DOE/NETL ADVANCED CARBON DIOXIDE CAPTURE R&D PROGRAM: TECHNOLOGY UPDATE

SEPTEMBER 2010

U.S. DEPARTMENT OF ENERGY

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DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update

September 2010

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ACKNOWLEDGEMENTS

This report was sponsored by the U.S. DOE's Existing Plants Program and Sequestration Program at the National Energy Technology Laboratory (NETL). The authors would like to express their appreciation to all those individuals who contributed to the successful preparation of the report. This especially includes Lynn Brickett, Director of Existing Plants Projects Division and John Litynski, Director of Sequestration Projects Division. Special thanks also to the following NETL project managers for their input and review of the individual project technology sheets included in this report: Andrew Jones, Timothy Fout, Susan Maley, Steven Markovich, Sara Zenner, Ronald Breault, Robin Ames, Robie Lewis, Robert Patton, Richard Read, Richard Dunst, Paula Flenory, Morgan Mosser, Kamalendu Das, Jose Figueroa, John Stipanovich, Jenny Tennant, Jason Hissam, Isaac Aurelio, Elaine Everitt, Edgar Klunder, Don Krastman, David Lang, Daniel Driscoll, Arun Bose, Arthur Baldwin, Andrew O'Palko, Bruce Lani, Norman Popkie, and Patricia Rawls. In addition, valuable information on work being conducted by NETL's Office of Research and Development was provided by Dave Luebke, Hank Pennline, and Tom Ochs. We would also like to acknowledge the invaluable critique of the draft report by Joe Giardina and Judy Gerba of Leonardo Technologies, Inc. The authors also want to thank Nick Fryer and Sara Lucas, Performance Results Corporation, for their work in providing the graphic design for the report. Finally, special thanks to all of the project researchers who contributed to the preparation of the individual CO_2 capture technology R&D status sheets that appear in the appendix to this report.

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MESSAGE TO STAKEHOLDERS

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 coal-based power plants. Under this program, DOE's National Energy Technology Laboratory (DOE/NETL) is funding the R&D of the next generation of advanced capture concepts for coal-based power plants. Research projects are carried out using various funding mechanisms – including partnerships, cooperative agreements, and financial assistance grants – with corporations, small businesses, universities, nonprofit organizations, and other national laboratories and government agencies. Current efforts cover not only improvements to state-of-the-art technologies, but also the development of several innovative concepts, such as metal organic frameworks and ionic liquids. In addition, DOE/NETL is conducting technical-economic analyses to establish the baseline cost and performance for current CO_2 capture technologies and determine the feasibility of advanced capture and compression technologies.

The overall goal of DOE/NETL's CO_2 capture R&D program is to develop advanced technologies that achieve 90 percent CO_2 capture at less than a 10 percent increase in the levelized cost of electricity (COE) of pre-combustion capture for integrated gasification combined cycle (IGCC) power plants and less than a 30 percent increase in COE of post- and oxy-combustion capture for new and existing conventional coal-fired power plants. Given the significant economic penalties associated with currently available CO_2 capture technologies, significant improvements in both cost and energy efficiency will be required to achieve these goals. Critical R&D milestones include the continuation of laboratory- through pilot-scale testing of a broad spectrum of CO_2 capture approaches including advanced solvents, sorbents, membranes, oxy-combustion, and chemical looping combustion that began in 2008; initiation of multiple slipstream tests of the most promising of these CO_2 capture technologies in 2010; and initiation of 25 MWe demonstrations of CO_2 capture technologies by 2016. It is anticipated that successful progression from laboratory- to large-scale demonstration will result in several of these advanced technologies being available for commercial deployment sometime between 2020 and 2030.

The purpose of this report is to provide an update on the R&D efforts of advanced CO_2 capture technologies for coal-based power systems being conducted by DOE/NETL. The report tracks the progress of DOE/NETL CO_2 capture related technology developments and is intended to be updated annually. Chapter 1 provides an overview of the importance of developing cost-effective advanced CO_2 capture technologies to enable the U.S. coal-based power generation industry comply with anticipated Federal and/or state regulations. A description of DOE/NETL's CO_2 capture R&D program is included in Chapter 2. A brief discussion of the three basic configurations for CO_2 capture – pre-combustion, post-combustion, and oxy-combustion – is provided in Chapter 3. Chapter 4 provides a brief explanation of some of the basic scientific principles and important operating parameters for the various CO_2 capture technologies. Chapters 5 through 10 report on the status of DOE/NETL's R&D efforts for pre-combustion capture; post-combustion capture; oxy-combustion; oxygen production; chemical looping; and advanced compression, respectively. Chapter 11 includes a discussion of DOE/NETL's CO_2 capture R&D collaborations. Finally, the Appendix provides detailed information on the status and results of the current portfolio of DOE/NETL's CO_2 capture R&D projects.

CHAPTER 1:

INTRODUCTION

The purpose of this report is to provide an update on the R&D of advanced CO_2 capture technologies for coal-based power systems being conducted by DOE/NETL. While efforts are focused on capturing CO_2 from the flue gas or synthesis gas (syngas) of coal-based power plants, these capture technologies should be applicable to natural-gas and oil-fired power plants and other industrial CO_2 sources. Intended to be updated annually, the report tracks the progress of DOE/NETL's CO_2 capture related technology developments. DOE/NETL's CO_2 capture R&D program currently funds a broad portfolio of research projects in three primary technology pathways – pre-, post-, and oxy-combustion. The majority of the technology options being considered are still in the laboratory- and bench-scale stages of development. Additional information on DOE/NETL's CO_2 capture R&D effort is available in a companion document, entitled "Carbon Capture and Storage 2010 Roadmap."

Coal-based power plants currently generate approximately 50 percent of the electricity in the United States (see Figure 1-1) and coal is expected to continue to play a critical role in powering the Nation's electricity generation for the foreseeable future. DOE's Energy Information Administration (EIA) projects that the 308 gigawatts (GW) of coal-based electricity generating capacity currently in operation will increase to 323 GW by 2030.[i] However, electricity production from coal-based power plants is under scrutiny due to concerns that anthropogenic emission of greenhouse gases (GHG), such as CO_2, are contributing to global climate change.

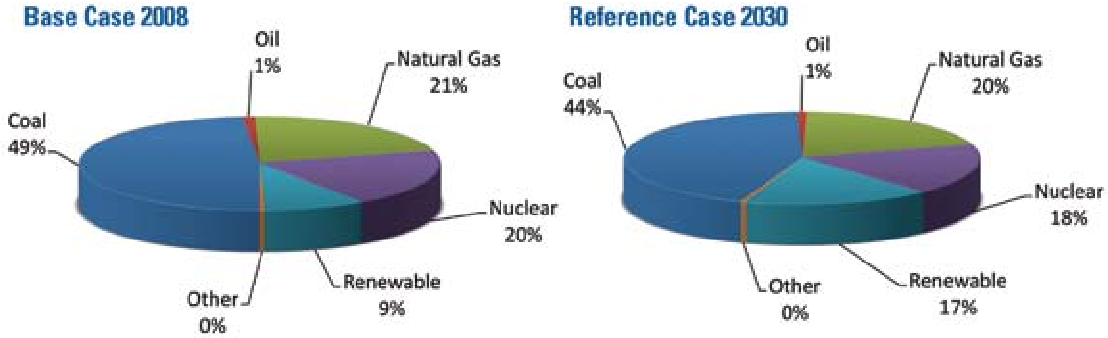


Figure 1-1: U.S. Electricity Generation by Fuel Type

Federal legislation and/or regulation could soon be enacted that would limit CO_2 emissions from the U.S. power generation sector to address these concerns. According to EIA estimates, fossil fuels accounted for approximately 71 percent of total U.S. electricity generation and produced over 40 percent of the 5.8 billion metric tons of total U.S. anthropogenic CO_2 emissions in 2008. Coal-based power plants consumed over 1 billion tons of coal that produced 1.9 billion metric tons of CO_2 emissions, which comprised almost 34 percent of total U.S. anthropogenic CO_2 emissions. Figure 1-2 shows the source of U.S. anthropogenic CO_2 emissions by fuel type. Moreover, EIA estimates that almost 95 percent of the coal-based CO_2 emissions projected to be released from today through 2030 will originate from existing coal-based power plants.[i] Therefore, both existing and new coal-based power plants would likely be targeted for reduction should Federal legislation and/or regulation be enacted to reduce CO_2 emissions from the power sector.

There are several options available to decrease CO_2 emissions from the power sector, including demand-side conservation, supply-side efficiency improvement, potential increases in nuclear and renewable energy supplies, and implementation of carbon capture and storage (CCS) on coal-based power plants. DOE/NETL and other scientific experts – such as the Environmental Protection Agency (EPA), the Electric Power Research Institute (EPRI), and the Intergovernmental Panel on Climate Change (IPCC) – believe that CCS represents the sole practical option to achieve considerable CO_2 emission reductions from fossil-fueled power plants. The CCS process includes three primary steps: CO_2 capture; compression and transport; and storage. The three general categories of CO_2 capture technologies that can be applied to coal-based power plants are pre-combustion; post-combustion; and oxy-combustion. Pre-combustion capture is applicable to integrated gasification combined cycle (IGCC) power plants, while post-combustion and oxy-combustion capture could be applied to conventional pulverized coal-fired (PC) power plants. These three methods for CO_2 capture will be discussed in more detail in Chapter 3. The captured CO_2 could be transported via pipeline or tanker car to a permanent storage site. The CO_2 would then be stored underground in geologic formations such as depleted oil and gas fields, saline formations, and unmineable coal seams.

