

APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS
POST-COMBUSTION SOLVENTS

BENCH-SCALE DEVELOPMENT OF A HOT CARBONATE ABSORPTION PROCESS WITH CRYSTALLIZATION-ENABLED HIGH PRESSURE STRIPPING FOR POST-COMBUSTION CO₂ 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 scale-up data to optimize the Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping (Hot-CAP) technology and demonstrate its capability to achieve the DOE goals of at least 90% carbon dioxide (CO₂) removal from coal-fired power plant flue gas with less than a 35% increase in the cost of electricity (COE), and that will help to advance the process to pilot-scale level within three 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 and scale-up, and commercial competitiveness of the Hot-CAP process with Monoethanolamine (MEA)-based processes and other emerging post-combustion CO₂ capture technologies.
- A combination of experimental, modeling, process simulation, and technical and economic analysis studies will be performed.

Technical Content

For this three-year project, UIUC and Energy Commercialization, LLC will investigate a Hot-CAP to overcome the energy use disadvantage of the MEA-based processes. A preliminary technical-economic evaluation shows that the energy use of the Hot-CAP is about 50% less than that of its MEA counterpart, and the process has the potential to meet or exceed DOE's technical and cost goals of $\geq 90\%$ CO₂ removal and $\leq 35\%$ increase in the COE.

The Hot-CAP is an absorption-based, post-combustion CO₂ technology that uses a carbonate salt (K₂CO₃ or Na₂CO₃) as a solvent. The process integrates a high-temperature (70–80 °C) CO₂ absorption column, a slurry-based high-pressure (up to 40 atm) CO₂ stripping column, a crystallization unit to separate bicarbonate and recover the carbonate solvent, and a declaimer to recover CaSO₄ as the byproduct of the sulfur dioxide (SO₂) removal.

Project objectives include performing a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the Hot-CAP technology to pilot-scale demonstration level within three years. The project tasks employ lab- and bench-scale test facilities to measure thermodynamics and reaction engineering data that can help evaluate technical feasibility and cost-effectiveness, performance and scale-up, and commercial competitiveness of the Hot-CAP compared to the MEA-based processes and other emerging post-combustion CO₂ capture technologies.

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Hot Carbonate Absorption Process

Participant:

University of Illinois at Urbana-Champaign

Project Number:

FE0004360

NETL Project Manager:

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Principal Investigator:

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Partners:

Energy Commercialization, LLC

Performance Period:

1/1/11 – 12/31/13

To meet project objectives, lab- and bench-scale tests will be performed by UIUC to measure the kinetics and phase equilibrium data associated with the major reactions and unit operations in the Hot-CAP including CO₂ absorption, bicarbonate crystallization, sulfate recovery, and CO₂ stripping. Energy Commercialization, LLC will use the results from the lab- and bench-scale studies to help create a process flow diagram, perform equipment and process simulations, and conduct a techno-economic study for a conceptual 500-MWe high-sulfur coal-fired power plant retrofitted with the Hot-CAP.

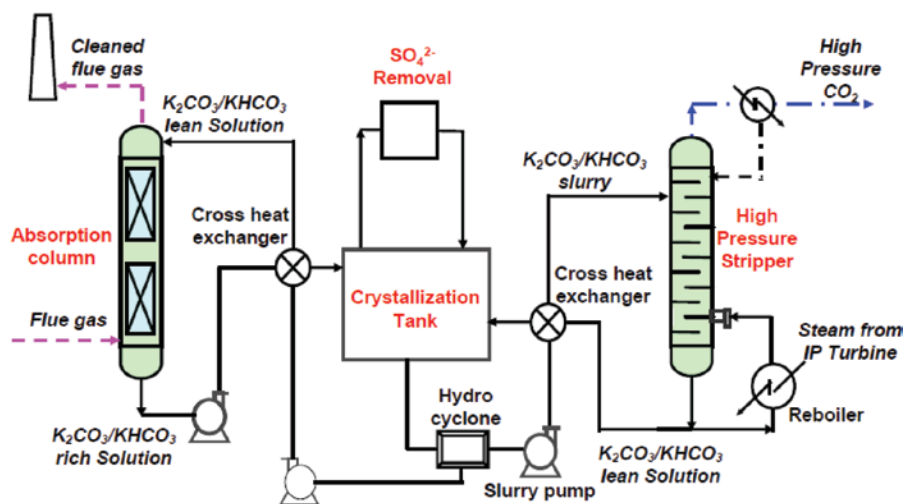


Figure 1: Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP): Process Flow Diagram

Table 1: Process Parameters for Carbonate Salt Solvent

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Carbonate salt (potassium or sodium carbonate)	
	Molecular weight	—	—
	Boiling point (°C)	—	—
	Heat of reaction (kJ/mole CO ₂)	7–17	—
	CO ₂ loading/working capacity, wt%	—	—
	Solvent concentration to stripper (mol/liter)	—	—
	Heat capacity of solution (kJ/K/kg)	—	—
	Viscosity, cP (glycol concentration)	—	—
Operating Conditions	Absorption temperature, °C	70–80	—
	Absorption pressure (CO ₂ partial pressure), atm	—	—
	CO ₂ capture efficiency, %	90	—
	Regeneration method	—	—
	Regeneration temperature, °C	130–200	—
	Regeneration pressure, atm	8–40	—
Heat Integration	Required regeneration steam temperature, °C	—	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	N/A	—
	N ₂ concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	N/A	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

- High stripping pressure which equates to low compression work and low stripping heat (high CO₂/H₂O ratio).
- Low sensible heat results in comparable working capacity to MEA and low C_p (½).
- Low heat of absorption, 7–17 kcal/mol CO₂ (crystallization heat included) versus 21 kcal/mol for MEA.
- Increased absorption rate by employing high concentration PC and high absorption temperature.
- Flue gas desulfurization (FGD) may be eliminated.
- No solvent degradation.
- Low-cost solvent.
- Less corrosiveness.

R&D Challenges

- Identifying favorable process conditions for absorption kinetics in carbonate solution.
- Identifying process conditions and solution properties for achieving the crystallization rate and desirable crystal size for solid separation.
- Identifying process conditions for potassium bicarbonate slurry to achieve stripping pressure ≥10 bar.
- Identifying process conditions for >95% SO₂ removal and continuous reclamation of the sulfate.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the December 2013 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/bench-scale-dev.html>

EVALUATION OF CONCENTRATED PIPERAZINE FOR CO₂ CAPTURE FROM COAL-FIRED FLUE GAS

Primary Project Goals

URS Group (URS) is gaining operational experience with the concentrated piperazine (PZ) solvent in coal-fired flue gas while employing the high-temperature, two-stage flash regeneration design. Results will be used to evaluate the technical and economic feasibility of a full-scale implementation of this process.

Technical Goals

Project objectives are to:

- 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, two-stage flash system.
- Identify and resolve other potential operational and design issues including process control, corrosion, foaming, and solids precipitation.

Technical Content

URS, in collaboration with the University of Texas (UT) and Trimeric Corporation, will investigate the use of concentrated PZ as a solvent for absorbing carbon dioxide (CO₂) from coal-fired power plant flue gas. Evaluations were previously performed on concentrated PZ for CO₂ removal through laboratory investigations, process modeling, and synthetic flue gas testing in a 0.1-megawatt (MW) unit. Results have indicated greater than 90% CO₂ capture with significant progress toward DOE's goal of less than 35% cost of electricity (COE) increase, as well as opportunities for further improvement. This project continues the development of the PZ-based CO₂ absorption process through a series of three field tests to gain operational experience with the solvent in coal-fired flue gas, while employing a novel, high-temperature, two-stage flash regeneration design. The tests will be conducted at Commonwealth Scientific and Industrial Research Organization's (CSIRO) Post-Combustion Capture (PCC) facility, UT's Separations Research Program (SRP) plant, and DOE's National Carbon Capture Center (NCCC). Results will be used to evaluate the technical and economic feasibility of full-scale implementation of the integrated absorber-flash regeneration system.

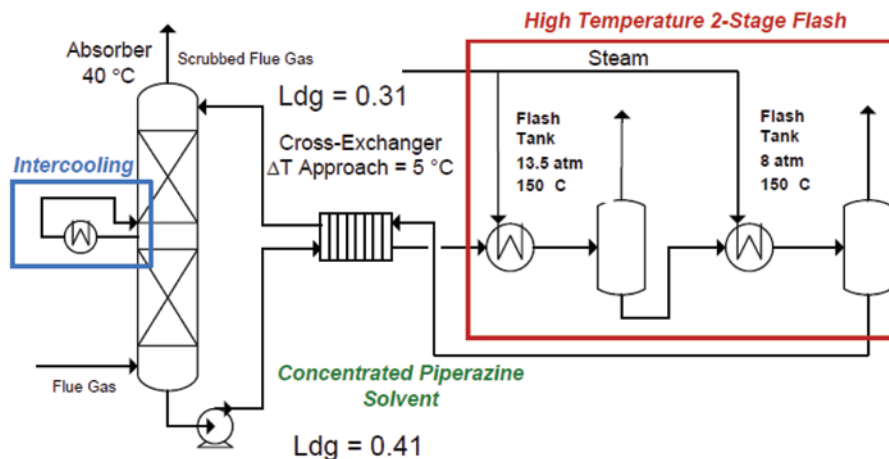


Figure 1: Diagram of Piperazine CO₂ Absorption Process

Technology Maturity:

Laboratory-scale, simulated flue gas and actual flue gas slipstream

Project Focus:

Piperazine Solvent with Flash Regeneration

Participant:

URS Group

Project Number:

FE0005654

NETL Project Manager:

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Principal Investigator:

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Partners:

Trimeric Corporation
 University of Texas at Austin

Performance Period:

9/27/10 – 3/31/14

This 42-month project will consist of a series of three field tests designed for continuous process improvement and scale-up of the PZ-based process. The first program will be a three-month test in coal-fired flue gas using CSIRO's 0.1-MW absorption column installed at a power station, coupled with the project team's 0.1-MW high-temperature, two-stage, flash solvent regeneration system. The second field test will entail refining the regenerator design based on the CSIRO test results in a three-week test in synthetic flue gas at UT's 0.1-MW pilot facility. The third field test will be a three-month test on coal-fired flue gas conducted with the 0.5-MW absorption column at NCCC in conjunction with a 0.5-MW regeneration skid built by the project team. The larger regeneration system design will be based on the operational experiences gained in the two prior testing programs. An engineering feasibility study will be performed on data obtained during the three testing programs to assess the feasibility of using concentrated PZ solvent for post-combustion CO₂ control. This analysis will include estimated capital and operating costs for installing and operating a full-scale system capable of achieving more than 90% CO₂ removal. Additionally, the next steps for research and development will be defined.

Technology Advantages

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

- Greater CO₂ absorption rate, greater working capacity, greater thermal stability, and less oxidative degradation—all of which point toward 10–20% less energy use.
- Lower capital costs.
- 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

- Robustness of concentrated PZ in flue gas must be demonstrated—PZ is more expensive to replace than monoethanolamine (MEA).
- Robustness of process to excursions in CO₂ loading, temperature, and water balance must be demonstrated, which will require quantification of the effect on solids precipitation and plant operation.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the March 2014 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/evaluation-concentrated-piperazine.html>

RECOVERY ACT: SLIPSTREAM DEVELOPMENT AND TESTING OF SIEMENS POSTCAP CAPTURE AND SEPARATION TECHNOLOGY

Primary Project Goals

Siemens Energy is designing, installing, and operating a pilot plant to treat a 2.5-MW flue gas slipstream from an operating coal-fired power plant to demonstrate the aqueous amino acid salt solvent-based, post-combustion carbon dioxide (CO₂) gas capture technology.

