigated at the bench-scale level for eliminating CAP liquid ammonium sulfate effluent stream and reducing CAP energy demand. GE Power plans to modify the CAP large pilot facility at the TCM in Norway for the implementation of these membrane systems once they are validated at bench-scale.

The first concept involves eliminating ammonium sulfate byproduct and reducing the consumption of ammonia and sulfuric acid reagents. In the CAP plant, as flue gas enters the conditioning section, residual SO_x in the direct contact column (DCC) reacts with ammonia to form ammonium sulfate byproduct. In the direct contact heating (DCH) column, residual ammonia in the treated flue gas from the absorption/water wash section is reduced to form ammonium sulfate using a sulfuric acid rinse. The ammonium sulfate byproduct generated in both unit operations is then transported as a concentrated liquid solution or processed on-site using crystallization technology to form a fertilizer, which requires high operating and capital costs. In this concept, a bipolar membrane electrodialysis (ED) unit converts the byproduct to sulfuric acid and anhydrous ammonia (process reagents). Figure 1 illustrates the ion exchange process through a bipolar membrane ED unit and Figure 2 shows an ED unit implemented into the CAP plant. Through electrodialysis, ions are transported through cation and anion exchange membranes from one solution to another under the influence of an electrical driving force. The ammonium sulfate bleed stream is dissociated into acidic and basic ionic species. Bipolar membranes consisting of an anion exchange membrane and a cation exchange membrane bonded together dissociate water into hydrogen and hydroxyl ions for combining with the ionic species, forming sulfuric acid and ammonia. Eliminating the ammonium sulfate byproduct stream is beneficial for power plants that are not able to use the byproduct as commercial fertilizer and reducing process reagent consumption solves the problems of on-site storage for substantial amounts of reagents.

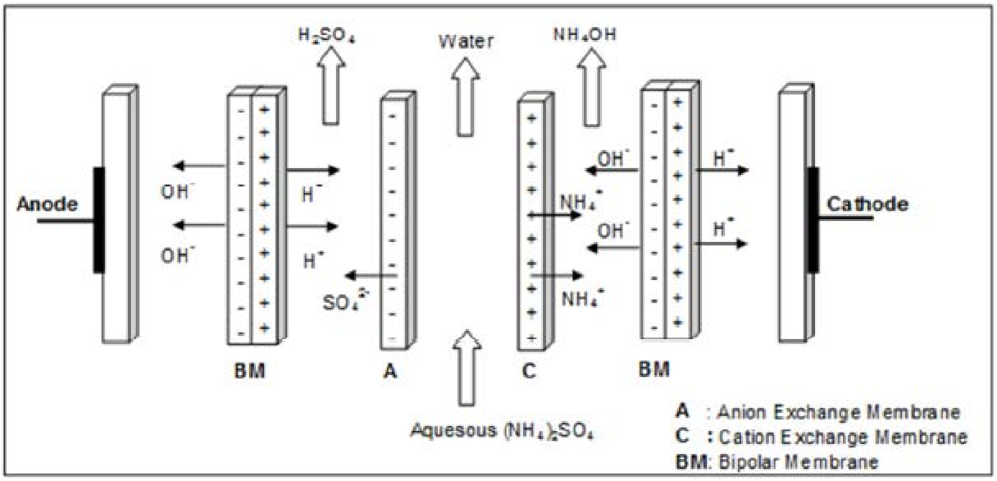


Figure 1: Bipolar membrane electrodialysis

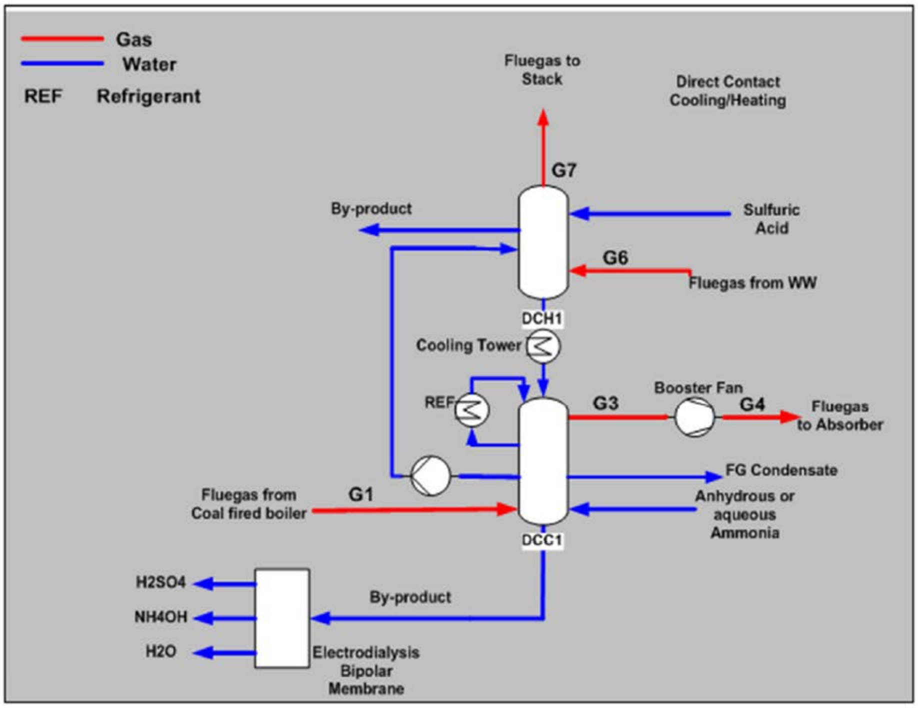


Figure 2: Bipolar membrane electrodialysis for byproduct elimination and reagent recovery

The second concept involves reducing the ammonia stripper energy. In the CAP plant, ammonia in the flue gas leaving the CO_2 absorber is first captured in a water wash vessel and then regenerated in an ammonia recovery stripper by heating the rich solution with saturated steam. In this concept, as shown in Figure 3, a reverse osmosis membrane separator is used to increase the ammonia concentration in the feed to the ammonia stripper, resulting in reduced feed flow rate, which minimizes stripper duty. As a result, stripper and heat exchanger sizes are reduced as well as steam energy demand. Also, the improvement in stripper performance potentially allows the CO_2 absorber to operate at a higher temperature resulting in lower refrigeration duty.

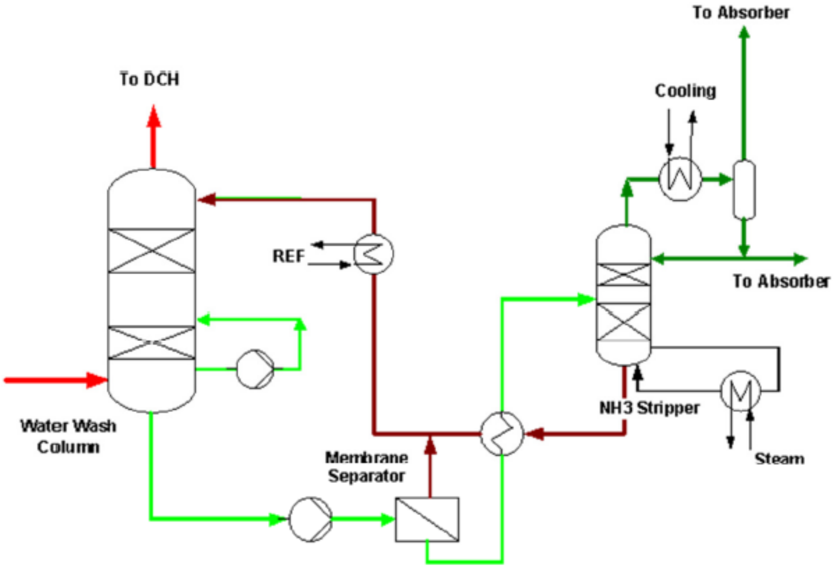


Figure 3: Reverse osmosis membrane for ammonia stripper energy reduction

The third concept involves reducing the CO_2 regeneration energy by recovering absorbent. In the CAP plant, a large amount of circulation flow between the CO_2 absorber and the CO_2 regenerator is required due to low CO_2 loading, which leads to high capital and operating costs of the plant. In this concept, as shown in Figure 4, a reverse osmosis membrane separator is used to recover the water and some portion of the ionic absorbent that passes through the CO_2 wash column after leaving the regenerator. The wash water with recovered ammonium is sent to the absorber for CO_2 capture, while the remaining carbon-containing ionic species that does not permeate through the membranes is returned to the CO_2 wash section to capture ammonia. This process allows for operation of the regenerator at lower pressure and higher ammonia emissions. In the current plant, the CO_2 is regenerated at high pressure, which reduces the ammonia content in the CO_2 product and minimizes the downstream compressor duty. However, this requires relatively high-pressure steam, which affects the power production capability of the power plant. Operating the regenerator at lower pressure allows for use of lower quality steam, which reduces the energy losses associated with high pressure steam utilization, but also increases the amount of ammonia emission from the CO_2 regenerator. This excess ammonia is captured in the CO_2 wash section and then processed in the reverse osmosis membrane system as described above.

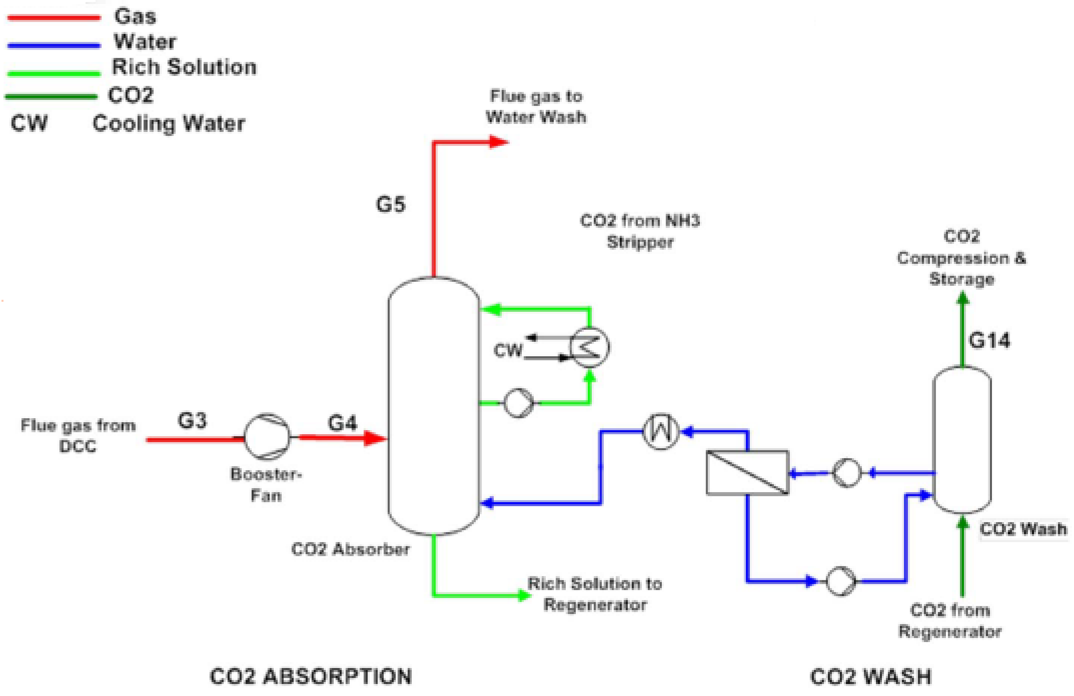


Figure 4: Reverse osmosis membrane for increased ammonium recovery from CO_2 wash

Each of these membrane systems were tested previously at laboratory-scale and bench-scale using process streams consistent with those within the CAP plant. A bench-scale electrodialysis test apparatus consisting of ion specific membranes with a total surface area of 0.152 m^2 was used to assess the first concept at ElectroSep. A sulfuric acid product tank was used to accumulate the sulfuric acid produced by the electrodialysis stack and confirmed an increase in sulfuric acid concentration, indicating that the initial membrane selection is feasible. Through testing of the commercial reverse osmosis membranes at Georgia Institute of Technology, it was determined that a higher osmotic pressure is needed; however, higher pressure membranes are not robust and are associated with high operating and capital costs. An alternate concept was developed utilizing a low-pressure reverse osmosis membrane design that is expected to improve costs by eliminating the stripper and steam consumption. The development program was revised to allow for further testing of this new concept at bench-scale and a decision was made to not proceed with modifications to the large pilot plant.

Definitions:

Membrane Geometry **–** Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux **–** For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU **–** Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement **–** Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

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

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

technology advantages

- Uses ammonia—a low-cost, stable, readily available chemical—as a reagent.
- Uses commercially available membranes that can be scaled up using conventional methods.
- The incorporation of bipolar membrane technology eliminates the CAP byproduct stream (ammonium sulfate) and associated disposal/processing costs as well as recovers reagents (ammonia and sulfuric acid).
- The incorporation of reverse osmosis membrane technology minimizes the CAP regenerator steam consumption and reduces the stripper and associated heat exchanger sizes by ~50 percent.

R&D challenges

- Utilizing lower pressure membranes for reverse osmosis concept.

status

Bipolar membrane electrodialysis for the CAP is prepared for large pilot-scale testing based on the successful completion of bench-scale testing at ElectroSep, Inc. Bench-scale testing of the reverse osmosis concept determined that the low-pressure membrane rejection rate is insufficient, and therefore, modification of the initial process scheme is required along with bench-scale testing to validate the new process before proceeding to large pilot-scale testing. A preliminary techno-economic analysis was completed based on the bench-scale tests, showing an improvement in power plant steam cycle efficiency and a small reduction in cost of electricity (COE) from the DOE baseline case. The COE improvement was not sufficient to justify further development of the original reverse osmosis concept. Bench-scale testing along with an economic assessment for the alternate concept using low pressure reverse osmosis membranes is required to allow consideration of the membrane technology for CAP improvements.

available reports/technical papers/presentations

Muraskin, David, "Improvement of GE Power's Chilled Ammonia Process using Membrane Technology," Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/D-Muraskin-GE-Alstom-Chilled-Ammonia-Large-Pilot.pdf*

"Improvement of Alstom's Chilled Ammonia Process using Membrane Technology," Project kickoff meeting presentation, October 28, 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026589-Kickoff-Presentation.pdf*

Novel Flow Sheet for Low Energy CO_2 Capture Enabled by Biocatalyst Delivery System

primary project goals

Akermin developed an advanced biocatalyst enabled solvent system for lower cost carbon dioxide (CO_2) capture. The project focused on the development of encapsulated carbonic anhydrase (CA) biocatalyst technology. The project combines an improved biocatalyst delivery system (BDS), a new solvent, and process improvements tested in a modified bench-scale system incorporating these new advancements.

technical goals

- Demonstrate a second-generation biocatalyst that has lower production costs, is more readily scaled up, and enables on-stream catalyst replacement.
- Optimize production of the BDS.
- Demonstrate consistent long-term performance in lab-scale closed loop reactor.
- Design and modify bench-scale test unit to incorporate the next-generation BDS and to accommodate the novel process improvements.
- Optimize the process flow sheet to utilize low grade steam for solution regeneration and to achieve parasitic power less than 220-kWh/t CO_2.
- Evaluate performance of advanced AKM24 solvent.
- Complete field testing with the bench-scale test unit at the National Carbon Capture Center (NCCC) using coal-derived flue gas.
- Demonstrate on-stream biocatalyst maintenance.
- Perform techno-economic assessment and engineering study to demonstrate viability of the new technology, targeting at least 30 percent reduction in cost of CO_2 capture.

technical content

Akermin is developing a low-energy, enzyme-catalyzed solvent system for CO_2 capture and testing in a bench-scale unit to continue advancing the technology that was previously developed under project DE-FE0004228. The novel system combines the next-generation BDS and a non-volatile salt solution (AKM24 "solvent"). Updates to an existing 500 standard liters per minute (SLPM) bench-scale test unit incorporated the process and solvent advancements. The process scheme is shown in Figure 1.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Carbonic Anhydrase Catalyzed Advanced Carbonate and Non-Volatile Salt Solution ("Solvents")

participant:

Akermin, Inc.

project number:

FE0012862

predecessor projects:

FE0004228

NETL project manager:

Andrew Jones
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principal investigator:

Alex Zaks
Akermin, Inc.
zaks@akermin.com

partners:

Worley Parsons; Novozymes

start date:

10.01.2013

percent complete:

100%

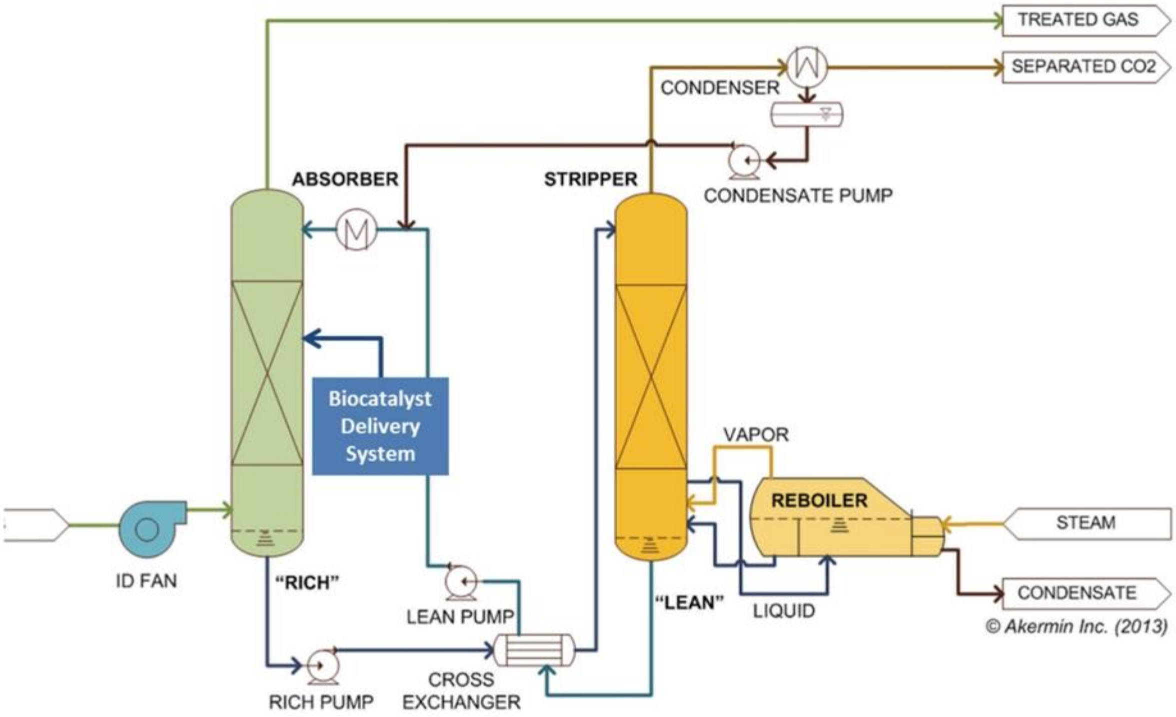

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Figure 1: Akermin's CO_2 capture process

The technology uses a next-generation BDS, in which, the CA enzyme is immobilized within proprietary polymeric microparticles. CA accelerates hydration of CO_2 to bicarbonate to enhance the performance of the solvent for CO_2 capture. The microparticles have high surface area to enable higher mass transfer rates and provide a protective environment for the enzymes against inactivation by temperature, solvent and shear forces. The catalyst can be delivered by two potential concepts: (1) by recirculation in the absorber only, which requires particle separation, or (2) by continuous circulation in the absorber and stripper, which would not require particle separation, but would require lower temperature stripping to avoid denaturation of the enzyme-based biocatalyst. By incorporating the non-volatile salt solution that has significantly lower regeneration energy combined with using lower temperature steam from the power plant, the result is significant reductions in parasitic power requirements and also lower capital costs for the power plant and integrated CO_2 capture system. Since AKM24 operates with higher CO_2 loading capacity, lower circulation rates can be realized. The modified bench-unit was operated with actual coal-derived flue gas at the NCCC to evaluate performance and validate process modeling performance estimates.

The solvent and process parameters are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	not disclosed	not disclosed
Normal Boiling Point	°C	107	107
Normal Freezing Point	°C	-8	-8
Vapor Pressure @ 15 °C	bar	non-volatile	non-volatile
Manufacturing Cost for Solvent	$/kg	not disclosed	not disclosed
Working Solution			
Concentration	kg/kg	not disclosed	not disclosed
Specific Gravity (15 °C/15 °C)	—	1.18	1.18
Specific Heat Capacity @ STP	kJ/kg-K	3.33	3.33
Viscosity @ STP	cP	3.98	33.98
Absorption			
Pressure	bar	1.07	1.07
Temperature	°C	50	50
Equilibrium CO_2 Loading	mol/mol	0.80	0.80
Heat of Absorption	kJ/mol CO_2	52	52
Solution Viscosity	cP	2.01	2.01
Desorption			
Pressure	bar	1.07	1.07
Temperature	°C	107	107
Equilibrium CO_2 Loading	mol/mol	0.40	0.40
Heat of Desorption	kJ/mol CO_2	70	70
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	40	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 >99 1.05	
Absorber Pressure Drop	bar	<0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

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

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

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120 °C). Measured data at other conditions are preferable to estimated data.

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Chemical/Physical Solvent Mechanism – The reaction of CO_2 with water (H_2O) in the presence of CA and base (B) is as follows:

$$H_2O + CO_2 \text{ <--> } HCO_3^- + H \qquad \text{(slow without catalyst)}$$

$$H^+ + B \text{ <--> } BH^+ \qquad \text{(fast)}$$

$$H_2O + CO_2 + B \text{ <--> } BH^+ + HCO_3^- \qquad \text{(overall reaction)}$$

The presence of CA increases the rate of conversion of CO_2 to bicarbonate (improving the slow step above), but does not affect the equilibrium properties of the solvent. The rate of hydration of CO_2 (i.e., the reaction with H_2O) in the absence of the enzyme is exceedingly slow; however, the enzyme provides dramatic acceleration of the reaction (kcat ≈1/microsecond) and is limited only by diffusion.

Solvent Contaminant Resistance – Studies with K_2CO_3 and CA in solution indicate that the enzyme is not inhibited by sulfate, sulfite, nitrite, nitrate, or chloride ions in solution at levels expected for coal flue gas. Divalent metal ions (e.g., mercury [Hg^{2+}], lead [Pb^{2+}]) inhibit the activity of soluble CA, because the active site in the enzyme itself contains a divalent metal ion (mainly zinc). However, the low solubility of their hydroxide and carbonate salts in carbonate solutions and the stabilizing role of the immobilization system alleviate some of the decrease in CA activity.

Solvent Foaming Tendency – The presence of soluble enzyme can contribute to foaming, especially in the stripper, whereas the tendency to foam is mitigated by using immobilized enzyme. Previous work has used small quantities of anti-foam.

Flue Gas Pretreatment Requirements – Standard sulfur oxides (SO_x), nitrogen oxides (NO_x), and mercury control systems that meet local air emission requirements will be sufficient.

Solvent Make-Up Requirements – The capture of acid gases, such as sulfur dioxide (SO_2) and nitrogen dioxide (NO_2), will reduce carrying capacity over time. Initial tests indicated the loss of capacity to be on the order of 2 percent per year or less. K_2CO_3 is non-volatile and has excellent oxidative stability (an inorganic salt solution). Akermin's new solvent (AKM24) is based on a non-volatile salt solution; therefore, it is expected to have similar benefits.

Waste Streams Generated – In the first-generation technology, the deactivated packing would need to be replaced (recycled) to maintain CA activity on an ongoing basis. Notably, the second-generation BDS provides for on-stream biocatalyst maintenance as a microparticle, which reduces the volume and cost of solid waste management.

Process Design Concept – Figure 1 presents the basic process flow sheet.

technology advantages

- Advanced solvent in the presence of Akermin's BDS has high CO_2 absorption rates and higher capacity relative to first generation. It also has significantly lower regeneration energy compared to amine-based solvents.
- Solvent is non-volatile, oxidative stable, and environmentally benign.
- Advanced solvent uses lower-grade steam with lower regeneration temperatures than amine solvents; resulting in lower auxiliary power requirements, more power generated, lower unit capital costs, and lower CO_2 capture costs.

R&D challenges

- Scaling up and manufacturing of the immobilized biocatalyst batches that consistently achieve the critical performance metrics (cost, efficiency, ease of integration with BDS, etc.).
- Determining the optimal catalyst recirculation option.
- Demonstrating an effective BDS in the lab- and bench-scale test units to achieve stable and consistent long-term performance.

status

Akermin has produced and tested multiple biocatalyst batches on the kilogram scale. They have demonstrated an average 90 percent CO_2 capture over extended testing in the lab-scale closed loop reactor. An enzyme kinetic model was built in Aspen and validated with test data. The 500 SLPM bench unit located at the NCCC was modified and commissioned in June 2016, and testing was initiated. The project ended in July 2016, prior to the planned September 30, 2016, end date, due to unexpected circumstances.

available reports/technical papers/presentations

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http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/J-Reardon-Akermin-Enzyme-Catalyzed-Solvent-for-CO2.pdf

Reardon, J., et al., "Enzyme-Catalyzed Process for Low-Cost CO_2 Separation and Capture," presented at the 2012 MEGA Conference, Baltimore, MD, August, 2012.
http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/enzyme-catalyzed-process-aug2012.pdf.

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http://www.netl.doe.gov/File%20Library/research/coal/cross-cutting%20research/advanced%20materials/advanced-low-energy-enzyme-catalyzed-solvent-july2012.pdf.

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http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/23Aug11-Zaks-Akermin-Enzyme-Catalyzed-Solvent.pdf.

Gifford, P., "Advanced Low Energy Enzyme Catalyzed Solvent for CO_2 Capture," Presented at the 2010 NETL Annual CO_2 Capture Technology Meeting, September, 2010, Pittsburgh, PA.
http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/Paul-Gifford---Akermin-Inc.pdf.

Carbon Absorber Retrofit Equipment (CARE)

primary project goals

Neumann Systems Group, Inc. (NSG) has designed, constructed, and tested a 0.5-MW scale patented NeuStream® absorber at the Colorado Springs Utilities (CSU) Martin Drake #7 power plant. The absorber employs nozzle technology proven during a previously completed 20-MW NeuStream-S flue gas desulfurization (FGD) pilot project, as well as a 6-m piperazine (PZ) solvent, which is an efficient solvent for capturing carbon dioxide (CO_2). The goal of the project is to show that the absorber system is capable of significantly reducing the process equipment footprint and the CO_2 capture system cost.

Due to an unrelated turbine fire at the Martin Drake plant in May of 2014, the project scope was revised to relocate the system to NSG's facility, where a natural gas steam boiler will provide the flue gas and stripping heat. Stripped CO_2 was recycled to increase the incoming CO_2 concentration to ≈13 percent to simulate flue gas from a coal-fired boiler.

technical goals

- Design a 0.5-MW_e slipstream CO_2 scrubber to minimize parasitic power through efficient design.
- Demonstrate a 2-month steady-state operation with a three-stage absorber and a multistage stripper.
- Demonstrate 90 percent CO_2 capture efficiency utilizing the best available solvent.
- Show unit traceability/scalability to commercial scale.

technical content

The NSG Carbon Absorber Retrofit Equipment (CARE) project includes design, construction, and testing of a 0.5-MW NeuStream® CO_2 capture system, based on NSG's patented flat jet, modular absorber technology. The NeuStream® absorber uses a proven technology with an array of flat jets and an advanced solvent (6 m PZ) to capture CO_2. The CARE absorber design is based on modeling (computational fluid dynamics [CFD] and Aspen Plus™) and analysis of carbon capture data from slipstream experiments, where experimental specific surface areas of 440 m^2/m^3 have been achieved. The CARE system slipstream test includes compact NeuStream® modules, as well as sulfur oxide (SO_x) scrubbing and amine washing equipment that also utilizes the NeuStream® flat jet technology.

The SO_x scrubbing equipment uses compact modular NeuStream® technology and can be adjusted to residual SO_x level (1–30 parts per million [ppm]) prior to CO_2 capture. The CARE project employs slipstream nitrogen oxide (NO_x) removal; a four-stage, 0.5-MW_e NeuStream® high-performance absorber unit for scrubbing; a novel stripper design that reduces heat waste; and a flue gas heat-recovery method to offset a portion of steam usage.

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

Carbon Absorber Retrofit Equipment

participant:

Nuemann Systems Group

project number:

FE0007528

predecessor projects:

N/A

NETL project manager:

Andy O'Palko
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principal investigator:

Eric Klein
Neumann Systems Group
erick@neumannsystemsgroup.com

partners:

Colorado Springs Utilities, UNDEERC, Industrial Constructor Managers, University of Texas

start date:

01.02.2012

percent complete:

100%

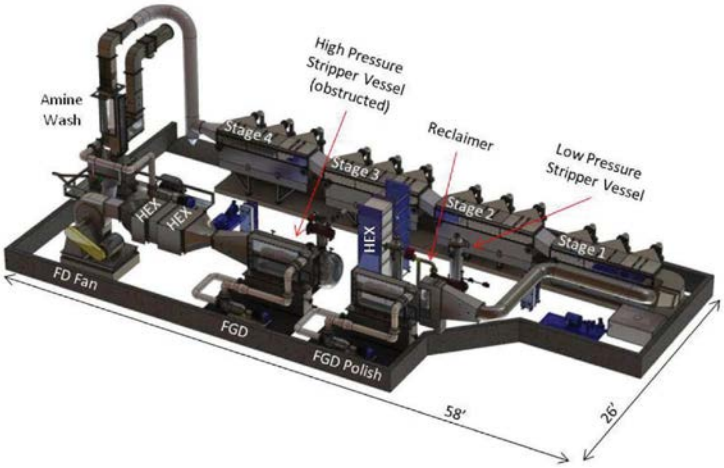

Figure 1: The system layout of the 0.5-MW NeuStream®-C demonstrator system

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	86.14	86.14
Normal Boiling Point	°C	146	146
Normal Freezing Point	°C	106	106
Vapor Pressure @ 15 °C	bar	<0.001	<0.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	34%	34%
Specific Gravity (15 °C/15 °C)	—	0.99 (50 °C)	0.99 (50 °C)
Specific Heat Capacity @ STP	kJ/kg-K	3.6 (50 °C)	3.6 (50 °C)
Viscosity @ STP	cP	3.6 cP at 50 °C	3.6 cP at 50 °C
Absorption			
Pressure**	bar	0.101	0.101
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.38	0.38
Heat of Absorption	kJ/mol CO_2	73	73
Solution Viscosity	cP	4.7	4.7
Desorption			
Pressure***	bar	2/4	2/4
Temperature	°C	150	150
Equilibrium CO_2 Loading	mol/mol	0.28	0.28
Heat of Desorption	kJ/mol CO_2	73	73
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2,370	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 >95 4/8	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

*unloaded PZ solution is a solid at 15 °C; **CO_2 partial pressure in the flue gas at Drake plant; ***CO_2 partial pressure exiting stripper

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 into concentrated PZ follows a carbamate mechanism, which is typical of primary and secondary amines. The overall chemical reaction of PZ with CO_2 is

$$2PZ + CO_2 \Leftrightarrow PZH^+ + PZCOO,$$

while the full aqueous reaction pathway is [3]

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$2H_2O + CO_2 \Leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$$

$$PZH^+ + H_2O \Leftrightarrow PZ + H_3O^+$$

$$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$$

$$HPZCOO + H_2O \Leftrightarrow PZCOO^- + H_3O^+$$

$$PZCOO^- + HCO_3^- \Leftrightarrow PZ(COO)_2^{2-} + H_2O.$$

Solvent Contaminant Resistance – 6-m PZ is thermally stable at 150 °C with negligible oxidative degradation. The total amine loss is estimated to be 0.4 percent/week when stripping at 150 °C. At 135 °C, the reported thermal degradation of PZ is 0.07 percent as compared to 8.1 percent in the case of an MEA solvent.[4] The main degradation products of PZ are nitrates (0.13 mM/hr) and ethylenediamine (0.09 mM/hr).

Flue Gas Pretreatment Requirements – The flue gas is passed through a NeuStream® NO_x- and SO_x-removal system before being fed to the CARE system. The SO_x concentration is kept below 10 ppm using two stages of NeuStream® FGD absorbers. The polishing scrubber for SO_x removal has a high volumetric mass-transfer coefficient and 90 percent removal efficiency. The polishing scrubber also cools the flue gas from 57 °C to ≈32 °C by contacting the flue gas with cold sorbent. This helps maintain water balance while also reducing the volumetric flow rate through the CO_2 absorber and counteracting some of the heat from the exothermic CO_2 absorption reaction, reducing the PZ solvent temperature and decreasing the equilibrium vapor pressure, both of which help to reduce the size of the CO_2 absorber.

Waste Streams Generated ––Solid waste streams are generated by the reclaimer, which removes heat stable salts formed by NO_x and SO_2 absorption, and by the inline filters. Fugitive liquid amine emissions will be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Amine slip is minimized through the use of an amine water wash absorber unit, also based on NeuStream® technology. The FGD unit generates a gypsum by-product suitable for landfill.

Process Design Concept – Process flow diagram is shown in Figure 2 below.

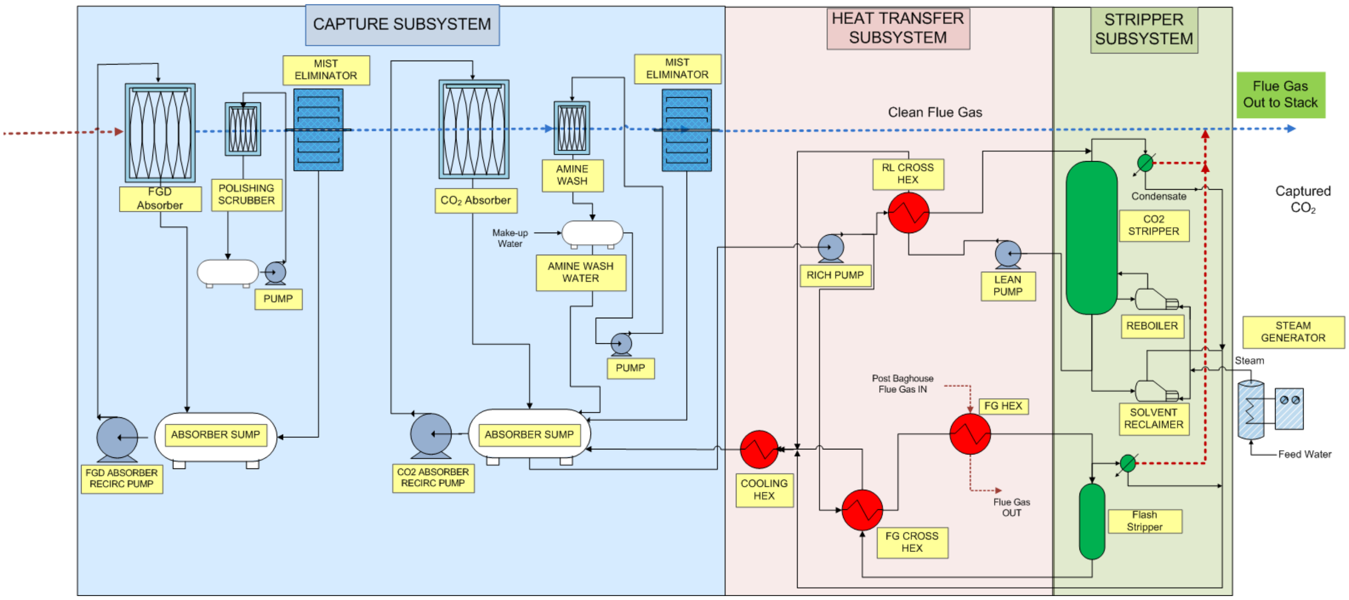

Figure 2: Process flow diagram of CARE system

Proposed Module Design – The heart of the NeuStream® system is NSG's patented, high specific surface area NeuStream® flat jet nozzle technology (shown in Figure 3) engineered into modular, scalable, and efficient cross-flow gas liquid contactor (absorber) units. The modular absorber units are arranged in parallel into full scale systems. Several areas of innovation make this gas-liquid contactor extremely effective for absorbing CO_2 from flue gas. First, a high specific surface area (400–800 m^{-1}) absorption zone is achieved over a large volume from an array of flat jets driven by low liquid-side pressure (<34 kPa). Secondly, the flat jets are aerodynamically shaped, which allows for a high gas flow parallel to the jets while maintaining a low gas-side pressure drop (0.25 kPa/m). Packaging of the NeuStream® absorber takes advantage of the high specific surface area and high gas velocities (typically 5 m/s for CO_2 capture) to reduce the footprint of the system by up to 90 percent and booster fan power requirements by up to 70 percent when compared to conventional packed towers.

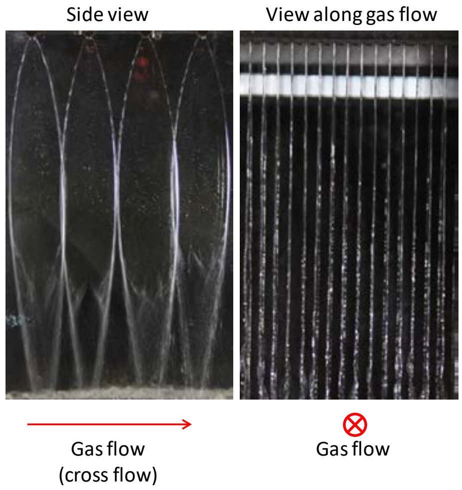

Figure 3: NeuStream® flat jet technology

The system layout is shown above in Figure 1 and the process flow diagram is shown above in Figure 2. Ozone is introduced upstream of a forced draft to oxidize NO_X to more soluble components. The fan moves the flue gas through a heat exchanger to heat the slipstream flow back up to a representative temperature (350 °F). The flue gas then passes through a second heat exchanger, which heats loaded solvent and reduces steam usage in the regeneration subsystem. The flue gas then passes through a NeuStream® FGD system to reduce the SO_x concentration to 15 ppm and the NO_x by 80–90 percent. A polishing/direct contact cooler (DCC) NeuStream® scrubber is used to further reduce the SO_x to 1 ppm, and to cool the flue gas to <35 °C. After the polishing/DDC scrubber, the gas passes through a four-unit NeuStream® CO_2 absorber (shown in Figure 4), where each unit has three stages. This 12-stage absorber reduces the CO_2 by 90 percent prior to contacting the flue gas with a NeuStream® amine wash, which cleans the amine slip from the gas before reintroducing it into the plants main flue gas stream. Due to space constraints, only 3 of the 4 absorber units were relocated to NSG's facility following the unrelated turbine fire at the Drake plant, such that the expected capture efficiency at design gas flow rates would decrease from 90 percent to ≈75 percent and the gas flow would need to be de-rated in order to realize 90 percent CO_2 capture.

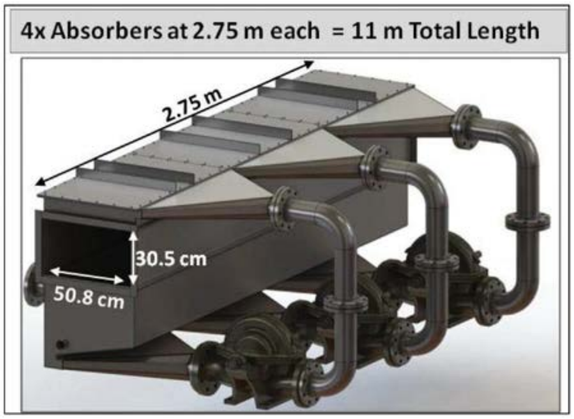

Figure 4: Solid model of one of four NeuStream® CO_2 absorber stages utilized in Project CARE (Cross-sectional area scales with system size, but length remains unchanged.)

The regeneration system contains all typical components, such as cross heat exchangers, solvent cooler exchanger, rich pump, reclaimer, and condenser. A custom-designed stripper vessel is utilized to lower steam usage during operation. Additionally, approximately 10 percent of the rich flow is directed to a lower-pressure flash vessel to desorb the CO_2 from the solvent using only heat provided by the flue gas.

technology advantages

- The NeuStream® CO_2 capture technology integrates a highly-efficient, compact absorber design with an advanced solvent, leading to substantial (≈90 percent) reduction in absorber volume as well as significant savings in both capital and operating costs compared to conventional systems.
- The high surface areas of the NeuStream® flat jets and low-pressure drop in the absorber lower the capital cost of the absorber considerably, leading to significant reductions in the increase in levelized cost of electricity (LCOE) over MEA.
- The NeuStream® technology is adaptable to a wide range of solvents encompassing a large spectrum of properties such as surface tension, viscosity and mass transfer rates.
- The NeuStream® flat jets are engineered into modular absorber units, which are arranged in parallel to meet the flue gas flow rate requirements for specific applications, facilitating rapid, low-risk scale-up of the technology.
- The NeuStream® technology incorporates PZ regeneration at high pressures, leading to lower CO_2 compression power requirements.
- The CARE system utilizes an alternative NO_x-removal strategy to demonstrate the viability of this option over selective catalytic reductions (SCRs).
- The CARE system utilizes a flue gas heat-recovery strategy to reduce the steam usage in the regeneration subsystem.
- A novel stripper design developed by NSG with Dr. Rochelle and Dr. Chen at the University of Texas is incorporated into the CARE system to minimize steam usage.

R&D challenges

- Ensuring optimal distribution of gas in the absorber and avoiding gas bypassing the jets in large-scale absorbers may be an issue, which is addressed via CFD modeling.
- Results from tests on the design verification stand indicate that the specific surface area is not fully preserved with increasing jet length; this may lead to larger absorbers, increasing capital costs. It is possible this decrease is due to the wall effects that become more prevalent at longer jet lengths in the design verification test stand.

status

NSG designed, built and tested a 0.5-MW NeuStream® CO_2 capture system using flue gas from a natural gas boiler. The system exhibited 90 percent capture at the CSU's Martin Drake PC power plant, regenerated CO_2 purity was measured to be 98.6 percent. The NeuStream® absorbers tested support a 90 percent reduction in absorber volume compared to packed towers and with an absorber parasitic power of less than 1 percent when configured for operation with a 550-MW coal plant. Figure 5 shows a size comparison between a 110-MW (net) NeuStream® CO_2 absorber and a commercial 110-MW (net) CO_2 absorber, which was recently commissioned at SaskPower's Boundary Dam Unit #3.[5] As can be seen, NeuStream® technology provides a significant size advantage over conventional CO_2 capture technology, resulting in a volume reduction of 82 percent for the 160-MW Boundary Dam application. The preliminary techno-economic analysis predicted a cost of CO_2 capture at $25.73/tonne, with a corresponding COE increase of 40 percent. Project complete as of December 31, 2015.

Figure 5: CO_2 absorber size comparison: 110 MW (net) NeuStream® vs. CanSolv's 110 MW (net) SaskPower Boundary Dam Unit #3 Project (Includes flue gas desulfurization, CO_2, and amine wash absorbers.)

available reports/technical papers/presentations

"Carbon Absorber Retrofit Equipment (CARE) Final Scientific/Technical Report," December 2015. https://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007528-Neumann-Final-Report.pdf.

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[2] Van Wagener, David H., "Stripper Modeling for CO_2 Removal Using Monoethanolamine and Piperazine Solvents," PhD Thesis, University of Texas, 2011.

[3] Bishnoi, S., and Rochelle, G. T., "Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility," Chemical Engineering Science 55 (2000) 5531-5543.

[4] Dombrowski, K, "Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas," DOE-NETL Contractor's Meeting, 2010.

[5] Couturier, Guy and DMello, Mark, (SNC-Lavalin), "From Engineering to Procurement to Construction of the Boundary Dam Carbon Capture System," SaskPower CCS Consortium, 2013 Information and Planning Symposium, May 21, 2013.

Combined Pressure, Temperature Contrast and Surface-Enhanced Separation of Carbon Dioxide for Post-Combustion Carbon Capture

primary project goals

William Marsh Rice University developed a novel process for the separation of carbon dioxide (CO_2) from flue gas from conventional, pulverized coal-fired power plants. The process combines the solvent absorber and stripper columns into a single integrated unit. The combined absorber and stripper system benefited from using a high surface area ceramic foam gas-liquid contactor for enhanced mass transfer. The project included bench-scale testing of the system.

technical goals

- Combine absorber and stripper columns into a single, integrated process unit to achieve significant cost savings in capital costs and to mitigate space availability constraints.
- Use a high surface area ceramic foam gas-liquid contactor for enhanced mass transfer.
- Use vacuum stripping in combination with waste heat for regeneration of a CO_2 solvent.
- Assess the potential to functionalize the ceramic gas-liquid contactors with solid catalyst for enhanced CO_2 desorption.
- Evaluate the use of catalysts for CO_2 desorption.
- Determine best absorbent and operating conditions for the process.
- Develop a two-dimensional (2D) model to simulate gas and liquid flow in the capture process.
- Perform a techno-economic analysis.

technical content

The technical approach involves the integration of the absorber and stripper sections into a single unit. Figure 1 shows a schematic of a combined absorber and stripper unit.

In Figure 1, the region shaded in blue represents a gas-liquid contactor on the absorption side whereas the region shaded in red represents the same on the stripping side. The gas-liquid contactor must possess a large geometric surface area for good gas-liquid contacting. For liquid to be transported from the absorption to stripping side, horizontal flow of the liquid is a requirement. This can take place in two ways, either by flow through the connected pores of a ceramic contactor or as a liquid film moving over the surface of a contactor with a complex three-dimensional structure.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Novel Absorption/Stripper Process

participant:

William Marsh Rice University

project number:

FE0007532

predecessor projects:

N/A

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N/A

start date:

10.01.2011

percent complete:

100%

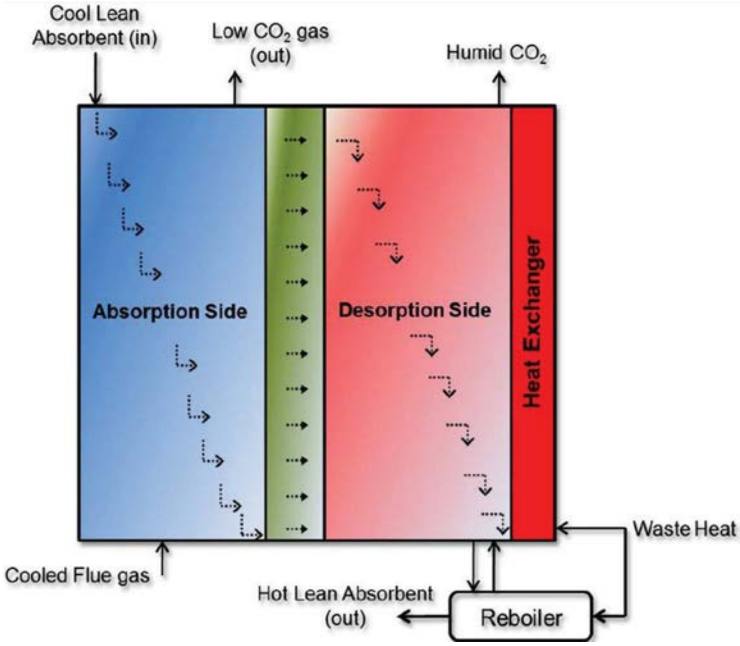

Figure 1: Schematic of combined pressure and temperature contrast and surface-enhanced separation of CO_2

A bench-scale prototype of the gas absorption process was developed to study various aspects of fluid flow in the system. A simulation model for the process was also developed to optimize the properties of ceramics being used and the process operating conditions.

The expected outcomes of this project include significant reduction in the capital and operating costs of the gas absorption process and a resulting decrease in cost of electricity (COE). The use of waste heat instead of high-quality steam provides a significant reduction in operating costs. An integrated absorber and stripper unit substantially reduces capital costs.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	86.14	86.14
Normal Boiling Point	°C	146	146
Normal Freezing Point	°C	106	106
Vapor Pressure @ 15 °C	bar	<0.001	<0.001
Manufacturing Cost for Solvent	$/kg	—	—
Working Solution			
Concentration	kg/kg	34%	34%
Specific Gravity (15 °C/15 °C)	—	0.99 (50 °C)	0.99 (50 °C)
Specific Heat Capacity @ STP	kJ/kg-K	3.6 (50 °C)	3.6 (50 °C)
Viscosity @ STP	cP	3.6 cP at 50 °C	3.6 cP at 50 °C
Absorption			
Pressure**	bar	0.101	0.101
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.38	0.38
Heat of Absorption	kJ/mol CO_2	73	73
Solution Viscosity	cP	4.7	4.7
Desorption			
Pressure***	bar	2/4	2/4
Temperature	°C	150	150

Equilibrium CO_2 Loading	mol/mol	0.28		0.28
Heat of Desorption	kJ/mol CO_2	73		73
Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		2,370	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	>95	4/8
Absorber Pressure Drop	bar		—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

*unloaded PZ solution is a solid at 15 °C; **CO_2 partial pressure in the flue gas at Drake plant; ***CO_2 partial pressure exiting stripper

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Provide brief description of the following items:

Chemical/Physical Solvent Mechanism – The absorption of CO_2 into concentrated PZ follows a carbamate mechanism, which is typical of primary and secondary amines. The overall chemical reaction of PZ with CO_2 is

$$2PZ + CO_2 \Leftrightarrow PZH^+ + PZCOO,$$

while the full aqueous reaction pathway is [3]

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

$$2H_2O + CO_2 \Leftrightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \Leftrightarrow CO_3^{2}- + H_3O^+$$

$$PZH^+ + H_2O \Leftrightarrow PZ + H_3O^+$$

$$PZ + HCO_3^- \Leftrightarrow PZCOO^- + H_2O$$

$$HPZCOO + H_2O \Leftrightarrow PZCOO^- + H_3O^+$$

$$PZCOO^- + HCO_3^- \Leftrightarrow PZ(COO)_2^{2-} + H_2O.$$

Solvent Contaminant Resistance –6-m PZ is thermally stable at 150 °C with negligible oxidative degradation. The total amine loss is estimated to be 0.4 percent/week when stripping at 150 °C. At 135 °C, the reported thermal degradation of PZ is 0.07 percent as compared to 8.1 percent in the case of an MEA solvent.[4]. The main degradation products of PZ are nitrates (0.13 mM/hr) and ethylenediamine (0.09 mM/hr).

Flue Gas Pretreatment Requirements – The flue gas is passed through a NeuStream® nitrogen oxides (NO_x)- and sulfur oxides (SO_x)- removal system before being fed to the CARE system. The SO_x concentration is kept below 10 ppm using two stages of NeuStream® FGD absorbers. The polishing scrubber for SO_x removal has a high volumetric mass-transfer coefficient and 90 percent removal efficiency. The polishing scrubber also cools the flue gas from 57 °C to ≈32 °C by contacting the flue gas with cold sorbent. This helps maintain water balance while also reducing the volumetric flow rate through the CO_2 absorber and counteracting some of the heat from the exothermic CO_2 absorption reaction, reducing the PZ solvent temperature and decreasing the equilibrium vapor pressure, both of which help to reduce the size of the CO_2 absorber.

Waste Streams Generated ––Solid waste streams are generated by the reclaimer, which removes heat stable salts formed by NO_x and SO_2 absorption, and by the inline filters. Fugitive liquid amine emissions will be controlled by incorporating seamless valves, rupture disks, closed-loop ventilation systems, pumps with dual mechanical seals, minimum welds, and correct gasket material selection. Amine slip is minimized through the use of an amine water wash absorber unit, also based on NeuStream® technology. The FGD unit generates a gypsum by-product suitable for landfill.

Process Design Concept – Process flow diagram is shown in Figure 2 below.

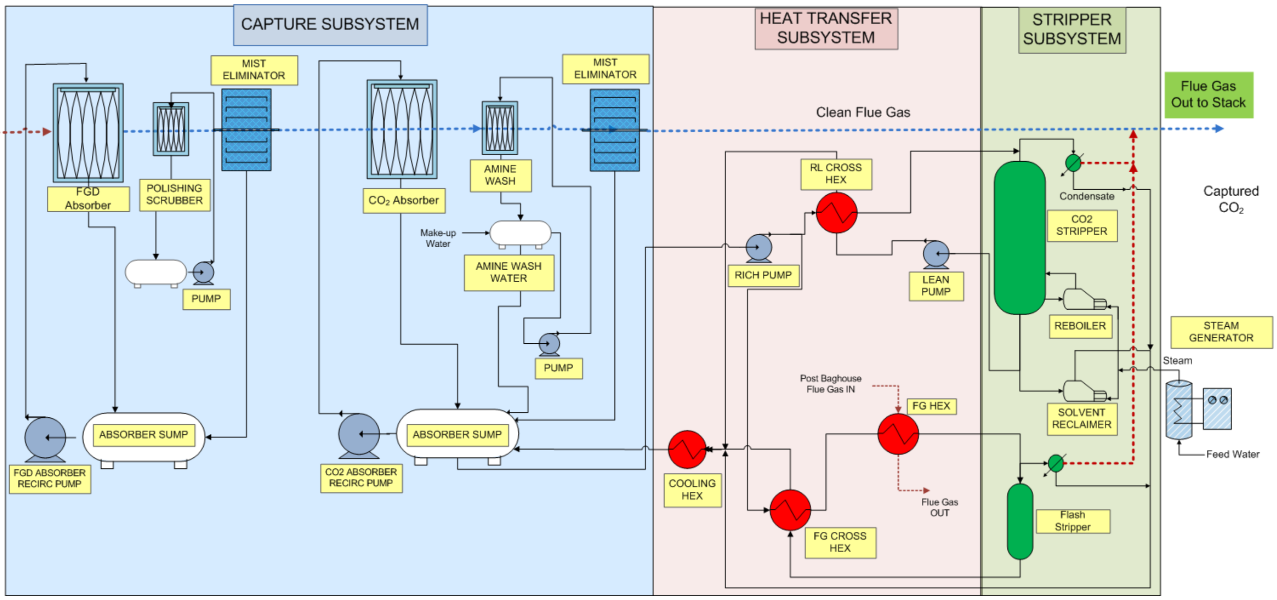

Figure 2: Process flow diagram of care system

Proposed Module Design – The heart of the NeuStream® system is NSG's patented, high specific surface area NeuStream® flat jet nozzle technology (shown in Figure 3) engineered into modular, scalable, and efficient cross-flow gas liquid contactor (absorber) units. The modular absorber units are arranged in parallel into full scale systems. Several areas of innovation make this gas-liquid contactor extremely effective for absorbing CO_2 from flue gas. First, a high specific surface area (400–800 m^{-1}) absorption zone is achieved over a large volume from an array of flat jets driven by low liquid-side pressure (<34kPa). Secondly, the flat jets are aerodynamically shaped which allows for a high gas flow parallel to the jets while maintaining a low gas-side pressure drop (0.25 kPa/m). Packaging of the NeuStream® absorber takes advantage of the high specific surface area and high gas velocities (typically 5 m/s for CO_2 capture) to reduce the footprint of the system by up to 90 percent and booster fan power requirements by up to 70 percent when compared to conventional packed towers.

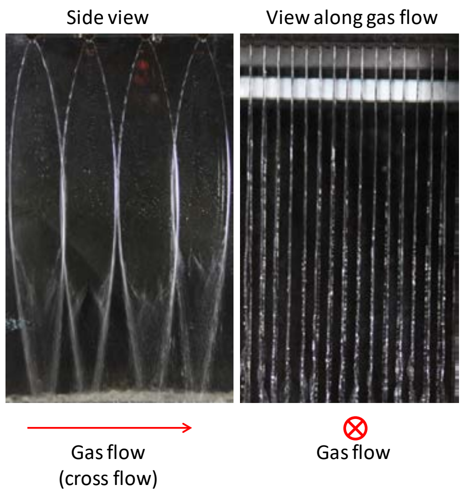

Figure 3: NeuStream® flat jet technology

The system layout is shown above in Figure 1 and the process flow diagram is shown above in Figure 2. Ozone is introduced upstream of a forced draft to oxidize NO_x to more soluble components. The fan moves the flue gas through a heat exchanger to heat the slipstream flow back up to a representative temperature (350 °F). The flue gas then passes through a second heat exchanger, which heats loaded solvent and reduces steam usage in the regeneration subsystem. The flue gas then passes through a NeuStream® FGD system to reduce the SO_x concentration to 15 ppm and the NO_x by 80–90 percent. A polishing/direct contact cooler (DCC) NeuStream® scrubber is used to further reduce the SO_x to 1 ppm, and to cool the flue gas to <35 °C. After the polishing/DDC scrubber, the gas passes through a four-unit NeuStream® CO_2 absorber (shown in Figure 4), where each unit has three stages. This 12-stage absorber reduces the CO_2 by 90 percent prior to contacting the flue gas with a NeuStream® amine wash, which cleans the amine slip from the gas before reintroducing it into the plants main flue gas stream. Due to space constraints, only 3 of the 4 absorber units were relocated to NSG's facility following the unrelated turbine fire at the Drake plant. The expected capture efficiency at design gas flow rates would decrease from 90 percent to ≈75 percent and the gas flow would to be de-rated in order to realize 90 percent CO_2 capture.

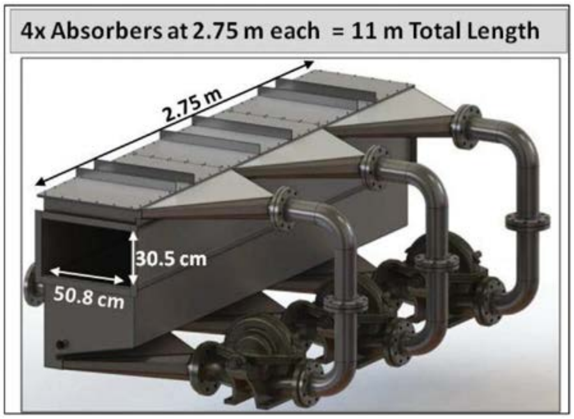

Figure 4: Solid model of one of four NeuStream® CO_2 absorber stages utilized in project CARE (cross-sectional area scales with system size, but length remains unchanged)

The regeneration system contains all typical components, such as cross heat exchangers, solvent cooler exchanger, rich pump, reclaimer, and condenser. A custom-designed stripper vessel is utilized to lower steam usage during operation. Additionally, approximately 10 percent of the rich flow is directed to a lower-pressure flash vessel to desorb the CO_2 from the solvent using only heat provided by the flue gas.

technology advantages

- The NeuStream® CO_2 capture technology integrates a highly-efficient, compact absorber design with an advanced solvent, leading to substantial (≈90 percent) reduction in absorber volume as well as significant savings in both capital and operating costs compared to conventional systems.
- The high surface areas of the NeuStream® flat jets and low-pressure drop in the absorber lower the capital cost of the absorber considerably, leading to significant reductions in the increase in levelized cost of electricity (LCOE) over MEA.
- The NeuStream® technology is adaptable to a wide range of solvents encompassing a large spectrum of properties such as surface tension, viscosity and mass transfer rates.
- The NeuStream® flat jets are engineered into modular absorber units which are arranged in parallel to meet the flue gas flow rate requirements for specific applications, facilitating rapid, low-risk scale-up of the technology.
- The NeuStream® technology incorporates PZ regeneration at high pressures, leading to lower CO_2 compression power requirements.
- The CARE system utilizes an alternative NO_x-removal strategy to demonstrate the viability of this option over selective catalytic reductions (SCRs).
- The CARE system utilizes a flue gas heat-recovery strategy to reduce the steam usage in the regeneration subsystem.
- A novel stripper design developed by NSG with Dr. Rochelle and Dr. Chen at the University of Texas is incorporated into the CARE system to minimize steam usage.

R&D challenges

- Ensuring optimal distribution of gas in the absorber and avoiding gas bypassing the jets in large-scale absorbers may be an issue which is addressed via computational fluid dynamics (CFD) modeling.
- Results from tests on the design verification stand indicate that the specific surface area is not fully preserved with increasing jet length; this may lead to larger absorbers, increasing capital costs. It is possible this decrease is due to the wall effects that become more prevalent at longer jet lengths in the design verification test stand.

status

NSG designed, built and tested a 0.5-megawatt (MW) NeuStream® CO_2 capture system using flue gas from a natural gas boiler. The system exhibited 90 percent capture at the CSU's Martin Drake PC power plant, regenerated CO_2 purity was measured to be 98.6 percent. The NeuStream® absorbers tested support a 90 percent reduction in absorber volume compared to packed towers and with an absorber parasitic power of less than 1 percent when configured for operation with a 550-MW coal plant. Figure 5 shows a size comparison between a 110-MW (net) NeuStream® CO_2 absorber and a commercial 110-MW (net) CO_2 absorber which was recently commissioned at SaskPower's Boundary Dam Unit #3.[5] As can be seen, NeuStream® technology provides a significant size advantage over conventional CO_2 capture technology, resulting in a volume reduction of 82percent for the 160-MW Boundary Dam application. The preliminary techno-economic analysis predicted a cost of CO_2 capture at $25.73/tonne, with a corresponding COE increase of 40 percent. The project was complete as of December 31, 2015.

Figure 5: CO_2 Absorber size comparison: 110-MW (net) NeuStream® vs. CanSolv's 110-MW (net) SaskPower Boundary Dam Unit #3 project (includes flue gas desulfurization, CO_2 and amine wash absorbers)

available reports/technical papers/presentations

"Carbon Absorber Retrofit Equipment (CARE) Final Scientific/Technical Report, December 2015. https://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007528-Neumann-Final-Report.pdf.

"Progress Update on the Carbon Dioxide Absorber Retrofit Equipment (CARE) Program," 2014 NETL CO_2 Capture Technology Meeting, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/A-Awtry-NSG-Progress-Update-On-NSGs-CARE.pdf*.

"Status of the Carbon Dioxide Absorber Retrofit Equipment (CARE) Program," 2013 NETL CO_2 Capture Technology Meeting, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO₂%20Capture/A-Awtry-NSG-Status-of-the-CARE-Program.pdf*

Brasseur, J., and Awtry, A., "Compact Absorber Retrofit Equipment (CARE)," presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA. *http://www.netl.doe.gov/publications/proceedings/12/CO₂capture/presentations/2-Tuesday/2-Brasseur-NeumannSG.pdf*.

Awtry, A., Klein, E., and Brasseur, J., "NeuStream®-C: Carbon Capture Progress Update", Air Quality IX, Arlington, VA, 2013.

Awtry, A., Klein, E., and Brasseur, J., "NeuStream®-C: Carbon Capture Progress Update", Power-Gen XXV, Orlando, FL, 2013.

references

[1] Dugas, Ross E., "CO_2 Absorption, Desorption, and Diffusion in Aqueous Piperazine and Monoethanolamine," PhD Thesis, University of Texas, 2009.

[2] Van Wagener, David H., "Stripper Modeling for CO_2 Removal Using Monoethanolamine and Piperazine Solvents," PhD Thesis, University of Texas, 2011.

[3] Bishnoi, S., and Rochelle, G. T., "Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility," Chemical Engineering Science 55 (2000) 5531-5543.

[4] Dombrowski, K, "Evaluation of Concentrated Piperazine for CO_2 Capture from Coal-Fired Flue Gas," DOE-NETL Contractor's Meeting, 2010.

[5] Couturier, Guy and DMello, Mark, (SNC-Lavalin), "From Engineering to Procurement to Construction of the Boundary Dam Carbon Capture System", SaskPower CCS Consortium, 2013 Information and Planning Symposium, May 21, 2013.

Development of a Novel Gas Pressurized Stripping-Based Technology for CO_2 Capture from Post-Combustion Flue Gases

primary project goals

Carbon Capture Scientific has performed bench-scale development, testing, and computer simulations of a novel solvent-based carbon dioxide (CO_2) capture technology, known as gas-pressurized stripping (GPS) process. The GPS technology has the potential to significantly reduce the energy penalty associated with solvent regeneration and compression by operating the regeneration step at higher pressures, which in-turn reduces the compression requirements for CO_2 storage.

technical goals

- Computer simulation to predict GPS column performance under different operating conditions.
- Lab-scale tests of individual process units to document experimental results and obtain necessary information to progress the technology to the next level.
- Experimental investigation of selected solvents to minimize the economic risk of the proposed technology.
- Design, build, and operate a bench-scale GPS unit capable of processing about 500 standard liters of actual coal-derived flue gas per minute (SLPM) at the National Carbon Capture Center (NCCC).
- Derive a techno-economic analysis (TEA) of the GPS process on a pulverized coal plant compared to a baseline pulverized coal plant.

technical content

The project conducted lab-scale individual process unit tests and integrated continuous bench-scale GPS system tests using actual coal-derived flue gas at the NCCC. The overall objective was to reduce the energy consumption and capital cost of the CO_2 capture process.

Computer simulation tasks investigated the GPS column behavior under different operating conditions, optimizing the column design and operating conditions, leading to a capital cost increase less than five percent over the baseline monoethanolamine (MEA) case. Solvent related tasks collected information on the solvent operating cost when a modified, commercially-available solvent is used in the GPS process. Experiment related tasks with the major individual units obtained information needed for the bench-scale unit design, and the integrated continuous bench-scale GPS system tests using actual coal-derived flue gas at the NCCC provided all the necessary information for the next level pilot-scale process and engineering design along with the GPS system performance data. Testing at the NCCC demonstrated that the GPS process can

technology maturity:

Bench-Scale, Real Flue Gas

project focus:

Gas-Pressurized Stripping

participant:

Carbon Capture Scientific

project number:

FE0007567

predecessor projects:

N/A

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partners:

CONSOL Energy, Inc., Nexant, Inc., Western Kentucky University

start date:

10.01.2011

percent complete:

100%

achieve 90 percent CO_2 removal from typical coal-derived flue gas. The GPS process can produce high-pressure CO_2 product with required purity. Finally, the GPS process has an energy consumption much lower than that of the DOE MEA baseline case. A TEA of the GPS process was derived, showing that a GPS-based pulverized coal (PC) plant has net power production of 647 MW, greater than the MEA baseline study. This increase is attributed to the lower steam requirement and smaller CO_2 compression auxiliary power consumption. The TEA also found that the 20-year levelized cost of electricity for a supercritical PC plant with GPS-based PCC is 52 percent more than the baseline supercritical PC plant without CO_2 capture but 23 percent lower than the baseline supercritical PC plant with MEA. Figure 1 is a flowchart for the GPS process. Figure 2 shows the GPS-based skid developed and tested at the NCCC. Table 1 lists the process parameters relevant to the GPS process.

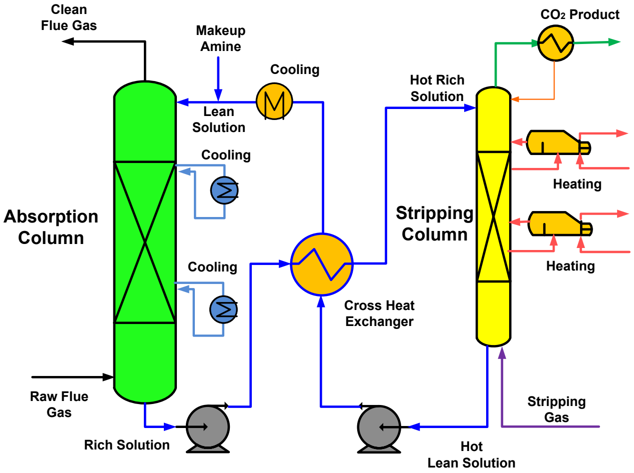

Figure 1: GPS-based absorption/stripping process

Figure 2: GPS-based skid used for bench-scale slipstream testing at NCCC

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	112.4	112.4
Normal Boiling Point	°C	226.8	226.8
Normal Freezing Point	°C	4.4	4.4
Vapor Pressure @ 15 °C	bar	<1.3E-05	<1.3E-05
Manufacturing Cost for Solvent	$/kg	3	3
Working Solution			
Concentration	kg/kg	—	—
Specific Gravity (15 °C/15 °C)	—	1.06	1.06
Specific Heat Capacity @ STP	kJ/kg-K	ca. 3	ca. 3
Viscosity @ STP	cP	N/A	
Absorption			
Pressure	bar	1.01	1.01
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.41	0.49
Heat of Absorption	kJ/mol CO_2	59.6	59.6
Solution Viscosity	cP	6.2	4
Desorption			
Pressure	bar	6	6
Temperature	°C	120	120
Equilibrium CO_2 Loading	mol/mol	0.19	0.19
Heat of Desorption	kJ/mol CO_2	58.5	58.5
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	40	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90% >95%	6 bar
Absorber Pressure Drop	bar	0.05	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

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

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

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

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

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

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

Concentration **–** Mass fraction of pure solvent in working solution.

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism **–** Pressurized stripping is a process applicable to different types of solvents. Chemistry of the GPS-based absorption/stripping process depends on the solvent used in the process. In the proposed research, a modified commercially-available amine solvent will be used. Therefore, the chemistry of the amine-based CO_2 capture process will apply to the GPS-based process.

The reaction kinetics of the GPS-based process also depends on the solvent selected. With the solvent currently selected, it is believed that the reaction kinetics of the modified commercially available solvent will perform better than the baseline monoethanolamine (MEA) process.

Solvent Contaminant Resistance **–** Since the selected solvent is an amine-based solvent, it will share common issues that other amine-based solvents have. Sulfur oxide (SO_x) and nitrogen oxide (NO_x) could be the major contaminants in flue gas, which will be detrimental to all amine-based solvents, including the solvent used in this process. Similar to other amine-based solvents, pretreatment of flue gas will be required to minimize amine degradations.

Solvent Foaming Tendency **–** The solvent is a commercially available solvent, with different strength. The solvent forming tendency should be manageable based on industrial experience.

Flue Gas Pretreatment Requirements **–** Similar to other amine-based solvents, pretreatment of flue gas will be required to minimize amine degradations.

Solvent Makeup Requirements **–** Solvent stability study has demonstrated that this commercially-available solvent will have solvent makeup rate of 1 kg solvent/tonne CO_2.

Waste Streams Generated **–** Waste stream of the GPS-based process is also similar to other amine-based absorption/stripping processes. The main waste material is amine degradation products.

Process Design Concept – Flowsheet/block flow diagram of the GPS process is shown in Figure 1. It is clear that the GPS process is virtually the same as a conventional absorption/stripping process except the two unique innovations: (1) using two side heat exchangers to replace a bottom reboiler, and (2) introducing a stripping gas (N_2 or other inert gas) into the GPS column from the bottom. This process configuration will reduce stripping heat significantly.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57 °C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

		Composition						
Pressure	Temperature	vol%					ppmv	
bara	°C	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1.014	57	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

- The use of off-the-shelf process equipment will accelerate process development.
- The use of absorption/stripping technology would be suitable for low-cost, large-scale applications.
- The higher stripper operating pressure reduces the stripping heat requirement and subsequent compression work. As a result, GPS process offers higher energy efficiency.