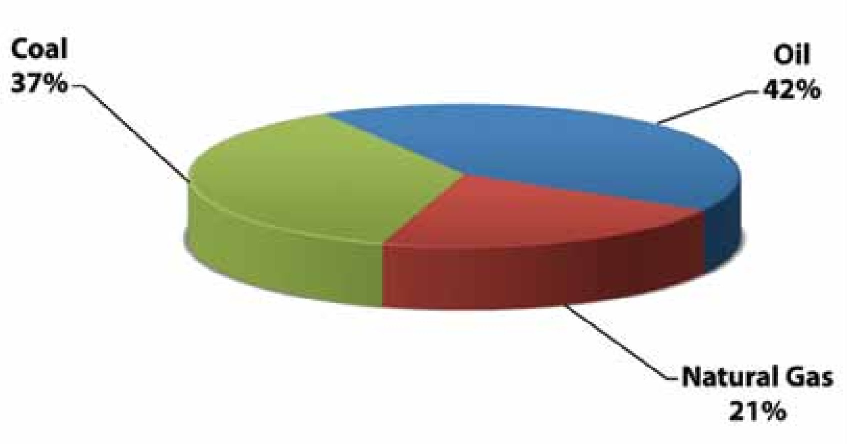


Figure 1-2: Source of U.S. CO_2 Emissions by Fuel Type in 2008

There are commercially-available CO_2 capture technologies that are being used in various industrial applications. However, in their current state of development these technologies are not ready for implementation on coal-based power plants for three primary reasons: 1) they have not been demonstrated at the larger scale necessary for power plant application; 2) the parasitic loads (steam and power) required to support CO_2 capture would decrease power generating capacity by approximately one-third; and 3) if successfully scaled-up, they would not be cost effective at their current level of process development.

Figure 1-3: Net Plant Efficiency with and without CO_2 Capture and Compression

The net electrical output from a coal-based power plant employing currently available CO_2 capture and compression technologies will be significantly less than that for the same plant without capture. This is because some of the energy – thermal and electrical – produced at the plant must be used to operate the CO_2 capture and compression processes. Steam usage decreases the gross electrical generation, while the additional auxiliary power usage decreases the net electrical output of the power plant. Figure 1-3 shows the change in net plant efficiency as a result of implementing currently available CO_2 capture and compression technologies on hypothetical conventional PC, IGGC, and NGCC power plants.

DOE/NETL analyses indicate that for a new 550 MWe net output power plant, addition of currently available pre-combustion CO_2 capture and compression technology increases the capital cost of an IGCC power plant by $290 million (20 percent) compared with the non-capture counterpart. For a similarly sized new supercritical PC plant, post-combustion and oxy-combustion capture would increase capital costs by $860 million (80 percent) and $708 million (65 percent) respectively. For post-combustion CO_2 capture on a similarly sized new NGCC plant, the capital cost would increase by $300 million or 80 percent.

Figure 1-4 presents a comparison of the levelized cost of electricity (LCOE) for various power plant configurations both with and without CO_2 capture. For example, the LCOE for a new IGCC plant is 110 $/MWh without CO_2 capture, but increases approximately 45 percent to almost 160 $/MWh with pre-combustion CO_2 capture. Likewise, the LCOE for a new PC plant is approximately 85 $/MWh without CO_2 capture, but increases approximately 80 percent to almost 155 $/MWh with post-combustion CO_2 capture. Figure 1-4 also shows the cost of CO_2 capture in terms of avoided cost as measured by $/ton CO_2. The avoided cost is calculated by dividing the difference in LCOE, $/MWh, by the difference in CO_2 emissions with and without CO_2 capture, ton/MWh.

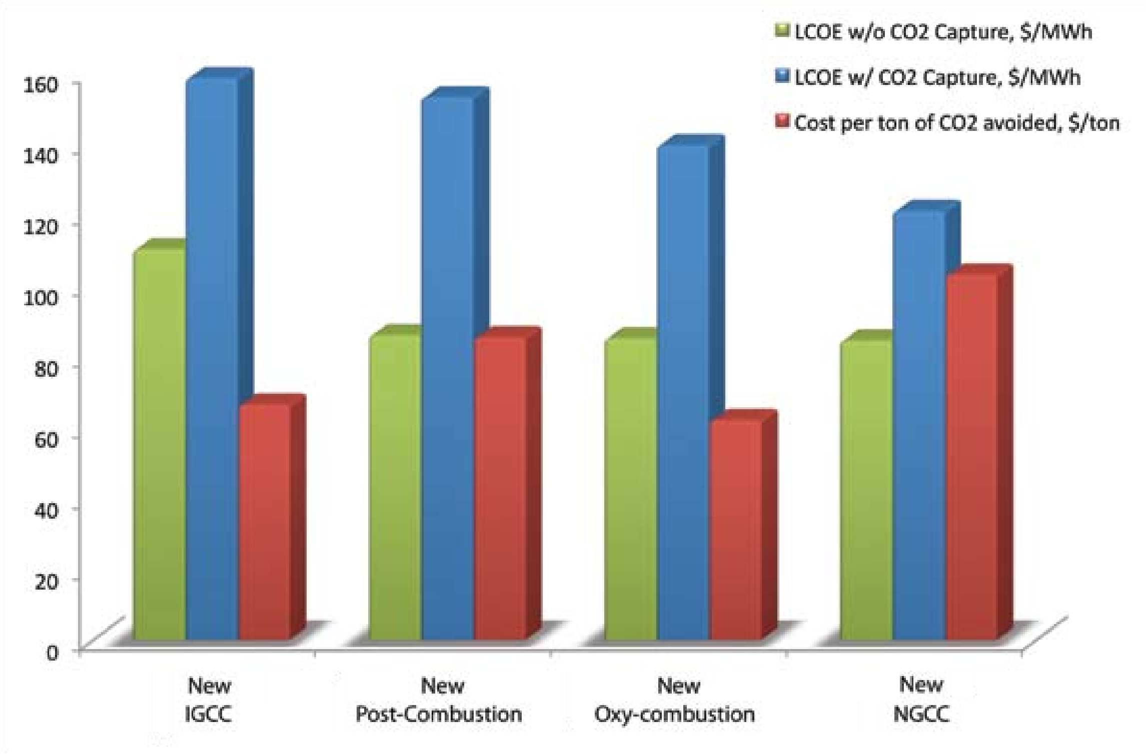


Figure 1-4: CO_2 Capture Costs for Different Types and Configurations of Power Plants

Other major technical challenges associated with the application of currently available CO_2 capture technologies to coal-based power plants include energy integration, flue gas contaminants, water use, CO_2 compression, and oxygen (O_2) supply for oxy-combustion systems. Therefore, further R&D of CO_2 capture technology is needed to ensure that this can be done cost-effectively. Table 1-1 provides an overview of the key technical challenges.

TABLE 1-1: CO_2 CAPTURE KEY TECHNICAL CHALLENGES

Parameter	Technical Challenge
Scale-Up	While industrial-scale CO_2 separation processes are now commercially available, they have not been deployed at the scale required for large power plant applications and consequently, their use could significantly increase electricity production costs.
Cost-Effectiveness	Recent studies conducted by NETL show that current technologies are expensive and energy-intensive, which seriously degrade the overall efficiency of both new and existing coal-fired power plants. For example, installing the current state-of-the-art post-combustion CO_2 capture technology – chemical absorption with an aqueous monoethanolamine (MEA) solution – is estimated to increase the levelized COE by about 75 to 80 percent.
Auxiliary Power	A significant amount of auxiliary power is required to operate currently available CO_2 capture technologies. The auxiliary power decreases the net electrical generation of the power plant.
Steam Usage	The large quantity of energy required to regenerate the solvent in commercially-available CO_2 capture technologies (~1,550 British thermal units [Btu] per pound of CO_2 removed) significantly reduces net power plant efficiency.
Energy Integration	The energy required to regenerate the solvent in commercially available CO_2 capture technologies would be provided by steam extraction from the power plant. This activity requires careful integration of the power plant steam cycle to the CO_2 capture technology.
Flue Gas Contaminants	Constituents in the flue gas, particularly sulfur, can contaminate CO_2 capture technologies, leading to increased operational expenses.
Water Use	A significant amount of water use is required for CO_2 capture and compression cooling.
CO_2 Compression	To enable sequestration, significant power is required to compress the captured CO_2 to typical pipeline levels (1,500 to 2,200 psia depending on sequestration scheme and location). Reducing this power requirement is essential to improving overall plant efficiency and facilitating CO_2 sequestration at both existing and future power plants.
Oxygen Supply	An oxy-combustion power plant requires a supply of high-purity oxygen. Currently available technology – cryogenic air separation unit (ASU) – is energy and capital intensive.

CHAPTER 2:

DOE/NETL CARBON DIOXIDE CAPTURE R&D PROGRAM

DOE's CCS R&D effort is conducted under the overarching Clean Coal Research Program. The Program is administered by the DOE Office of Clean Coal and 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.

DOE/NETL has adopted a comprehensive, multi-pronged approach to the R&D of advanced CO_2 capture technologies for coal-based power plants. The success of this research will enable cost-effective implementation of 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. As shown in Figure 2-1, there are numerous DOE/NETL R&D programs that are contributing to the CO_2 capture R&D effort.