Technical Goals

- Demonstrate the ability of Siemens Energy's POSTCAP technology to achieve 90% CO₂ removal while approaching a 35% increase in the cost of electricity (COE).
- Demonstrate the scalability and feasibility of developing the technology to a full-scale, commercial, post-combustion CO₂ capture (550 MW) application for coal-fired power plants and to full-scale commercial application for industrial sources of CO₂ emissions.

Technical Content

Siemens Energy is designing, installing, and operating an advanced CO₂ capture, solvent-based pilot plant. The Siemens POSTCAP CO₂ capture process utilizes an aqueous amino acid salt (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 will be installed at Tampa Electric Company's (TECO) Big Bend Station and will treat a flue gas slipstream equivalent to approximately 2.5 MWe. Although the CO₂ source for this slipstream pilot-scale testing is from a coal-fired power plant flue gas, it will provide an appropriate design and performance baseline for direct scale-up to many industrial applications.

The project encompasses the complete design, engineering, procurement, installation, operation, data analysis, and decommissioning of the CO₂ capture system and will be completed in four phases. In Phase I, the engineering design and permitting for the project will be completed. POSTCAP system mass and energy balances and pilot plant process flow diagrams will be generated, and the host site will be analyzed for integration of the pilot plant. Phase II will 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 will be commissioned and started up, the pilot program test campaigns will be conducted, and the resulting data will be analyzed. Phase IV will cover the pilot plant decommissioning and disassembly.



Figure 1: Siemens Lab Plant for CO₂ Capture Tests at Frankfurt Hoechst Industrial Park

Technology Maturity:

Pilot-scale, actual flue gas slipstream

Project Focus:

Amino Acid Salt

Participant:

Siemens Energy, Inc.

Project Number:

FE0003714

NETL Project Manager:

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Partners:

Siemens AG

Performance Period:

10/1/10 – 10/31/13

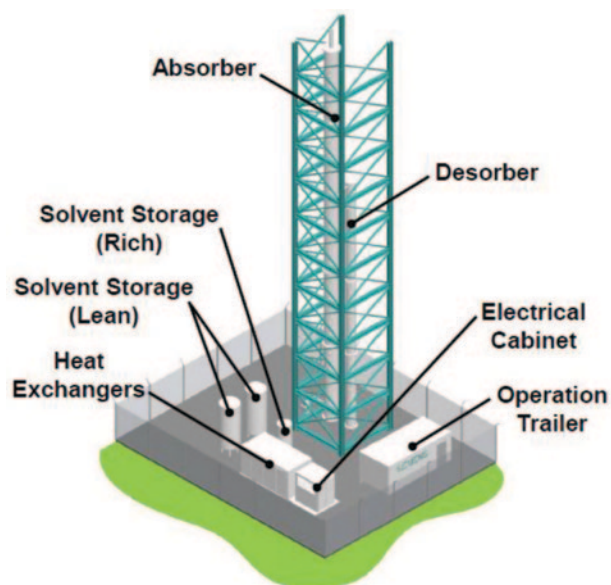


Figure 2: Basic POSTCAP Pilot Layout

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 CO₂ 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

Results from the project are not yet available.

Next Steps

Final test results will not be available until the October 2013 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/self-concentrating-amine.html>

POST-COMBUSTION CO₂ CAPTURE FOR EXISTING PC BOILERS BY SELF-CONCENTRATING AMINE ABSORBENT

Primary Project Goals

In this project, 3H Company is experimentally and analytically confirming the feasibility of the proposed Self-Concentrating Absorbent CO₂ Capture Process, with the goal of developing a sound engineering design, supported by laboratory data and economic justification, for a flue gas slip stream testing unit.

Technical Goals

- Perform laboratory screening experiments to identify different absorbent/solvent combinations that can exhibit the “self-concentrating” carbon dioxide (CO₂) 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 will examine an innovative and proprietary CO₂ 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 CO₂-rich liquid phase upon reaction with CO₂. The process is 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 CO₂ 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%.

The technology removes CO₂ 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 CO₂ (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 dual hydrophobic/hydrophilic functionality of the CO₂ absorbents (e.g., amine), the stability of the “CO₂-rich” reaction product, and its solubility behavior

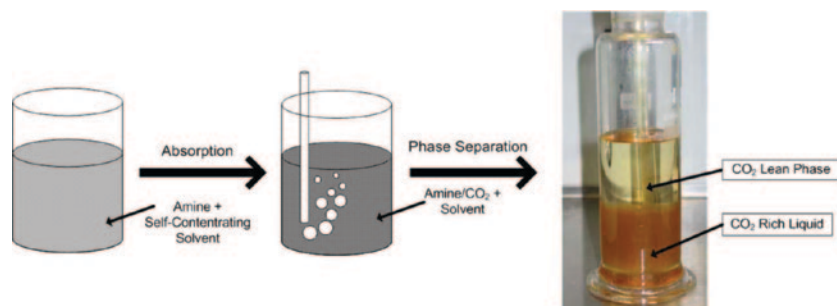


Figure 1: Concept of the Proposed Self-Concentrating Amine Absorbent Process

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Non-Aqueous, Amine-Based Solvent

Participant:

3H Company, LLC

Project Number:

FE0004274

NETL Project Manager:

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Partners:

Nexant, Inc.

Performance Period:

10/1/10 – 9/30/13

within the non-aqueous solvent system employed. When an amine is used as the CO₂ 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 CO₂: 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.

Conventional 30 wt% MEA-based CO₂ capture is considered to be the benchmark for performance. A typical heat of regeneration for a 30% MEA CO₂ capture process is about 1,934 Btu/lb CO₂ as cited in the literature. To better understand the inherent benefits of the 3H technology, it is important to examine the components that influence the heat of regeneration, heat of reaction, sensible heat, and latent heat. For a typical 30% MEA system, only about 1/3 of the regeneration energy is used to break the amine:CO₂ 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 CO₂ 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 CO₂ liquid” to be fully phase separated before sending it onto the stripper. Only the “rich CO₂ liquid” is subjected to regeneration, at a significant reduced volume as compared to a conventional MEA process. Overall, a 70% reduction in heat of regeneration can be achieved with the Self-Concentrating Absorbent process, taking into consideration that (1) only the “rich CO₂/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 non-aqueous process, will need to be investigated in more detail.

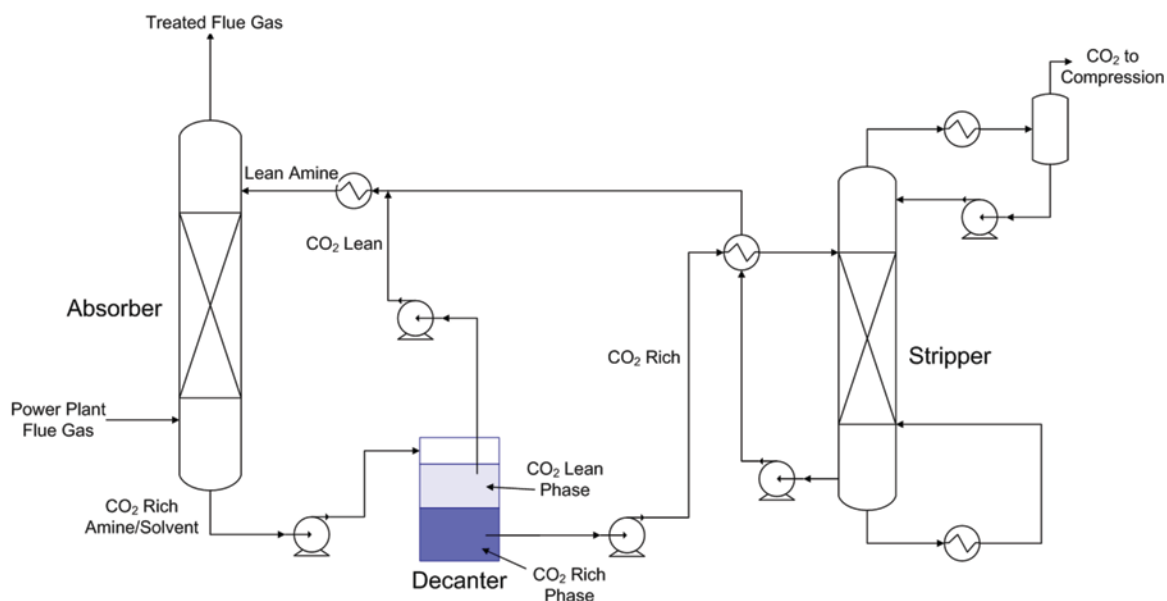


Figure 2: Simplified Flow Scheme of the Proposal Self-Concentrating Amine Absorbent Concept

Technology Advantages

- Lower regeneration energy requirements.
- Minimal degradation due to corrosion, oxygen degradation, and the formation of stable salts.

R&D Challenges

Not identified.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the September 2013 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/self-concentrating-amine.html>

ADVANCED LOW-ENERGY ENZYME CATALYZED SOLVENT FOR CO₂ CAPTURE

Primary Project Goals

Akermin is developing a bench-scale level reactor with the ability to capture up to 90% of carbon dioxide (CO₂) from a simulated flue gas using a solvent with significantly lower regeneration energy and at high reaction rates achieved by the use of an immobilized enzyme, carbonic anhydrase (CA), to catalyze the hydration reaction of CO₂.

Technical Goals

- Evaluate potential enzyme isoforms for stability to anticipated operating conditions and down-select to preferred option.
- Optimize micellar polymer to achieve high enzyme immobilization and stabilization.
- Develop detailed Aspen model of enzyme-catalyzed carbonate system and extrapolate to a power plant equivalent to 550 MWe, including mass and energy balances, electric power requirements, and projected chemical and maintenance costs.
- Build and test a closed-loop bio-reactor capable of processing up to 500 standard liters per minute (SLPM) of gas, the approximate equivalent of a 5-kWe power plant, and demonstrate continuous operation over a six-month period.

Technical Content

An advanced enzyme catalyzed low-energy solvent system is being developed for post-combustion CO₂ capture in this project. The core technology involves the integration of a proprietary immobilized CA enzyme into a packed column absorber to promote the hydration of CO₂ in lower reaction energy solvents. Chemical solvents of interest include potassium carbonate (K₂CO₃) and methyl diethanolamine (MDEA), both of which are known to produce bicarbonate as a product of reaction and therefore demonstrate accelerated rates of CO₂ capture with carbonic anhydrase enzymes.

The principal project objective is to demonstrate 90% CO₂ capture from simulated flue gas in a bench-scale unit at rates comparable to monoethanolamine (MEA) using a solvent that has significantly lower regeneration energy. Other key project objectives include evaluating the potential impact of minor contaminants, such as sulfur oxides and nitrogen oxides, common to coal-fired flue gases using lab-scale tests, and to demonstrate immobilized enzyme life in excess of 200 days in a bench-scale unit.

The current work plan is focused on establishing kinetic and lab-scale closed-loop reactor data to support design and scale-up from lab-scale ~20 SLPM to the bench-unit scale ~500 SLPM flue gas. Akermin is working to identify a preferred strain of CA that will have a long lifetime under industrial conditions, to optimize a micellar polymer for immobilization of this preferred enzyme, to develop and scale-up the immobilized enzyme packing material to the lab-scale closed-loop reactor system, and then to scale-up to a bench-scale system.