- The GPS technology is flexible in terms of operating pressures and temperatures, and is applicable to different types of solvents.

R&D challenges

The major challenge of the GPS-based process is its capital cost. The optimal GPS-based process has almost the same capital cost as the baseline process. New process equipment, which can significantly reduce capital cost, is needed to commercialize the GPS technology.

status

The project was completed on September 30, 2015. Carbon Capture Scientific and their partners determined that a combination of experimental, computer simulation, and techno-economic analysis was effective to identify optimal process configurations and operating conditions for the GPS technology and that the GPS-based post-combustion capture process is energy-efficient and cost-effective compared with the benchmark MEA process. Integrating the GPS process into a 550-MW_e PC-fired power plant will increase cost of electricity approximately 23 percent less than that for the benchmark MEA process.

available reports/technical papers/presentations

Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," Final Scientific/Technical Report, October 2015. *https://www.osti.gov/scitech/servlets/purl/1233208*.

Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," Project Closeout Meeting, Pittsburgh, PA, December 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007567-Final-Review-Presentation-12-18-2015.pdf*.

Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/S-Chen-CCS-Gas-Pressurized-Stripping.pdf*.

Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Chen-CCS-Development-Of-A-Novel-Gas-Pressurized-Stripping.pdf*.

Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Chen-CCS-Novel-GPS-Based-Technology.pdf*.

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Shiaoguo (Scott) Chen, "Development of a Novel Gas Pressurized Stripping (GPS)-Based Technology for CO_2 Capture from Post-Combustion Flue Gases," 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/development-novel-gas-pressurized-stripping-july2012.pdf*.

"Development of a Novel Gas Pressurized Stripping Process-Based Technology for CO_2 Capture," Project Kick-Off Meeting Presentation, November 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/development-novel-gas-pressurized-stripping-kickoff-nov2011.pdf*.

Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Vacuum Regeneration

primary project goals

Novozymes, together with the project partners, designed, built, and tested an integrated bench-scale system that combines the attributes of an enzyme catalyst (carbonic anhydrase [CA]) with low-enthalpy absorption liquids and vacuum regeneration in a solvent-based carbon dioxide (CO_2) capture process, and evaluated a novel ultrasonically enhanced regeneration concept.

technical goals

- Conduct preliminary evaluation of the potential for ultrasonic regeneration to deliver a lean-loading equivalent to the lean loading predicted with vacuum stripping at 70 °C.
- Optimize enzyme-promoted potassium carbonate (K_2CO_3)-based solvent for maximum CO_2 absorption rate.
- Demonstrate enzyme robustness for meeting targeted bench-scale test conditions.
- Design and build an integrated bench-scale unit incorporating the vacuum regeneration component to validate stripping performance at 70–80 °C.
- Demonstrate system performance and benefits based on completion of 500 hours of testing.
- Complete a full technology assessment of the process and potential for meeting reductions in net parasitic load compared to conventional technology for post-combustion CO_2 capture.

technical content

Novozymes, together with the project partners, designed, built, and tested an integrated bench-scale system that combines the attributes of the bio-renewable enzyme carbonic anhydrase (CA) with low-enthalpy aqueous potassium carbonate-based solvent and vacuum regeneration. Preliminary evaluation of a novel ultrasonically enhanced regeneration system was also made. The objective was to develop a CO_2 capture process with improved efficiency and economics when compared with existing CO_2 technologies.

The application of CA accelerates inter-conversion between dissolved CO_2 and bicarbonate ion, which is the rate-limiting step for absorption and desorption in low enthalpy of reaction solutions that rely on reactive absorption of CO_2. The mechanism for CO_2 absorption and desorption when using potassium carbonate solvent is:

$$CO_2 + H_2O + K_2CO_3 \leftrightarrow 2\,KHCO_3$$

The use of low enthalpy CO_2 absorption solvents offers the opportunity to regenerate the solvent at lower temperatures relative to existing CO_2 scrubber technologies. The

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Solvent + Enzyme and Vacuum Regeneration Technology

participant:

Novozymes

project number:

FE0007741

predecessor projects:

N/A

NETL project manager:

Andrew Jones
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principal investigator:

Dr. Sonja Salmon
Novozymes

partners:

University of Kentucky CAER; Pacific Northwest National Laboratory; Doosan

start date:

10.01.2011

percent complete:

100%

system was evaluated with respect to energy requirement and enzyme effects in a process where the enzyme is dissolved and recirculates through the absorber and reduced-temperature stripper. A replenishment program to compensate for active enzyme loss while maintaining system performance was also evaluated.

One method of achieving low temperature stripping is to apply vacuum to decrease the solvent boiling point to ≈70–80 °C, and provide driving force for the regeneration. Process simulations of this approach have been made indicating that the use of low-enthalpy solvents, which could require low-pressure steam during the regeneration cycle, together with vacuum has the potential to require 43 percent less parasitic power from a coal-fired power plant compared to NETL Case 10 MEA scrubbing technology. It is recognized that application of vacuum would have a corresponding compression penalty downstream of the CO_2 capture unit. Therefore, the aim of the evaluation was to demonstrate the feasibility of the vacuum approach by a combination of bench-scale system testing and corresponding projections of feasibility at 550-megawatt electric (MW_e) scale.

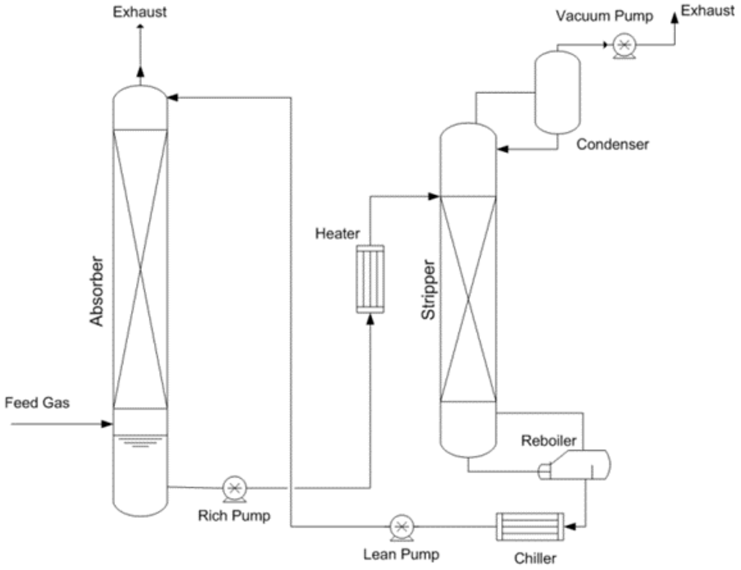

Figure 1: Bench-scale process schematic

In another method of low temperature stripping, application of ultrasonic energy transforms dissolved CO_2 into gas bubbles, thereby increasing the overall driving force of the solvent regeneration reaction. This is shown in Figure 2, where the effects of sonication can be seen on the loaded solvent. The ultrasonic effect known as rectified diffusion where expanding bubbles allow for a biased transfer of dissolved gas into the bubble from solution, could have the potential to yield lean solvent CO_2 loading equivalent to vacuum stripping. Several different configurations of the prototype ultrasonic regenerator were evaluated, including combination with vacuum and novel incorporation of a hydrocyclone to enhance gas-liquid separation. The magnitude of measured CO_2 release was within the range of temperature-dependent release, meaning that application of ultrasonics could provide thermal regeneration effects. However, additional work would be required to validate whether rectified diffusion could replace the vacuum requirement at low stripping temperatures.

Figure 2: Ultrasonic regeneration batch tests for loaded solvent at 70 °C – (L) no sonication; (R) with sonication

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	138.21	138.21
Normal Boiling Point	°C	—	—
Normal Freezing Point	°C	—	—
Vapor Pressure @ 15 °C	bar	—	—
Manufacturing Cost for Solvent	$/kg	1.3	<1.3
Working Solution			
Concentration	kg/kg	0.23	0.23
Specific Gravity (15 °C/15 °C)	-	1.21	1.21
Specific Heat Capacity @ STP	kJ/kg-K	~3.4[a]	~3.4[a]
Viscosity @ STP	cP	~1.4	~1.4
Absorption			
Pressure	bar	1	1
Temperature	°C	30–40	30–50
Equilibrium CO_2 Loading	mol/mol	0.55	0.67
Heat of Absorption	kJ/mol CO_2	27	27
Solution Viscosity	cP	~1.4	~1.4
Desorption			
Pressure	bar	0.35	0.35
Temperature	°C	77	70–80
Equilibrium CO_2 Loading	mol/mol	0.35	0.30
Heat of Desorption	kJ/mol CO_2	27	27
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Notes: Working solution additionally contains CA enzyme catalyst.

[a] Technical Data: Properties of Potassium Carbonate. Armand Products Company.

Definitions:

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

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

1. $CO_{2(g)} \leftrightarrow CO_{2(aq)}$ (gas-liquid physical mass transfer)
2. $CO_{2(aq)} + HO^- \leftrightarrow HCO_3^-$
3. $HCO_3^- + HO^- \leftrightarrow CO_3^= + H_2O$ ($pK_a = 10.3$)
4. $CO_{2(aq)} + H_2O \leftrightarrow H_2CO_3$
5. $H_2CO_3 + HO^- \leftrightarrow HCO_3^- + H_2O$ ($pK_a = 6.4$)
6. $H_2O \leftrightarrow H^+ + HO^-$

For the solvent system in the proposed operating range (pH 9-11), Reaction 2 and reactions 4 together with 5 are responsible for the absorption of CO_2 into the liquid phase as bicarbonate. CA enzyme catalyzes Reaction 6 in the enzyme active site to produce a zinc-hydroxide nucleophile that reacts with CO_2 to produce and release bicarbonate according to Reaction 2. The proton produced during Reaction 6 is transferred from the active site to the reaction medium where the proton is neutralized by the alkalinity and buffering capacity of the medium. The transfer of proton away from the active site has been determined in the literature as the rate limiting step for CA catalysis.

The kinetics of CO_2 absorption in CA enzyme/K_2CO_3 solution were measured using the wetted-wall column technique. The current enzyme/K_2CO_3 solvent supports a mass transfer rate ≥50 percent the rate of benchmark 30 percent MEA.

Solvent Contaminant Resistance – Publications by Akermin, Inc. (DE-FE0004228 and DE-FE0012862) and the University of Illinois (DE-FC26-08NT0005498) demonstrate the robustness of enzyme-promoted K_2CO_3 solvents to typical flue gas contaminants at lab scale.

Solvent Foaming Tendency – Based on bench-scale tests, solvent foaming can be mitigated by antifoam, as necessary.

Flue Gas Pretreatment Requirements – No special requirements expected beyond conventional pretreatment for particulate, sulfur oxide (SO_x), and nitrogen oxide (NO_x) removal.

Solvent Make-Up Requirements – Preliminary feasibility study assumed a K_2CO_3 makeup rate of 0.1 ton/day and continuous enzyme reclamation from 0.05 percent lean solvent slipstream. However, lower than targeted enzyme longevity in the bench scale test resulted in significant cost impact of solvent makeup requirements in the final TEA.

Waste Streams Generated – Waste stream consists of K_2CO_3 salts and biodegradable enzyme, which could be used as compost, fertilizer or boiler fuel.

Process Design Concept – Bench-scale process schematic is shown in Figure 1.

technology advantages

- The energy required for solvent regeneration is provided by low-pressure steam and vacuum.
- Enzyme helps overcome the inherently slow reaction rates of the K_2CO_3 based solvent, which have previously made its use for atmospheric CO_2 capture prohibitive. Enzyme-enhanced rates of CO_2 absorption compared to aqueous K_2CO_3 without CA could lead to capital cost savings.
- By providing enzyme in dissolved form, conventional liquid handling approaches can be used to adjust enzyme dose and replenishment rates to achieve optimal system performance.
- K_2CO_3 has chemical handling advantages due to negligible vapor pressure, no flash point, no odor, no degradation, good safety and environmental profile, and ready availability.

R&D challenges

- Scale-up of the vacuum and ultrasonic regeneration systems from lab- to bench-scale (10–30 standard liters/minute [SLPM] gas, 0.1–0.30 LPM solvent) to provide sufficient lean loading to support 90 percent capture.
- Ultrasonic test system showed tendency towards rapid CO_2 re-dissolution of generated gases and foaming phenomena, which pointed to the need for specialized gas removal in the continuous system. Further work is needed to verify predicted ultrasonic advantages.
- Enzyme dose required to achieve and maintain 90 percent capture.
- Accurate scale up of bench scale data to full scale predictions using process models.
- Practicality of vacuum equipment to handle CO_2 gas flow at 550-MW_e scale.
- Utilization of a very low pressure (VLP) turbine for extracting the solvent regeneration steam at 8 psia (and 85 °C).

status

This project was completed on June 30, 2015. A novel flow-through ultrasonic regenerator was designed and tested, confirming that CO_2 was released, however the release values were below the equilibrium projections. The highest ultrasonic results were explainable by the localized temperature increases in the liquid caused by the ultrasonic energy alone, therefore the remainder of the project focused on the use of vacuum regeneration. The fully integrated bench-scale system including vacuum regeneration was designed and fabricated, with parametric and alternative solvent testing completed. Overall, the system was operated successfully for an accumulated 500 hours of operation with vacuum conditions. An average of 84 percent CO_2 capture efficiency was attained during the period using enzyme replenishment. The presence of enzyme caused foaming in the stripper, which was controlled via antifoam addition. There was a faster decay rate of the enzyme activity at longer residence time at elevated temperatures in the cycle. TEA studies of the system indicated higher COE, higher cost of CO_2 captured, and slightly lower energy requirement compared to DOE Case 10 (Econamine solvent process), with the difference in costs primarily due to higher variable costs.

available reports/technical papers/presentations

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *http://netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007741-Final-Project-Meeting-09-23-15.pdf*

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *http://netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*

House, A., "Low-Energy Solvents for CO_2 Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," AIChE 2014 Meeting, Atlanta, GA, November 17, 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007741-AIChE-2014-Presentation-11-17-2014.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Vacuum Regeneration," Novozymes North America, Inc., 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Salmon-Novozymes-Low-Energy-Solvents.pdf*.

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Salmon, S., "Lab-Scale Assessment of a Post-Combustion Carbon Dioxide Capture Process Enabled by a Combination of Enzymes and Ultrasonics," 2012 Pittsburgh Coal Conference, Pittsburgh, PA, October 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/ipcc-oct2012-session11-salmon.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Ultrasonics," 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA. July 2012. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/enzymes-ultrasonics-july2012.pdf*.

Salmon, S., "Low-Energy Solvents for Carbon Dioxide Capture Enabled by a Combination of Enzymes and Ultrasonics," Project Kick-Off Meeting, November 2011. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/enzymes-ultrasonics-kickoff-nov2011.pdf*.

DEVELOPMENT OF AN ENERGY-EFFICIENT, ENVIRONMENTALLY FRIENDLY SOLVENT FOR THE CAPTURE OF CO_2

primary project goals

This Babcock & Wilcox Power Generation Group, Inc., (B&W) project focuses on identifying concentrated piperazine (PZ)-based solvent formulations that improve overall solvent and system performance.

technical goals

- Improve system operability and reliability.
- Minimize environmental impacts.
- Reduce corrosion potential.
- Maximize solvent durability.

technical content

B&W is characterizing and optimizing the formulation of a novel solvent for the capture of carbon dioxide (CO_2) at coal-fired utility plants. The solvent of interest has been identified through a 5-year solvent development program conducted at B&W. The solvent formulations of interest comprise concentrated solutions of a cyclic diamine, PZ. Testing at B&W indicates that blends of concentrated PZ with other compounds have the potential to perform substantially better than PZ itself. The objective is to lower the total cost of solvent-based CO_2 capture systems by identifying formulations that improve overall solvent and system performance.

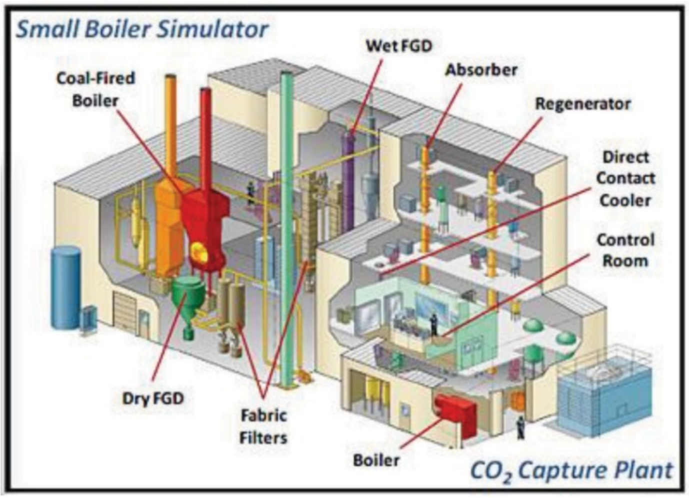

Figure 1: B&W 7-Ton/Day Pilot Facility

technology maturity:

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Optimized Solvent Formulation

participant:

Babcock & Wilcox

project number:

FE0007716

NETL project manager:

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principal investigator:

George Farthing
Babcock & Wilcox
gafarthing@babcock.com

partners:

University of Cincinnati, First Energy

performance period:

10/1/11 – 4/30/14

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The CO_2-reactive species (there may be other non-reactive species) in the solvent formulation may include amines, carbonates, or amino acid salts in combination with concentrated PZ. Amine solvents are grouped according to their molecular structure. Carbonate and amine reactions with CO_2 can be summarized as follows:

Carbonates: $CO_3^{=} + CO_2 + H_2O \leftrightarrow 2\ HCO_3^-$

Hindered and tertiary amines: $CO_2 + R_3N + H_2O \leftrightarrow HCO_3^- + R_3NH^+$

Primary and secondary amines: $CO_2 + 2R_2NH \leftrightarrow R_2NCOO^- + R_2NH_2^+$

Solvent Contaminant Resistance – Amine solvents chemically degrade in a variety of ways (thermal degradation due to exposure to the high temperatures of the regeneration process, oxidative degradation due the presence of oxygen in the flue gas, carbamate polymerization, etc.). Degradation reactions can be accelerated by the presence of degradation or corrosion products and heat-stable salts, and through the catalytic effects of various metals (possibly originating with the coal fly ash). Minimizing solvent degradation and the attendant production of potentially hazardous chemical species is a central objective of this project.

Flue Gas Pretreatment Requirements – Flue gas supplied to the CO_2 capture system must be cooled to approximately 40°C and relatively free of contaminants. Concentrations of sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) must be less than about 10 parts per million (ppm)—preferably around 1 ppm.

Solvent Makeup Requirements – Solvent makeup is required to offset solvent losses due to volatility, degradation, the formation of heat stable salts, etc. PZ-based solvents are expected to minimize such losses due to the lower volatility and better resistance to thermal degradation exhibited by PZ relative to solvents such as monoethanolamine (MEA). This project is focused on minimizing solvent losses in the system.

Waste Streams Generated – Waste streams generated by the process will be similar to those generated by convention amine processes, including reclaimer waste solids, spent carbon and particulate filter cake from solvent filtration equipment, and potentially waste water. It is an objective of this project to minimize the environmental impact of these streams through careful selection of the solvent formulation and operating conditions.

Process Design Concept – The CO_2 capture process, illustrated in Figure 2, comprises a relatively conventional absorption/stripping process.

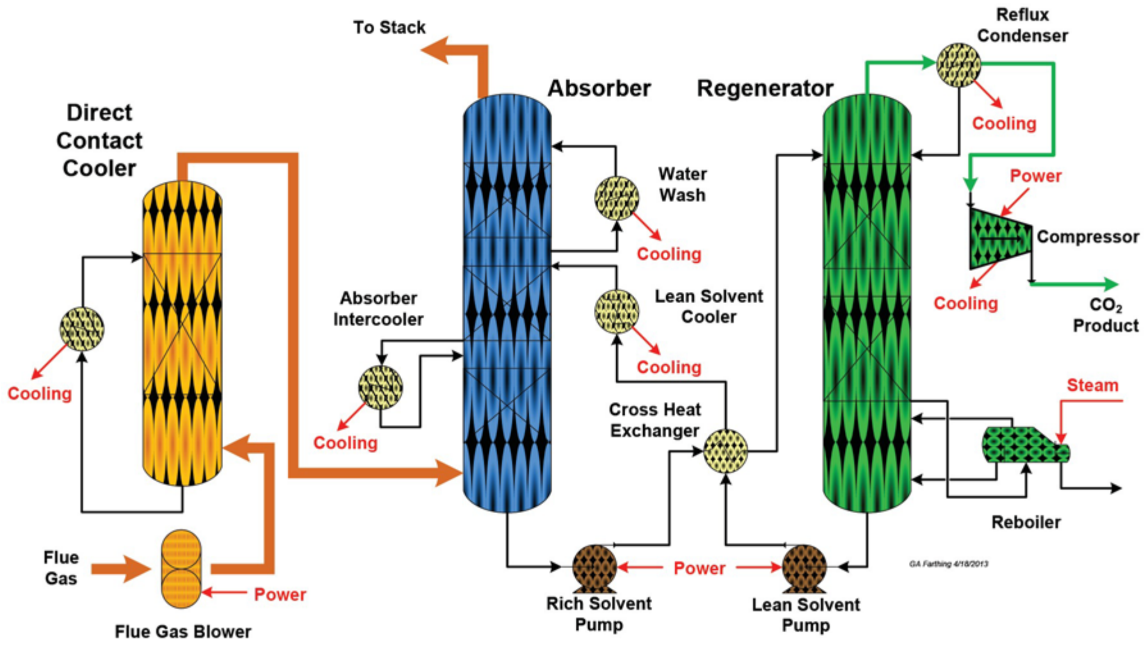

Figure 2: Schematic of Solvent-Based CO_2 Capture Process

technology advantages

Piperazine, used alone, has demonstrated high rates of absorption and low regeneration energy. Recent testing at B&W indicates that blends of concentrated PZ with other organic compounds may perform substantially better than PZ alone.

R&D challenges

- Selection of a solvent formulation involves compromises that seek to optimally balance competing effects. Using limited and potentially non-representative data generated in laboratory-scale equipment is extremely challenging. Previous solvent development work supports correlation of laboratory results with pilot-scale performance estimation to optimize solvent formulation.
- Goals include improved system operability and reliability, minimizing environmental impacts, reducing corrosion potential, and maximizing solvent durability.

results to date/accomplishments

- A list of candidate solvent formulations was developed and refined. This work comprised evaluations regarding overall solvent performance criteria, identification of primary active components, and verification of wet chemistry analytical techniques for CO_2 loading and alkalinity.
- Several modeling approaches were identified. Tools considered include equilibrium models, semi-empirical rate-based models, and rigorous rate-based models. Tools for the prediction of process economics were also evaluated.
- Characterization tests in B&W's wetted-wall column (WWC) were completed on a baseline concentrated PZ solvent and 12 candidate solvent formulations. The liquid film mass transfer coefficient (kg), as well as equilibrium partial pressure of CO_2 (P_{CO2}*), were obtained from each WWC test. Other parameters, such as heat of absorption and CO_2 working capacity, were also derived from these experimental data. Preliminary solvent formulation performance was then estimated with in-house, semi-empirical models.
- Solvent volatility and solubility testing was performed on several candidate formulations of concentrated PZ solutions containing salts of amino acids, carbonates, and other amines. Also evaluated were organic additives designed to improve the solubility of PZ and its carbamates. In addition, it was found necessary to characterize candidate formulations with respect to their viscosities in order to ensure good mass transfer performance and acceptable operability.
- Installation of the bench-scale continuous solvent degradation system (CSDS) was completed. The CSDS will enable comprehensive investigations of proposed solvent formulation degradation under representative operating conditions. It is intended to simulate key features of industrial CO_2 capture processes, including cyclical absorption and regeneration process conditions. The CSDS is designed for continuous, unattended operation for tests lasting 100 to 1,000 hours or more.

next steps

This project ended on April 30, 2013.

available reports/technical papers/presentations

Final Report, "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," June 2014. *http://www.osti.gov/scitech/servlets/purl/1136527*.

Farthing, G., "Optimized Solvent for Energy-Efficient, Environmentally Friendly Capture of CO_2 at Coal-Fired Power Plants," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

BENCH-SCALE DEVELOPMENT OF A HOT CARBONATE ABSORPTION PROCESS WITH CRYSTALLIZATION-ENABLED HIGH-PRESSURE STRIPPING FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

The University of Illinois at Urbana-Champaign (UIUC) is performing a proof-of-concept study that will generate process engineering and scaleup data to optimize the Hot Carbonate Absorption Process (Hot-CAP) with crystallization-enabled, high-pressure stripping technology. The study seeks to demonstrate its capability to achieve the U.S. Department of Energy (DOE) goals of at least 90 percent carbon dioxide (CO_2) removal from coal-fired power plant flue gas with less than a 35 percent increase in the cost of electricity (COE), helping to advance the process to pilot-scale level within 3 years.

technical goals

- Perform laboratory- and bench-scale tests to measure thermodynamic and reaction engineering data that will be used to evaluate technical feasibility and cost-effectiveness, performance of scaleup, and commercial competitiveness of the Hot-CAP with monoethanolamine (MEA)-based processes and other emerging post-combustion CO_2 capture technologies.
- Perform a combination of experimental, modeling, process simulation, and technical and economic analysis studies.

technical content

UIUC and Carbon Capture Scientific, LLC are investigating a Hot-CAP to overcome the energy use disadvantage of MEA-based processes. A preliminary technical-economic evaluation shows that the energy use of the Hot-CAP is about 40 percent less than that of its MEA counterpart, and the process has the potential to meet or exceed DOE's technical and cost goals of greater than or equal to 90 percent CO_2 removal and less than or equal to a 35 percent increase in the COE.

The Hot-CAP is an absorption-based, post-combustion CO_2 technology that uses a carbonate salt (K_2CO_3 or Na_2CO_3) as a solvent. The process integrates a high-temperature (70–80 °C) CO_2 absorption column, a slurry-based high-pressure (up to 40 atm) CO_2 stripping column, a crystallization unit to separate bicarbonate and recover the carbonate solvent, and a reclaimer to recover $CaSO_4$ as the byproduct of the sulfur dioxide (SO_2) removal.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping

participant:

University of Illinois at Urbana-Champaign

project number:

FE0004360

NETL project manager:

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principal investigator:

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partners:

Carbon Capture Scientific, LLC

performance period:

1/1/11 – 3/31/14

Project objectives include performing a proof-of-concept study aimed at generating process engineering and scaleup data to help advance the Hot-CAP technology to pilot-scale demonstration level. The project tasks employ lab- and bench-scale test facilities to measure thermodynamic and reaction engineering data that can help evaluate technical feasibility and cost-effectiveness, performance of scaleup, and commercial competitiveness of the Hot-CAP compared to the MEA-based processes and other emerging post-combustion CO_2 capture technologies.

To meet project objectives, lab- and bench-scale tests include measurement of the kinetics and phase equilibrium data associated with the major reactions and unit operations in the Hot-CAP, including CO_2 absorption, bicarbonate crystallization, sulfate recovery, and CO_2 stripping. The results from the lab- and bench-scale studies support development of a process flow diagram, equipment and process simulations, and a techno-economic study for a conceptual 550-MWe high-sulfur coal-fired power plant retrofitted with the Hot-CAP.

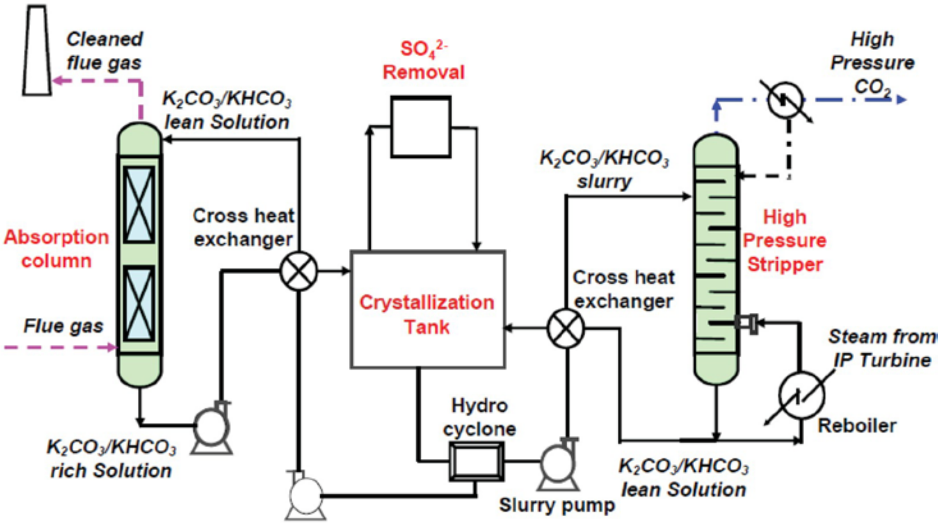

Figure 1: Hot Carbonate Absorption Process with High-Pressure Stripping Enabled by Crystallization (Hot-CAP)—Process Flow Diagram

TABLE 1: PROCESS PARAMETERS FOR CARBONATE SALT SOLVENT
(based on 40 wt% [K_2CO_3 equivalent] $K_2CO_3/KHCO_3$ solution)

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	138 g/mol	N/A
Normal Boiling Point	°C	105–115 (depending on % K_2CO_3 to $KHCO_3$ conversion, i.e., CO_2 loading)	N/A
Normal Freezing Point	°C	<0 (estimated)	N/A
Vapor Pressure at 15 °C	bar	N/A (not volatile)	N/A
Manufacturing Cost for Solvent	$/kg	0.4–1.0 (dry, pure K_2CO_3)	0.8
Working Solution			
Concentration	kg/kg	0.4	0.4
Specific Gravity (15 °C/15 °C)	—	1.42	N/A
Specific Heat Capacity at STP	kJ/kg-K	2.72	N/A
Viscosity at STP	cP	5.1	N/A
Absorption (Rich Solution at Bottom)			
Pressure (CO_2 partial)	bar	0.09 (1.32 psia)	<0.1
Temperature	°C	60–80	60–80
Equilibrium CO_2 Loading	mol/mol	0.4–0.45	0.4–0.45
Heat of Absorption	kJ/kg CO_2	609	609
Solution Viscosity	cP	1.5	N/A

TABLE 1: PROCESS PARAMETERS FOR CARBONATE SALT SOLVENT

(based on 40wt% [K_2CO_3 equivalent] K_2CO_3/$KHCO_3$ solution)

	Units	Current R&D Value	Target R&D Value
Desorption (Lean Solution at Bottom)			
Pressure (CO_2 partial)	bar	0.3-1.7 (4-12 total pressure)	>0.6 (>6 total pressure and CO_2/H_2O>3:1)
Temperature	°C	140–200	<200
Equilibrium CO_2 Loading	mol/mol	0.20-0.40 (60 wt% slurry concentration)	0.20-0.40
Heat of Desorption	kJ/kg CO_2	600–1,500 (including heat of crystallization)	<1,500
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	1,600,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99%, 10 bar	
Absorber Pressure Drop	bar	0.07 (structured packing)	

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

The overall reaction for CO_2 absorption into potassium carbonate solution at 70–80 °C is:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3$$

The CO_2-rich solution from the absorber is cooled to 30–35 °C to crystallize $KHCO_3$:

$$KHCO_3\ (aq) = KHCO_3(s)$$

The overall reaction for CO_2 stripping using $KHCO_3$ slurry at 140–200 °C is:

$$2KHCO_3 = K_2CO_3 + CO_2 + H_2O$$

Solvent Contaminant Resistance – K_2CO_3 reacts with the flue gas contaminants (e.g., SO_2, nitrogen oxide [NO_x], and hydrogen chloride [HCl]), to form K_2SO_4, KNO_3, and KCl, respectively, resulting in solvent losses if the salts are not reclaimed.

Solvent Foaming Tendency – K_2CO_3/$KHCO_3$ solution itself does not have a foaming problem. If an organic promoter is used, foaming may occur for the K_2CO_3/$KHCO_3$ + promoter solution. However, the foaming tendency is expected to be less severe than the conventional amine-based processes because the promoter concentration is generally low.

Flue Gas Pretreatment Requirements – If an organic promoter is used, pretreatment of the flue gas is required to reduce the concentration of SO_2 to below 30 parts per million by volume (ppmv). If an inorganic promoter or a catalyst is used, flue gas pretreatment can be eliminated by a K_2SO_4 reclamation process under development in this project.

Solvent Makeup Requirements – Stoichiometric loss of K_2CO_3 due to reactions with acidic gases in the flue gas (SO_2, NO_x, etc.) is estimated 1.46 kg K_2CO_3/tonne CO_2 captured based on the assumed 42 ppmv SO_2 and 74 ppmv NO_x in the flue gas exiting a wet flue gas desulfurization (FGD) unit.

If an organic promoter is used, the promoter has tendency to degrade. Since the promoter concentration is low and most of the promoter does not enter the Hot-CAP stripping column, nominal losses due to promoter degradation is estimated to be less than10 percent of that in the conventional MEA-based processes.

Waste Streams Generated – Waste streams include sludge of inorganic salts (e.g., sulfate, nitrate, chloride, etc.) as a result of K_2CO_3/$KHCO_3$ reactions with acid gases in the flue gas and liquid blowdown from the process to avoid accumulation of chlorine, metals, etc.

Process Design Concept – Shown in Figure 2 below.

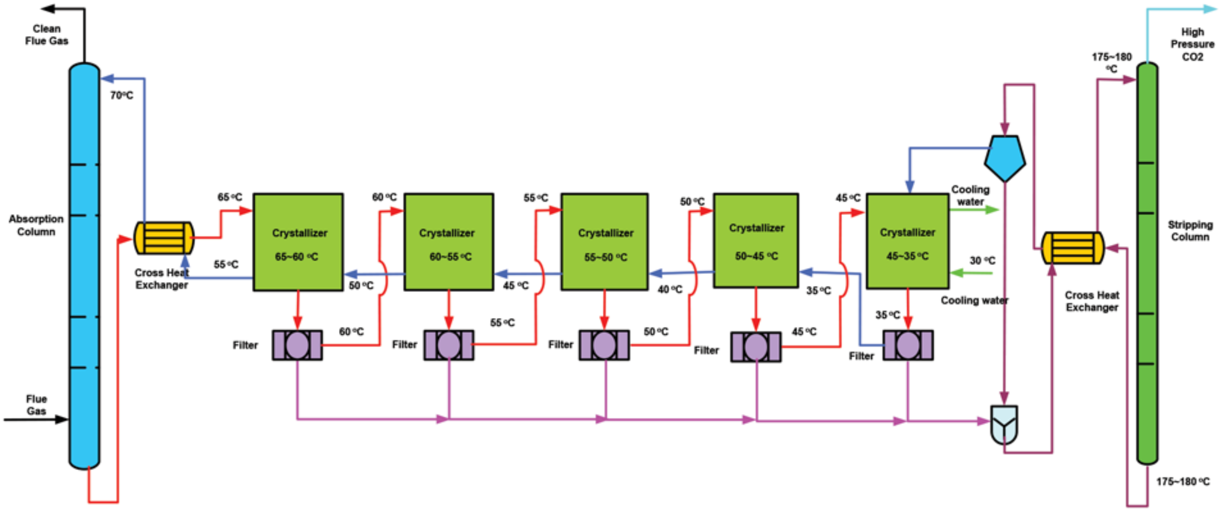

Figure 2: Process Design Concept

technology advantages

- High stripping pressure, which equates to low compression work and low stripping heat (high CO_2/H_2O ratio).
- Low sensible heat as a result of higher working capacity and lower Cp (1/2) compared with MEA.
- Low heat of absorption: 7–17 kcal/mol CO_2 (crystallization heat included) versus 21 kcal/mol for MEA.
- Increased absorption rate by employing high K_2CO_3 concentration and high absorption temperature.
- FGD may be eliminated.
- No degradation of the carbonate solution and low degradation of the promoter.
- Low-cost solvent.
- Less corrosiveness.

R&D challenges

- Identifying favorable process conditions and promoters/catalysts for achieving fast absorption kinetics in carbonate solution.
- Identifying process conditions and solution properties for achieving a fast crystallization rate and a desirable crystal size for solid separation.
- Identifying process conditions for potassium bicarbonate slurry to achieve stripping pressure ≥6 bar.
- Identifying process conditions for >95 percent SO_2 removal and continuous reclamation of the sulfate.
- Identifying risk mitigation strategies to prevent fouling on surfaces of heat exchangers and crystallizers due to bicarbonate crystallization.

results to date/accomplishments

- Three inorganic catalysts and five amine and three amino acid salt promoters were evaluated using a batch-stirred tank reactor.
- A bench-scale, packed-bed column was designed and fabricated to investigate the kinetics, mass transfer, and hydrodynamic performance of CO_2 absorption. Absorption column tests revealed that CO_2 removal efficiency by 40 wt% $K_2CO_3/KHCO_3$ solution promoted by either of two selected promoters at 70 °C was higher than that of the counterpart 5M MEA solution at 50 °C at the CO_2 loading levels typical of the two processes.
- Absorption column tests also showed that $KHCO_3$ precipitation could occur when the CO_2 loading reached a level equivalent to 40–45 percent of K_2CO_3 conversion. However, the accumulation of precipitates in the solution did not result in a pronounced decrease in CO_2 removal efficiency.
- Mixed suspension-mixed product removal (MSMPR) crystallization tests revealed that pure $KHCO_3$ crystals could be obtained and the crystallization of $KHCO_3$ was kinetically fast and a residence time of as few as 15 minutes was sufficient to obtain large crystal particles (>80 µm) required for efficient solid-liquid separation.
- Vapor Liquid Equilibrium (VLE) measurements for concentrated $KHCO_3/K_2CO_3$ aqueous systems with high levels of K_2CO_3 conversion at temperatures of 140–200 °C revealed the thermodynamic feasibility of high-pressure stripping (achieving both a high total pressure and a low H_2O/CO_2 pressure ratio).
- Parametric tests of reclaiming the potassium sulfate desulfurization byproduct were performed and results provided guidance for developing a modified process concept for the combined SO_2 removal and CO_2 capture. The feasibility of the modified process was preliminarily demonstrated. A bench-scale, packed-bed stripping column with a temperature rating of 200 °C and pressure rating of 500 pounds per square inch absolute (psia) was fabricated and installed at the UIUC laboratory.
- Parametric testing of high-pressure CO_2 stripping with concentrated bicarbonate-dominant slurries at high temperatures (≥140 °C) in the bench-scale stripping column demonstrated lower heat use than with MEA. For example, it was observed that compared with the 5 M MEA solution at 120 °C, the heat duty for CO_2 stripping at 160 °C from the 30 to 50 wt% $KHCO_3/K_2CO_3$ feed solutions with the CO_2 loading equivalent to 80 percent of carbonate conversation was two-to-three times lower.

- In addition to the experimental studies, the technical challenges pertinent to fouling of slurry-handling equipment and the design of the crystallizer and stripper were addressed through consultation with vendors and engineering analyses.
- A techno-economic analysis for the baseline Hot-CAP integrated with a 550-MWe power plant showed that the net power produced in the PC + Hot-CAP is 609 MWe, greater than the PC + MEA (550 MWe). The LCOE (levelized cost of electricity) increase for the Hot-CAP, including CO_2 transportation and storage, incurs a 60 percent increase over the base PC plant without CO_2 capture. The LCOE increase caused by the Hot-CAP is 29 percent lower than that for MEA.

next steps

This project ended on March 31, 2014.

available reports/technical papers/presentations

Shihan Zhang, Xinhuai Ye, Yongqi Lu. Development of a Potassium Carbonate-based Absorption Process with Crystallization-enabled High-pressure Stripping for CO_2 Capture: Vapor–liquid Equilibrium Behavior and CO_2 Stripping Performance of Carbonate/Bicarbonate Aqueous Systems. *Energy Procedia* 2014, 63: 665-675.

Final Report, “Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High-Pressure Stripping for Post-Combustion CO_2 Capture,” April 2014.

Final Project Review Presentation, May 2014.

Lu, Y., O’Brien K.; and Chen, S., “Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture,” presented at the Project Review Meeting, Pittsburgh, PA, February 15, 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/HotCAP-review-meeting-021513.pdf*.

Lu, Y., “Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture,” 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/Y%20Lu-ISGS-Hot%20CAP.pdf*.

Lu, Y., “Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion CO_2 Capture,” 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

DEVELOPMENT OF CHEMICAL ADDITIVES FOR CO_2 CAPTURE COST REDUCTION

primary project goals

Lawrence Berkeley National Laboratory (LBNL) is investigating a novel mixed solvent system that integrates amine-based, potassium-based, and ammonia-based solvents to provide benefits of three systems while avoiding many of their drawbacks.

technical goals

- Develop chemical additives for solvent systems to reduce the cost of post-combustion capture of carbon dioxide (CO_2).
- Determine the optimal process configuration and operating condition for the transfer of CO_2 in amine solvent to potassium carbonate (K_2CO_3), and then to an ammonium species, resulting in the production of NH_4HCO_3.

technical content

The new solvent system uses a novel solvent transfer approach after the capture of CO_2 from flue gas. Using this approach, the energy demand and the capital cost of solvent regeneration are expected to be significantly reduced compared to the monoethanolamine (MEA) system.

An aqueous solution of amine is used as an absorbent to facilitate favorable CO_2 absorption kinetics. The amine is chosen such that the CO_2 absorbed in an absorber can be readily transferred to potassium carbonate (K_2CO_3) in a recirculation tank to produce $KHCO_3$ solids. Subsequently, $KHCO_3$ solids enter into a regenerator by gravitation, where it reacts with an ammonia catalyst to regenerate K_2CO_3 for reuse and generate a concentrated CO_2 stream suitable for sequestration.

The approach contains the benefits of three solvent systems: amine, K_2CO_3 and ammonia systems. The benefits are: (1) amine's fast CO_2 absorption kinetics; (2) K_2CO_3 and ammonium species' low reagent cost, high chemical stability, and small heat capacity; and (3) ammonium bicarbonate's low decomposition temperature, fast decomposition kinetics, and amenable for high-pressure CO_2 production. The employment of solids significantly reduces the sensible and latent heat consumed by water in solvent regeneration. The low decomposition temperature of ammonium bicarbonate enables waste heat and/or low-quality steam to be used for the production of concentrated CO_2 gas.

technology maturity:
Bench-Scale, Simulated Flue Gas

project focus:
Chemical Additives for CO_2 Capture

participant:
Lawrence Berkeley National Laboratory

project number:
FWP-ED33EE

NETL project manager:
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partners:
N/A

performance period:
6/1/08 – 5/31/13

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	100–212	100–212
Normal Boiling Point	°C	165–252	165–252
Normal Freezing Point	°C	(-50)–28	(-50)–28
Vapor Pressure at 15 °C	bar	0–0.0013	0–0.0013
Manufacturing Cost for Solvent	$/kg	30–250	30–250
Working Solution			
Concentration	kg/kg	0.3–0.6	0.3–0.6
Specific Gravity (15 °C/15 °C)	-	0.9–1.7	0.9–1.7
Specific Heat Capacity at STP	kJ/kg-K	3–4	3–4
Viscosity at STP	cP	20–40	20–40
Absorption			
Pressure	bar	1.01	1–1.5
Temperature	°C	40–70	30–80
Equilibrium CO_2 Loading	mol/mol	0.7–0.9	0.7–0.9
Heat of Absorption	kJ/mol CO_2	65–75	65–75
Solution Viscosity	cP	10–15	10–15
Desorption			
Pressure	bar	2.7	1–75
Temperature	°C	80–120	80–300
Equilibrium CO_2 Loading	mol/mol	0.4–0.6	0.4–0.6
Heat of Desorption	kJ/mol CO_2	85–92	85–92
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 99%, 75 bar	
Absorber Pressure Drop	bar		

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

Absorber: $\text{Amine} + CO_2 \leftrightarrow \text{Amine-}CO_2$

Recirculation tank: $\text{Amine-}CO_2 + K_2CO_3 + H_2O \leftrightarrow \text{Amine} + 2\ KHCO_3\downarrow$

Regenerator: $2\ KHCO_3 + (NH_4+) \rightarrow K_2CO_3 + H_2O + CO_2\uparrow + (NH_4+)$

Solvent Contaminant Resistance – Sulfur dioxide (SO_2) has little impact to the amine. The amine is regenerated by chemical rather than thermal methods. The amine employed should be much more resistant to oxygen (O_2) and nitrogen oxides (NO_x) than MEA. Nevertheless, the reaction kinetics and products of O_2 and NO_x with amine need to be investigated.

Solvent Foaming Tendency – Solvent foaming was not observed in laboratory experiments.

Flue Gas Pretreatment Requirements – Flue gas from coal-fired power plants equipped with conventional pollution control systems does not require additional pretreatment. Residual SO_2 after dissolution can be separated from the liquid stream as K_2SO_3/K_2SO_4 precipitates. The formation of heat-stable salts with amine should not be an issue, as amine is regenerated by chemical rather than thermal methods involving steam.

Solvent Makeup Requirements – Amine is confined in the low-temperature absorber and recirculation tank loop. As a result, the thermal degradation, chemical degradation (due to the reactions with flue gas trace constituents), and emission loss (due to the volatility) are expected to be insignificant compared to the benchmark MEA process. Absorber is not expected to exhibit a plugging problem resulting in operation breakdown and reagent loss as $KHCO_3$ solid is produced in the recirculation tank located above the K_2CO_3 regeneration tank (i.e., the stripper). A long-term integration test that lasts a significant number of hours will be needed to determine the amine's makeup requirements. $KHCO_3$ and K_2CO_3 are stable chemicals and do not degrade under high-temperature operation in the regenerator.

Waste Streams Generated – Waste streams from the absorber/recirculation tank low-temperature loop may contain trace amount of fly ash, dissolved NO_x, and amine degradation products. Waste streams from the stripper are expected to contain K_2SO_3 and K_2SO_4, if SO_2 polishing is not equipped ahead of the CO_2 capture system.

Process Design Concept – Shown in Figure 1 below.

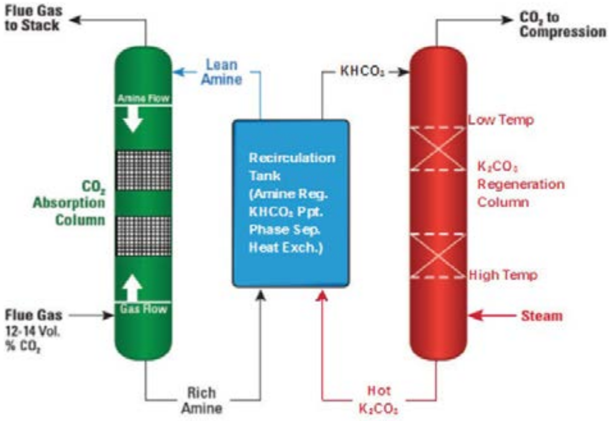

Figure 1: Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bar, temperature is 57 °C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Possession of high-CO_2 absorption kinetics, resulting in an acceptable absorber capital cost.
- Reduction of processing water, resulting in reduced solvent regeneration energy demands.
- Employment of low-heat capacity $KHCO_3$/K_2CO_3, resulting in reduced sensible heat demands.
- Reduction of reagent loss and equipment corrosion, resulting in reduced operation costs.
- Reduction of emission as $KHCO_3$ can be treated at high temperature without any emissions of heat degradable harmful products.
- Reduction of CO_2 compression ratio, resulting in reduced CO_2 compression energy and compressor capital costs.

R&D challenges

- Development of a new system for the transfer of $KHCO_3$ solid from the recirculation tank to the stripper by the gravitation method and with pressurized steam.
- Determination of the optimal operation condition to regenerate K_2CO_3 and to produce high pressure CO_2 gas for enhanced oil recovery (EOR) or methanol production.

results to date/accomplishments

- Evaluated more than 50 amines and amino acid salts for CO_2 absorption amenable for the new solvent regeneration approach.
- Compared relative CO_2 absorption efficiencies of various lean amines regenerated by chemical methods.

- Investigated conditions required for phase separation and determined phase diagrams following chemical regeneration of lean amine in the recirculation tank in attempt to understand its chemical and physical behaviors.
- Elucidated the kinetics and mechanisms of CO_2 absorption and chemical regeneration involved in the new solvent system.
- Constructed a stripper system equipped with a calorimeter for the determination of K_2CO_3 regeneration rates and energy demands. Preliminary results indicated that K_2CO_3 regeneration energy demand was 2,079 kJ/kg CO_2 at steady-state conditions, which is approximately 40 percent less than that of MEA.
- Performed a semi-continuous integration test encompassing CO_2 absorption in the absorber, amine regeneration in the recirculation tank, and K_2CO_3 regeneration and CO_2 production in the stripper.
- Performed mass and water balances, and developed a stream table of the bench-scale new solvent system.

next steps

Project completed May 31, 2013.

available reports/technical papers/presentations

“Developing Chemical Additives for Aqueous Ammonia to Reduce CO_2 Capture Cost,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants Meeting, Pittsburgh, PA, March 2009.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/monday/Ted%20Chang-LBNL.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/CO2capture/presentations/2-Tuesday/23Aug11-Chang-LBNL-Additives%20for%20Reducing%20CO2%20Capture%20Costs.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2012. *http://www.netl.doe.gov/publications/proceedings/12/CO2capture/presentations/2-Tuesday/T%20Chang-LBNL-Additives.pdf*.

“Development of Chemical Additives for CO_2 Capture Cost Reduction,” presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/events/2013/CO2%20capture/Y-Li-LBNL-Additives-for-Reducing-CO2-Capture-Costs.pdf*.

POST-COMBUSTION CO_2 CAPTURE FOR EXISTING PC BOILERS BY SELF-CONCENTRATING AMINE ABSORBENT

primary project goals

3H Company set out to experimentally and analytically confirm the feasibility of the proposed Self-Concentrating Absorbent CO_2 Capture Process, with the goal of developing a sound engineering design, supported by laboratory data and economic justification, for a flue gas slipstream-testing unit.

technical goals

- Perform laboratory screening experiments to identify different absorbent/solvent combinations that can exhibit the "self-concentrating" carbon dioxide (CO_2) absorption effect, and conduct fundamental absorption/regeneration rates and physical and chemical property measurements to allow its process design and techno-economic feasibility to be evaluated.
- Conduct experiments to demonstrate the process under dynamic column testing conditions and to develop a process design package for a slipstream testing facility.

technical content

This project examined an innovative and proprietary CO_2 capture technology developed by 3H Company. The process is based on amine and/or other chemical absorbents in a non-aqueous solvent that can phase separate into a distinct CO_2-rich liquid phase upon reaction with CO_2. The process was demonstrated using commercially available amines and solvents. The technology has the potential of not only greatly reducing the energy penalty associated with regeneration compared to conventional monoethanolamine (MEA)-based processes, but it can also increase the amine CO_2 absorption rate. Preliminary experimental data shows that the proposed Self-Concentrating Amine Absorbent process has the potential of reducing the total regeneration energy by as much as 70 percent.

The technology removes CO_2 from power plant flue gas, using an absorbent (e.g., amine or special designed chemical species) and a matched solvent, which rapidly forms two immiscible liquid phases upon absorbing CO_2 (Figure 1). The process has been demonstrated in the laboratory for a number of specific amine/solvent pairs. The solvents employed are non-aqueous. The novelty of the concept rests on the duel hydrophobic/hydrophilic functionality of the CO_2 absorbents (e.g., amine), the stability of the "CO_2-rich" reaction product, and its solubility behavior within the non-aqueous solvent system employed. When an amine is used as the CO_2 absorbent, it is reasonable to assume that the chemistry follows that for an aqueous-based system. However, in the presence of a Self-Concentrating Solvent, the CO_2:amine reaction forms a stable product that can be solvated in higher concentration within the solvent system. The chemistry and mechanism of the process requires additional research and development (R&D).

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

CO_2 Capture with Self-Concentrating Amine Absorbent

participant:

3H Company

project number:

FE0004274

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partners:

Nexant, Inc.
LG&E and KU Energy LLC
EPRI

performance period:

10/1/10 – 1/31/13

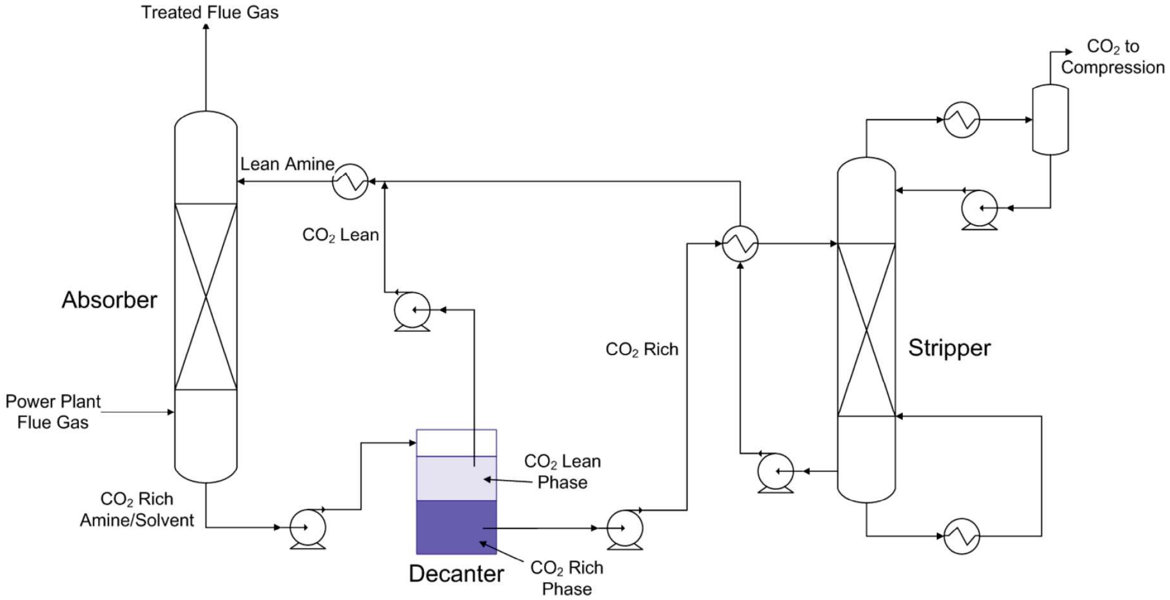

Figure 1: Concept of the Proposed Self-Concentrating Amine Absorbent Process

Conventional 30 wt% MEA-based CO_2 capture is considered to be the benchmark for performance. A typical heat of regeneration for a 30 percent MEA CO_2 capture process is about 1,934 Btu/lb CO_2, as cited in the literature, and only about 1/3 of the regeneration energy is used to break the amine:CO_2 bonds. Minimizing the overall heat of regeneration by using a unique absorbent/solvent system is the key to the Self-Concentrating Absorbent process. Figure 2 shows a flow scheme for the concept, using amine as the CO_2 absorbent. The flow scheme is similar to a conventional MEA process, with the exception that a decanter is incorporated downstream of the absorber to allow the "rich CO_2 liquid" to be fully phase separated before sending it onto the stripper. Only the "rich CO_2 liquid" is subjected to regeneration, at a significant reduced volume as compared to a conventional MEA process. Overall, a 70 percent reduction in heat of regeneration can be achieved with the Self-Concentrating Absorbent process, taking into consideration that (1) only the "rich CO_2/solvent liquid" will be sent onto regeneration with minimum excess solvent, and (2) the solvent has a lower heat capacity and heat of vaporization than water. Because the process uses a non-aqueous system, many of the problems associated with MEA, including degradation due to corrosion, oxygen degradation, and the formation of stable salts, are expected to be mitigated. These types of effects, along with the potential environmental emissions and health problems associated with the use of the non-aqueous process, will need to be investigated in more detail.

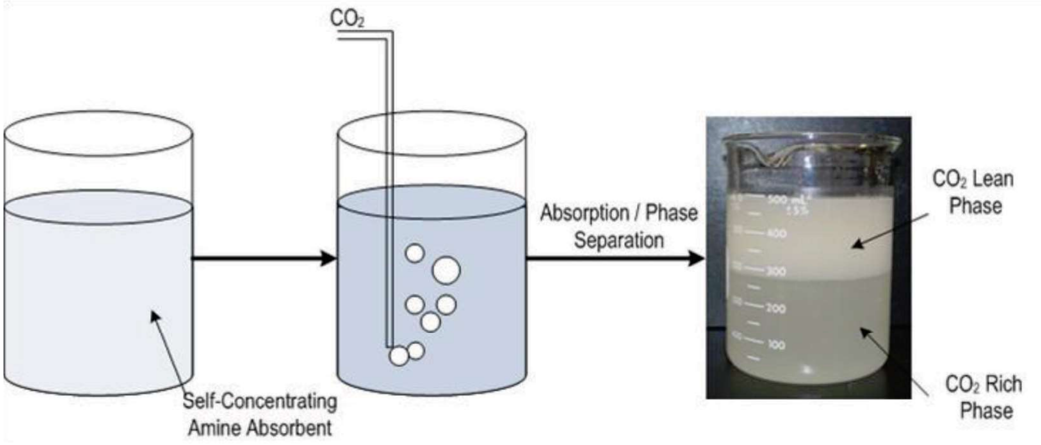

Figure 2: Simplified Flow Scheme of the Proposal Self-Concentrating Amine Absorbent Concept

technology advantages

- Lower regeneration energy requirements.
- Minimal degradation due to corrosion, oxygen degradation, and the formation of stable salts.

R&D challenges

- The chemistry, kinetics, and mass-transfer characteristics governing the diffusion of CO_2 into the liquid phase where it reacts with amine within the non-aqueous solvent, etc., are unknown.
- The self-concentrating process involves the phase separation of the "CO_2 rich" reaction product from the solvent system, of which its stability, composition, phase behavior, thermodynamic miscibility, and solubility limit are unknown.
- It is necessary to develop some basic theoretical and mechanistic understanding of the process so that R&D will not have to be based purely on an empirical approach.

results to date/accomplishments

- Completed preliminary system analysis and process design study comparing the 3H process to 30 percent MEA.
- Completed bench-scale screening, property measurement, and testing to identify all four promising Self-Concentrating Absorbent/Solvent pairs for more detailed characterization and evaluation.
- Completed down-selection to two promising Self-Concentrating Absorbent/Solvent pairs and commenced detailed characterization and analysis of these two final absorbent/solvent pairs.

next steps

This project ended on January 31, 2013.

available reports/technical papers/presentations

Hu, L., "Post-Combustion CO_2 Capture for Existing PC Boilers by Self-Concentrating Absorbent," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2012. *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/L%20Hu-%203H%20Company-Self-concentrating%20Absorbent.pdf*.

IONIC LIQUIDS: BREAKTHROUGH ABSORPTION TECHNOLOGY FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

The University of Notre Dame set out to develop a new ionic liquid (IL) solvent capture process resulting in a small increase in cost of electricity (COE) compared to currently available capture technologies by overcoming viscosity and capacity issues impacting cost and performance of ILs via "proof-of-concept" exploration and laboratory-/bench-scale testing of a variety of IL formulations.

technical goals

- Design and synthesize one or more IL absorbents tailored for post-combustion carbon dioxide (CO_2) capture.
- Perform atomistic-level classical and quantum calculations to engineer IL structures maximizing CO_2 carrying capacity with minimal regeneration costs.
- Measure or accurately estimate all physical solvent properties essential for detailed engineering and design calculations:
    - Gas solubility, viscosity, heat of absorption, heat capacity, mass transfer coefficients, thermal decomposition, chemical stability, and corrosivity.
- Complete detailed systems and economic analysis.
- Demonstrate CO_2 capture technology on a continuous lab-scale unit.

technical content

ILs are salts that are liquid at room temperature. They are known to have high intrinsic physical solubility for CO_2. Examples of ILs are illustrated in Figure 1.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Ionic Liquids

participant:

University of Notre Dame

project number:

FC26-07NT43091

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partners:

Babcock and Wilcox
DTE
Trimeric Corporation
Koei Chemical

performance period:

2/28/07 – 9/30/12

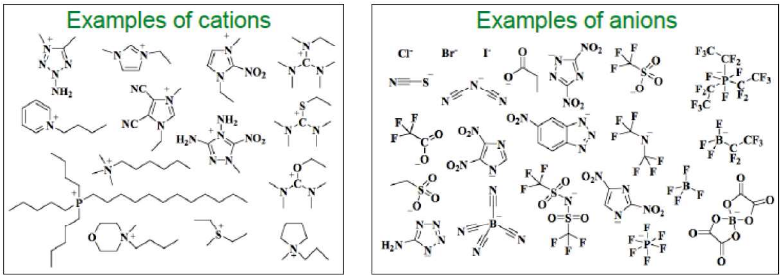

Figure 1: Examples of Ionic Liquids

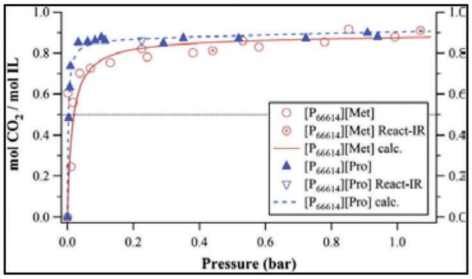

Figure 2: Isotherms confirming 1:1 binding

A close-to-conventional absorber/stripper process is assumed for process modeling and costing. Process simulation has been used to evaluate the sensitivity of a representative 500-MW (gross capacity), coal-fired power plant CO_2 capture process for the properties of ILs. The results were used to guide the development of the next generation of ILs. Salient project details include:

- Anion/cation functionalization: Notre Dame has developed both 1:1 and 2:1 (IL:CO_2) stoichiometries by adding chemical functionality to the anion and cation, respectively. Molecular modeling calculations were used to identify anion-functionalized ILs with minimal increase in solvent viscosity after CO_2 absorption. Two ILs (NDIL0046 and NDIL0157) were identified. NDIL0046 was used for lab-scale experimental tests, and data on NDIL0157 was used for techno-economic analysis.
- Enthalpy of reaction: Process modeling indicated that the binding strength of NDIL0046 needed to be improved, and a new IL (NDIL0157) with optimal enthalpy of reaction and lower heat capacity was identified. Optimal reaction enthalpy leads to higher CO_2 solvent capacities, reduced solvent circulation rate, and lowered sensible heating load.

Results show much lower parasitic energy compared with a monoethanolamine (MEA) system. From techno-economic analysis, it was estimated that the parasitic electricity losses in the reboiler are reduced by 36 percent, compression load increased by 14 percent, and the auxiliary losses in CO_2 capture are lowered by 34 percent. The best-case IL (NDIL0157) has almost the same increase in levelized cost of electricity (LCOE) compared with MEA due to higher capital costs for the CO_2 capture system.

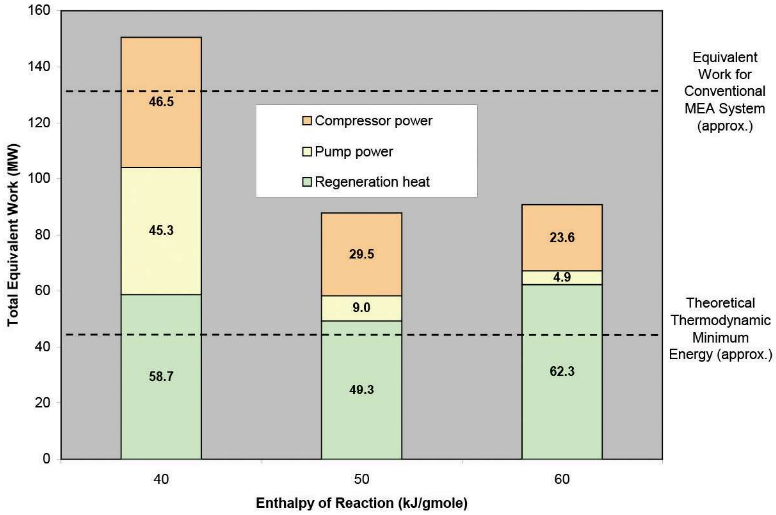

Figure 3: Results from Sensitivity Studies on the Parasitic Power Requirement of Ionic Liquid Solvents

TABLE 1: PROCESS PARAMETERS FOR IONIC LIQUID SOLVENTS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	575	322
Normal Boiling Point	°C	N/A - does not boil	N/A - does not boil
Normal Freezing Point	°C	< -10oC	< -10oC
Vapor Pressure @ 15°C	bar	Essentially zero	Essentially zero
Manufacturing Cost for Solvent	$/kg	$20/kg	< $15/kg
Working Solution			
Concentration	kg/kg	0.998	> 0.9
Specific Gravity (15°C/15°C)	-	0.907	≈1.0
Specific Heat Capacity @ STP	kJ/kg-K	2.25	<2.3
Viscosity @ STP	cP	158 @40 c	< 100
Absorption			
Pressure	bar	1.03	1
Temperature	°C	40-52	40-52
Equilibrium CO_2 Loading	mol/mol	0.167	0.988
Heat of Absorption	kJ/mol CO_2	43	54
Solution Viscosity	cP	129	< 100
Desorption			
Pressure	bar	1.3	1-3
Temperature	°C	120-188	120-204
Equilibrium CO_2 Loading	mol/mol	0.041	0.51
Heat of Desorption	kJ/mol CO_2	43	54
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A	
Adsorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – A 1:1 reaction with CO_2 and the basic group on the anion of the IL.

Solvent Contaminant Resistance – Resistant to air; have not evaluated resistance to other contaminants.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – Flue gas desulfurization (FGD) plus polishing column to get to 10 parts per million (ppm) sulfur oxide (SO_x).

Solvent Make-Up Requirements – 3.15 tons/day for a 550-MW net plant.

Waste Streams Generated – Degraded solvent waste; negligible vapor emissions.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

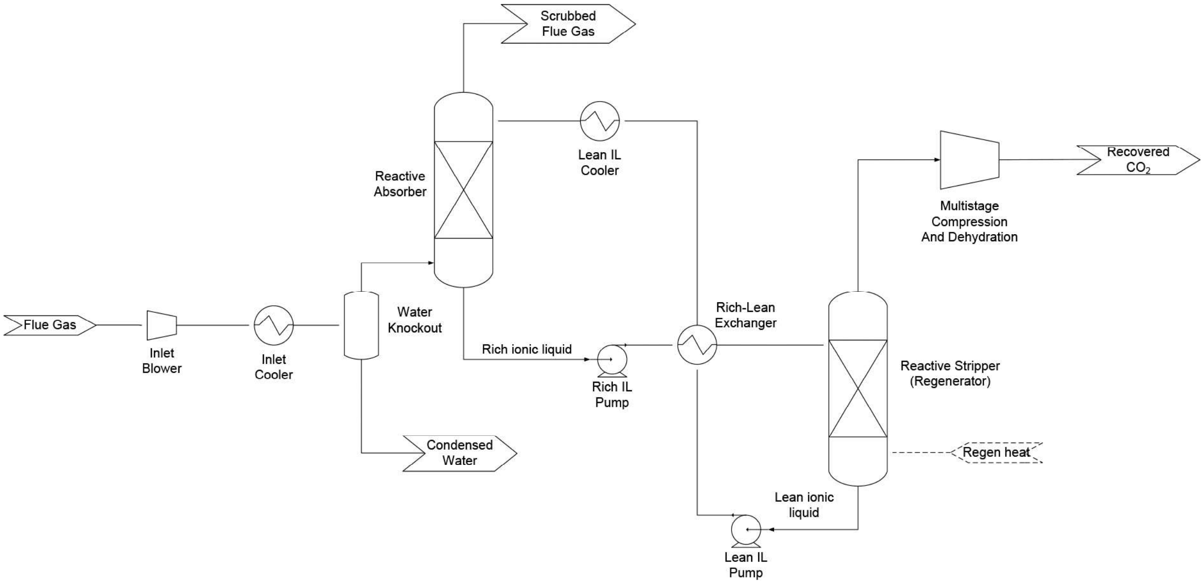

Figure 4: Schematic of Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Low volatility and good thermal stability.
- Wide liquidus range.
- Net-CO_2 uptake by solvent can be varied by tuning the enthalpy of CO_2 absorption (10 to 80 kJ/mol) through a combination of computational methods and experimental synthesis.
- Anhydrous absorption process.
- The viscosity of the current generation of ILs (NDIL0046) does not change significantly with CO_2 absorption.

R&D challenges

- The solvent CO_2 capacity (on a weight basis) should be higher than that for the best-case scenario (NDIL0157) to lower-solvent recirculation rates and reduce absorber costs.
- The effects of water on the corrosion behavior and CO_2 reactivity of the ILs need to be examined in greater detail, though preliminary results show negligible corrosion for NDIL0046 + carbon steel.
- The chemically functionalized IL solvent mass-transfer characteristics/viscosity need to be improved to lower capital and operating costs.
- Low-cost commercial synthesis routes for Generation III ILs are required to lower operating costs.

results to date/accomplishments

All project phases (I, II, and III) are complete. Key accomplishments to date include:

- Discovered and synthesized a new class of non-aqueous ILs reacting with 1:1 stoichiometry, and with no increase in viscosity following CO_2 absorption.
- Developed molecular modeling techniques that enabled the computation of key properties of ILs from first principles, and tuned the binding strength of ILs to optimize process economics.
- Demonstrated that the NDIL0046 IL had significantly lower corrosion rates compared to aqueous MEA, indicating that lower-cost materials could be used for absorber and heat exchangers.
- Techno-economic analysis on the best IL to date (NDIL0157) suggests favorable COE and significantly lower parasitic energy losses compared to aqueous MEA (U.S. Department of Energy [DOE]/National Energy Technology Laboratory [NETL] Baseline Case 12).
- Developed unique experimental techniques, including the ability to monitor the infrared spectrum of the IL as it absorbs CO_2, and then use this information to determine reaction rates and mechanisms.

next steps

The project ended on September 30, 2012. Recommendations for further steps include:

- Scale-up of experiments to the next level using synthetic flue gas and slipstream tests.
- The operating performance of ILs (mass-transfer characteristics, viscosity) would be improved.
- Process chemistry improvements needed to make ILs at tonne-scales for lower cost would be investigated.
- IL toxicity and long-term stability would also be examined.

available reports/technical papers/presentations

M. McCready et al., “Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO_2 Capture,” presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July, 2012. Available at: *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/M%20McCready-Notre%20Dame-Ionic%20Liquids.pdf*.