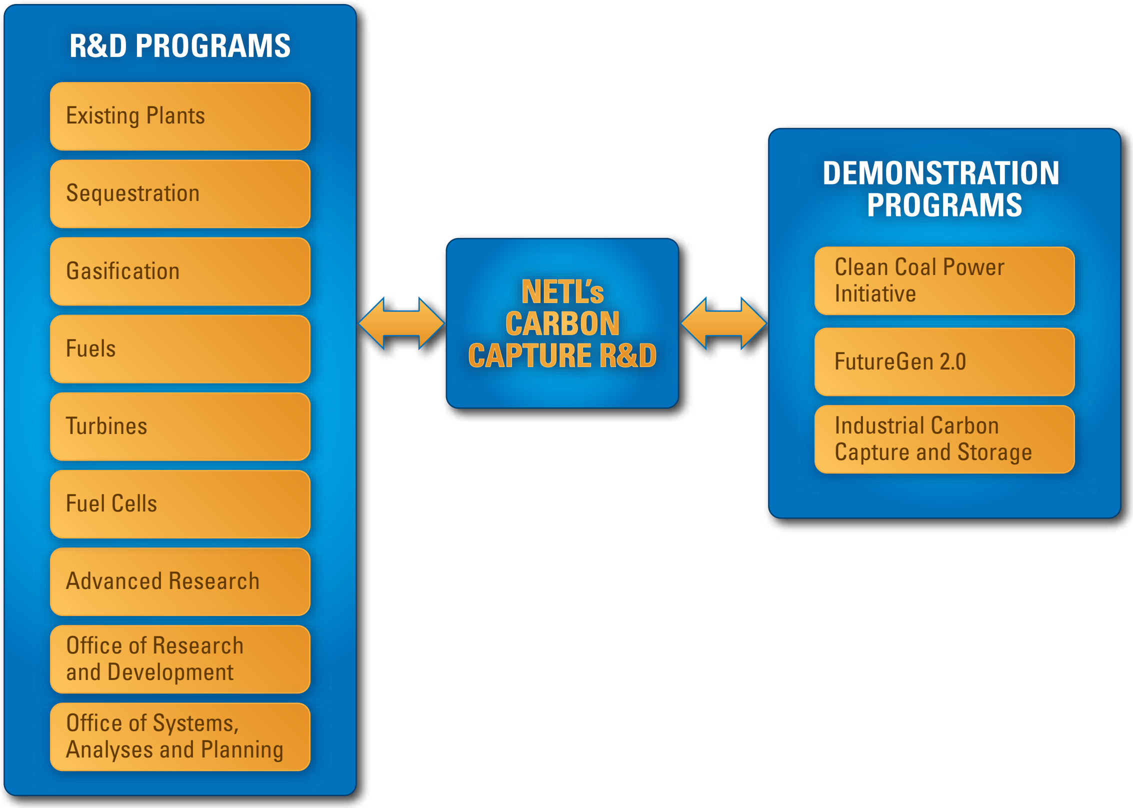


Figure 2-1: NETL Programs Associated with Carbon Capture R&D

Currently, the Clean Coal Research Program comprises nine distinct program areas: Innovations for Existing Plants (IEP), Advanced Integrated Gasification Combined Cycle (IGCC), Advanced Turbines, Carbon Sequestration (CS), Solid State Energy Conversion Alliance (SECA) Fuel Cells, Fuels, FutureGen, CCPI, and Advanced Research (AR). The IEP program area focuses on developing post- and oxy-combustion CO_2 capture technologies and advanced compression technologies that are applicable to new and existing pulverized coal (PC) power plants. The CS program area plays a lead role in pre-combustion CO_2 emissions control for IGCC power plants and CO_2 storage technology development with a focus on geological sequestration and its associated monitoring, verification, and accounting. Additional R&D of pre-combustion CO_2 capture technologies also conducted under the IGCC and Fuels program areas is focused on advanced membrane-based systems for the separation of H_2 and CO_2 in coal-derived syngas. In addition, DOE/NETL's Office of Systems, Analyses, and Planning (OSAP) is conducting technical-economic analyses to establish the baseline cost and performance for current CO_2 capture technologies; track the cost and performance of new CO_2 capture technologies under development relative to DOE/NETL's goals; and determine the feasibility of novel capture and compression technologies.

NETL's CO_2 capture R&D program is pursuing a wide variety of advanced CO_2 capture technologies, including liquid solvents, solid sorbents, membranes, oxy-combustion, and chemical looping combustion. Current R&D studies also include development of several innovative concepts, such as metal organic frameworks (MOFs) and ionic liquids (ILs). It is anticipated that successful progression from laboratory- to full-scale demonstration will result in several of these technologies being available for commercial deployment by 2030.

The overall goal of DOE/NETL's carbon capture R&D is to develop advanced technologies that achieve 90 percent CO_2 capture at less than a 10 percent increase in COE for pre-combustion capture for IGCC power plants and less than a 30 percent increase in COE for post- and oxy-combustion capture for new and existing coal-fired power plants. Given the significant economic penalties associated with currently available CO_2 capture technologies, step-change improvements in both cost and energy efficiency will be required to achieve this goal.

DOE/NETL CO_2 CAPTURE R&D PROCESS

The development of an advanced CO_2 capture technology includes more than just a laboratory-scale evaluation of the process chemistry and associated operating parameters before it can be commercialized. The research effort can also require the development of a new or improved manufacturing process to commercially produce the chemicals and/or devices used to support the process. Just as important is conducting systems analyses to evaluate the cost-effective integration of the process into the power plant thermodynamic cycle. Figure 2-2 presents the various R&D components that might be necessary to take a capture technology from concept to commercial reality.

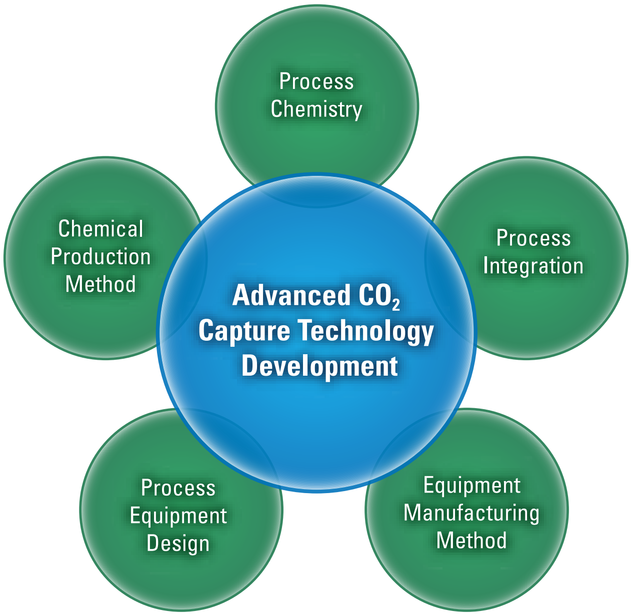


Figure 2-2: Components of CO_2 Capture Technology Development

Upon completion of laboratory- and bench-scale testing, it is necessary to conduct pilot-scale slipstream testing using actual flue gas to determine potential adverse effects on the process from minor constituents in the coal that are present in the syngas or combustion flue gas. For example, low concentrations of sulfur dioxide (SO_2) are known to degrade the performance of currently available solvent-based technologies. In addition, potential problems with excessive scaling, plugging, and/or corrosion of process equipment can only be evaluated and solutions developed via operating experience during long-term, pilot-scale slipstream or full-scale testing. After successful completion of pilot-scale testing, the process equipment can be further scaled-up to conduct large-scale field testing prior to commercial deployment of the technology.

Laboratory- and bench-scale testing is usually conducted with simulated flue gas at relatively low gas flow rates ranging from one to 100 standard cubic feet per minute (scfm). Small pilot-scale testing can also be conducted in a laboratory setting using coal combustors to generate flue gas for process testing with equivalent gas flow rates of approximately 10 scfm to 125 scfm. Based on previously announced field testing projects being conducted or planned by other organizations, it is anticipated that the flue gas design flow rate for DOE/NETL's large pilot-scale slip-stream testing would be in the range of 1,000 scfm to 12,000 scfm. For comparison, one megawatt (MW) gross electric generation produces approximately 2,500 scfm of combustion flue gas.