Pacific Northwest National Laboratory (PNNL) and Battelle Memorial Institute (Battelle) are collaborating to perform necessary wetted wall kinetic and mass transfer studies, chemical process modeling, and relevant cost estimation to determine how such a system would scale and cost-ef-

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Carbonic Anhydrase-Potassium Carbonate Mixture

Participant:

Akermin, Inc.

Project Number:

FE0004228

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Pacific Northwest National
Laboratory

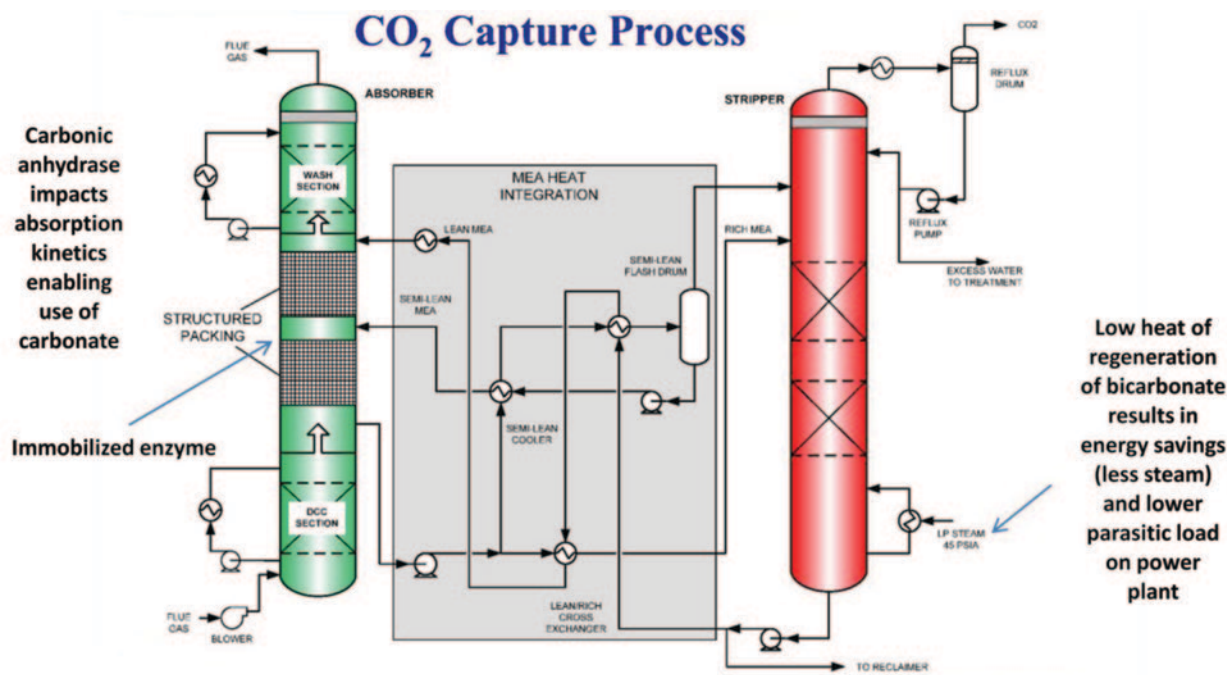
Performance Period:

9/30/10 – 9/30/12

ffectively integrate into an existing coal-fired power plant compared to DOE's goal of less than a 35% increase in cost of electricity with post-combustion CO₂ capture.

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POST-COMBUSTION SOLVENTS

Figure 1: Akermin's CO₂ Capture Process

Akermin's activities are distributed in parallel as needed to address: proof-of-concept testing and thermodynamic analysis; laboratory-scale process development and testing; bench unit design; immobilized enzyme scale-up; and bench unit installation, commissioning, and operation.

The four main areas of development in this project include: identification of preferred enzyme; optimization of immobilization polymer/enzyme system in catalyst support systems suitable for the bench-scale unit; definition of operating limits through analysis of lab-scale reactor data and process modeling; and process design, detailed engineering, fabrication and commissioning of a bench-scale unit capable of processing simulated flue gas, or interfacing directly to a commercial slip-stream.

Table 1: Solvent Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Potassium carbonate	
	Molecular weight	138.2 g/mol	—
	Boiling point (°C)	105 °C	—
	Heat of reaction (kJ/mole CO ₂)	28.2	—
	CO ₂ loading/working capacity, wt%	N/A	—
	Solvent concentration to stripper (mol/liter)	N/A	—
	Heat capacity of solution (kJ/K/kg)	N/A	—
	Viscosity, cP	5.6	—
Operating Conditions	Absorption temperature, °C	60	—
	Absorption pressure (CO ₂ partial pressure), atm	N/A	—
	CO ₂ capture efficiency, %	N/A	—
	Regeneration method	N/A	—
	Regeneration temperature, °C	120	—
	Regeneration pressure, atm	N/A	—

Table 1: Solvent Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Heat Integration	Required regeneration steam temperature, °C	N/A	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	N/A	—
	N ₂ concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	N/A	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

Ability to capture CO₂ using a solvent with significantly lower regeneration energy and at rates comparable to the solvent MEA.

R&D Challenges

- Enzyme immobilization, greater than 80% physical retention in flow liquid.
- Enzyme stabilization under anticipated absorber conditions (40–60 °C, pH 9–10, high ionic strengths).
- Flexible immobilization technology needed, which can easily adapt to improved enzymes and is adaptable to varied carbonate chemistries (K₂CO₃/KHCO₃, ammonium carbonate, MDEA, etc.).
- Demonstrate tolerance to sulfur and nitrogen oxides in bench-scale flow system.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the September 2012 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/adv-low-energy-enzyme.html>

NOVEL SOLVENT SYSTEM FOR POST-COMBUSTION CO₂ CAPTURE

Primary Project Goals

The overall project goals are to demonstrate ION Engineering's ionic liquid (IL)-amine solvents and carbon dioxide (CO₂) capture process design at a bench-scale level using coal-fired power plant flue gas, to evaluate process improvements to reduce costs, and to further evaluate the ability to achieve DOE cost and performance targets at commercial scale.

Technical Goals

- Process design objectives are to evaluate key parameters for the design of a 1.0-gallon per minute (gpm) CO₂ capture unit through laboratory work, process modeling, and performance tests.
- Process operation and evaluation objectives are to fabricate, install, and operate the portable bench-scale unit with simulated flue gas at ION's laboratories
- Subsequently operate continuously the portable bench-scale unit using actual flue gas at Xcel Energy's Valmont Station for at least 72 hours and with greater than 90% CO₂ capture.

Technical Content

ION Engineering, in collaboration with its partners, will design, construct, operate, and evaluate a bench-scale CO₂ capture system using simulated flue gas at ION Engineering's laboratories and then using actual flue gas at Xcel Energy's Valmont Power Station. The project will demonstrate ION's solvent approach for amine-based CO₂ capture, using amines as chemical solvents with ILs as the physical solvent. ION's IL-amine solvent system is related to well-understood aqueous amine solvent-based processes in that it utilizes proven amines as chemical solvents for CO₂ capture; however, it differs significantly with the use of an IL rather than water as the physical solvent. As ILs do not incur the high energy penalties of an aqueous system, utilizing ILs in place of water can reduce energy requirements by approximately 45% compared to aqueous amine systems. By selectively balancing the amines and ILs, higher CO₂ loading capacities can be achieved as well.

The 18-month project will demonstrate the ability of the IL-amine solvent system to capture CO₂ using a 1.0-gpm bench-scale process unit, and will include simulation modeling to finalize process designs, laboratory evaluations, solvent selection, and scale-up from the existing laboratory units to the bench-scale process unit. Design, construction, installation, integration, operation, monitoring, and decommissioning of the bench-scale unit will be performed, as well as commercial and operational assessments of the technology's ability to perform at full-scale. The evaluation of the IL-amine system in an operating environment with actual flue gas will provide data to confirm performance levels and evaluate additional opportunities to improve performance at commercial scale.

Technology Maturity:

Laboratory-scale, simulated flue gas and actual flue gas slipstream

Project Focus:

Ionic Liquid-Amine Mixture

Participant:

ION Engineering

Project Number:

FE0005799

NETL Project Manager:

Isaac Aurelio
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Principal Investigator:

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Partners:

Electric Power Research Institute
 Eltron Research
 Evonik Goldschmidt Corporation
 University of Alabama
 WorleyParsons Group, Inc.
 Xcel Energy

Performance Period:

10/1/10 – 4/30/12

The project is divided into two phases, as follows:

Phase I:

- Laboratory testing will be conducted on ION solvents to characterize vapor-liquid equilibrium and the requisite physical and chemical properties of the solvents for simulation modeling and process design.
- A process simulation model will be selected and customized to more effectively represent unique characteristics of IL and amine solvents versus current models.
- A laboratory-scale continuous process unit will be fabricated and used for tests with simulated flue gas to validate solvent performance, calibrate the simulation model, and develop the field test process design.
- Process design options will be evaluated considering system performance under varying flue gas conditions and requirements for corrosion, sulfur dioxide (SO₂), and thermal stability.
- A 5–15 liter-per-minute (1–3 gpm) system for CO₂ capture will be designed for field tests with actual flue gas.

Phase II:

- The final design, fabrication, installation, and shake-down of the field test unit will be completed.
- A series of test runs using the preferred ION solvent will be conducted in the field test unit at Xcel Energy's Valmont Station with data captured for monitoring and analysis.
- Aspen Plus® process modeling will be refined and expanded to evaluate potential commercial and operational performance. Capital expenditures and operating expenditures will be estimated.
- A final report will be completed that integrates the commercial and operational assessment, process modeling outcomes, and an assessment of potential savings in the use of waste steam, lower-cost materials, and other process improvement opportunities that were identified as the project proceeded.

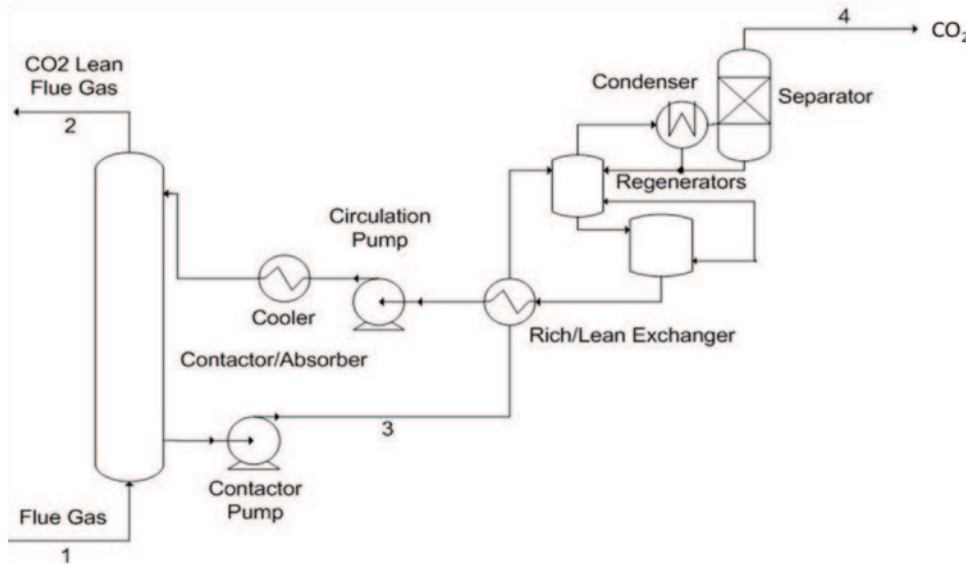


Figure 1: IL-Amine Solvent CO₂ Capture Process Diagram

Technology Advantages

Relative to state-of-the-art aqueous amine technology, IL-amine solvents offer:

- A 45% reduction in energy requirements.
- Higher CO₂ loading capacities.
- Reduced corrosion and solvent losses.
- Smaller units with reduced CAPEX.
- Ability to use lower-quality steam in regeneration.