W. F. Schneider and E. Mindrup, “First-Principles Evaluation of CO_2 Complexation In Functionalized Ionic Liquids,” Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 17-21, 2008.

K. E. Gutowski and E. J. Maginn, “Amine-Functionalized Task Specific Ionic Liquids for CO_2 Capture,” Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 17-21, 2008.

Joan F. Brennecke, “CO_2 Capture – Challenges and Opportunities,” Energy, Citizens and Economic Transformation for Indiana and America, University of Notre Dame, July 7, 2008.

Joan F. Brennecke, Jessica L. Anderson, Alexandre Chapeaux, Devan E. Kestel, Zulema K. Lopez-Castillo, and Juan C. de la Fuente, “Carbon Dioxide Capture Using Ionic Liquids,” 236th ACS National Meeting, Philadelphia, Pennsylvania, August 17, 2008.

E. M. Mindrup and W. F. Schneider, “Comparison of Functionalized Amine Energetics for CO_2 Capture,” poster presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

Wei Shi and E. J. Maginn, “Molecular simulation of pure and mixture gases absorption in ionic liquids,” presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

Wei Shi and E. J. Maginn, “Molecular simulation and regulation solution theory modeling of pure and mixed gas absorption in the ionic liquid 1-n-butyl-3- methylimidazolium Bis(Trifluoromethylsulfonyl)amide ([hmim][Tf2N]),” Journal of Physical Chemistry B, 112(51), 16710-16720.

Fisher, K.S., et al. Advanced Amine Solvent Formulations and Process Integration for Near-Term CO_2 Capture Success. Final Report to DOE/NETL. Grant No. DE-FG02-06ER84625, June 2007.

Christina Myers, Henry Pennline, David Luebke, Jeffery Ilconich, JaNeille Dixon, Edward J. Maginn, and Joan F. Brennecke, “High Temperature Separation of Carbon Dioxide/Hydrogen Mixtures Using Facilitated Supported Liquid Membranes,” Journal of Membrane Science, 2008, 322, 28-31.

Xiaochun Zhang, Feng Huo, Zhiping Liu, Wenchuan Wang, Edward Maginn and Wei Shi, “Absorption of CO_2 in the Ionic Liquid 1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FEP]): A Molecular View by Computer Simulations,” Journal of Physical Chemistry B, 2009, 113, 7591-7598.

Keith Gutowski and Edward J. Maginn, “Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity Upon Complexation with CO_2 from Molecular Simulation,” Journal of the American Chemical Society, 2008, 130, 14690-14704.

E. J. Maginn, Developing New Ionic Liquids for CO_2 Capture: A Success Story for Thermodynamics and Computational Molecular Design, GE Global Research Symposium on Emissions and Aftertreatment, GE Global Research Center, Niskayuna, New York, Sept. 17, 2009.

Marcos Perez-Blanco and Edward J. Maginn, "Molecular Dynamics Simulations of CO_2 at an Ionic Liquid Interface: Adsorption, Ordering and Interfacial Crossing," Journal of Physical Chemistry B (cover article), 2010, 36, 11827.

W. F. Schneider, "Ionic Liquids for CO_2 Capture from First-Principles," CECAM workshop on Carbon Capture, Lausanne, Switzerland, July 26-28, 2010.

W. F. Schneider and E. Mindrup, "AHA! Computational design of aprotic heterocyclic anions for ionic-liquid-based CO_2 separations," Division of Fuel Chemistry, American Chemical Society National Meeting, Boston, Massachusetts, August 22-26, 2010.

Burcu E. Gurkan, Juan C. de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, and Joan F. Brennecke, "Equimolar CO_2 absorption by anion-functionalized ionic liquids," J. Am. Chem. Soc., 132, 2010, 2116-2117.

Burcu E. Gurkan, Juan de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, Edward J. Maginn and Joan F. Brennecke, "Chemically Complexing Ionic Liquids for Post-Combustion CO_2 Capture," Clearwater Clean Coal Conference, Clearwater, FL, June 6-10, 2010.

Edward J. Maginn, "Molecular engineering of new ionic liquid sorbents for CO_2 capture" at the 9th Annual Carbon Capture and Sequestration Meeting, Pittsburgh, Pennsylvania, May 2010.

Edward J. Maginn, Joan F. Brennecke, William F. Schneider, and Mark J. McCready, "Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture," presented at the NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September, 2010.

DEVELOPMENT AND EVALUATION OF A NOVEL INTEGRATED VACUUM CARBONATE ABSORPTION PROCESS

primary project goals

The Illinois State Geological Survey (ISGS) set out to prove the novel Integrated Vacuum Carbonate Absorption Process (IVCAP) concept and further improve the energy efficiency of the process for post-combustion carbon dioxide (CO_2) capture.

technical goals

- Test the proof-of-concept of the IVCAP.
- Identify an effective catalyst for accelerating CO_2 absorption.
- Identify an effective additive for reducing the stripping heat.
- Evaluate a modified IVCAP as a multi-pollutant control process for combined sulfur dioxide (SO_2) and CO_2 capture.

technical content

The proposed IVCAP employs a potassium carbonate (K_2CO_3) aqueous solution for CO_2 absorption. While the absorption takes place at atmospheric pressure, the stripper is operated under a vacuum condition. As seen in Figure 1 and Table 1, the low heat of reaction between CO_2 and K_2CO_3 favors a stripping process operated at a low temperature and the low-quality steam (close to the exhaust end of low-pressure turbine in the power plant) can be used as a heat source for the stripping process as a result.

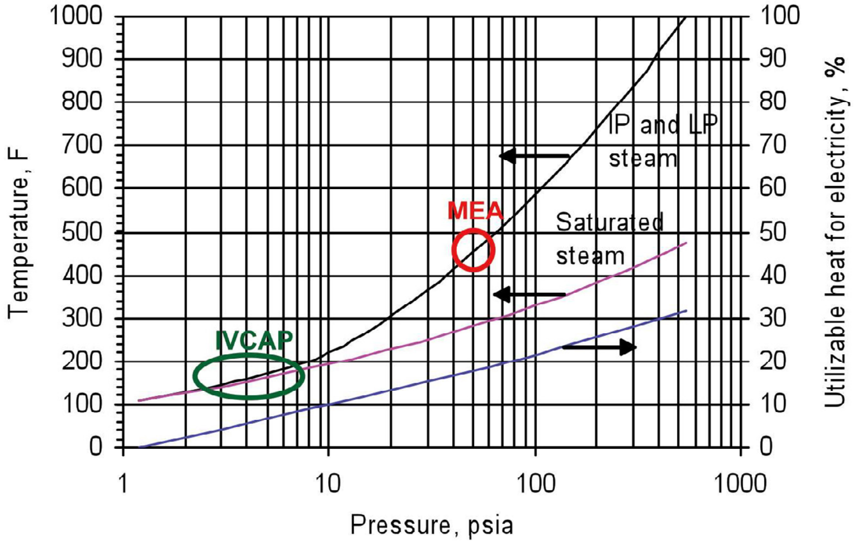

Figure 1: Steam Properties During Expansion in the Intermediate- and Low-Pressure Turbines

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Novel Integrated Vacuum Carbonate Process

participant:

Illinois State Geological Survey

project number:

NT0005498

NETL project manager:

Andrew Jones
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principal investigator:

Yongqi Lu
Illinois State Geological Survey
yongqilu@illinois.edu

partners:

Calgon Carbon Corporation
Illinois Clean Coal Institute
University of Illinois

performance period:

10/1/08 – 4/30/12

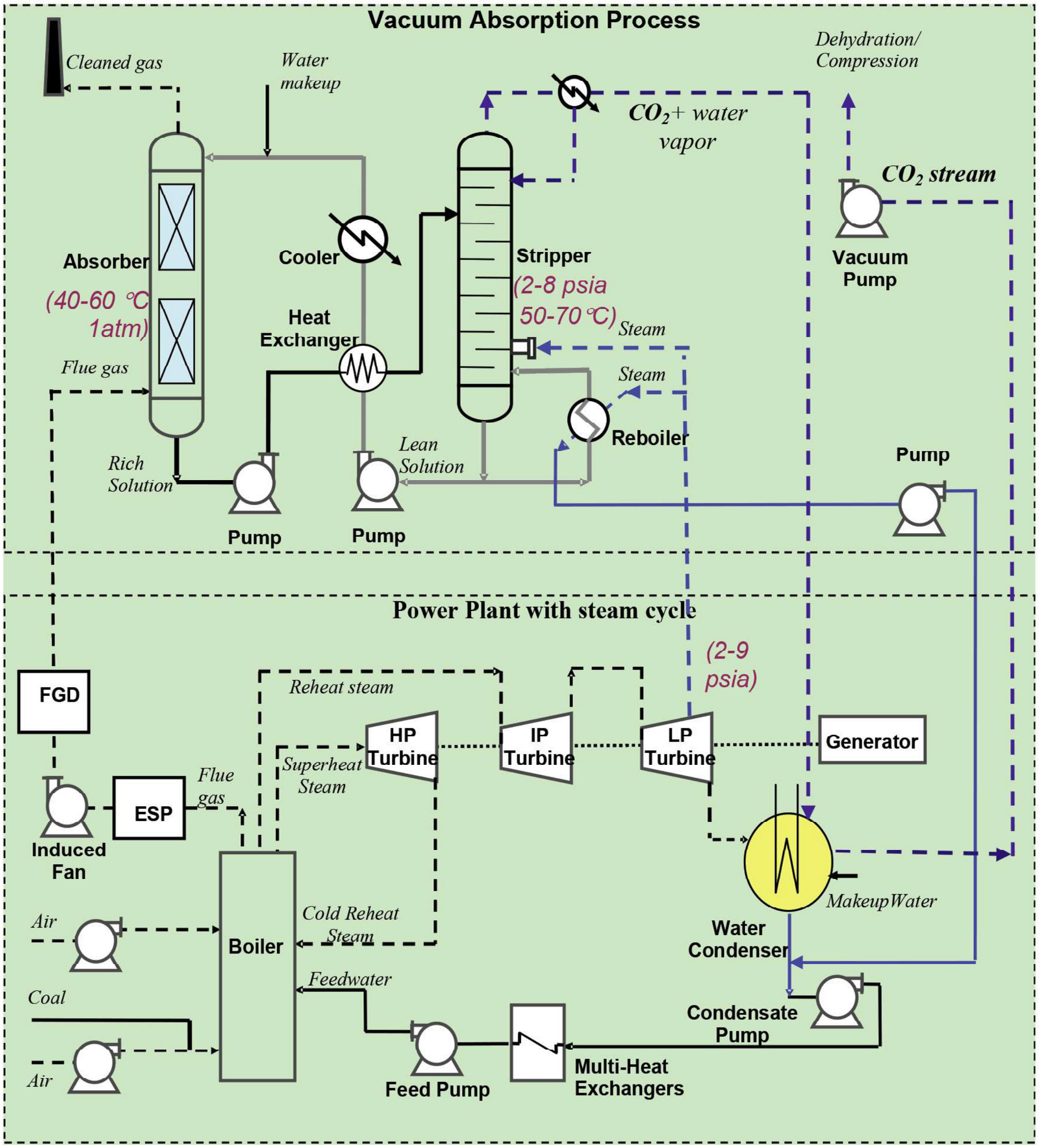

Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low-Quality Steam From the Power Plant

TABLE 1: A COMPARISON OF HEATS OF ABSORPTION FOR CO_2 SOLVENTS

Solvent	Main Reaction	Heat of Absorption
Primary/Secondary Amines	$2RR'NH + CO_2 = RR'NCOO^- + RR'NH_2+$	MEA: 1,900 kJ/kg
Tertiary Amine	$RR'R''N + CO_2 + H_2O = HCO_3^- + RR'R''NH^+$	MDEA: 1,200 kJ/kg
Carbonate	$CO_32- + CO_2 + H_2O = 2 HCO_3^-$	600 kJ/kg

The intrinsic rate of CO_2 absorption into the K_2CO_3 solution is much slower than that in a monoethanolamine (MEA) solution; therefore, enzyme catalysts were developed to promote the absorption rate. Unlike the mixing of another solvent into a primary solvent, a catalyst accelerates the absorption rate without increasing the heat of absorption of the solvent.

The enzyme catalysts will need to be immobilized in order to:

- Reduce enzyme leakage in a flow system.
- Improve chemical stability of enzymes.
- Improve thermal stability of enzymes.

Three supportive matrices (i.e., carbon-, controlled pore glass [CPG]-, and silica-based materials) were evaluated for enzyme immobilization.

Since more than 60 to 70 percent of the process heat in the IVCAP is the stripping heat, an additive able to suppress water vaporization of the CO_2-loaded solution can reduce the stripping heat in the stripper. Successful screening and development of an additive can further reduce the heat use in the IVCAP.

The IVCAP has the flexibility to integrate SO_2 removal in the CO_2 capture process. In the amine-based and amine-promoted absorption processes, the flue gas must be treated to reduce the concentration of SO_2 and other acid gases to below 20 parts per million (ppm) to prevent/minimize the formation of heat-stable salts that are difficult to reclaim. In the IVCAP, SO_2 can be removed by the reaction with the solvent to form a sulfate salt that can be further processed to reclaim the solvent.

TABLE 2: PROCESS PARAMETERS FOR IVCAP PROCESS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	138	N/A
Normal Boiling Point	°C	103	N/A
Normal Freezing Point	°C	≤0	N/A
Vapor Pressure @ 15°C	bar	Not volatile	N/A
Manufacturing Cost for Solvent	$/kg	0.4-1.0	≤0.8
Working Solution			
Concentration	kg/kg	0.2	0.2
Specific Gravity (15°C/15°C)	-	1.24	N/A
Specific Heat Capacity @ STP	kJ/kg-K	3.34	N/A
Viscosity @ STP	cP	1.9	N/A
Absorption (Rich Solution at Bottom)			
Pressure	bar	0.06-0.08 (0.8-1.2 psia)	<0.1
Temperature	°C	40-60	40-60
Equilibrium CO_2 Loading	mol/mol	0.5	0.5
Heat of Absorption	kJ/mol CO_2	600	N/A
Solution Viscosity	cP	0.95 (at 50°C)	N/A
Desorption (Lean Solution at Bottom)			
Pressure (CO_2 equilibrium pressure)	bar	0.007-0.02 (0.1-0.3 psia)	≥0.01
Temperature	°C	50-70	50-70
Equilibrium CO_2 Loading	mol/mol	0.12-0.20	≤0.2
Heat of Desorption	kJ/mol CO_2	600	N/A
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	500,000 (100,000 kg/hr CO_2)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 99%, 0.14–0.54 (prior to vacuum pump)	
Adsorber Pressure Drop	bar	0.04 (structured packing)	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The main reactions involving in the IVCAP include:

CO_2 absorption: $CO_2+H_2O^{+}K_2CO_3 = 2KHCO_3$
Solvent regeneration: $2KHCO_3=K_2CO_3+H_2O^{+}CO_2$

Solvent Contaminant Resistance – Since the potassium carbonate solution is used as a solvent, no solvent degradation and little corrosion problems are expected. The $K_2CO_3/KHCO_3$ solution reacts with the flue gas contaminants (e.g., SO_2, nitrogen oxides [NO_x], hydrogen chloride [HCl], etc.). No SO_2 scrubbing pretreatment is needed prior to the IVCAP, since SO_2 removal can be combined with CO_2 capture and the potassium sulfate desulfurization product can be potentially reclaimed in the IVCAP.

Solvent Foaming Tendency – The $K_2CO_3/KHCO_3$ solution itself does not have a foaming problem. The addition of a carbonic anhydrase (CA) enzyme biocatalyst in the $K_2CO_3/KHCO_3$ solution will not incur a foaming tendency due to its low dosage (<3 g/l) and low contents of impurities.

Flue Gas Pretreatment Requirements – Sulfur dioxide removal can be combined with CO_2 capture in the IVCAP. The carbonate solution absorbs SO_2 to form a sulfate salt, which is reclaimable using a reclamation approach developed in this project. Therefore, a separate flue gas desulfurization (FGD) unit currently required in the power plant can be potentially downsized or even eliminated in the IVCAP. No other flue gas pretreatments (such as for particulate matter [PM], NO_x) are required either.

Solvent Make-Up Requirements – A thermophilic CA enzyme tested in the project demonstrated to be stable at 40°C. At 50°C, the enzyme had a half-life of approximately two months. After immobilization, the thermal stability of the enzyme has been significantly improved. The enzyme also demonstrated excellent chemical stability against the most abundant flue gas impurities. It is estimated that two to three replacements of the enzyme is required annually if the absorption operates at 50°C and 30 percent replacements is required at 40°C.

Waste Streams Generated – Waste streams mainly include the process blowdown streams, such as the carbonate/bicarbonate aqueous solution from the absorber/stripper and water condensate saturated with CO_2.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Uses lower-quality steam than amine-based processes (e.g., MEA), consequently increasing net power output.
- Lower heat of absorption.
- Less energy required for CO_2 stripping.
- Modified IVCAP may be able to remove SO_2 without an FGD unit.
- Approximately 25 percent lower electricity loss.

R&D challenges

- Slow kinetics of CO_2 absorption into the K_2CO_3 solution; thus, a high-activity catalyst is required.
- Potentially large capital and operating cost of the vacuum pump and vacuum stripper.
- Suppressing water vaporization in the stripper.
- Chemical and thermal stability of the absorption enzymes.

results to date/accomplishments

- Reactivity tests of two CA enzymes (ACA1 and ACA2) from a leading enzyme manufacturer and eight inorganic and organic catalysts commercially available were evaluated in a laboratory-stirred tank reactor (STR). The CA enzymes were identified to be the most-effective catalyst for promoting CO_2 absorption into $K_2CO_3/KHCO_3$ solution.
- Rates of CO_2 absorption into a 20 wt% $K_2CO_3/KHCO_3$ solution were increased by approximately three to nine times at temperatures between 25 and 50°C with the addition of 300 mg/l CA enzyme. Further increase in absorption rate was observed at higher CA concentrations (>300 mg/l CA). Absorption rates into CO_2-rich $K_2CO_3/KHCO_3$ solutions were comparable to those into CO_2-lean $K_2CO_3/KHCO_3$ solutions at the same CA dosage. Modeling predictions suggested that in a packed-bed column configuration, the IVCAP absorber at 2 g/l CA dosage was 23 to 40 percent larger than the equivalent equipment for the MEA process employing 5M MEA as a solvent.
- The CA enzymes demonstrated excellent chemical stability to resist flue gas impurities. Presence of flue gas impurities at their typical concentrations resulted in <11 percent loss of initial CA activity.
- The ACA1 enzyme had satisfactory stability at 25°C, but not at temperatures higher than 40°C. The ACA2 enzyme (a thermophilic CA) demonstrated excellent thermal stability at 40°C, losing only about 15 percent of its initial activity after six months. At 50°C, the ACA2 enzyme had a half-life of about two months.
- Covalent bonding methods were successfully developed to immobilize the CA enzymes onto different carbon-, CPG-, and silica-based support materials. All of the immobilized CA enzymes exhibited significantly improved thermal stability.
- Process simulation studies showed that the IVCAP integrated with a 528 MWe (gross) coal-fired, subcritical power plant at a baseline condition lowered parasitic power losses by 24 percent compared to the conventional MEA process.

- Techno-economic studies showed that the capital cost of the baseline IVCAP was about 33 percent higher than that for the MEA process due to the requirements for a vacuum pump and a larger stripper under a vacuum condition, but its operation and maintenance (O&M) cost was about 40 percent lower due to its lower solvent cost and reduced parasitic power losses. The levelized cost of electricity (LCOE, about $46/MWh) of the baseline IVCAP was a 71 percent increase over the reference power plant without CO_2 capture, about 17 percent less than that of the MEA process.

next steps

This project ended on April 30, 2012.

available reports/technical papers/presentations

Zhang, S., et. al, “Catalytic Behavior of Carbonic Anhydrase Enzyme Immobilized onto Nonporous Silica Nanoparticles for Enhancing CO_2 Absorption into a Carbonate Solution,” Int. J. Greenhouse Gas Control 2013, 13: 17-25.

Lu, Y., et. al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” Final Project Closeout Review, Pittsburgh, Pennsylvania, July 13, 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/IVCAP-Closeout-Mtg-0713.pdf*.

Lu, Y., et al, “An Integrated Vacuum Carbonate Absorption Process Enabled with an Enzyme Biocatalyst for CO_2 Absorption,” proceedings of the Clearwater Clean Coal Conference, Tampa, Florida, June 2012. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Clearwater-IVCAP-YLu.pdf*.

Zhang S., et. al, “Activity and Stability of Immobilized Carbonic Anhydrase for Promoting CO_2 Absorption into A Carbonate Solution for Post-Combustion CO_2 Capture,” Bioresources Technology 2011, 102(22): 10194-10201.

Lu, Y., et. al, “Development of a Carbonate Absorption-Based Process for Post-Combustion CO_2 Capture: The Role of Biocatalyst to Promote CO_2 Absorption Rate,” Energy Procedia 2011, 4: 1286-1293.

Lu, Y., et. al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011.

Lu, Y., et.al, “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010.

Lu, Y., “Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process,” presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.

SLIPSTREAM DEVELOPMENT AND TESTING OF SIEMENS POSTCAP CAPTURE AND SEPARATION TECHNOLOGY

primary project goals

Siemens Energy set out to design, install, and operate a pilot plant to treat a 2.5-megawatt (MW) flue gas slipstream from an operating coal-fired power plant to demonstrate the aqueous amino acid salt (AAS) solvent-based, post-combustion carbon dioxide (CO_2) gas capture technology.

technical goals

- Demonstrate the ability of Siemens Energy's POSTCAP technology to achieve 90 percent CO_2 removal while approaching a 35 percent increase in the cost of electricity (COE).
- Demonstrate the scalability and feasibility of developing the technology to a full-scale, commercial, post-combustion CO_2 capture (550 MW) application for coal-fired power plants and to full-scale commercial application for industrial sources of CO_2 emissions.

technical content

Siemens Energy worked to design, install, and operate an advanced CO_2 capture, solvent-based pilot plant. The Siemens POSTCAP CO_2 capture process utilizes an aqueous AAS solution as the solvent that offers cost and performance advantages when compared to state-of-the-art, amine-based solvents. The POSTCAP pilot plant was to be installed at Tampa Electric Company's (TECO) Big Bend Station and treat a flue gas slipstream equivalent to approximately 2.5 megawatt electric (MWe). Although the CO_2 source for this slipstream pilot-scale testing is from a coal-fired power plant flue gas, it would have provided an appropriate design and performance baseline for direct scale-up to many industrial applications.

The project encompassed the complete design, engineering, procurement, installation, operation, data analysis, and decommissioning of the CO_2 capture system and was to be completed in four phases. In Phase I, the engineering design and permitting for the project were completed. POSTCAP system mass and energy balances and pilot plant process flow diagrams were to be generated, and the host site was to be analyzed for integration of the pilot plant. Phase II was to encompass the equipment procurement, fabrication, delivery, and installation of the components at the host site with required tie-ins to plant interfaces. In Phase III, the pilot plant was to be commissioned and started up, the pilot program test campaigns were to be conducted, and the resulting data were to be analyzed. Phase IV was to cover the pilot plant decommissioning and disassembly.

technology maturity:

Pilot-Scale, Actual Flue Gas Slipstream

project focus:

POSTCAP Capture and Separation

participant:

Siemens Energy

project number:

FE0003714

NETL project manager:

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partners:

Siemens AG

performance period:

10/1/10 – 2/29/12

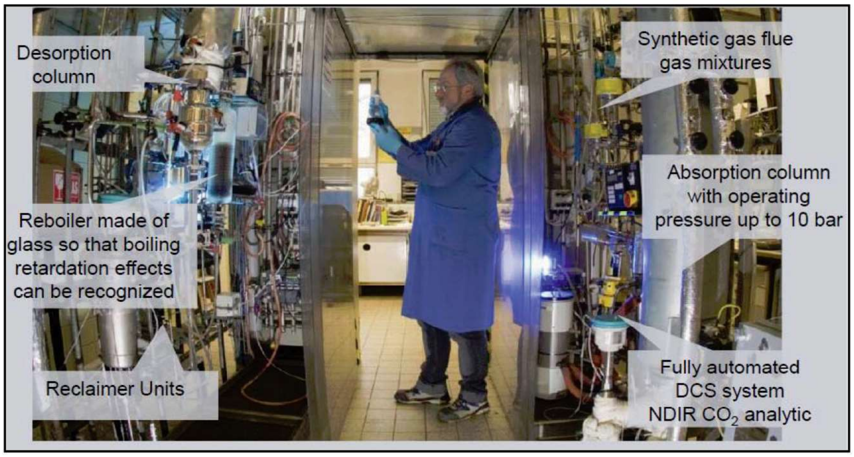

Figure 1: Siemens Lab Plant for CO_2 Capture Tests at Frankfurt Hoechst Industrial Park

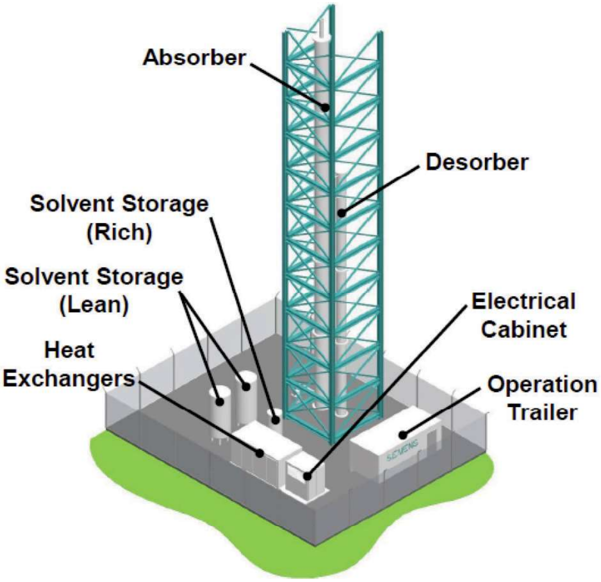

Figure 2: Basic POSTCAP Pilot Layout

technology advantages

- Lower energy consumption.
- Negligible solvent emission and degradation.
- High absorption capacity.
- Low environmental impact.

R&D challenges

- Developing solvent suppliers on a large, commercial scale.
- Minimize energy consumption.
- Available footprint for large-scale carbon capture retrofits.
- Combined cycle challenges to be overcome:
    - Low CO_2 concentration in flue gas.
    - High oxygen content in flue gas.
    - Operation with frequent load changes.
    - Fewer integration options for low-temperature heat from the capture plant.

results to date/accomplishments

Completed a preliminary design for a 2.5-MW POSTCAP pilot plant that was to be installed at the TECO Big Bend Power Station.

next steps

This project ended on February 29, 2012.

available reports/technical papers/presentations

Winkler, J.L., "Slipstream Development & Testing of Post Combustion CO_2 Capture and Separation Technology for Existing Coal-Fired Plants," presented at 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/2-Tuesday/23Aug11-Winkler-Siemens-Technology%20Slipstream%20Testing.pdf*.

REVERSIBLE IONIC LIQUIDS AS DOUBLE-ACTION SOLVENTS FOR EFFICIENT CO_2 CAPTURE

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Reversible Ionic Liquids

participant:

Georgia Tech Research Corporation

project number:

NT0005287

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partners:

N/A

performance period:

10/1/08 – 9/30/11

primary project goals

The primary project goal was to develop a novel class of solvents for the recovery of carbon dioxide (CO_2) from post-combustion flue gases that would achieve a substantial increase in CO_2 working capacity with a reduction in cost.

technical goals

- Synthesis of silyl amine-based ionic liquids (ILs) with minimal viscosity.
- Measure heat of absorption and desorption.
- Measure rates of CO_2 absorption and desorption.
- Identify solvents that will consume the minimal amount of energy.
- Use simulation tools, such as ASPEN, to design an economic absorption/desorption process.

technical content

Reversible ionic liquids (RevILs) are neutral molecules that react with CO_2 to form an IL, which then dissolves additional CO_2 by a physisorption mechanism. Subsequently, modest elevations in temperature reverse the reaction and yield pure CO_2 for disposal; because of this dual mode, capacity can be large.

In a two-component RevIL, CO_2 at 1 atmosphere acts as a "switch," as shown in Figure 1.

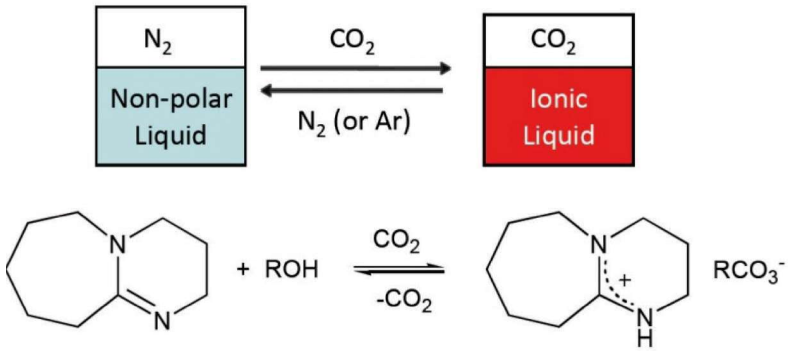

Figure 1: CO_2 Will Switch a Non-Polar Liquid to an Ionic Liquid

Two-component RevILs have the disadvantage of being too complex and requiring alcohol. Light alcohol would evaporate with the CO_2, while a heavy alcohol would have too much heat capacity. A single-component RevIL would eliminate the need for alcohol.

Figure 2 shows an example based on silylated amine. The chemistry must work well in the presence of water, considering that water is a component of flue gas. The RevILs will be tested for their chemical stability with 0 and 10 % water present. Stability will also be tested at 4, 25, and 50°C. High viscosity could also be an issue; however, viscosity in RevILs is highly nonlinear (as shown in Figure 3) and can be reduced with impurities, such as water or dissolved gases.

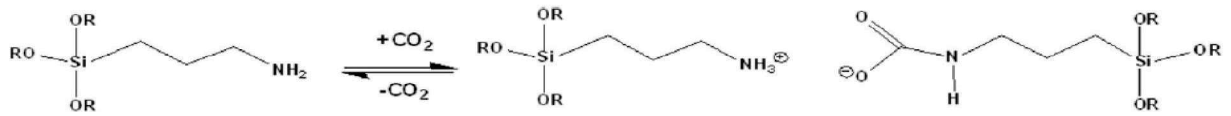

Figure 2: An Example of a Single-Component RevIL

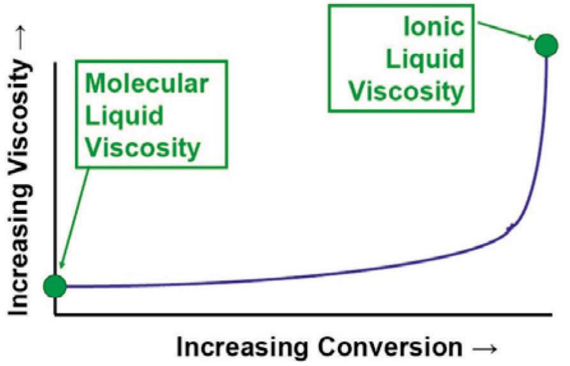

Figure 3: Ionic Liquids are More Viscous Than Their Respective Molecular Liquids

TABLE 1: PROCESS PARAMETERS FOR REVIL SOLVENTS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	170-220	150
Normal Boiling Point	°C	150 or greater	200
Normal Freezing Point	°C	< -77	
Vapor Pressure @ 15°C	bar	0.5-1x10-3	
Manufacturing Cost for Solvent	$/kg	TBD	
Working Solution			
Concentration	kg/kg	0.95	
Specific Gravity (15°C/15°C)	-	≈0.82	
Specific Heat Capacity @ STP	kJ/kg-K	2.2	<4.2
Viscosity @ STP	cP	>1,000	<80
Absorption			
Pressure	bar	1.2	1.2
Temperature	°C	25-40	>50
Equilibrium CO$_2$ Loading	mol/mol	Avg. 0.63	
Heat of Absorption	kJ/mol CO$_2$	80-90	
Solution Viscosity	cP	Variable (often <1,000)	<1,000
Desorption			
Pressure	bar	2	2
Temperature	°C	115	75
Equilibrium CO$_2$ Loading	mol/mol	< 0.01	
Heat of Desorption	kJ/mol CO$_2$	≈120	

TABLE 1: PROCESS PARAMETERS FOR REVIL SOLVENTS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical reaction for the CO_2 capture process is shown in Figure 2.

Solvent Contaminant Resistance – Since amine groups are involved in the reaction, sulfur oxides (SO_x) and nitrogen oxides (NO_x), as well as other acid gases, have to be removed. However, solvents have been shown to be stable in wet and oxygen-rich environments for a period of two months.

Solvent Foaming Tendency – No foaming observed.

Flue Gas Pretreatment Requirements – Flue gas pretreatment should be similar to the amine-based absorption processes since the RevIL is resistant to moisture.

Solvent Make-Up Requirements – Only required for process leakage in large plant.

Waste Streams Generated – None anticipated.

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Use both physical absorption (dissolution in RevILs) and chemical absorption (reaction with RevILs); amines utilize only chemical absorption.
- Structure can be modified to optimize properties.
- Silylation will decrease viscosity.
- Function in the presence of water.
- Greater capacity than current solvents.
- Smaller energy penalty than current solvents.

R&D challenges

- New compounds must be designed, synthesized, and characterized.
- Optimum equilibria and heats must be achieved.
- Rapid reaction rates must be achieved.
- Favorable transport rates must be achieved.
- Results from new process must meet U.S. Department of Energy goals.

results to date/accomplishments

- Have demonstrated greater capacity than current solvents.
- Successful synthesis and chemical characterization of 10 precursors for novel RevILs:
  - (3-aminopropyl) trimethoxysilane.
  - (3-aminopropyl) triethoxysilane.
  - (3-aminopropyl) triethylsilane.
  - (3-aminopropyl) tripropylsilane.
  - (3-aminopropyl) trihexylsilane.
  - (3-aminopropyl) diisopropyl silane.
  - (3-aminopropyl) cyclohexyldimethyl silane.
  - (3-aminopropyl) phenyldimethyl silane.
  - (E)-3-(triethylsilyl) prop-2-en-1-amine.
  - 4-(triethylsilyl) butan-2-amine.
- Completed examination of the chemical and physical absorption of CO_2 in the six silyl-amine-based RevILs at operating pressures of up to 1,000 pounds per square inch (psi) and temperatures of 35, 50, 75, and 100°C.
- Established recyclability of silyl-amine-based reversible ILs.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

Rohan, A. L., et.al, "The Synthesis and the Chemical and Physical Properties of Non-Aqueous Silylamine Solvents for Carbon Dioxide Capture," Chemsuschem 2012, 5 (11), 2181-2187.

Eckert, C. A., and Liotta, C. L., "Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture," Final Report, December 2011. *http://www.osti.gov/bridge/servlets/purl/1048880/1048880.pdf*.

Eckert, C. A., and Liotta, C. L., "Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture," presented at 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Charles%20Eckert-NT0005287.pdf*.

Blasucci, V., et.al, "Single Component, Reversible Ionic Liquids for Energy Applications," Fuel, 89, 1315–1319, 2010.

Blasucci, V., et.al, "Reversible Ionic Liquids Designed for Facile Separations," Fluid Phase Equilibria, 294, 1-6, 2010.

Hart, R., et.al, "Benign Coupling of Reactions and Separations with Reversible Ionic Liquids," Tetrahedron, 66, 1082-1090, 2010.

Eckert, C. A., and Liotta, C. L., "Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO_2/pdfs/5287%20Georgia%20Tech%20reversible%20IL%20solvent%20%28Eckert%29%20mar09.pdf*.

Blasucci, V., et.al, "One Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," Chem Comm, 116-119, 2009.

CO_2 CAPTURE FROM FLUE GAS BY PHASE TRANSITIONAL ABSORPTION

primary project goals

Hampton University set out to conduct the kinetic study for its novel technology, phase transitional absorption, which has the potential to reduce operation costs by at least half (possibly by 80%) and significantly cut capital investment (compared with current monoethanolamine [MEA]-carbon dioxide [CO_2] absorption technologies).

technical goals

To understand the mechanisms of phase transitional absorption by measuring absorption kinetics, regeneration rate, and loading capacity, as well as to further compare with other methods, such as the state-of-art MEA absorption.

technical content

The phase transitional absorption process is radically different from the conventional absorption processes. It uses an activated agent, which, when mixed with a special solvent, forms a special phase transitional absorbent for CO_2 capture. The absorbent, after absorbing CO_2 from flue gas in an absorber, flows into a settler where it is separated into two phases: a CO_2-rich phase and a CO_2-lean phase. The CO_2-rich solvent is then sent to a regenerator for regeneration. After regeneration, the solvent is cooled and mixed with the CO_2-lean phase and sent to an absorber to complete the cycle.

A schematic diagram of the process is shown in Figure 1. It may be noted that the process is similar to a conventional MEA process, except that a settler is added for separating the two phases.

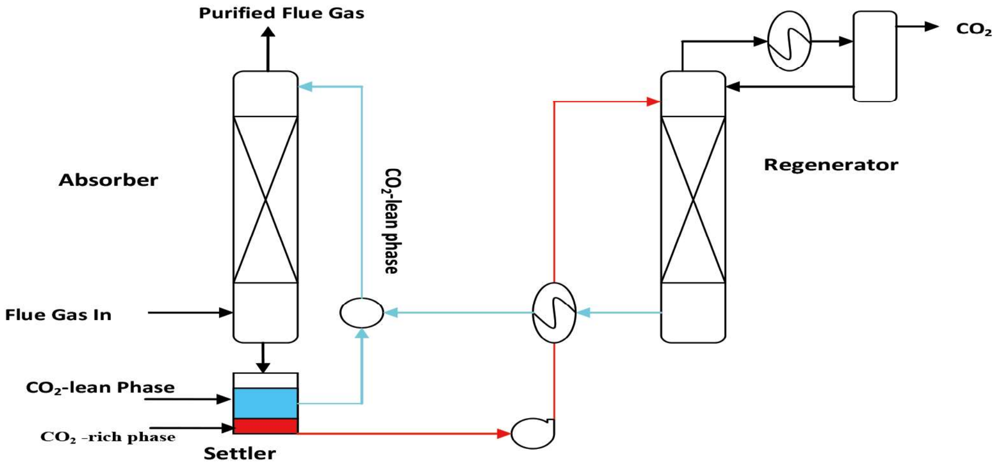

Figure 1: Concept Flow Diagram of Phase Transitional Absorption

In the conventional absorption process, such as an MEA process, the entire solvent is sent to the regenerator for regeneration, which necessitates a large circulation pump and a large amount of regeneration energy. In contrast, in the phase transitional absorption process, the

technology maturity:

Laboratory-Scale, Using Simulated Flue Gas

project focus:

Phase Transitional Absorption

participant:

Hampton University

project number:

FG26-05NT42488

NETL project manager:

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isaac.aurelio@netl.doe.gov

principal investigator:

Liang Hu
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partners:

None

performance period:

6/15/05 – 6/30/09

absorbent separates into two phases, and only the CO_2-rich phase needs to be regenerated. The CO_2-rich phase is only approximately 20 percent of the total absorbent. Thus, the pumping and heating requirements are significantly less compared to the MEA process.

Another important feature of the phase transitional absorption is that the absorption rate of CO_2 will be enhanced by selecting the proper solvent, as shown in Figure 2.

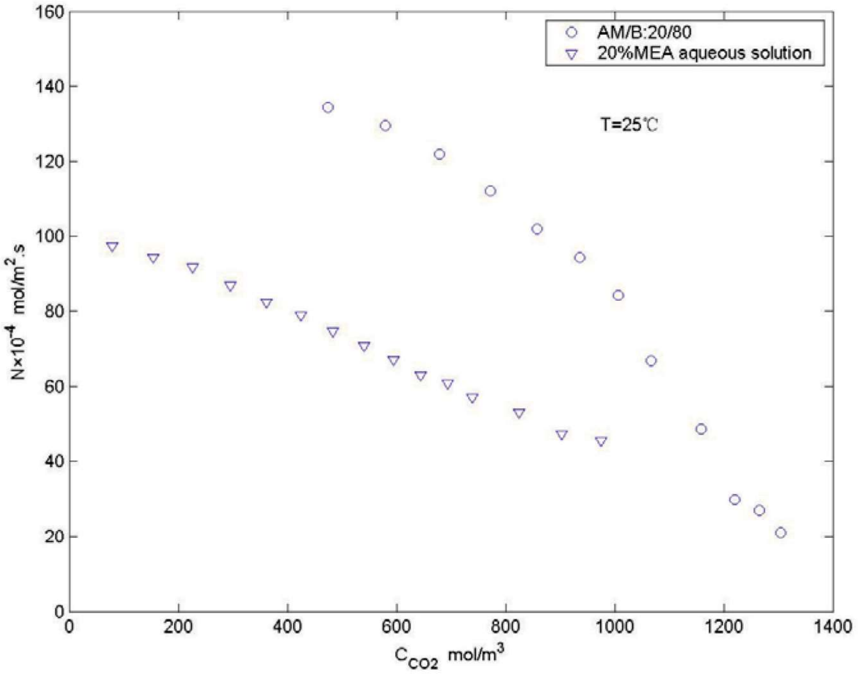

Figure 2: Absorption Rate Comparison (Phase Transitional Absorption vs. MEA Technology)

T = 25°C; P_{CO2} = 1 atm; N=60 rpm; VL = 900 ml.
Phase Transitional Absorption: activated agent: AM 20 percent by volume; solvent: B 80 percent.
MEA Technology: 20 percent (by volume) MEA aqueous solution.

Experimental results also showed that the temperature did not have strong impact on the absorption rate for the several absorbents studied. The small effect on the absorption rate by temperature could be attributed to the much smaller reaction heat.

The highest absorption rate is found when the activated agent was in the range of 30 to 40 percent by volume. The range may vary if the different activated agents and solvents are used. The range of activated agents with the highest absorption rate is highly related to the physical and chemical properties of the absorbent (i.e., activated agents and solvents), as well as the combination.

It was determined from these results that the mechanism of the absorption is a fast chemical reaction controlled by the liquid-side mass transfer. Therefore, an absorber with large gas-liquid interface and sufficient liquid turbulence is recommended in order to have a higher absorption rate, such as a packed column.

TABLE 1: PARAMETERS FOR PHASE TRANSITIONAL ABSORPTION PROCESSES

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	varies	
Normal Boiling Point	°C	varies	
Normal Freezing Point	°C	N/A	
Vapor Pressure @ 15°C	bar	N/A	
Manufacturing Cost for Solvent	$/kg	N/A	

TABLE 1: PARAMETERS FOR PHASE TRANSITIONAL ABSORPTION PROCESSES

	Units	Current R&D Value	Target R&D Value
Working Solution			
Concentration	kg/kg	20/80 by volume	
Specific Gravity (15°C/15°C)	-	N/A	
Specific Heat Capacity @ STP	kJ/kg-K	N/A	
Viscosity @ STP	cP	N/A	
Absorption			
Pressure	bar	1	
Temperature	°C	25-50	
Equilibrium CO_2 Loading	mol/mol	0.4 – 0.5	
Heat of Absorption	kJ/mol CO_2	N/A	
Solution Viscosity	cP	N/A	
Desorption			
Pressure	bar	1	
Temperature	°C	90-120	
Equilibrium CO_2 Loading	mol/mol	≈ 0	
Heat of Desorption	kJ/mol CO_2	N/A	
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A	
Adsorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	N/A	

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

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

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

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

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

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

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

Concentration – Mass fraction of pure solvent in working solution.

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The mechanism of the absorption is a fast chemical reaction controlled by the liquid-side mass transfer.

technology advantages

- Greatly reducing regeneration energy compared with the MEA process.
- Higher absorption rate, resulting in lower capital investment for absorption equipment.
- Higher CO_2 working capacity, which will reduce sensible heat and solvent volume in circulation.
- Low corrosion rate to carbon steel compared to the MEA process.
- Potentially less solvent loss.
- Non-toxic, environmentally safe.

R&D challenges

- Process exists only at the laboratory scale and needs to be scaled-up.
- Moisture in flue gas may have impact on the process.

results to date/accomplishments

- Measured the absorption rate at 15, 25, 35, 45, and 55 °C.
- Measured the effect of absorbent concentration in solution (from 10 to 50 percent by volume) on absorption rate and loading capacity.
- Measured the effect of solution agitation speed (30, 60, and 90 rpm) on absorption rate.
- Measured the absorption rate at 1 atm of CO_2 partial pressure.
- Conducted the regeneration tests; measured the regeneration rate at different temperature.
- Conducted the corrosion tests for carbon steel coupon.
- Conduct the initial process evaluation based on the lab results and made the comparison with MEA absorption.

next steps

This project ended on June 30, 2009.

available reports/technical papers/presentations

Hu, L., "CO_2 Capture from Flue Gas by Phase Transitional Absorption." Final Report June 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/phase-transitional-absorption-final-report-june2009.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
POST-COMBUSTION SORBENT TECHNOLOGIES

Bench-Scale Development and Testing of Aerogel Sorbents for CO_2 Capture

primary project goals

Aspen Aerogels designed an innovative aerogel sorbent for carbon dioxide (CO_2) capture with improved CO_2 capacity, high adsorption/desorption cyclic stability, and resistance to contaminants in the flue gas, improving the performance and economics of CO_2 capture.

technical goals

- Optimize Amine Functionalized Aerogel (AFA) to maximize CO_2 adsorption, decrease regeneration temperature, maintain kinetics for fluidized bed operation, and maintain high cyclic-adsorption stability.
- Develop pellet- and bead-forming processes.
- Develop a sulfur oxide (SO_x)-resistant coating to minimize aerogel degradation due to flue gas contaminants.
- Develop optimum AFA pellet/binder (SO_x coating) formulations.
- Develop aerogel production process.
- Test and evaluate aerogel sorbent technology at the bench-scale to determine CO_2 capture performance and optimize operating conditions.
- Complete a techno-economic analysis of the system.

technical content

Aspen Aerogels has designed an AFA sorbent for CO_2 capture with improved CO_2 capacity, high adsorption/desorption cyclic stability, and resistance to contaminants in the flue gas to achieve an overall reduction in total carbon capture cost. The AFA contains amine groups bonded to an aerogel backbone. AFA benefits include high surface area, high porosity, hydrophobicity to enhance CO_2 adsorption selectivity, low specific heat for lower energy regeneration, and high temperature stability. The unique, specific aerogel structural morphology is shown in Figure 1, along with the AFA beads, shown in Figure 2.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Advanced Aerogel Sorbents

participant:

Aspen Aerogels, Inc.

project number:

FE0013127

predecessor projects:

SC0004289

NETL project manager:

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principal investigator:

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rbegag@aerogel.com

partners:

University of Akron; ADA Environmental Solutions, Longtail Consulting, LLC

start date:

10.01.2013

percent complete:

100%

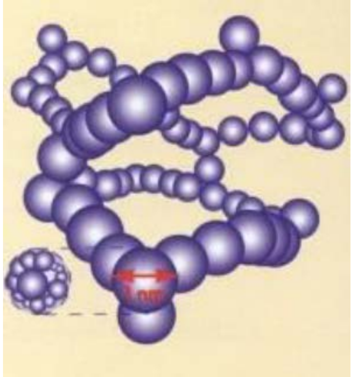

Figure 1: Structural morphology of an aerogel

Figure 2: AFA sorbent in bead form

This project maximized those benefits via bench-scale evaluation of the aerogel sorbents. Optimization of the initial sorbent formulations aimed to increase CO_2 loading capacity, improve resistance to flue gas contaminants, maintain kinetics for fluidized bed operation, and maintain high cyclic stability. Initial testing on aerogel powders provided performance data to determine optimal formulations. For use in larger scale applications, the use of AFA pellets or beads is necessary instead of powders. The AFA pellets are formed by adding binder to the aerogel powder. Further development optimized the process of aerogel bead fabrication. Bead performance was compared to AFA pellet performance, with not only the optimization of CO_2 capacity, cycle life, and stability to contaminants, but also for parameters important to high performance in a fluidized bed, including particle size, density, attrition index, and crush strength. Bench-scale cold-flow fluidized bed testing on the final AFA formulations provided hydrodynamic properties and heat transfer coefficients.

Upon testing, both the AFA bead and pellet forms demonstrated comparable CO_2 capture performance. Pellets showed superior stability during long term CO_2 capture testing. The pellet form was chosen moving forward primarily due to scale-up production capabilities of the aerogel at Aspen and the pelletization capabilities at the University of Akron for future large-scale production.

Opportunities to improve the sorbent in terms of advancing the production process include: (1) reducing the mass of the pellet binder to increase the CO_2 mass loading by using lightweight aerogel beads, needing minimal binder as coating for SO_2 resistance, and (2) lowering density of AFA and using the bead form to reduce capital costs and sorbent circulation rate, directly tied to sorbent costs due to attrition.

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,150	1,200–1,300
Bulk Density	kg/m^3	250-800	≈1,000
Average Particle Diameter	mm	0.2–1.0	0.3–0.6
Particle Void Fraction	m^3/m^3	0.56	
Packing Density	m^2/m^3	not measured	
Solid Heat Capacity @ STP	kJ/kg-K	≈1.3	0.7
Crush Strength	kg_f	3.8–6.4	
Manufacturing Cost for Sorbent	$/kg	N/A	7- 10
Adsorption			
Pressure	bar	0.8 (in Colorado)	1.0
Temperature	°C	40	<70
Equilibrium Loading	g mol CO_2/kg	100-200	>250
Heat of Adsorption	kJ/mol CO_2	55-62	60
Desorption			
Pressure	bar	0.8 (in Colorado)	1.0
Temperature	°C	100-120	<130
Equilibrium CO_2 Loading*	g mol CO_2/kg	20–100	<100
Heat of Desorption	kJ/mol CO_2	55–62	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	— — —	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*Under 100 percent CO_2

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The primary mechanism of CO_2 capture on AFA sorbents occurs by chemisorption. The homogenous distribution of amine grafted on the high surface area aerogel structure facilitates mass transfer of CO_2 to and from receptor sites. Adsorption/desorption of CO_2 occurs by temperature swing, between 40 °C and 100–120 °C.

Sorbent Contaminant Resistance – Development of a series SO_2 resistant coatings was initiated. Preliminary studies of the performance of the coatings were carried out. These coatings reduced the effect of SO_2 poisoning on the AFA sorbent and increased the stability of the sorbent in the presence of SO_2. The effectiveness of the newly developed coatings shows a CO_2 capacity reduction of only 4 percent after 20-cycle exposure to 40 ppm SO_2 in simulated flue gas, versus 55–61 percent reduction with no coating on the sorbent.

Sorbent Attrition and Thermal/Hydrothermal Stability – Selected AFA pellets were subjected to ASTM D5757 (Standard Test Method for Determination of Attrition and Abrasion of Powdered Catalysts by Air Jets), to measure the attrition index (AI). The initial sizes of the tested pellets are above 500 µm. AI is lower for AFA pellets relative to a reference of fluidized catalytic cracker (FCC). The attrition index was higher for < 20 micron particles at 300 ft/s than the reference FCC sample. The AI index indicates that the sorbent is suitable for a fluidized bed process where it will not only encounter mechanical attrition from the fluidized bed at relatively low velocities, but it will also be subject to high gas velocity cyclones needed to separate the sorbent from the gas flow.

Flue Gas Pretreatment Requirements – Protecting sorbents from SO_2 poisoning and generating high-purity CO_2 from the process are two unavoidable tasks for CO_2 Capture and Sequestration (CCS). The economic feasibility considerations are also important to the scale-up and commercialization of the CO_2 capture process. SO_2-resistant coating was verified effective to reduce the SO_2 poisoning of the AFA sorbent pellets. However, it was determined that a SO_2 polishing scrubber was needed prior to the CO_2 capture process, based on the maximum SO_2 concentration that the AFA sorbent can tolerate.

As for temperature of the flue gas entering the adsorber, for example for an adsorption temperature of 40 °C, some cooling was required due to inevitable gas heating in the blower (to overcome the pressure drop of the sorbent bed in the adsorber).

Sorbent Makeup Requirements – This has not yet been determined.

Waste Streams Generated – None known.

Process Design Concept – The solid sorbent capture case utilizing AFA sorbent was modeled using ADA-ES's general process design reported in their 1 MW pilot testing report[1] (Figure 3). However, individual reactors were specifically designed and sized for use with Aspen Aerogel's sorbent (AFA).

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[1] Sjostrom, S. (2016). *Evaluation of Solid Sorbents as a Retrofit Technology for CO2 Capture*. ADA-ES, Inc. U.S. Department of Energy

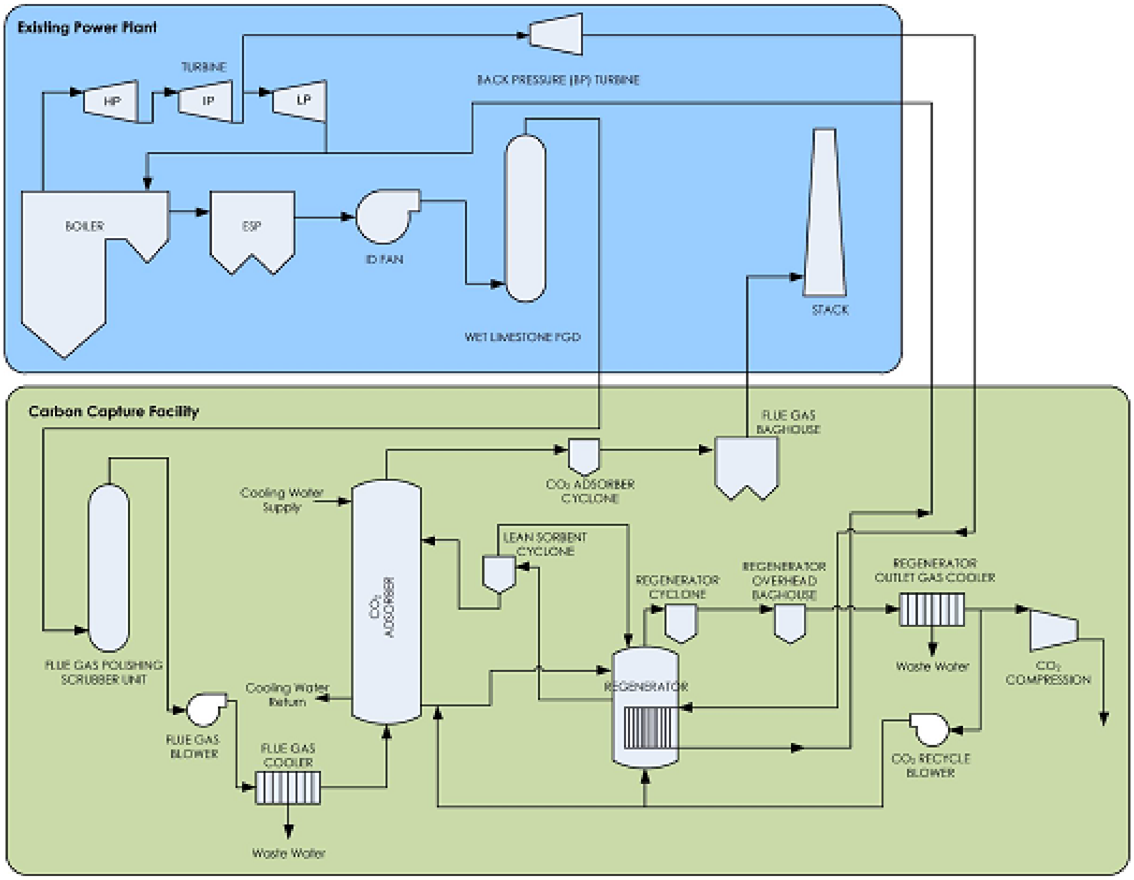

Figure 3: ADA-ES solid sorbent CO2 capture process flow diagram

technology advantages

- AFA sorbent has high CO_2 capacity and long life, reducing equipment size requirements and process costs.
- High sorbent selectivity allows for reduced sorbent cycling times, which allows for reductions in sorbent quantity, reactor size, and cost.
- Low specific heat results in low energy regeneration.
- High moisture resistance.
- High temperature stability.
- Reduced delta T for adsorption/desorption.

R&D challenges

- Optimizing pellet formulation to balance properties for optimum performance, including CO_2 capacity, attrition and SO_x resistance, thermal conductivity to improve kinetics, as well as selecting the optimal particle size and density for use in a fluidized bed.
- Optimizing pellet and bead fabrication to match performance of the aerogel powder.
- Reducing attrition.
- Overcoming the issue of reduced CO_2 capacity for AFA beads due to some amine leaching out during the fabrication process.

status

The project was completed on December 31, 2016. Aspen Aerogels tested bead and pellet formulations of the AFA, with both showing comparable CO_2 capture performance, with total CO_2 capacity between 11–14 wt%, CO_2 working capacity between 6.0–6.5 wt%, and cyclic stability over 500 cycles in a fixed bed. The AFA production and pelletization processes were scaled up, with 30 kg of pelletized sorbent prepared. The pellet form was chosen for scale-up and testing based primarily on the pelletization capabilities at the University of Akron for future large-scale production. The pelletized AFA sorbent was tested on the bench-scale in a cold-flow fluidized bed and showed good fluidization could be attained at bed velocity of 1.5 ft/s and pellet density of 1150 kg/m^3.

available reports/technical papers/presentations

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/3-Wednesday/R-Begag-Aspen-Testing-of-Aerogel-Sorbents.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/R-Begag-AAI-Aerogel-Sorbents.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbents," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File Library/Events/2014/2014 NETL CO2 Capture/G-Gould-AAI-Bench-Scale-Development.pdf*

Begag, R., et al. "Development and Testing of Aerogel Sorbents for CO_2 Capture," presented at BP1 Review Meeting, July 2014. *http://www.netl.doe.gov/File Library/Research/Coal/carbon capture/post-combustion/BP1-NETL-presentation-Final-Rev-2-nonproprietary.pdf*

Begag, R., et al. "Bench-Scale Development and Testing of Aerogel Sorbent for CO_2 Capture," presented at Project Kick-Off Meeting, Pittsburgh, PA, November 8, 2013. *http://www.netl.doe.gov/File Library/Research/Coal/ewr/CO2/Aspen-Aerogels-NETL-DOE--Kick-Off-Final-Non-proprietary.pdf*

NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology

primary project goals

NRG Energy proposed to develop a post-combustion carbon dioxide capture project utilizing the Inventys VeloxoTherm^{TM} technology utilizing a structured adsorbent in a rotary bed adsorber using rapid cycle temperature swing adsorption. The project would have included developing the scope, configuration, and design basis of a pilot-scale system.

technical goals

- Develop the scope, configuration, and design basis for a pilot plant using the VeloxoTherm^{TM} process sized for a 10-megawatt electric (MW_e) or greater slipstream of flue gas from an NRG coal plant.
- Determine optimal size and host site location at one of NRG's coal plants.
- Complete a techno-economic analysis and identify technology gaps.

technical content

NRG Energy was working to establish the technical and economic feasibility of the Inventys VeloxoTherm^{TM} post-combustion carbon dioxide (CO_2) capture process. VeloxoTherm^{TM} is an intensified temperature swing adsorption process using a proprietary combination of structure sorbent and process design using a rotary adsorption machine, as depicted in Figure 1.

The structured sorbents provide high surface area along with mass and heat transfer kinetics allowing for low pressure drop, immobilization with no fluidization, and high surface area. The VeloxoTherm^{TM} process is based on rotary air preheaters, which have been used in process industries. The process implements a cycle design without the need of discrete vessels, multiple large switching valves, and complicated interconnecting piping and ducting. The VeloxoTherm^{TM} technology has previously been validated for capturing CO_2 from a natural gas-fired boiler. The current project is aimed at determining the size, scope, configuration, and design basis for a pilot plant using a slipstream of flue gas from one of NRG Energy's coal plants.

technology maturity:

Conceptual Design of Pilot-Scale, Actual Flue Gas Slipstream (equivalent to 10 MW_e or greater)

project focus:

Temperature Swing Adsorption with Structured Sorbent

participant:

NRG Energy, Inc.

project number:

FE0026581

predecessor projects:

N/A

NETL project manager:

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principal investigator:

David Greeson
NRG Energy, Inc.
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partners:

Inventys

start date:

10.01.2015

percent complete:

100%

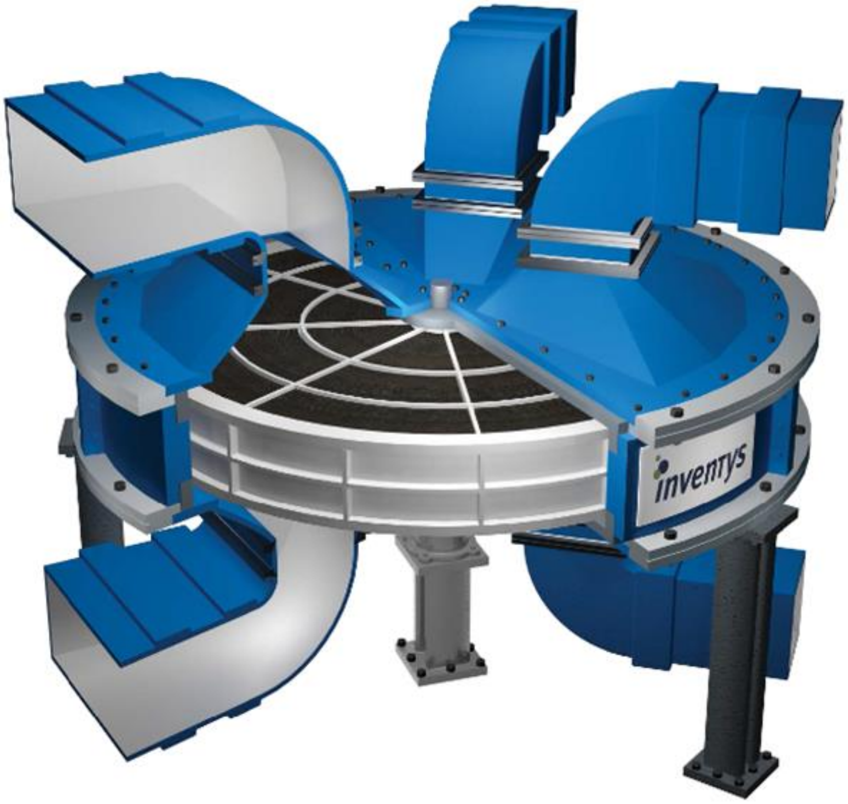

Figure 1: Inventys VeloxoTherm™ rotary adsorption machine concept

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

technology advantages

- Technology proven at 0.5 MW_e pilot scale using natural gas feed.
- Structured adsorbents have high surface area per reactor volume and low pressure drop.
- Structured adsorbents allow for high heat and mass transport due to short diffusion paths within structured materials.
- High heat retention due to anisotropic heat transfer properties.
- Laminate design allows degrees of freedom for adjusting void fraction, packing densities, and hydrodynamics.
- Rapid cycle temperature swing adsorption (TSA) with structured adsorbents shows good resistance to sulfur oxides (SO_x) and other flue gas contaminants.

R&D challenges

- Risk of scale up to a large-scale rotary adsorption machine.
  - Maintaining flow distribution.
  - Size of adsorbent beds.
  - Scale-up of gas seal design.
  - Rotor imbalances/process asymmetry.
- Developing the technology for a coal-based flue gas feed.

status

During the initial phase of the project NRG and Inventys conducted a six-week test exposing the adsorbent to flue gas from one of NRG coal-fired boilers and determined that further work was needed to improve the economics before a large scale pilot demonstration could be attempted. Consequently, the project was wrapped up September 30, 2016. NRG completed conceptual design of a 15 m diameter large scale pilot rotary adsorption machine, along with a preliminary EH&S risk assessment and technology gap analysis. Increased structured adsorbent bed density and use of a vacuum-assisted regeneration strategy was determined to be necessary to achieve process performance targets for the coal flue gas TSA cycle.

available reports/technical papers/presentations

Armpriester, A. and Stevenson, M. “NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/2-Tuesday/A-Armpriester-NRG-CO2NCEPT.pdf*

Armpriester, A. “NRG CO_2NCEPT – Confirmation of Novel Cost-Effective Emerging Post-Combustion Technology,” presented at the Project Kickoff Meeting, Pittsburgh, PA, November 2015. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0026581-NRG-Inventys-DOE-Kickoff-Meeting.pdf*

Bench-Scale Development and Testing of Rapid Pressure Swing Adsorption for Carbon Dioxide Capture

primary project goals

W.R. Grace developed a rapid pressure swing adsorption (rPSA) process to evaluate concept cost and performance benefits by testing a bench-scale system using a low-cost, structured adsorbent with low-pressure drop, high mass-transfer rates, high capacity, and high availability that will enable large feed throughputs.

technical goals

- Develop an attrition-resistant and low-pressure drop structured adsorbent based on a commercial zeolite that is compatible with the high velocities associated with rapid PSA operation.
- Design, develop, and test a bench-scale rapid PSA process using the structured adsorbent to deliver efficient and cost-effective separation of carbon dioxide (CO_2) from flue gas.

technical content

W.R. Grace worked to develop a rapid PSA process with a much shorter cycle time compared to conventional PSA, which could potentially reduce the cycle time from 300 seconds (conventional PSA cycle) to 30 seconds or less. This would increase the feed throughput, and thus decrease the size of the columns by a factor of 10 or more, significantly reducing both the capital and operating costs, as well as the plant footprint. Pressure swing adsorption is attractive because it requires only electricity and not any of the power plant's steam.

The key challenge to the success of this concept is two-fold: (1) an attrition-resistant and low-pressure drop structured adsorbent must be developed based on commercial zeolite that is compatible with the high velocities associated with rapid PSA operation; and (2) a rapid PSA cycle configuration must be developed in concert with the structured adsorbent so that the resulting rapid PSA process achieves necessary cost and performance metrics.

One advantage of a rapid PSA process over other CO_2 adsorption processes is simplified heat management. The rapid cycle times minimize temperature swings. Thus, the columns will heat up only slightly during adsorption and cool down only slightly during desorption, approaching nearly isothermal operation, which is optimal.

Management of water will provide some operational challenges. Degradation of the PSA process performance in the presence of water is well documented. It is anticipated that for a rapid PSA CO_2 removal process, up to 95 percent of the water in the flue gas will need to be removed using commercial desiccant technology. This will increase capital and operating costs; however, any increases are more than offset by cost savings in other parts of the process.

The structured adsorbent to be developed will consist of zeolite crystals coated on a

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid Pressure Swing Adsorption

participant:

W.R. Grace and Co.

project number:

FE0007639

predecessor projects:

N/A

NETL project manager:

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partners:

University of South Carolina;
Catacel Corporation;
Battelle Memorial Institute

start date:

10.01.2011

percent complete:

100%

metal support. This process has been successfully demonstrated using metal foil, as shown in Figure 1.

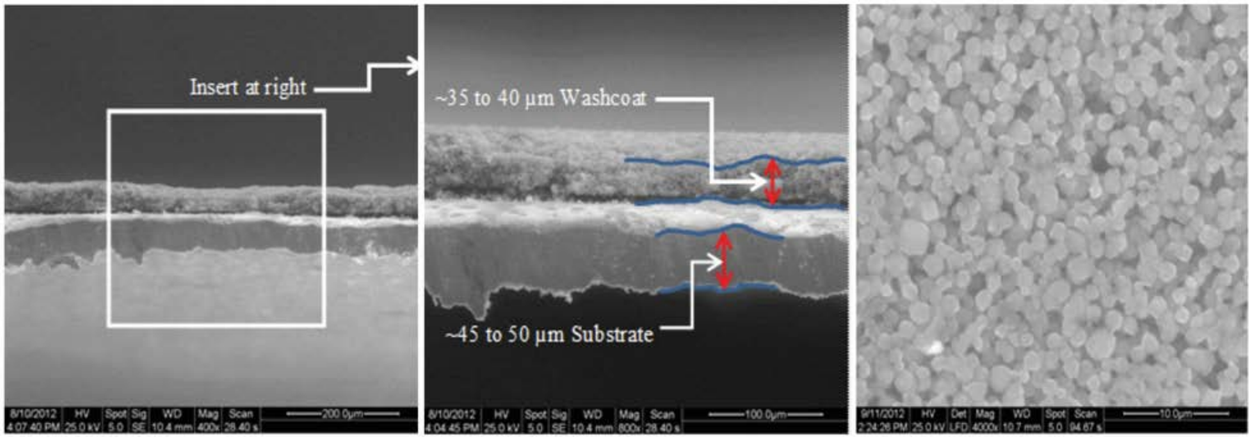

Figure 1: Edge view of zeolite-coated metal substrate at 400x magnification (left); edge view of zeolite-coated metal substrate at 800x magnification indicating washcoat is 35–40 µm thick (center); top view of zeolite-coated metal foil substrate at 4,000x magnification (right)

Corrugated cores have been fabricated (Figure 2) to serve as the metal substrate for testing the rapid PSA process. These cores were tested to evaluate pressure drop, and coated with zeolite crystals for process testing.

Figure 2: Side view of 1.5” x 6” x 289 psi corrugated cores

In addition, a dynamic volumetric frequency response (DVFR) apparatus (Figure 3) that is being used to characterize adsorbate mass-transfer rates in various adsorbents at cycle times up to 10 Hz, as well as a single-column rapid pressure swing adsorption (S-C rPSA) system (Figure 4), is being used to study the effect of cycle time on the mass-transfer rates at step times as short as 0.25 seconds.