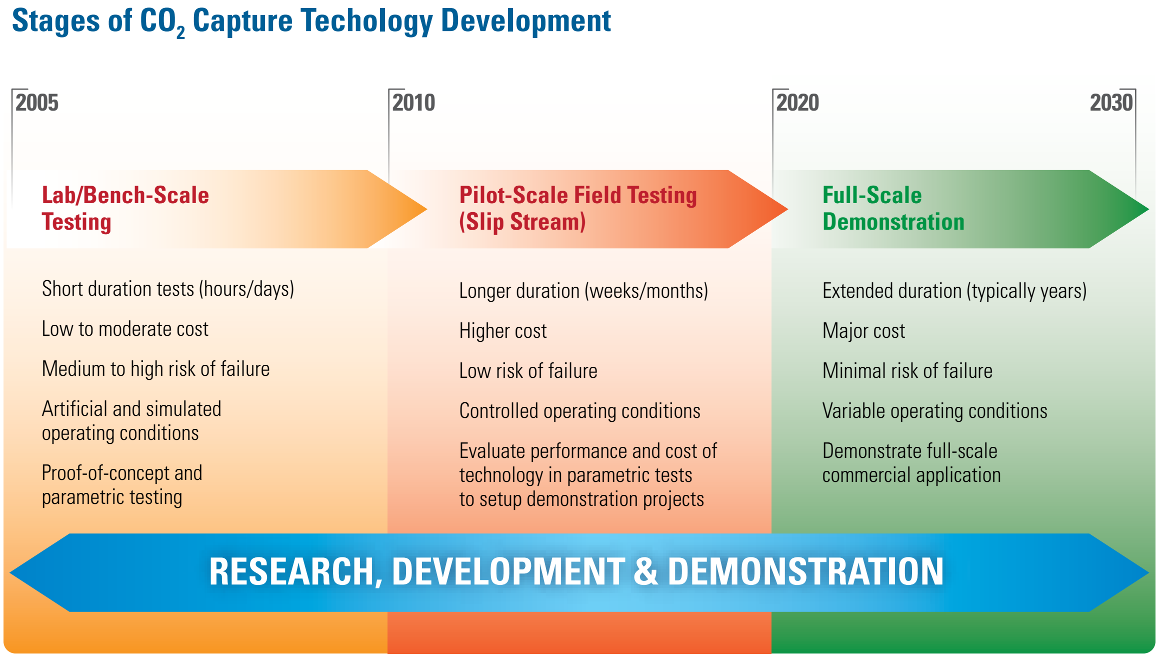


Figure 2-3: Stages of CO_2 Capture Technology R&D

Figure 2-3 describes the various stages of R&D scale-up. An example of the scale-up process is the R&D being conducted by Membrane Technology and Research, Inc. (MTR) to develop a new membrane-based post-combustion CO_2 capture technology. In April 2007, MTR initiated a two-year R&D project with DOE/NETL. MTR's first phase of R&D included bench-scale testing of various membrane designs using a simulated gas flow rate of approximately 2.5 scfm. Based on successful bench-scale testing, MTR initiated a follow-up project with DOE/NETL in October 2008 to conduct a small pilot-scale field test that should be completed in 2010. The approximately 175 scfm pilot-scale slipstream testing is being conducted at the Arizona Public Services coal-fired Cholla Power Plant located near Holbrook, Arizona. Upon successful completion of the small pilot-scale testing, MTR plans to conduct large pilot-scale testing of a proof-of-concept system based on a gas flow rate of approximately 5,000 scfm to 10,000 scfm.

DOE/NETL IN-HOUSE CO_2 CAPTURE RESEARCH

DOE/NETL's Office of Research and Development (ORD) is developing new breakthrough concepts for CO_2 capture that could lead to dramatic improvements in cost and performance relative to today's technologies. ORD's research portfolio includes projects conducted at NETL laboratories, as well as research conducted through partnerships, cooperative research and development agreements (CRADAs), and contractual arrangements with universities and the private sector. The ORD research includes activities led by research scientists based at NETL sites in Pittsburgh, PA, Morgantown, WV, and Albany, OR, as well as faculty investigators from the NETL-Regional University Alliance (NETL-RUA), which includes Carnegie-Mellon University, the University of Pittsburgh, West Virginia University, Penn State University, and Virginia Tech. ORD is conducting experimental studies with numeric simulations to guide CO_2 capture technology development. The following is a brief overview of some of ORD's CO_2 capture research activities.

Pre-Combustion CO_2 Capture

ORD is investigating the use of ionic liquids both as solvents and as complexing agents within membranes. Ionic liquids tested at NETL have shown a capacity for CO_2 that exceeds existing commercial solvents, and can operate at high temperature. Testing is being conducted to characterize the ability of the ionic liquids to selectively absorb CO_2 over the water vapor in synthesis gas. Assuming significant water absorption can be avoided, ORD plans to conduct a system study to determine the application of ionic liquid solvents for synthesis gas CO_2 capture.

ORD researchers are also developing a CO_2 membrane technology using "facilitated transport" in supported ionic liquids. These membranes have demonstrated excellent permeability and selectivity. Further developments will improve membrane supports and tolerance to gas impurities. The goal of the research is to develop a practical membrane module for testing on coal synthesis gas, possibly at the DOE National Carbon Capture Center.

ORD has also developed several different types of sorbents that can capture CO_2 in warm synthesis gas. These sorbents can operate at higher temperatures and can be used to capture CO_2 while at the same time promoting hydrogen production through the water-gas-shift reaction. The goal of the research is to propose a virtual reactor design that can use the sorbents and, based on laboratory test data, evaluate the potential benefit of continued development.

New sorbent classes for syngas CO_2 separation are also being developed. A new class of metal organic frameworks (MOFs) has been developed that responds to changes in CO_2 pressure with a change in lattice geometry that allows or excludes CO_2 based on the pressure. Phase-change sorbents have been identified that show the ability to capture CO_2 with a concurrent phase transition from solid to liquid. In these materials, the solid phase essentially dissolves in CO_2, and the CO_2 can be released from the liquid with a modest pressure reduction. ORD is also exploring the potential of zeolitic imidazolate frameworks (ZIFs) that may have superior CO_2 capacity and durability compared to the mature MOFs.

Post-Combustion CO_2 Capture

ORD has developed sorbents that appear to show advantages in regeneration energy compared to conventional solvent scrubbing. The emphasis of continuing work is to develop both the sorbent and reactor system. ORD's success in sorbent development is illustrated by recent interest in testing and licensing sorbents or sorbent reactor systems patented by NETL. Ongoing tests focus on quantifying the effect of flue gas moisture on sorbent regeneration energy. ORD is using numeric modeling to devise and optimize the reactors needed for the multi-phase flow process.

Computational chemistry models are being used to screen a multitude of materials for the optimal balance between regeneration energy, working capacity and absorption kinetics. ORD is also evaluating techniques based on pharmaceutical nano-technology to control adsorption film deposition for rapid commercial manufacture of sorbents with ideal chemistry and surface area. Additional fundamental studies are being used to understand how CO_2 interacts with surfaces so that future sorbents can be designed with maximum performance with minimal degradation and regeneration energy. New concepts like amino acids are being studied to determine if biomimetic techniques can be used to produce stable sorbents based on natural compounds that absorb CO_2.

Oxy-Combustion

ORD is conducting research focused on developing supporting technologies for oxy-combustion CO_2 capture. ORD is using lab-scale fundamental studies to address basic issues associated with combustion and heat transfer in the oxy-combustion environment. Heat transfer data and combustion data from larger-scale tests are used to evaluate/validate numeric model predictions so that future oxy-combustion designs can be based on validated numeric model predictions. NETL has also licensed an emissions control technology known as integrated pollutant removal (IPR) to Jupiter Oxygen Corporation that is being tested in a pilot-scale oxy-combustion boiler.

ORD is also studying the impact of ash and combustion products unique to the oxy-combustion environment on the component materials of construction. Research is focusing on the impact of increases in the levels of these constituents and potentially higher operating temperatures on material life times to determine whether existing materials can meet these more demanding performance criteria, or whether more corrosion- and temperature-resistant materials will be required. Another ORD research activity is development of sensors that can be used to characterize and control oxygen levels in the boiler. Oxygen distribution is expected to be more critical in oxy-combustion systems (compared to air firing) because of the desire to operate with minimal excess oxygen. One effort is aimed at developing a wireless sensor system that could be used to evaluate oxygen levels on oxy-combustion boiler applications. Another ORD research activity is focused on developing oxygen separation membranes/concepts specifically for pulverized coal oxy-combustion systems.

Chemical Looping

ORD is also conducting research focused on developing chemical looping combustion and supporting technologies for CO_2 capture. The current emphasis of the research is to define a virtual demonstration of a chemical looping combustion power plant based on laboratory data. Chemical looping is a highly complex, nonlinear process for which traditional methods of scale-up design are not appropriate due to the large number of dimensionless parameters. Accordingly, a reliable predictive tool is needed that numerically includes these nonlinear interactions. ORD is developing a working lab-scale solid fuel chemical looping reactor that will be a key to developing and validating the model to evaluate and scale-up the process, testing promising oxygen carrier materials, assessing attrition and makeup rates, assessing separation/recycle processes for O_2 carriers, testing advanced instrumentation, and providing input for economic analysis. ORD is also conducting experiments needed to define the kinetics and transport behavior of chemical looping carriers. These data will be used to develop the virtual model and also guide laboratory development of the needed oxygen carriers.

In addition to chemical looping combustion, ORD is conducting basic studies of chemical looping applied to gasification systems. One of the key issues with gasification is enhancing gasification rates by means of improved surface chemistry. Fundamental studies for gasification schemes of oxygen carriers include development of high-surface area nano-particles of metals on hexaluminate supports, as well as development of so-called “aerogel” supports. The aerogels are a unique class of materials which could provide a high-surface area support for metal oxides, or even CO_2 sorbents.

DOE/NETL CO_2 CAPTURE TECHNOLOGY DEMONSTRATIONS

DOE/NETL’s Clean Coal Power Initiative (CCPI) and restructured FutureGen Programs are designed to provide incentives for the early deployment of advanced CO_2 capture technologies. The CCPI is an innovative technology demonstration program that fosters more efficient clean coal technologies for use in new and existing coal-based power plants. The intent of CCPI is to accelerate technology adoption and thus rapidly move promising new concepts to a point where private-sector decisions on deployment can be made. CCPI is currently conducting three pre-combustion and three post-combustion CO_2 capture demonstration projects (see Table 2-1) designed to capture, compress, transport and store the CO_2 in a saline formation or for beneficial reuse such as enhanced oil recovery. The pre-combustion projects involve CO_2 capture from IGCC power plants. The generating capacities at the demonstration facilities range from 257 to 582 MW. The demonstrations will be initiated between 2014 and 2016 and will operate for 2-3 years. The post-combustion projects will capture CO_2 from PC plant slipstreams representing the equivalent of 60 to 235 MW of power production. In August 2010, DOE/NETL announced the selection of an oxy-combustion CO_2 capture demonstration project that is being conducted under the FutureGen Initiative that will repower an existing 200 MW power plant located in Illinois.