R&D Challenges

- Solvent lifetime in actual flue gas conditions.
- Heat stable salt (HSS) formation, foaming, and corrosion.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the April 2012 project completion date.

Available Reports/Technical Papers/Presentations

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/novel-solvent-system.html>

NOVEL HIGH-CAPACITY OLIGOMERS FOR LOW-COST CO₂ CAPTURE

Primary Project Goals

GE Global Research is developing a novel oligomeric solvent and process for carbon dioxide (CO₂) capture from post-combustion flue gases.

Technical Goals

- Use molecular modeling to design new compounds with optimal heats of reaction (-8.5 to -10 kcal/mol).
- Design new oligomer solvents that have higher CO₂ solubility than current solvents.
- Achieve 25% greater CO₂ capacity than aqueous MEA.
- Achieve low solvent volatility.
- Achieve high reaction rate.

Technical Content

Silicone based solvents, which may be either oligomeric (defined as short-chain polymers containing 2–20 repeat units) or small molecule species, will be developed. Silicones are known in the literature to be CO₂-philic. These materials are advantageous compared to aqueous amine technology because they have low volatility, do not require a carrier fluid such as water, and can be synthesized with a number of CO₂ capture sites per molecule, increasing the overall CO₂ capacity. In addition, silicones have a high degree of thermal stability, allowing the system to operate at higher temperatures. Polymer-CO₂ interactions have been extensively studied in the literature and several CO₂-philic functional groups, such as acetates, carbonates, and ketones, have been identified.

The development of the capture solvent has taken the following approach:

- Identify solvent backbones and functional groups (Figure 1), using a literature review, that are potentially CO₂-philic (see Table 1 and Table 2).
- Use molecular modeling to predict favorable structures and heats of reaction.
- Synthesize Generation 1 solvents.
- Screen silicone solvents using high throughput screening (HTS) techniques.
- Confirm materials by:
 - Nuclear magnetic resonance (NMR).
 - Boiling point, vapor pressure, flash point, viscosity, thermal stability, and CO₂ release characteristics.
- Downselect candidate solvents and synthesize.

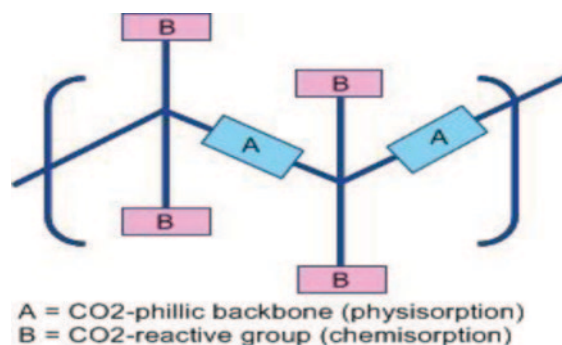


Figure 1: Solvent Concept

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

High-Capacity Oligomers

Participant:

GE Global Research

Project Number:

NT0005310

NETL Project Manager:

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Principal Investigator:

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GE Global Research

grocela@ge.com

Partners:

GE Energy

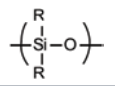
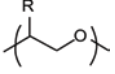
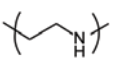
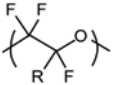
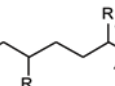
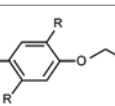
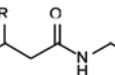
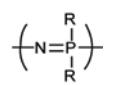
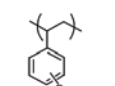
University of Pittsburgh

Performance Period:

10/1/08 – 9/30/10

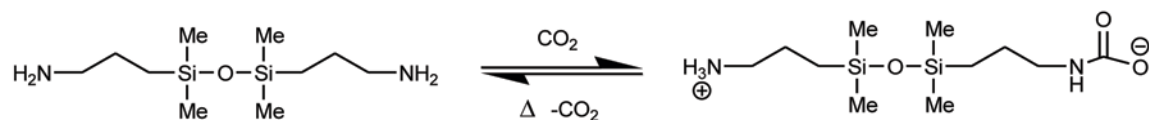
- Estimate physical, chemical, and thermodynamic properties using modeling to further select candidates.
- Physically measure solvent properties.
- Conduct degradation and stability tests in the presence of CO₂, water, sulfur dioxide (SO₂), etc.
- Determine minimized cost of energy (COE) and an optimized capture process using power plant models.

Table 1: Examples of Solvent Backbone Candidates

Backbone	Structure	Attribute						Total
		Physical State	Cost (inexpensive)	Synthetic Availability	Ease of Derivatization	CO ₂ -philic	Stability	
Siloxane		9	5	9	9	9	9	50
Alkyl Ether		9	9	9	5	5	9	46
Alkyl Amino		5	9	9	5	9	9	46
Perfluoroether		9	1	5	1	9	9	34
Alkyl		9	9	9	5	1	9	42
Aryl Ether		1	5	5	5	5	5	26
Alkylamido		5	5	9	5	5	5	34
Phosphazene		5	1	5	5	5	1	22
Polystyrene		1	9	9	9	1	9	38
Physical State Cost (inexpensive) Synthetic Availability Ease of Derivatization CO ₂ -philic		must be low viscosity liquid should be <\$10/lb able to be made on large scale must be easily functionalized physisorption	9=liquid, 5=viscous liquid, 1=solid 9=<\$10/lb, 5=\$10-20/lb, 1=>\$20/lb 9=commercial, 5=small scale, 1=laboratory 9=easy, 5=moderate, 1=difficult 9=high, 5=moderate, 1=low					

The solvent selection process splits the oligomers into backbones and functional groups so that physisorption and chemisorption are decoupled in the modeling of CO₂ solubility. Higher total scores indicate more promising candidates.

After HTS of various materials, one candidate solvent that showed much promise was 1,3-bis(3-aminopropyl)-1,2,3,3-tetramethyldisiloxane. The reaction of it and CO₂ is shown below:



Currently, the absorption process involves contacting the aminosilicone/glycol solvent system with gas phase CO₂. The viscosity of the system increases as CO₂ reacts until maximum CO₂ absorption is achieved. The solvent system remains a liquid and is transferred to a pressurized desorption chamber where it is heated, the CO₂ is released, and the lean solvent system is regenerated.

Table 2: Examples of Solvent Functional Group Candidates





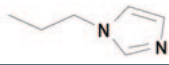
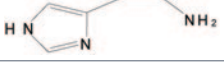
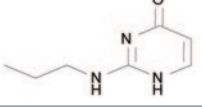
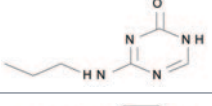

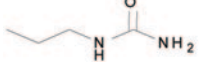
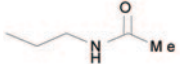
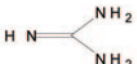
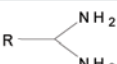
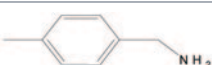
Backbone	Structure	Attribute					Total
		CO ₂ Capacity	Heat of Reaction	Kinetics	Ease of Attachment	Cost	
Aminoethyl		5	5	9	5	9	33
Aminopropyl		5	5	9	9	9	37
Aminoethylaminopropyl		9	9	9	9	9	45
Bis(aminoethyl)aminopropyl		9	9	9	9	9	45
Imidazole		1	1	1	9	5	17
Histamine		5	9	1	5	1	21
Isocytosine		5	5	5	5	1	21
5-Azacytosine		9	5	5	5	1	25
Piperazine		9	9	9	9	5	41
Urea		5	5	1	5	9	25
Acetamide		1	5	1	5	5	17
Guanidine		9	5	9	1	5	29
Amidine		9	5	9	9	5	37
Benzylamine		5	9	5	9	5	33
CO ₂ capacity Heat of Reaction Kinetics Ease of Attachment		9=high, 5=moderate, 1=low 9=moderate, 5=low, 1=high 9=fast, 5=moderate, 1=slow 9=easy, 5=doable, 1=difficult (Reaction with CO ₂)					

Table 3: Process Parameters for Aminosilicone/Glycol Solvents

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Amino silicone/glycol	
	Molecular weight	248/150	—
	Boiling point (°C)	132 °C at 11 mm Hg/125 °C at 0.1 mm Hg	—
	Heat of reaction (kJ/mole CO ₂)	45	—
	CO ₂ loading/working capacity, wt%	5.5–6%	—
	Solvent concentration to stripper (mol/liter)	—	—
	Heat capacity of solution (kJ/K/kg)	~2.1	—
	Viscosity, cP	At 40 °C <50 (0%) <4,500 (100%)	—
Operating Conditions	Absorption temperature, °C	—	—
	Absorption pressure (CO ₂ partial pressure), atm	0.1~0.15	—
	CO ₂ capture efficiency, %	>90	—
	Regeneration method	Thermal	—
	Regeneration temperature, °C	100~150	—
	Regeneration pressure, atm	5~20	—
Heat Integration	Required regeneration steam temperature, °C	120~170	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	N/A	—
	N ₂ concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	N/A	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

- Low volatility.
- Water not required as a carrier fluid, thus lowering heat capacity.
- Silicones have a high degree of thermal stability.

R&D Challenges

Flexible short chain silicones have not been previously demonstrated as CO₂ absorbing solvents, and thus a number of potential risks have been identified. The most significant technical risks include:

- Insufficient chemical and thermal stability of the solvents.
- Low CO₂ absorption and desorption rates.
- Excessively high heat of reaction.

Results To Date/Accomplishments

- Selected solvent classes.
- Calibrated plant model for absorption cycles, stripping cycles, and cost calculations.
- Downselected aminosilicones solvent classes.
- Found that a glycol co-solvent aids in physisorption of CO₂ and decreases viscosity.
- Shown thermal regeneration of solvent after CO₂ capture.
- Demonstrated continuous CO₂ absorption by aminosilicone solvent system.
- Discovered aminosilicone solvent systems that show a >25% increase in loading compared to 30% MEA.
- Determined thermal stability and tolerance to impurities of selected solvents.
- Constructed a continuous absorption/desorption unit which created ability to determine mass transfer coefficients, robustness of the solvent system, and special heating or cooling needs.
- Calculated 41% increase in COE vs. 74% for optimized MEA system.

Next Steps

Project is complete.

Available Reports/Technical Papers/Presentations

Xie, H-B, Johnson, J. K., Perry, R., Genovese, S., Wood, B., "A Computational Study of the Heats of Reaction of Substituted Monoethanolamine with CO₂," J. Phys. Chem. A, 2011, Vol 115, Issue 3, pp. 342–350.

Perry, R., Grocela-Rocha, T., O'Brien, M., Genovese, S., Wood, B., Lewis, L., Lam, H., Soloveichik, G., Rubinsztajn, M., Kniajanski, S., Draper, S., Enick, R., Johnson, J., Xie, H.-b. and Tapriyal, D., "Aminosilicone Solvents for CO₂ Capture." Chem-SusChem, 2010, 3: 919–930.