Figure 3: Photograph DVFR apparatus

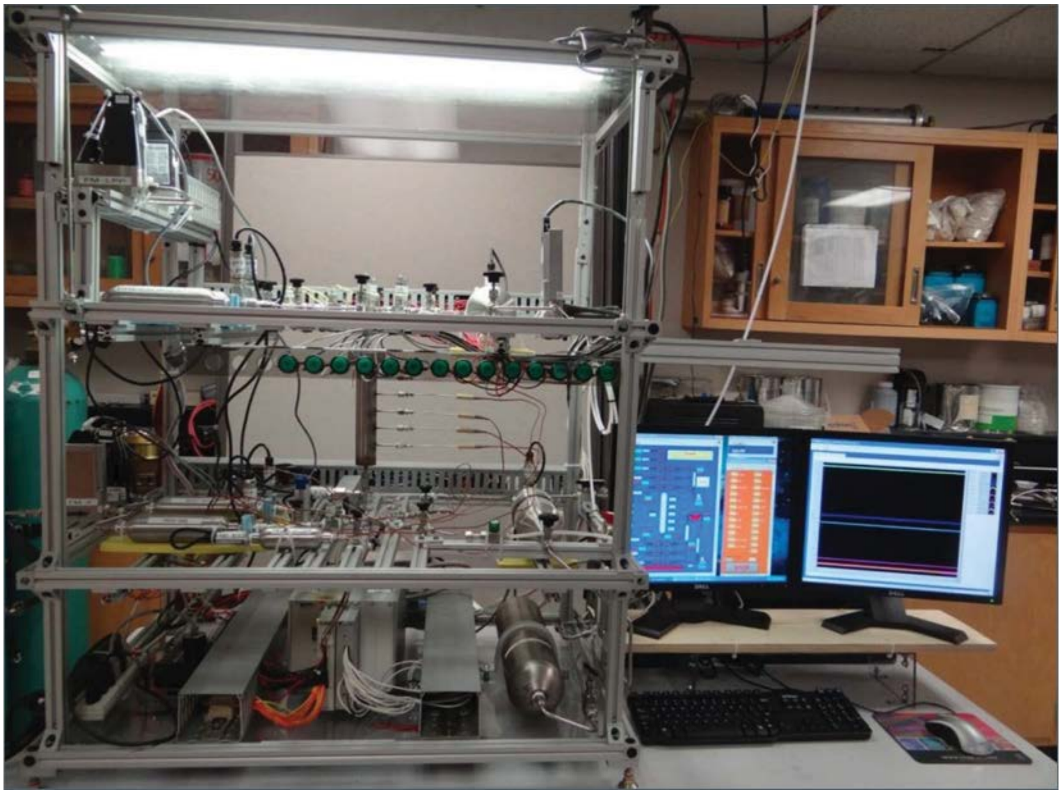

Figure 4: Photograph of S-C rPSA system

TABLE 1: SORBENT PROCESS PARAMETERS[1]

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP[2]	kg/m^3	1,090	2,518
Bulk Density[3]	kg/m^3	688	400
Average Particle Diameter[4]	mm	5.0	0.100
Particle Void Fraction	m^3/m^3	0.47	0.47
Packing Density	m^2/m^3	750	6,070
Solid Heat Capacity @ STP[2]	kJ/kg-K	0.92	0.82
Crush Strength[5]	kg$_f$	3.6	N/A
Manufacturing Cost for Sorbent	\$/kg	20	37.4
Adsorption[6]			
Pressure[7]	bar	1.2/1.14	1.2/1.14
Temperature	°C	50	50
Equilibrium Loading[8]	g mol CO$_2$/kg	4.18	4.18
Heat of Adsorption	kJ/mol CO$_2$	37.5–46.0	37.5–46.0
Desorption			
Pressure[7]	bar	0.05/0.00085	0.05/0.00085
Temperature	°C	50	50
Equilibrium CO$_2$ Loading[9]	g mol CO$_2$/kg	0.14	0.14
Heat of Desorption	kJ/mol CO$_2$	37.5–46.0	37.5–46.0
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed bed/cyclic	
Flue Gas Flowrate	kg/hr	2.32×10^6	
CO2 Recovery, Purity, and Pressure	% / % / bar	90 95 1.38	
Adsorber Pressure Drop	bar	0.15	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

1. For the Current R&D Value, the calculation is based on 5-mm 13X beads. For the Target R&D Value, the calculation is based on a 52-micron thick stainless steel support containing a 100-micron thick zeolite crystal coating at each side.
2. The Target R&D Value includes the stainless steel support.
3. The Target R&D Value corresponds to mass of adsorbent (zeolite) per volume of bed.
4. The Target R&D Value corresponds to coating thickness.
5. The structured support for the target will be unaffected by PSA dynamic stresses.
6. The adsorption step is considered as the Heavy Reflux step, which follows the feed step in the PSA cycle and is highly enriched in CO$_2$ and obtained from another desorption step in the PSA cycle.
7. First value is total pressure; second value is partial pressure of CO$_2$.
8. The value corresponds to conditions of the heavy product gas.
9. The value corresponds to conditions of the light product gas.

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO$_2$-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The relative thermodynamic adsorption selectivity toward CO_2 over other gases such nitrogen (N_2), oxygen (O_2), and argon (Ar) on a commercial zeolite at partial pressures of CO_2 at around or below 1.0 bar.

Sorbent Contaminant Resistance – The effect of the contaminant sulfur dioxide (SO_2) is not clear yet; tests are planned. It is expected, however, that the 42 parts per million (ppm) in the fresh flue gas will be significantly reduced at the condensing heat exchanger that will be located upstream of the PSA unit. It is not expected that the zeolite will be irreversibly affected by nitrogen oxides (NO_x).

Sorbent Attrition and Thermal/Hydrothermal Stability – The sorbent will be deposited on the surface of a metal structured support; thus, thermal or mechanical stresses present in pelletized/beaded systems will not be observed.

Flue Gas Pretreatment Requirements – The flue gas requires a blower to bring the pressure up to 120 kPa and then a condensing heat exchanger followed by a dryer to bring the content of water to less than 0.1 vol% prior to entering the PSA unit.

Sorbent Makeup Requirements – There are no sorbent makeup requirements in PSA units. The structured adsorbent is expected to last at least 5 years and possibly 10 years before it needs to be replaced. This is common in commercial PSA systems.

Waste Streams Generated – There are no waste streams generated in the flowsheet. All potential waste streams are recycled and used in the process somewhere. For example, the condensing heat exchanger will produce about 460,000 lb/h of condensed water that is recycled back as makeup water for the flue gas desulfurization (FGD) unit. It may contain up to 1,125 mg/L of dissolved SO2 and no other contaminants. In addition, about 3.69 x 106 lb/h of N_2-rich product at about 80 °C is vented into the air. This stream will contain, by volume, about 1.8 percent CO_2, 4.0 percent H_2O, 3.3 percent O_2, 1.09 percent Ar, and balance N_2.

technology advantages

- Established large-scale technology for other applications.
- Requires no steam or water, only electricity.
- Tolerant to trace contaminants; possibly with use of guard or layered beds.
- Zeolite adsorbent is commercial and widely available.
- Increase in cost of electricity (COE) lower than other capture technologies.
- If research and development (R&D) is successful, beds could be installed under a parking lot.

R&D challenges

- Energy-intensive (but better than current amines).
- Reducing bed size; larger bed implies large pressure drop, requiring more power.
- Minimizing pressure drop, mass transfer issues, and adsorbent attrition.

status

The project has ended. Three 6-inch Catacel core structures were successfully coated with a 50 µm thick layer of Zeolite crystals, with a density of 240 kg/m^3. One-bed and three-bed bench-scale PSA apparatuses were constructed. Testing of the structured adsorbent began using these units. The dynamic adsorption process simulator was validated with experimental data from the testing.

available reports/technical papers/presentations

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/J-Ritter-USCarolina-Rapid-PSA.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.
http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/J-Ritter-USCarolina-Rapid-Pressure-Swing-Adsorption.pdf

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO$_2$%20Capture/J-Ritter-USC-Rapid-Pressure-Swing-Adsorption.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-july2012.pdf*

Ritter, J. "Bench-Scale Development and Testing of Rapid PSA for CO_2 Capture," presented at the Project Kickoff Meeting, Pittsburgh, PA, May 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/rapid-pressure-swing-adsorption-kickoff-july2012.pdf*

Bench-Scale Development of an Advanced Solid Sorbent-Based CO_2 Capture Process for Coal-Fired Power Plants

primary project goals

RTI International addressed the technical and economic hurdles to developing a sorbent-based carbon dioxide (CO_2) capture process by transitioning a promising sorbent chemistry, based on molecular basket sorbent (MBS) materials, to a low-cost sorbent suitable for use in a fluidized-bed process and developing a scalable circulating fluidized, moving-bed reactor (FMBR) process arrangement.

technical goals

- Improve the thermal and chemical stability of the base polyethyleneimine (PEI) reactant while transitioning the current fixed-bed form MBS material into a fluidizable form.
- Collect critical process engineering data using a bench-scale test unit to allow for a detailed design of a CO_2 capture prototype system based on improved MBS materials.
- Improve reactor design, optimize operability, and optimize heat integration strategies for the FMBR system.
- Scale-up advanced MBS materials production for use in the CO_2 capture prototype system.
- Demonstrate the technical and economic feasibility of a commercial embodiment of the MBS-based CO_2 capture process through a detailed technology feasibility study.

technical content

The project team developed an advanced sorbent process that utilizes a polymeric amine-based CO_2 sorbent developed by Pennsylvania State University (PSU) under a previous project (DE-FE-0000458) to capture CO_2 from coal-fired power plant flue gas. This molecular basket sorbent consists of a high-surface area support, such as silica, impregnated with branched PEI polymer, as exhibited in Figure 1.

The branched polymer contains primary, secondary, and tertiary amine sites that adsorb CO_2. Carbon dioxide absorption is favored between 50 and 90 °C (122 and 194 °F), with a heat of reaction of $\Delta Habs = 66$ kJ/mol- CO_2 (645 Btu/lb- CO_2). At temperatures greater than 110 °C (230 °F), the reverse reactions predominate and the sorbent releases CO_2.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Advanced Solid Sorbents and Processes for CO_2 Capture

participant:

RTI International

project number:

FE0007707

predecessor projects:

N/A

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partners:

Pennsylvania State University; Masdar New Ventures; Masdar Institute

start date:

10.01.2011

percent complete:

100%

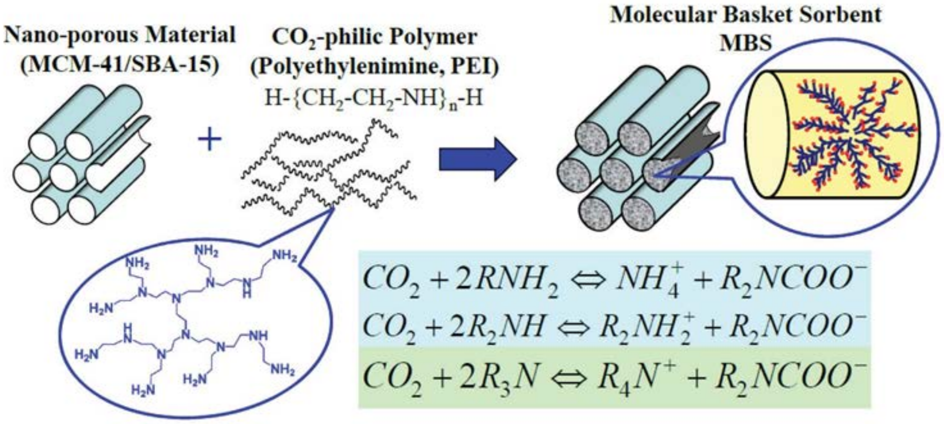

Figure 1: Molecular basket sorbent concept

This advanced sorbent CO_2 capture process operates as a cyclic adsorption-regeneration thermal swing process where the solid sorbent is continuously circulated between two FMBRs—a CO_2 adsorber and a sorbent regenerator. A basic block flow diagram of this process, installed within a pulverized coal (PC)-fired power plant, is provided in Figure 2.

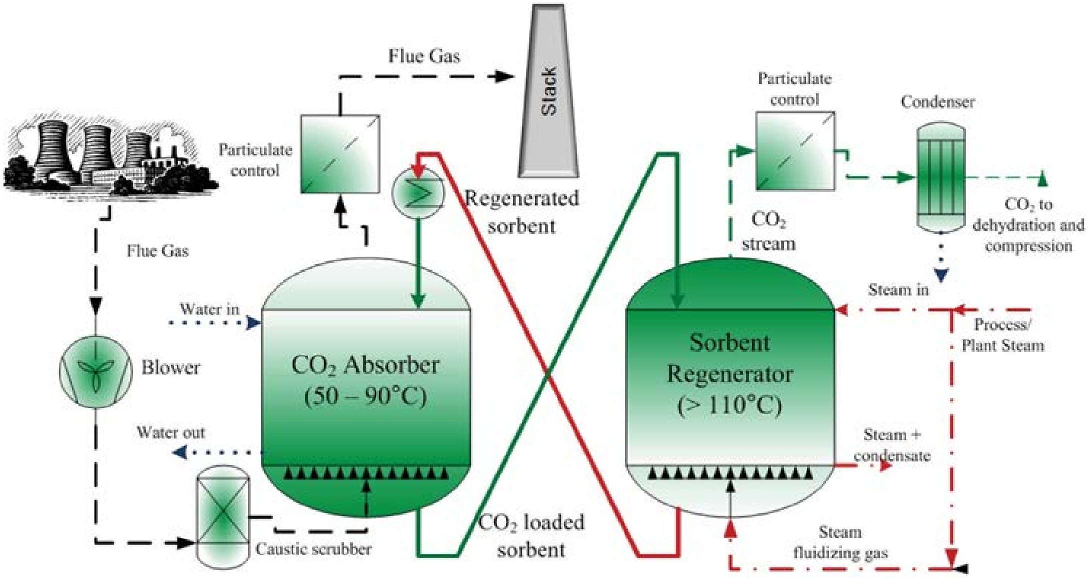

Figure 2: Block flow diagram of advanced solid sorbent CO_2 capture process

Carbon dioxide-rich flue gas from the PC power plant goes through a caustic scrubbing system to remove strong acid gases prior to entering the CO_2 adsorber. The CO_2 adsorber is designed as an FMBR. Within the adsorber, flue gas comes in contact with lean sorbent that is fed to the adsorber from the sorbent regenerator. The sorbent selectively removes CO_2 and generates heat due to the heat of reaction for CO_2 removal. In order to control the sorbent bed temperature, cooling water is used to cool the sorbent through indirect contact. Treated flue gas exits the CO_2 adsorber and enters a baghouse filter for removal of particulates, primarily attrited sorbent particles. Following particulate removal, the flue gas is then directed to the stack and vented.

The CO_2-rich sorbent exits the adsorber and is transported to the sorbent regenerator. The sorbent regenerator design and operation is similar to the CO_2 adsorber, except that the sorbent bed is indirectly heated with condensing steam in order to strip the sorbent of the adsorbed CO_2. The regenerated sorbent produces a concentrated CO_2 gas stream that is swept out of the sorbent regenerator with a CO_2 sweep gas. The concentrated CO_2 gas stream is then sent to a dehydration and compression unit, and the sorbent is transferred through a sorbent cooling unit and on to the CO_2 adsorber for continued CO_2 removal. Fresh sorbent is added to this stream to make up for attrited sorbent and diminished sorbent performance.

RTI led an effort to conduct process evaluations in a bench-scale, single-stage, fluidized-bed unit capable of sustained CO_2 capture and sorbent regeneration, followed by the design and fabrication of a bench-scale, continuous-flow CO_2 capture prototype system. This system is integrated and commissioned at RTI's Energy Technology Development Facility (ETDF) using simulated flue gas.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value		Target R&D Value
True Density @ STP	kg/m^3	N/A		N/A
Bulk Density	kg/m^3	≈500		≈1,000
Average Particle Diameter	mm	≈0.1		0.05 to 0.2
Particle Void Fraction	m^3/m^3	not measured		TBD
Packing Density	m^2/m^3	not measured		TBD
Solid Heat Capacity @ STP	kJ/kg-K	1.53		1.1 to 1.5
Crush Strength	kg_f	N/A		N/A
Manufacturing Cost for Sorbent	$/kg	N/A		<10
Adsorption				
Pressure	bar	1.01		1.01
Temperature	°C	75		60 to 90
Equilibrium Loading	g mol CO_2/kg	2.27		3.18
Heat of Desorption	kJ/mol CO_2	66		60 to 70
Desorption				
Pressure	bar	1.01		1.01
Temperature	°C	100		>110
Equilibrium CO_2 Loading	g mol CO_2/kg	0.68		0.45
Heat of Desorption	kJ/mol CO_2	78		70 to 80
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement/Operation	—		—	
Flue Gas Flowrate	kg/hr		—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	—	—	—
Adsorber Pressure Drop	bar		—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – see Figure 1.

Sorbent Contaminant Resistance – Most, if not all materials used for CO_2 capture, including aqueous amine solvents, alkaline and alkali-based solvents and sorbents, and the amine-based sorbents being developed in this project, have a high affinity for strong acid gases, including sulfur oxide (SO_x), nitrogen oxide (NO_x), and hydrogen chloride (HCl). Considerations have been made regarding how to implement contaminant control within the overall CO_2 capture system. Resistance to trace metal contaminants is unknown at this point.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent attrition will be a function of the process operating environment and physical strength of the sorbent. These will be measured and observed during larger-scale testing campaigns. The base PEI reagent suffers from performance instability at temperatures greater than 110 °C. One of the focuses of this project is to improve the sorbent performance stability.

Flue Gas Pretreatment Requirements – Most likely, the flue gas will require a scrubbing of acid gases prior to entering the CO_2 adsorber containing the sorbent being developed in this project.

Sorbent Makeup Requirements – Continuous sorbent makeup will be required during operation of a commercial system in order to replenish sorbent lost to attrition, entrainment, and deactivation by reaction with contaminants.

Waste Streams Generated – As a whole, the process generates few waste streams. It is expected that a continuous purge of sorbent will be required to maintain a desired level of CO_2 removal within the sorbent bed. In addition, sorbent will be lost from the process through attrition and entrainment. The sorbent can either be treated and reused, or disposed of following minimal treatment.

Process Design Concept – See Figure 2.

technology advantages

- Potential for reduced parasitic loads and lower capital and operating costs than conventional technology.
- High CO_2 loading capacity.
- Relatively low heat of absorption with no heat of vaporization penalty.
- Reactor design offers superior gas-solid heat and mass transfer characteristics.

- Counter current gas-solids flow maximizes CO_2 driving force.
- Required process equipment exists and is used industrially.

R&D challenges

- Heat management / temperature control.
- Solids handling / solids circulation control.
- Sorbent attrition resistance.
- Stability of sorbent performance.
- Heat management and novel heat integration strategies are critical to reduce parasitic power losses.

status

The project was completed on December 31, 2015. RTI has produced a fluidizable form of a high capacity sorbent and has optimized and scaled up sorbent production to 135 kg scale. The multi-stage fluidized bed bench-scale test unit with a flue gas processing capacity of 13 standard cubic feet per minute (scfm) was operated with several hundred hours of parametric and long-term performance testing, identifying optimal operating conditions and achieving 90 percent CO_2 capture using a simulated flue gas. The sorbent maintained CO_2 working capacity between 4 and 7 wt% during 100+ hours of continuous testing. The techno-economic analysis indicated an estimated cost of CO_2 capture for a conceptual commercial layout of the process to be approximately \$45.0/tonne CO_2.

available reports/technical papers/presentations

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2016. *https://www.netl.doe.gov/File%20Library/Events/2016/c02%20cap%20review/4-Thursday/T-Nelson-RTI-Solid-Sorbent-Based-CO2-Capture.pdf*

Nelson, T., et al. "Bench-Scale Development of an Advanced Solid Sorbent-Based CO_2 Capture Process for Coal-Fired Power Plants," Final Scientific/Technical Report, June 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/fe0007707-final-report.pdf*

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/T-Nelson-RTI-Advanced-Solid-Sorbents.pdf*

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/T-Nelson-RTI-Advanced-Solid-Sorbents-and-Process-Designs.pdf*.

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/T-Nelson-RTI-Advanced-Solid-Sorbents.pdf*.

Nelson, T., et al. "Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/advanced-solid-sorbents-process-designs-july2012.pdf*

Nelson, T., et al. "Advanced Solid Sorbent CO_2 Capture," presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2011. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/novel-solid-sorbents-kickoff-dec2011.pdf*

Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration

primary project goals

ADA Environmental Solutions (ADA-ES) investigated heat recovery for a temperature-swing-adsorption (TSA) capture process, including the use of a cross-heat exchanger to recover sensible heat from the sorbent leaving the regenerator. Recovering heat generated by the sorbent during the capture process reduces the energy penalty and overall cost for carbon dioxide (CO_2) capture.

technical goals

- Evaluate options to reduce the plant heat rate and levelized cost of electricity (LCOE) associated with the ADAsorb™ process through heat integration with the plant and use of a cross-heat exchanger.
- Optimize approach temperature and cross-heat exchanger design.
- Assess two different sorbents with preliminary design and techno-economics.
- Assess two cross-heat exchanger designs with laboratory testing, preliminary design and techno-economics.

technical content

ADA-ES, along with partners Solex Thermal Science, Technip Stone and Webster Process Technologies, and the Energy Research Center at Lehigh University, optimized its promising dry sorbent-based post-combustion capture process—the ADAsorb™ process—developed under another DOE-funded project (DE-FE0004343), by evaluating heat integration opportunities as well as working to develop an overall optimized process. In prior project DE-NT0005649, ADA-ES evaluated multiple solid sorbents at the lab- and bench-scale. In prior project DE-FE0004343, ADA-ES evaluated the ADAsorb™ process at the 1 megawatt electric (MW_e) pilot-scale. The ADAsorb™ process is shown in Figure 1. The concepts, however, will be applicable to other TSA processes. The optimization study includes a sensitivity analysis across a range of sorbent properties to identify cost and energy demand trends so that the general conclusions can be applied to most sorbent-based CO_2 capture processes.

technology maturity:

Bench-Scale Testing at Simulated Full-Scale Process Conditions

project focus:

Cross-Heat Exchanger for Sorbent-Based CO_2 Capture

participant:

ADA-ES, Inc.

project number:

FE0012914

predecessor projects:

FE0004343
NT0005649

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partners:

Solex Thermal Science; Lehigh University–Energy Research Center; Technip Stone and Webster Process Technologies

start date:

10.01.2013

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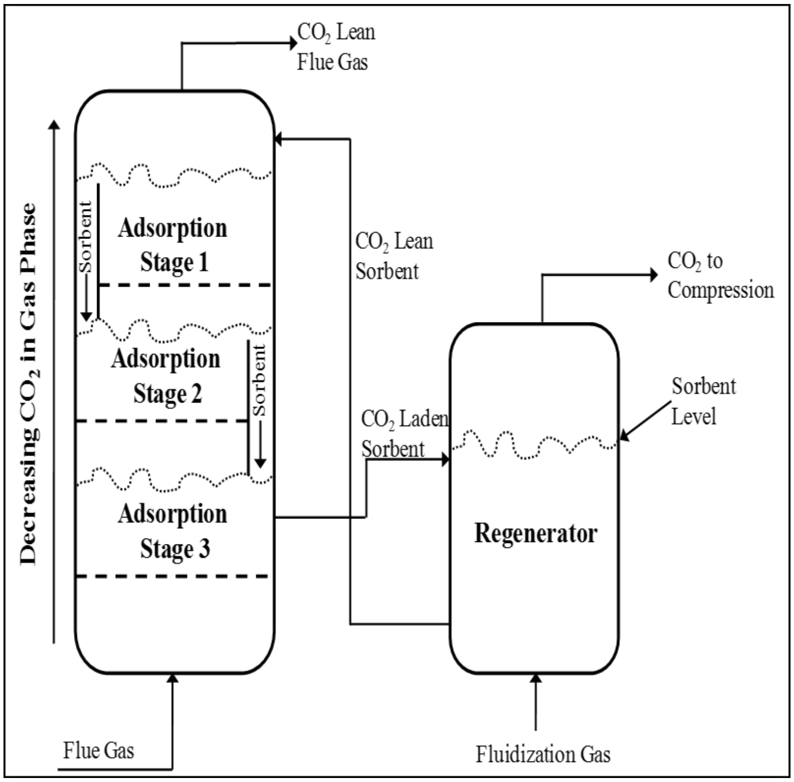

Figure 1: ADAsorb™ process overview

Cross-heat exchangers are standard features of solvent-based processes; large-scale heat exchangers appropriate for solids in this application currently do not exist. Although the fundamental components for solids-based heat exchangers are commercially available, the design details and integration approach are being developed and optimized to ensure that the additional equipment capital costs do not outweigh benefits associated with reduced overall energy penalty. Figure 2 is a concept drawing for the cross-heat exchanger.

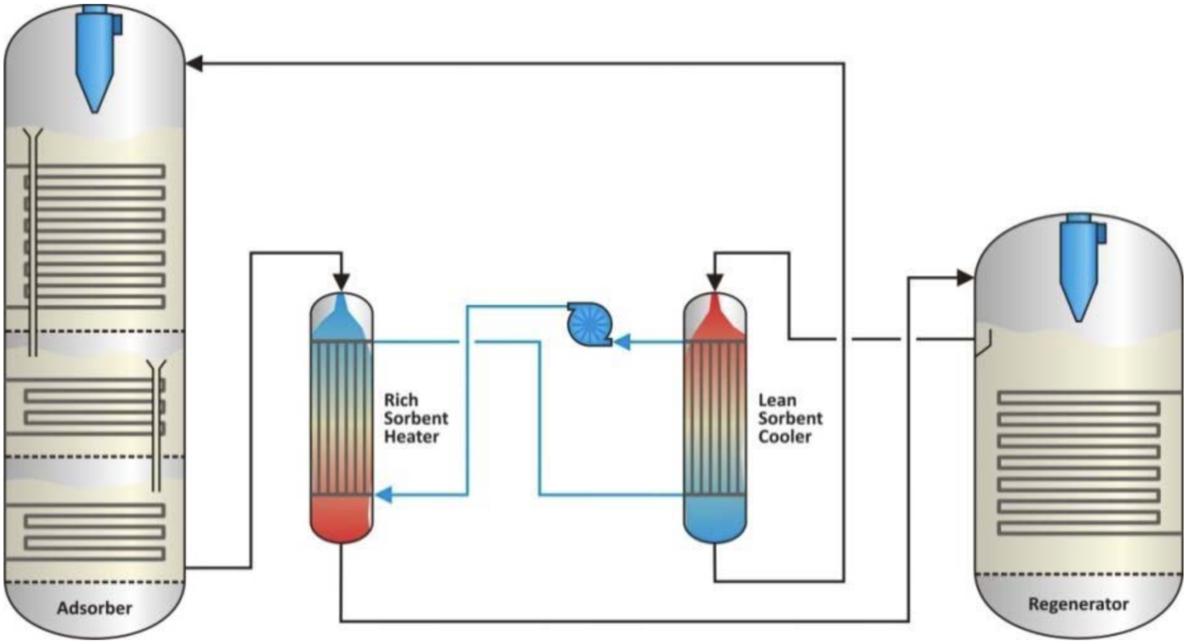

Figure 2: Cross-heat exchanger concept

The team evaluated heat integration opportunities and optimizing the process by:

- Bench-scale testing the heat exchanger concept with a single sorbent to collect the data required for scale-up modeling and the subsequent computational modeling.
- Modeling using ASPEN Plus and custom tools to determine the optimal operating conditions for the heat exchanger in a moving-bed and fluidized bed arrangements integrated into the overall CO_2 capture process to minimize capital and operating cost.
- Process modeling to assess the viability of heat integration options (with the power plant and the CO_2 compressors).
- Optimization of the flue gas moisture level.
- Adsorber and regenerator design assessment to reduce pressure drop.

The sorbent and process properties are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	646	646
Bulk Density	kg/m^3	453	453
Average Particle Diameter	mm	0.18	0.18
Particle Void Fraction	m^3/m^3	0.418	0.418
Packing Density	m^2/m^3	N/A	N/A
Solid Heat Capacity @ STP	kJ/kg-K	1.05	1.05
Crush Strength	kg_f	2.2	2.2.
Manufacturing Cost for Sorbent	$/kg	150	10
Adsorption			
Pressure	bar	1	1
Temperature	°C	40	40
Equilibrium Loading	g mol CO_2/kg	2.4	7.2
Heat of Adsorption	kJ/mol CO_2	-60	-60
Desorption			
Pressure	bar	1	1
Temperature	°C	120	<100
Equilibrium CO_2 Loading	g mol CO_2/kg	0.8	0.6
Heat of Desorption	kJ/mol CO_2	60	60
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fluidized bed, temperature swing adsorption	
Flue Gas Flowrate	kg/hr	3,500	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 85(CO_2)/15(H_2O) ambient	
Adsorber Pressure Drop	bar	0.55	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism **–** The sorbent selected for this project is an ion exchange resin with a primary benzyl amine that removes CO_2 in a TSA process. It is important to note that other supported amine sorbents with similar enthalpy of adsorption and physical properties could also be used in the same process without major equipment changes.

One of the most important sorbent properties for post-combustion CO_2 capture is the CO_2 working capacity. Isotherms were generated using experimental data and the Langmuir isotherm model, which are provided in Figure 3. To calculate the CO_2 working capacity of this sorbent, the adsorption conditions are assumed to be 40 °C and pCO_2 (partial pressure of carbon dioxide) = 0.15 bar, while the regeneration conditions are assumed to be 120 °C and 0.81 bar (note that the CO_2 in the regenerator exhaust will be slightly diluted with desorbing moisture). Using the isotherms provided in Figure 3, the CO_2 loading under adsorption conditions is approximately 10.5 g CO_2/100 g fresh sorbent, while the CO_2 loading under the regeneration conditions is approximately 3.5 g CO_2/100 g fresh sorbent; the CO_2 working capacity is approximately 7 g CO_2/100 g fresh sorbent, which is nearly an 80 percent improvement versus the working capacity of aqueous monoethanolamine provided in the 2010 version of the DOE baseline report.

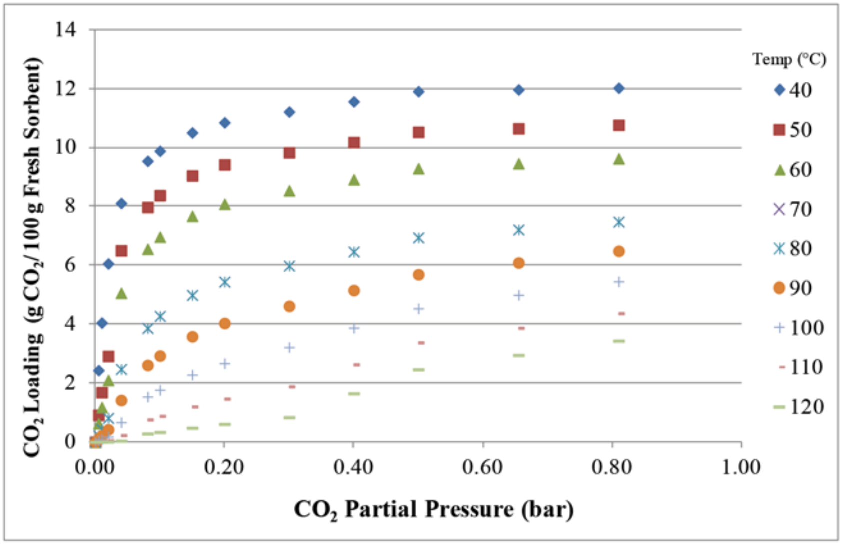

Figure 3: Sorbent isotherms

Sorbent Contaminant Resistance – Amines will react with sulfur dioxide (SO_2) in the flue gas. The selected sorbent will react with SO_2 and, as a result, the overall working capacity for CO_2 will decrease. However, this is a reversible reaction and the sorbent can be regenerated to recover CO_2 capture effectiveness.

Sorbent Attrition and Thermal/Hydrothermal Stability – Based on laboratory testing, the selected sorbent is expected to have low mechanical attrition. Comparisons to fluid catalytic cracking (FCC) catalyst attrition are favorable. The moisture uptake on the sorbent is important because it results in an increase in the regenerator heat duty due to the enthalpy of vaporization/condensation (assuming that the water (H_2O) is physically adsorbed). In addition, in the regenerator, the released H_2O will necessitate the addition of condensers to separate the H_2O from the CO_2 exhaust. This sorbent demonstrates a small (≈0.9 g H_2O/100 g fresh sorbent under expected 1-MW_e pilot operating conditions) H_2O working capacity.

Flue Gas Pretreatment Requirements – A secondary scrubber has been incorporated into the pilot design to reduce the flue gas SO_2. An assessment of the cost-benefit of scrubbing SO_2 versus regenerating the sorbent that has reacted with SO_2 to recover CO_2 capture effectiveness must be conducted to determine the commercial process design and operating details. Additional work has examined the possibility of regenerating sorbents contaminated by acid gases such as SO_2 so that the sorbents may be reused in the process.

Sorbent Makeup Requirements – Current estimates used in cost projections are to replace the sorbent nominally once per year. Further testing is required, including pilot testing to refine the makeup requirements.

Waste Streams Generated – Waste streams will include spent sorbent, flue gas scrubber blow-down, and flue gas cooler condensate.

Process Design Concept – Flowsheet/block flow diagram included above.

Proposed Module Design – The CO_2 capture module will be located downstream of the plant's existing SO_2 scrubber. The gas stream from which CO_2 will be removed is representative of that from a coal-fired power plant with nominal conditions of $pCO_2 = 0.13$ bar and $T = 55$ °C. The adsorber is designed to operate isothermally at 40 °C. The exhaust pressure for regeneration is approximately ambient pressure. The minimum superficial velocity of the flue gas will be limited to 1.2 m/s (4.0 ft/s) to minimize the number and footprint of reactors, and thus capital costs. Pneumatic conveying will be utilized for all required material conveying to increase reliability, decrease operations and maintenance (O&M) costs, and increase technology acceptance. Because the sorbent and flue gas are contacted in a system that approaches counter-current flow, CO_2 working capacity can be maximized. In addition, the heat transfer has been optimized through the use of bubbling fluidized beds. The optimal mixing that is characteristic of bubbling fluidized beds also translates into effective gas/solids contacting. The design of the system employed established methods and principles used for gas-solid systems, including gas distribution, in-bed heat transfer, risers, standpipes, cyclones, and diplegs. Large-scale, two-stage fluidized beds have been used commercially for FCC processes. However, not all aspects of the design are commercially available.

In addition, the cross-heat exchanger module will consist of a further module based upon two concepts. The first concept is a moving bed plate and frame heat exchanger which transfers sensible heat from the hot CO_2 lean sorbent to cold CO_2 rich sorbent via a working fluid within the plates. As the sorbent flows between the plates heat is either transferred from hot sorbent to cool plates and the working fluid in the plates or cool sorbent flows past plates being warmed by the hot heat transfer fluid circulating within the plates.

The second concept uses a fluidized bed system with heat exchanger coils to extract heat from the hot CO_2 lean sorbent and transfer heat to the cold CO_2 rich sorbent. This system is analogous to a shell and tube heat exchanger where the fluidized sorbent in a vessel flows past coils with a heat transfer fluid circulating through the coils. The sensible heat of the hot CO_2 lean sorbent is then rejected to the heat transfer fluid in the coils which then is used in another exchanger to heat the cool CO_2 rich sorbent before it enters the regenerator.

technology advantages

- Sensible heat recovery.
- Reduced adsorber pressure drop.
    - Sorbent is currently cooled in top adsorber bed.
    - Reduced cooling requirements, smaller bed, reduced flue gas blower power, and reduced thermal regeneration input and cooling duty.
- Reduced regenerator pressure drop.
    - Sorbent enters regenerator at higher temperature.
    - Less heat transfer surface required.

R&D challenges

- Benefits of heat recovery must outweigh the increase in capital costs.
- The addition of a cross-heat exchanger may increase the footprint of the existing capture unit.
    - For many existing power plants, overall site footprint may be a limiting factor.
- A heat exchanger will necessitate more sorbent residence time and increase the amount of sorbent required for the process.
- Sorbent cycling time flexibility will be limited by heat exchange requirements.

status

The project ended on December 31, 2015. Two cross-heat exchanger designs—moving bed and fluidized bed—were evaluated for use between the adsorber and regenerator. The initial assessment indicated that the fluidized bed concept was not a practical approach due to the prohibitively high additional electric load associated with fluidization. The techno-economic assessment indicated that addition of a cross-heat exchanger and heat integration significantly improved net unit heat rate, but the additional equipment costs required almost always outweighed the performance improvement. Sorbent BN with the cross-heat exchanger had lower cost of electricity (COE) than for the case without. Sorbent OJ with cross-heat exchanger alone lowered the COE by 0.2 percent, however it showed thermodynamic benefits over the other sorbent. The lowest cost sorbent OJ case had a 15 percent lower COE than the lowest cost sorbent BN case.

available reports/technical papers/presentations

Sjostrom, S. "Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration," presented at Project Closeout Meeting, Pittsburgh, PA, March 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/7017-DOE-Closeout-DE-FE0012914-Final.pdf*

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Sjostrom, S. and Morris, W. "Optimizing the Costs of Solid Sorbent-Based CO_2 Capture Process through Heat Integration," presented at 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Sjostrom-ADA-Optimizing-the-Costs-of-Solid-Sorbent-Based-CO2.pdf*.

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Sjostrom, S.; Krutka, H.; Starns, T.; and Campbell, T., "Pilot Test Results of Post-Combustion CO_2 Capture Using Solid Sorbents," Energy Procedia, 2011, 4, 1584-1592.

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Low-Cost High-Capacity Regenerable Sorbent for Carbon Dioxide Capture from Existing Coal-Fired Power Plants

primary project goals

TDA Research, Inc. (TDA) developed a low-cost, high-capacity carbon dioxide (CO_2) adsorbent to demonstrate its technical and economic viability through sorbent evaluation and optimization, development of sorbent production techniques, and bench-scale testing of the process using actual flue gas.

technical goals

- Optimize sorbent chemical composition.
- Optimize physical properties and mechanical integrity of the sorbent to meet the specific requirements of the process.
- Design and test performance on moving-bed and fixed-bed units.
- Identify optimum operating conditions and process parameters for design calculations.
- Assess the economic viability of the new carbon capture process.

technical content

TDA developed a low-cost, high-capacity CO_2 adsorbent and demonstrated its technical and economic viability for post-combustion CO_2 capture for existing pulverized coal (PC)-fired power plants. The sorbent consists of a carbon material modified with surface functional groups that remove CO_2 via physical adsorption. It exhibits a much higher affinity to adsorb CO_2 than nitrogen, water, or oxygen, enabling effective CO_2 separation from the flue gas. The sorbent binds CO_2 more strongly than common adsorbents, providing the chemical potential needed to remove the CO_2. However, because CO_2 does not form a true covalent bond with the surface sites, regeneration can be carried out with only a small energy input. The heat input to regenerate the sorbent is only 4.9 kcal/mol of CO_2, which is much lower than that for chemical absorbents (e.g., 29.9 kcal/mol CO_2 for sodium carbonate) or amine-based solvents (e.g., 14.2 kcal/mol CO_2 for monoethanolamine [MEA]).

Initial sorbent testing under conditions simulating the environment downstream of a wet flue gas desulfurization unit showed stable CO_2 capacity for more than 220 cycles with no sign of degradation (Figure 1).

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Low-Cost, High-Capacity Regenerable Sorbent

participant:

TDA Research, Inc.

project number:

FE0007580

predecessor projects:

N/A

NETL project manager:

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TDA Research, Inc.
galptekin@tda.com

partners:

Babcock & Wilcox; Gas Technology Institute; University of California, Irvine

start date:

10.01.2011

percent complete:

100%

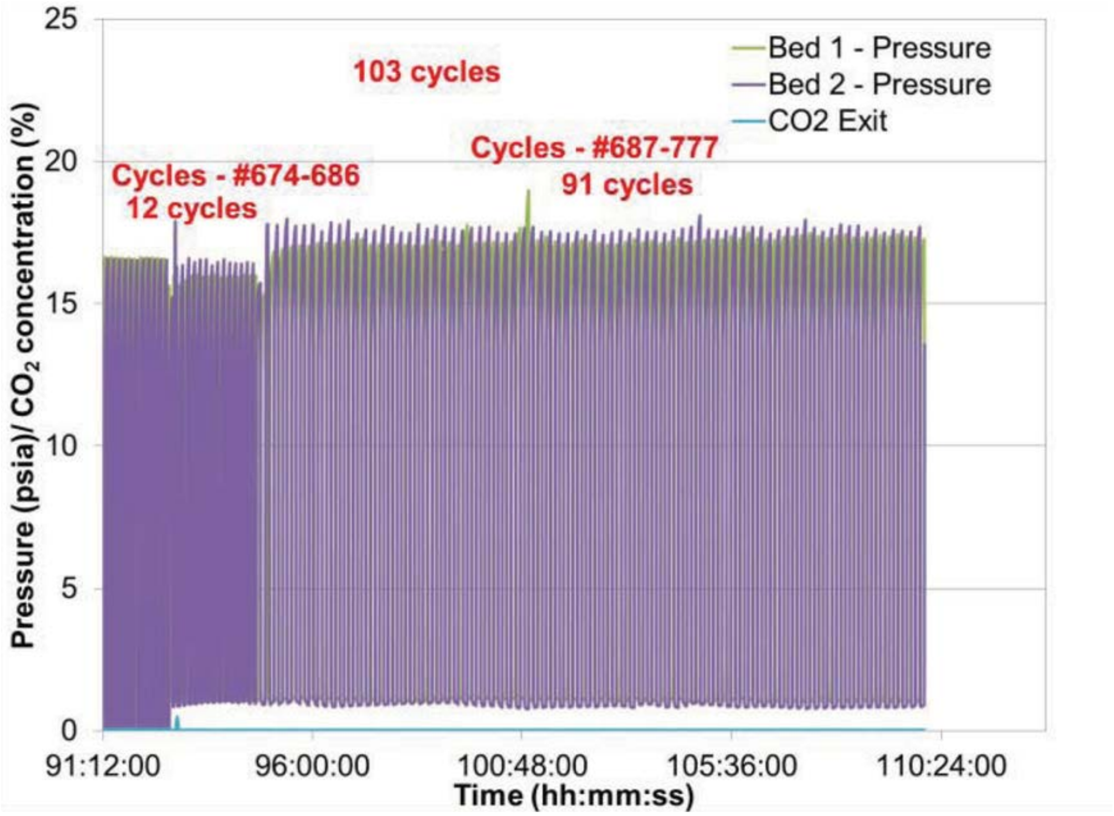

Figure 1: Capacity testing under multiple VSA cycles—capacity maintained over 770 cycles (T = 22 °C; half-cycle time = 4–8 min.; P_{ads} = 16 psia; P_{des} = 1 psia; simulated flue gas, 17 vol% CO_2, H_2O = 1.2 vol%)

The presence of acid gases, such as sulfur dioxide (SO_2) and nitrogen oxide (NO_x), and water (H_2O) vapor up to 15 vol% caused no adverse effect on the CO_2 capacity (Figure 2).

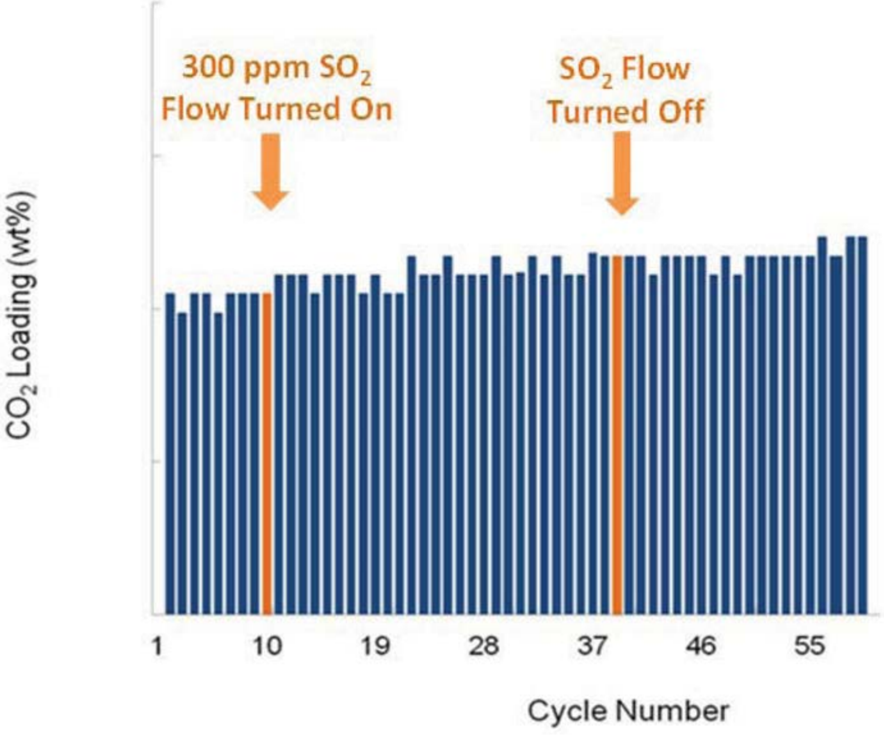

Figure 2: Capacity analysis in presence of SO_2 and water (adsorption T = 62 °C, 15.2 percent CO_2, 2.8 percent O_2, bal. N_2, sat. with H_2O, 300 ppmv SO_2)

Both a moving-bed and fixed-bed vacuum swing adsorption unit were designed for proof-of-concept testing. The 4-bed vacuum swing adsorption (VSA) system is shown in Figure 3.

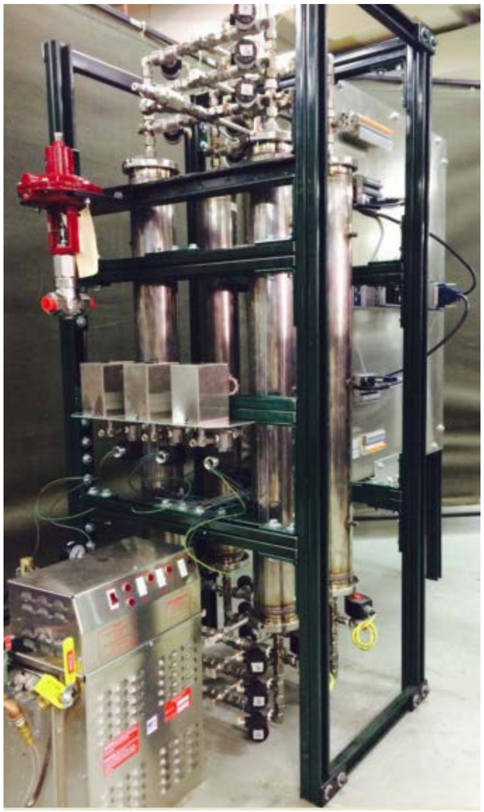

Figure 3: 4-bed VSA prototype

The regeneration of the sorbent and the recovery of CO_2 and its pressurization can then be achieved by several approaches, including temperature swing and vacuum swing. Figure 4 shows a schematic diagram of the process. The sorbent and process parameters are shown in Table 1.

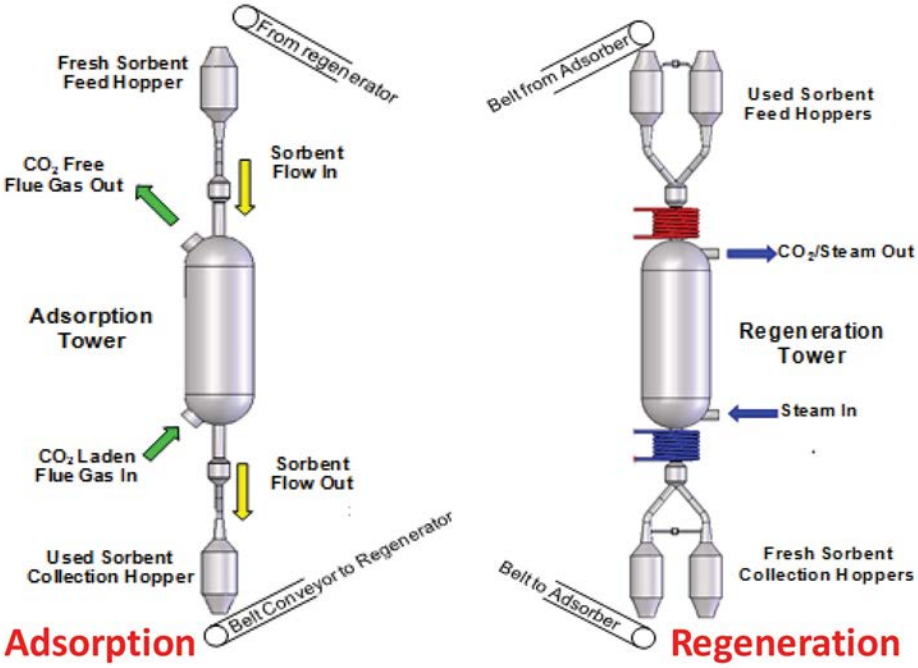

Figure 4: TSA process schematic

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	—	—
Bulk Density	kg/m^3	—	—
Average Particle Diameter	mm	—	—
Particle Void Fraction	m^3/m^3	—	—
Packing Density	m^2/m^3	—	—
Solid Heat Capacity @ STP	kJ/kg-K	0.93	0.93
Crush Strength	kg$_f$	—	—
Manufacturing Cost for Sorbent	$/kg	—	—
Adsorption			
Pressure	bar	1.02	1.02
Temperature	°C	70	58
Equilibrium Loading	g mol CO_2/kg	0.3	0.4
Heat of Adsorption	kJ/mol CO_2	-20.5	-20.5
Desorption			
Pressure	bar	0.204	0.15–0.2
Temperature	°C	70	58
Equilibrium CO_2 Loading	g mol CO_2/kg	—	—
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	—	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— — —	
Adsorber Pressure Drop	bar	—	
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

technology advantages

- The sorbent competitively adsorbs CO_2 over water.
- The heat of adsorption of CO_2 is low (much lower than amine-based solvents; comparable to that of Selexol).
- The net energy loss in sorbent regeneration is expected to be lower than amine scrubbers.

R&D challenges

- Mechanical integrity of the sorbent material at the conditions of use must be demonstrated.
- The gas-solid contactor design must be proven with full capabilities to be demonstrated.

status

The project was completed on September 30, 2015. Proof-of-concept testing was completed on both a moving-bed and a fixed-bed VSA unit. B&W estimated the total plant cost for the moving-bed system as approximately $424 million (2011 basis) and a total plant cost for the fixed-bed system to be approximately $276 million. A 4-bed VSA system was tested for over 750 hours on a 4-standard cubic feet per minute (scfm) slipstream of actual flue gas at Gas Technology Institute's Combustion Facility, showing stable performance and achieving >90 percent CO_2 capture.

available reports/technical papers/presentations

Alptekin, G., Jayaraman, A., and Copeland, R., "Post-Combustion CO_2 Capture System for Existing Coal-Fired Power Plant," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/G-Alptekin-TDA-New-Sorbent-Process.pdf.*

Alptekin, G., Jayaraman, A., and Copeland, R., "Post-Combustion CO_2 Capture System for Existing Coal-Fired Power Plant," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/G-Alptekin-TDA-A-New-Sorbent-For-Post-Combustion.pdf*.

Alptekin, G., Jayaraman, A., and Copeland, R., "Post-Combustion CO_2 Capture System for Existing Coal-Fired Power Plant," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/G-Alptekin-TDA-New-Sorbent-for-Post-Combustion.pdf*.

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Alptekin, G., "Post-Combustion CO_2 Capture System for Existing Coal-fired Power Plant," presented at the Project Kickoff Meeting, Pittsburgh, PA, December 2011. *https://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/low-cost-high-capacity-regenerable-sorbent-dec2011.pdf.*

Rapid Temperature Swing Adsorption Using Polymeric/Supported Amine Hollow Fiber Materials

primary project goals

Georgia Tech Research Corporation developed a rapid temperature swing adsorption (RTSA) carbon dioxide (CO_2) process and evaluated the cost and performance benefits of this novel hybrid capture approach via bench-scale testing of a module containing polymeric/supported amine hollow fibers, which are loaded with supported adsorbents and surround an impermeable lumen layer that allows for cooling and heating.

technical goals

- Produce polymeric hollow fiber contactors loaded with amine adsorbent particles for post-combustion (CO_2 capture.
- Develop a computational model of the fiber module and validate it in parallel with the experimental program.
- Assess adsorption/desorption and heat-exchange performance of hollow fiber modules using simulated clean and simulated dirty flue gas.

technical content

Supported amine adsorbents have many promising properties with regard to CO_2 capture from post-combustion flue gas. However, most previous studies of supported amine materials focus only on CO_2 adsorption, ignoring desorption. In addition, essentially all published studies describe the use of supported amine materials in fixed beds. This process configuration is difficult to use at practical scales due to heat integration challenges. This is especially important for supported amines; whose heats of adsorption are among the highest of known CO_2 adsorbents (50–80 kJ/mol), but which enables large swings in capacity with temperature. Thus, practical process designs for amine sorbents must include effective heat transfer.

Recently, the use of novel polymeric hollow fiber contactors loaded with CO_2 adsorbents has been introduced as a scalable process configuration for CO_2 capture. In this approach, polymeric hollow fibers, similar to those used for commercial-scale membrane gas separation, are prepared and loaded with large volumes of solid CO_2 adsorbing materials. However, unlike those used for membrane applications, these hollow fibers have several unique aspects. First, high volumes of adsorbent materials are included, typically 60–75 percent by volume. Second, the polymeric phase is designed to have many large voids, allowing rapid mass transfer to the sorbent particles. Third, a dense lumen layer is installed in the fiber bore to largely shutdown transport from the shell side of the fibers to the bore. This design yields fibrous structures that are ideally suited for application as combined sorption and heat transfer modules in an RTSA process. Total cycle times are in the order of 3 minutes.

In the amine-hollow-fiber RTSA process, flue gases flow over the shell of the fibers while cooling water flows through the bore. Given the small diameter of the fibers, the fibers

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Rapid Temperature Swing Adsorption

participant:

Georgia Tech Research Corporation

project number:

FE0007804

predecessor projects:

N/A

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partners:

Trimeric Corporation; Algenol Biofuels; Southern Company Services; GE Energy

start date:

10.01.2011

percent complete:

100%

and adsorbents can be maintained in nearly isothermal conditions, with the cooling fluid providing an effective reservoir for heat of adsorption (Figure 1). At the appropriate time, the flue gas can be rerouted to another bed and the fibers can be switched to desorption mode by passing hot water through the fiber bore, driving off the CO_2.

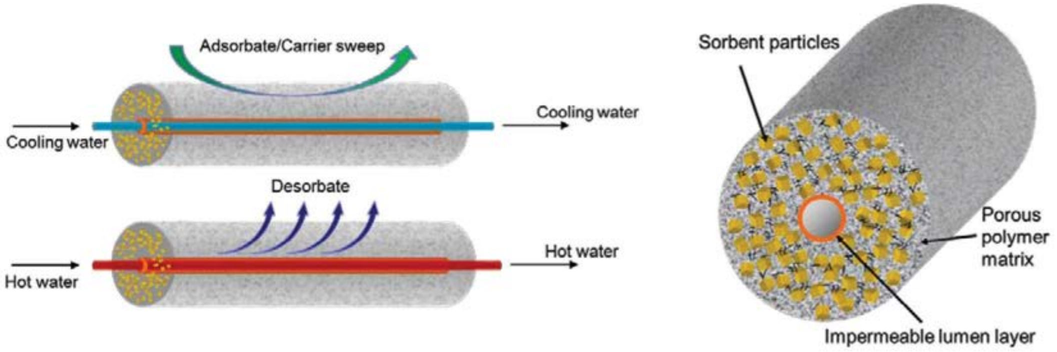

Figure 1: Sorption (top) and desorption (bottom) modes in hollow fiber sorbents

This RTSA approach was previously demonstrated using cellulose acetate fibers and zeolite 13X as the adsorbent in the fibers. Zeolite 13X is not an ideal sorbent for wet post-combustion CO_2 capture streams, but supported amines may be well suited for the task.

The hollow fiber architecture has three key attributes: (1) it provides the adsorption surface area needed to handle large volumes of flue gas, (2) it enables efficient heat transfer needed to handle the high heat of adsorption of supported amines, and (3) it is readily scalable given the current commercial capability to produce large surface area hollow fibers on an industrial scale.

The RTSA process based on hollow fibers containing supported amine adsorbents represents a novel new process configuration for post-combustion CO_2 capture. In a commercial process, multiple hollow fiber modules would be used, and modules would cycle synergistically between adsorption and desorption modes in a continuous process, as shown in Figure 2.

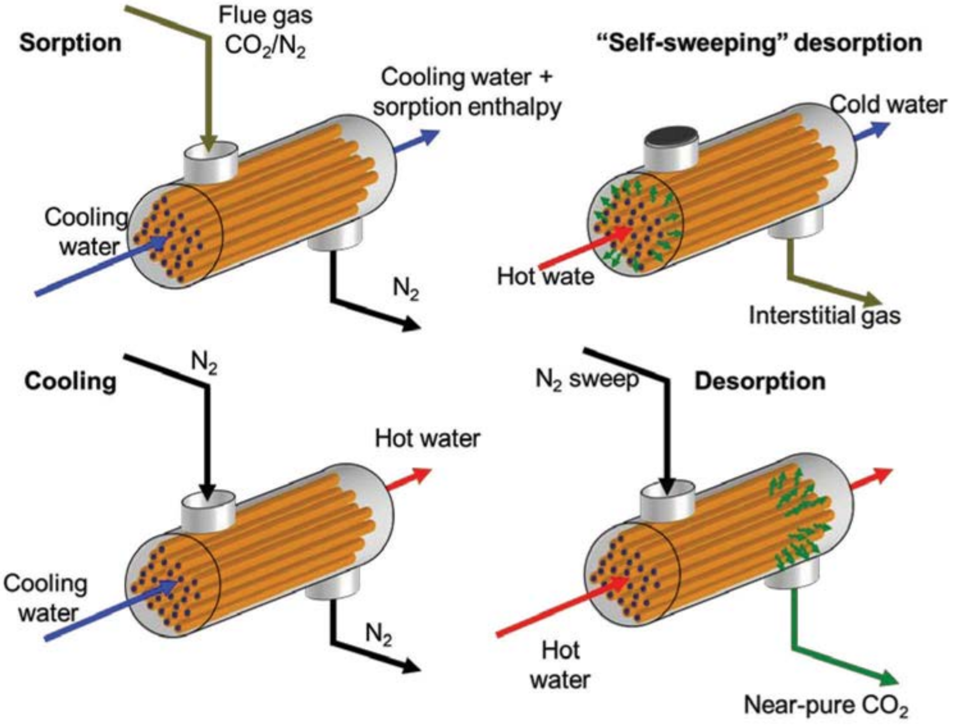

Figure 2: Potential RTSA process configuration

The sorbent and process parameters are shown in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,100	1,100
Bulk Density	kg/m^3	1,100	1,100
Average Particle Diameter	mm	1.2	1.0
Particle Void Fraction (void fraction of fiber bed)	m^3/m^3	0.4–0.5	0.28–0.3
Packing Density (packing density of fiber bed)	m^2/m^3	1,000	1,600
Solid Heat Capacity @ STP	kJ/kg-K	1,800	3,000
Crush Strength	kg$_f$	1.140	1.140
Manufacturing Cost for Sorbent	$/kg	unknown	unknown
Manufacturing Cost for Fiber Module (includes hardware, fibers, sorbent)	$/kg	unknown	$10/m^2 or $25–$35/kg
Adsorption			
Pressure (partial pressure of CO_2)	bar	0.159	0.13
Temperature	°C	55	35
Equilibrium Loading	g mol CO_2/kg fiber	0.84	1.0–1.5
Heat of Adsorption	kJ/mol CO_2	59	55–65
Desorption			
Pressure	bar	0.2	1.0
Temperature	°C	120	90
Equilibrium CO_2 Loading	g mol CO_2/kg fiber	0.34	0.1
Heat of Desorption	kJ/mol CO_2	59	55–65
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	shell and tube	
Flue Gas Flowrate	kg/hr	200 sccm (lab), ≈2,900 (full scale, per module)	0.5 (lab), ≈2,900 (full scale, per module)
CO_2 Recovery, Purity, and Pressure	% / % / bar	91%/96 mol%/0.2 bar (0.19 bar partial pressure)	90%/95 mol%/1 bar or 80 mol% at 5.5 bar
Adsorber Pressure Drop	bar	<0.1	<0.15
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The underlying mechanism is primary and secondary amines reacting with CO_2 to produce carbamates or (bi)carbonates, depending on the nature of the amines, amine loading, and humidity level. Under most conditions, a mixture of species is formed on the adsorbent surface.

Sorbent Contaminant Resistance – Thus far, the solid supported amines developed for this project have displayed excellent oxidative stability, stability in humid conditions (5–90 percent relative humidity [RH]), and resistance to nitric oxide. The active amine fillers are poisoned by high concentrations of sulfur oxide (SO_x, 200 parts per million [ppm]), and extensive sulfur removal is needed.

Sorbent Attrition and Thermal/Hydrothermal Stability – Due to the sorbents being "protected" within the walls of the hollow fiber sorbents, the Georgia Institute of Technology has yet to experience any mechanical issues (such as attrition) in their studies. The fibers themselves are quite temperature-resistant, but the amines have a realistic upper temperature limit of ≈130 °C. The amines contained within the fiber walls exhibit higher CO_2 uptake capacities in the presence of water; moreover, the fibers themselves have been continuously cycled between 35°C and 120°C without damage to the fiber structure. These suggest that the materials are hydrothermally stable within the operating ranges of the RTSA process.

Flue Gas Pretreatment Requirements – Current analysis indicates that flue gas cooling to approximately 35 °C is required for low-cost CO_2 capture. Experimental work suggests that partial dehydration of the flue gas may prolong fiber lifetimes (i.e., 90 percent RH vs. 100 percent RH). Finally, further wet FGD may be required for additional SO_x removal for optimum long-term performance of the amines.

Sorbent Makeup Requirements – Analyses investigating the amine loss rates are needed. It has been demonstrated that deactivated amines can be removed when required, and fresh amines redeposited in the fibers, allowing fiber recycling and reuse.

Waste Streams Generated – Spent fiber sorbents represent the only process waste stream. Currently, the fibers are assumed to last 3 years before replacement is required. With appropriate flue gas scrubbing, such lifetime may be achievable.

Process Design Concept – See Figure 2.

technology advantages

- Deleterious thermal effects typically associated with packed-bed sorption can be mitigated and higher sorption efficiencies can be achieved by utilizing the hollow fiber morphology to supply cooling agents in the bore of the fiber during adsorption.
- The thin porous walls of the fiber sorbent allow for rapid heat and mass transfer equilibration, thereby allowing for more rapid thermal cycles and thus reducing device volume.
- Pressure drops through these beds will be correspondingly lower than those of packed or fluidized solid sorbent beds, which will reduce draft fan costs.
- Heat transfer fluids in the bore of the fibers can be as simple as hot water and cold water, providing an environmentally friendly overall process.
- Rapid heat transfer enables potential recovery of heat of adsorption and reuse of sensible heat of the bed. This affords heat integration both within the capture process and may facilitate heat integration with the boiler feed water preheat. This can dramatically reduce the overall parasitic thermal load of the RTSA process.

R&D challenges

- High heat of adsorption, with heat management improved by contactor design.
- Deactivation of sorbents upon exposure to SO_x and exposure to saturated humidity and temperature.
- Low-working capacity in more conventional contactors.
- Efficient heat integration with power plant.
- Long-term operation of complete cycles with bore-side heating and cooling.
- Manufacturing cost estimates of fibers have significant uncertainty.
- Design of efficient multibed cycles to improve recovery and purity.
- Adaptive scheduling and control to manage slow degradation over many cycles and variability between modules.

status

The project was completed on March 31, 2015. Georgia Tech has developed a post-spinning amine infusion method to create and recharge sorbents. A dual layer spinning method was developed for constructing a barrier lumen layer in the fiber bore, which allows the fiber to be used as an adsorbing shell-in-tube heat exchanger. Testing has been completed on hollow fiber RTSA modules. Heat integration in the RTSA process has allowed for up to 70 percent recovery of the heat of adsorption and the RTSA cycle time has been reduced to 3 minutes. A detailed process model of the cyclic pressure temperature swing adsorption module was developed and validated against experimental data. The process model was integrated with costing models for the overall process that included compression and flue gas conditioning. The CO_2 capture cost was estimated to be $44.8/tonne CO_2.

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Bench-Scale Development and Testing Of A Novel Adsorption Process for Post-Combustion CO_2 Capture

primary project goals

InnoSepra, LLC developed a sorption-based carbon dioxide (CO_2) capture technology using a combination of novel microporous materials and process cycles to determine the impacts of these combinations on capture costs and performance via bench-scale testing of system components using actual coal-based flue gas.

technical goals

- Confirm the design basis for bench-scale testing based on lab-scale results and process modeling.
- Build and mechanically test the bench-scale unit in the lab.
- Test the bench-scale unit on an actual coal-based flue gas at NRG Indian River plant for a period of 6–8 weeks.
- Develop capital cost, operating cost, and levelized cost of electricity (LCOE) estimates for a commercial, 550-megawatt (MW) power plant.

technical content

InnoSepra demonstrated the effectiveness of an innovative, adsorption-based carbon dioxide capture technology utilizing a combination of novel microporous materials and process cycles. The process utilizes physical sorbents with much lower heats of adsorption (around 38 kJ/mol, less than 25 percent of the total energy needed for amine-based systems) compared to competing processes. Bench-scale testing has produced greater than 99 percent CO_2 purity and greater than 90 percent CO_2 recovery from the actual coal-fired plant flue gas. Projections based on detailed engineering evaluations show that at commercial scale, the technology can reduce the power consumption for CO_2 capture by more than 40 percent, and reduce the capital cost for the CO_2 capture equipment by more than 40 percent; this results in a more than 40 percent reduction in the CO_2 capture cost compared to alternate technologies such as amines and chilled ammonia. Since the steam for regeneration is extracted at a temperature of less than 105 °C for the InnoSepra process compared to a steam extraction temperature of >250 °C for the amine process (MEA) the power loss due to steam extraction for the InnoSepra process is about 75 percent lower than MEA-based amine process (power generation efficiency for steam at 105 °C is about 15 percent compared to a power generation efficiency of >30 percent for the steam extraction at >250 °C).

The overall process schematic including its integration with the power plant is shown in Figure 1.

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Novel Adsorption Process

participant:

InnoSepra, LLC

project number:

FE0007948

predecessor projects:

N/A

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partners:

Adsorptech; New Mexico State University; Electric Power Research Institute; NRG Energy, Inc.; Pacific Northwest National Laboratory

start date:

10.01.2011

percent complete:

100%

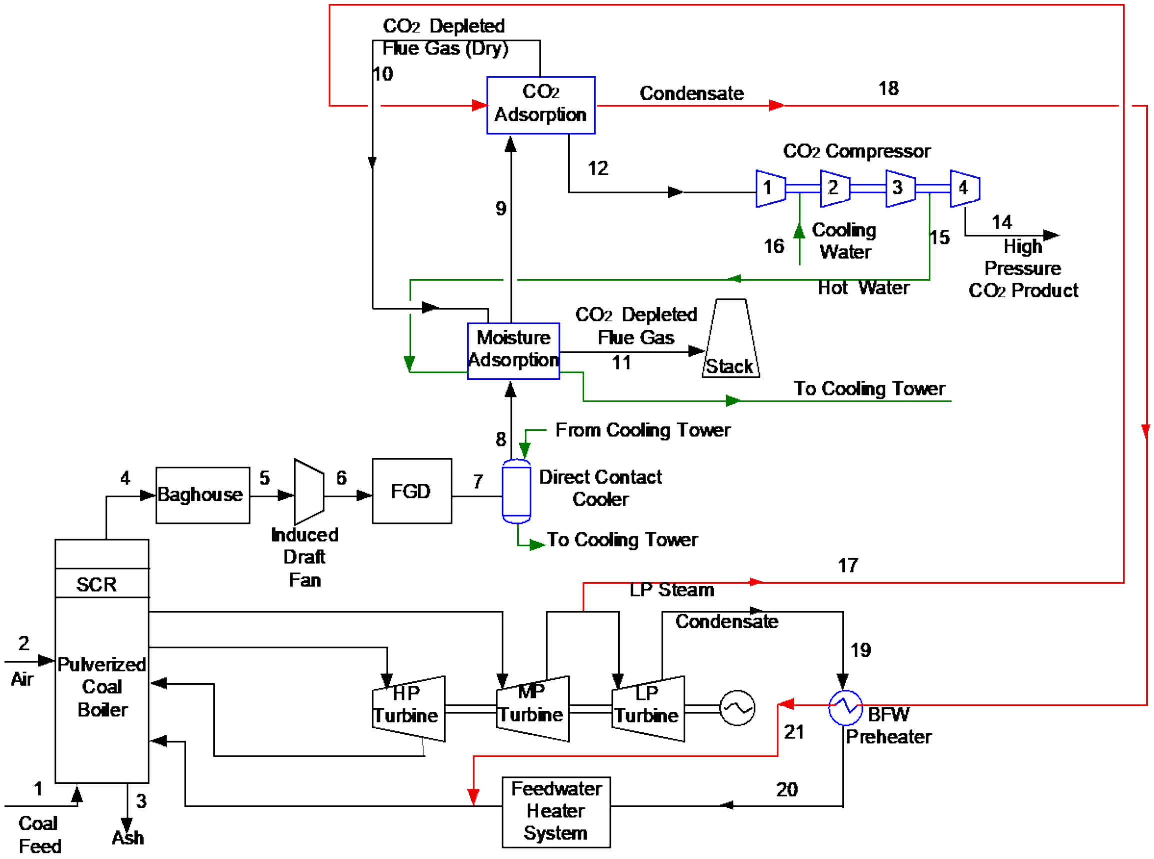

Figure 1: InnoSepra capture process schematic

Figure 2 provides a schematic representation focusing on the CO_2 removal process. After the removal of moisture and sulfur oxides (SO_x) in a pretreatment system, the CO_2 is captured in an adsorber. A high-purity CO_2 is produced during sorbent regeneration. The sorbents are heated and cooled using both direct and indirect cooling. Some of the heat of adsorption is removed during the adsorption process; the remaining heat is removed during the cooling steps. Regeneration heat is supplied via low-pressure steam, as well as by utilizing other process waste heat in the system

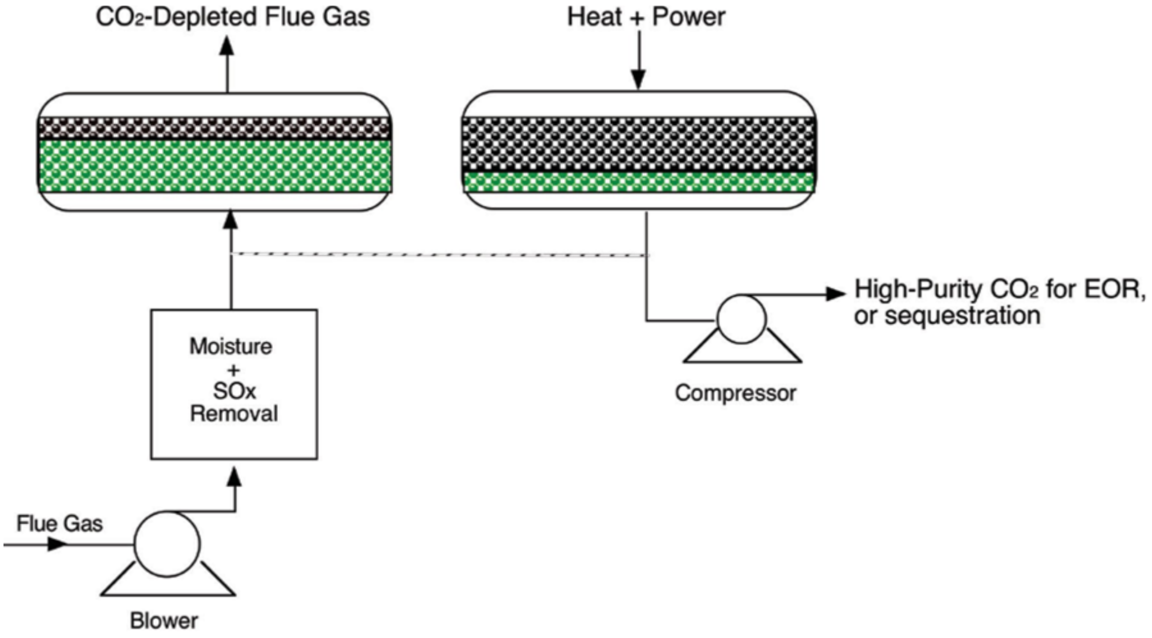

Figure 2: CO_2 capture process schematic

The test unit is shown in Figure 3. Field-testing of the process at a 1-ton-per-day scale in an actual power plant, as well as independent verification of process economics, has provided a firmer basis for techno-economic evaluation.