TABLE 2-1: CO_2 CAPTURE DEMONSTRATION PROJECTS BEING CONDUCTED UNDER CCPI AND FUTUREGEN 2.0

Performer	Location	Capture Technology	Capture Rate (tonnes/year)	Start Date
Pre-Combustion Capture				
Summit Texas Clean Energy	Odessa, TX	Selexol	3,000,000	2014
Southern Company	Kemper County, MS	Selexol	2,000,000	2014
Hydrogen Energy California	Kern County, CA	Rectisol	2,000,000	2016
Post-Combustion Capture				
Basin Electric	Beulah, ND	Amine	500,000 - 1,000,000	2014
NRG Energy	Thompson, TX	Amine	~500,000	2015
American Electric Power	New Haven, WV	Chilled Ammonia	1,500,000	2015
Oxy-Combustion Capture				
FutureGen 2.0	Meredosia, IL	Oxy-Combustion	1,000,000	2015

In addition to the demonstrations under the CCPI program, additional CO_2 capture demonstration projects are being conducted under the Industrial Carbon Capture and Storage (ICCS) program. Several of the ICCS projects are pursuing capture technologies that are similar to those that are being demonstrated for power plants. These projects are of similar magnitude to the CCPI capture demonstrations (90 percent capture, 0.9-4 million tonnes/year captured).

TABLE 2-2: PROJECTS SELECTED UNDER THE INDUSTRIAL CARBON CAPTURE AND STORAGE INITIATIVE

Performer	Location	Capture Technology	Product	Capture Rate (tonnes/year)	Start Date
Leucadia Energy, Lake Charles	Lake Charles, LA	Rectisol	Methanol	4,000,000	2014
Archer Daniels Midland	Decatur, IL	Amine	Power, Ethanol	900,000	2014
Air Products	Port Arthur, TX	Amine	Hydrogen	900,000	2013

CHAPTER 3:

GENERAL APPROACHES TO CARBON DIOXIDE CAPTURE

In general, CO_2 capture technologies can be categorized into three approaches – pre-, post-, and oxy-combustion. Pre-combustion systems are designed to separate CO_2 from H_2 and other constituents in the high-pressure syngas stream produced for the IGCC power plant cycle. Post-combustion systems are designed to separate CO_2 from the flue gas – primarily nitrogen (N_2) – produced by fossil-fuel combustion in air. Oxy-combustion separates the O_2 from N_2 (via an air separation unit) before coal combustion takes place in the boiler. Removing the N_2 from the oxidant stream before combustion results in a CO_2 concentrated flue gas stream that, after a purification step, is essentially sequestration ready.

DOE/NETL is investigating a broad portfolio of research pathways in the three CO_2 capture technology approaches. Research efforts also address critical challenges to cost-effective commercial deployment including key enabling technologies such as O_2 supply for oxy-combustion and IGCC power plants. At this time, the majority of the technology options being considered are still in the laboratory- and bench-scale stage of development.

3.A PRE-COMBUSTION CO_2 CAPTURE

Pre-combustion capture is mainly applicable to gasification plants, where fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric O_2. A simplified process schematic for pre-combustion CO_2 capture is shown in Figure 3-1. By carefully controlling the amount of O_2, only a portion of the fuel burns to provide the heat necessary to decompose the remaining fuel and produce syngas, a mixture of H_2 and carbon monoxide (CO), along with minor amounts of other gaseous constituents. To enable pre-combustion capture, the syngas is further processed in a water-gas shift (WGS) reactor, which converts CO into CO_2 while producing additional H_2, thus increasing the CO_2 and H_2 concentrations. An acid gas removal system, such as Selexol™ , can then be used to separate the CO_2 from the H_2. Because CO_2 is present at much higher concentrations in syngas (after WGS) than in flue gas, and because the syngas is at higher pressure, CO_2 capture should be easier to achieve and therefore less expensive for pre-combustion capture than for post-combustion capture. After CO_2 removal, the H_2 is used as a fuel in a combustion turbine combined cycle to generate electricity. Another application, currently being developed under DOE's Fuel Cell Program, is to utilize the H_2 to power fuel cells with significantly increased overall plant efficiency. The advantage of this type of system is the higher CO_2 concentration (and corresponding partial pressure) and the lower volume of syngas to be handled, which results in smaller equipment sizes and lower capital costs. A more detailed description of pre-combustion CO_2 capture processes is provided in Chapter 4.

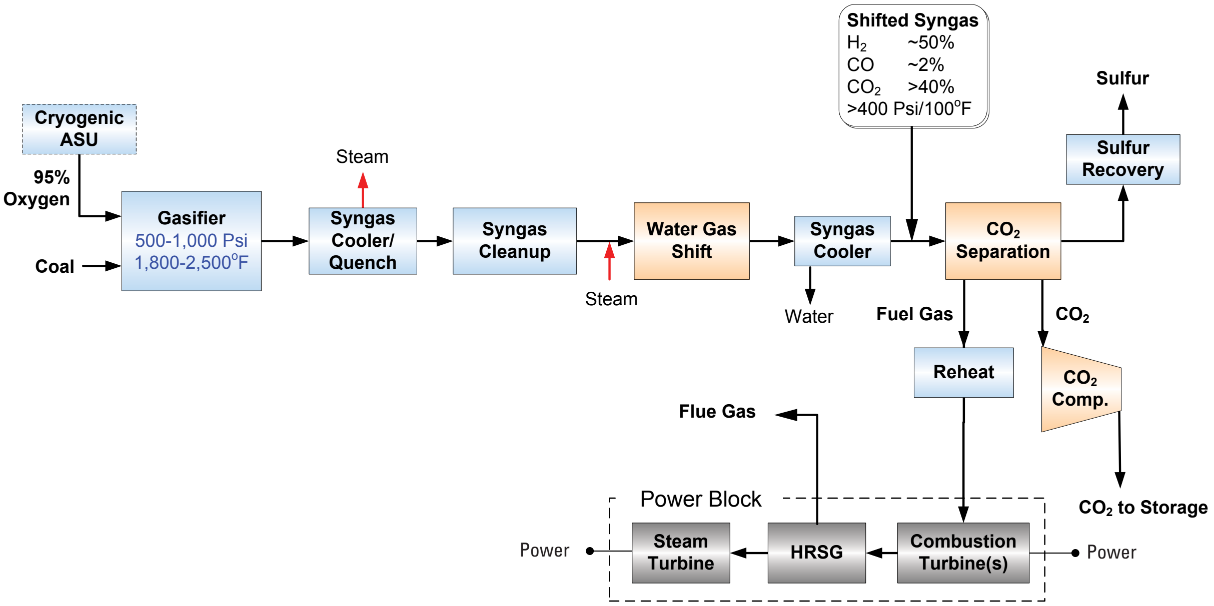


Figure 3-1: Block Diagram Illustrating Pre-Combustion System

3.B POST-COMBUSTION CO_2 CAPTURE

Post-combustion CO_2 capture refers to removal of CO_2 from combustion flue gas prior to discharge to the atmosphere. A simplified process schematic of post-combustion CO_2 capture is shown in Figure 3-2. In a typical coal-fired power plant, fuel is burned with air in a boiler to produce steam that drives a turbine/generator to produce electricity. Flue gas from the boiler consists mostly of N_2 and CO_2. The CO_2 capture process would be located downstream of the conventional pollutant controls. Chemical solvent-based technologies currently used in industrial applications are being considered for this purpose. The chemical solvent process requires the extraction of a relatively large volume of low pressure steam from the power plant's steam cycle, which decreases the gross electrical generation of the plant. The steam is required for release of the captured CO_2 and regeneration of the solvent. Separating CO_2 from this flue gas is challenging for several reasons: a high volume of gas must be treated because the CO_2 is dilute (13 to 15 volume percent in coal-fired systems, three to four volume percent in gas-fired turbines); the flue gas is at low pressure (15 to 25 pounds per square inch absolute [psia]); trace impurities (particulate matter [PM], sulfur oxides [SO_X], nitrogen oxides [NO_X], etc.) can degrade the CO_2 capture materials (i.e., solvents/sorbents/membranes); and compressing captured CO_2 from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load.

Post-combustion CO_2 capture offers the greatest near-term potential for reducing power sector CO_2 emissions because it can be retrofit to existing coal-based power plants and can also be tuned for various levels of CO_2 capture, which may accelerate market acceptance. Although post-combustion capture technologies would typically be applied to conventional coal-fired power plants, they can also be applied to the combustion flue gas from IGCC power plants, natural gas combined cycle (NGCC) power plants, and industrial facilities that combust fossil fuels. A more detailed description of post-combustion CO_2 capture processes is provided in Chapter 4.