"Novel Aminosilicones for CO₂ Capture," Fuel Preprints, 2010, 55(1), 282.

ACS National Meeting, March 24, 2010 "Novel Aminosilicone Solvents for CO₂ Capture."

43rd Silicon Symposium, May 21, 2010 "Aminosilicone Solvents for Low Cost CO₂ Capture."

2010 NETL CO₂ Capture Technology Meeting, September 15, 2010 "Novel High Capacity Solvents for CO₂ Capture."

AIChE Meeting, November 8, 2010 "Characteristics of Aminosilicones for CO₂ Capture."

AIChE Meeting, November 12, 2010 "CO₂-Capture Process Using Aminosilicone-Based Absorbents."

PacifiChem 2010, December 17, 2010 "Aminosilicones as CO₂-Capture Solvents."

Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, March 24–26, 2009, Pittsburgh, PA.

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/oligomers.html>

DEVELOPMENT AND EVALUATION OF A NOVEL INTEGRATED VACUUM CARBONATE ABSORPTION PROCESS

Primary Project Goals

The goal of this project is for the Illinois State Geological Survey 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 (CO₂) capture.

Technical Goals

- Test the proof-of-concept of the IVCAP.
- Identify an effective catalyst for accelerating CO₂ absorption.
- Identify an effective additive for reducing the stripping heat.
- Evaluate a modified IVCAP as a multi-pollutant control process for combined sulfur dioxide (SO₂) and CO₂ capture.

Technical Content

The proposed IVCAP employs a potassium carbonate (K₂CO₃) aqueous solution for CO₂ 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 CO₂ and K₂CO₃ 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.

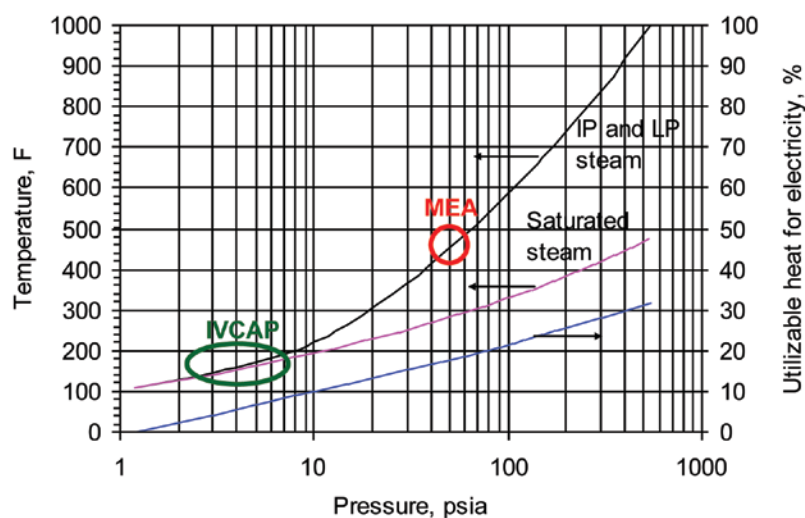


Figure 1: Steam Properties During Expansion in the Intermediate and Low-Pressure Turbines

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Integrated Vacuum Carbonate Absorption

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

lu@isgs.illinois.edu

Partners:

Calgon Carbon Corporation
Illinois Clean Coal Institute
University of Illinois

Performance Period:

9/26/08 – 4/30/12

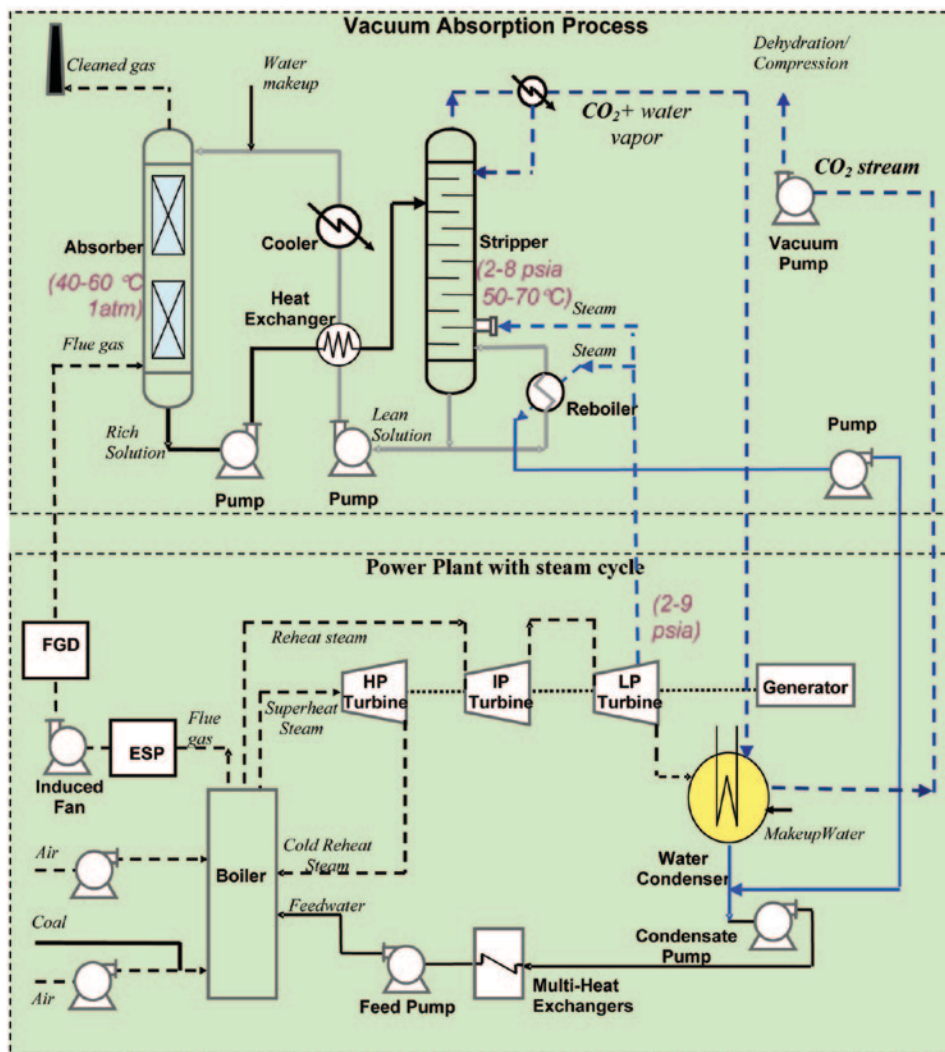


Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low-Quality Steam From the Power Plant

Table 1: A Comparison of Heats of Absorption for CO₂ 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	$CO_3^{2-} + CO_2 + H_2O = 2 HCO_3^-$	600 kJ/kg

The intrinsic rate of CO₂ absorption into the K₂CO₃ solution is much slower in an MEA solution; therefore, enzyme catalysts will be 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-, ceramic-, and polymer-based materials) will be evaluated for enzyme immobilization.

Since more than 60% of the process heat in the IVCAP is the stripping heat, an additive able to suppress water vaporization of the CO₂-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 SO₂ removal in the CO₂ capture process. In the amine-based and amine-promoted absorption processes, the flue gas must be treated to reduce the concentration of SO₂ 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, SO₂ can be removed by the reaction with the solvent to form a sulfate salt which can be further processed to reclaim the solvent.

Table 2: Process Parameters for IVCAP Process

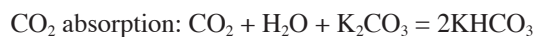
	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	K ₂ CO ₃ /KHCO ₃	—
	Molecular weight	138	—
	Boiling point (°C)	103	—
	Heat of reaction (kJ/mole CO ₂)	26.4	—
	CO ₂ loading/working capacity ¹ , wt%	2.7–4.0 wt%	—
	Solvent concentration to stripper (mol/liter)	20–25 wt%	—
	Heat capacity of solution (kJ/K/kg)	3.35	—
	Viscosity, cP	0.95 (50 °C)	—
Operating Conditions	Absorption temperature, °C	40–60	—
	Absorption pressure, atm	1	—
	CO ₂ capture efficiency, %	90%	—
	Regeneration method	Pressure swing	—
	Regeneration temperature, °C	50–70	—
	Regeneration pressure, atm	0.14–0.54	—
Heat Integration	Required regeneration steam temperature, °C	60–100	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	Negligible	—
Product Quality	CO ₂ purity, %	>99	—
	N ₂ concentration, %	Negligible	—
	Other contaminants, %	0.1%	—
Process Performance	Electricity requirement, kJ/kg CO ₂	460–580	—
	Heat requirement, kJ/kg CO ₂	240–550 (electricity equivalent)	—
	Total energy (electricity equivalent), kJ/kg CO ₂	800–1,130	~800

Note:

1. Working capacity is the loading difference CO₂-rich solution before and after it is regenerated.

Equations Describing Chemical Reaction:

The main reactions involving in the IVCAP include:



Solvent Reaction Kinetics: Based on the experimental results to date, the overall CO₂ absorption rate measured for a 20 wt% potassium carbonate (PC) solution mixed with 300 mg/l free carbonic anhydrase (CA) enzyme was about 1.5 to five times lower than that of the MEA, depending on the CO₂ loading in the solution. The CA enzyme promotes the absorption more significantly when the CO₂ loading in the solution is higher. The CO₂ absorption rate into the CA-promoted PC solution can be close to the MEA if a higher enzyme dosage level (>300 mg/l), an additive to increase CO₂ solubility in the solution, and an absorber configuration with large liquid holdup are further employed.

Solvent Heating/Cooling Method: There are two process configurations for heating and cooling the carbonate solvent in the IVCAP. If the stripper is operated at close to 70 °C, a heat exchanger is employed for exchanging heat between the CO₂-rich solution from the absorber and CO₂-lean solution from the stripper. If the stripping temperature is chosen at close to 50 °C, the heat exchange between the rich and lean solution can be eliminated, and only a cooler (using cooling water as medium) is used to cool down the lean solution before it enters the absorber.

Solvent Contaminant Resistance: Since the potassium carbonate solution is used as a solvent, no solvent degradation and little corrosion problems are expected. No SO₂ scrubbing is needed prior to the IVCAP, since SO₂ removal can be combined with CO₂ capture. Therefore, there is also no problem related to SO₂ contamination.

Flue Gas Pretreatment Requirements: Sulfur dioxide removal can be combined with CO₂ capture in the IVCAP. The carbonate solution absorbs SO₂ 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 eliminated in the IVCAP. No other flue gas pretreatments [such as for particulate matter (PM), nitrogen oxides (NO_x)] are required either.

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 CO₂.

Technology Advantages

- Uses lower quality steam than amines (MEA), consequently increasing net power output.
- Lower heat of absorption.
- Higher absorption capacity.
- Less energy required for stripping.
- Modified IVCAP may be able to remove SO₂ without a FGD unit.
- Approximately 25% lower electricity loss.

R&D Challenges

- Slow kinetics of CO₂ absorption into the K₂CO₃ solution and thus a high-activity catalyst is required.
- Potentially large capital and operating cost of the vacuum pump.
- Suppressing water vaporization in the stripper.
- Chemical and thermal stability of the absorption enzymes.
- Materials need to be developed to immobilize the enzymes.