Figure 3: Adsorption skid (left) and heating and cooling skid (right)

The sorbent and process parameters are provided in Table 1.

TABLE 1: SORBENT PROCESS PARAMETERS

Sorbent	Units	Current R&D Value	Target R&D Value
True Density @ STP	kg/m^3	1,990	1,990
Bulk Density	kg/m^3	690	690
Average Particle Diameter	mm	1.5–3.0	0.5–1.5
Particle Void Fraction	m^3/m^3	0.45	0.45
Packing Density	m^2/m^3	1.79e8	1.79e8
Solid Heat Capacity @ STP	kJ/kg-K	0.96	0.96
Crush Strength	kg_f	2.9	2.9
Manufacturing Cost for Sorbent	$/kg	4.0	3.0–4.0
Adsorption			
Pressure	bar	1.15	1.1
Temperature	°C	25–32	25–32
Equilibrium Loading	g mol CO_2/kg	3.25	3.5–4.0
Heat of Adsorption	kJ/mol CO_2	38	38
Desorption			
Pressure	bar	0.3–1.0	0.3–1.0
Temperature	°C	100	90–110
Equilibrium CO_2 Loading	g mol CO_2/kg	1.5	1.5–2.0
Heat of Desorption	kJ/mol CO_2	38	38
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fixed/cyclic	
Flue Gas Flowrate	kg/hr	2,320,000	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90 99 1.0	
Adsorber Pressure Drop	bar	0.14	0.10
Estimated Adsorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	336	

Definitions:

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

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either *continuous*, *cyclic*, or *semi-regenerative* operation.

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

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

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – The adsorption is physical sorption based on weak van der Waals forces. This leads to low heats of adsorption.

Sorbent Contaminant Resistance – Under normal operation the sorbent is not irreversibly damaged by any contaminant in the flue gas. If substantial quantities of SO_2 are present in the feed to the CO_2 adsorption section the sorbent may require higher than normal regeneration temperature to restore performance.

Sorbent Attrition and Thermal/Hydrothermal Stability – The process design protects the adsorbent from moisture and potential hydrothermal degradation. If moisture should breakthrough onto the adsorbent, the adsorbent can be regenerated completely. The adsorbent is thermally stable at temperatures of more than 300 °C.

Flue Gas Pretreatment Requirements – No special flue gas pretreatment is required. A conventional FGD and a Direct Contact Cooler (DCC) are sufficient for normal process operation.

Sorbent Makeup Requirements – Based on prior experience with similar sorbents in similar operating environments, the adsorbent life would be between 5 and 10 years. An adsorbent life of 5 years has been assumed to estimate the makeup requirements.

Waste Streams Generated – Except for the sorbents loaded with flue gas components, SO_x and mercury, no other waste streams are generated in the process. These can be disposed of as per current power plant practices for materials loaded with SO_x and Hg.

Process Design Concept – The commercial process configuration is shown in Figure 4. The adsorption equipment is modular in nature and five adsorption skids are needed for a 550 MW power plant. The rest of the process equipment such as the feed blower, direct contact cooler and the CO_2 compressor is very similar to the amine process.

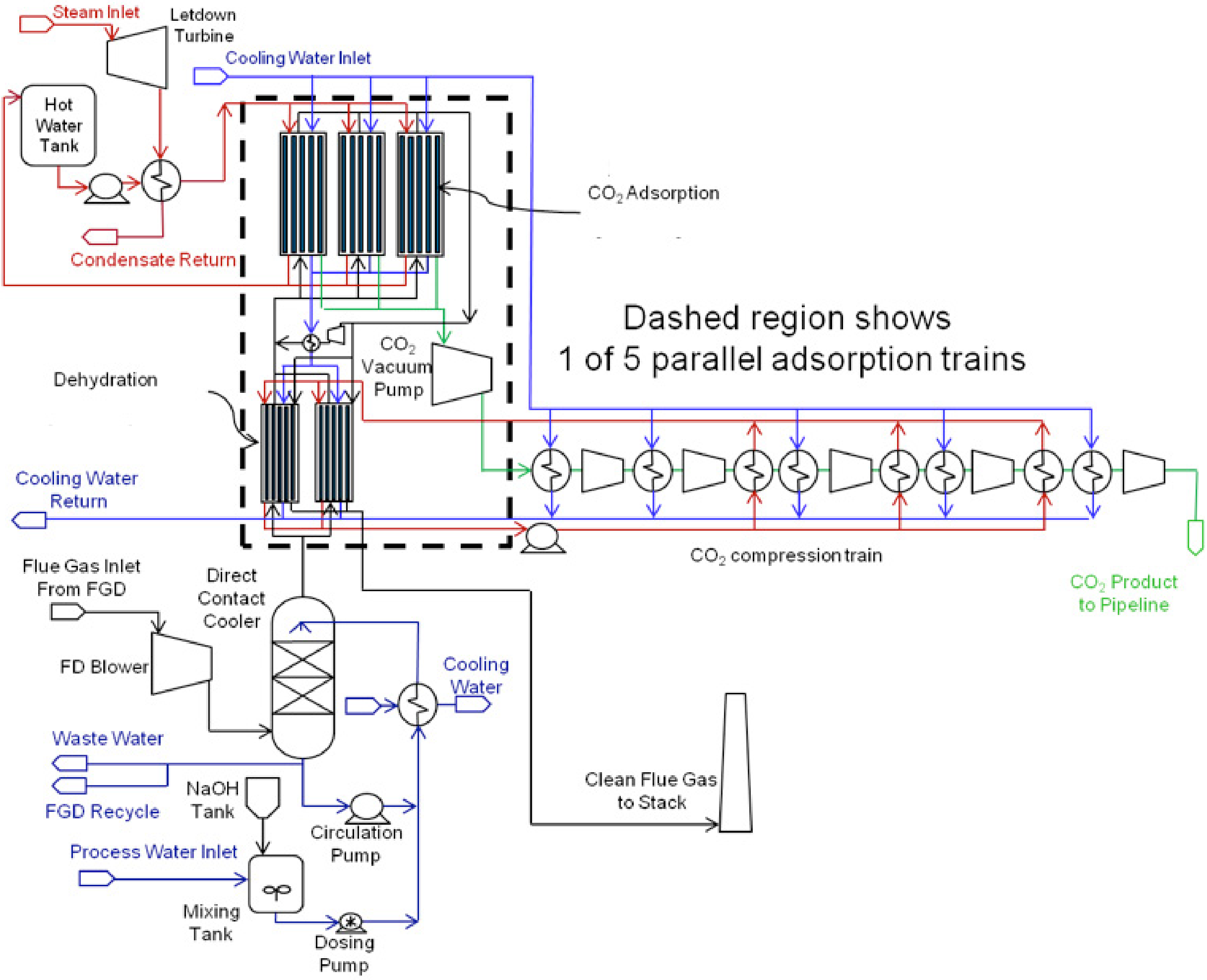

Figure 4: Commercial Process Configuration

Proposed Module Design – The CO_2 capture modules will be designed to capture CO_2 from a 550-MW PC power plant. Multiple modules will be used to minimize field fabrication and maximize offsite fabrication. The separation skid will consist of a feed preparation section (flue gas compression and cooling), the CO_2 adsorption section (removal of impurities, CO_2 adsorption, and desorption), and the CO_2 compression section.

technology advantages

- The technology is able to utilize physical sorbents to obtain the same purity and recovery as chemical sorbents and amine-based absorption.
- The sorbents have much lower heats of adsorption compared to reaction-based systems.
- The technology can produce >99 percent purity CO_2 at >90 percent recovery with a thermal energy penalty of less than 60 percent of the energy penalty for the monoethanolamine (MEA) systems. The steam is extracted at <105 °C leading to more than 75 percent reduction in power loss due to steam extraction compared to MEA.
- The process is non-corrosive and can utilize carbon steel construction for the most part.

R&D challenges

- Heat management during both adsorption and regeneration.
- Water management.

status

The project was completed on March 31, 2015. InnoSepra completed bench-scale testing using actual flue gas at the NRG Energy plant, indicating >94 percent CO_2 recovery, 98.5–99.5 percent CO_2 purity and between 8–10.5 wt% net CO_2 capacity for a feed between 10–12 percent CO_2. Results indicated the field performance is superior to the performance in the lab. The estimated total energy required for the process, excluding compression, is 450–500 kcal/kg of CO_2. The TEA for a 550-megawatt electric (MW_e) plant indicated 38 percent lower capital cost, including the CO_2 compressor, compared to MEA, and 18 percent parasitic power load compared to 28 percent parasitic load for MEA.

available reports/technical papers/presentations

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EVALUATION OF CARBON DIOXIDE CAPTURE FROM EXISTING COAL-FIRED PLANTS BY HYBRID SORPTION USING SOLID SORBENTS

primary project goals

The University of North Dakota (UND) and Envergex LLC are developing a solid sorbent technology—Capture from Existing Coal-Fired Plants by Hybrid Sorption (CACHYS™)—that is based on the following principles:

- Reduction of energy for sorbent regeneration.
- Utilization of novel process chemistry.
- Contactor conditions that minimize sorbent-CO_2 heat of reaction and promote fast CO_2 capture.
- Low-cost method of heat management.
- Low-cost, carbon-based sorbent impregnated with an alkali carbonate salt and an active promoter.

technical goals

- Sorbent selection and formulation, as well as the determination of heat of sorption, sorbent capacity (CO_2 loading), and sorbent physical properties for process design definition.
- Conduct lab-scale, fixed-bed tests to investigate adsorption and desorption kinetics, working capacity, heats of adsorption and desorption and a relative measure of attrition during multiple cycles.
- Establish the optimum process conditions (e.g., temperatures, pressures, and residence times), preferred sorbent compositions, and bench-scale equipment design (e.g., size, energy duties, and material feed rates).
- Design, build, and operate a bench-scale CACHYS™ adsorption and desorption system designed for a flue gas flow rate of 30 actual cubic feet per minute (acfm) obtained as a slipstream from a sub-bituminous coal-fired stoker boiler at the UND campus steam plant.

technical content

The project was intent on developing key information for the CACHYS™ process - sorbent performance, energy for sorbent regeneration, physical properties of the sorbent, the integration of process components, sizing of equipment, and overall capital and operational cost of the integrated CACHYS™ system. The bench-scale CACHYS™ test unit includes a flue gas conditioning system to remove particulate matter and sulfur dioxide via a fabric filter and a wet packed-bed scrubber using sodium hydroxide solution, respectively. Two circulating fluidized beds are employed for CO2 adsorption. The Solex Thermal regenerator system consists of three functional units capable of operating at elevated pressure—the

technology maturity:

Bench-Scale, Actual Flue Gas

project focus:

Solid Sorbent-Based CO_2 Capture

participant:

University of North Dakota

project number:

FE0007603

NETL project manager:

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partners:

Industrial Commission of North Dakota
Envergex LLC
Barr Engineering
Solex Thermal Science Incorporated
ALLETE Incorporated
SaskPower

performance period:

10/1/11 – 12/31/14

preheater, the regenerator, and the cooler. Sorbent transferred from the adsorber system is heated to the desired regeneration temperature in the preheater and transferred to the regenerator unit where the CO_2 is desorbed from the sorbent. The sorbent then transfers to the cooler, where the temperature of the sorbent is returned to the adsorption temperature. The sorbent is then transferred back to the adsorber system via pneumatic conveyance.

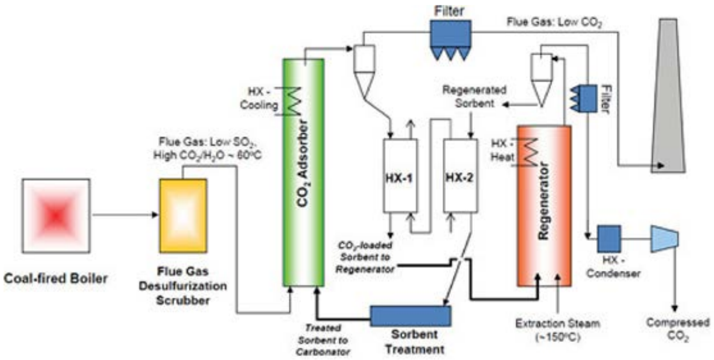

Figure 1: CACHYS™ Sorption Process

TABLE 1: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density at STP	kg/m^3	1,800–2,200	1,800–2,200
Bulk Density	kg/m^3	400–700	400–700
Average Particle Diameter	mm	0.1–1	0.1–1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	230	230
Solid Heat Capacity at STP	kJ/kg-K	1.2	1.2
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg	1.65	1.00
Absorption			
Pressure (partial of CO_2)	bar	0.1	0.1
Temperature	°C	50–80	50–80
Equilibrium CO_2 Loading	g mol CO_2/kg	2.1	2.1
Heat of Absorption	kJ/mol CO_2	30–80	30–80
Desorption			
Pressure (partial of CO_2)	bar	1.9	1.9
Temperature	°C	140–160	140–160
Equilibrium CO_2 Loading	mol/mol	0.5	0.5
Heat of Desorption	kJ/mol CO_2	30–80	30–80
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	fluidized bed	
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, 95–99%	
Adsorber Pressure Drop	bar		

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

technology advantages

- Low heat of sorption.
- Increased sorption kinetics.
- Low-cost sorbent.
- Commercially-available and easily-scalable equipment.

R&D challenges

- Confirmation of energetics.
- Sorbent integrity.
- Sorbent handling.
- Achievement of 90% CO_2 capture.

results to date/accomplishments

- Performed laboratory-scale testing that showed heat of desorption was 30–80 kJ/mol CO_2, depending on process conditions. Sorbent CO_2 working capacity ranged from 70–100 g/kg sorbent. Both metrics exceeded the target levels.
- 100-cycle tests demonstrated excellent chemical stability and no detectable loss in capacity.
- The CACHYS™ bench-scale test facility was constructed at UND's coal-fired steam plant. The system captures CO_2 from 30 acfm of flue gas with a sorbent throughput of 200-400 lb/hr.
- Bench-scale parametric testing resulted in a maximum CO_2 capture of 85 percent and demonstrated the significant benefits of hybrid sorption compared to standard carbonate sorption: Much higher capture and reaction rates (≈2–3X) and excellent control of exothermic heat of adsorption.
- Continuous and integrated bench-scale testing demonstrated sustainable (5–7 hours) capture of 70–80 percent with 4 percent CO_2 in flue gas and 40–60 percent with 8 percent CO_2 in flue gas. A 15-hour continuous test with stable operations was completed.
- Based on the testing data gathered over the course of the project, a final technical and economic feasibility study was completed. Results indicate a modest improvement over the benchmark MEA process and progress towards the DOE goals.

next steps

This project ended December 31, 2014.

available reports/technical papers/presentations

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/S-Benson-UNDakota-S-Srinivasachar-Envergex-Evaluation-of-CO2.pdf*.

Presentation at the Thirteenth Annual Conference on Carbon Capture, Utilization, and Storage, Pittsburgh, PA, April 28–May 1, 2014. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/2014-CCUS-Presentation-7603.pdf*.

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July 2013, *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/S-Benson-UND-Hybrid-Sorption-Using-Solid-Sorbents.pdf*.

Benson, S., et al., "Evaluation of CO_2 Capture from Existing Coal-fired Plants by Hybrid Sorption Using Solid Sorbents," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

Preliminary Carbon Dioxide Capture Technical and Economic Feasibility Study—Topical Report (November 2012).

Project Review Meeting Presentation (September 2012). *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/und-CO2-capture-budget-period1.pdf*.

Evaluation of CO_2 Capture from Existing Coal-Fired Power Plants by Hybrid Sorption Using Solid Sorbents (CACHYS™) Project Kick-Off Meeting Presentation, November 21, 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO2/und-CO2-capture-budget-period1.pdf*.

METAL MONOLITHIC AMINE-GRAFTED SILICA FOR CO_2 CAPTURE

primary project goals

The University of Akron set out to develop a low-cost carbon dioxide (CO_2) capture technology by integrating metal monoliths with a grafted amine sorbent.

technical goals

- 1.5 mmol-CO_2/g-sorbent.
- 1.0 mmol-sulfur dioxide (SO_2)/g-sorbent.
- 500 repeated thermal cycles of sorbent between CO_2 adsorption at 25°C and desorption at 110°C with less than a 10 percent degradation in original CO_2 capture capacity.

technical content

The key innovation of this project is the utilization of metal foils with amine-grafted porous silica to fabricate a highly efficient and low-cost CO_2 adsorption system. Porous silica, alumina, zeolite, and carbon, which are used as commercial adsorbents for a wide range of applications, are impregnated with alkyl amine molecules such as monoethanolamine (MEA)/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was determined to be greater than 1.5 mmol-CO_2/g-sorbent because of the abundance of available amine functional groups on the amine-grafted silica. The adsorption and desorption can be further optimized by the sorbent preparation procedures with additives.

The metal monolithic structure allows the rapid removal of heat of CO_2 adsorption. The surface of the metal monolith is coated with a layer of silica, carbon fibers, and a binder. Calcination of the metal monolith with this coating produces the silica or zeolite layers structure with 10-µm diameter channels. The binder and carbon fiber concentration is fine-tuned to optimize the number of the micro channel pathways for CO_2 diffusion into the amine-grafted silica and zeolite.

The University of Akron, as part of this project, has also investigated using coal fly ash treated first with sodium hydroxide (NaOH) and/or hydrochloric acid (HCl), and then impregnated with the amine tetraethylenepentamine. Coal fly ash was investigated as a support for amine due to its ready availability and low cost.

technology maturity:

Pilot-Scale Using Simulated Flue Gas, 15 kW

project focus:

Metal Monolithic Amine-Grafted Zeolites

participant:

University of Akron

project number:

FC26-07NT43086

NETL project manager:

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partners:

FirstEnergy

performance period:

2/21/2007 – 3/31/11

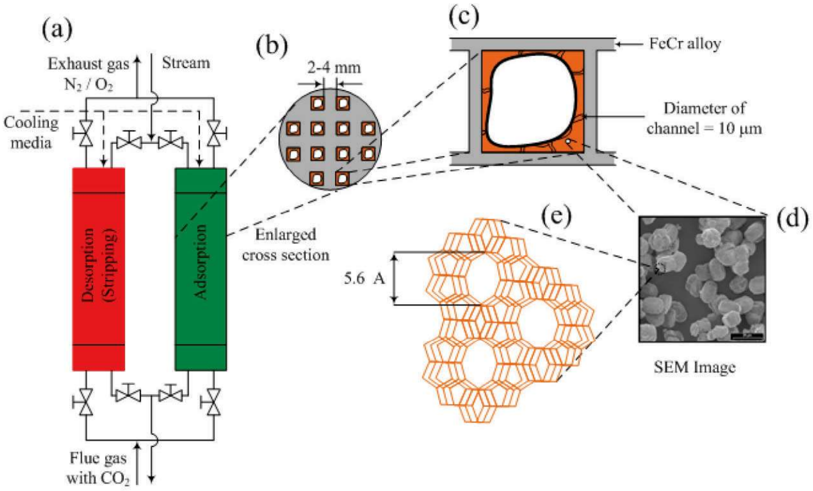

Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

Figure 1 displays the amine-grafted zeolite structure (5.6 Angstroms in length) inside an adsorption unit. The amine is located in the adsorption (a) chamber within holding tubes. The tubes housed in the adsorption unit holds the individual metal (b) tubes with the amine approximately 2 to 4 mm apart. The silica or zeolite is coated inside the square metal tube. Gas enters the tube and flows through the channels (d) of the amine grafted silica, which are 10 µm in diameter. Heating for CO_2 desorption (i.e., regeneration) and cooling for adsorption are achieved by 40 pounds per square inch gauge (psig) steam and cooling water flowing through the jacket side of the adsorber. Desorbed CO_2 is purged from the channels of metal monoliths by pulses of steam and hot air. The goal is that CO_2 and SO_2 adsorption capacity of the amine will be greater than 1.5 mmol-CO_2/g-sorbent and 1.0 mmol-CO_2/g-sorbent, respectively. The amine is capable of greater than 500 times regeneration with less than 10 percent degradation in CO_2 capacity. The amine-grafted silica sorbent is expected to exhibit a heat capacity of 1.5 kJ/kg K. The CO_2 will be captured at an approximate temperature of 50°C (140°F) and then released at approximately 110°C (230°F).

TABLE 1: PROCESS PARAMETERS FOR METAL MONOLITHIC AMINE-GRAFTED SILICA SORBENTS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3		
Bulk Density	kg/m^3	0.5	0.5
Average Particle Diameter	mm	0.05-1	<1
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	.43	<0.5
Solid Heat Capacity @ STP	kJ/kg-K		
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg	14	12
Adsorption			
Pressure	bar	1	1
Temperature	°C	50	<55
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Adsorption	kJ/mol CO_2	60	55
Desorption			
Pressure	bar	1-1.05	1-1.05
Temperature	°C	100-110	100-110
Equilibrium Loading	g mol CO_2/kg	2.4	3.1
Heat of Desorption	kJ/mol CO_2		

TABLE 1: PROCESS PARAMETERS FOR METAL MONOLITHIC AMINE-GRAFTED SILICA SORBENTS

	Units	Current R&D Value	Target R&D Value
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar		
Adsorber Pressure Drop	bar		
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

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

Other Parameter Descriptions:

Chemical/Physical Sorbent Mechanism – $CO_2 + R\text{-}NH_2 \rightarrow$ Carbamate/ammonium ions and Carbamic acid

Sorbent Contaminant Resistance – Sorbent capacity decreased by more than 50 percent after 30 cycles in 15 percent CO_2 and 250 parts per million (ppm) SO_2.

Sorbent Attrition and Thermal/Hydrothermal Stability – Sorbent capacity decreased by less than 10 percent after more than 500 cycles under thermal/hydrothermal conditions.

Flue Gas Pretreatment Requirements – Less than 20 ppm SO_2.

Sorbent Makeup Requirements – Less than 10 percent after 500 cycles.

Waste Streams Generated – Degraded sorbents will be re-activated.

Proposed Module Design –

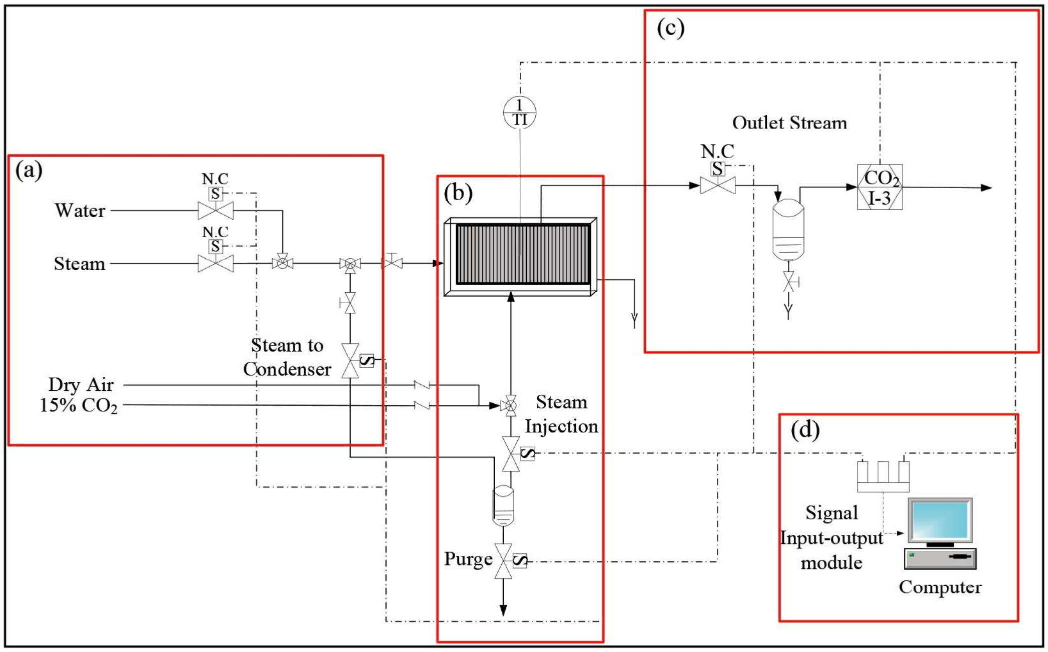

Figure 2: Process Schematic of the Monolith Adsorber

Adsorption temperature: < 40°C; desorption temperature: 105 to 115°C; pressure: 1 to 1.3 atm.

technology advantages

- High stability for CO_2 adsorption and desorption.
- Accelerated removal of the heat of adsorption.
- Low regeneration heat duty due to the low heat capacity of the sorbent.
- Low-cost immobilized amine sorbent.

R&D challenges

- The scale-up transition from lab- to bench-scale tests.
- Temperature swing adsorption requires a long cycle time due to the heating and cooling of the sorbent.
- Contaminants, such as sulfur oxides (SO_x), will react with amine functional groups similar to the MEA process.
- Currently, the CO_2 capture capacity of the sorbent is too low.

results to date/accomplishments

- The first generation of immobilized amine sorbents underwent 500 CO_2 capture cycles with less than 15 percent degradation. Refining in composition and preparation method resulted in sorbents with high stability for more than 1,100 CO_2 capture cycles, but lower capture capacity.
- Zeolite was shown to not be an effective support because of its hydrophilicity and small pore sizes.
- Developed a pilot-scale sorbent manufacturing process at a rate of 1 kg/hr.
- Enhanced the sorbent resistance to SO_2 poisoning by adding a proprietary additive to the CO_2 sorbent.

- A binder agent allows to agglomerate powder sorbents into rod or spherical pellets while maintaining the CO_2 capture capacity of the sorbent and yielding to low attrition rates.
- The operation under fixed-bed conditions present limitations in heat transfer: (1) slowing down the CO_2 capture process and (2) causing the sorbent to degrade.
- The CO_2 capture capacity could be increased 1.6 to 1.9 times when H_2O is present in the flue gas as compared to capture in dry conditions.
- Demonstrated the sorbent at pilot-scale, a 5-kg fixed bed. Adsorption was carried out at 55°C and desorption was with steam at 110°C.

next steps

This project ended on March 31, 2011.

available reports/technical papers/presentations

Chuang, S.S.C., "Amine absorber for carbon dioxide capture and processes for making and using the same,"

US 8377173 B_2, US Patent, Publication date: Feb. 19, 2013.

Chuang, S.S.C., "Metal Monolithic Amine-Grafted Zeolites for CO_2 Capture Power Plants," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/monday/Steven%20Chuang-NT43086.pdf*.

Chuang, S.S.C.; Fisher, J.; and Tanthana, J., "Metal Monolithic Amine-grafted Zeolites for CO_2 Capture," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO_2/pdfs/43086%20Akron%20amine-zeolite%20sorbent%20%28Chuang%29%20mar09.pdf*.

Tanthana, J., and Chuang, S.S. C., "In Situ Infrared Study of the Role of PEG in Stabilizing Silica-Supported Amines for CO_2 Capture," Chemical & Sustainability Energy & Materials, 3, 957-964, 2010. *http://onlinelibrary.wiley.com/doi/10.1002/cssc.201000090/abstract*.

Fisher II, J.C.; Tanthana, J.; and Chuang, S.S.C., "Oxide-supported Tetraethylenepentamine for Carbon Dioxide Capture," Environmental Progress & Sust Energy, 28 (4), 589-598, 2009. *http://onlinelibrary.wiley.com/doi/10.1002/ep.10363/abstract*.

CO_2 REMOVAL FROM FLUE GAS USING MICROPOROUS METAL ORGANIC FRAMEWORKS

primary project goals

UOP set out to design and develop a carbon dioxide (CO_2) removal system that employs metal organic framework (MOF) sorbents.

technical goals

- Use combinatorial chemistry to systematically synthesize and characterize a wide range of MOF and related materials.
- Screen materials for hydrothermal stability.
- Collect isotherm data for subsequent development and optimization.
- Determine the effects of water on CO_2 adsorption.
- Develop and validate material scale-up and forming procedures.
- Select the best one or two materials for final optimization and scale-up.
- Determine the effects of contaminants on the performance of scaled-up materials.
- Understand detailed kinetic and equilibrium data for incorporation in a process design and an economic analysis.

technical content

MOFs are extremely high surface area, crystalline, microporous, and thermally stable materials that have shown exceptional storage capacity for CO_2, methane, hydrogen, and other gases. MOFs typically consist of transition metal vertices, or hubs, attached three-dimensionally to other metal vertices by organic “linker” molecules. After removal of reaction solvent, the resulting porosity can be adjusted by simply changing the length or composition of the molecules used to link the metal vertices. Well-ordered openings, channels, and pockets in the structures are from a few angstroms to tens of angstroms. Figure 1 represents the building blocks used to create prototypical MOF-5, in which the green ball represents the metal-containing hub, and the yellow cylinder represents the organic linker.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

CO_2 Removal from Flue Gas Using Microporous MOFs

participant:

RTI International

project number:

FC26-07NT43092

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Vanderbilt University
Northwestern University

performance period:

3/12/07 – 6/30/10

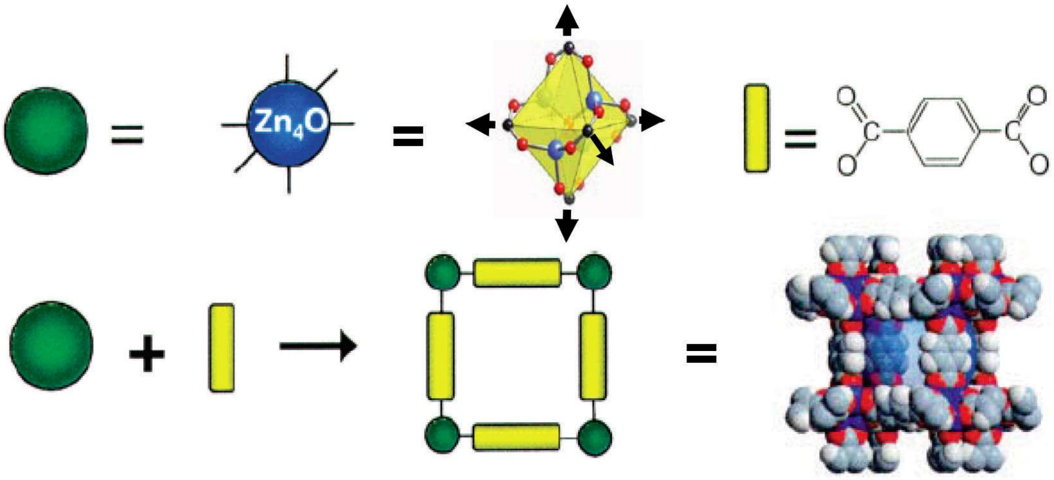


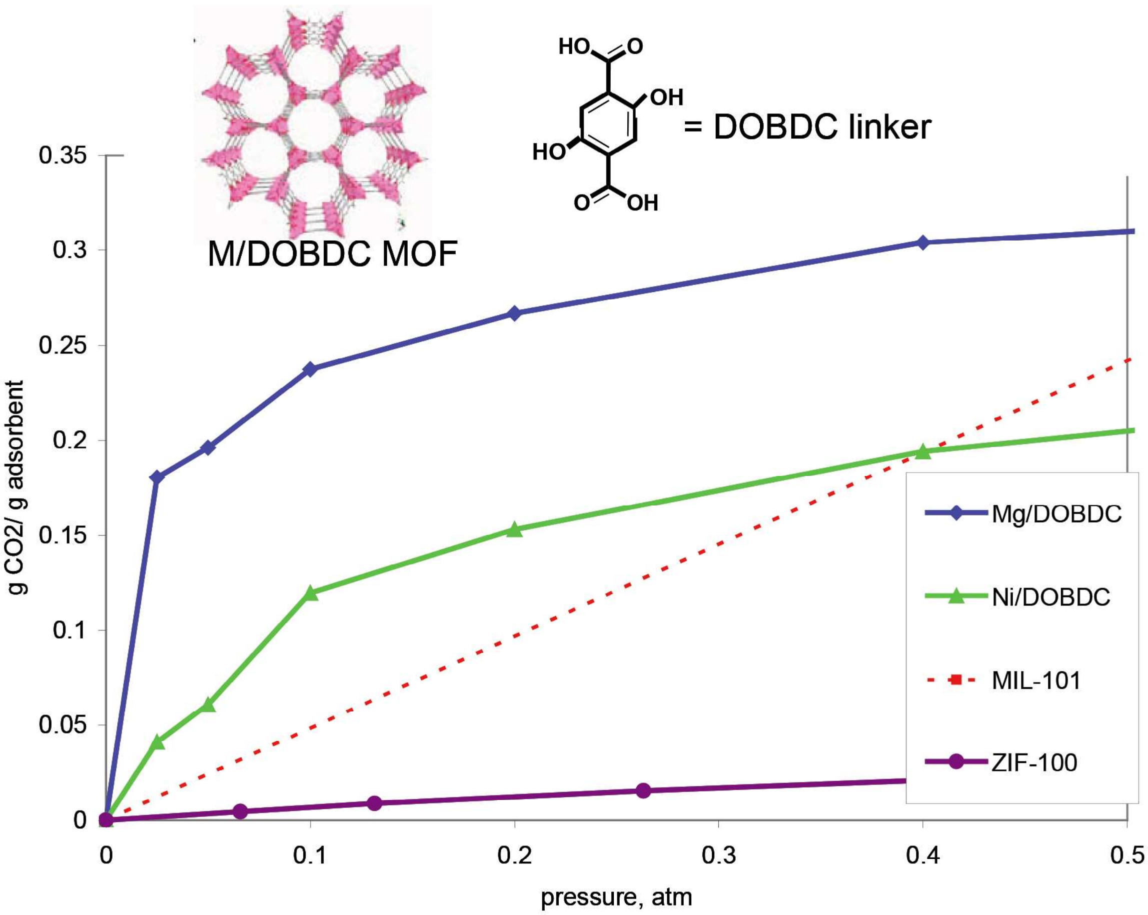
Figure 1: Building Blocks Used to Create Prototypical MOF-5

More than 50 MOFs for CO_2 adsorption were prepared from literature reports or designed by the experimenters. Table 1 displays the top MOFs for CO_2 capture.

TABLE 1: TOP 10 MOFS FOR CO_2 CAPTURE

Sample	Loading (mol/kg)	Loading (wt%)	Heat of Absorption (kJ/mol)
Mg\DOBDC (2)	4.73	20.9	60.1
Ni\DOBDC	3.40	15.0	27.2
Co\DOBDC	1.84	8.1	19.9
Mg\DOBDC (1)	1.28	5.6	21.3
HKUST-1 (CuBTC)	0.42	1.8	23.3
Zn\DOBDC	0.41	1.8	22.9
A1-MIL-110	0.24	1.1	21.7
Cr-MIL-101	0.18	0.8	13.3
Tb-MOF-76	0.18	0.8	21.7
A1-MIL-53	0.17	0.7	26
Zn-IRMOF-1	0.13	0.6	13.5

MOF-based adsorbents will be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO_2 from flue gas. Figure 2 represents an example of MOF CO_2 adsorption capabilities as a function of pressure (for M/DOBDC, M represents the metal).



ZIF-100 data from Wang, et al, *Nature* **2008**, *453*, 207

Figure 2: Example of MOF CO_2 Adsorption Capabilities as a Function of Pressure

The MOF-based VPSA CO_2 recovery system will be located after a contaminant-removal section and before the final CO_2 compression and drying section. The nitrogen (N_2)-rich waste stream (raffinate) will be sent to the stack. A process schematic is provided in Figure 3.

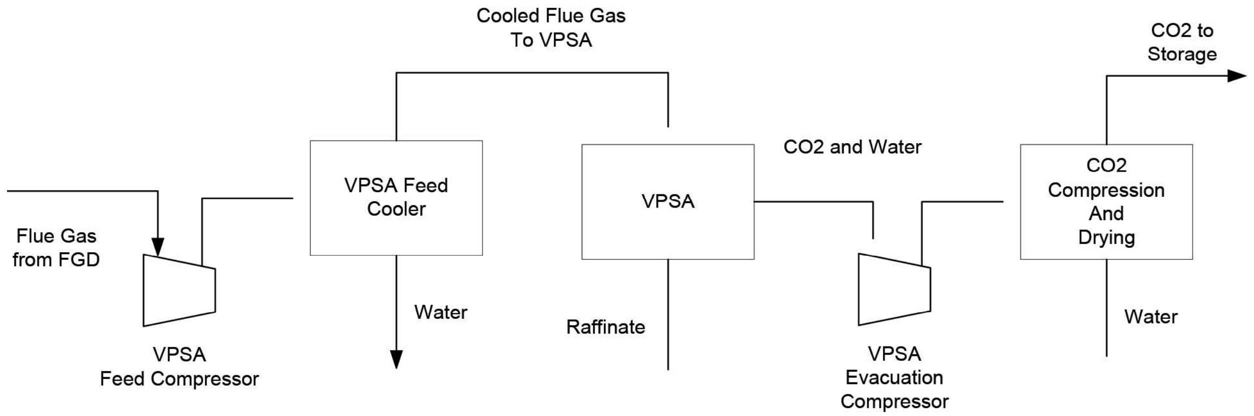


Figure 3: The MOF-Based CO_2 Capture System Process Schematic

Downstream from the flue gas desulfurization (FGD) and polishing scrubber, flue gas pressure is boosted in the VPSA feed compressor by approximately 4.8 pounds per square inch (psi) to make up for pressure drop in the contaminant-removal section and to maximize the adsorption of CO_2 in the VPSA unit. The VPSA feed compressor will be followed by a VPSA feed cooler to lower the temperature of the flue gas to approximately 100°F. It is likely that two parallel operating VPSA feed compressor and VPSA feed cooler trains will be required. Compressing and cooling the flue gas to 100°F will reduce the flue gas volume flow rate (actual cubic feet per minute [ACFM]) by up to 35 percent, and concurrently knock out at least 75 percent of the water vapor originally present in the flue gas. The combined lower-volume, lower-temperature, and lower-water content will allow the VPSA unit to operate more efficiently and effectively on the resultant flue gas stream.

The cooled flue gas enters the VPSA unit and will flow in a radial fashion through a short bed of adsorbent in either a vertical or horizontal configuration, depending upon the particular power plant's requirements. The adsorbent beds will consist of alumina for moisture polishing, and MOF for CO_2 removal. In the VPSA conceptual design at the end of the adsorption step, the vessel first vents N_2 raffinate to the stack to reduce the bed pressure to atmospheric pressure; pressure then equalizes with another vessel that had just completed the vacuum regeneration step. This would reduce the bed pressure to 7 to 8 pounds per square inch absolute (psia). These steps also reduce the N_2 stored in the vessel voids and minimize the amount that would be co-produced with the CO_2. The adsorbent bed would then be evacuated to 0.5 psia to produce the CO_2. For the purposes of the calculations, it was assumed that there was negligible co-adsorption of N_2 on the CO_2-loaded adsorbent and that the N_2 was primarily stored in the voids of the adsorbent vessel. The target CO_2 delta loadings were based on producing a >90 percent CO_2 purity stream during the regeneration step. The parasitic load for regeneration of the adsorbent is the compression energy associated with evacuating the vessel to 0.5 psia and compressing the contents to at least 8.8 pounds per square inch gauge (psig). The contribution of the N_2 stored in the voids is quite small compared to the compression energy associated with desorbing the CO_2. A purge step was not used in this process since the primary concern is producing a high-purity CO_2 stream.

The VPSA evacuation compressor will be used to remove CO_2 streams at 95 to 97 percent purity from the adsorbent beds. The water that comes along with the CO_2 will be removed during the CO_2 compression and drying stage of the process. In order to facilitate the gas compression and drying section CAPEX estimate, the VPSA evacuation compressor discharge pressure is 8.8 psig. This is the same pressure that the Econamine process delivers captured CO_2 to the gas compression and drying section. In the compression section, the CO_2 is compressed to 2,215 psia by a six-stage centrifugal compressor with inter-stage cooling to 100°F. The discharge pressures of the stages were balanced to give reasonable power distribution and discharge temperatures across the various stages. During compression in the multiple-stage, intercooled compressor, the CO_2 stream is dehydrated to a dew point of -40°F with triethylene glycol. The virtually moisture-free supercritical CO_2 stream is delivered to the plant battery limit as sequestration-ready.

There are no heating or cooling steps within the VPSA unit operation, which is typical of VPSA processes. Since this is still a conceptual design, however, there remain other types of processes to consider depending upon future pilot study and other experimental results. In a VPSA process, the heat of adsorption is released and is stored in the bed by a sensible temperature rise. The heat is removed during the desorption step as the adsorbent bed cools. Approximately 90 percent of the CO_2 in the feed gas is adsorbed onto the MOF adsorbent, and the rest leaves the VPSA section to the stack. Further, other than spent adsorbent, there is no waste generated in this process. The MOF-based VPSA process should generate little waste because the adsorbent itself is not hazardous waste, nor is it expected that the MOF will generate any hazardous waste products via degradation.

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density @ STP	kg/m^3	0.8	1.0
Bulk Density	kg/m^3		
Average Particle Diameter	mm	0.5 – 2.0	1.0
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3	0.5	0.7
Solid Heat Capacity @ STP	kJ/kg-K	≈ 1	< 1
Crush Strength	kg_f		
Manufacturing Cost for Sorbent	$/kg		

TABLE 2: ADSORPTION-BASED POST-COMBUSTION CO_2/N_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Adsorption			
Pressure	bar	0.1	0.1 – 0.15
Temperature	°C	25 – 45	25 – 45
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Adsorption	kJ/mol CO_2	45	45 – 55
Desorption			
Pressure	bar	0.01 – 0.05	0.05
Temperature	°C	Ambient	Ambient
Equilibrium Loading	g mol CO_2/kg-sorbent		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	-	—-	—-
Flue Gas Flowrate	kg/hr	—-	—-
CO_2 Recovery, Purity, and Pressure	% / % / bar	90–98	
Adsorber Pressure Drop	bar	—-	—-
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—-	—-

Definitions:

STP – Standard Temperature and Pressure (15°C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

Manufacturing Cost for Sorbent – “Current” is market price of material, if applicable; “Target” is estimated manufacturing cost for new materials, or the estimated cost of bulk manufacturing for existing materials.

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

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

technology advantages

- High CO_2 adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D challenges

- Effects of water, sulfur oxides (SO_x), and nitrogen oxides (NO_x) on the MOF material.
- Need for large vacuum pumps to compress the CO_2 from the outlet of the VPSA.

results to date/accomplishments

- More than 50 MOF materials were evaluated; two were selected for further development and testing. The CO_2 capacity for these MOFs was determined in the presence of water and other contaminants and measured at several temperatures. Hydrothermal stability testing at accelerated conditions was also carried out for these MOFs.
- Mg/DOBDC outperformed all MOF and zeolite materials evaluated, with about 25 wt% CO_2 captured by this MOF at flue gas conditions (≈0.13 atm CO_2 pressure, 311°K).
- UOP's techno-economic analysis indicated that an MOF-based VPSA process has potential to be a less-expensive option than using amines to capture CO_2. Their analysis indicated a 65 percent increase in cost of electricity (COE) compared to a reference power plant without CO_2 capture.

next steps

This project ended on June 30, 2010. The final report was issued in October 2010.

available reports/technical papers/presentations

Carbon Dioxide Removal from Flue Gas Using Microporous Metal Organic Frameworks [PDF-2.7MB] (Oct 2010) Final Technical Report.

Benin, A., et al., "CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43092%20UOP%20MOF%20sorbent%20%28Benin%29%20public%20version%20mar09.pdf*

DEVELOPMENT OF A DRY SORBENT-BASED POST-COMBUSTION CO_2 CAPTURE TECHNOLOGY FOR RETROFIT IN EXISTING POWER PLANTS

primary project goals

Research Triangle Institute (RTI) developed and tested a carbon dioxide (CO_2) capture process that utilizes a dry sodium carbonate (Na_2CO_3) sorbent that is based on the reaction of Na_2CO_3 with CO_2 and water vapor present in the flue gas from a coal-fired power plant.

technical goals

- Determine the optimal process configuration for the dry carbonate process.
- Construct and demonstrate a bench-scale CO_2 capture process using Na_2CO_3.
- Construct and demonstrate a pilot-scale, dry carbonate process that captures 0.9 tonnes of CO_2/day (1 ton of CO_2/day).
- Demonstrate the long-term chemical and mechanical stability of the sorbent.
- Update the economic analyses of the CO_2 sorbent capture process.
- Develop a commercialization plan for instituting the CO_2 capture process.

technical content

In an effort to develop a pre-pilot scale facility, RTI has been collecting data needed for designing, constructing, and operating the dry sorbent-based capture unit. RTI has designed and constructed a bench-scale heat transfer evaluation unit, shown in Figure 1, which is used to experimentally determine realistic gas and solid circulation rates and overall heat transfer coefficients for new reactor designs. A schematic diagram of the process is shown in Figure 1.

technology maturity:

Bench-Scale/Small Pilot-Scale

project focus:

A Dry Sorbent-Based Post Combustion CO_2 Capture

participant:

RTI International

project number:

FC26-07NT43089

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performance period:

3/7/07 – 12/31/09

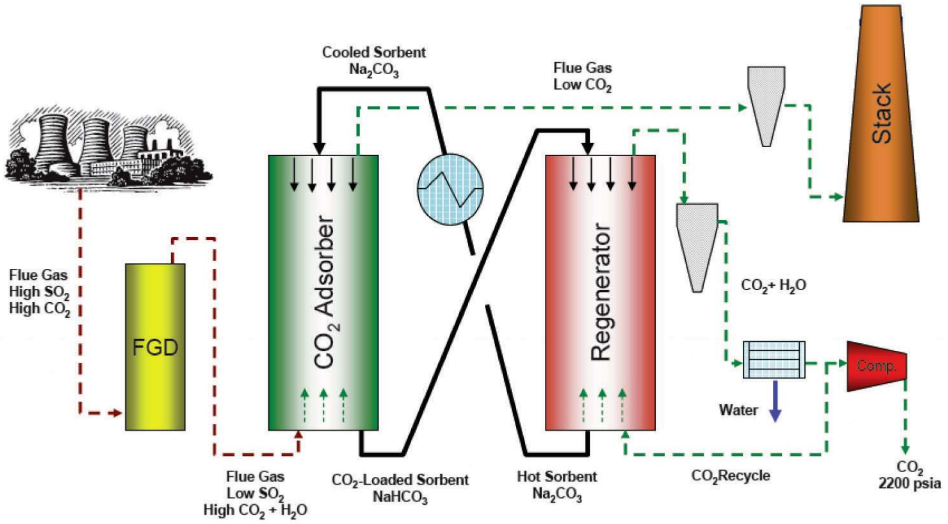

Figure 1: Schematic Diagram of CO_2 Capture Process

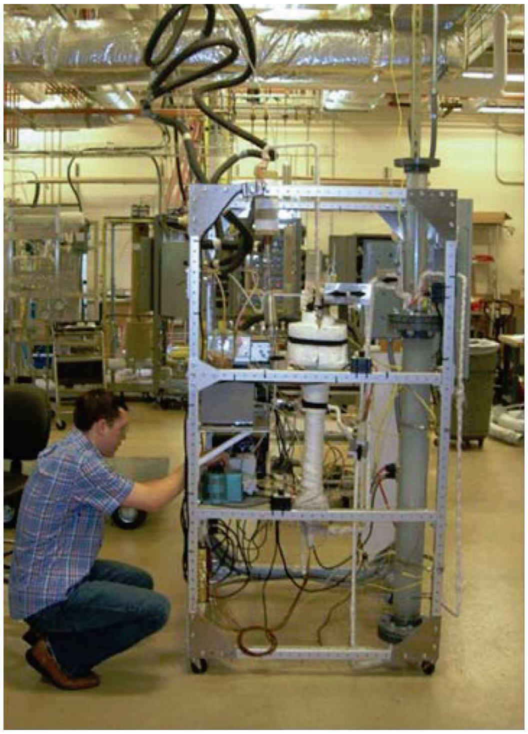

Figure 2: Lab-Scale CO_2 Absorption Reactor Skid

Pilot-scale testing will be performed on a slipstream from the air-blown gasifier at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. SRI has designed a pilot-scale, continuous, integrated test system. The equipment is being procured and will be assembled. The pilot-scale test will emphasize stability of integrated operation. The effects of trace contaminants will be observed, as the pilot tests will use a gas stream from an operating gasifier that has undergone minimum cleanup and will contain trace contaminants.

The CO_2 capture unit is located after the wet flue gas desulfurization (FGD) unit. The Na_2CO_3 sorbent reacts with the CO_2 and water (H_2O) located in the gas stream through a cyclic temperature swing cycle by adsorbing the CO_2 and H_2O at 60°C and releasing the constituents at 120°C during the sorbent regenerating stage. Considering the high exothermic heat of absorption (3.08 MJ/kg), significant cooling fluid is required to maintain the adsorption temperature at the desired value.

Utilizing the information gathered from the bench-scale unit, as well as the lab-scale unit shown in Figure 2, RTI has developed engineered sorbents that exhibit improved CO_2 capture rate and physical characteristics (e.g., attrition resistance, fluidizibility, and density) over the supported (multi-layer) sorbents. These improvements will have a significant impact on a commercial, dry carbonate system by lowering the solids handling requirements and minimizing the heating and cooling duties in a commercial process. A long-term, multi-cycle testing of these sorbents to demonstrate chemical stability has been undertaken. Initial results indicate that the engineered sorbents are highly stable in the presence of contaminates such as hydrochloric acid (HCl), nitrous oxides (NO_x), H_2O, and oxygen (O_2). While sulfur dioxide (SO_2) forms irreversible chemical bonds to the sorbent, it is considered a minor issue, considering the rate of attrition is generally greater than the rate of deactivation due to SO_2.

TABLE 1: PHYSICAL PROPERTIES OF SODIUM CARBONATE SORBENTS

Property	Value
Bulk Density	1.0 – 1.1 g/mL
Average Particulate Size	65 – 75 µm
Surface Area	100 – 120 m^2/g
Physical Strength (A)	0.77
Na_2CO_3 Strength	10 – 40 wt%
Heat of Absorption	3.08 MJ/kg
Regeneration Energy	3.08 MJ/kg

The heat transfer experiments will be conducted in a fluidized bed contactor, as shown in Figure 2. The conveyors (one heated, the other cooled) will be used to move the Na_2CO_3 through the fluidized bed to introduce a simulated flue gas (from coal or natural gas) to the sorbent. The instrument is used to analyze the adsorption effectiveness and the attrition rate of the Na_2CO_3 sorbent. Data from the fluidized bed will be used to validate and develop the computational fluid dynamic (CFD) model called MFIX.

Some physical properties of the sorbent are provided in Table 1.

As seen in the aforementioned table, the theoretical maximum CO_2 loading for the sorbent is ≈40 wt%. While RTI has achieved loading as high as 30 wt%, it requires a cycle time much greater than would be practical. Allowing only 30 minutes per cycle phase results in loading capacities of ≈20 to 25 percent.

technology advantages

- Lower capital and operating costs for CO_2 removal.
- Sorbent is inexpensive and easy to acquire (≈$200/ton).
- Sorbent is non-hazardous, non-toxic, and does not produce hazardous waste.

R&D challenges

- Circulation of solids may be problematic.
- The reaction of Na_2CO_3 with H_2O is highly exothermic and requires effective heat transfer.
- Removal of CO_2 requires equimolar amounts of H_2O.
- Irreversible reactions of Na_2CO_3 with SO_2 and HCl during process conditions.
- Raw Na_2CO_3 is not a physically strong material, leading to high attrition rates.
- Raw Na_2CO_3 agglomerates upon contact with condensed H_2O.

results to date/accomplishments

- Constructed a heat transfer evaluation system used to evaluate the hydrodynamics and heat transfer characteristics of the reactor designs.
- Constructed a packed-bed reactor system to demonstrate sorbent stability over many adsorption and regeneration cycles and provide insight into reaction kinetics.
- Validated the operation of a bench-scale, coupled cold-flow system and collected data on gas-solid contactor bed height control, range of operability, sorbent bed densities, bed void volumes, and fluidization characteristics.
- Measured the heat transfer limitations of the existing screw conveyor system and determined that the screw conveyors cannot be used for sorbent regeneration in a 1-ton/day CO_2 capture pre-pilot system.
- Developed updated process simulations for the new dry carbonate process design using ASPEN Plus.

next steps

This project ended on December 31, 2009. The final report was completed in April 2010.

available reports/technical papers/presentations

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants – Final Report – April 2010.

Nelson, T., et al., "Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology Retrofit in Existing Power Plants," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2/pdfs/43089%20RTI%20sorbent%20%28Nelson%29%20mar09.pdf*.

The Dry Carbonate Process: Carbon Dioxide Recovery from Power Plant Flue Gas, 7th Annual Conference on Carbon Capture and Sequestration in Pittsburgh, Pennsylvania, May 2008.

The Dry Carbonate Sorbent Technology for CO_2 Removal from Flue Gas of Existing Coal-Fired Power Plants – Power Plant Air Pollutant Control "Mega" Symposium in Baltimore, Maryland, August 2008.

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants Fact Sheet, April 2008.

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents, Topical Report, November 2004.

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
POST-COMBUSTION MEMBRANE TECHNOLOGIES

Novel Inorganic/Polymer Composite Membranes for CO_2 Capture

primary project goals

Ohio State University developed an inorganic/polymer composite membrane consisting of a thin, selective inorganic-containing layer embedded in a polymer structure. The project developed the new membrane design to improve system performance through laboratory, bench-scale, and pilot-scale testing, and developed a continuous manufacturing process to decrease costs.

technical goals

- Develop membrane synthesis process that incorporates a thin, selective inorganic-containing layer embedded in a polymer structure.
  - Membranes were developed and down-selected to achieve the Department of Energy (DOE) target of <$40/tonne carbon dioxide (CO_2) captured for 2025 (for a CO_2/nitrogen [N_2] selectivity of >100 and a CO_2 permeance of >800 gas permeation units [GPU]).
  - Continuous fabrication of the proposed hybrid membrane morphology was performed with the use of a continuous membrane fabrication machine.
- Conduct membrane characterization via bench-scale testing.
  - Functional hybrid membranes were synthesized for incorporation into three prototype membrane modules for parametric and continuous testing with simulated or actual flue gas.
- Complete system and cost analysis of the membrane system.

technical content

Ohio State University developed a cost-effective design and manufacturing process for new membrane modules that capture CO_2 from flue gas. In one approach, the membranes are comprised of a thin, selective inorganic particle-containing layer embedded in a polymer structure so that it can be made in a continuous manufacturing process. In another approach, a continuous zeolite membrane is rapidly synthesized on a polymer support. Figures 1 and 2 show the two hybrid membrane concepts studied in this project. The membrane of the first approach was incorporated in spiral-wound modules for testing with simulated and actual coal-fired flue gas. Preliminary cost calculations showed that a single-stage membrane process is economically unfavorable, primarily because of the low concentration of CO_2 (≈14 percent) in the flue gas stream. A two-stage process is more economical, but requires plant operation with a CO_2-enriched recycle stream. An important cost driver in current carbon capture membrane technologies is the energy requirement for maintaining the driving force for the membrane separation. The flue gas must be kept at atmospheric pressure and the concentrated CO_2 stream kept under vacuum (approximately 3 pounds per square inch [psi]) conditions. Preliminary calculations showed that the carbon capture energy requirement can be sufficiently reduced in a two-stage process. In the first stage, CO_2 is removed from flue gas by evacuation; in the second stage, remaining CO_2 is removed using an air-sweep such that the 90 percent capture target is met.

technology maturity:
Pilot-Scale, Actual Flue Gas

project focus:
Inorganic/Polymer
Composite Membranes

participant:
Ohio State University

project number:
FE0007632

predecessor projects:
N/A

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partners:
Gradient Technology, TriSep Corporation, American Electric Power (AEP)

start date:
10.01.2011

percent complete:
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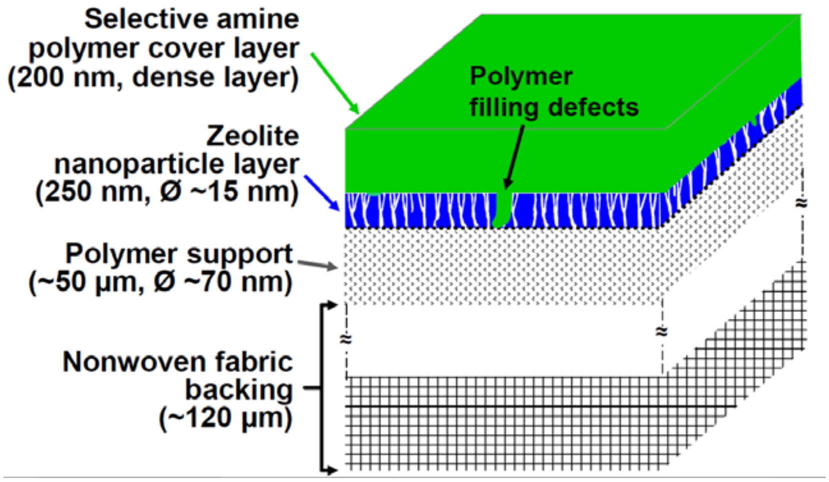

Figure 1: Membrane concept with selective amine polymer layer on zeolite nanoparticles embedded in polymer support

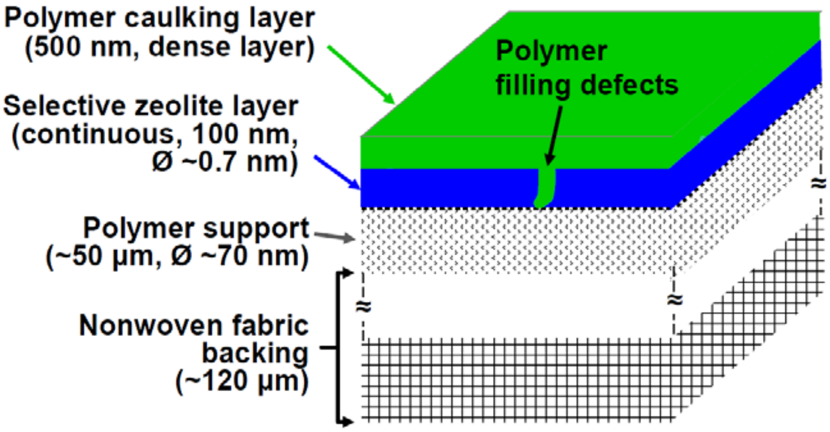

Figure 2: Membrane concept with polymer caulking layer on selective zeolite membrane grown on polymer support

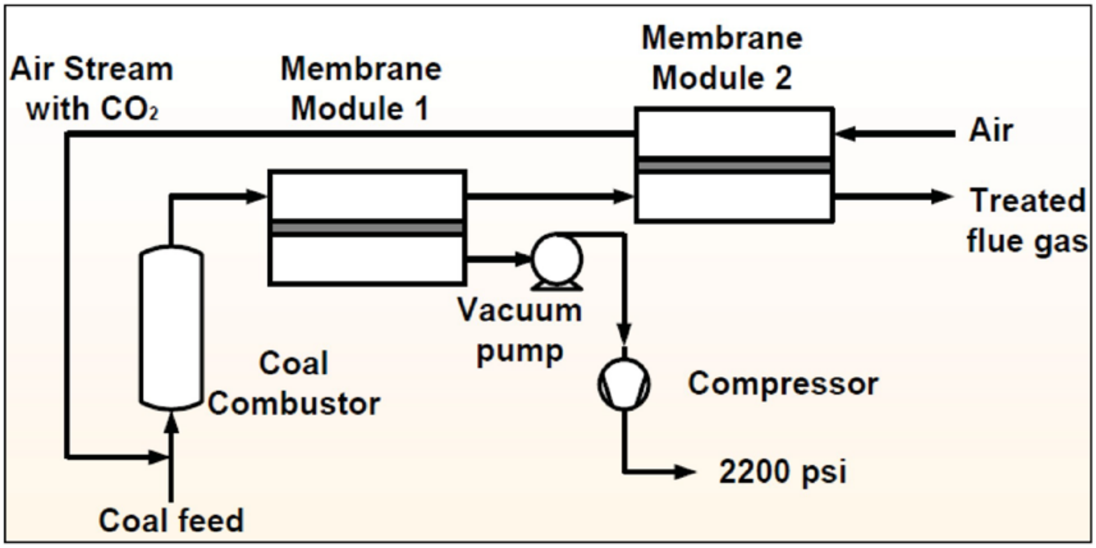

Figure 3: Process concept for two-stage membrane system

The entrance sweep flow is the same as the combustion air used in the current plant; the now CO_2-enriched stream is subsequently used for combustion. The 95 percent pure CO_2, captured in the first stage, is then compressed to 15 MPa (≈2,200 psi). DOE's cost targets can be met with a membrane that has a selectivity ≈170, a permeance of 1,100 GPU, and full stability against flue gas contaminants. This combination cannot be achieved with fully polymeric membranes. Fully inorganic, micro-porous membranes are sufficiently selective and stable, but generally too expensive due to high manufacturing costs. The focus of this project was a design that combines favorable inorganic membrane selectivity with the cost-effectiveness resulting from the manufacture of a composite membrane in continuous mode. The micro-porous membranes are aluminosilicates. Fully inorganic structures have CO_2/N_2 selectivities of >200, and permeances of <3,000 gas GPU. The latter can be improved by reducing membrane thickness, in combination with defect abatement with a thin polydimethylsiloxane (PDMS) layer. Two types of inorganic selective layers including alumina and zeolite Y (zeolite Y has a silica-to-alumina ratio of their framework of three or greater) were investigated. Membrane fabrication with growth of zeolite Y (ZY) into a continuous layer offers better selectivity, lower processing cost, and is easier to scale-up than membrane fabrication with rapid modification of the top aluminum oxide layer to form a microporous layer. A zeolite Y/polymer composite membrane was down-selected for further studies. Zeolite Y layers can be grown from solutions at 95 °C; however, the zeolite Y layer requires long growth time, which was reduced to 1 hour via application of a novel zeolite synthesis approach. The membrane system can be deposited on available polyethersulfone supports, which are fabricated into 14-inch supports with a continuous fabrication machine.

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value	Target R&D Value
Materials of Fabrication for Selective Layer	—	zeolites and/or amine-containing polymer	
Materials of Fabrication for Support Layer	—	polyethersulfone or polysulfone on non-woven fabric	
Nominal Thickness of Selective Layer	nm	150–250	150–250
Membrane Geometry	—	flat sheet	spiral-wound sheet
Max Trans-Membrane Pressure	bar	can be 0.2–50	0.2–1.5
Hours Tested without Significant Degradation	—	200 hours	200 hours
Manufacturing Cost for Membrane Material	$\$/m^2$	20	20
Membrane Performance			
Temperature	°C	57 °C and 102 °C	57 °C
CO_2 Pressure Normalized Flux	GPU or equivalent	800 GPU	>800 GPU
CO_2/H_2O Selectivity	—	not determined	not determined
CO_2/N_2 Selectivity	—	α = 140–800 for 20 CO_2/80 N_2 with p_{tot} = 101 kPa	α >100 for flue gas conditions
CO_2/SO_2 Selectivity	—	not determined	not determined
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	about 1800	
Shell-Side Fluid	—	air sweep	
Flue Gas Flowrate	kg/hr	about 0.2	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90%, >95%, 0.2–1.2 bar	
Pressure Drops Shell/Tube Side	bar	about 0.05/0.05	
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa (SI units).

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in desulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

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

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Surface adsorption and diffusion and molecular sieving for the zeolite selective layer; solution-diffusion for the polymer cover layer; facilitated transport for amine-containing selective layer.

Contaminant Resistance – Fully resistant polymer and inorganic materials.

Flue Gas Pretreatment Requirements – Removal of particulates, possibly dehydration.

Membrane Replacement Requirements – Estimated approximately 4 years.

Waste Streams Generated – N_2 with water (H_2O), about 1 percent CO_2 and minor impurities.

Process Design Concept – See Figure 3.

technology advantages

High CO_2/N_2 selectivity and cost-effective separation principle.

R&D challenges

Synthesis and scale-up of sufficiently selective and permeable membranes.

status

The project was completed on December 31, 2015, resulting in the development of a pilot-scale continuous casting machine for the fabrication of 14-inch polymer substrates and the development of a pilot-scale continuous membrane fabrication machine for the deposition of zeolite particles on polymer substrates using a vacuum-assisted dip coating method, followed by coating of the amine-containing polymer cover layer on the zeolite/polymer substrates. The pilot-scale amine-containing composite membranes were rolled into spiral-wound modules and implemented in a two-stage CO_2 capture process. These membrane modules were tested with real flue gas at the National Carbon Capture Center (NCCC), achieving >800 GPU of CO_2 permeance and >150 CO_2/N_2 selectivity. A process for rapid (1 hour) zeolite membrane growth, involving a continuous zeolite layer grown within polymer support, was also developed.

available reports/technical papers/presentations

Ho, W., "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," Final project review meeting presentation, Pittsburgh, PA, February 2016. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/FE0007632-Project-Meeting-Final-public-release-2-26-16.pdf.*

Ho, W. "Novel Inorganic/Polymer Composite Membranes for CO_2 Capture," presented at the 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015. *https://www.netl.doe.gov/File%20Library/Events/2015/co2captureproceedings/W-Ho-OSU-Inorganic-Polymer-Composite-Membranes.pdf.*

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BENCH-SCALE, HIGH-PERFORMANCE, THIN FILM COMPOSITE HOLLOW FIBER MEMBRANE FOR POST-COMBUSTION CARBON DIOXIDE CAPTURE

primary project goals

General Electric Global Research (GE) is developing high-performance, thin film polymer composite hollow fiber membranes and advanced processes for economical post-combustion carbon dioxide (CO_2) capture. The project includes bench-scale testing to tune the properties of a novel phosphazene polymer membrane and decrease costs through development of innovative fabrication techniques.

technical goals

- Optimize phosphazene polymer and coating solution: Synthesize phosphazene polymer, optimize separation performance, and develop processable coating solutions.
- Fabricate hollow fiber support layer: Produce highly porous, robust hollow fiber supports with controlled surface porosity from commercially available materials.
- Fabricate composite coated hollow fiber membranes: Develop processes to apply thin layer coatings on hollow fiber supports and elucidate fundamental polymer properties.
- Test membranes at bench-scale under flue gas conditions: Exposure and performance test materials and membranes under flue-gas conditions.
- Conduct process evaluation and module design: Conduct technical and economical process evaluation and module design and fabrication.

technical content

GE and partners are developing a high-performance, thin film polymer composite hollow fiber membrane and advanced process for economical post-combustion CO_2 capture. The project utilizes novel phosphazenepolymeric materials to produce an economical and scalable composite hollow fiber membrane module.

The membrane will be optimized at bench-scale, including tuning the properties of the phosphazene polymer in a coating solution and fabricating highly engineered porous hollow fiber supports. The project will also define the processes for coating the fiber support to manufacture thin, defect-free composite hollow fiber membranes.

technology maturity:

Bench-Scale, Simulated Flue Gas

project focus:

Composite Hollow Fiber Membranes

participant:

General Electric Global Research Center

project number:

FE0007514

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partners:

Idaho National Laboratory,
Western Research Institute,
Georgia Institute of Technology

performance period:

10/1/11 – 12/31/14

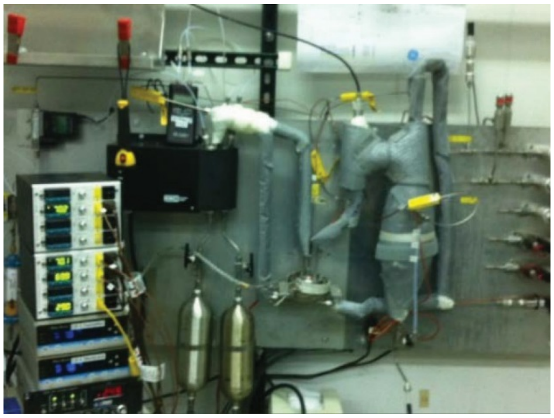

Figure 1: GE Test Rig – Flat Sheet and Hollow Fiber Membranes

The physical, chemical, and mechanical stability of the materials (individual and composite) to flue gas components will be evaluated using exposure and performance tests. Membrane fouling and cleanability studies will define long-term performance.