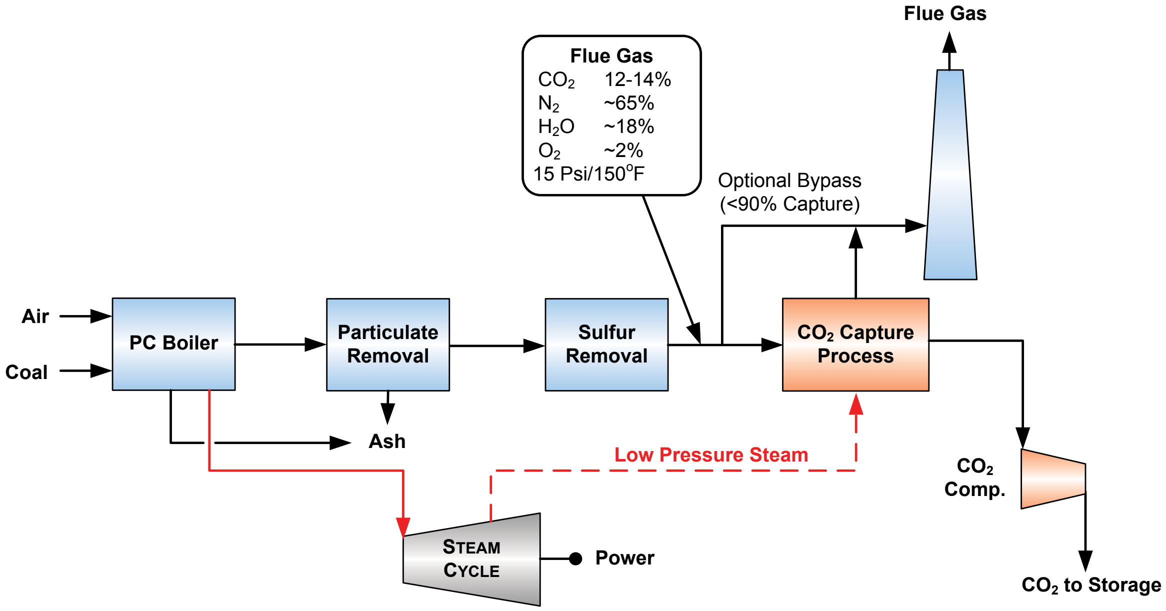


Figure 3-2: Block Diagram Illustrating Post-Combustion System

3.C OXY-COMBUSTION CO_2 CAPTURE

Oxy-combustion systems for CO_2 capture rely on combusting coal with relatively pure O_2 diluted with recycled CO_2 or CO_2/steam mixtures. Under these conditions, the primary products of combustion are water (H_2O) and CO_2, with the CO_2 separated by condensing the H_2O (see Figure 3-3). Oxy-combustion overcomes the technical challenge of low CO_2 partial pressure normally encountered in coal combustion flue gas by producing a highly concentrated CO_2 stream (~60 percent), which is separated from H_2O vapor by condensing the H_2O through cooling and compression. Flue gas recycle is necessary for oxy-combustion to approximate the boiler combustion and heat transfer characteristics of combustion with air. An additional purification stage for the highly concentrated CO_2 flue gas may be necessary to remove other minor gas constituents such as N_2, O_2, and argon in order to produce a CO_2 stream that meets pipeline and storage requirements. This purification step should have significantly less cost than a conventional post-combustion capture system due to the high CO_2 concentration and reduced flue gas volume. A more detailed description of oxy-combustion is provided in Chapter 4.

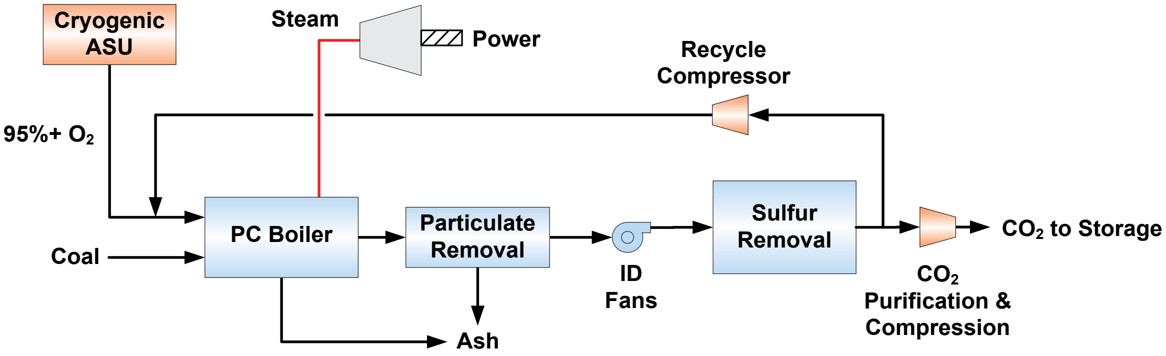


Figure 3-3: Block Diagram Illustrating Oxy-Combustion System

3.D CHEMICAL LOOPING

Chemical looping is an advanced technology similar to oxy-combustion in that it relies on combustion/gasification of coal in a N_2-free environment. However, rather than using an ASU, chemical looping involves the use of a metal oxide or other compound as an oxygen carrier to transfer O_2 from the air to the fuel. Subsequently, the products of combustion (primarily CO_2 and H_2O) are kept separate from the rest of the flue gases. Chemical looping can be applied in either coal combustion or coal gasification processes. A more detailed description of the chemical looping combustion and gasification CO_2 capture processes is provided in Chapter 4.

CHAPTER 4:

PRINCIPLES OF OPERATION FOR CARBON DIOXIDE CAPTURE

This chapter provides a brief overview of some of the basic scientific principles and important operating parameters for the various processes under development as CO_2 capture technologies under each of the general approaches discussed above in Chapter 3.

4.A SOLVENT-BASED PROCESSES

Gas-liquid absorption is a widely used and mature process in the chemical industry for gas separation and purification that can be used in both pre- and post-combustion power plant applications for CO_2 capture. There are two general categories of solvents that can be used for CO_2 absorption – chemical and physical. As the name implies, a chemical solvent relies on the chemical reaction of CO_2 in the solvent to enhance absorption, whereas a physical solvent absorbs molecular CO_2 without a chemical reaction. Physical solvents are well suited for pre-combustion capture of CO_2 from syngas at elevated pressures; whereas, chemical solvents are more attractive for CO_2 capture from dilute low-pressure post-combustion flue gas.

In an absorption process, a gaseous component dissolves into a liquid solvent forming a solution. Due to different solubility of gas components in a particular solvent, the solvent can be used to selectively separate the gas components. Chemical absorption involves the formation of chemical bonds between specific components of the gas and solvent molecules and thus can be highly selective. The main benefit of a physical solvent, as compared to a chemical solvent, is that it requires less energy for regeneration, since the CO_2 only weakly interacts with the solvent.

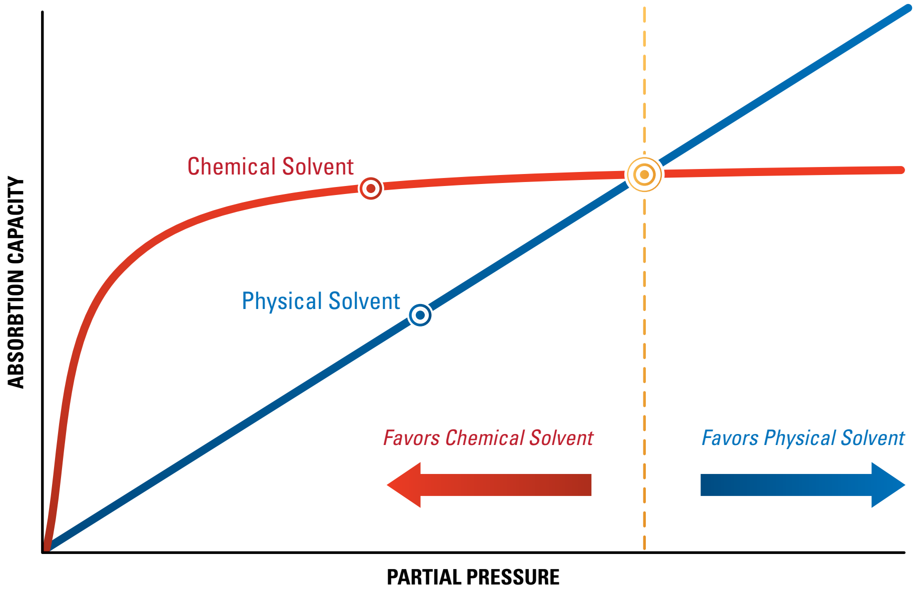


Figure 4-1: Comparison between Chemical and Physical Solvents

Figure 4-1 illustrates the general behavior of chemical and physical solvents. At lower CO_2 partial pressure, chemical solvents have a higher absorption capacity, which makes them more attractive for use for post-combustion flue gas conditions. However, at higher partial pressures their capacity levels off. The relationship between solvent capacity and partial pressure is nearly linear for physical solvents (Henry's Law behavior). Thus, at higher partial pressure, physical solvents are preferred. Selexol and similar physical solvents outperform chemical solvents such as amines and carbonate solutions, when the CO_2 partial pressure is above about 10 atmospheres (atm). In pre-combustion IGCC applications, the syngas CO_2 partial pressure is typically around 20 atm, therefore a physical solvent is usually preferred over a chemical solvent.

In a CO_2 absorption process, the CO_2 containing gas is contacted with the solvent in an absorption column also referred to as an absorber, and CO_2 in the gas is transferred to the solvent. The CO_2-rich solvent from the absorber is then regenerated so that it can be re-used. Chemical solvents are usually regenerated by raising the temperature to release CO_2, while with physical solvents pressure is reduced. Solvent regeneration is often accomplished in a desorption column, also referred to as a stripper. A stripping gas, typically steam, is used to enhance desorption. Any water vapor in the CO_2-rich gas stream leaving the stripper is condensed, and the high-purity CO_2 is sent to compression.

In addition to the operating pressure and temperature discussed above, many other parameters can impact the performance of an absorption process, including solvent working capacity; heats of absorption and reaction; mass transfer and chemical reaction rates; CO_2 selectivity; co-solvent concentrations; and contamination resistance. The following is a brief discussion of some of those parameters:

Working Capacity – The solvent working capacity is the difference between the concentration of CO_2 in the rich solvent exiting the absorber (entering the stripper) and the lean solvent entering the absorber (exiting the stripper). The working capacity is often reported in units of moles of CO_2 per moles of solvent. The working capacity is a function of the operating pressures and temperatures of the absorber and stripper. A higher working capacity will not only reduce the required solvent circulation rate between absorber and stripper, it can also reduce the incremental sensible heat required to heat the solvent to the stripper temperature.