Results To Date/Accomplishments

- Completed the reactivity test of CA enzyme from a leading enzyme manufacturer and the evaluation of existing inorganic catalysts. The results showed that the CA is a promising catalyst for accelerating CO₂ absorption into the K₂CO₃ solution.

- Results have shown that the CA enzyme:
 - Effective catalyst to promote CO₂ absorption into PC.
 - 300 mg/l CA promotes rate by 2–20 times.
 - Activity comparable at 25–50 °C.
 - Rates comparable at different CO₂ loadings.
 - Rate could further increase at higher CA dosage (>300 mg/l).
 - Stable at tested pH range (9–11.5).
- Rate into PC+CA (at 300 mg/l) 2–5 times less than MEA in a packed-bed column.
- Presence of flue gas impurities resulted in <11% loss of initial CA activity.
- CA immobilized onto silica/glass materials with high Immobilization Factor.

Next Steps

- Investigate catalytic methods to enhance the CO₂ absorption rate in the K₂CO₃ solution.
 - Evaluate and optimize activity of enzyme catalysts.
 - Investigate enzyme immobilization.
 - Evaluate other potential catalysts.
- Screen and develop additives for suppressing water vaporization in the stripper.
 - Measure vapor-liquid phase equilibrium for the CO₂-H₂O-K₂CO₃-KHCO₃ systems with and without additives at a temperature range of 25–70 °C.
 - Inorganic and organic additives to be examined.
- Combine SO₂ removal in the CO₂ capture process.
 - Evaluate reclamation reagents.
 - Conduct parametric tests in the batch and semi-continuous lab systems.
- Conduct techno-economic analysis of the IVCAP.

Available Reports/Technical Papers/Presentations

Presentation at the Annual NETL CO₂ Capture Technology R&D Meeting, September 2010.

Presentation at the Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, March 2009.

Poster presentation at the Eighth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 2009.

Presentation at the 2009 AIChE Annual Meeting, Nashville, TN, November 2009.

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/vacuumcarbonate.html>

REVERSIBLE IONIC LIQUIDS AS DOUBLE-ACTION SOLVENTS FOR EFFICIENT CO₂ CAPTURE

Primary Project Goals

Georgia Tech Research Corporation is developing a novel class of solvents for the recovery of carbon dioxide (CO₂) from post-combustion flue gases that will achieve a substantial increase in CO₂ 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 CO₂ 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 CO₂ to form an IL, which then dissolves additional CO₂ by a physisorption mechanism. Subsequently, modest elevations in temperature reverse the reaction and yield pure CO₂ for disposal; because of this dual mode, capacity can be large.

In a two-component RevIL, CO₂ at 1 atmosphere acts as a “switch,” as shown in Figure 1.

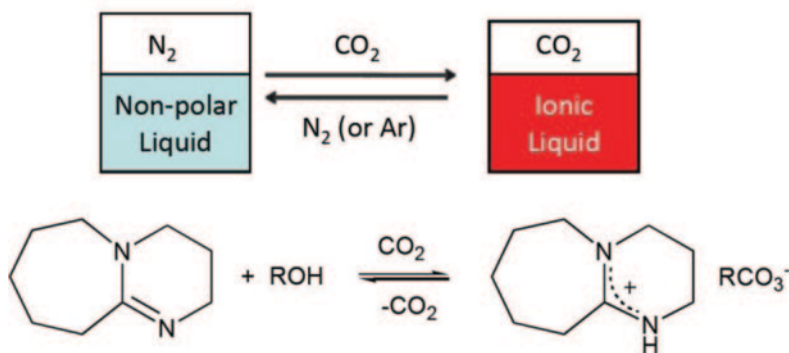


Figure 1: CO₂ Will Switch a Non-Polar Liquid to an Ionic Liquid

Two-component RevILs have the disadvantage of being too complex and requiring alcohol. Light alcohol would evaporate with the CO₂, 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

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Ionic Liquids

Participant:

Georgia Tech Research Corporation

Project Number:

NT0005287

NETL Project Manager:

David Lang

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Principal Investigator:

Charles A. Eckert

Georgia Tech Research Corporation

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Partners:

None

Performance Period:

10/1/08 – 9/30/11

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.

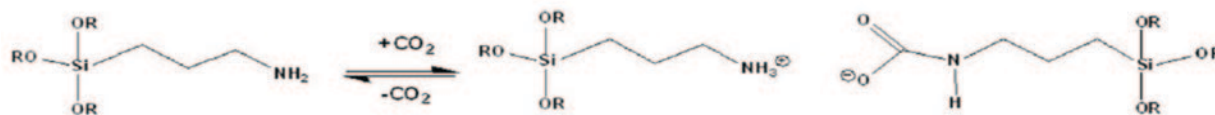


Figure 2: An Example of a Single Component RevIL

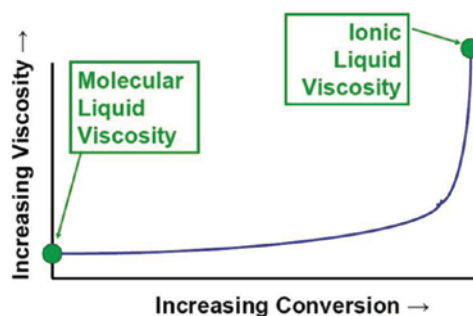


Figure 3: Ionic Liquids are More Viscous Than Their Respective Molecular Liquids

Table 1: : Process Parameters for RevIL Solvents

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Reversible ionic liquid	
	Molecular weight	170–220	150
	Boiling point (°C)	130	200
	Heat of reaction (kJ/mole CO ₂)	Unknown	50
	CO ₂ loading/working capacity ¹ , wt%	Unknown	100
	Solvent concentration to stripper (mol/liter)	4.5	7
	Heat capacity of solution (kJ/K/kg)	—	<4.2
	Viscosity, cP	>1,000	<80
Operating Conditions	Absorption temperature, °C	35	>50
	Absorption pressure, atm	1.2	1.2
	CO ₂ capture efficiency, %	—	90
	Regeneration method	Thermal	Thermal
	Regeneration temperature, °C	115	75
	Regeneration pressure, atm	2	2
Heat Integration	Required regeneration steam temperature, °C	135	100
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	—	<0.003
Product Quality	CO ₂ purity, %	—	>99
	N ₂ concentration, %	—	<1
	Other contaminants, %	—	<1
Process Performance	Electricity requirement, kJ/kg CO ₂	—	500
	Heat requirement, kJ/kg CO ₂	—	1,500
	Total energy (electricity equivalent), kJ/kg CO ₂	—	950

Note:

1. Working capacity is the loading difference CO₂-rich solution before and after it is regenerated.

Equations Describing Chemical Reaction:

Chemical reaction for the CO₂ 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.

Flue Gas Pretreatment Requirements: Flue gas pretreatment should be similar to the amine-based absorption processes since the RevIL is resistant to moisture.

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 DOE goals.

Results To Date/Accomplishments

- Have demonstrated greater capacity than current solvents.
- Successful synthesis and chemical characterization of ten 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 CO₂ in the 6 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

- Successfully synthesize and characterize silylated one-component RevILs.
 - Demonstrate function in presence of water.
- Measure candidate RevIL's thermodynamic properties.
- Measure candidate RevIL's absorption and desorption rates.
- Identify and produce optimum capture solvent.
- Show that energy penalty is smaller than with current solvents.
- Design of capture process.
- Conduct an economic analysis.

Available Reports/Technical Papers/Presentations

Presentation from Kickoff Meeting held on December 2, 2009.

Presentation: Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, March 24–26, 2009, in Pittsburgh, PA.

Vittoria Blasucci, Cerag Dilek, Hillary Huttenhower, Ejae John, Veronica Llopis-Mestre, Pamela Pollet, Charles A. Eckert, and Charles L. Liotta, "One Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," *Chem Comm*, 116–119, 2009.

Vittoria Blasucci, Ryan Hart, Veronica Llopis-Mestre, D. Julia Hahne, Melissa Burlager, Hillary Huttenhower, Reginald Thio, Charles L. Liotta, and Charles A. Eckert, "Single Component, Reversible Ionic Liquids for Energy Applications," *Fuel*, **89**, 1315–1319, 2010.

Vittoria M. Blasucci, Ryan Hart, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids Designed for Facile Separations," *Fluid Phase Equilibria*, **294**, 1–6, 2010.

Ryan Hart, Pamela Pollet, Dominique J. Hahne, Ejae John, Veronica Llopis-Mestre, Vittoria Blasucci, Hillary Huttenhower, Walter Leitner, Charles A. Eckert, and Charles L. Liotta, "Benign Coupling of Reactions and Separations with Reversible Ionic Liquids," *Tetrahedron*, **66**, 1082–1090, 2010.

Presentation: Annual NETL CO₂ Capture Technology Meeting, September 13–17, 2010, in Pittsburgh, PA.

General project information is available on DOE/NETL website at: <http://www.netl.doe.gov/technologies/coalpower/ewr/co2/post-combustion/double-action.html>

DEVELOPMENT OF CHEMICAL ADDITIVES FOR CO₂ CAPTURE COST REDUCTION

Primary Project Goals

Lawrence Berkeley National Laboratory (LBNL) is developing a novel solvent system that will integrate amine, potassium carbonate (K₂CO₃), and ammonium solvents to obtain as much carbon dioxide (CO₂) absorption and as little solvent regeneration energy demand as possible.

Technical Goals

- Develop additives to promote CO₂ absorption by K₂CO₃ solution.
- Develop methods to convert KHCO₃ to NH₄HCO₃.
- Develop additives to allow conversion of KHCO₃ to K₂CO₃ with low energy demand.
- Investigate chemistry involved, develop process configuration, determine energy demand, and prepare for scale-up demonstration.

Technical Content

LBNL is performing a bench-scale investigation of novel solvents for post-combustion CO₂ capture. The goal is to enhance CO₂ absorption by the solvent and reduce the cost of regenerating solvents. To date, a bench-scale CO₂ absorber has been set up and calibrated, and parametric tests to determine baseline kinetic performance for methylethanolamine (MEA), ammonia, and chilled ammonia have been conducted as a reference for tests with advanced solvents. LBNL will now investigate a new solvent with CO₂ absorption kinetics reportedly at least twice as fast as MEA. They believe that this should allow CO₂ absorber and packing sizes to be reduced by 50%. The new solvent will produce a CO₂-bearing salt, ammonium bicarbonate. LBNL expects that the energy required to decompose the ammonium bicarbonate for separation of CO₂ will be much less than that required for conventional MEA carbamate salt. During the decomposition process, LBNL will separate ammonia gas from CO₂ and investigate ways to reduce ammonia emissions from the CO₂ capture process.