GE and the Georgia Institute of Technology (Georgia Tech) will work together on developing processes to apply the thin layer coating formulations onto the hollow fiber supports. GE will leverage the knowledge gained from using its flat sheet film coating apparatus to enable development of the continuous dip process for coating of hollow fiber membrane supports. Georgia Tech will use the in situ process developed to coat porous cellulose acetate hollow fibers with defect-free layers as a benchmark, which will be further adapted to obtain thin, defect-free coated layers. Both the continuous dip coating and batch in situ processes will be optimized to provide economical and scalable coated composite hollow fiber membranes.

Figure 2: Georgia Tech Hollow Fiber Fabrication Line

Working with Idaho National Laboratory, Georgia Tech will characterize phosphazene material properties in films cast on porous polymer supports to elucidate polymer properties including aging, membrane fouling, and cleanability. The characterization techniques will enable a better understanding of polymer and composite membrane performance. Membrane performance validation testing under flue-gas conditions will be performed at Western Research Institute's coal combustion test facility. Module design and technical and economic feasibility analyses will be conducted to evaluate the overall performance and impact of the process on the cost of electricity.

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	phosphazene	
Materials of Fabrication for Support Layer	—	polymer	
Nominal Thickness of Selective Layer	µm	1–10	<1
Membrane Geometry	—	flat sheet/hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	2–5	up to 10
Hours Tested Without Significant Degradation	—	200 (flat sheet) 100 (hollow fiber)	100–1,000
Manufacturing Cost for Membrane Material	$/m^2	—	—
Membrane Performance			
Temperature	°C	30 and 65	30 and 60
CO_2 Pressure Normalized Flux	GPU or equivalent	50–275 Barrer (flat sheet 30 °C) 100–425 Barrer (flat sheet 65 °C) up to 70 GPU (hollow fibers 35 °C)	1,000–2,500 GPU (hollow fibers)
CO_2/H_2O Selectivity	—	8–10	8–10
CO_2/N_2 Selectivity	—	15–20 (65 °C) flat sheet 30–40 (30 °C) flat sheet 10–35 (35 °C) hollow fibers	30–40
CO_2/SO_2 Selectivity	—	not tested	non tested
Type of Measurement	—	mixed gas	mixed gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	countercurrent	
Packing Density	m^2/m^3	>1,000	
Shell-Side Fluid	—	retentate	
Flue Gas Flowrate	kg/hr	<1	
CO_2 Recovery, Purity, and Pressure	%/%/bar	>90%, 60–80%, 0.2–1 bar	
Pressure Drops Shell/Tube Side	bar	1–4	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cmHg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution-diffusion mechanism.

Contaminant Resistance – Phosphazene-based membranes have been tested to be resistant to contaminant species such as oxygen (O_2), nitrogen oxide (NO_x), sulfur dioxide (SO_2), and moisture present in coal flue gas.

Flue Gas Pretreatment Requirements – Fly ash particulate removal.

Membrane Replacement Requirements – Membranes found to be stable with up to 200 hours of testing. Long-term stability tests are currently in progress.

Waste Streams Generated – Acidic water condensate stream.

technology advantages

- Surface property optimization to reduce fly ash adhesion.
- Highly scalable, low-cost hollow fiber support platform.
- Ease of cleaning should provide longer membrane life.
- Phosphazene polymer with high permeability and selectivity.

R&D challenges

- Fouling potential from fly ash/particulates.
- Permeability and selectivity at 60 °C lower than anticipated.
- Large membrane area requirements and process integration.

results to date/accomplishments

- Synthesized phosphazene polymer, characterized separations performance under realistic flue gas conditions, and developed hollow fiber support coating solutions.
- Developed engineered, high-porosity, hollow fiber supports.
- Built/upgraded bench-scale membrane coating and testing facilities.
- Completed initial process technical and economic feasibility study.
- Fabricated phosphazene coated defect-free hollow fiber membranes.
- Membrane performance studies conducted showed stability over >100 hours of testing.

next steps

- Optimize phosphazene polymer coatability on hollow fiber supports.
- Optimize the continuous dip and batch coating processes to provide economical and scalable coated composite hollow fiber membranes.
- Continue testing of coated composite hollow fiber membranes at bench scale under flue gas conditions.
- Conduct final technical and economic feasibility analyses and an environmental, health, and safety assessment.

available reports/technical papers/presentations

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/D-Ajit-Bhandari-GE-Composite-Hollow-Fiber-Membranes.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO₂/DBhandari-GEGR-2013-CO₂-NETL-Conference.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2013 North American Membrane Society Meeting, Boise, ID, June 2013. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/CO₂/GEGR-2013-CO₂-NAMS-Conference.pdf*.

Bhandari, D., et al., "Composite Hollow Fiber Membranes for Post Combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

LOW-PRESSURE MEMBRANE CONTACTORS FOR CO_2 CAPTURE

primary project goals

Membrane Technology and Research (MTR) is developing a new type of membrane contactor (or mega-module) to decrease capture costs, energy use, and system footprint through bench-scale testing of a module with a membrane area that is 100 m^2, 5 times larger than that of current modules used for carbon dioxide (CO_2) capture.

technical goals

- Develop a module design to reduce energy cost by lowering module pressure drop.
- Develop a module design with a large membrane area.
- Develop a module design to reduce manifold complexity, footprint, and cost.

technical content

MTR is developing a new type of membrane contactor (or mega-module) to separate CO_2 from power plant flue gas. This module membrane area is 100 m^2, which is 4–5 times larger than that of current modules used for CO_2 capture. The countercurrent sweep module is crucial to the MTR-developed CO_2 removal from flue gas process, as this membrane module permits the use of air as a sweep gas, which increases the CO_2 flux through the membrane without requiring additional compression energy. This means the CO_2 concentration in the flue gas is increased at a minimal energy cost.

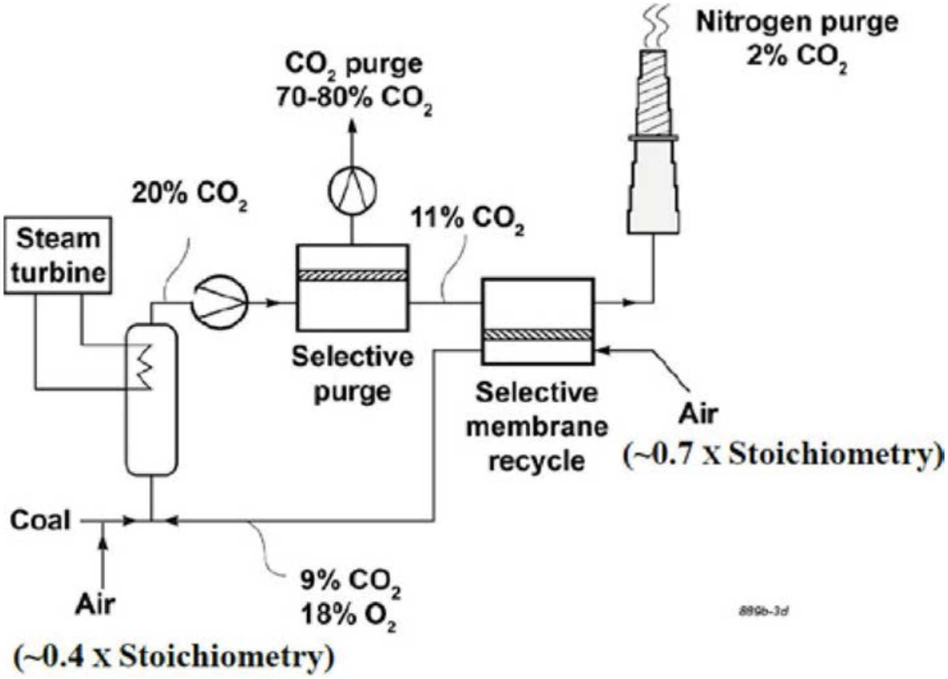

Figure 1: Two-Stage Membrane CO_2 Capture Process

technology maturity:

Bench-Scale, Simulated and Actual Flue Gas

project focus:

Low-Pressure Membrane Contactors (mega-module)

participant:

Membrane Technology and Research, Inc.

project number:

FE0007553

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partners:

University of Toledo

performance period:

10/1/11 – 9/30/14

TABLE 1: PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		proprietary polymer	
Materials of Fabrication for Support Layer		proprietary polymer	
Nominal Thickness of Selective Layer	µm	<1	<1
Membrane Geometry		plate-and-frame	plate-and-frame
Max Trans-Membrane Pressure	bar	70	70
Hours Tested Without Significant Degradation		500	500
Manufacturing Cost for Membrane Material	$\$/m^2$	100	10
Membrane Performance			
Temperature	°C	30	30
CO_2 Pressure Normalized Flux	GPU or equivalent	1,500	>2,500
CO_2/H_2O Selectivity	—	0.5	0.5
CO_2/N_2 Selectivity	—	50	50
CO_2/SO_2 Selectivity	—	0.5	0.5
Type of Measurement	—	pure gas	pure gas
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	cross-flow	
Packing Density	m^2/m^3	1,000	
Shell-Side Fluid	—	N/A	
Flue Gas Flowrate	kg/hr	5,000	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%, >96%, 140 bar	
Pressure Drops Shell/Tube Side	bar	feed: 0.1; sweep:0.2	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

Other Parameter Descriptions:

Contaminant Resistance – The membranes are known to be unaffected by water (H_2O), oxygen (O_2), and sulfur dioxide (SO_2). The effect of trace contaminants, such as mercury, arsenic, etc., is unknown and is being examined in the ongoing field demonstration at the National Carbon Capture Center (NCCC) in Wilsonville, AL, under a different U.S. Department of Energy National Energy Technology Laboratory (DOE/NETL)-sponsored project (DE-FE0005795).

Flue Gas Pretreatment Requirements – Currently, pretreatment requirements are unknown. The current demonstration tests at NCCC treat post-flue gas desulfurization (FGD) flue gas and will help determine the need for gas treatment prior to entering the membrane system. The greatest concern of species present in flue gas is that particulate matter will foul the membranes, reducing module lifetimes. Particulate filters that can achieve an order of magnitude better ash removal than a standard bag house, and are used today to treat refinery and gasification streams, may be needed.

Waste Streams Generated – The membrane process will recover >95 percent of the H_2O in flue gas as liquid. The quality of this H_2O and its potential to be reused in the plant will be studied in future work.

technology advantages

- In flue gas applications, the novel countercurrent sweep module recycles CO_2 to the boiler with an air sweep, which increases the CO_2 concentration in the flue gas with minimal energy input.
- The recycle of CO_2 to the boiler increases the concentration of CO_2 in the flue gas, which could make the CO_2 capture process easier for technologies other than membranes.
- The novel countercurrent sweep module design has low-pressured drop, which reduces the energy costs.
- Mega-modules (500 m^2 or larger) reduce the manifolding complexity, footprint, and cost of the membrane system.

R&D challenges

- The novel sweep plate and framed design will need to overcome several issues, including sweep-side pressure drop, poor utilization of the membrane area due to module geometry, and non-uniform flow patterns.
- Spacer design and selection needs to maximize packing density and mechanical support while minimizing pressure drop.
- Scaleup issues associated with building membrane modules 10–20 times larger than conventional modules.

results to date/accomplishments

- Completed design and fabrication of various 20-m^2 prototype membrane modules.
- Completed pressure drop and CO_2 separation performance testing of various 20-m^2 prototype membrane modules with bench-scale lab test system
- Completed design and construction of larger lab test system, sized for parametric studies of 100-m^2 membrane modules.
- Conducted CFD simulations of various sweep module designs that incorporate pressure drop, velocity profiles, and mass transfer.
- A large sweep module test unit was designed and assembled at MTR for all pure-gas, pressure drop, and CO_2 separation performance testing of 100 m^2 modules. The pressure drop through the plate-and-frame module is more than 10-fold lower than that through the best modified spiral module, significantly lower than the project target of 1.5 psi, and demonstrate substantial energy savings for the membrane capture process.
- A CFD comparative analysis of crossflow and countercurrent sweep membrane modules demonstrated that countercurrent/sweep modules require 35 percent less membrane area than crossflow modules to remove the same amount of CO_2, but the pressure drop through crossflow modules was lower.
- A 500-m^2 sweep membrane module skid was designed and fabricated for field testing. A pressure vessel with five 100-m^2 membrane modules can be run individually or as a group. The skid was designed for integration into the existing MTR 20-tpd CO_2 capture pilot test unit for testing at NCCC in Wilsonville, AL. The 500-m^2 sweep module skid is to be tested at NCCC in early 2015.

- A detailed performance and economic analysis of the MTR membrane CO_2 capture process with low-pressure sweep modules was performed. The methodology used by MTR to evaluate the membrane process is consistent with Case 10 of the 2010 DOE report: Econamine was used to capture 90 percent of the flue gas CO_2. The "all membrane" case demonstrates savings over the Econamine CO_2 capture process, but the cost is still higher than the DOE target of $40/tonne CO_2 captured.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO2%20Capture/R-Baker-MTR-Low-Pressure-Membrane-Contactors.pdf*.

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/R-Baker-MTR-Low-Pressure-Membrane-Contactors.pdf*.

Baker, R., et.al, "Low-Pressure Membrane Contactors for CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

CO_2 CAPTURE MEMBRANE PROCESS FOR POWER PLANT FLUE GAS

primary project goals

Research Triangle Institute (RTI) set out to develop an advanced hollow-fiber, polymeric membrane-based process that can be cost-effectively retrofitted into current pulverized coal (PC)-fired power plants to capture at least 90 percent of the carbon dioxide (CO_2) from the plant's flue gas.

technical goals

- Develop new fluorinated polymers as membrane materials that have superior CO_2 separation properties compared to conventional and competitive membrane platforms. A minimum selectivity of 30 for CO_2 over nitrogen (N_2) and CO_2 permeance in excess of 300 gas permeance unit (GPU) are targeted. Fluorinated polymers are a promising material platform because they exhibit excellent chemical stability to moisture, sulfur dioxide (SO_2), and nitrogen oxide (NO_x) contaminants present in flue gas.
- Develop next-generation polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current commercial polycarbonate membranes.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and high CO_2 permeate flow rates with minimal pressure drop.
- Identify and develop CO_2 capture membrane process design and integration strategies suitable for retrofit installation.

technical content

Project research efforts include development of membrane materials and membrane hollow fibers, membrane module design and fabrication, and process design.

RTI pursued the development of two membrane material platforms. As a near-term membrane platform solution, RTI worked with Generon to develop next-generation, high-flux polycarbonate hollow-fiber membranes and membrane modules with higher CO_2 permeance than current-generation, commercial polycarbonate membranes. Hollow-fiber membranes made from the high-flux polycarbonate have been successfully developed, scaled up, and fabricated into module separation devices. Laboratory-scale membrane modules have been studied with simulated flue gas mixtures with and without flue gas contaminants.

For a longer-term membrane platform solution, RTI worked with Arkema to develop improved CO_2 capture membrane materials based on the polymer chemistry of polyvinylidene fluoride [PVDF], the chemical structure of which is shown in Figure 1 and comprises the $[CH_2\text{-}CF2]n$ repeat unit. PVDF is well suited for contact with flue gas, possessing high chemical resistance to acids and oxidants, specific affinity for CO_2 for high CO_2 solubility, and high thermal stability (Td ≈ 340°C). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the fiber extrusion process used to fabricate mem-

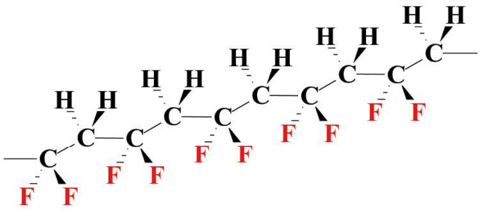

Figure 1: Chemical Structure of PVDF

technology maturity:

Bench-Scale, Using Simulated Flue Gas

project focus:

Hollow-Fiber, Polymeric Membrane

participant:

Research Triangle Institute

project number:

NT0005313

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partners:

Arkema
Generon IGS

performance period:

10/1/08 – 9/30/11

brane hollow fibers. However, conventional PVDF is a homopolymer that is semicrystalline and has CO_2/N_2 selectivity of ≈23 and low CO_2 permeance of ≈10 GPU. Arkema has pursued synthesizing and developing advanced, PVDF based copolymers possessing improved CO_2 permeance and selectivity.

In this project, the membrane under development was in the form of hollow fibers that are packaged into compact, high surface area-to-volume module devices. Multiple modules were utilized in a given CO_2 capture membrane system for power plant applications due to the large quantity of flue gas to be processed. The modularity of the membrane separation devices allows for easy adaptation to different levels of CO_2 removal desired by simply adding or subtracting the number of membrane modules used. Figure 2 shows a cross-section of a hollow-fiber membrane module. A single-membrane module consists of hundreds of thousands to more than a million micron-sized diameter hollow fibers bundled together. A couple of individual membrane hollow fibers, a small bundle loop of fibers, and modules of different sizes are shown in Figure 3. As flue gas flows through the membrane fibers, the feed is split into two streams. A permeate stream enriched in CO_2 is produced by the preferential transport of CO_2 across the fiber walls. The remaining flue gas (non-permeate) flows out of the membrane module as a CO_2-depleted retentate stream that is sent to the plant stack for discharge to the atmosphere.

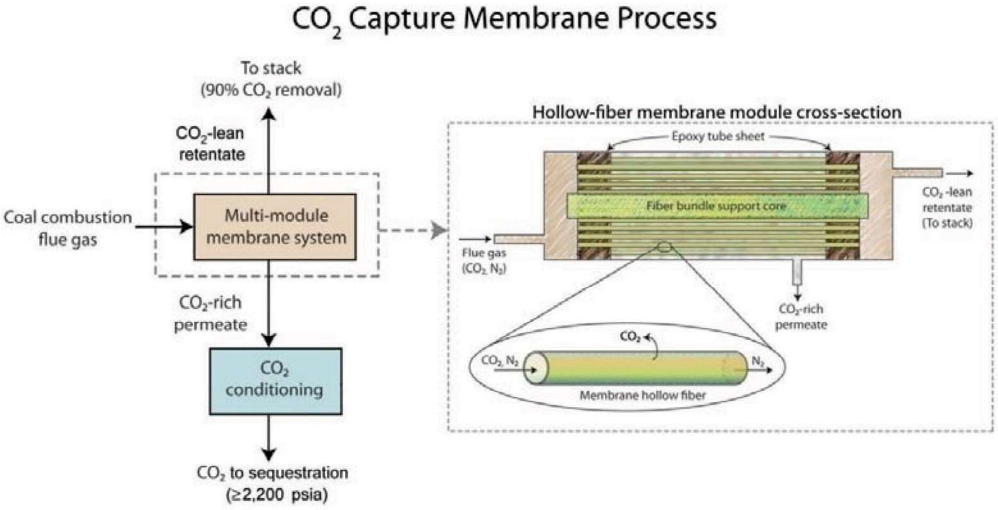

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module


Individual Membrane Hollow Fibers **Small Bundle Loop of Hollow Fibers** **Various Membrane Module Sizes**

Figure 3: Membrane Hollow Fibers

Process simulations for a single-stage membrane process were conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity to different parameters, including membrane flux (permeance), membrane selectivity, membrane fiber dimensions, and membrane pressure driving force. An important outcome of this sensitivity analysis was the understanding that membrane property development should focus on improving both permeance and selectivity together rather than individually.

To achieve high levels of CO_2 capture and purity, RTI developed the three-stage membrane process shown in Figure 4, where the membrane stages are represented by M1, M2, and M3. The flue gas is compressed and fed to the first membrane stage M1. To obtain a net 90 percent removal of CO_2 from the stream ultimately sent to the stack, the CO_2-depleted retentate exiting M1 is fed to M3, which is operated with a permeate-side air sweep to enhance removal of more CO_2. Before being released into the stack, the pressurized M3 retentate is sent to an expander to recover the energy associated with high pressure. The resulting M3 permeate is a CO_2 enriched air stream that is sent back to the boiler. In the second membrane stage M2, the CO_2 captured in the M1 permeate is further concentrated. The resulting CO_2-rich M2 permeate is then compressed and dehydrated to produce the final, sequestration-ready CO_2 capture stream. The M2 retentate is recycled and fed back to M1. The numbers shown in Figure 4 are for a 550-MW coal-fired power plant to achieve 90 percent CO_2 capture and 95 percent CO_2 purity in the capture stream using the high-flux polycarbonate membrane (400 GPU; $CO_2/N_2 = 35$).

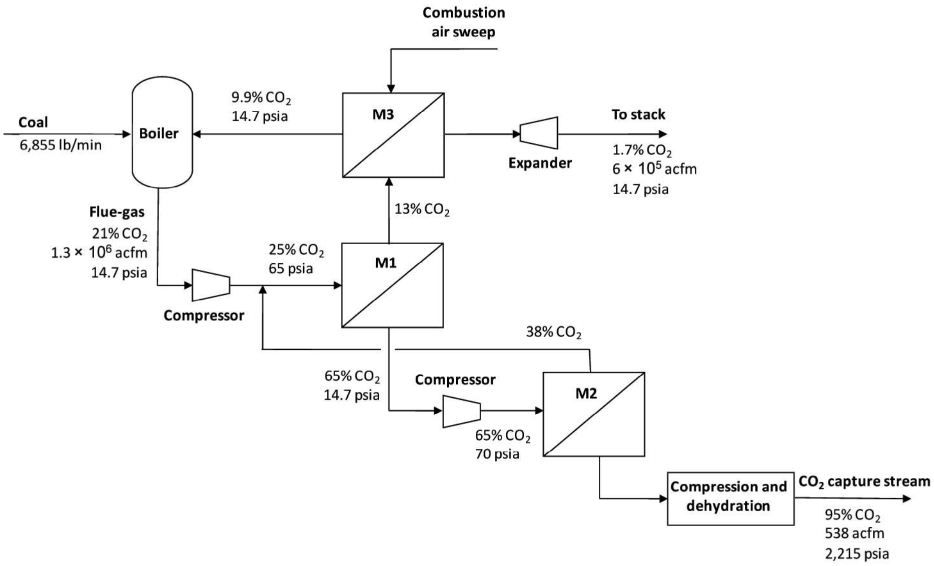

Figure 4: RTI's Three-Stage CO_2 Capture Membrane Process Design

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Polycarbonate-based and Vinylidene fluoride-based	
Materials of Fabrication for Support Layer	-	N/A	
Nominal Thickness of Selective Layer	μm	0.05	0.05
Membrane Geometry	-	Hollow-fiber	Hollow-fiber
Max Trans-Membrane Pressure	bar	15 (Not tested higher)	15
Hours Tested Without Significant Degradation	-	165	300 (coal)
Manufacturing Cost for Membrane Material	$/m^2	32	8
Membrane Performance			
Temperature	°C	25 – 30	50
CO_2 Pressure Normalized Flux	GPU or equivalent	400	1,000
CO_2/H_2O Selectivity	-	0.04	0.01 – 0.02
CO_2/N_2 Selectivity	-	35	50
CO_2/SO_2 Selectivity	-	≈1	<0.5 or >2
Type of Measurement	-	Ideal and mixed	Ideal and mixed
Proposed Module Design			
Flow Arrangement	-	Countercurrent	
Packing Density	m^2/m^3	9,000	
Shell-Side Fluid	-	Permeate	
Flue Gas Flowrate	kg/hr	(Unknown at this stage)	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95+%, 1 bar	

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pressure Drops Shell/Tube Side	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	(Unknown at this stage)	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Gas permeation in the high-flux polycarbonate and PVDF-based membrane platforms occurs due to a partial pressure driving force across the membrane. The specific permeation mechanism obeyed is the solution-diffusion model for gas transport in nonporous polymers. According to this model, preferential permeation of certain gas species occurs because they are more soluble in the polymer membrane, have a higher diffusion coefficient in the polymer membrane, or both. In this project, the preferentially permeated species CO_2 has both greater diffusivity and greater solubility than N_2 in the polycarbonate- and PVDF-based membranes.

Contaminant Resistance – Membrane resistance to contaminant species (NO_x, SO_2, moisture) found in flue gas was investigated in continuous, seven-day, bench-scale separation performance stability tests with contaminant-containing CO_2/N_2 mixtures. The permeance of the high-flux polycarbonate membrane showed some sensitivity to contaminants such as NO_x, but its selectivity was stable. The new PVDF-based membrane material platform, because of its intrinsically high-chemical resistance, exhibited excellent permeability (permeance) and selectivity stability in the contaminant tests.

Flue Gas Pretreatment Requirements – Before being fed to the membrane system, the flue gas from the plant stack must be conditioned to remove solid particulates and any condensed/entrained liquids (essentially liquid water).

Membrane Replacement Requirements – Based on seven-day, bench-scale contaminant resistance testing results, replacement cycle for high-flux polycarbonate membranes is anticipated to be roughly every five years. In the presence of flue-gas contaminants, the high-flux polycarbonate membrane has shown gradual permeance loss without loss in selectivity in continuous, seven-day testing. For PVDF-based membranes, the replacement cycle is anticipated to be every 10 years because of the excellent chemical and separation performance stability exhibited by them in the presence of flue-gas contaminants in seven-day tests. Much longer-term contaminant exposure testing of these membranes to real coal-derived flue gas, however, is recommended to confirm/refine the above membrane replacement requirements.

Waste Streams Generated – Because the membrane permeates and concentrates water into the CO_2 capture stream, a liquid water stream is recovered by the membrane process during compression of the capture stream to sequestration pressure. A water condensate stream is also produced upstream of membrane stages M1 and M2 because of compression of their feed gas streams, followed by cooling of this compressed gas with cooling water to the optimum membrane operating temperature. The quality of these liquid water streams is not known and will need to be determined.

technology advantages

Membrane-based processes have the potential to provide PC-fired power plants with a cost-effective technology option for CO_2 capture. They are inherently energy-efficient because the membrane enables passive separation of gases. Their compact footprint and modular nature allows for easy installation into an existing PC-fired plant, and, with no moving parts, they are simple to operate and maintain. In addition, the hollow fiber membrane approach taken in this project is particularly well suited for high-volume applications such as the large flue gas volumes that must be handled in post-combustion carbon capture. Hollow-fiber modules have much higher membrane packing density and lower cost-per-membrane area than other module types. The hollow-fiber membrane tubes are economically produced on a commercial scale by using existing fiber manufacturing equipment technology.

R&D challenges

Flue gas properties, such as low CO_2 concentration of 13 to 15 percent, low flue gas pressure of 1 atm, large flue gas volumes, and the presence of moisture and contaminants (sulfur oxides [SO_x], NO_x, and particulate matter), can pose certain challenges for a conventional membrane separation process. These technology challenges are being addressed in this project through the development of new membrane materials with improved CO_2 separation properties and chemical resistance, improved membrane module design and engineering, and novel process design and integration strategies.

results to date/accomplishments

- Development and scale-up of Generon next-generation, high-flux polycarbonate membrane hollow fibers with up to four times higher CO_2 flux (410 GPU) than that of Generon standard polycarbonate membrane fibers.
    - CO_2/N_2 selectivity of high-flux polycarbonate hollow-fiber membrane was comparable to that of standard (current-generation) polycarbonate hollow-fiber membrane. However, it was only 60 to 70 percent of its intrinsic CO_2/N_2 selectivity (35 to 37), meaning that the high-flux polycarbonate membrane properties could still be improved.
    - Fibers of high-flux polycarbonate with 25 percent larger dimensions were successfully spun as an option for managing parasitic axial pressure drops in the module.
    - High-flux polycarbonate membrane would be best operated at temperatures below room temperature to benefit from substantial increase in CO_2/N_2 selectivity without much decrease in CO_2 permeance due to its weak temperature dependence.
    - High-flux polycarbonate membrane displayed some sensitivity to flue-gas contaminants (NO_x and SO_2), which led to a permeance decline but had minimal to no effect on CO_2/N_2 selectivity. This observed sensitivity did not seem to degrade the membrane as it recovered much of its original properties when the contaminants were removed. In practice, therefore, feed pretreatment should be considered for this membrane.
- Successful formation of Generon high-flux polycarbonate membrane fibers into lab-scale modules and larger prototype (2,200 ft^2) modules.
- Development and synthesis of novel Arkema VDF-based copolymers with improved CO_2 permeance and improved CO_2/N_2 selectivity.
    - Copolymerization of a bulky, low-dipole Comonomer A into the VDF chain backbone can increase gas permeability by disrupting chain packing density and crystallinity in the polymer matrix.
    - VDF-co-A copolymer family was developed with up to 17 to 18 times higher CO_2 permeability than the base PVDF homopolymer, while maintaining the CO_2/N_2 selectivity of 24 of the base PVDF.
    - Copolymerization of a bulky, high-dipole Comonomer B into the VDF chain backbone can increase CO_2/N_2 selectivity by enhancing the CO_2 affinity of the polymer while also improving gas permeability relative to the base PVDF homopolymer.

  - VDF-co-B copolymer family was developed with 2.5 to 3 times higher CO_2/N_2 selectivity and six times higher CO_2 permeability than base PVDF homopolymer.
  - Strong temperature dependence of CO_2 permeance in VDF-based polymers could be exploited as a key process variable for increasing and optimizing CO_2 permeance to increase gas processing throughput in the capture process while maintaining reasonable CO_2 removal.
  - VDF-based polymer platform demonstrated excellent stability of its gas separation properties to contaminants SO_2, NO_x, and water vapor.
- Fabrication of the first developmental hollow fibers from new Arkema VDF-based copolymer platform.
  - VDF-A.2 was down-selected for fiber development because it had among the best balance of CO_2 permeability and selectivity of the new copolymers in this fluorinated platform.
  - Synthesis of VDF-A.2 was successfully scaled up to pilot scale to prepare 200 pounds of this resin for fiber development.
  - Fiber tackiness, fiber shape stability, and solvent extraction kinetics were identified as key issues that must be addressed and managed for the VDF-based polymers.
  - Hollow-fiber cores of the VDF-based materials were successfully spun on commercial fiber-spinning equipment. Fibers had good gas flux but exhibited no gas selectivity. Development of a membrane structure with gas selectivity will require additional research and development (R&D) effort.
- Development of three-stage CO_2 capture membrane process design to achieve 90 percent CO_2 capture and 95 percent CO_2 purity.
- Completed techno-economic evaluation of three-stage CO_2 capture membrane process design based on Generon's high-flux polycarbonate hollow-fiber membrane assuming a CO_2 permeance of 400 GPU and CO_2/N_2 selectivity of 35.
  - Increase in levelized cost of electricity (LCOE) estimated for subcritical coal power plant with RTI membrane process was estimated to be ≈73 to 82 percent over that of a plant with no capture, with the LCOE increase depending strongly on compressor cost.
  - Compressor costs made up the majority of equipment costs for the process, with 64 percent of costs attributed to compressors needed for the CO_2 separation process and 10 percent to the compressor for compression/drying of the captured CO_2 product.
  - Cost of CO_2 capture was estimated to be ≈\$42/ton-CO_2.
  - The energy penalty was the biggest contributor to the LCOE.

next steps

This project ended on September 30, 2011.

available reports/technical papers/presentations

"CO_2 Capture Membrane Process for Power Plant Flue Gas," Final Report, April 2012. *http://www.netl.doe.gov/publications/factsheets/program/05313%20Final%20Report%20April%202012.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/22Aug11-Toy-RTI-CO2-Capture-Membrane-Process.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/Lora-Toy---NT0005313.pdf*.

Toy, L., et al., "CO_2 Capture Membrane Process for Power Plant Flue Gas," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/5313-RTI-membrane--Toy--mar09.pdf*.

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

technology maturity:

Laboratory-Scale, with Simulated Flue Gas

project focus:

Dual Functional, Silica-Based Membrane

participant:

University of New Mexico

project number:

FG26-04NT42120

NETL project manager:

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partners:

T3 Scientific LLC

performance period:

8/23/04 – 4/30/09

primary project goals

The University of New Mexico set out to develop a new, dual-functional, silica-based membrane for carbon dioxide (CO_2) emissions capture from coal-fired power plants.

technical goals

- Achieve a membrane CO_2/nitrogen (N_2) selectivity of 100 and a CO_2 permeance of 1,000 gas permeance units (GPU) or greater.
- Formulate a sol-gel composition to be used in the preparation of clear aminosilicate coatings for membrane deposition onto the siliceous support matrix.
- Setup multi-component gas separation tests for preliminary membrane performance analysis.
- Refine the sol-gel compositions for optimal membrane deposition.
- Study the influence of sulfur dioxide (SO_2), water vapor, and trace oxygen (O_2) on membrane performance.
- Optimize membrane deposition on alternative economical membrane supports.
- Conduct preliminary economic analysis of the membrane process for post-combustion CO_2 capture.
- Identify a processing window that allows reproducible preparation of an asymmetric microporous silica membrane.
- Stabilize membrane performance through a nickel (Ni)-doping approach.
- Prepare an ultra-thin silica membrane using a plasma-assisted, atomic layer deposition technique (PA-ALD).

technical content

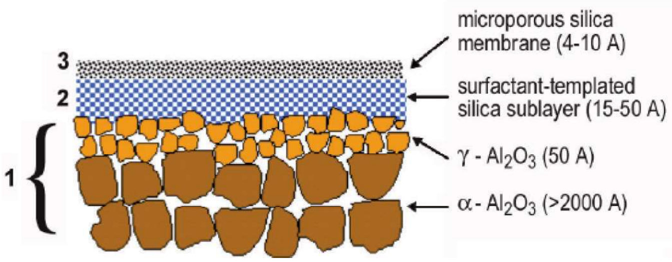

Figure 1: Cross-Section of Membrane

The dual-functional, silica-based membrane is prepared by a unique sol-gel dip-coating process for depositing a microporous amino-silicate membrane on a porous tubular ceramic support. It consists of a microporous inorganic siliceous matrix, with amine functional groups physically immobilized or covalently bonded on the membrane pore walls. Strong interactions between the permeating CO_2 molecules and the amine functional membrane pores enhance surface diffusion of CO_2 on the pore wall of the membrane, subsequently blocking other gases. The membrane is composed of three distinct layers as shown in Figure 1: (1) a commercially available tubular or hollow-fiber ceramic support; (2) a mesoporous surfactant-templated silica sub-layer with pore size 15-50 Å; and (3) a microporous aminosilicate gas separation membrane layer with pore size 4-10 Å.

TABLE 1: MEMBRANE PROCESS PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	-	Aminosilicate/doped-silicate	
Materials of Fabrication for Support Layer	-	Surfactant-templated silica on alumina	
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	-	Plate-and-frame	Hollow-fiber
Max Trans-Membrane Pressure	bar	3 bar	N/A
Hours Tested Without Significant Degradation	-	168 hrs	100 hrs
Manufacturing Cost for Membrane Material	$/m^2		
Membrane Performance			
Temperature	°C	25 – 250°C	25 – 80°C
CO_2 Pressure Normalized Flux	GPU or equivalent	CO_2: 400 GPU	CO_2: 1,000 GPU
CO_2/H_2O Selectivity	-		
CO_2/N_2 Selectivity	-	CO_2/N_2=80-100 (dry feed); CO_2/N_2 = 50-60 (humidified feed)	CO_2/N_2 = 100
CO_2/SO_2 Selectivity	-		
Type of Measurement	-	Mixed gas	Mixed gas
Proposed Module Design			
Flow Arrangement	-		
Packing Density	m^2/m^3	980	
Shell-Side Fluid	-		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	% / % / bar	>90%	
Pressure Drops Shell/Tube Side	bar	0.01 – 0.02	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in de-sulfurized flue gas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

Other Parameter Descriptions:

Contaminant Resistance – $SO_2 > 10$ parts per million (ppm).

Flue Gas Pretreatment Requirements – Particulate removal.

Waste Streams Generated – None.

technology advantages

The dual-functional, silica-based membrane will have a higher CO_2 selectivity and permeance compared to conventional membranes that separate gases based on differences in molecular size only.

R&D challenges

- The permeance of the new membrane will need to be increased by a factor of five to meet the research and development (R&D) target.
- The selectivity for the new membrane must remain constant under temperatures of 50 to 70°C and high humidity conditions.
- The presence of particulates in the flue gas could adversely affect membrane performance.
- Previous membrane designs suffered from a gradual reduction in permeance and selectivity under elevated temperature and humidity conditions due to pore shrinkage/blockage.

results to date/accomplishments

- Three classes of microporous, sol-gel derived, silica-based membranes were developed for CO_2 removal under simulated flue gas conditions.
- A novel class of amine-functional, microporous silica membranes was prepared using an amine-derivatized alkoxysilane precursor, exhibiting enhanced CO_2:N_2 selectivity (>70) in the presence of water vapor, but its CO_2 permeance (<1.25 cm^3[STP]/cm^2-min-atm [≈275 GPU]) was below the target.
- Pure siliceous membranes showed higher CO_2 permeance (1.5-2 cm^3[STP]/cm^2-min-atm [≈330-440 GPU]), but subsequent densification occurred under prolonged simulated flue gas conditions.
- Nickel oxide (NiO) was incorporated into the membrane's microporous network to retard densification and achieved CO_2 permeance of 0.5 cm^3(STP)/cm^2-min-atm (≈110 GPU) and CO_2:N_2 selectivity of ≈50 after 163 hours exposed to simulated flue gas conditions.
- The implementation of a novel ALD processing scheme shows evidence that a vapor-processed membrane can exhibit higher thermal/structural stability combined with higher flux and selectivity compared to the traditional liquid phase processing approach (sol-gel).

next steps

This project ended on April 30, 2009.

available reports/technical papers/presentations

"Novel Dual-Functional Membrane for Controlling Carbon Dioxide Emissions from Fossil Fuel Power Plants," Final Scientific/Technical Report, August 2009. *http://www.netl.doe.gov/File%20Library/Research/Coal/ewr/co2/2009Novel-Dual-Functional-Membrane-for-Controlling-Carbon-Di.pdf*.

"Tubular Ceramic-Supported Sol-Gel Silica-Based Membranes for Flue Gas Carbon Dioxide Capture and Sequestration," J. Memb. Sci., 341 (2009) 30-36.

"Novel Dual-Functional Membrane for CO_2 Capture," Seventh Annual Carbon Capture and Sequestration Conference, Pittsburgh, Pennsylvania, May 2008.

"Anodic Alumina Supported Dual-Layer Microporous Silica Membranes," J. Memb. Sci., 287, (2007) 157-161.

"Microporous Sol-Gel Derived Aminosilicate Membrane for Enhanced Carbon Dioxide Separation," Separation and Purification Technology, 42(3) (2005) 249-257.

DEVELOPMENT OF BIOMIMETIC MEMBRANES FOR NEAR-ZERO PC POWER PLANT EMISSIONS

primary project goals

Carbozyme set out to develop an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO_2) from coal and natural gas combustion flue gas. Carbozyme also set out to evaluate a state-of-the-art electrodialytic (EDI) method for CO_2 capture, comparing its performance with that of the CLM.

technical goals

- Scale-up the enzyme-catalyzed, CLM permeator design (4 to 400 m^2) to include multiple units organized as a skid (3×40 m^2) for testing with various coal ranks and natural gas.
- Implement a pretreatment conditioner to ensure that the flue gas constituents will not adversely impact the CLM permeator.
- Validate technology to cost-effectively produce carbonic anhydrase (CA) enzymes for the CLM.
- Test and analyze three different EDI test cells: a controlled pH resin wafer, a hollow fiber fed bipolar membrane (BPM), and an ion exchange membrane-resin wafer (IEM-RW).
- Conduct a commercialization study for both the CLM and EDI technologies.

technical content

The enzyme-based CA CLM membrane process mimics the natural process for removing CO_2 from an organism. An organism's blood stream is used to transport oxygen (O_2) and CO_2 to and from its cells, respectively. CA is an enzyme in the blood that captures the CO_2 from the cells and converts it to bicarbonate (HCO_3^-). The enzyme reverses this reaction in the lungs, allowing the CO_2 to be exhaled. Figure 1 shows the configuration for the enzyme-based CA CLM membrane process Carbozyme set out to develop. The CA CLM membrane is able to incorporate the absorption and stripping processes into a single unit. A membrane module consists of two groups of hollow fibers – one group contains the incoming CO_2 lean flue gas, and the second group contains the CO_2 rich permeate stream. The CA enzyme is contained in a thin-film liquid between the two groups of fibers. The CA helps catalyze the CO_2 to HCO_3^- to pro-

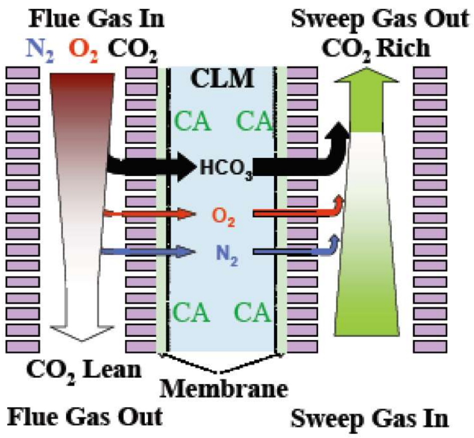

Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

technology maturity:

Laboratory/Bench-Scale, Using Simulated Flue Gas

project focus:

Biomimetic Membrane

participant:

Carbozyme

project number:

FC26-07NT43084
FG26-06NT42824

NETL project manager:

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EERC
Electrostep
Kansas State University
Siemens
SRI
Visage Energy

performance period:

3/28/07 – 7/31/09

mote permeation across the CO_2 lean membrane and reverses the process, promoting permeation across the CO_2-rich membrane. CA is one of the fastest acting enzymes with a turnover rate of 600,000 katals (catalyzes the hydration of 600,000 molecules of CO_2 per second per molecule of CA).

Figure 2 shows a process schematic for the CA CLM. Pretreated combustion flue gas from the boiler enters the membrane. A vacuum system is used to provide the driving force across the membrane. After the CO_2 is separated from the flue gas, it goes through a knockback condenser for water removal prior to compression. The resulting product is a 95 percent pure CO_2 stream. The remaining flue gas is sent to the plant stack.

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This technique reduces the size of the CO_2 stripper and operates at high pressure, reducing CO_2 compression needs; both reduce electric power consumption. AC has high net CO_2 loading, is a low-cost and readily available reagent, and requires little solvent makeup; the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in absorber solution is extremely low.

The project, in its first phase, constructed a bench-scale batch reactor unit to test the technology at SRI's facility in California. Testing was performed to validate the concept and to determine the optimum operating conditions.

Absorber testing was conducted to first determine the solubility of shifted-gas components (H_2, CO, nitrogen [N_2], argon [Ar]), then to determine the reactivity of CO_2 and H_2S; mixed-gas testing was performed to determine the relative reaction kinetics.

Regenerator testing was conducted to determine CO_2 and H_2S release characteristics, as well as the relative kinetics of CO_2 and H_2S release. Optimal operating conditions derived in bench-scale testing will be used at the pilot-scale test.

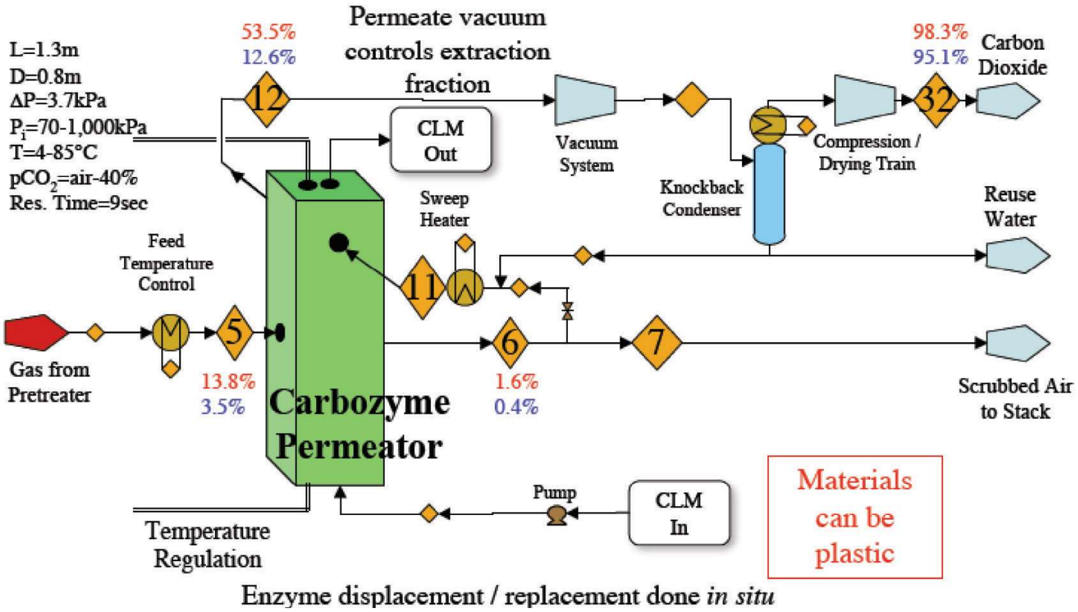

Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

technology advantages

- The CA enzyme catalyst does not contain any toxic chemicals or byproducts, making it more environmentally friendly than competing technologies.
- The CA enzyme catalyst has a fast CO_2 production rate with low energy requirements and boosts separation and purification due to its low nitrogen (N_2) and O_2 solubility.
- The enzyme catalyst is not vulnerable to oxidation or the formation of stable salts.
- The CA CLM system requires only minimal pumping and no heat exchangers, allowing it to consume 30 to 50 percent less energy compared to competing technologies.
- The CA CLM system recycles nearly all of its water and a portion of its waste heat.
- The modular design of the membrane makes it easy to manufacture, install, and scale up.

R&D challenges

- The cost of the purified CA enzyme remains high and production costs will need to be reduced in order to be considered economically viable.
- Early immobilization of the CA enzyme needs to be addressed.
- Sulfur dioxide (SO_2) acidification of the carbonate carrier fluid needs to be addressed via flue gas pretreatment.
- Ionized mercury in the flue gas could reduce enzyme activity.

results to date/accomplishments

Development progress for the CA CLM process was made in several categories, such as flue gas stream analysis and conditioning, enzyme selection, enzyme immobilization, membrane module construction, and economic analysis.

Specific accomplishments include:

- Developed an immobilized CA enzyme catalyst based on a thermophilic form of CA that can maintain a high activity at elevated temperature (≈50°C). The enzyme was immobilized using a proprietary surface activation method using an ultrathin polyamino acid (PAA) layer that can be removed and replaced, as needed. Enzyme testing indicated up to 80 percent of initial activity was retained over a 60-day period.
- Developed a 0.5-m^2 bench-scale CLM permeator that combines absorption and desorption in a single house through use of dual hollow-fiber, spiral-wound, polymer membranes. In this configuration, CO_2 capture is driven by a combination of pressure, vacuum, and temperature. More than 90 percent CO_2 capture was achieved during testing.
- Developed an alternate process technology based on separate absorption/desorption modules using single hollow-fiber, spiral-wound, polymer membranes.
- Fabricated an 11-m^2 CLM module for scale-up testing.
- Developed and tested a flue gas pre-treatment system for the CLM process.
- Developed computer modeling for CLM process components and integrated systems.
- Developed and tested a second technology based on a resin-wafer EDI system that uses a pH shift to accomplish CO_2 absorption/desorption.

next steps

This project ended on July 31, 2009.

available reports/technical papers/presentations

"Development of Biomimetic Membranes for Near Zero PC Power Plant Emissions," Final Report for Project #43084, March 2011.

"Capture of CO_2 by the Carbozyme Permeator," 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2009.

"Development of Biomimetic Membranes for Near-Zero Power Plant Emissions," Annual NETL CO_2 Capture Technology for Existing Plants R&D meeting, Pittsburgh, Pennsylvania, March 2009.

"Membrane-based, Enzyme Facilitated, Efficient, Carbon Dioxide Capture," 9th International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 2008.

"Progress on Carbozyme's HFCLM Permeator Technology Scale-up Project," 7th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2008.

"Biomimetic Membrane for CO_2 Capture from Flue Gas," Final Report for Project #42824, August 2007.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
POST-COMBUSTION NOVEL CONCEPTS

NOVEL CONCEPTS FOR THE COMPRESSION OF LARGE VOLUMES OF CO_2

primary project goals

Southwest Research Institute (SwRI) is developing novel compression technology concepts to reduce carbon dioxide (CO_2) compression power requirements by 10 percent compared to conventional compressor designs. The basic concept is a semi-isothermal compression process where the CO_2 is continually cooled using an internal cooling jacket rather than using conventional interstage cooling. The project includes thermodynamic testing (Phase I), prototype testing (Phase II), and a full-scale demonstration of a multistage, internally cooled diaphragm pilot test (Phase III).

technical goals

Phase III

- Design and construct a pilot-scale demonstration of a multistage internally cooled compressor diaphragm design.
- Complete a comprehensive thermodynamic and cost analysis of both pulverized coal (PC) and integrated gasification combined cycle (IGCC) plant incorporating the new compression technology.
- Design a multistage diaphragm and test loop.
- Design, fabricate, and test a third-generation cooled diaphragm and test in a single-stage test rig.

technical content

In the cooled diaphragm concept, the gas is continually cooled after each stage in the flow path through the compressor. A cooling jacket insert is used in the diaphragm of each stage to provide continuous cooling. Figure 1 shows a conceptual design for an internally cooled compressor. The flow of the CO_2 is shown in red, while the cooling liquid is shown in blue.

SwRI examined a number of different compression options to find the ones that would consume the least amount of power. Figure 2 shows how two hypothetical compression processes can achieve the same pressure, but still consume different quantities of power. The isothermal compression, even at 60 percent efficiency, requires less power than the isentropic compression at 100 percent efficiency. Therefore, efficiency alone cannot be used as a figure of merit for the compression process.

Figure 3 shows the pressure/enthalpy curves for six of the options examined by SwRI. While liquefaction and pumping is a viable option and may be superior to a pure compression route in cold climates, the semi-isothermal compression proved to be superior when all of the heat exchanger performance and other losses were taken into account.

technology maturity:

Pilot-Scale, 90 tonnes/hr

project focus:

Evaluation of Compression Efficiency Improvements

participant:

Southwest Research Institute

project number:

FC26-05NT42650

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partners:

Dresser-Rand

performance period:

9/28/2005 – 6/30/2014

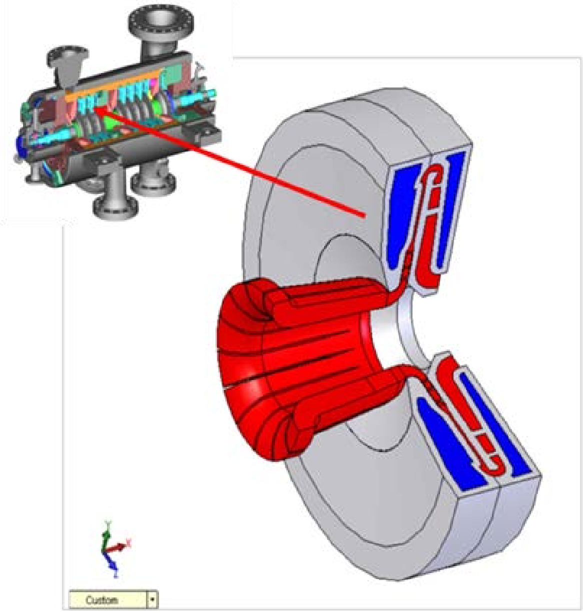

Figure 1: Design for an Internally Cooled Compressor

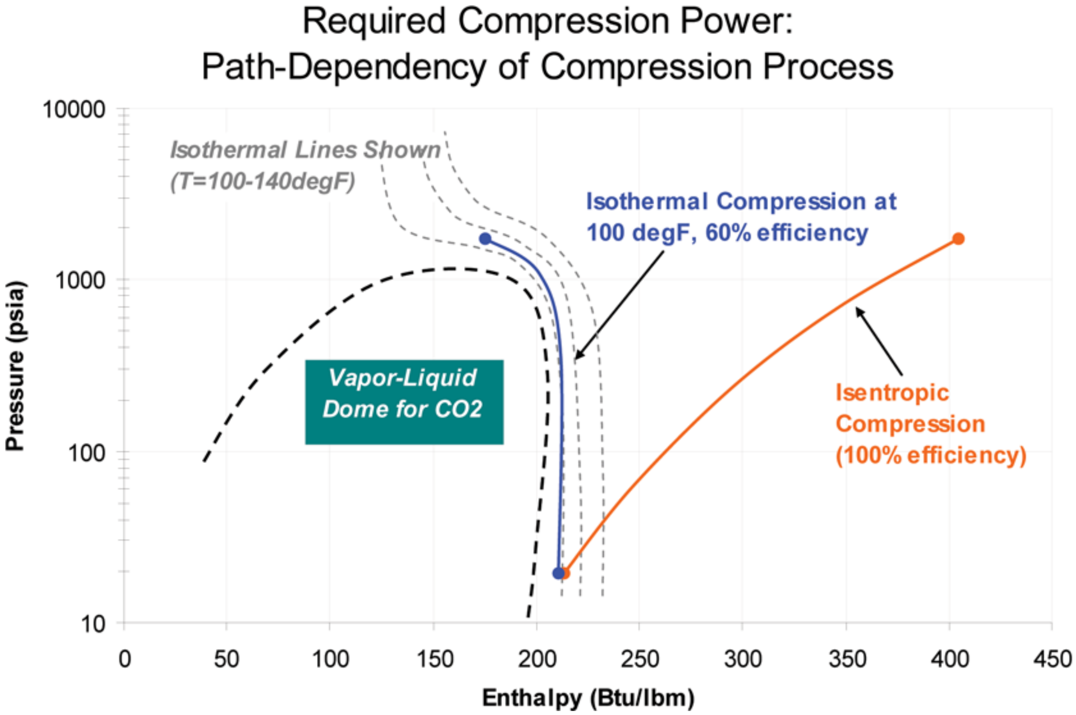

Figure 2: Example of Path Dependency of Compression Power

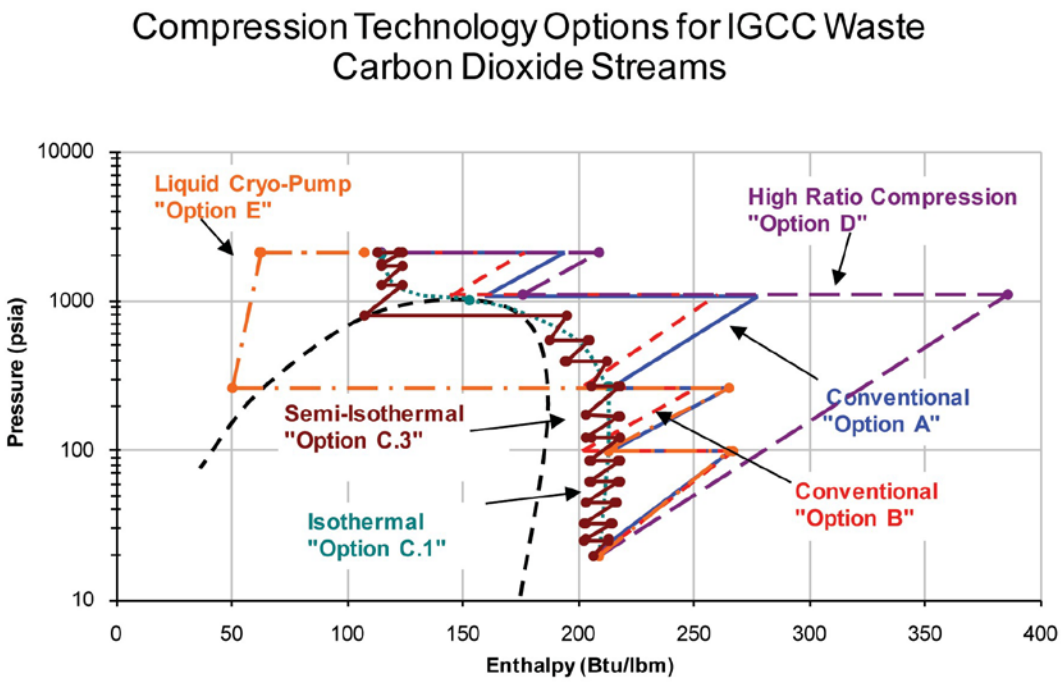

Figure 3: Required Compression Power for the Investigated Technology Options

Table 1 presents a description of the compression and cooling technology options and the resultant power requirements for the U.S. Department of Energy (DOE) 550-megawatt (MW) PC reference power plant with carbon capture using an amine process (≈1.3 million lb/hr CO_2 stream, Ramezan 2007)

- Single stream inlet pressure/temperature = 14.8 psia/115 °F
- Discharge pressure = 2,150 psia
- Intercooler/after-cooler exit temperature = 115 °F

The following configurations were analyzed for power comparisons:

1. DOE baseline (efficiencies and refrigeration/ liquefaction cycle performance calibrated to match data in [1])
2. Back-to-back LP and HP compressors with uncooled diaphragms
3. Back-to-back LP and HP compressors with cooled diaphragms, 15 percent effectiveness, 85 °F cooling water
4. Back-to-back LP and HP compressors with cooled diaphragms, 20 percent effectiveness, 85 °F cooling water

The power calculations in this analysis include gas horsepower for compression, cooling horsepower required for liquefaction, pumping horsepower, and gearbox power losses of 2 percent. The estimates exclude bearing and windage losses and power required for the pumping and chilling of cooling water.

The overall compression system analysis results for the methods shown above are displayed in Table 1. A back-to-back compressor with a cooled diaphragm is expected to achieve 10.4–11.7 percent power savings (15–20 percent effectiveness) relative to the DOE baseline case.

TABLE 1. OVERALL COMPRESSION POWER SAVINGS ANALYSIS RESULTS

Case Description	Assumed HX Effectiveness	Power Savings
DOE Baseline	NA	0%
D-R B2B LP and HP Uncooled Diaphragm	0%	6.6%
D-R B2B LP and HP with Cooled Diaphragm	15%	10.4%
D-R B2B LP and HP with Cooled Diaphragm	20%	11.7%

The goal of the current work was to develop and construct a pilot-scale demonstration compression plant to optimize CO_2 compression, as well as perform a balance of plant measurement for total power required and savings realized by improving on the technology developed in Phase II, but in a multi-stage version of the cooled diaphragm design. A new compressor, based on a Dresser-Rand DATUM® D12 frame size, consisted of a six-stage, back-to-back centrifugal compressor (D12R6B) that incorporated the cooled diaphragms. A new test loop with required coolers, valves, and piping was constructed to test this new compressor. The cooled diaphragm, compressor, and loop design, commissioning, and testing will be discussed in this paper. The compressor impeller selection was made for an adiabatic compressor for the design point of 15 psia (1.03 bara) to 250 psia (17.2 bara) for a mass flow of 15.1 lbm/sec (6.85 kg/s). This flow is equivalent to the CO_2 produced by a 35 MW coal fired power plant. The design speed of the compressor is 11,403 rpm and is driven by a 3 MW electric motor through a speed increasing gearbox.

The compressor package was delivered and set, leveled, and bolted to 20 sub-sole plates (Figure 4). Hand valves, control valves, orifice plates, flow conditioners, strainers, and the cooling tower were received and installed. The heat exchangers and piping were assembled and the cooling water supply was tested through the process heat exchangers. The completed pipe assembly is shown in Figure 5. A venting control valve is also used to maintain the desired suction pressure to the compressor. Cooling water was provided to the heat exchangers and compressor diaphragm via an 800 gpm evaporative cooling tower.

Figure 4. Installed Dresser-Rand Datum Compressor Package

The compressor package and pipe loop were commissioned, including oil flush, pipe alignment, shaft alignment, and mechanical testing. All mechanical parameters of the compressor met manufacturer's specifications.

Figure 5. Pipe Loop Assembly Aerial View

Several compressor operating configurations were tested in order to verify compressor performance and determine the effects of the cooled diaphragms. The adiabatic tests (with no cooling water) showed close correlation to the predicted aerodynamic performance maps. These tests established a baseline temperature distribution and power. The liquid cooling system was commissioned and tuned to provide the correct flow distribution to the diaphragms. The subsequent cooled diaphragm testing showed similar head-flow characteristic curves, but slightly higher head and pressure ratio for a given flow due to the increased volume reduction caused by lower stage discharge temperatures.

The polytropic head for varying flow rates from Test 1 is plotted in Figure 6 for the two sections. The adiabatic test points are shown in blue, and the data points for testing with cooling water at the two different flow rates are shown in red and green. The solid black line denotes the predicted adiabatic curve. All data are normalized with respect to the adiabatic test data at the design flow.

The measured adiabatic data were reasonably close to the predicted adiabatic curve, with polytropic head for Sections 1 and 2 measured to be slightly lower and higher than predicted near the design point, respectively. The data also showed that diaphragm cooling changed the characteristics of the speed line slightly by increasing the volume flow capacity for each section, particularly near the choke side of the map. This performance change is attributed to the gas volume reduction that occurred as the gas was cooled in the diaphragm, which caused the latter stages in each section to stay out of choke and operate closer to their design point. The opposite would be true at low flow operation allowing the flow range to be extended by shutting off cooling flow when operating near the surge line. Since the introduction of cooling water affected the head characteristics, the speed during the cooled tests was reduced to match identical discharge pressure as the adiabatic test in order to allow a direct comparison on power.

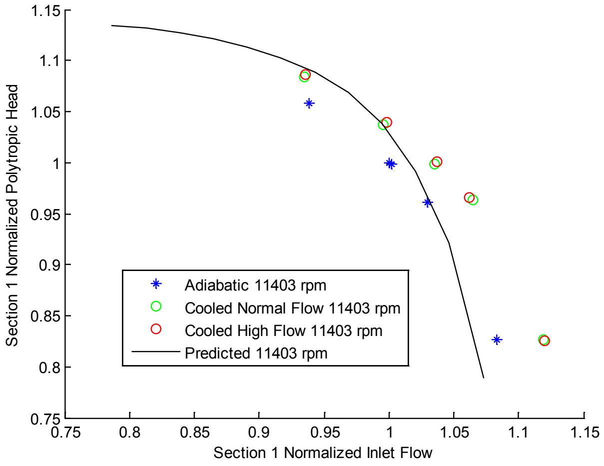

Figure 6. Section 1 Normalized Polytropic Head vs. Normalized Flow (Test 1)

Internal temperature measurements were taken at various points along the compressor. At each of these points, several temperature and pressure measurements were taken at different circumferential locations. These data points were averaged to get a temperature and pressure at each location. For both the adiabatic and cooled cases, the predicted design point temperature was plotted against the actual design point temperature in Figure 7 for Section 1. These results indicate that the adiabatic temperature rise was slightly higher than predicted and cooled temperatures were slightly lower than predicted but showed good agreement overall. The measured discharge temperature was over 100 °F lower for the cooled case.

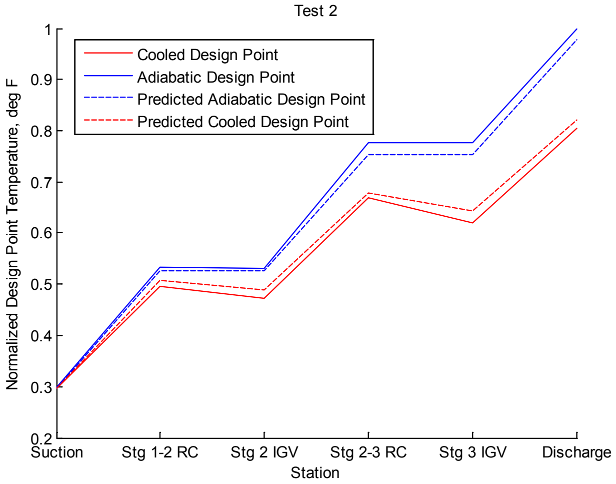

Figure 7. Section 1 Comparison with Predicted Normalized Temperature for Design Flow Conditions

The data show that the cooled diaphragms reduce power consumption by 3–8 percent when the compressor is operated as a back-to-back unit, with the higher power savings at high flow operating points using the high speed torquemeter for reference as shown in Table 2. Additional performance savings could be realized by adding more stages and running the compressor at a slower speed.

TABLE 2. HORSEPOWER PERCENT SAVINGS WITH INTERCOOLER

Point	Adiabatic versus Cooled Diaphragm Difference (%)
1	7.99
2	6.28
3 (design PR)	3.24 (predicted 2.9%)
4	3.03
5	3.01
6	3.32

The results from Test 3 (no intercooling to simulate a straight-through compressor), as shown in Table 3, showed even higher power savings of 9 percent at the design point when matching pressure ratio and speed. Based on the trends seen in back-to-back testing, power savings are expected to be even higher at higher flows exceeding the 10 percent goal of this program.

TABLE 3. HORSEPOWER PERCENT SAVINGS WITH NO INTERCOOLER

Power Savings (%) A. Matching speed and pressure ratio	Power Savings (%) B. Matching flow and pressure ratio
5.64	9.00

technology advantages

- New compression process could use up to 10 percent less power compared to commercially available inline centrifugal compressors.
- Applicable to all types of power plants, including PC, IGCC, and oxy-fuel.
- Could result in significant capital savings and reliability improvement compared to an integrally geared compressor.
- Inline compressors are scalable to large power plants, and their reliability is well proven in LNG and Ethylene service.

R&D challenges

- The wide range of CO_2 output from the power plant based on required electrical output.
- Carbon dioxide compression technology must have high reliability.
- IGCC plants contain multiple CO_2 streams at different pressures.
- The volume reduction during the compression can exceed 500:1.

results to date/accomplishments

- Development complete of multistage internally cooled diaphragm.
- Detailed design of Dresser-Rand DATUM compressor with multistage cooled diaphragms is complete.
- Design of a closed-loop to test back-to-back compressor is complete.
- Pilot-scale demonstration compression plant was developed and constructed.
- Measured the CO_2 baseline compressor performance with and without diaphragm cooling.
- Comparative testing of adiabatic and cooled tests at equivalent inlet conditions shows that the cooled diaphragms reduce power consumption by 3–8 percent when the compressor is operated as a back-to-back unit and over 9 percent when operated as a straight-through compressor with no intercooler.
- The power savings, heat exchanger effectiveness, and temperature drops for the cooled diaphragm were all slightly higher than predicted values.

next steps

This project ended on June 30, 2014.

available reports/technical papers/presentations

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2," presented at the 2013 NETL CO_2 Capture Technology Meeting, July 2013. *http://www.netl.doe.gov/File%20Library/events/2013/CO2%20capture/J-Moore-SWI-Concepts-for-Compression-of-Large-Volumes-of-CO2.pdf*.

Moore, J.J.; et al., "Advance Centrifugal Compression and Pumping for CO_2 Applications," presented at the 2012 NETL CO_2 Capture Technology Meeting, July 2012. *http://www.netl.doe.gov/File%20Library/Events/2012/CO2%20Capture%20Meeting/J-Moore-SRI-CO2-Compression.pdf*.

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.

Moore, J.J.; et al., "Novel Concepts for the Compression of Large Volumes of CO_2 – Phase II," presented at the Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 2009.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
PRE-COMBUSTION SOLVENT TECHNOLOGIES

CO_2 Capture from IGCC Gas Streams Using the AC-ABC Process

primary project goals

SRI International (SRI)'s goal was development of a carbon dioxide (CO_2) capture technology for integrated gasification combined cycle (IGCC)-based power plants that uses a high-capacity and low-cost aqueous solution containing ammonium carbonate (AC) that reacts with CO_2 to form ammonium bicarbonate (ABC). SRI partnered with Bechtel Hydrocarbon Technology Solutions (BHTS) to use the Bechtel Pressure Swing Claus (BPSC) process to remove sulfur species from the recovered CO_2 stream.

technical goals

- Test the technology on a bench-scale batch reactor to validate the concept.
- Determine the optimum operating conditions for a small pilot-scale reactor.
- Design and build a small pilot-scale reactor capable of continuous, integrated operation.
- Perform pilot-scale tests to evaluate the process in a coal gasifier environment.
- Perform a technical and economic evaluation of the technology.

technical content

The technology is based on the use of an aqueous ammoniated solution containing AC, which reacts with CO_2 to form ABC.

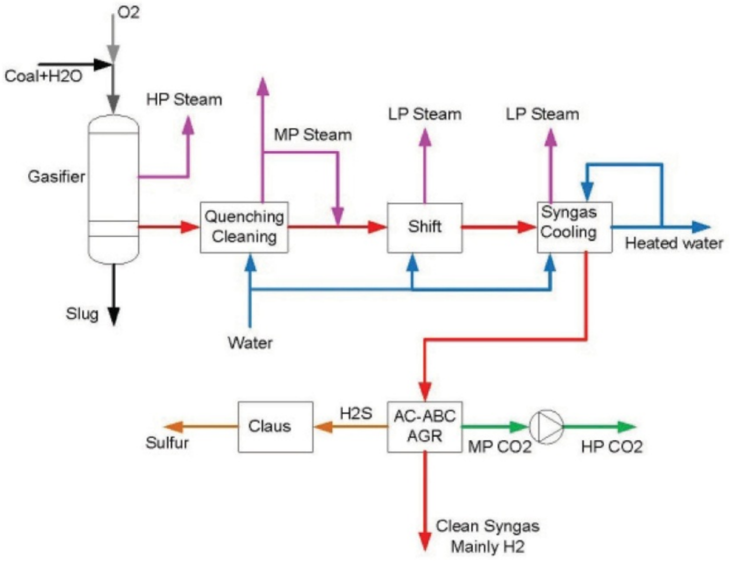

Figure 1: Acid gas removal in a gasification system

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This high-pressure separation technique reduces the size of the CO_2 stripper, the CO_2 compression needs, and the

technology maturity:

Pilot-Scale, Actual Syngas (equivalent to 0.15 MW_e)

project focus:

CO_2 Capture Using AC-ABC Process

participant:

SRI International

project number:

FE0000896

predecessor projects:

N/A

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Anoop Nagar
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partners:

Bechtel Hydrocarbon Technology Solutions, Inc.; EIG, Inc.; National Carbon Capture Center

start date:

09.30.2009

percent complete:

100%

electric power consumption relative to capture at lower syngas pressures. Figure 1 depicts the AC-ABC acid gas removal process in the larger context of a coal gasification and syngas cleanup system.