Heats of Absorption and Reaction – The heat of absorption is the energy released when the solvent absorbs CO_2. The heat of reaction is the energy released when the absorbed CO_2 reacts with a chemical solvent. Heats of absorption and reaction impact the energy required during regeneration because the same amount of heat that is released during absorption and reaction is required to drive off CO_2 from the solvent. A higher energy requirement indicates stronger bonding between CO_2 and the solvent, and often translates to a higher working capacity. Thus, CO_2 working capacity and the heats of absorption and reaction are interrelated.

Depending on the solvent properties, as the CO_2 is absorbed into the solvent and forms bonds, heat can be produced (exothermic) or consumed (endothermic). Considering that the operating temperature will be a carefully monitored variable, heating or cooling will be required in order to maintain optimum conditions. Due to the significant cost of heating and cooling large volumes of liquids, it will be a focal point of solvent research to minimize the heat of absorption.

Reaction Rates – Mass transfer and chemical reaction rates impact the size of the absorber and stripper required to perform the separation. The absorption and regeneration reaction rates are important variables due to their impact on the volume of solvent required. If the solvent does not absorb or regenerate at a fast rate, large volumes of solvent will be required in order to supply solvent for the duration necessary to reach loading capacity. This adds to the capital and operation cost of the system.

Selectivity – The degree that one substance is absorbed in comparison to others is defined as selectivity. The greater the solvent's CO_2 selectivity, the purer the product stream will be. Solvent CO_2 selectivity is a function of the relative solubility and transfer rates of the components in the feed gas. Chemical solvents generally exhibit higher selectivity than physical solvents.

Solvent Concentration – Depending on other solvent characteristics, such as corrosiveness, a single solvent or co-solvents may be used. For example, amine solvents are aqueous mixtures. The amount of water circulated with the solvent will impact the process material and energy balances.

Contaminant Resistance – Contaminant resistance is another important variable. Solvents such as amines and ionic liquids form heat-stable salts when reacting with SO_2. Developing solvents that are resistant to contamination or to its effects will reduce costs by reducing the volume of solvent make-up. Additionally, developing an efficient method of removing the by-products will aid in maintaining the efficiency of the system.

Table 4-1 and Table 4-2 present a summary of the technical advantages and challenges related to pre- and post-combustion solvent-based technologies, respectively.

TABLE 4-1: TECHNICAL ADVANTAGES AND CHALLENGES FOR PRE-COMBUSTION SOLVENT TECHNOLOGIES

Advantages	Challenges
• CO_2 recovery does not require heat to reverse a chemical reaction. • Common for same solvent to have high H_2S solubility, allowing for combined CO_2/H_2S removal. • System concepts in which CO_2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems.	• CO_2 pressure is lost during flash recovery. • Must cool down synthesis gas for CO_2 capture, then heat it back up again and re-humidify for firing to turbine. • Low solubilities can require circulating large volumes of solvent, resulting in large pump loads. • Some H_2 may be lost with the CO_2.

TABLE 4-2: TECHNICAL ADVANTAGES AND CHALLENGES FOR POST-COMBUSTION SOLVENT TECHNOLOGIES

Advantages	Challenges
• Chemical solvents provide fast kinetics to allow capture from streams with low CO_2 partial pressure. • Wet-scrubbing allows good heat integration and ease of heat management (useful for exothermic absorption reactions). • Experience--More than 70 years of experience in CO_2 gas separation using solvent systems in industrial applications.	• Significant amount of energy (in the form of heat) required to reverse chemical reaction derates power plant. • Energy required to heat, cool, and pump non-reactive carrier liquid (usually water) is often significant. • Vacuum stripping can reduce regeneration steam requirements but is expensive.

4.B SORBENT-BASED PROCESSES

Sorbent-based processes (or “dry scrubbing”) can also be used for both pre- and post-combustion CO_2 capture. Adsorption refers to the phenomenon of a fluid (gas, vapor, or liquid) component being concentrated at the surface, or in the pores, of a solid. The solid is called the sorbent or adsorbent, and the fluid is called the sorbate or adsorbate. Although adsorption takes place only on the surface of a material, this surface can be quite large in a porous material, meaning that industrial sorbents will nearly always be micro-porous so as to maximize surface area and minimize volume. Different chemical molecules have different affinity to the surface of a solid, which allows for the separation of a specific fluid molecule from a mixture. Based on the interaction between fluid molecules and the sorbent surface, adsorption can be characterized as chemical adsorption or physical adsorption. Chemical adsorption – via chemical bond – has a strong interaction between the fluid molecule and sorbent, and is selective. Physical adsorption – via van der Waals forces – has a weaker interaction between the fluid molecule and sorbent, and is non-selective. Adsorption is commonly used in industrial applications for removing impurities (e.g., separation of CO_2 from gaseous streams such as hydrogen-rich gases resulting from gasification, steam reforming, and shift of fossil hydrocarbons). Adsorption can be selective in that polar and/or condensable species like CO_2 will be strongly retained, together with sulfur compounds and hydrocarbons, while “light” components such as N_2, O_2, and CO will be less retained, or not retained at all on the adsorbent.

Aside from chemistry, the main difference between solvent absorption and sorbent adsorption lie in the process design. Because adsorption involves a solid sorbent, the operation of an adsorption process is more difficult to accomplish compared to a gas/liquid absorption process. This distinction could be critical when the process scale is extremely large, such as a power plant. Solid adsorbents require desorption, just like liquid absorbents in a solvent-based process. The sorbent regeneration is typically accomplished using a thermal or pressure cycle. There are basically three process configurations available for an adsorption process to handle the solids: fixed bed, moving bed, and fluidized bed. Solid adsorbents are usually packed as fixed beds, submitted to successive adsorption and desorption steps, resulting in a time-cycle. Since the adsorption process is transient instead of steady-state, multiple packed-beds are often used in shifted time-cycles to achieve continuous production. A fixed-bed configuration is the most commonly used option when the fluid component is only in trace amount and temperature swing adsorption (TSA) is used for thermal regeneration. In TSA the adsorbent is regenerated by raising its temperature. When the fluid component has a high concentration in the feed stream (e.g., 10 percent or more), a pressure swing adsorption (PSA) mechanism is more appropriate. In PSA the gas mixture containing CO_2 flows through a packed bed of adsorbent at elevated pressure until the adsorption of the desired gas approaches equilibrium with the solid. The bed is then regenerated by stopping the feed mixture and reducing the pressure. A fluidized-bed configuration is usually selected when intensive heat transfer is required and the sorbent attrition is not an issue. A moving bed is the least commonly used configuration because of its equipment complexity.

Sorbent properties that will influence an adsorption process include, but are not limited to, the mechanical/thermal/chemical stability, porosity, particle size, adsorption capacity, and heat of adsorption. While many of these properties will impact the design and cost of an adsorption process, adsorption capacity and heat of adsorption impact energy consumption. Other characteristics that differentiate adsorption from absorption can include: more drastic pre-treatment of gases, especially for particle removal; lower purity of the produced CO_2; appropriateness of desorbing below atmospheric pressure (vacuum-swing cycles); and different trade-offs between purity and recovery. Major factors that influence the performance and cost of a sorbent are listed below.

Surface Area – The larger the surface area of a sorbent, the more adsorption can take place per mole of sorbent. It is desirable for sorbents to be porous so as to maximize adsorption with the smallest amount of sorbent resulting in lower sorbent costs and lower process equipment costs. Reported values range between 0.5 and 1,500 square meters of surface area per gram of sorbent.

Working Capacity – Adsorption working capacity, which is the CO_2 loading difference between the spent sorbent and regenerated sorbent, will influence the required sorbent inventory of the process and hence equipment size. If TSA is utilized for regeneration, then the energy consumption will be impacted as well. Should other sorbent properties be the same, a higher working capacity is always beneficial. Working capacity is measured by how many grams of CO_2 are captured per gram of sorbent. In other words, a CO_2 working capacity of one percent would mean that 1 kg of sorbent would capture 10 g of CO_2 in a given cycle. Reported CO_2 working capacity can reach as high as 21 percent by weight.

Heat of Adsorption – Heat of adsorption determines the energy requirement during sorbent regeneration (i.e., desorption). A higher heat of adsorption will require more energy for regeneration. Heat of adsorption will also influence the regeneration mode of an adsorption process. Higher heat of adsorption also implies a higher sensitivity of the adsorption working capacity to the regeneration temperature (i.e., a small change in temperature will cause a large change in capacity, and thus TSA regeneration is more favorable). A chemical sorbent typically uses a TSA regeneration design, while a physical sorbent uses PSA regeneration. Reported values for heat of adsorption can range between 11.7 and 1,760 kJ/mole.

Crush Strength – The strength of the sorbent is important in a process that stresses it, such as a fluidized bed. A physically weak sorbent will too quickly undergo attrition that will reduce it to an ineffective powder. The result is that it will need to be replaced more frequently.

Cycle Time – The cycle time of an adsorption process is critical for fixed-bed configurations, especially when the process scale is large. Even if a sorbent has a very large CO_2 working capacity, if it must remain in the adsorption reactor of the cycle for too long, it will result in too little CO_2 being captured, more sorbent being needed, larger equipment, and a larger footprint.

Number of Expected Cycles – Sorbents are expected to degrade over time, either through physical attrition or chemical degradation such as from sulfur or oxygen. It is desirable for a sorbent to be cycled a large number of times before needing to be replaced. The reported expectation of cycles range between 1,800 and 10,000 cycles before replacement.

Sorbent Costs – An ideal sorbent would be very inexpensive to produce and would be composed of materials that are readily available. An example would be a material that could be mined and put into service with minimal processing requirements.