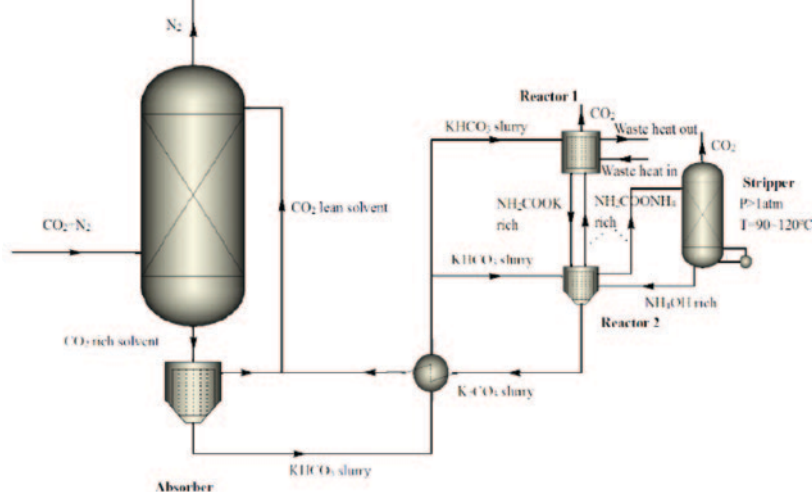


Figure 1: Conceptual Process Configuration #1

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Mixed Solvent

Participant:

Lawrence Berkeley National Laboratory

Project Number:

FWP-ED33EE

NETL Project Manager:

David Lang
David.Lang@netl.doe.gov

Principal Investigator:

Shih-Ger Chang
 Lawrence Berkeley National Laboratory
sgchang@lbl.gov

Partners:

None

Performance Period:

6/1/08 – 5/31/13

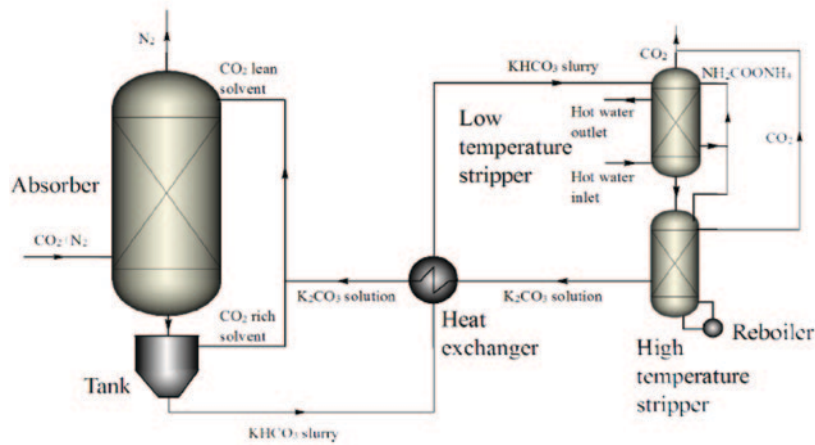


Figure 2: Conceptual Process Configuration #2

Table 1: Solvent Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Amine, potassium carbonate, and ammonium solvent	
	Molecular weight	N/A	—
	Boiling point (°C)	N/A	—
	Heat of reaction (kJ/mole CO ₂)	N/A	—
	CO ₂ loading/working capacity, wt%	N/A	—
	Solvent concentration to stripper (mol/liter)	N/A	—
	Heat capacity of solution (kJ/K/kg)	N/A	—
	Viscosity, cP	N/A	—
Operating Conditions	Absorption temperature, °C	55	—
	Absorption pressure (CO ₂ partial pressure), atm	N/A	—
	CO ₂ capture efficiency, %	N/A	—
	Regeneration method	Thermal	—
	Regeneration temperature, °C	120	—
	Regeneration pressure, atm	N/A	—
Heat Integration	Required regeneration steam temperature, °C	N/A	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	N/A	—
	N ₂ concentration, %	N/A	—
	Other contaminants, %	N/A	—
Process Performance	Electricity requirement, kJ/kg CO ₂	N/A	—
	Heat requirement, kJ/kg CO ₂	4,503	—
	Total energy (electricity equivalent), kJ/kg CO ₂	N/A	—

Technology Advantages

- Low energy demand.
 - Slurries, reduce sensible and latent heat.
 - NH_4HCO_3 , low solvent decomposition temperature.
 - Waste heat, CO_2 production.
- Reduced reagent loss and equipment corrosion.
 - Organic rate promoters not exposed to H.T. stripping.
- Avoid NH_3 emissions.

R&D Challenges

- CO_2 absorption rate promoters.
- Reaction mechanisms, kinetics, and thermodynamics involving many chemical species, three phases, high concentrations, elevated temperatures, and pressure.
- Most appropriate process configuration.

Results To Date/Accomplishments

- Bench-scale CO_2 absorber has been set up and calibrated.
- Parametric tests to determine baseline kinetic performance for MEA, ammonia, and chilled ammonia.
- Developed a conceptual process configuration.

Next Steps

Final test results will not be available until the May 2013 project completion date.

Available Reports/Technical Papers/Presentations

Annual NETL CO_2 Capture Technology Meeting, September 13–17, 2010, Pittsburgh, PA.

IONIC LIQUIDS: BREAKTHROUGH ABSORPTION TECHNOLOGY FOR POST-COMBUSTION CO₂ CAPTURE

Primary Project Goals

The University of Notre Dame is developing a new ionic liquid (IL) solvent and accompanying capture process that will incur a small increase in cost of electricity (COE) compared to currently available capture technologies.

Technical Goals

- ILs will have low water solubility and will be used in essentially an anhydrous state.
- The target selectivity of carbon dioxide (CO₂) over nitrogen (N₂) for the IL will be 50.
- The complexing ratio of CO₂: IL will be at least 1:1.
- Desired IL properties include:
 - Liquid at room temperature or slightly above.
 - Thermally stable to 300 °C.
 - Minimal viscosity increase upon complexation with CO₂.
 - Binding strength tuned to yield optimal capture and regeneration performance.

Technical Content

ILs are salts that are liquid at room temperature. They are known to have high intrinsic physical solubility for CO₂. Examples of ILs are illustrated in Figure 1.

Previous experiments have shown a potential for high CO₂ solubility and low oxygen (O₂), N₂ solubility (see Figure 2). ILs as CO₂ absorbents are promising for reducing costs by developing a process with higher CO₂ loading in the circulating liquid and lower heat requirements for regeneration. Both of these effects would lower process costs.

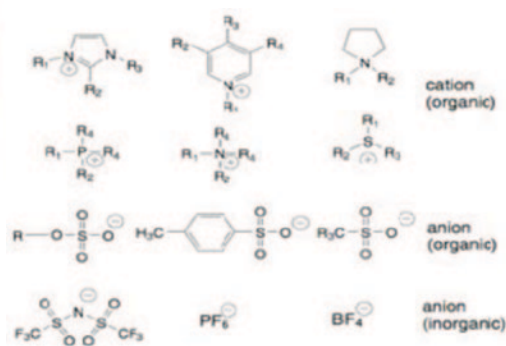


Figure 1: Examples of Ionic Liquids

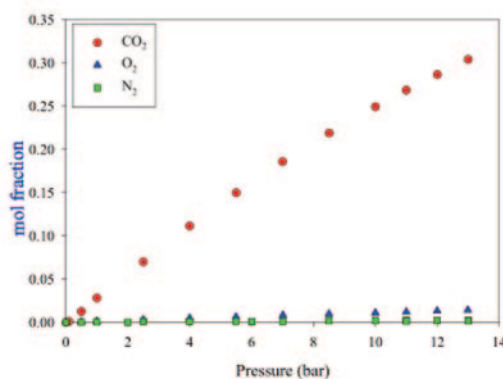


Figure 2: CO₂ Solubility in Ionic Liquids

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Ionic Liquids

Participant:

University of Notre Dame

Project Number:

NT43091

NETL Project Manager:

David Lang

David.Lang@netl.doe.gov

Principal Investigator:

Edward J. Maginn

University of Notre Dame

ed@nd.edu

Partners:

Babcock & Wilcox

DTE

EMD

Trimeric Corporation

Performance Period:

2/28/07 – 2/29/12

A suitable capture process cannot be identified until the best IL candidate is selected. However, the following is a base case absorber/stripper process.

Process simulation has been used to evaluate the sensitivity of a representative 500-MW, coal-fired power plant CO₂ capture process for the properties of ILs. The results will be used to guide the development of the next generation of ILs. Variables include:

- Stoichiometry: Notre Dame has developed both 1:1 and 2:1 (IL: CO₂) stoichiometries; to date, preliminary modeling assumed 1:1 since this should yield the best performance.
- Enthalpy of reaction: Notre Dame proposed a range of low to high based on molecular modeling.
- Loading (K_{eq}): Sensitivity includes a range of CO₂ loadings that result from the above enthalpies of reaction.
- Water miscibility: Both partially and fully miscible systems are included. Activities coefficients modeled with Nationally Recognized Testing Laboratory (NRTL) using experimental data.

Preliminary results show much lower parasitic energy compared with an MEA system.

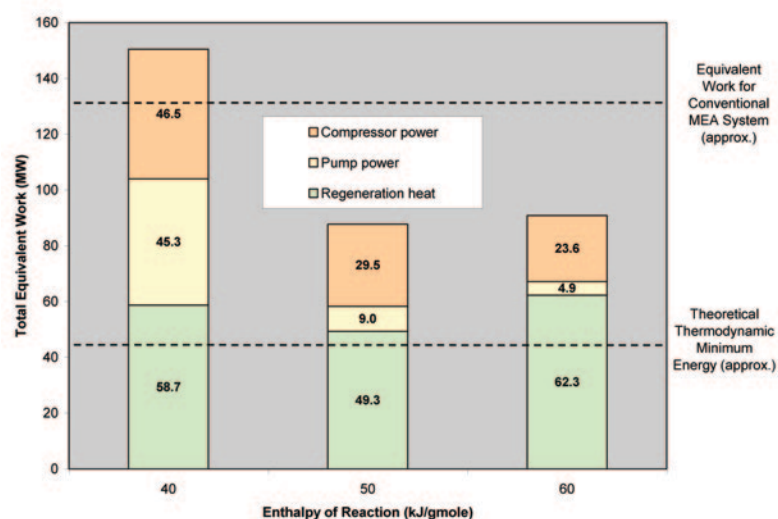


Figure 3: Preliminary Results on the Parasitic Power Requirement of Ionic Liquid Solvents

Table 1: Process Parameters for Ionic Liquid Solvents

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Ionic liquid	Ionic liquid
	Molecular weight	575 g/mol	<575 g/mol
	Boiling point (°C)	N/A, do not boil	N/A, do not boil
	Heat of reaction (kJ/mole CO ₂)	35–75	35–75
	CO ₂ loading/working capacity ¹ , wt%	1.6–2.6%	>2.6%
	Solvent concentration to stripper (mol/liter)	1.8	1–2
	Heat capacity of solution (kJ/K/kg)	2.1	<2
	Viscosity, cP	100 at 40 °C	<100 at 40 °C

Table 1: Process Parameters for Ionic Liquid Solvents

	Parameter	Current R&D Value	Target R&D Value
Operating Conditions	Absorption temperature, °C	40–50	40–50
	Absorption pressure, atm	0.15 of CO ₂	0.15
	CO ₂ capture efficiency, %	90	90
	Regeneration method	Thermal	Thermal
	Regeneration temperature, °C	120–160	120–204
	Regeneration pressure, atm	1–3	>2
Heat Integration	Required regeneration steam temperature, °C	126–218 °C	126–218 °C
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	0.001	<0.001
Product Quality	CO ₂ purity, %	>95%	>95%
	N ₂ concentration, %	<3%	<3%
	Other contaminants, %	Unknown	<2%
Process Performance	Electricity requirement, kJ/kg CO ₂	390–560	Minimize
	Heat requirement, kJ/kg CO ₂	1,650–1,850	Minimize
	Total energy (electricity equivalent), kJ/kg CO ₂	890–950	Minimize

Note:

- Working capacity is the loading difference CO₂-rich solution before and after it is regenerated.