Figure 2 depicts the flows within the AC-ABC process, showing how acid gases are removed from the syngas in the absorber column, and how they are recovered as a separate gas stream in the stripping column. AC is a low-cost and readily available reagent with high net CO_2 loading capacity, requiring relatively low circulation of solvent between the CO_2/H_2S absorber and CO_2/H_2S stripper. The ammonium carbonate is highly selective to CO_2 and H_2S at the lower temperatures of the gas and solvent in the absorber (solvent entering column at 85 °F), while the solubility of hydrogen (H_2), carbon monoxide (CO), and methane (CH_4) in the absorber solution is extremely low, resulting in minimal losses of syngas species in the absorber. Rich solvent exiting the absorber is regenerated in the stripping column by increasing its temperature (solution entering column at 250 °F), causing the CO_2 and H_2S to evolve as a relatively pure gas stream from the stripper. The pressure is relatively constant in this cycle, with only the temperature being varied, classifying this a temperature-swing absorption cycle for acid gas removal from syngas.

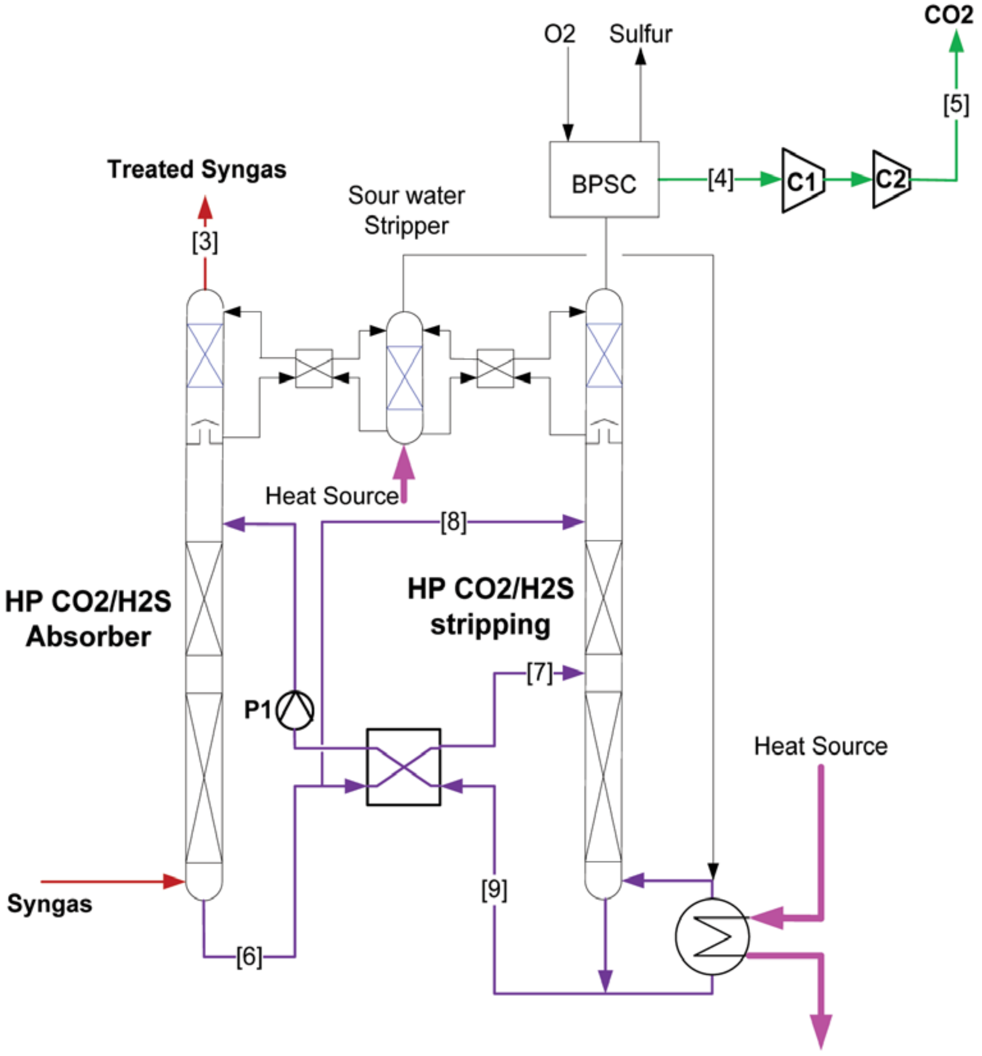

Figure 2: Schematic of the CO_2 and H_2S capture system

Because the AC-ABC process removes a mixture of CO_2 and H_2S, it is necessary to separate the H_2S to enable utilization or storage of the CO_2. Accordingly, the BPSC process was chosen for this purpose downstream from the AC-ABC unit. BPSC is a high-pressure, sub dew point Claus system which recovers H_2S directly from an acid gas stream in the form of elemental molten sulfur, using SO_2 as an oxidant. In this technology, multiple sub dew point reactors are used in rotation (Lead/Lag/Regeneration) similar to a molecular sieve dehydration unit, a pressure swing absorption unit, or a low-pressure sub dew point Claus system. BPSC allows recovery of sulfur species as elemental sulfur while maintaining system pressure. Due to the higher pressures compared to traditional Claus units, equipment size is reduced. Figure 3 shows the basic process scheme of the BPSC system.

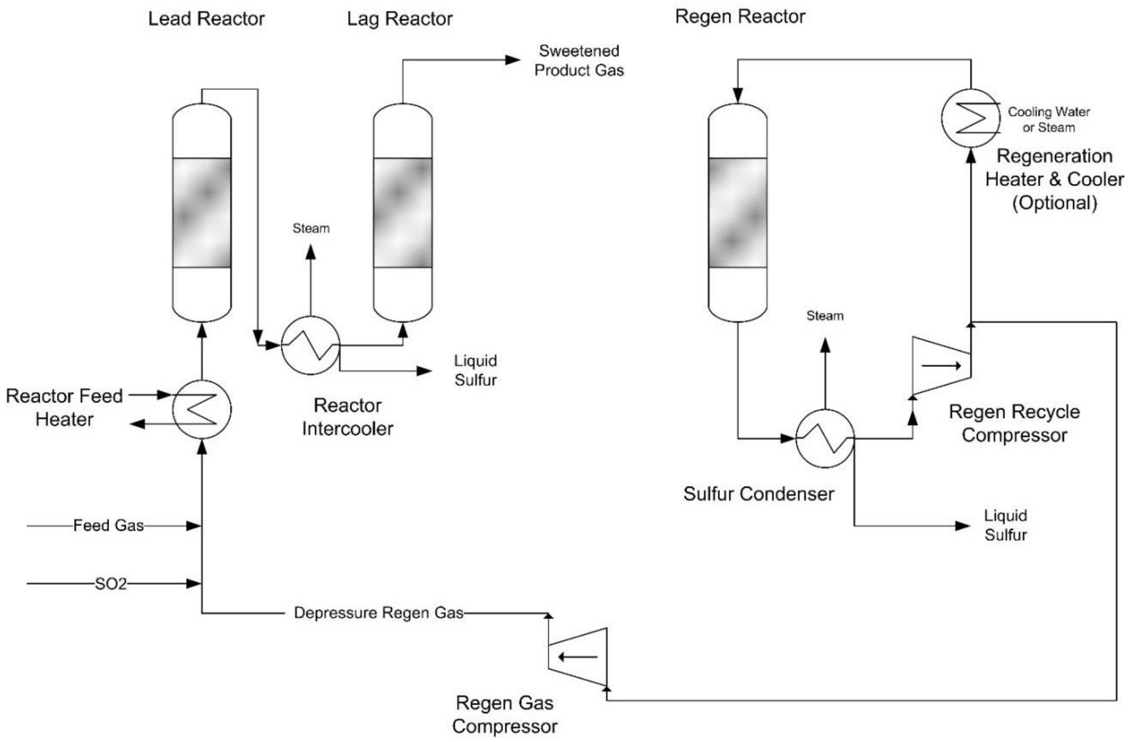

Figure 3: Schematic of the Bechtel pressure swing Claus H_2S removal system

In the BPSC process, SO_2 (produced by oxidizing some of the product sulfur) is introduced to the acid gases ("feed gas") and they are heated indirectly by steam in the "reactor feed heater". Then the mixture is fed to the first or primary on-line reactor ("primary reactor"), where most of the H_2S, carbonyl sulfide (COS), and SO_2 are converted to sulfur and adsorbed on the catalyst. The gas flows through a cooler ("reactor intercooler"), where it is cooled by generating steam. Provisions are made to accommodate any sulfur that may condense at this location. Any recovered sulfur drains to a sulfur pit, and the vapor goes to the next reactor ("secondary reactor/sulfur trap"), which acts as a sulfur trap/guard bed. The product gas is returned to the facility for compression. After about 8–12 hours online, the primary reactor is rotated to regeneration, the secondary reactor moves up to the primary position, and the regenerated reactor is switched to the secondary reactor position. The sulfur-loaded bed is partially regenerated by pressure let down. Flash gas passes through a sulfur condenser and is recompressed in the Regen Recycle Compressor and Regen Gas Compressor prior to being mixed into the BPSC feed stream. There is a heating and cooling cycle ("Regeneration Heater & Cooler") using recycled sweep gas to complete the reactor regeneration.

In 2016, SRI International and EIG Inc. were awarded a patent on the technology for simultaneous high-efficiency capture of CO2 and H2S from pressurized gas, which is at the core of the AC-ABC Process. For further information, refer to U.S. Patent No. 9,463,416 B2, dated October 11, 2016.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	nominal 18	nominal 18
Normal Boiling Point	°C	varies with pressure: 100 °C at 1 atm	varies with pressure: 100 °C at 1 atm
Normal Freezing Point	°C	nominal 0 °C, varies with composition	nominal 0 °C, varies with composition
Vapor Pressure @ 15°C	bar	NH_3 vapor pressure varies with composition and temperature	NH_3 vapor pressure varies with composition and temperature
Manufacturing Cost for Solvent	$/kg	—	cost of anhydrous ammonia typically $200–$400/ton
Working Solution			
Concentration	kg/kg	0.1 kg NH_3/kg	0.15 kg NH_3/kg
Specific Gravity (15 °C/15 °C)	-	1.1	1.1
Specific Heat Capacity @ STP	kJ/kg-K	3.5	3.5
Viscosity @ STP	cP	nominal 1	nominal 1
Absorption			
Pressure	bar	20	30
Temperature	°C	25	25–40
Equilibrium CO_2 Loading	mol/mol	varies with the composition of the solution	varies with the composition of the solution
Heat of Absorption	kJ/mol CO_2		40-60
Solution Viscosity	cP	nominal 1	nominal 1
Desorption			
Pressure	bar	30	30
Temperature	°C	<200°C	—
Equilibrium CO_2 Loading	mol/mol	varies with the composition of the solution	varies with the composition of the solution
Heat of Desorption	kJ/mol CO_2	—	—
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr	225	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90% >95% 30 bar	
Absorber Pressure Drop	bar	<1 bar	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	—	

Definitions:

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

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

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

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

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

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

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

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

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism –

$$NH_4OH + CO_2 \leftrightarrow NH_4HCO_3$$

$$(NH_4)_2CO_3 + CO_2 + H_2O \leftrightarrow 2NH_4HCO_3$$

$$NH_4(NH_2CO_2) + CO_2 + 2H_2O \leftrightarrow 2NH_4HCO_3$$

Solvent Contaminant Resistance – The solvent is expected to be resistant to several contaminants nominally present in an IGCC gas stream. Hydrogen sulfide reacts with the solvent, but it can be removed during the regeneration. The ammonia (NH_3) in the IGCC may negate any NH_3 loss from the solvent. The resistance of the solvent to trace metals is not known yet.

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

Syngas Pretreatment Requirements – The IGCC gas stream needs to undergo a water gas shift (WGS) reaction to convert CO to CO_2 and to be cooled to a temperature of 25–50 °C.

Solvent Makeup Requirements – The AC is a readily available commodity chemical, and the makeup requirements are estimated to be small. However, the actual amount will be determined in the field test.

Waste Streams Generated – Ammonium sulfate solution from the capture of trace residual NH_3 in the gas.

Process Design Concept – See Figures 1–3.

Proposed Module Integration – Note the module location, as well as the pressure, temperature, and composition of the gas entering the module.

Pressure	Temperature	Composition						
		vol%						ppmv
psia	°F	CO_2	CO	CH_4	N_2	H_2	Ar	H_2S
185	68	13.4	0.03	0.6	74.4	10.1	0.6	2000

technology advantages

- Low-cost and stable reactive solution/solvent—low ammonia loss demonstrated in testing.
- Ammoniated solution is very effective in rapid absorption of CO_2 at elevated pressure—CO_2 capture efficiency greater than 99 percent demonstrated in testing.
- The reactive ammoniated solution has a high CO_2 loading capacity (12 percent CO_2 effective loading).
- H_2S can be simultaneously absorbed along with CO_2 in a single absorber column—H_2S capture efficiency greater than 99 percent demonstrated in testing.

- The absorption/loss of fuel gas species like H_2, CO, and CH_4 was very low as shown in testing—therefore high conversion of CO in the syngas is not required to achieve 90 percent reduction of carbon emissions.
- CO_2 stripping in the AC-ABC process can be accomplished at elevated pressures in the range of 20–50 bar, resulting in a 3–7.5 pressure ratio to compress the gas to the pipeline pressure of 150 bar pressure—i.e., the availability of regenerated CO_2 at elevated pressure significantly reduces the compressor requirements for CO_2 sequestration.
- The AC-ABC process does not require compressors other than the CO_2 compressor.
- Both the absorber and regenerator are operated at similar elevated pressure, reducing the need for pumping solvents across pressure boundaries.
- Hot syngas from the shift reactor can be used as the main heat source for the CO_2 stripping, reducing the power output penalty.
- The BPSC process removes H_2S from the high-pressure CO_2 (or syngas) stream with minimal reduction in pressure, which reduces the power output penalty.
- The BPSC process combines the function of three units (solvent, Claus, and Claus tail gas) into one. The thermal oxidizing unit needed for the traditional approach is not needed with BPSC, reducing total carbon footprint.

R&D challenges

- Possible sulfating problem on beds of BPSC process catalyst.
- Difficulty in measurement/quantification of sulfur produced in the BPSC process at pilot scale.
- Difficulties in engineering packing or trays to effectively control ammonia emissions from the absorber at pilot scale.

status

The project was completed in September 2016. In the culmination of project activities, a 0.15-megawatt electric (MW_e) integrated pilot plant was constructed and operated, processing 500 lb/hr of shifted syngas from an air blown gasifier at the National Carbon Capture Center in Wilsonville, Alabama, with total testing duration of over 700 hours. This successfully demonstrated use of the AC-ABC process for carbon dioxide and sulfur capture from actual coal-derived syngas. System availability was considered to be favorable, even at the pilot-scale level.

The results of the techno-economic analysis (with baseline case 750-MW IGCC plant using CO_2 capture using conventional Selexol and traditional Claus plant) indicate that the increase in cost of electricity (COE) with the AC-ABC process will be ~30 percent, and the cost of CO_2 captured is projected to be less than $27/metric ton of CO_2 while meeting DOE's 90 percent CO_2 capture goal.

available reports/technical papers/presentations

Nagar, A. et al., "*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process,*" Final Report, SRI Project P19207 and P21321, Cooperative Agreement No. DE-FE0000896, SRI International, Menlo Park, CA, 16 February 2017.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2011 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, August 2011.

"*CO_2 Capture from IGCC Gas Streams Using AC-ABC Process*," presented at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010.

"CO_2 Capture from IGCC Gas Streams Using the AC-ABC Process," presented at the Pre-Combustion CO_2 Capture Kick-Off Meetings, Pittsburgh, PA, November 2009.

"Analysis of SRI AC-ABC and Bechtel Pressure Swing Claus Technologies for Pre-Combustion Carbon Capture," presented at the Eleventh Annual Conference on Carbon Capture, Utilization and Sequestration, Pittsburgh, PA, May 2012.

"Bechtel Pressure Swing Claus Sulfur Recovery," presented at the International Pittsburgh Coal Conference, Pittsburgh, PA, September 2009.

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
PRE-COMBUSTION SORBENT TECHNOLOGIES

EVALUATION OF DRY SORBENT TECHNOLOGY FOR PRE- COMBUSTION CO_2 CAPTURE

primary project goals

URS Group and the University of Illinois at Urbana-Champaign (UIUC) are developing dry carbon dioxide (CO_2) sorbent materials, through the coupling of thermodynamic, molecular simulation, as well as process simulation modeling with novel synthesis methods, that possess superior adsorption and regeneration properties at conditions applicable to water gas shift (WGS) systems. If successful, this project will demonstrate that one or more sorbent materials are able to remove greater than 90 percent of the CO_2 from a simulated synthesis gas (syngas) at conditions applicable to a WGS reactor, thus meeting a key U.S. Department of Energy (DOE) program objective.

technical goals

Specific technical objectives of this project include:

- Determination of optimal CO_2 sorbent properties and operating conditions for CO_2 removal and regeneration and carbon monoxide conversion in a simulated syngas using a combination of computational and experimental methods.
- Development of one or more sorbents that recover high-quality heat during CO_2 adsorption, regenerate at elevated pressure, have minimal deactivation over multiple cycles, have high selectivity at high temperatures, have high adsorption capacity, and have acceptable thermal stability and mechanical integrity. This will result in sorbents capable of 90 percent CO_2 removal with high loading capacities and able to operate at the high temperatures and pressures typically encountered upstream of a WGS reactor. If successful, the sorbents developed in this program will augment or replace the carbon monoxide conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.
- Determine the techno-economic feasibility of the sorption-enhanced WGS (SEWGS) process for removing CO_2.

technical content

URS Group is leading development of a dry sorbent process configured to combine the WGS reaction with CO_2 removal for coal gasification systems. The result will be an SEWGS technology.

A novel approach integrates the use of multiple computational models with sorbent synthesis and characterization activities to develop sorbents with optimal CO_2 removal properties at high temperatures and pressures applicable to WGS applications. Tests evaluate sorbent performance in simulated WGS gas mixtures at commercially relevant conditions. Appropriate data reduction and analysis provides suitable data for a techno-economic analysis to evaluate the feasibility and scaleup potential of the SEWGS technology.

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Sorbent Development for WGS

participant:

URS Group, Inc.

project number:

FE-0000465

NETL project manager:

Elaine Everitt
elaine.everitt@netl.doe.gov

principal investigator:

Carl Richardson
URS Group, Inc.
carl.richardson@urs.com

partners:

Illinois Clean Coal Institute University of Illinois at Urbana-Champaign

performance period:

1/1/10 – 9/30/13

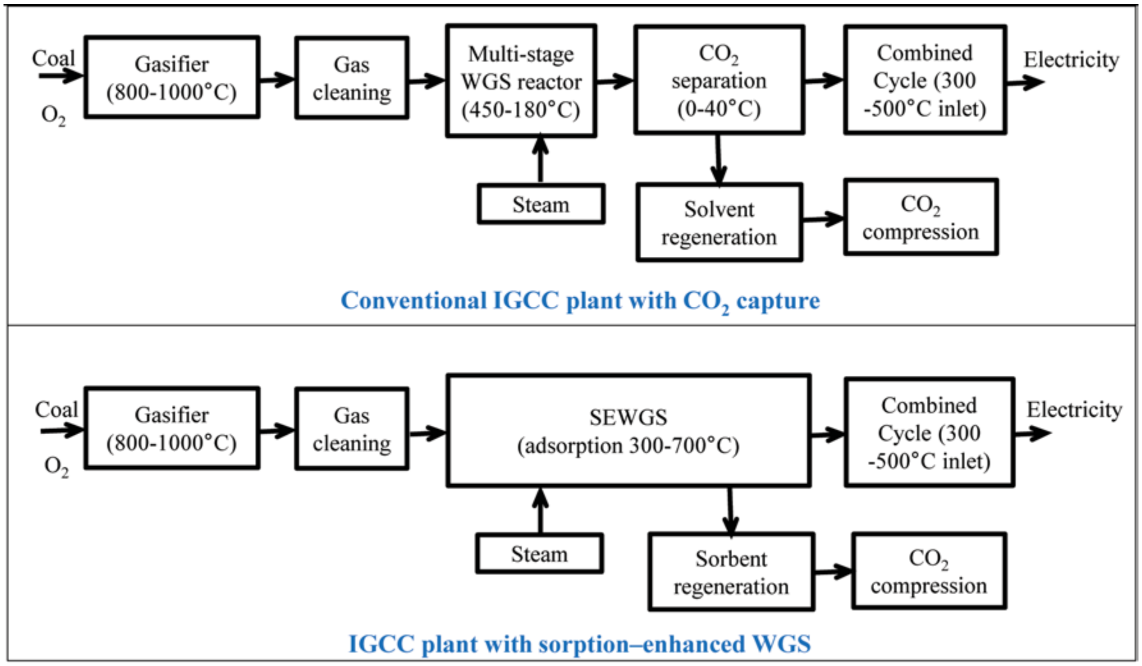

Figure 1: IGCC with SEWGS vs. Conventional IGCC

Process simulation modeling and sorbent molecular and thermodynamic analyses by UIUC allow prediction of optimal sorbent properties and identification of optimal operating temperature and pressure windows to maximize the energy efficiency of the combined WGS and CO_2 capture processes. The thermodynamic study includes developing phase equilibrium diagrams for potential sorbents, identifying optimum operating conditions for CO_2 capture, understanding impacts of syngas impurities, and identifying promising sorbents. Molecular simulation predicts isotherms and properties, kinetics, and dynamics, and identifies sorbents with desired properties using quantum chemistry/mechanics, force field-based molecular dynamics (MD), and reactive dynamics (RD) simulations. Process simulation analyzes various process scenarios for heat integration between SEWGS and integrated gasification combined cycle (IGCC) and process energy performance for individual sorbents.

The first phase testing and modeling efforts guide the synthesis of sorbents with desired pore structure and composition. Synthesis includes use of various precursors, including calcium, magnesium, and other metal oxides, as well as zirconates, titanates, silicates, aluminates, and adsorbent-shift catalyst hybrid. The sorbent down-selection process is guided by the decision tree shown in Figure 2.

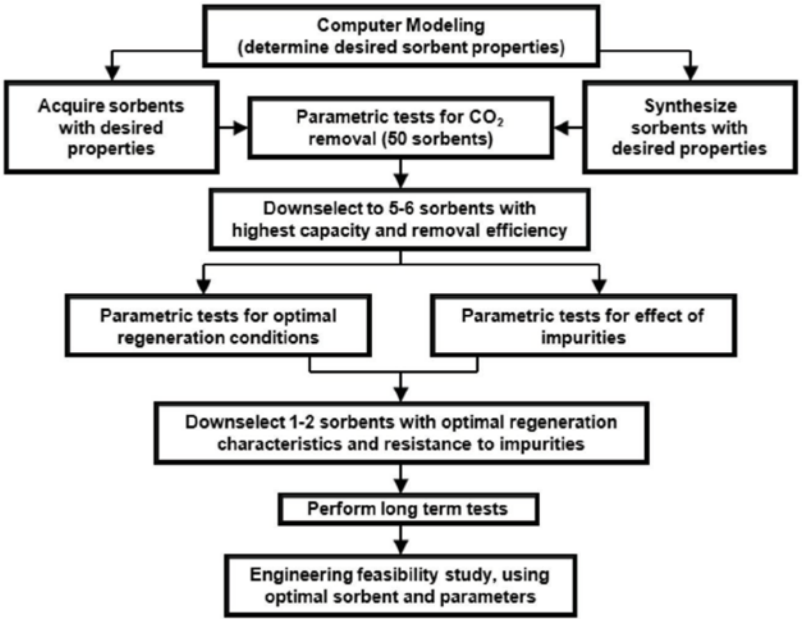

Figure 2: Sorbent Development and Analysis Decision Tree

An atmospheric-pressure thermogravimetric analyzer (TGA) and high temperature and pressure reactor (HTPR) system, capable of 300 pounds per square inch gauge (psig) and 950 °C, are UIUC's primary tools for screening sorbents for CO_2 removal. A URS HTPR provides the capability to evaluate five to seven down-selected sorbents' adsorption performance in the presence of syngas impurities and regeneration performance. Long-term testing is limited to a down-selection of one to two sorbents.

A preliminary engineering study of process feasibility for adsorbing and removing CO_2 as part of the WGS process, and comparison to base WGS operation and other CO_2 removal strategies, is informed by the preceding laboratory test results. Parameters under evaluation include costs of >90 percent removal (cost of electricity [COE], operation and maintenance [O&M]), sorbent costs, anticipated lifetime (i.e., replacement rate), estimated future market costs of precursor materials, handling equipment, sorbent regeneration costs, heat/energy integration, compression costs with SEWGS, unit footprint, and capital costs and scalability.

TABLE 1: SOLID SORBENT PARAMETERS

	Units	Current R&D Value	Target R&D Value
Sorbent			
True Density at STP	kg/m^3		TBD
Bulk Density	kg/m^3		TBD
Average Particle Diameter	mm	nano (20–70 nm) or micro meter (0.5–10 µm) level; particles can be pelletized if needed	TBD based on the reactor design analysis
Particle Void Fraction	m^3/m^3		
Packing Density	m^2/m^3		
Solid Heat Capacity at STP	kJ/kg-K	<1	<1
Crush Strength	kg_f		
Manufacturing Cost for Solvent	$/kg		
Absorption			
Pressure	bar	30–40	40
Temperature	°C	300–700	550–650
Equilibrium CO_2 Loading	g mol CO_2/kg		
Heat of Absorption	kJ/mol CO_2	100–200	TBD

Desorption			
Pressure	bar	up to 30	highest possible up to 30
Temperature	°C	depends on individual sorbent and highest regeneration pressure achievable	TBD; optimization based on minimal energy limit
Equilibrium CO_2 Loading	mol/mol		
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement/Operation	—	temperature swing	temperature swing
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	90 percent, 99 percent	
Adsorber Pressure Drop	bar	depending on sorbent properties, to be determined during project	TBD

Definitions:

STP – Standard Temperature and Pressure (15 °C, 1 atm).

Sorbent – Adsorbate-free (i.e., CO_2-free) and dry material as used in adsorption/desorption cycle.

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

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

Desorption – The conditions of interest for desorption are those that prevail at minimum sorbent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-dependent. Measured data at other conditions are preferable to estimated data.

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

Packing Density – Ratio of the active sorbent area to the bulk sorbent volume.

Loading – The basis for CO_2 loadings is mass of dry, adsorbate-free sorbent.

Flow Arrangement/Operation – Gas-solid module designs include fixed, fluidized, and moving bed, which result in either continuous, cyclic, or semi-regenerative operation.

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

This is a research and development (R&D) program involving fairly immature technology. As such, many target R&D values will be determined during execution of the test program and will be impacted by a number of key process parameters, including sorbent type and cost, sorbent performance and loading capacity, sorbent lifetime, regeneration conditions and cycling parameters, and complexity of integration of optimal adsorption and regeneration processing steps.

Sorbent Heating/Cooling Method – For sorbent regeneration, the sorbent is heated in a fluidized-bed or moving-bed configuration with heat supplied by either hydrogen (H_2) (or syngas) oxy-combustion or steam extracted from the gasification plant steam cycle. Before entering the adsorption bed, the regenerated sorbent is cooled by exchanging heat with inlet regeneration H_2/oxygen (O_2) or syngas. In the adsorption bed, a heat exchanger (such as a boiler tube bundle used in the fluidized-bed boiler) is used for recovering heat generated from CO_2 adsorption.

Heat of Adsorption Handling – Adsorption heat is recovered during CO_2 adsorption by using a heat exchanger to generate steam, which is combined into the gasification plant's steam cycle for electricity generation.

Heat Supply Method for Regeneration – Two methods are considered. One is to burn a small amount of the H_2 or syngas using O_2 to supply heat directly. Another approach is to use the steam from the gasification plant's steam cycle if the regeneration temperature is below 1,000 °F.

Contamination Resistance – This program will evaluate the impact of various syngas impurities on the adsorption and regeneration performance of promising CO_2 sorbents. Sorbents may not be resistant to sulfur species (hydrogen sulfide [H_2S], carbon disulfide [CS_2], etc).

Syngas Pretreatment Requirements – The pretreatment of H_2S/CS_2 is needed for sorbents with no sulfur resistance. If it is determined that the performance of identified sorbents is inhibited by sulfur species present in the syngas, additional work will focus on the development of sorbents materials that are resistant to sulfur; the objective will be to avoid the need for syngas pretreatment associated with this technology.

Waste Streams Generated – Desulfurization byproducts.

technology advantages

- High carbon monoxide conversion with reduced stream addition.
- No or limited WGS catalyst use.
- High-quality adsorption heat usable for generation of high-quality steam.
- Limited gas cooling/reheating requirement downstream.
- No separate CO_2 capture unit required.
- Reduced energy requirement for CO_2 compression.

R&D challenges

- Sorbent pores may be plugged during adsorption, causing capacity and activity loss.
- Long-term capacity and activity stability after multiple cycles.
- Selectivity at high temperature.
- System/reactor issues, such as material transport and handling at high temperature and pressure.

results to date/accomplishments

- More than 40 sorbents were modeled and subsequently down-selected to seven candidates (magnesium oxide [MgO], calcium oxide [CaO], lithium zirconate [Li_2ZrO_3], calcium zirconium oxide [$CaZrO_3$], barium zirconate [$BaZrO_3$], barium titanate [$BaTiO_3$], and barium silicate [$BaSiO_3$]) for further development.
- Process simulations were performed for a baseline IGCC plant with WGS and a Selexol process and compared to an IGCC with SEWGS. These showed a 0.5–2.4 percentage point increase in net thermal efficiency for the simulated plant with SEWGS.
- Molecular simulation studies included quantum chemical (QC) calculations and MD simulations with reactive field force
- (ReaxFF). Molecular simulation was successfully applied to assess carbonation and calcination reactions (CaO).
- The impacts of sorbent structure and the sintering of calcium oxide particles with and without CO_2 chemisorption, and the role of a dopant in reducing the sintering of CaO particles, were also determined.
- More than 60 SEWGS sorbents were synthesized using mechanical alloying (MA), ultrasonic spray pyrolysis (USP), and flame spray pyrolysis (FSP) techniques.
- CaO sorbents prepared by dry and wet ball-milled MA methods exhibited improved CO_2 adsorption capacities and stabilities over commercial $CaCO_3$ materials. The performance of $CaCO_3$ sorbents was improved by doping with inert MgO.
- Hollow, porous $CaCO_3$ sorbents synthesized using the USP method were spheres of ≈1 µm with a shell thickness of 50–100 nm. The CaO generated upon calcination of the $CaCO_3$ exhibited a high surface area (up to 75 m^2/g).

- A 75:25 w/w $CaO:Ca_{12}Al_{14}O_{33}$ (mayenite) sorbent retained 91 percent of its initial CO_2 capacity after 15 cycles and 79 percent after 50 cycles, while a USP CaO only retained 43 percent after 15 cycles.
- The surface area of nano-sized (<70 nm) CaO, ZrO_2-doped CaO, MgO, MgO-doped CaO, and ZrO_2-doped MgO sorbents synthesized using the FSP method ranged between 21 and 54 m^2/g. ZrO_2 was found to be an effective dopant to improve the stability of CaO-based sorbents. A ZrO_2-CaO (Zr:Ca=0.2:1) sorbent maintained its capacity at 0.5 g CO_2/g sorbent over 15 adsorption-desorption cycles.
- An HTPR tube reactor with quarter-inch ID and 1-foot length was also used to test sorbents at UIUC. These tests were performed at 650 °C and CO_2 partial pressures up to 4 bar adsorption conditions.
- Results from the HTPR testing showed sorbents with as high as 0.4 grams of CO_2 per grams of sorbent capacity with the ability to initially shift the WGS completely toward CO_2/H_2.
- A longer term experiment with a simple syngas matrix and N_2/steam regeneration stream showed a USP sorbent (#199) to be stable through 50 adsorption-regeneration cycles, though the sorbent tested had a somewhat diminished initial capacity.

next steps

This project ended on September 30, 2013.

available reports/technical papers/presentations

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"Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture," Carl Richardson, URS Corporation, 2013 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO2%20Capture/C-Richardson-URS-Dry-Sorbent-Technology.pdf*.

Hong Lu, Yongqi Lu, Massoud Rostam-Abadi, "CO_2 Sorbents for a Sorption-Enhanced Water-Gas-Shift Process in IGCC plants: A Thermodynamic Analysis and Process Simulation Study," International Journal of Hydrogen Energy, Volume 38, Issue 16, 30 May 2013, Pages 6663-6672. *http://www.sciencedirect.com/science/article/pii/S0360319913006770*.

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Richardson, C., and Lu, Y., "Evaluation of Dry Sorbent Technology," Presentation at the 2010 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/CO2capture/presentations/thursday/Carl%20Richardson%20-%20FE0000465.pdf*.

"Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture," Pre-Combustion CO_2 Capture Kick-Off Meetings, Pittsburgh, PA, November 2009. *http://www.netl.doe.gov/publications/proceedings/09/CO2capture/7-URS%20Dry%20Sorbent%20Kickoff%20Presentatin-111309.pdf*.

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CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
PRE-COMBUSTION MEMBRANE TECHNOLOGIES

Polymer-Based Carbon Dioxide Capture Membrane Systems

primary project goals

Los Alamos National Laboratory (LANL) developed and demonstrated polymer-based membrane structures, deployment platforms, and sealing technologies for attaining a combination of high selectivity, high permeability, chemical stability, and mechanical stability at elevated temperatures (>150 °C) and packaged in a scalable, economically viable, high area density system amenable to incorporation into an integrated gasification combined cycle (IGCC) plant for pre-combustion carbon dioxide (CO_2) capture.

technical goals

- Minimize membrane support costs, maximize membrane flux, retain thermo-mechanical and thermo-chemical stability characteristics, and increase the area density achievable in a commercial module design.
- Produce an asymmetric polybenzimidazole (PBI) hollow fiber comprised of a thin, dense, defect-minimized PBI selective layer and an open, porous underlying support structure with morphology characteristics tailored to optimize transport and mechanical property requirements (use and lifetime).
- Develop materials and methods to further mitigate defects in ultra-thin selective layers for use under process relevant conditions.
- Reduce perceived technical risks of utilizing a polymeric membrane based technology in challenging (thermal, chemical, mechanical) syngas environments.

technical content

LANL work, from a previously funded project FWP-10-002, demonstrated that PBI and other benzimidazole-based materials show promise as membranes for pre-combustion-based capture of CO_2. PBI is a unique polymer family that is stable to temperatures approaching 500 °C. PBI possesses excellent chemical resistance, a high glass transition temperature (>460 °C), good mechanical properties, and an appropriate level of processability. The PBI-based membranes developed by LANL have demonstrated operating temperatures significantly higher than 150 °C (up to 450 °C) with excellent chemical, mechanical, and hydrothermal stability, and outperformed any polymer-based membrane available commercially or reported in the literature for separations involving hydrogen. This achievement is validated via membrane productivity (separation factor and flux) comparisons (Figure 1). The improved performance of this technology in an application such as IGCC-integrated capture is further substantiated by the accessible operating temperature range (up to 400 °C), long-term hydrothermal stability, sulfur tolerance, and overall durability of the proposed membrane materials in these challenging pre-combustion environments. These characteristics have been validated via extensive evaluations of LANL's polymer-based membrane in simulated syngas environments containing hydrogen (H_2), CO_2, methane (CH_4), nitrogen (N_2), carbon monoxide (CO), steam (H_2O), and hydrogen sulfide (H_2S), from 25 to 400 °C, and demonstration of the membrane's thermal stability

technology maturity:

Bench-Scale, Simulated Syngas (single hollow fiber testing)

project focus:

High-Temperature Polymer-Based Membrane

participant:

Los Alamos National Laboratory

project number:

FWP-FE-308-13

predecessor projects:

FWP-FE-10-002
04FE13-AC24

NETL project manager:

David Lang
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principal investigator:

Kathryn A. Berchtold
Los Alamos National Laboratory
berchtold@lanl.gov

partners:

PBI Performance Products,
NETL

start date:

10.01.2008

percent complete:

100%

via 300-plus days in operation at 250 °C. These achievements and material/membrane property validations were largely conducted on flat sheet and tubular platform membranes.

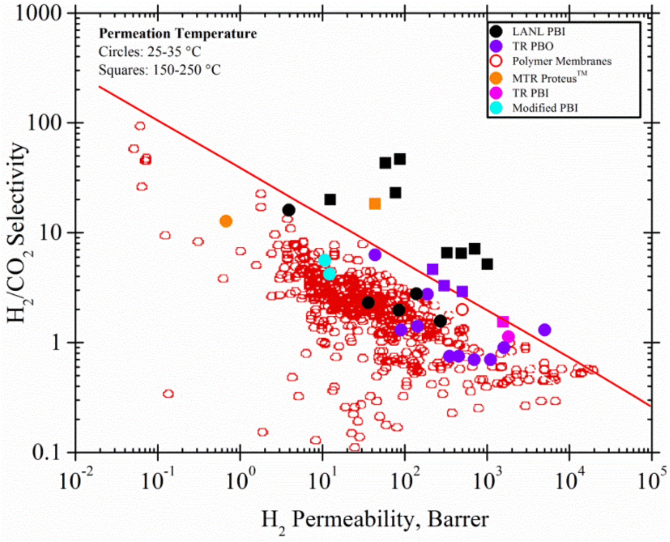

Figure 1: Robeson plot comparing PBI composite membrane with other polymeric membranes tested for H_2/CO_2 separation

The line represents the 2008 upper bound and Red symbols are the corresponding experimental data from Robeson JMS 320 (2008) 390-400. Data taken from LANL PBI: Berchtold *et al.*, JMS 415 (2012) 265-270, Xin *et al.*, JMS 461 (2014) 59-68 & Pesiri *et al.*, JMS 218 (2003) 11-18; Modified PBI: Kumbharkar *et al.*, JMS 286 (2006) 161-169; Membrane Technology & Research (MTR) Proteus: Merkel *et al.*, JMS 389 (2012) 441-450; Thermally Rearranged Polybenzoxazole (TR PBO): Han *et al.*, PCCP 14 (2012) 4365-4373 & Park *et al.*, JMS 359 (2010) 11-24; TR-PBI: Hans *et al.*, JMS 357 (2010) 143-151.

Previous R&D efforts were focused on the utilization of the PBI formulations as a selective layer deposited on and supported by a unique porous metal substrate (fabricated by Pall Corporation). Systems, economic, and commercialization analyses conducted by NETL, LANL, and others, combined with in- and out-of-laboratory testing, established the technical viability of the technology and indicated the strong potential for the membrane-based capture technology to meet and exceed the DOE Carbon Capture Program goals. However, these analyses also made clear the need to cut the costs of the support material and increase the area density realized by the ultimate module design in order to realize the desired step-change in both performance and cost of CO_2 capture associated with the use of this membrane-based capture technology. One promising option for achieving a substantial increase in active membrane area density and mitigating the cost of a metal or inorganic material-based support is the use of a hollow fiber membrane (HFM) platform. A HFM is the membrane configuration with the highest achievable packing density (i.e., the highest membrane selective area density). Commercial HFM modules have been fabricated to obtain selective area densities as high as 30,000 m^2/m^3. This affords the opportunity to achieve several orders of magnitude improvement over the density achievable with the previous polymeric-metallic membrane platform (ca. 250 m^2/m^3) which will reduce the size requirement of the costly, high temperature-tolerant membrane module housings, will minimize membrane support costs through their all-polymeric design, and will facilitate membrane flux maximization through processing facilitated selective layer thickness minimization (Figure 2). Realization of such increases in membrane area density and flux with the materials previously developed would lead to substantial economic and technical benefits.

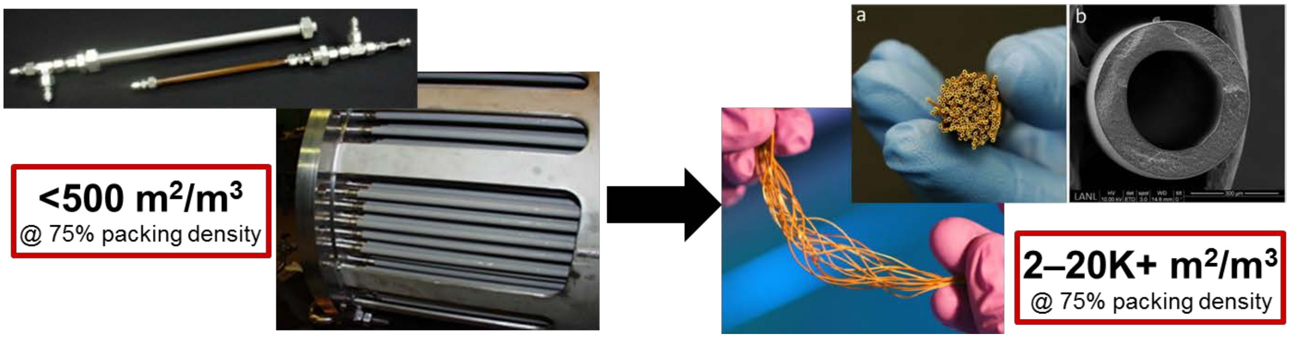

Figure 2: Illustration of the transition from the technology development state at project onset (PBI-metallic composite membrane in a tubular platform) to the technology end state (high area density all-polymeric PBI hollow fiber membrane platform)

The focus of recent technology development has been translation of the previously developed membrane materials chemistries into a high area density HFM platform via commercially viable HFM manufacturing methods; developing and deploying defect mitigation strategies for optimizing membrane performance and durability; and demonstrating the produced membranes in simulated and actual process environments with the overarching goal of technology progression toward commercialization.

Technology advancement has now been extended to realization of polybenzimidazole (PBI)-based membrane chemistries, structures, deployment platforms, and sealing technologies that achieve the critical combination of high permselectivity and durability at elevated temperatures (up to 350 °C, the highest ever reported viable operating temperature of a polymer based membrane). The work conducted as part of this development and demonstration effort includes the translation of these unique PBI materials into a commercially viable, all polymeric HFM platform (Figure 3). Results also demonstrated that the developed materials not only function at significantly higher temperatures than current commercially available polymeric membranes (which are limited to <150 °C) but also provide improved performance while exhibiting long-term temperature stability, sulfur tolerance, and overall durability in industrially relevant operating conditions. For the most detailed documentation of recent work available, the reader is referred to the project final report for FWP-FE-308-13 (see the list of available reports below).

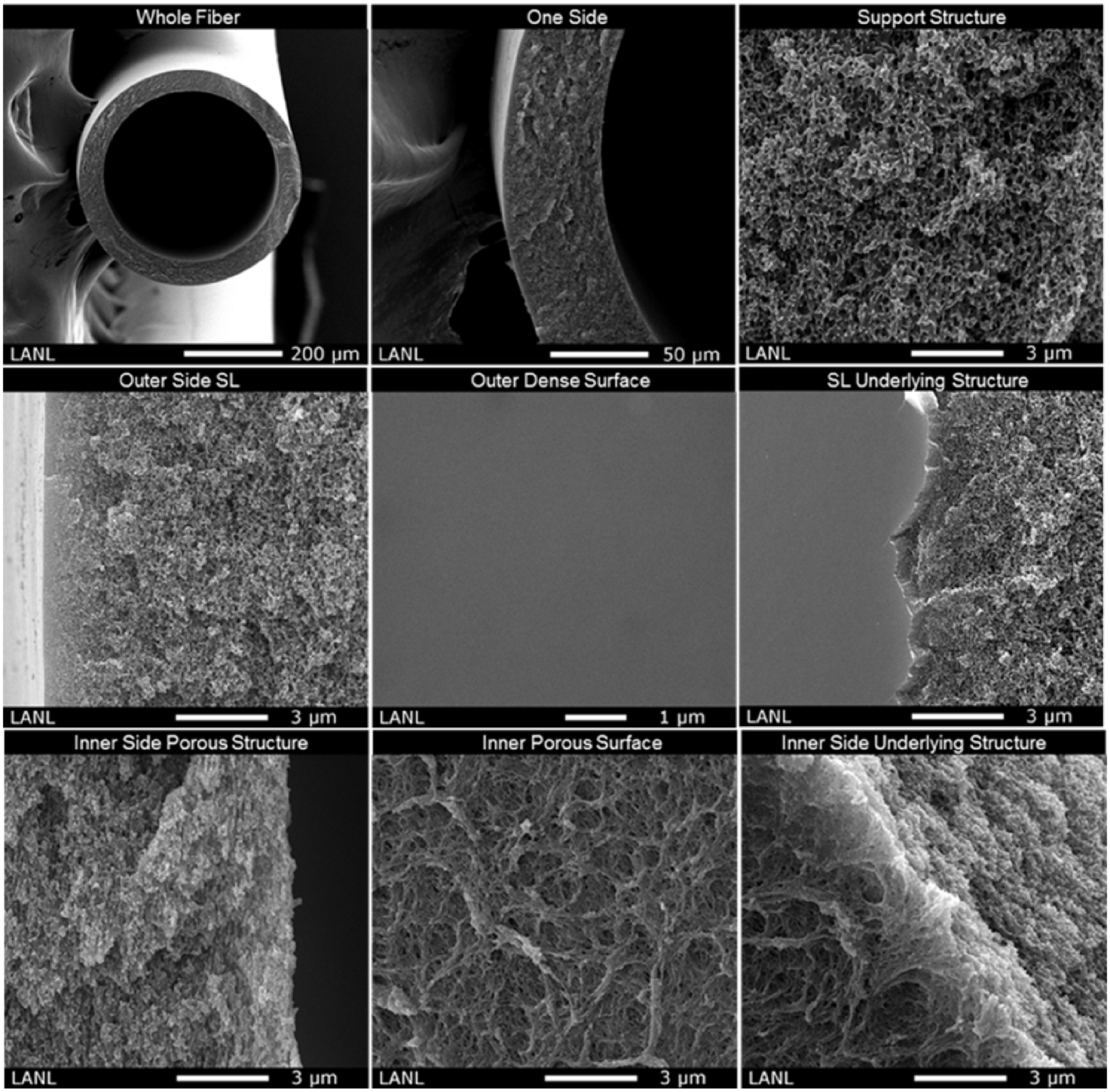

Figure 3: The state-of-the-art PBI HFM having ideal morphology: thin (ca. 160 nm) selective layer, macrovoid free, porous inner surface and fiber wall, and fabricated in an environmentally benign external coagulant (water).

TABLE 1: MEMBRANE PROCESS PARAMETERS

Materials Properties	Units	Current R&D Value		Target R&D Value
Materials of Fabrication for Selective Layer	—	m-PBI, high T_g polymer		
Materials of Fabrication for Support Layer	—	metallic composite	high T_g polymer	high T_g polymer
Nominal Thickness of Selective Layer	µm	0.6	0.2–0.5	0.1–0.5
Membrane Geometry	—	tubular	hollow fiber	hollow fiber
Max Trans-Membrane Pressure	bar	30[1]	12.5[1]	30
Hours Tested without Significant Degradation	—	8,400 (at 250 °C)[2]	3,000 (at ≥250 °C)[2]	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	>100	≤15	15
Membrane Performance				
Temperature	°C	250	150–350	150–350
H_2 Pressure Normalized Flux	GPU or equivalent	170	200–275	250
H_2/H_2O Selectivity	—	≈1	≈0.3	
H_2/CO_2 Selectivity	—	42	25	25–40
H_2/H_2S Selectivity	—	>1,800	>1,800	>1,800
Sulfur Tolerance	ppm	10,000[3]	10,000[3]	1,000
Type of Measurement	—	mixed and pure	mixed[4] and pure	mixed
Proposed Module Design			*(for equipment developers)*	
Flow Arrangement	—	counter	counter/complex	
Packing Density	m^2/m^3	250	2,000–15,000	
Shell-Side Fluid	—	feed/retentate		
Syngas Flowrate	kg/hr	210-240		
CO_2 Recovery, Purity, and Pressure	%/%/bar	75-90%[6], HPD[5,6], 50 bar[6]		
H_2 Recovery, Purity, and Pressure	%/%/bar	80-99%[6,7], HPD[5,7], 20 bar[7]		

[1] Max TMP tested, not max achievable TMP.

[2] No degradation observed during testing.

[3] Max sulfur content tested with current generation HFMs was 100 ppm, not a measure of sulfur tolerance. Materials testing in other platforms indicates a tolerance to ≥10,000 ppm

[4] Typical Mixed gas conditions: simulated syngas 50.3% H_2, 19.2% H_2O, 29.4% CO_2, 1.1% CO with 0, 20, & 100 ppm H_2S.

[5] Highly process dependent (HPD).

[6] Gasifier, coal feedstock, upstream unit operation (e.g., water gas shift [WGS]), and downstream unit operation (e.g., CO_2 purification) specifications dependent.

[7] Tailored to match the turbine inlet specifications (e.g., 125 LHV Btu/ft^3 and 20 bar permeate).

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas permeation unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm mercury (Hg). For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Other Parameter Descriptions:

Membrane Permeation Mechanism – Solution diffusion where at the proposed elevated separation temperatures, permeability is dominated by gas diffusivity in the selective layer.

Contaminant Resistance – Excellent resistance to syngas contaminants.

Syngas Pretreatment Requirements – Particulate removal.

Waste Streams Generated – Particulate removal.

Process Design Concept – Multiple location possibilities largely influenced by gasifier type (syngas pressure and quality), the employed WGS technology, and the presence or lack thereof of a warm temperature gas cleanup for sulfur removal prior to the capture step. For performance benchmark purposes, the membrane separation is conducted post-low temperature (250 °C) WGS. Nitrogen from the air separation unit (ASU) is used as a membrane sweep gas, with the sweep flows specified based on the turbine inlet heating value specification. Initial evaluations have utilized GE F-class turbine specifications and GE (Texaco) gasifier-radiant operation.

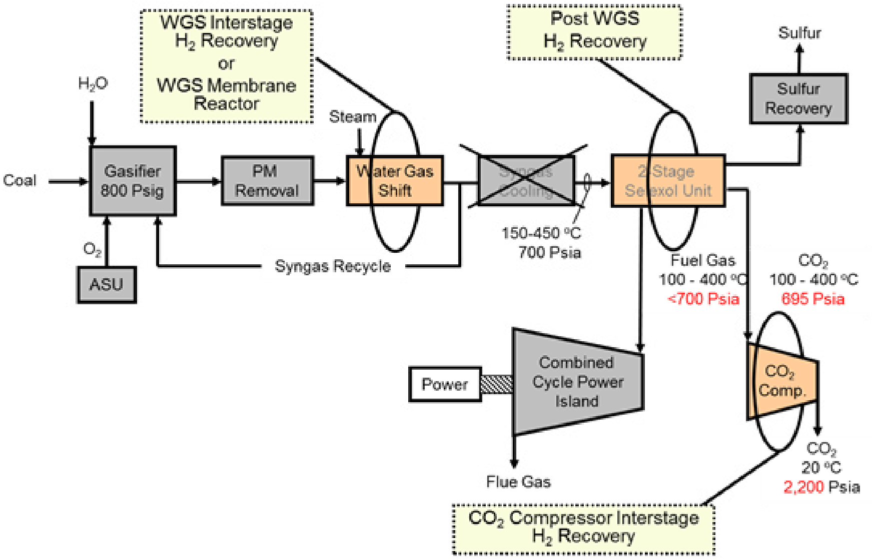

Figure 4: Proposed design concept identifying multiple location opportunities for PBI membrane separation technology integration

Proposed Module Integration – Hollow fiber module design comprised of high-pressure, high-temperature housings and components. The syngas will be processed at process temperature and pressure (see conditions and composition below). The conditions of the primary separation position will be matched to those at the exit of the low-temperature WGS reactor. The pressure drop utilized will be tailored based on the turbine inlet pressure. This process favors conditions created by gasifiers that operate at higher pressure.

technology advantages

- Broad accessible membrane operating temperature range (150–350 °C) facilitating increased opportunity for process integration/optimization.
- Demonstrated long-term hydrothermal stability, sulfur tolerance, and overall durability of selective layer materials.
- Membrane-based technology competitive advantages: modularity, low-maintenance operations, small footprint, low/no waste process, and flexible design opportunities.
- CO_2 produced at higher pressure enables reduced compression costs.

R&D challenges

- Design, control, prediction, and synthesis of tailored material morphologies in hollow fiber format.
- Realizing high-permeance, defect-free gas separation viable hollow fibers.
- Realizing sealing materials and methods compatible with the target material and process thermal, chemical, and mechanical characteristics/environments.

status

At the project's end, production of mechanically robust PBI hollow fibers suitable for industrial use was attained, taking advantage of a novel continuous spinning process, defect sealing layer material and deposition method, and environmentally benign coagulation solvent and modified commercial dope to ensure macro-void free fiber fabrication. A novel potting material for multi-fiber module fabrication with promising properties to withstand typical syngas operating conditions and chemical environments was developed. In fiber testing, long-term stable performance in simulated syngas containing H_2S, steam and CO at elevated temperatures (250–350 °C) of syngas was demonstrated.

Challenges remaining for successful industrial deployment include (1) further development and demonstration of potting material for multi-fiber modules (current industrial materials lack hydrothermal stability, material developed in this work requires further development and demonstration), and (2) further improvement in H_2/CO_2 selectivity is needed to meet carbon capture targets without relying on supplemental downstream processing/purification.

available reports/technical papers/presentations

Berchtold, K. A. and Singh, R. P., "*Polymer-Based Carbon Dioxide Capture Membrane Systems*," Final Technical Report DOE/NETL FWP-FE-308-13, 2017.

"*High Temperature Polymer-Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Rajinder P. Singh & Kathryn A. Berchtold, NETL Final Project Review Meeting, January 2017.

"*High-Temperature Polymer Based CO_2 Capture Membrane Systems for Pre-Combustion CO_2 Capture*," presented by Rajinder Singh, Los Alamos National Laboratory, 2016 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2016.

Berchtold, K. A., Dudeck, K. W., Singh, R. P., and Dahe, G. J., "Polybenzimidazole hollow fiber membranes and method for making an asymmetric hollow fiber membrane," US 15/190,011, 2016

Radcliffe, A. J., Singh, R. P., Berchtold, K. A., and Lima, F., "Modeling and Optimization of High-Performance Polymer Membrane Reactor Systems for Water–Gas Shift Reaction Applications," Processes, 4 (2016) 8.

"*High-Temperature Polymer Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Kathryn A. Berchtold, Los Alamos National Laboratory, 2015 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, June 2015.

Singh, R. P and Berchtold, K. A., "H_2 Selective Membranes for Pre-combustion Carbon Capture," in: F.S. Morreale (Ed.) Novel Materials for Carbon Dioxide Mitigation Technology, Elsevier, Amsterdam, 2015, pp. 177-206.

"*High-Temperature Polymer Based Membrane Systems for Pre-Combustion Carbon Dioxide Capture*," presented by Kathryn A. Berchtold, Los Alamos National Laboratory, 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014.

Singh, R. P., Dahe, G. J., Dudeck, K. W., Welch, C. F., and Berchtold, K. A., "High Temperature Polybenzimidazole Hollow Fiber Membranes for Hydrogen Separation and Carbon Dioxide Capture from Synthesis Gas," *Energy Procedia* **63** (2014) 153-9.

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Stauffer, P.; Keating, G.; Middleton, R.; Viswanathan, H.; Berchtold, K.A.; Singh, R.P.; Pawar, R.; and Mancino, A., "Greening Coal: Breakthroughs and Challenges in Carbon Capture and Storage," *Environmental Science & Technology* **45** (2011) 8597-604.

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O'Brien, K.C.; Krishnan, G.; Berchtold, K.A.; and Figueroa, J.D., et al., "Toward a Pilot-Scale Membrane System for Pre-Combustion CO_2 Separation," *Energy Procedia* **1** (2009) 287-94.

PRE-COMBUSTION CARBON DIOXIDE CAPTURE BY A NEW DUAL-PHASE CERAMIC-CARBONATE MEMBRANE REACTOR

primary project goals

Arizona State University is developing a dual-phase, membrane-based separation device that will separate carbon dioxide (CO_2) from typical water-gas shift (WGS) mixture feeds and produce hydrogen (H_2), which can be introduced into the combustion turbines of integrated gasification combined cycle (IGCC) plants.

technical goals

- Synthesize chemically and thermally stable dual-phase, ceramic-carbonate membranes with CO_2 selectivity (with respect to [H_2], carbon monoxide [CO], or water [H_2O]) larger than 500 and CO_2 permeance larger than 5×10^{-7}mol/m^2/s/Pa.
- Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications.
- Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93 percent purity and the CO_2 stream with at least 95 percent purity.

technical content

A membrane separation device consisting of a porous metal phase and a molten carbonate phase can conduct carbonate ions (CO_3^{2-}) at a high rate. The metal-carbonate membranes only conduct electrons implying oxygen (O_2) should be mixed with CO_2 in the feed in order to convert CO_2 to $CO_3^{=}$ ions. However, the presence of O_2 can also oxidize the metallic support and reduce its electronic conductivity, and thus CO_2 permeability. The problem is addressed by the proposed dual-phase, ceramic-carbonate membrane configuration consisting of a porous ionic conducting ceramic phase and a molten carbonate phase.

At the upstream surface, CO_2 reacts with oxygen ions supplied from the ceramic phase to form $CO_3^{=}$, which transports through the molten carbonate phase towards the downstream surface of the membrane. On the downstream surface, the reverse surface reaction takes place, converting $CO_3^{=}$ to CO_2, with $O^{=}$ released and transported back through the ceramic phase towards the upstream surface of the membrane. The net effect is permeation of neutral CO_2 through the membrane driven by the CO_2 pressure gradient. The dual-phase membrane will be made of continuous thin mesoporous oxygen ionic-conducting ceramic layer filled with a molten carbonate, supported on porous stainless steel or other metal, with an intermediate layer of sub-micron, pore-sized oxygen ionic conducting material.

technology maturity:

Lab-Scale Using Simulated Syngas

project focus:

Dual-Phase Ceramic-Carbonate Membrane Reactor

participant:

Arizona State University

project number:

FE0000470

NETL project manager:

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principal investigator:

Jerry Y.S. Lin
Arizona State University
jerry.lin@asu.edu

partners:

None

performance period:

10/1/09 – 9/30/14

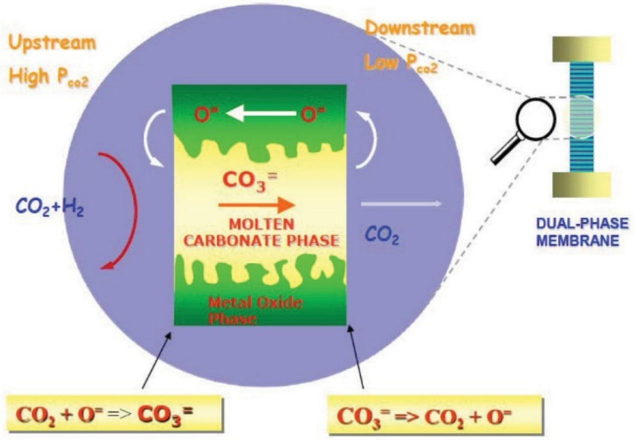

Figure 1: Concept of Dual-Phase Membrane

Development of this dual-phase membrane will be divided in to two phases. Phase I work will include identifying optimum conditions for synthesis of adequate membrane supports and the dual-phase membranes in disk geometry and studying gas permeation properties of the membranes. The second part of the Phase I work will be focused on fabrication of the dual-phase membranes in tubular geometries and the study of permeation, chemical, and mechanical stability of the tubular membranes relevant to their uses in membrane reactors for WGS reaction.

Phase II work will be directed towards studying the dual-phase membrane reactor performance for WGS reaction for hydrogen production and CO_2 capture. The work includes synthesis and kinetic study of a high-temperature WGS catalyst and experimental and modeling study of WGS reaction on the dual-phase membrane reactors. The experimental data will be compared with modeling results to identify optimum operating conditions for WGS reaction. The project will perform an economic analysis using the dual-phase membrane as a WGS reactor for hydrogen production and CO_2 capture for an IGGC plant.

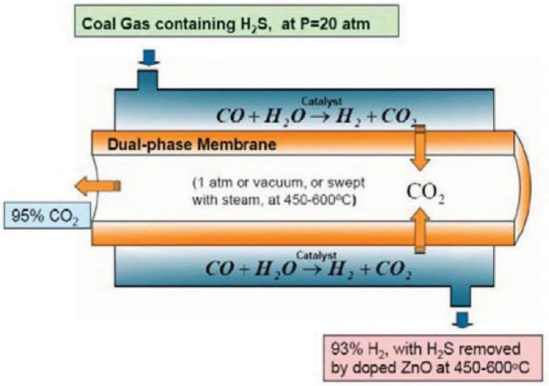

Figure 2: Proposed Membrane Reactor for WGS Reaction

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	Li_2/K_2CO_3	doped Li_2/K_2CO_3
Materials of Fabrication for Support Layer	—	porous stainless steel	fast-ionic conductors (doped ZrO_2, CeO_2)
Nominal Thickness of Selective Layer	µm	2,000	10-200
Membrane Geometry	—	disk	tube
Max Trans-Membrane Pressure	bar	2	>6
Hours Tested Without Significant Degradation	—	N/A	>700
Manufacturing Cost for Membrane Material	$/m^2	/	500
Membrane Performance			
Temperature	°C	700–900	700–900
CO_2 Pressure Normalized Flux	GPU or equivalent	600	>1,000
CO_2/H_2O Selectivity	—	300	>500
CO_2/H_2 Selectivity	—	300	>500
CO_2/SO_2 Selectivity	—	—	>500
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	flat disk	Tube – counter-flow
Packing Density	m^2/m^3	10	>60
Shell-Side Fluid	—		steam
Syngas Flowrate	L(STP)/min (per tube)	>0.2	
CO_2 Recovery, Purity, and Pressure	%/%/bar	90%/99.5%/1 atm	
H_2 Recovery, Purity, and Pressure	%/%/bar	99.9%/93%/>6 atm	
Pressure Drops Shell/Tube Side	bar	>6	

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Carbon dioxide permeates through by combined transport of carbonate ions in the molten carbonate phase and oxygen ions in the solid metal-oxide phase.

Contaminant Resistance – The membrane to be stable in 0.1–1 percent atmosphere containing hydrogen sulfide (H_2S).

Proposed Module Design – Shell-tube module.

technology advantages

- WGS reaction at one temperature (above 400 °C).
- Separation of CO_2 and H_2 mixture in one step.
- Production of high-pressure hydrogen stream.

R&D challenges

- Failure to obtain sufficiently high CO_2 permeance due to a rate-limiting surface reaction.
- Undesired surface properties of ceramic supports resulting in instability of the carbonate in the support pores.

results to date/accomplishments

- Synthesis of dual-phase membrane disks.
- Tubular membranes were prepared via pressing technique using graphite powders.
- Fabrication techniques of pressing-sintering and centrifugal casting were successfully modified to optimize support micro-structure.
- Thin, dual-phase membranes on porous support of disk and tubular geometries were successfully fabricated.
- High CO_2 selectivity and good CO_2 permeance through the membranes were demonstrated.
- Separation and permeation properties of dual-phase membranes under syngas conditions was modeled and analyzed. CO_2 permeation mechanism and factors affecting CO_2 permeation of the dual-phase membranes have been identified.
- WGS reaction in the dual-phase membrane reactor was studied. Conditions to produce hydrogen of 93 percent purity and CO_2 stream of >95 percent purity, with 90 percent CO_2 capture were identified.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

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Lu, B.; and Lin, Y.S., "Sol-Gel Synthesis and Characterization of Mesoporous Yttria Stabilized Zirconia Membranes with Graded Pore Structure," *J. Materials Sci*., 46, 7056-7066 (2011).

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Dong, X.; Ortiz-Landeros, J.; Lin, Y.S., "An asymmetric tubular ceramic-carbonate dual phase membrane for high temperature CO_2 separation", *Chem. Commun*, 49, 9654-9656 (2013)

Ortiz-Landeros, J., Norton, T.; Lin, Y.S., "Effects of support pore structure on carbon dioxide permeation of ceramic-carbonate dual-phase membranes", *Chem. Eng. Sci*., 104, 891-898 (2013)

Norton, T.T., Ortiz-Landeros, J., Lin, Y.S., "Stability of La-Sr-Co-Fe oxide-carbonate dual-phase membranes for carbon dioxide separation at high temperatures", *Ind. Eng. Chem. Res.,* 53, 2432-2440 (2014)

Norton, T.T.; Lu, B.; Lin, Y.S., "Carbon dioxide permeation properties and stability of samarium-doped-ceria carbonate dual-phase membranes", *J. Membr, Sci*., 467, 244-252(2014)

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DESIGNING AND VALIDATING TERNARY PD-ALLOYS FOR OPTIMUM SULFUR/CARBON RESISTANCE

primary project goals

Pall Corporation is developing an economically viable hydrogen (H_2)/carbon dioxide (CO_2) separation membrane system that would allow efficient capture of CO_2 at high temperature and pressure from gasified coal in the presence of typical contaminants using a ternary palladium (Pd)-alloy. Membranes were fabricated and tested in simulated coal gasification conditions. The final objective is a membrane with high hydrogen flux and excellent resistance to syngas contaminants.

technical goals

- Create an advanced Pd-alloy for optimum H_2 separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability under long-term testing of a pilot membrane in laboratory-scale.
- Understand long-term effects of the coal gasifier environment on the metallurgy of the membrane components by comparing controlled diffusion studies with in-service membranes.

technical content

The project developed an advanced Pd-alloy for optimum H_2 separation performance to demonstrate long-term durability under coal synthesis gas (syngas) conditions. Ternary Pd-alloys with potential for favorable performance were selected based on a literature search. This large set of ternary Pd-alloys underwent combinatorial alloy spreads on thin film support disks. These disks were tested in a syngas environment using in situ Raman spectroscopy to measure H_2 separation factor and permeability, as well as characterize sulfur and carbon resistance of best candidate alloys. These alloys were compared to baseline tests of traditional Pd-gold (Au) alloy membranes.

The best alloys were fabricated into 15-cm^2 tubular membranes and tested. As with the combinatorial disks, the 15-cm^2 active area tubes were exposed to conditions representative of a coal gasifier environment: high temperature and high pressure in the presence of contaminating species. Emphasis was placed on identification and characterization of membrane defects, surface analysis of the regions affected by the contaminants, and assessment of the surface quality of the ceramic substrate

technology maturity:

Laboratory-Scale Using Simulated Syngas

project focus:

Pd-Alloys for Sulfur/Carbon Resistance

participant:

Pall Corporation

project number:

FE0001181

NETL project manager:

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principal investigator:

Scott Hopkins
Pall Corporation
scott_d._hopkins@pall.com

partners:

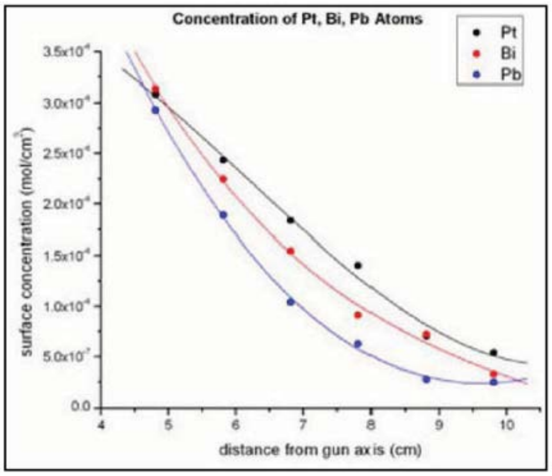
Cornell University,
Georgia Institute of Technology,
Colorado School of Mines,
Southern Company

performance period:

10/1/09 – 9/30/14

Figure 1: A Co-Sputtering Chamber

Scale-up of membranes to75-cm^2 was initially planned but was not conducted. The 15-cm^2 active area tubes were subjected to a 100+ hour continuous testing.



Membrane Figure 2: Graph of Atom Concentration as a Function of Distance from the Gun Axis for Pt, Bi, and Pb Targets

Figure 3: A 75-cm^2

Technical Targets:

- Membrane would be tolerant of up to 20 parts per million (ppm) hydrogen sulfide (H_2S).
- Hydrogen flux of 200 $ft^3/hr/ft^2$ at 400 °C and 20 pounds per square inch (psi) H_2 partial pressure differential.
- Total pressure differential operating capability 400 psi.
- The membrane cost must be in the range of $500/$ft^2$.
- Permeate H_2 purity should be at a level of 99.5 percent.
- The membrane must be resistant to coking with relatively low steam-to-carbon ratio.
- The system should be stable for a minimum of 3 years in service.

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	palladium-gold alloys	palladium alloys
Materials of Fabrication for Support Layer	—	zirconia coated porous stainless steel tubes	zirconia coated porous stainless steel tubes
Nominal Thickness of Selective Layer	µm	3–5 µm	3–7 µm
Membrane Geometry	—	shell and tube	shell and tube
Max Trans-Membrane Pressure	bar	400 psi at 400 °C	400 psi at 400 °C
Hours Tested Without Significant Degradation	—	1,000	5,000
Manufacturing Cost for Membrane Material	$/m^2	1,000	500
Membrane Performance			
Temperature	°C	400	450
H_2 Pressure Normalized Flux	GPU or equivalent	170	200
H_2/H_2O Selectivity	—		
H_2/CO_2 Selectivity	—		
H_2/SO_2 Selectivity	—		
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—	outside – in	
Packing Density	m^2/m^3		
Shell-Side Fluid	—		
Flue Gas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar		

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane’s permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – Palladium-based alloy membranes should tolerate moderate levels of coal gas contaminants after advanced hot syngas cleanup. Primary contaminants include H_2S and carbon monoxide (CO). A typical hot gas cleanup process can bring residual level of sulfur into the range of 0.5–20 parts per million volume (ppmv). After a single-stage water-gas shift (WGS) reactor, CO can be as low as a few percent.

Waste Streams Generated – No waste streams are generated since H_2 is extracted by a Pd-alloy membrane system with primarily CO_2 and water (H_2O) left at high pressure. After steam is condensed, CO_2 is sent for sequestration.

technology advantages

- Researchers use a proprietary process to create ultrathin, economical, Pd-alloy membranes in virtually any alloy system.
- The project applied combinatorial methods to continuous ternary alloy spreads and use a novel characterization method to rapidly scan the alloys after syngas exposure to identify the most resistant compositions.
- A customized composite substrate from Pall was used to deposit ultrathin Pd-alloy membranes. The substrate is porous stainless steel tubes with ceramic coating on the outside surface as a diffusion barrier; thus, membrane elements can be assembled into the module by a conventional welding technique.

R&D challenges

- Hydrogen separation performance may not achieve target performance by membrane design alone. Supplements such as additional gas reforming capabilities may be required either upstream or downstream of the membrane module.
- Scale-up of the Pd-alloy surface area from 15 to 75 cm^2; was planned but will not be conducted under this project.
- Membrane durability during thermal cycling and its effect on stability; the stability of the ceramic coated support has been demonstrated, but not the long-term stability with a Pd-alloy membrane in place.

results to date/accomplishments

- Identified six candidate ternary alloys that had little adsorption of sulfur and carbon after exposure.
- Added Colorado School of Mines as a subcontractor to create six ternary alloys for hydrogen permeance testing and sulfur/carbon exposure testing.
- Made 5 cm^2 membranes for exposure testing.
- Conducted preliminary tests on active area membranes.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Lewis, A., Hopkins, S.; and H. Zhao "Identifying Pd-Based Ternary Membranes for Carbon and Sulfur Applications," 2014 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO₂%20Capture/A-Lewis-Pall-Pd-Based-Ternary-Membranes.pdf*.

Hopkins, S.; and H. Zhao. "High Throughput Design of Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems," presented at 2013 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File%20Library/Events/2013/CO₂%20Capture/H-Zhao-Pall-Ternary-Pd-Alloys.pdf*.

Hopkins, S.; and H. Zhao. "High Throughput Design of Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance in Hydrogen Separation and Carbon Capture Membrane Systems," presented at 2012 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2012.

Hopkins, S. "Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance," presented at 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, August 2011.

Henkel, D., "Combinatorial Design of Pd Ternary Alloys for Sulfur/Carbon Tolerant Hydrogen Separation," presented at 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, September 2010.

HYDROGEN-SELECTIVE EXFOLIATED ZEOLITE MEMBRANES

primary project goals

The University of Minnesota researchers are further developing exfoliated zeolite coating technology for hydrogen (H_2) separation membranes, including membrane production methodology, and determining the feasibility of integration of the membrane into a water-gas shift (WGS) reactor model.

technical goals

- Develop and optimize a membrane production method for the exfoliated zeolite coating.
- The membrane must demonstrate high flux, high selectivity, and stable performance.
- Determine the feasibility of integrating these membranes in WGS reactors and integrated gasification combined cycle (IGCC) flow sheets.
- Perform a techno-economic analysis.

technical content

This project will further develop a novel silica molecular sieve membrane using exfoliated zeolite coatings with the potential to contribute to carbon capture by high-temperature separation of H_2 from carbon dioxide (CO_2) and other gases present in shifted synthesis gas (syngas). The project will establish procedures for the production of the required supply of these layered silicates, first optimizing the synthesis process of the exfoliated zeolite, then the layer-by-layer coating process.

The pore structure of the zeolite that is currently studied (MCM-22) includes ultra-small (potentially H_2-selective) sized pores defined by six SiO_4 tetrahedra (6-Member Ring pores: 6MR) along the c-axis. Therefore, c-out-of-plane oriented films are promising for H_2-separation membranes. MCM-22 has highly anisotropic plate or disk-like crystal shape, thin along the c-crystallographic axis and appropriate for achieving c-oriented films. Among available compositions, an all-silica and potentially hydrothermally stable composition has been reported, which could enable H_2-separations in applications like WGS reactors.

Membrane Microstructures Achieved Currently: MCM-22/silica composite films were fabricated using layer-by-layer deposition towards a nanoscale realization of the selective flake concept. The repetition of appropriate deposition cycles (i.e., particle deposition and subsequent silica coating) led to the gradual increase of separation performance achieving H_2/nitrogen (N_2) ideal selectivity as high as 120. The scanning electron microscope (SEM) cross-section image of a five-layer membrane along with its schematic is shown in Figure 1. The aim of the ongoing work is to improve performance using thinner flakes (exfoliated zeolite layers).

technology maturity:
Bench-Scale, Simulated Syngas

project focus:
Hydrogen-Selective Zeolite Membranes

participant:
University of Minnesota

project number:
FE0001322

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partners:
None

performance period:
10/1/09 – 9/30/14

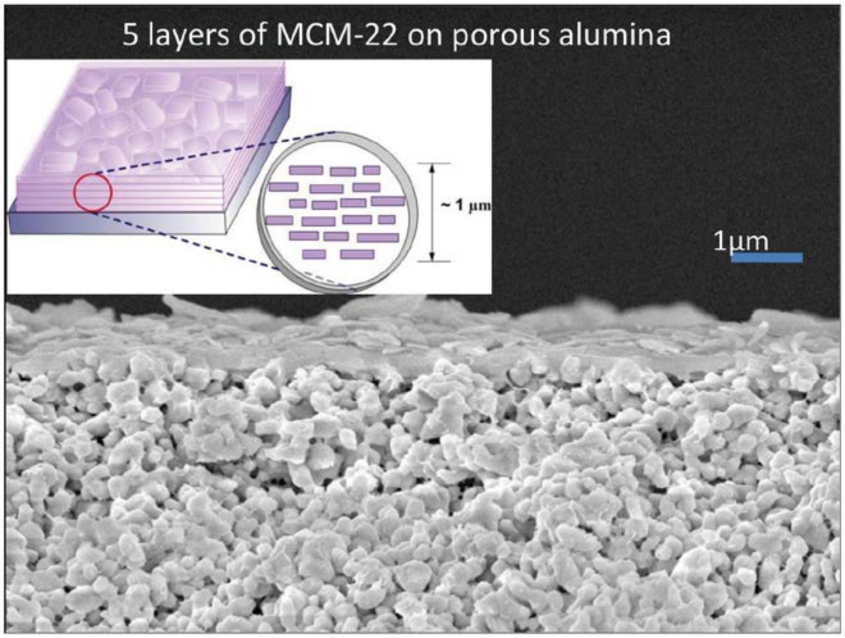

Figure 1: SEM Cross-Section Image of a Five-Layer Membrane Along with Schematic

The H_2 permeance and selectivity to CO_2 and other gases, as well as hydrothermal stability, will be determined for the developed membrane. A series of tests will determine membrane separation performance. Performance testing configurations will include flat alumina supports up to 220 °C; tubular membrane testing using single gases up to 600 °C; tubular membrane testing using simulated feeds up to 600 °C; and high-temperature, high-pressure testing of tubular supports. The membrane stability will be determined in a WGS environment. The three stability test configurations are in steam containing simulated feeds for exfoliated powders; in steam containing simulated feeds for alumina supported films; and in steam containing simulated feeds for stainless steel supported films.

The project will also integrate the membrane into a WGS membrane reactor model, integrate the model in an IGCC flow sheet, and perform techno-economic analysis and operability evaluation and analysis.

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	MCM-22 plate like crystals	exfoliated MCM-22 layers
Materials of Fabrication for Support Layer	—	porous alumina discs (homemade)	porous stainless steel tubes (commercial)
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	—		
Max Trans-Membrane Pressure	bar		
Hours Tested Without Significant Degradation	—	48	250
Manufacturing Cost for Membrane Material	$/m^2		
Membrane Performance			
Temperature	°C	200	500
H_2 Pressure Normalized Flux	GPU or equivalent		
H_2/H_2O Selectivity	—		
H_2/CO_2 Selectivity	—	20	80–800
H_2/H_2S Selectivity	—		
Sulfur Tolerance			
Type of Measurement	—		

Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—		
Packing Density	m^2/m^3		
Shell-Side Fluid	—		
Syngas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar	1–2	10

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – These materials are crystalline silicates and the main issue is stability to steam. Other contaminants are not expected to create problems.

Syngas Pretreatment Requirements – To be determined as project progresses.

Waste Streams Generated – To be determined as project progresses.

technology advantages

This membrane technology will form the selective film using a coating process and premade components, and will have high selectivity, flux, and stability.

R&D challenges

- Dispersible exfoliated layers.
- Simple and efficient coatings process.

results to date/accomplishments

- Synthesis of high aspect ratio exfoliated MCM-22 layers while preserving structure.
- Layer-by-layer coatings of exfoliated MCM-22 layers were fabricated.
- Membranes were tested for separation performance.
- Stability testing was conducted on exfoliated MCM-22 membranes in WGS environment.
- Simulation and optimization studies for IGCC-Membrane Reactor (MR) plant were performed and a techno-economic assessment of IGCC-MR process was completed.

next steps

This project ended on September 30, 2014.

available reports/technical papers/presentations

Tsapatis, M; Daoutidis, P.; Elyassi, B.; Lima, F; Iyer, A.; Agrawal, K.; Sabnis, Sanket, Final Report, “Hydrogen Selective Exfoliated Zeolite Membranes,” *http://www.osti.gov/scitech/biblio/1178537*, Publication date 09/30/2014.

Tsapatsis, M.; Daoutidis, “Hydrogen Selective Exfoliated Zeolite Membranes,” Final Project Presentation. *http://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/pre-combustion/2014-12-12-Final-Presentation-DOE-CO$_2$.pdf*.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. Iyer, A, “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2014 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2014. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO$_2$%20Capture/A-Iyer-UMinnesota-Zeolite-Membranes.pdf*.

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Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. “ Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2012 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, July 2012. *http://www.netl.doe.gov/File%20Library/Events/2012/CO$_2$%20Capture%20Meeting/F-Lima-UMn-Exfoliated-Zeolite-Membranes.pdf*.

Lima, Fernando V.; Daoutidis, Prodromos; Tsapatsis, Michael; et al., “Modeling and Optimization of Membrane Reactors for Carbon Capture in Integrated Gasification Combined Cycle Units,” Industrial & Engineering Chemistry Research, Volume: 51 Issue: 15 Pages: 5480-5489, April 18, 2012. Tsapatsis, Michael, Toward High-Throughput Zeolite Membranes, Science, Volume: 334 Issue: 6057 Pages: 767-768, November 11, 2011.

Varoon, Kumar; Zhang, Xueyi; Elyassi, Bahman; et al., “Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane,” Science, Volume: 333 Issue: 6052 Pages: 72-75, October 7, 2011.

Tsapatsis, M.; Daoutidis, P.; Lima, F.; Elyassi, B. “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, August 2011. *http://www.netl.doe.gov/File%20Library/Events/2011/CO$_2$capture/26Aug11--Lima-UMinn-H$_2$-Selective-Zeolite-Membranes.pdf*.

Tsapatsis, M.; Daoutidis, P., “Hydrogen Selective Exfoliated Zeolite Membranes,” presented at the 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, PA, September 2010. *http://www.netl.doe.gov/File%20Library/Events/2010/CO$_2$capture/Michael- Tsapatsis-FE0001322.pdf*.

Maheshwari, S.; Kumar, S.; Bates, F.S.; Penn, R.L.; Shantz, D.F.; Tsapatsis, M. Journal of the American Chemical Society 130, 1507-1516 (2008), “Layer Structure Preservation during Swelling, Pillaring and Exfoliation of a Zeolite Precursor.”

Choi, J.; Tsapatsis, M. Journal of the American Chemical Society 132(2), 448-449 (2010), “MCM-22/Silica Selective Flake Nanocomposite Membranes for Hydrogen Separations.”

PRESSURE SWING ABSORPTION DEVICE AND PROCESS FOR SEPARATING CO_2 FROM SHIFTED SYNGAS AND ITS CAPTURE FOR SUBSEQUENT STORAGE

primary project goals

The New Jersey Institute of Technology (NJIT) is developing, via laboratory-scale experiments, a pressure swing membrane absorption-based (PSMAB) device using a non-dispersive, membrane-based gas-liquid contactor that produces hydrogen at high pressure for integrated gasification combined cycle (IGCC), as well as a carbon dioxide (CO_2) stream, between 1 and 5 atm, that contains at least 90 percent of the CO_2 from a feed gas at ≈200 °C and 300 pounds per square inch gauge (psig).

technical goals

- Develop, via laboratory experiments, an advanced PSMAB device and a cyclic process to produce helium (He) (a surrogate for hydrogen) at high pressure from low-temperature, post-shift reactor synthesis gas (syngas), as well as a CO_2 stream containing at least 90 percent of the CO_2 and suitable for sequestration.
- Provide data and analysis of the cyclic process and device to facilitate subsequent scaleup.
- Develop a detailed analysis for the process and device to allow economic evaluation for potential larger-scale use.

technical content

In the first phase of research, an experimental setup will be developed for studying the PSMAB process. NJIT will work with Media and Process Technology, Inc., Porogen Inc. and Applied Membrane Technologies (AMT), Inc. to develop microporous hydrophobized ceramic tubule-based, microporous hydrophobized Polyetheretherketone (PEEK) hollow fiber-based and microporous Polytetrafluoroethylene (PTFE) hollow fiber-based absorption devices. The absorption device will be explored on a preliminary basis for performance of PSMAB separation of a moist CO_2-He gas mixture at 150–200 °C and 200–300 psig, simulating a low-temperature, post-shift reactor syngas stream.

technology maturity:

Laboratory-Scale Using Simulated Syngas

project focus:

Pressure Swing Membrane Absorption Device and Process

participant:

New Jersey Institute of Technology

project number:

FE0001323

NETL project manager:

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partners:

Applied Membrane Technologies,
Media and Process Technology,
Porogen,
Techverse

performance period:

10/1/09 – 3/31/13

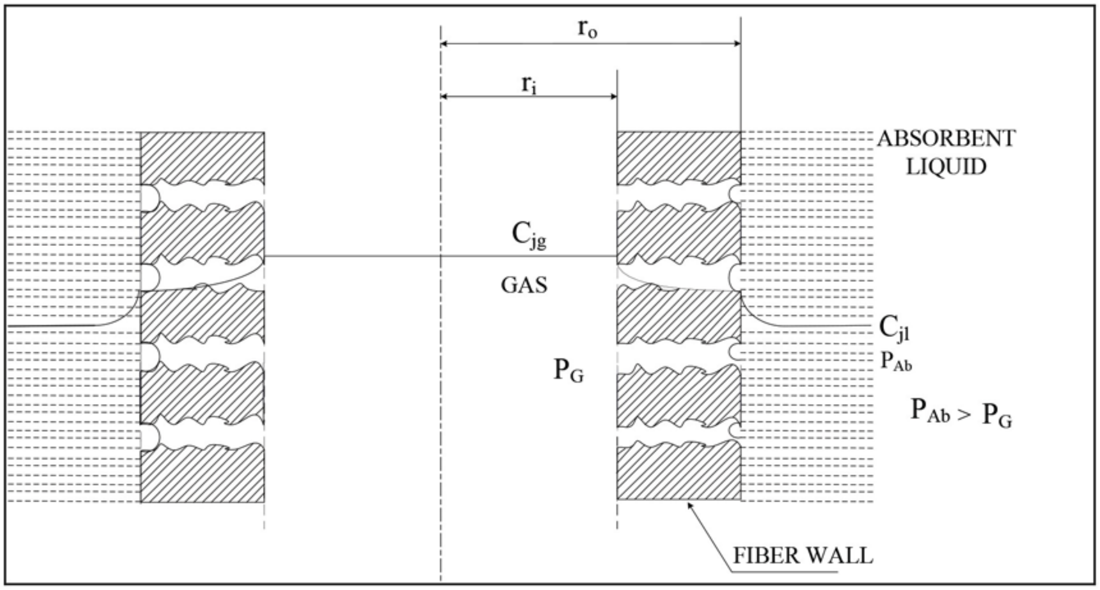

Figure 1: Concentration Profile of Absorbed Species in Gas and Liquid Phases.

In Phase II, NJIT will explore, in detail, the purification and separation performance of the PSMAB process for selected absorbents vis-à-vis purification of the feed gas stream to obtain a high-pressure, purified He stream and a low-pressure, purified CO_2 stream.

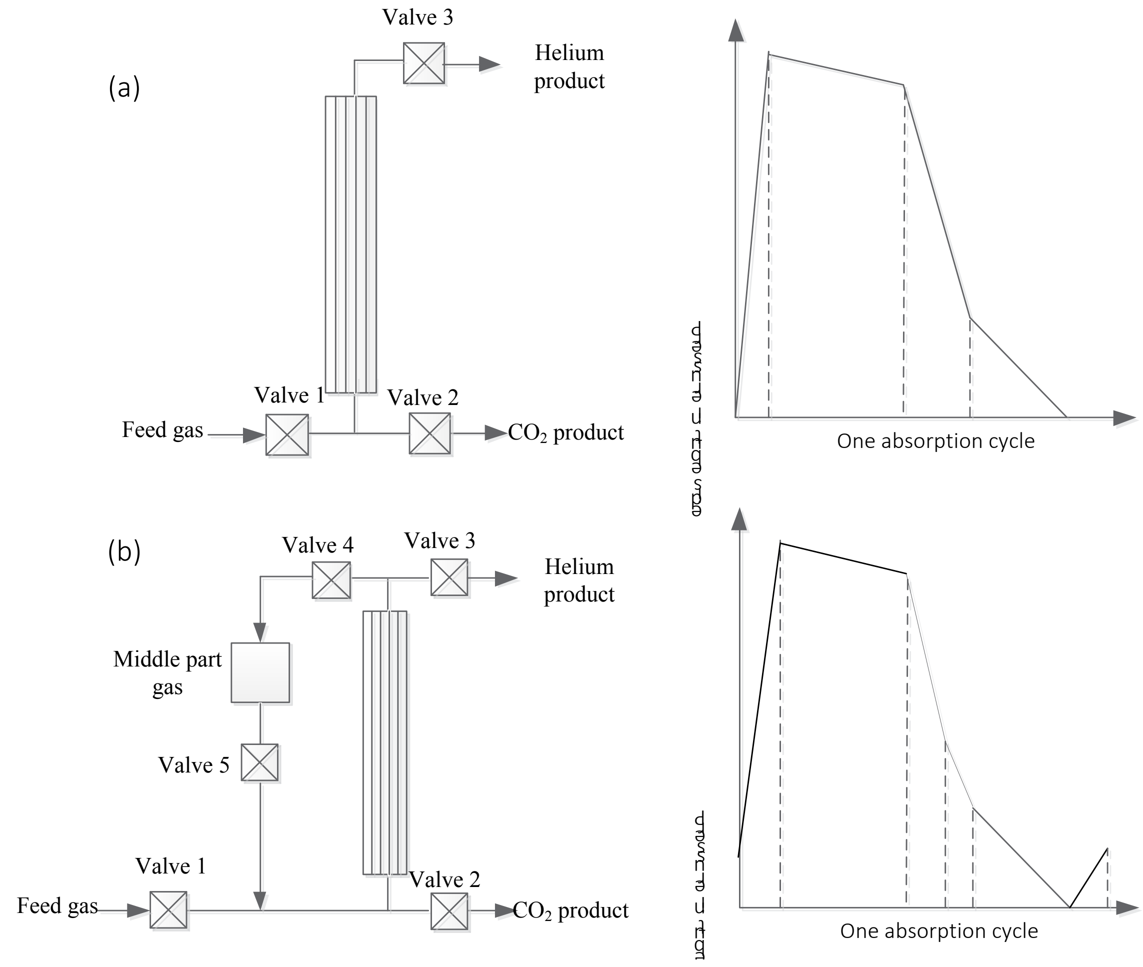

Figure 2: Schematic Diagrams of (a) 3-Valve and (b) 5-Valve Pressure Swing Membrane Absorption Process and the Corresponding Pressure vs. Time Profile in the Bore of the Tubule or Hollow Fiber.

Experimental setups will be developed to measure the solubility and diffusion coefficients of CO_2 and He at the appropriate ranges of temperature and pressure for selected absorbents. Researchers will develop a mathematical model of the PSMAB device and process.

In Phase III, NJIT will generate experimental data on the solubility and diffusion coefficient for CO_2 and He for the selected absorbents. This will allow comparison of the results of simulation of the mathematical model with the observed purification and separation in the PSAB process and device for selected absorbents. Simulations of the model will be performed to explore scale up of the process and facilitate process evaluation. The extent of loss/deterioration of the absorbents over extended periods of operation will be determined.

TABLE 1: LIQUID SORBENT BED PARAMETERS

	Units	Current R&D Value	Target R&D Value
Pure Sorbent			
Molecular Weight	mol^{-1}	205.26	205.26
Normal Boiling Point	°C	N/A	N/A
Normal Freezing Point	°C	-6	-6
Vapor Pressure at 15 °C	bar	None	None
Manufacturing Cost for Sorbent	$/kg	Not available	
Working Solution			
Concentration 20% PAMAM dendrimer Gen 0 in [bmim]	Kg/kg	0.25 (dendrimer/[bmim][DCA])	
Specific Gravity (15 °C/15 °C)	g/cm^3	1.08 at room temp.; 1.06 at 65 °C 1.092 (20 wt% dendrimer-[bmim][DCA] mixture) at room temperature	
Specific Heat Capacity at STP	kJ/kg-K	N/A	N/A
Viscosity at STP	cP	106.7 at room temp	
Absorption			
Pressure	bar	13.8–17	13–20
Temperature	°C	100–125	150–200
Equilibrium CO_2 Loading	mol/mol	0.13	
Heat of Absorption	kJ/mol CO_2		
Solution Viscosity	cP	25.4 at 65 °C	
Desorption			
Pressure	bar	0.9	1.0
Temperature	°C	100–125	150–200
Equilibrium CO_2 Loading	mol/mol	0.019	
Heat of Desorption	kJ/mol CO_2		
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr		
H_2 Recovery, Purity, and Pressure	%/%/bar		
Pressure Drops Shell/Tube Side	bar		

TABLE 2: MEMBRANE-CONTACTOR PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer	—	fluoropolymer	
Materials of Fabrication for Support Layer	—	ceramic, Teflon, PEEK	
Nominal Thickness of Selective Layer	µm		
Membrane Geometry	—	hollow fiber, shell and tube	
Max Trans-Membrane Pressure	bar	20.4 bar	21 bar
Hours Tested Without Significant Degradation	—	100	1,000
Manufacturing Cost for Membrane Material	$\$/m^2$	100	
Type of Measurement	—		
Proposed Module Design		*(for equipment developers)*	
Flow Arrangement	—		
Packing Density	m^2/m^3		ceramic: 900 Teflon: 2,000 PEEK: 5,000
Shell-Side Fluid	—		
Syngas Flowrate	kg/hr		
CO_2 Recovery, Purity, and Pressure	%/%/bar	N/A/85≈90.7/0.2≈1.0	90/95/1.0
H_2 Recovery, Purity, and Pressure	%/%/bar	N/A/93≈95/5.0≈6.0	95/98/6.0–10.0
Pressure Drops Shell/Tube Side	bar	N/A	N/A

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0 °C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0 °C)/cm^2/s with pressures measured in cm Hg.
Note: 1 GPU = 3.3464 × 10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either cocurrent, countercurrent, crossflow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

Other Parameter Descriptions:

Contaminant Resistance – Hydrogen sulfide (H_2S) will not affect the ceramic substrate, nor will it affect the fluoropolymer coating on ceramic and PEEK materials; the Teflon hollow fibers will also remain unaffected. PEEK material is also unlikely to be affected.

Syngas Pretreatment Requirements – Syngas may need to be cooled to 100–125 °C, unless the next round of membrane modules can withstand higher temperature on a continuous basis.

Membrane Replacement Requirements – Device has not been run long enough continuously to define the replacement time. Device will need to run for at least 1,000–3,000 hours.

Waste Streams Generated – Degraded absorption solvent.

Proposed Module Design – Porous hydrophobic hollow-fiber based membrane modules having very limited dead volume at the tube-side headers and tube sheets and connections; the outside diameters of contiguous hollow fibers should not touch each other to allow absorbent in between at the closest distance between adjacent hollow fibers

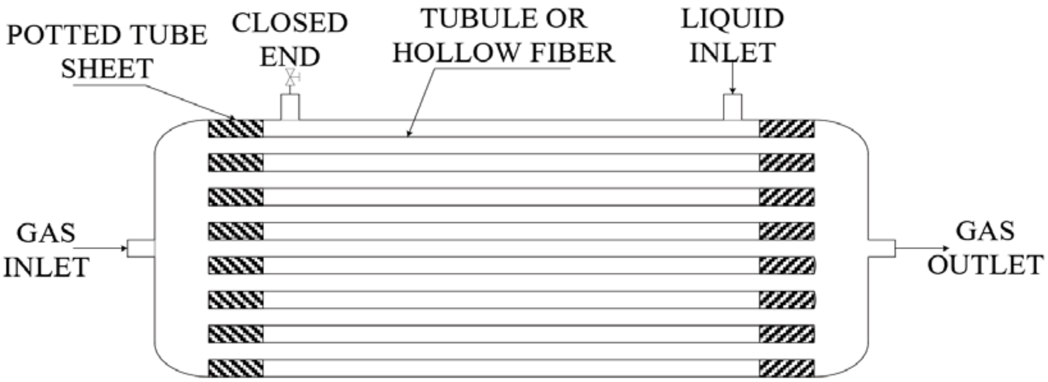

Figure 3: Schematic of Absorber Containing Ceramic Tubules or Hollow Fibers

technology advantages

- High solubility selectivity of novel selected liquid absorbents, high purification ability of the PSA process, and high gas-liquid contacting surface area per unit device volume.
- Compact, membrane-like device.
- Will deliver highly purified hydrogen (H_2) at nearly its partial pressure and temperature in the post-shifted reactor syngas feed.
- Purified CO_2 stream (>90 percent CO_2) will be available at 1 atm.

R&D challenges

- Continuous production of both a higher-purity He stream and a highly purified CO_2 stream requires more modules and altered module configurations. The PEEK hollow-fiber module design has to be changed to achieve higher purification. There is considerable dead volume in the design provided to us resulting in lower CO_2 concentration in the CO_2-rich stream and higher CO_2 concentration in the He-rich stream.
- Absorbent leaks through microporous PTFE hollow fibers that have a plasma polymerized microporous fluorosilicone coating. These fibers did not develop a high-enough pressure capability and need further development.
- The ceramic tubules have considerable pressure capability but have low surface area per unit volume and are therefore not suitable with current tubule dimensions.

results to date/accomplishments

- Successful testing of PEEK membrane in lab at 250 psig and 100 °C with He/CO_2 stream.
- Successful testing of ceramic membrane modules in lab at 300 psig without any leakage; extended operation at 120 °C.
- Scale-up of process and device was conducted, including implementation of improved hollow-fiber module design with regard to inter-fiber spacing and fiber surface area in a given module.
- Absorbent liquid was characterized and degradation determined.
- Polyethylene glycol (PEG) 400 is capable of replacing the ionic liquid as the solvent especially in the presence of the dendrimer.
- The PSMAB process was stable with time; the PEEK membrane modules performed much better than ceramic membrane modules to separate CO_2 since PEEK hollow fibers had much higher gas-liquid contacting area per unit gas volume.
- A mathematical model was developed to describe the pressure swing membrane absorption process.

next steps

This project ended on March 31, 2013.

available reports/technical papers/presentations

Jie, X., Chau, J., Obuskovic G. and Sirkar, K. K., "Preliminary Studies of CO_2 Removal from Precombustion Syngas through Pressure Swing Membrane Absorption Process with Ionic Liquid as Absorbent," I&EC Res., 52, 8783-8799 (2013).

Chau, J., Obuskovic, G., Jie, X., Mulukutla, T. and Sirkar, K. K., "Solubilities of CO_2 and Helium in an Ionic Liquid Containing Poly(amidoamine) Dendrimer Gen 0," I&EC Res., 52, 10484-10494 (2013).

Chau, J., Obuskovic, G., Jie, X. and Sirkar, K.K., "Pressure Swing Membrane Absorption Process for Syngas Separation in a 3-valve System: Modeling vs. Experiments," J. Membrane Sci., 453, 61-70 (2014).

Jie, X., Chau, J., Obuskovic, G. and Sirkar, K.K., "Enhanced Pressure Swing Membrane Absorption Process for CO_2 Removal from Shifted Syngas with Dendrimer-Ionic Liquid Mixture as Absorbent," I&E Chem. Res., 53(8), 3305-3320 (2014).

Sirkar, K; Jie, X; Chau, J; Obuskovic, G.; Final Technical Report, June 2013, "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage." *http://www.osti.gov/scitech/servlets/purl/1097081*.

Sirkar, K.K., "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage," presented at 2012 NETL CO_2 Capture Technology Meeting, July 2012.

Chau, J.; Xingming, J.; Obuskovic, G.; and Sirkar, K.K., "Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage," presented at 2011 NETL CO_2 Capture Technology Meeting, August 2011. *http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/26Aug11-Sirkar-NJIT-PSA-CO₂-from-Syngas.pdf*.

PRE-COMBUSTION CARBON CAPTURE BY A NANOPOROUS, SUPERHYDROPHOBIC MEMBRANE CONTACTOR PROCESS

technology maturity:

Bench-Scale Using Simulated Syngas

project focus:

Nanoporous, Superhydrophobic Membrane Contactor Process

participant:

Gas Technology Institute

project number:

FE0000646

NETL project manager:

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principal investigator:

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partners:

PoroGen Corporation
Aker Process Solutions

performance period:

10/1/09 – 3/31/12

primary project goals

Gas Technologies Institute set out to develop cost-effective separation technology for carbon dioxide (CO_2) capture from synthesis gas (syngas) based on a hollow-fiber membrane contactor.

technical goals

- Design an energy-efficient, CO_2 recovery process that minimizes hydrogen loss.
- Tailor highly chemical-inert and temperature-stable, superhydrophobic, hollow-fiber poly (ether ether ketone) (PEEK) membrane for pre-combustion CO_2 capture.
- Manufacture a low-cost integrated membrane module.

technical content

The membrane contactor is a novel gas separation technology, advanced mass transfer device that operates with a liquid on one side of the membrane and gas on the other. Unlike gas separation membranes where a differential pressure across the membrane provides the driving force for separation, the membrane contactor can operate with pressures that are almost the same on both sides of the membrane. The driving force is the chemical potential of CO_2 absorption into the liquid. This process is thus easily tailored to suit the needs for pre-combustion CO_2 capture.

The hollow-fiber membrane is manufactured from an engineered material, called PEEK by PoroGen Corporation, using a patented process. Some key characteristics that make PEEK attractive for this process are: high heat resistance, high rigidity, high dimensional stability, good strength, excellent chemical resistance, excellent hydrolytic stability, an average pore size of 1 to 50 nm, an average porosity of 40 to 70 percent, and an 800-pound per square inch (psi) water breakthrough pressure.

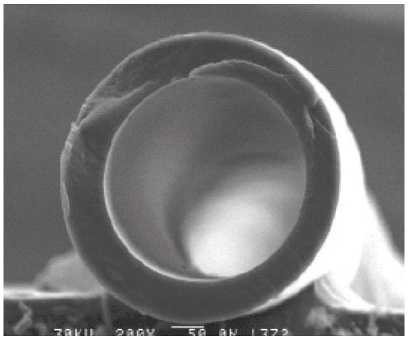
Figure 1: PEEK Hollow Fiber

The PEEK hollow-fiber membrane is nanoporous and can be surface modified to achieve superhydrophobicity; fiber OD can range from 200µm to 1mm; and fibers can be made with thin wall (<25µ) due to the strength of PEEK. The PEEK membrane pore size can be controlled from 1 to 50 nm, and asymmetric membrane structures can be utilized for high performance. The hollow fiber has a high burst pressure of greater than 500 pounds per square inch gauge (psig), and a high collapse pressure of greater than 1,000 psig.

The advanced hollow-fiber module is constructed by computer-controlled helical winding. The modules exhibit favorable flow dynamics with minimal pressure drop, high uniform packing density, and thermodynamically efficient counter-current flow configuration.

The project was divided into two phases. The activities of Phase I included the development of hollow-fiber membranes suitable for the membrane contactor application with improved mass transfer, establishing feasibility of the proposed technology for syngas CO_2 separation, and performing initial process design and economic analysis based on test data.

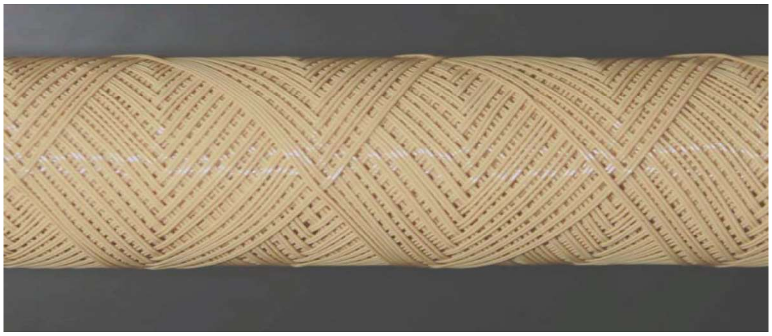

Figure 2: Advanced Hollow-Fiber Module Design

The focus of the Phase II activity was to scale-up the process from lab to bench scale. This included scale-up of the membrane module fabrication process so that membrane modules of the size suitable for large-scale application could be manufactured; bench-scale testing of the membrane contactor process stability and sensitivity to process variations; and refinement of the process economics based on bench-test data.

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Perfluoro-oligomer	Perfluoro-oligomer/Polymer
Materials of Fabrication for Support Layer		PEEK	PEEK
Nominal Thickness of Selective Layer	µm	100	100
Membrane Geometry		Hollow Fiber	Hollow Fiber
Maximum Trans-Membrane Pressure	bar	3.4	Maximize
Hours Tested Without Significant Degradation		120	120
Manufacturing Cost for Membrane Material	$\$/m^2$	Proprietary	Proprietary
Membrane Performance			
Temperature	°C	0 – 50	Maximize
H_2 Pressure Normalized Flux	GPU or equivalent		
CO_2 Removal Rate	$kg/m^2/h$	6	1.5
H_2/H_2O Selectivity	-	$3.7x10^{-6}$	$3.7x10^{-6}$
H_2/CO_2 Selectivity	-	$2.65x10^{-7}$	$2.65x10^{-7}$
H_2/H_2S Selectivity	-	7.5x10-5	7.5x10-5
Sulfur Tolerance	ppm	>100,000	>100,000
Type of Measurement	-	Equilibrium Calculation	Gas Analysis
Proposed Module Design		-	
Flow Arrangement	-	Counter-Current	Counter-Current
Packing Density	m^2/m^3	500 – 1,000	500 – 1,000
Shell-Side Fluid	-	Water, methanol, aMDEA	Water, methanol, Selexol

TABLE 1: GTI MEMBRANE PARAMETERS

	Units	Current R&D Value	Target R&D Value
Membrane Area/Module	m^2	1	100
Syngas Gas Flowrate	L/min	12	1,200
Solvent Flowrate	L/min	1.2	120
CO_2 Recovery, Purity, and Pressure	% / % / bar	90/96/5	90/96/5
H_2 Recovery, Purity, and Pressure	% / % / bar	99/91/50	99/91/50
Pressure Drops Shell/Tube Side	bar	0.4/0.04	0.4/0.04
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{m^2}$	$100	$40

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cm Hg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; projected permeance and selectivities should be for mixture of gases found in pre-conditioned syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (H_2-rich) or retentate (syngas) stream.

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

Contaminant Resistance – Membrane is resistant to all contaminants. Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column.

technology advantages

- Counter-current flow allows for the most efficient mass transfer, thermodynamically.
- Computer-controlled winding provides structured packing to enable enhanced turbulence flow at fiber surface.
- High temperature stability for the desorption step.
- High liquid breakthrough pressure (no liquid wet out), high membrane integrity.
- High membrane productivity.

R&D challenges

- Membrane hydrophobic properties change with solvent contact, causing leakage.
- Mass transfer coefficient of 1.5 kg/m^2hr used in the economic evaluation was not sufficiently high for gas absorption in the membrane contactor.

results to date/accomplishments

- Membrane contactor stability and life testing completed.
- 90 percent CO_2 removal from simulated syngas demonstrated.
- High mass transfer coefficients achieved.
- Commercial size membrane contactor designed.
- Slipstream testing completed.

next steps

- The project ended on March 31, 2012.
- Additional module design and testing required to operate with more viscous solvents.
- Scale-up testing with 8-in diameter modules with coal-derived syngas.

available reports/technical papers/presentations

Meyer, H.; Zhou, J.; Bikson, B.; and Ding, Y., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2011 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, August 2011. *http://www.netl.doe.gov/publications/proceedings/11/co2capture/presentations/5-Friday/26Aug11-Meyer-GTI-Pre-Combustion%20Capture%20by%20Nanoporous%20Membr.pdf*.

Zhou, J.; Meyer, H.; and Bikson, B., "Pre-combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process," presented at the 2010 NETL CO_2 Capture Technology Meeting in Pittsburgh, Pennsylvania, September 2010. *http://www.netl.doe.gov/publications/proceedings/10/co2capture/presentations/friday/Shaojun%20Zhou%20-%20FE0000646.pdf*.

Meyer, H.; Zhou, J.; and Leppin, D., "Advanced H_2S and CO_2 Removal Technologies for Synthesis Gases", presented at the 4th International Freiberg Conference of IGCC and XtL Technologies, Dresden, Germany, May 2010. *http://www.gasification-freiberg.org/PortalData/1/Resources/documents/paper/IFC_2010/14-2-Meyer.pdf*.

Zhou, S.J.; Meyer, H.; Bikson, B.; and Ding, Y., "Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture." AIChE Spring Meeting, San Antonio, Texas, March 2010. *http://www.aiche.org/cei/resources/chemeondemand/conference-presentations/hybrid-membrane-absorption-process-post-combustion-co2-capture*.

NOVEL POLYMER MEMBRANE PROCESS FOR PRE-COMBUSTION CO_2 CAPTURE FROM COAL-FIRED SYNGAS

primary project goals

Membrane Technology & Research, Inc. (MTR) set out to develop a new polymer membrane and membrane separation process to capture carbon dioxide (CO_2) from shifted synthesis gas (syngas) generated by a coal-fired integrated gasification combined cycle (IGCC) power plant.

technical goals

Initial technical goals of this project were as follows:

- Investigate novel, high-temperature-stable polymers for use in hydrogen (H_2)/CO_2-selective membranes.
- Prepare composite polymer membranes and bench-scale modules that have H_2/CO_2 selectivities of 10 or higher and hydrogen permeances of greater than 200 gas permeation units (GPU) at syngas cleanup temperatures of 100 to 200°C.
- Optimize membrane process designs, investigate the sensitivity of different proposed processes to membrane performance, and assess the optimal integration of a membrane system into the syngas cleanup train.
- Conduct bench-scale testing of optimized membranes and membrane modules at MTR laboratories with simulated syngas mixtures to evaluate membrane performance and lifetime under expected operating conditions.
- Prepare a comparative evaluation of the cost of the polymer membrane-based separation process versus current cleanup technologies (Rectisol®, Selexol®, and PSA) and proposed future membrane reactors.

technical content

The objective of this project was the development of novel, H_2-selective polymer membranes for use in pre-combustion CO_2 capture. The first phase of the project was focused on down-selecting promising membrane materials and scaling-up their production. The optimized membranes produced by this effort (designated as Proteus membranes) show excellent H_2/CO_2 separation properties compared to conventional polymeric membranes. For example, hydrogen permeance of up to 800 GPU and H_2/CO_2 selectivity of greater than 12 were achieved using a simulated syngas mixture at 150°C and 50 pounds per square inch gauge (psig). These values are compared to literature data and the original project target (200 GPU for hydrogen permeance and 10 for H_2/CO_2 selectivity) in Figure 1 in the form of a tradeoff plot. These promising membranes were scaled-up and fabricated into lab-scale modules using high-temperature-stable module components identified during the project. Laboratory testing with simulated syngas mixtures confirmed that the modules (with 100 times the area of membrane stamps) performed as expected.

technology maturity:

Bench-Scale Using Actual Syngas

project focus:

Polymer Membrane Process Development

participant:

Membrane Technology & Research, Inc. (MTR)

project number:

FE0001124

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partners:

Southern Company
Tetramer Technologies, LLC

performance period:

9/14/09 – 9/14/11

Following laboratory scale-up, field tests of the optimized membranes and modules using coal-derived syngas were conducted at the National Carbon Capture Center (NCCC) in Wilsonville, Alabama. The main objective of the field tests was to evaluate the long-term stability of membrane or module components at elevated temperatures in the presence of water, sulfur-containing compounds, and heavy hydrocarbons. Figure 2 shows a module housing and one of the bench-scale Proteus membrane modules tested at NCCC. Field results indicate that all membrane and module components were stable in coal-derived syngas (feed pressures: 150 to 175 psig; feed temperatures: 120 to 135°C) for more than 600 hours. The field performance of both Proteus membrane stamps and modules was consistent with the results obtained in the lab, suggesting that the presence of sulfur-containing compounds (up to 780 parts per million [ppm] hydrogen sulfide [H_2S]), water vapor, and heavy hydrocarbons in the syngas feed stream had no adverse effect on performance.

Comparative economic analyses for a number of membrane process designs developed in this project (using H_2-selective membranes, alone or in the combination with CO_2-selective membranes) were also performed. The current field performance for Proteus membranes was used in the design analysis. A possible process design for pre-combustion CO_2 capture is shown in Figure 3. It uses a combination of H_2-selective Proteus membranes and CO_2-selective membranes. The economic study showed this design has the potential to reduce the increase in Levelized Cost of Electricity (LCOE) for 90 percent CO_2 capture to approximately 15 percent if co-sequestration of H_2S is viable, or 20 percent if H_2S must be removed separately. This value is still higher than the U.S. Department of Energy (DOE) target for increase in LCOE (10%); however, compared to the base-case Selexol process that gives a 30 percent increase in LCOE at 90 percent CO_2 capture, the membrane-based process appears promising. Future improvements in membrane performance have potential to lower the increase in LCOE further.

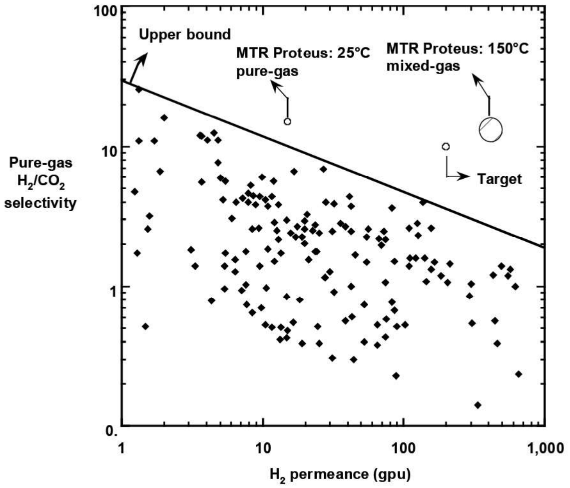


Figure 1: Trade-Off Plot of H_2/CO_2 Selectivity Versus H_2 Permeance

All data points below the upper bound line are for polymeric membranes reported in the membrane literature, and have been translated from pure-gas permeability at 25°C assuming a selective layer thickness of 1 micron. For the mixed-gas measurement, the feed gas is a H_2/CO_2 (50:50 vol%) mixture at 50 psig and 150°C.

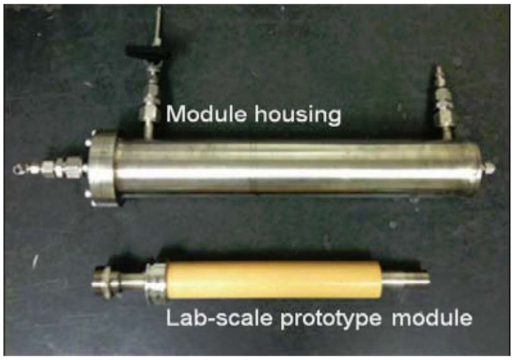
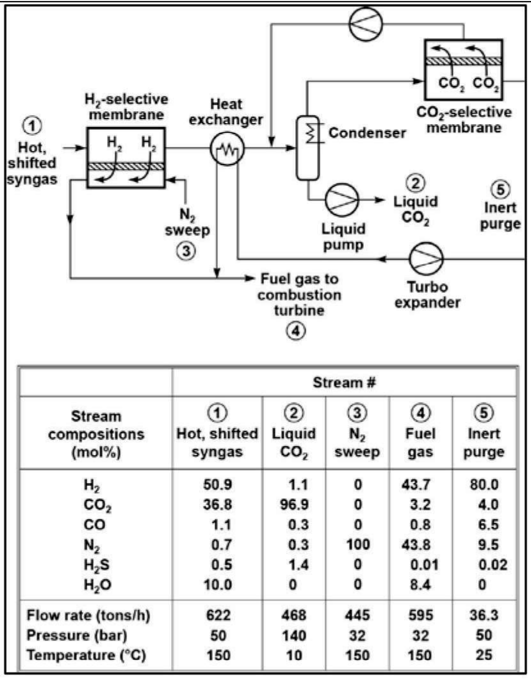


Figure 2: Photos of Module Housing and a Lab-Scale Proteus Membrane Module Tested at NCCC



	Stream #				
Stream compositions (mol%)	① Hot, shifted syngas	② Liquid CO_2	③ N_2 sweep	④ Fuel gas	⑤ Inert purge
H_2	50.9	1.1	0	43.7	80.0
CO_2	36.8	96.9	0	3.2	4.0
CO	1.1	0.3	0	0.8	6.5
N_2	0.7	0.3	100	43.8	9.5
H_2S	0.5	1.4	0	0.01	0.02
H_2O	10.0	0	0	8.4	0
Flow rate (tons/h)	622	468	445	595	36.3
Pressure (bar)	50	140	32	32	50
Temperature (°C)	150	10	150	150	25

Figure 3: Possible Membrane Process for Pre-Combustion CO_2 Capture that Uses Both H_2- and CO_2-Selective Membranes

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Materials Properties			
Materials of Fabrication for Selective Layer		Polymer	Polymer
Materials of Fabrication for Support Layer		Polymer	Polymer
Nominal Thickness of Selective Layer	µm	0.1	N/A
Membrane Geometry		Spiral wound	Spiral wound
Maximum Trans-Membrane Pressure	bar	12	N/A
Hours Tested Without Significant Degradation		600	N/A
Manufacturing Cost for Membrane Material	$\$/m^2$	500	N/A
Membrane Performance			
Temperature	°C	120 – 150	150 – 200
H_2 Pressure Normalized Flux	GPU or equivalent	800	200
H_2/H_2O Selectivity	-	0.3	N/A
H_2/CO_2 Selectivity	-	15	10
H_2/H_2S Selectivity	-	30	N/A
Sulfur Tolerance	ppm	780	N/A
Type of Measurement	-	Mixed-gas	Mixed-gas
Proposed Module Design			
Flow Arrangement	-	Cross-flow	Cross-flow
Packing Density	m^2/m^3	700	700
Shell-Side Fluid	-	N/A	N/A
Syngas Gas Flowrate	kg/hr	4	N/A
CO_2 Recovery, Purity, and Pressure	% / % / bar	90%, 95%, 140 bar	
H_2 Recovery, Purity, and Pressure	% / % / bar	99%, 92%, 30 bar	

TABLE 1: MEMBRANE-BASED CO_2 SEPARATIONS

	Units	Current R&D Value	Target R&D Value
Pressure Drops Shell/Tube Side	bar	N/A	N/A
Estimated Module Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	20	N/A

Definitions:

Membrane Geometry – Flat discs or sheets, hollow fibers, tubes, etc.

Pressure Normalized Flux – For materials that display a linear dependence of flux on partial pressure differential, this is equivalent to the membrane's permeance.

GPU – Gas Permeation Unit, which is equivalent to 10^{-6} cm^3 (1 atm, 0°C)/cm^2/s/cm Hg. For non-linear materials, the dimensional units reported should be based on flux measured in cm^3 (1 atm, 0°C)/cm^2/s with pressures measured in cmHg. Note: 1 GPU = 3.3464×10^{-6} kg mol/m^2-s-kPa [SI units].

Type of Measurement – Either mixed or pure gas measurements; target permeance and selectivities should be for mixture of gases found in shifted syngas.

Flow Arrangement – Typical gas-separation module designs include spiral-wound sheets, hollow-fiber bundles, shell-and-tube, and plate-and-frame, which result in either co-current, counter-current, cross-flow arrangements, or some complex combination of these.

Packing Density – Ratio of the active surface area of the membrane to the volume of the module.

Shell-Side Fluid – Either the permeate (CO_2-rich) or retentate (flue gas) stream.

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

N/A – Not available or not applicable for this project.

Other Parameter Descriptions:

Membrane Permeation Mechanism – Hydrogen-permeable polymeric membranes developed in this project are rigid glassy materials, where permeation occurs by the solution-diffusion mechanism. The mobility selectivity (which favors hydrogen) governs the separation of H_2 and CO_2.

Contaminant Resistance – The greatest concern would be fouling of the membrane surface due to residual particulate matter or heavy hydrocarbons/tars. Preliminary results from tests at NCCC suggest that existing syngas filters upstream of the membranes will be sufficient to protect the membranes from such surface fouling.

Syngas Pretreatment Requirements – As described above, existing syngas filters should be adequate protection for the membranes. Current temperature limitations on the polymeric membranes require the syngas to be cooled to ≈150°C prior to treatment.

Membrane Replacement Requirements – Periodic module replacement is required. The expected lifetime of membrane modules is three to five years.

Waste Streams Generated – The membrane process will not generate any waste streams. Periodic module replacement (expected lifetime of three years) will produce a small amount of solid waste. Typically, for the large membrane applications like sea water desalination by reverse osmosis, these membrane modules are sent to a landfill.

Process Design Concept – A possible process design for pre-combustion CO_2 capture using a combination of hydrogen-permeable Proteus membranes and CO_2-selective membranes is shown in Figure 3. The field performance obtained at NCCC for Proteus membranes was used in the design analysis. Composition and operating conditions for the shifted syngas feed are shown in Table 2.

Proposed Module Design – A spiral-wound membrane module design was used. The hydrogen-enriched stream is produced at lower pressure in the permeate, while the CO_2-enriched stream on the retentate side maintains pressures near those of the syngas feed stream.

TABLE 2: COMPOSITION AND OPERATING CONDITIONS FOR SHIFTED SYNGAS FEED USED IN FIGURE 3 PROCESS DESIGN

Syngas Components	Composition of Shifted Syngas (wet basis, mol %)
H_2	50.9
CO_2	36.8
CO	1.1
N_2	0.7
H_2S	0.5
H_2O	10.0
Shifted Syngas Feed Operating Conditions	
Pressure	50 bar
Temperature	150°C

technology advantages

- Membranes developed in this project are based on polymer materials that show higher hydrogen permeance and higher H_2/CO_2 selectivity than conventional polymer materials. These membranes can be fabricated into robust, stable, and inexpensive modules of the type currently used commercially in the refinery and natural gas industries to separate gas mixtures at high pressures.
- These polymeric membranes are not sensitive to sulfur species in the syngas feed.
- The process design using both H_2- and CO_2-selective membranes will create a high-pressure CO_2 stream capturing greater than 90 percent of CO_2 in post-shift syngas and fuel gas stream containing greater than 99 percent of the syngas hydrogen. This membrane process has the potential to reduce the increase in LCOE for 90 percent CO_2 capture to approximately 15 percent if co-sequestration of H_2S is viable, and 20 percent if H_2S is removed separately.
- Membranes offer the advantages of simple, passive operation; no use of hazardous chemicals and the subsequent waste handling and disposal issues; no steam use; and a small footprint.

R&D challenges

- Polymer materials that are used in the selective layer and the support layer need to be thermally stable at high operating temperatures.
- Membrane modules to be developed for this application have to endure the extended long-term operations at high temperatures (≈150°C). All the module components, including feed and permeate spacers, support papers, and glues, require new development for this application.
- There is little membrane operational experience with real coal-derived syngas.

results to date/accomplishments

- Confirmed that composite membranes made from novel polymers give hydrogen permeances of at least 200 GPU and H_2/CO_2 selectivities of greater than 10 in bench-scale tests as well as in field tests.
- Completed scale-up of composite membranes on a commercial coater. Lab-scale Proteus membrane modules were also developed using scaled-up Proteus membranes and high-temperature-stable module components identified during this project.
- Completed five, 500-hour slipstream tests of membrane stamps and/or bench-scale membrane modules with coal-derived syngas at NCCC. Both membrane stamps and membrane modules show stable performance treating syngas containing up to 780 ppm H_2S. The average membrane field performance (H_2/CO_2 selectivity of 15 to 25; H_2 permeance of 200 to 300 GPU) exceeds project targets.
- Performed an economic analysis of a number of membrane process designs developed in this project (using H_2-selective membranes, alone or in the combination with CO_2-selective membranes). The field performance at NCCC for Proteus membranes was used in the design analysis. The study showed the current best design has the potential to reduce the increase in LCOE for 90 percent CO_2 capture to approximately 15 percent if co-sequestration of H_2S is viable. This value is still higher than the DOE target for increase in LCOE (10%); however, compared to the base-case Selexol process that gives a 30 percent increase in LCOE at 90 percent CO_2 capture, the membrane-based process appears promising.

next steps

- This project ended on September 14, 2011.
- Future activities should include: (1) continued scale-up of Proteus modules to commercial size elements; (2) increasing the maximum operating temperature of the membrane modules to 200°C; and (3) field testing of an integrated membrane process using H_2- and CO_2-selective membranes.

available reports/technical papers/presentations

T. C. Merkel, M. Zhou, and R. W. Baker; "Carbon Dioxide Capture with Membranes at an IGCC Power Plant;" J. Membr. Sci. 389, 441 (2012).

T. C. Merkel, M. Zhou, S. Thomas, H. Lin, A. Serbanescu, and K. Amo, "Novel Polymer Membrane Process For Pre-Combustion CO_2 Capture From Coal-Fired Syngas," presented at 2011 NETL CO_2 Capture Technology Meeting, August 2011.

T.C. Merkel, M. Zhou, S. Thomas, H. Lin, A. Serbanescu, J. Vu, and K. Amo; Novel Polymer Membrane Process for Pre-Combustion CO_2 Capture from Coal-Fired Syngas; Final report submitted to DOE NETL, December 2011.

T. C. Merkel, S. Thomas, M. Zhou, H. Lin, and A. Serbanescu, "Novel Polymer Membrane Process For Pre-Combustion CO_2 Capture From Coal-Fired Syngas," presented at 2010 NETL CO_2 Capture Technology Meeting, September 2010.

M. Zhou, S. Thomas, H. Lin, A. Serbanescu, and T. Merkel, Polymer Membranes For Pre-Combustion CO_2 Capture, 2010 NAMS Annual Meeting & International Conference on Inorganic Membranes.

M. Zhou, S. Thomas, H. Lin, A. Serbanescu, and T. Merkel, Polymer Membranes For Pre-Combustion CO_2 Capture, 2010 AIChE Spring Meeting & 6th Global Congress on Process Safety.

CARBON CAPTURE TECHNOLOGY SHEETS

APPENDIX:
R&D COLLABORATIONS

Advancing CO_2 Capture Technology: Partnership For CO_2 Capture

primary project goals

The University of North Dakota Energy and Environmental Research Center (UNDEERC) conducted pilot-scale testing to evaluate and validate a range of carbon dioxide (CO_2) capture technologies to develop key technical and economic information that can be used to examine the feasibility of capture technologies as a function of fuel type and system configuration.

technical goals

- Integrate a high-efficiency, flexible post-combustion capture system with existing pilot-scale combustion and emission control systems to evaluate the performance of several capture techniques and technologies in flue gas streams derived from selected fossil fuels, biomass, and blends.
- Conduct testing of oxy-combustion for selected fuels and blends in one or more of UNDEERC's existing pilot-scale units.
- Evaluate the performance of emerging CO_2 capture technologies under development and identify key challenges associated with each for both pre-combustion and post combustion platforms
- Perform systems engineering modeling to examine efficient and cost-effective integration of CO_2 capture technologies in existing and new systems.

technical content

UNDEERC constructed two pilot-scale systems and performed experiments on several advanced CO_2 capture technologies and compared them to monoethanolamine (MEA). Flue gas derived from one of two pilot combustors was used as the CO_2 source. The pilot combustors are highly versatile; able to fire virtually any fuel and configurable with all of the primary pollution control devices including electrostatic precipitators, fabric filters, selective catalytic reduction for nitrogen oxide (NO_x) control, and flue gas desulfurization.

Baseline testing was conducted using MEA to gather information to characterize each of the units. The results obtained by using MEA in the CO_2 absorption system were used as a standard by which all other solvents were compared. Data collected included CO_2 removal, CO_2 purity, required regeneration heat, and effects of sulfur oxide (SO_x), NO_x, particulate matter, and trace metals.

Baseline testing of the oxy-combustion system followed similar procedures as the absorption system. The data collected can be used to identify potential challenges concerning this technology. These challenges include effects of mercury (Hg) capture, flame stability, fouling, slagging, and heat-transfer issues.

technology maturity:

Pilot Scale

project focus:

Partnership for CO_2 Capture

participant:

University of North Dakota
Energy and Environmental
Research Center

project number:

FC26-08NT43291

predecessor projects:

N/A

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start date:

05.01.2008

percent complete:

100%

Figure 1: UNDEERC post-combustion CO_2 capture test facility

Carbon dioxide capture technologies were selected and tested. Two flue gas pretreatment technologies were evaluated. The Partnership for CO_2 Capture worked with Cansolv Technologies Inc. to test the operability of a benchmark solvent and an improved formulation for sulfur dioxide (SO_2) removal. The testing indicated that choice of solvent should be made based on both SO_2 removal effectiveness and energy input required for regeneration rather than on solvent operability. The second pretreatment technology tested was a flue gas filtration technology manufactured by Tri-Mer Corporation which combines particulate, NO_X, and SO_2 control. This test showed that their capture was highly dependent on temperature, ammonia injection rate, and amount of sorbent used. The Sorbacal sorbent SPS achieve higher levels of SO_2 removal than their SP sorbent, and the Tri-Mer system effectively removed impurities prior to post-combustion CO_2 capture (though SO_2 levels may need additional trimming).

Two post-combustion solvents were also tested. Korea Carbon Capture and Sequestration R&D Center's (KCRC) Solvent-B showed 90 percent capture with approximately 40 percent lower liquid/gas ratio and 30 percent lower regeneration energy input than MEA at the same capture level. CO_2 Solutions Incorporated proprietary technology uses the enzyme carbonic anhydrase as a catalyst with a salt solution. Testing showed no degradation in performance of the enzyme catalyst, no generation of toxic waste by-products, and showed the ability to use low-grade heat for regeneration, allowing for reduction of cost of CO_2 capture.

Nine membranes for hydrogen/CO_2 separation were provided by Commonwealth Scientific and Industrial Research Organization (CSIRO) for pre-combustion testing using syngas from EERC's fluidized-bed gasifier with warm-gas cleanup. Membrane performance increased with increases in temperature.

A detailed process-modelling effort was undertaken using Aspen Plus software to develop the basis for determining cost of CO_2 capture using advanced post-combustion capture technologies and techniques including the solvents from KCRC and CO_2 Solutions. Also, three power plants were modeled using Carnegie Mellon's Integrated Environment Control model to show the effects that capture would have on net power production, water usage, and revenue requirements for various levels of capture.

Laboratory testing was performed to determine the feasibility of measuring residual amine and nitrosamines potentially emitted in stack flue gases using Fourier transform infrared spectroscopy (FT-IR).

This project placed a strong emphasis on the integration of total systems so that the economic and environmental benefits of carbon capture could be further understood and potentially implemented by utility stakeholders.

Testing of proprietary solvents was conducted on a small industrial 1 tonne/day CO_2 catch and release test system. The system utilized real combustion flue gas generated in a pilot combustor located adjacent to the capture system with typical flue gas conditions given in Table 1. Proprietary membrane testing was conducted utilizing UNDEERC's gasification pilot systems. Table 2 lists the typical conditions of the syngas for membrane testing.

Table 1: Typical Flue Gas Conditions

Flue Gas Flow 250 kg/hr		Composition						
Pressure	Temperature	vol%				ppmv		
psia	°C	CO_2	H_2O	N_2	O_2	CO	SO_x	NO_x
14.7	40	15.6	11.0	80.1	4.2	25	295	200

Table 2: Typical Syngas Conditions

Syngas Flow 2,200 kg/hr		Composition						
Pressure	Temperature	vol%						ppmv
psig	°C	CO	H_2	O_2	N_2	CO_2	CH_4	hydrocarbons	H_2S
309	325	2.63	37.64	0.12	11.96	47.92	2.83	0.04	4,095

technology advantages

UNDEERC has obtained experimental data for a variety of advanced CO_2 capture technologies and oxy-combustion systems. Beyond showing a clear comparison of various approaches, this work has resulted in several improvements to solvents and membranes. Data from this program led directly to an improved sulfur capture solvent being produced by Cansolv Technologies. KCRC took the data obtained to focus their development pathway, focusing on a solvent which displays potential for future performance improvement. CO_2 Solutions Incorporated utilized data generated to further develop their technology to take advantage of waste heat availability which shows potential to reduce capture costs. Finally, CSIRO advanced their early stage development of a membrane that shows great promise for pre-combustion CO_2 capture. These advancements are moving concepts toward application, producing concepts and technologies that reduce the cost of CO_2 capture.

R&D challenges

Retrieving enough information on existing technologies to make appropriate selections for testing and integrating the technologies into total systems.

status

Final report is completed.

available reports/technical papers/presentations

SUBTASK 2.18 – ADVANCING CO_2 CAPTURE TECHNOLOGY: PARTNERSHIP FOR CO_2 CAPTURE (PCO_2C) PHASE III, Final Report, J.P. Kay, at al. March 2016.*https://www.osti.gov/scitech/servlets/purl/1320560*

Kay, J.P.; Jensen, M.D.; Fiala, N.J., "Pilot-Scale Evaluations of Advanced Solvents for Postcombustion CO_2 Capture," Energy Procedia 2014, 63, 1903–1910.

Kay, J.P.; Fiala, N.J., "Comparative Evaluation of Advanced Postcombustion CO_2 Capture Technologies," Paper presented at the 38th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, June 2–6, 2013.

Pavlish, B.M.; Kay, J.P.; Laumb, J.D.; Strege, J.R.; Fiala, N.J.; Stanislowski, J.J.; Snyder, A.C., "Subtask 2.5 – Partnership for CO_2 Capture – Phases I and II", Final Report (September 1, 2010–April 30, 2013) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; EERC Publication 2013-EERC-08-17; Energy & Environmental Research Center: Grand Forks, ND, August 2013.

Hildebrandt, K.; Kay, J.P., "Integration of Postcombustion CO_2 Capture into Existing Coal-Fired Power Plants," Topical Report for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-08NT43291; Energy & Environmental Research Center: Grand Forks, ND, March 2012.

Laumb, J.D.; Stanislowski, J.J.; Kay, J.P.; Pavlish, B.M., "Evaluation of Advanced Solvents and Other Technologies for CO_2 Capture from Fossil Fuel-Fired Systems'" Presented at the 2012 International Pittsburgh Coal Conference, Pittsburgh, PA, October 15–18, 2012.

Pavlish, B.M.; Kay, J.P.; Stanislowski, J.J.; Laumb, J.D., "The Partnership for CO_2 Capture: Final Evaluation Results of Advanced Solvents and Oxy-Fired Combustion Pilot-Scale Testing," Presented at the 36th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, FL, June 5–9, 2011.

Chen, S.G.; Lu, Y.; and Rostam-Abadi, M., "Carbon Dioxide Capture and Transportation Options in the Illinois Basin," Topical Report October 1, 2003–September 30, 2004 for U.S. Department of Energy Contract No. DE-FC26-03NT41994.

Metz, B.; Davidson, O.; Coninik, H.; Loos, M.; and Meyer, L. "IPCC Special Report Carbon Dioxide Capture and Storage Technical Summary," ISBN 92-9169-119-4, September 2005.

Narula, R.; Wen, H.; and Himes, K., "Economics of Greenhouse Gas Reduction – The Power Generating Technology Options," Presented at the World Energy Congress, Buenos Aires, Brazil, October 2001.

FUTURE OF CCS TECHNOLOGY ADOPTION AT EXISTING PC PLANTS

primary project goals

Argonne National Laboratory (ANL) is constructing scenarios that affect carbon capture and storage (CCS) adoption as combinations of cases for the following dimensions: electricity demand, nuclear growth, renewable energy growth, higher or lower gas price factors, and alternative policies.

technical goals

- Extension of ANL's previous work in project FWP49539, "Evaluation of CO_2 Capture/ Utilization/Disposal Options."
- Simulate oxy-combustion and amine-based processes using ASPEN.
- Expand the scenario analyses to focus on the value of coal-based CCS for existing pulverized coal (PC) plants and for other technologies, such as coal-to-liquids with CCS.
- ANL will examine pathways that expedite CCS adoption, such as accelerated research and development (R&D) and carbon dioxide (CO_2) utilization for enhanced oil recovery (EOR).
- ANL will examine opportunities for R&D related to shale gas, such as developing CCS specifically for natural gas combined cycle (NGCC) units.

technical content

In a previous project (FWP49539), ANL conducted engineering assessments and economic evaluations on retrofitting PC boilers with oxy-combustion, and then eventually repowering the site with integrated gasification combined cycle (IGCC). The engineering assessment for oxy-combustion was conducted with the ASPEN process model and the economic evaluations with the AMIGA macroeconomic model. The assessment investigated the entire life cycle of the plant, which included the mining of the coal, coal transportation, coal preparation, power generation, environmental controls, water use, pipeline CO_2 conditioning, and pipeline transport of CO_2 for sequestration.

ANL also conducted ASPEN modeling for 18 different oxy-combustion and air-fired cases. Three different power production ratings (150 MW, 300 MW, and 450 MW) were investigated. The model included a selective catalytic reduction (SCR) system and a flue gas desulfurization (FGD) system for flue gas cleanup.

technology maturity:

Systems Analysis and Macroeconomic Modeling

project focus:

Analysis of CCS Technology Adoption

participant:

Argonne National Laboratory

project number:

FWP49806
continued from
FWP49539

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partners:

None

performance period:

2/1/11 – 3/31/14

The analysis in the current project will demonstrate and, to the extent possible, quantify the role and benefit of R&D related to the utilization and environmental control of fossil fuels. The impacts of R&D will be shown by comparing model results such as deployment rates, emissions reductions, and electricity costs across various scenarios. The scenarios will capture a number of CO_2 control regimes, R&D programs, and economic conditions in order to fully understand the role that R&D plays in each. With widespread deployment of CCS under a CO_2 reduction target, R&D that lowers cost of CO_2 capture and increases efficiency will be shown to have a high economic payoff.

Other topics to be analyzed with the ANL model are as follows: the value of coal-based CCS in high natural gas price scenarios; opportunities and obstacles for R&D, on NGCC with CCS, including cost and performance parameters; the conditions under which CO_2-EOR enables faster deployment of CCS systems; the market opportunity for coal and biomass to liquid fuels and power co-production with CCS; and impacts on PC units, especially those retrofitted with CCS, from cycling due to intermittent grid generation from renewables.

technology advantages

The ANL model is especially designed to analyze the issues and scenarios described above.

R&D challenges

Capturing the impacts and costs of high intermittent renewable generation as it affects dispatchable coal generators, especially those that have adopted CCS.

results to date/accomplishments

- Ran Electricity Supply and Investment Model (ESIM) for high, mid, and low gas supply scenarios to identify retirement of existing PC power plants which do not retrofit with CCS and to identify the retrofit with CCS of other current PC plants.
- Modeled predicted increased CO_2 capture and decreased CO_2 emissions for the scenarios.
- Simulated the benefit of higher utilization (i.e., capacity factor) for PC plants that retrofit CCS because of rising up the loading order (i.e., dispatch order).
- Analyzed the value of coal-based CCS in high natural gas price scenarios.
- Analyzed opportunities and obstacles for R&D, specifically regarding CCS, including cost and performance parameters.
- Analyzed market opportunity for coal and biomass to liquid fuels and power co-production with CCS.
- Analyzed impacts on PC units, especially those retrofitted with CCS, from cycling due to intermittent grid generation from renewables.
- Concluded funding for R&D for CCS, nuclear, and biochemical technologies can help meet CO_2 reduction goals.
- Concluded credits for reducing CO_2 or small price on emitting CO_2 will provide incentive to operate units with CCS at higher utilization than units without capture.
- Concluded electricity prices can be moderated for consumers and businesses if revenue from a modest price on CO_2 is recycled back to help fund investments in advanced generation capacity.

next steps

This project ended on March 31, 2014.

available reports/technical papers/presentations

Hanson, D. and Schmalzer, D, "An Adoption Scenario for Carbon Capture in Pulverized Coal Power Plants in the USA," Greenhouse Gases Science and Technology (3:p.303-308), 2013.

Hanson, D. "Future of CCS Technology Adoption at Existing PC Plants," presented at CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2013. *http://www.netl.doe.gov/File Library/events/2013/CO_2 capture/D-Hanson-ANL-Future-of-CCS.pdf*.

Hanson, D., and Schmalzer, D., "CCS Adoption Under Alternative Market Conditions," presented at U.S. Association for Energy Economics Conference, Austin, TX, November 2012.

Hanson, D., "Economics and Adoption of CO_2 Capture for Existing PC Plants in a Power System Context," Eleventh Annual Conference on Carbon Capture, Utilization & Sequestration, Pittsburgh PA, May 2012.

Hanson, D., "Future of CCS Technology Adoption at Existing PC Plants," presented at CO_2 Capture Technology Meeting, Pittsburgh, PA, July 2012.

Hanson, D.; Marano, J.; and Fout, T., "Economic Analysis of Existing Coal Plant Retrofits with CCS," Energy, Utility, & Environmental Conference, Phoenix AZ, January 2012.

Hanson, D., "A Market Scenario Approach to Managing Existing Power Plant Assets," 13th Annual Electric Power Conference and Exhibition, Rosemont, IL, May 2011.

Hanson, D., and Doctor, R., "Future of CCS Technology Adoption at Existing PC Plants," presented at CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, August 2011.

"ANNUAL REPORT 2009: Evaluation of CO_2 Capture and Sequestration Using Oxyfuels with AMIGA Economic Modeling," November 23, 2009.

Doctor, R.; Hanson, D. A.; and Molburg, J. C., "Evaluation of CO_2 Capture and Sequestration Using Oxyfuels with AMIGA Economic Modeling," presented at 2009 NETL Capture Technology Meeting, March 2009.

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