Technology Advantages

- Low volatility and good thermal stability.
- Wide liquidus range.
- Adjustable enthalpy of absorption (10–80 kJ/mol).

R&D Challenges

- Maintain high thermal stability with good reaction kinetics and capacity.
- Unknown corrosion behavior.
- Determine mass transfer characteristics.
- Gain operational experience in lab-scale units.
- Cost of solvent made on large-scale unknown.

Results To Date/Accomplishments

Phase I and Phase II of the project are complete; Phase III is in progress. Key accomplishments to date include:

- Synthesized and tested a total of 17 new “Generation 1” ILs during the first year of the project; synthesized a total of 7 “Generation 2” ILs during the second year of the project.
- Developed molecular modeling techniques that have enabled Notre Dame researchers to compute key properties of ILs from first principles.
- Developed a way to tune the binding strength of CO₂ to optimize the ILs using process modeling as a guide.

- Developed unique experimental techniques, including the ability to monitor the IR spectrum of the IL as it absorbs CO₂, and then use this information to determine reaction rates and mechanisms.
- Evaluated alternative process configurations; selected a viscosity modified absorber stripper process for continued study.
- Developed a detailed understanding of the mechanism responsible for the large viscosity increase observed upon complexing CO₂, and designed new molecules that do not show viscosity increase.
- Synthesized several “Generation 3” ILs that exhibit low viscosity and whose viscosity does not significantly increase upon reaction with CO₂, unlike the case with “Generation 2” ILs.
- Selected “optimal” IL(s) for lab-scale testing.
- Conducted bench-scale tests to evaluate process design.
- Designed and contrasted a laboratory-scale test system.

Next Steps

- Continued synthesis and testing of “Generation 3” ILs.
- Construct and operate lab-scale test system using conventional solvent and Phase III IL.
- Finalize economic, engineering, and systems analyses.

Available Reports/Technical Papers/Presentations

W. F. Schneider and E. Mindrup, “First-Principles Evaluation of CO₂ Complexation In Functionalized Ionic Liquids,” Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, PA, August 17–21, 2008.

K. E. Gutowski and E. J. Maginn, “Amine-Functionalized Task Specific Ionic Liquids for CO₂ Capture,” Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, PA, August 17–21, 2008.

Joan F. Brennecke, “CO₂ 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, PA, August 17, 2008.

E. M. Mindrup and W. F. Schneider, “Comparison of Functionalized Amine Energetics for CO₂ Capture,” poster presented at the AIChE Annual Meeting, Philadelphia, PA 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, PA 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 CO₂ Capture Success*. Final Report to U.S. Department of Energy, National Energy Technology Laboratory (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 CO₂ 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 CO₂ from Molecular Simulation," *Journal of the American Chemical Society*, 2008, 130, 14690–14704.

E. J. Maginn, Developing New Ionic Liquids for CO₂ Capture: A Success Story for Thermodynamics and Computational Molecular Design, GE Global Research Symposium on Emissions and Aftertreatment, GE Global Research Center, Niskayuna, NY, Sept. 17, 2009.

Marcos Perez-Blanco and Edward J. Maginn, "Molecular Dynamics Simulations of CO₂ 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 CO₂ 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 CO₂ separations," Division of Fuel Chemistry, American Chemical Society National Meeting, Boston, MA, 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 CO₂ 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 CO₂ Capture," Clearwater Clean Coal Conference, Clearwater, FL, June 6–10, 2010.

Edward J. Maginn, "Molecular engineering of new ionic liquid sorbents for CO₂ capture" at the 9th Annual Carbon Capture and Sequestration Meeting, Pittsburgh, PA, May 2010.

Edward J. Maginn, Joan F. Brennecke, William F. Schneider, and Mark J. McCready, "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO₂ Capture", NETL CO₂ Capture Meeting, Pittsburgh, PA, Sept 13, 2010.

CO₂ CAPTURE FROM FLUE GAS BY PHASE TRANSITIONAL ABSORPTION

Primary Project Goals

Hampton University is demonstrating the techno-economic viability of the phase transitional absorption process, which is a novel, innovative, low-cost, and low-energy-consuming carbon dioxide (CO₂) capture technology relative to the mainstream amine-based technology.

Technical Goals

To understand the mechanisms of phase transitional absorption by measuring absorption kinetics, regeneration rate, loading capacity, absorbent losses, and regeneration energy losses; and further to compare with other methods, such as the state-of-art monoethanolamine 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 CO₂ capture. The absorbent, after absorbing CO₂ from flue gas in an absorber, flows into a settler where it is separated into two phases: a CO₂-rich phase and a CO₂-lean phase. The CO₂-rich solvent is then sent to a regenerator for regeneration. After regeneration, the solvent is cooled and mixed with the CO₂-lean phase and sent to an absorber to complete the cycle. The absorbent is characterized as phase transitional absorbent due to its ability to separate the concentrated CO₂-rich phase from CO₂-lean phase. 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.

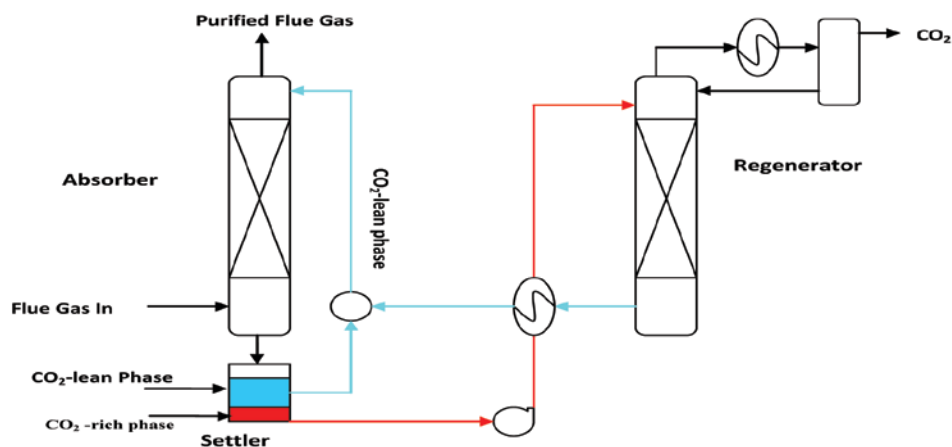


Figure 1: Concept Flow Diagram of Phase Transitional Absorption

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 absorbent separates into two phases, and only the CO₂-rich phase needs to be regenerated. The CO₂-rich phase is only approximately 20% of the total absorbent. Thus, the pumping and heating requirements are significantly less compared to the MEA process.

Technology Maturity:

Laboratory-scale, simulated flue gas

Project Focus:

Phase Transitional Absorption

Participant:

Hampton University

Project Number:

NT42488

NETL Project Manager:

Isaac Aurelio

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Partners:

None

Performance Period:

6/15/05 – 6/30/09

Another important feature of the phase transitional absorption is that the absorption rate of CO₂ will be enhanced by selecting the proper solvent, as shown in Figure 2.

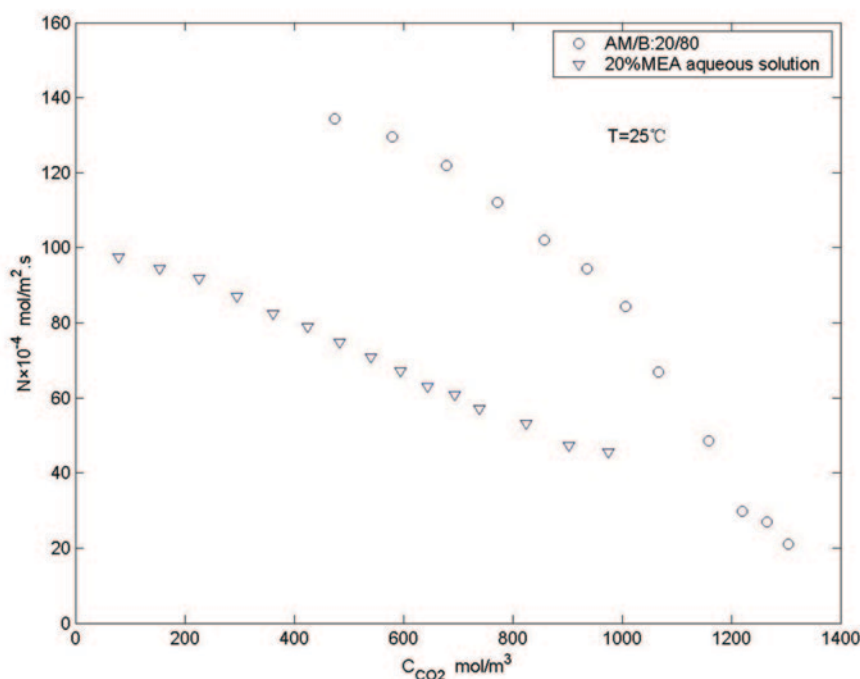


Figure 2: Absorption Rate Comparison (Phase Transitional Absorption vs. MEA Technology)

T = 25 °C; P_{CO₂} = 1 atm; N = 60 rpm; V_L = 900 ml.

Phase Transitional Absorption: activated agent: AM 20% by volume; solvent: B 80%.

MEA Technology: 20% (by volume) MEA aqueous solution.

Experimental results also showed that the temperature did not have strong impact on the absorption rate for the several absorbent 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 between 30 and 40% 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), and also 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

Parameter	Current R&D Value	Target R&D Value
Type of solvent	Non-aqueous amine	
Molecular weight	Varies	—
Boiling point (°C)	Varies	—
Heat of reaction (kJ/mole CO ₂)	—	—
CO ₂ loading/working capacity ¹ , wt%	20%	—
Solvent concentration to stripper (mol/liter)	—	—
Heat capacity of solution (kJ/K/kg)	—	—
Viscosity, cP	—	—

Table 1: Parameters for Phase Transitional Absorption Processes

	Parameter	Current R&D Value	Target R&D Value
Operating Conditions	Absorption temperature, °C	25–50	—
	Absorption pressure, atm	Atmospheric	—
	CO ₂ capture efficiency, %	>90	—
	Regeneration method	Thermal	—
	Regeneration temperature, °C	90–120	—
	Regeneration pressure, atm	Vacuum, 2 or 3	—
Heat Integration	Required regeneration steam temperature, °C	120	—
Miscellaneous	Solvent make-up rate, kg/kg CO ₂	N/A	—
Product Quality	CO ₂ purity, %	99.9%	—
	N ₂ concentration, %	—	—
	Other contaminants, %	—	—
Process Performance	Electricity requirement, kJ/kg CO ₂	—	—
	Heat requirement, kJ/kg CO ₂	1,000 (heat)	—
	Total energy (electricity equivalent), kJ/kg CO ₂	—	—

Note:

1. Working capacity is the loading difference CO₂-rich solution before and after it is regenerated.

Technology Advantages

- Greatly reducing regeneration energy comparing with MEA process.
- Higher absorption rate, resulting in lower capital investment for absorption equipment.
- Higher CO₂ working capacity, which will reduce sensible heat and solvent volume in circulation.
- Low corrosion rate to carbon steel compared to 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% 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 CO₂ 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

The project is completed.

Available Reports/Technical Papers/Presentations

Hu, Liang, Monica Wood, Joseph Hoque. "CO₂ Capture from Flue Gas by Phase Transitional Absorption." <http://www.netl.doe.gov/publications/proceedings/07/ucr/abstracts/Hu.pdf> (Accessed 9/28/2009).