An ideal sorbent would exhibit all desirable properties such as large surface area, low cost, short cycle times, and small swings between pressure or temperature. However, it is not expected that any one sorbent will exhibit all of the best properties, meaning that economic analyses will be vital in the determination of which sorbent and which combination of properties will result in the lowest costs for a particular plant. While the ultimate goal is to capture CO_2 with minimal impact on COE, the total capture cost for each sorbent and associated process can come from a number of different factors and be heavily influenced by various properties of the sorbents.

Table 4-3 and Table 4-4 present a summary of the technical advantages and challenges related to pre- and post-combustion sorbent-based technologies, respectively.

TABLE 4-3: TECHNICAL ADVANTAGES AND CHALLENGES FOR PRE-COMBUSTION SORBENT TECHNOLOGIES

Advantages	Challenges
• CO_2 recovery is primarily based on pressure swing (versus heat energy). • Common for H_2S to also have high solubility in the same sorbent, meaning CO_2 and H_2S capture can be combined. • System concepts in which CO_2 is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems.	• CO_2 pressure is lost during flash recovery. • Must cool synthesis gas for CO_2 capture, then heat it back up again and re-humidify for firing to turbine. • Some H_2 may be lost with the CO_2.

TABLE 4-4: TECHNICAL ADVANTAGES AND CHALLENGES FOR POST-COMBUSTION SORBENT TECHNOLOGIES

Advantages	Challenges
• Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO_2 partial pressure. • Higher capacities on a per mass or volume basis than similar wet-scrubbing chemicals. • Lower heating requirements than wet-scrubbing in many cases (CO_2 and heat capacity dependant).	• Heat required to reverse chemical reaction (although generally less than in wet-scrubbing cases). • Heat management in solid systems is difficult, which can limit capacity and/or create operational issues when absorption reaction is exothermic. • Pressure drop can be large in flue gas applications • Sorbent attrition.

SPECIAL CONSIDERATIONS FOR PRE-COMBUSTION CO_2 CAPTURE WITH SORBENTS

There is no commercially-available adsorption process for pre-combustion (IGCC) CO_2 capture. The closest application of an adsorption process for CO_2 separation is the PSA process for H_2 purification from syngas. However, H_2 purification is different from a CO_2 removal process. In H_2 purification, the purity of H_2 is the key parameter, whereas the recovery of H_2 is not as critical. For an IGCC power plant with CO_2 capture, H_2 recovery rate and CO_2 purity are both important, but the H_2 purity (above 93 percent) and CO_2 recovery rate (above 90 percent) can be compromised. As a result, an H_2 purification process designed to produce highly pure H_2 would require modification to facilitate the new requirement of CO_2 capture and sequestration.

Due to the high partial pressure of CO_2 in IGCC syngas, a physical sorbent with low heat of adsorption should be sufficient for ambient temperature CO_2 capture. Both the large scale of an IGCC power plant and the low heat of adsorption favor PSA regeneration. The cycle time of the PSA process should be less than an hour – a longer time might not be cost-effective. If a fluidized-bed configuration is to be used then extremely attrition resistant sorbent would be necessary, or the price of the sorbent should be relatively low.

One of the advantages of a sorbent for IGCC applications is that it can be used at higher temperatures than a solvent. A sorbent-based hot/warm CO_2 capture process that can operate at a temperature above the combustion turbine entrance temperature will improve the IGCC cycle efficiency and potentially result in a decrease in power production costs. An adsorption process could also be combined with the WGS reaction to shift the chemical equilibrium. In addition to the thermal efficiency improvement, such a sorbent-based CO_2 capture process would provide additional benefit to the IGCC CO_2 capture power plant by accelerating the WGS reaction rate and reducing the excess steam required for the traditional WGS reaction.

4.C MEMBRANE-BASED PROCESSES

In general, membranes refer to a barrier or medium, which has the potential to effect the selective permeation of the desired chemical species. Based on membrane material, a membrane can be organic (e.g., polymeric membranes) or inorganic (e.g., metallic, ceramic, and zeolitic membranes). A membrane can separate the individual chemical constituents of a gas mixture because the constituents permeate through the membrane at different rates. Diffusion mechanisms in membranes differ depending on the type of membrane used. Generally, gas separation is accomplished by some physical or chemical interaction between the membrane and the gas being separated. Membrane separation uses partial pressure as the driving force and is usually more favorable when the feed gas stream is at a high pressure.

Figure 4-2 shows a simplified process schematic for a post-combustion gas separation membrane. The feed stream contains the CO_2, N_2, and other minor flue gas constituents. The gas stream that passes through the membrane is called permeate and the retained stream is called the residue or retentate stream. A pressure differential across the membrane surface area serves as a driving force for a portion of the CO_2 to selectively diffuse through the membrane, creating a CO_2-rich permeate stream. The remaining CO_2, N_2, and other gas constituents make-up the CO_2-lean residue stream that exits the membrane.

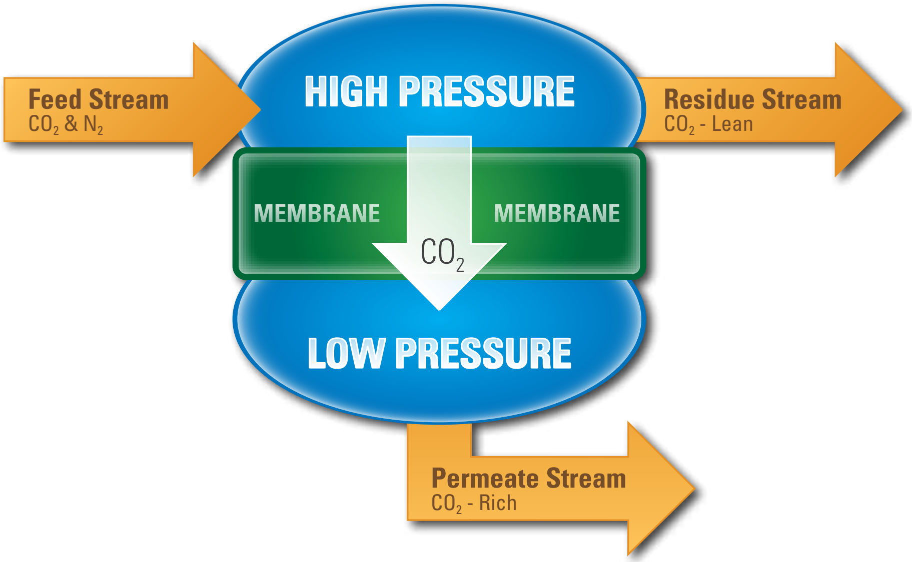


Figure 4-2: Membrane Process Schematic

Membrane properties such as permeability, selectivity, chemical/thermal/mechanical stability, and packing density will all influence the performance of a membrane system. Permeability determines the required membrane surface area, and therefore, the capital cost and footprint of a membrane CO_2 capture system. A related parameter, which is more closely related to membrane productivity, is known as permeance. Permeance equals the permeability divided by the thickness of the membrane. The thinner the membrane, the higher the permeance will be. For this reason a thinner membrane is beneficial. The membrane selectivity – the ratio of the two individual gas permeabilities (or permeances) – will also impact the performance of a membrane system. A high selectivity for a component will facilitate the membrane system to achieve a high recovery rate for that component under similar operating conditions (feed gas composition, total pressure, and pressure ratio between retentate stream and permeate stream). Generally, there is a trade-off between membrane permeance and selectivity. A membrane that has a high selectivity tends to have a low permeance and vice versa. However, it is desirable that a membrane have both high permeability and high selectivity. Usually the selectivity of the membrane is insufficient to achieve the desired purities and recoveries, therefore multiple stages and recycle streams may be required in an actual operation, leading to increased complexity, energy consumption, and capital costs. The following is a brief explanation of the three most important membrane design parameters – permeance, selectivity, and pressure ratio – as well as other process design considerations.

Permeance – A membrane's design permeance, also known as flux, is an important performance parameter that determines the required membrane surface area, and therefore, the capital cost and footprint of a membrane CO_2 capture system. Increasing CO_2 permeance proportionally decreases the required membrane surface area – a ten-fold increase in permeance results in a ten-fold decrease in area. Permeance is equal to the permeability times the thickness of the membrane. The permeability, P [cm^3(STP)·cm/cm^2·s·cmHg], of a membrane is defined as the rate at which a particular gas moves through a standard thickness and area of the membrane under a standard pressure differential. A commonly used metric of permeance is known as the gpu, where 1 gpu equals 10^{-6} cm^3 (STP)/cm^2·s·cmHg. Membrane permeance, surface area, and pressure ratio determine percentage CO_2 removal from the feed stream.

Selectivity – The ability of a membrane to separate two gases (e.g., CO_2 and N_2) is measured as the selectivity, α, which is defined as the ratio of the individual gas permeability or permeance. The highest practical CO_2/N_2 selectivity is about 50 for conventional post-combustion membranes because the CO_2 separation process is pressure ratio limited and increasing selectivity would require a large increase in membrane surface area. Increasing selectivity has a minimal affect on reducing membrane surface area, but can increase the percentage CO_2 concentration (purity) in the permeate stream. Overall, membrane permeance is the more important design parameter. Membrane selectivity and pressure ratio determine CO_2 purity.

Pressure Ratio – Membrane pressure ratio is defined as the ratio of feed pressure to permeate pressure. As mentioned previously, membrane pressure ratio and permeance determine percentage CO_2 removal, while pressure ratio and selectivity determine CO_2 purity. By design, membrane CO_2 enrichment (purity divided by feed concentration) will be less than the pressure ratio, regardless of selectivity. Therefore, the pressure ratio determines the maximum CO_2 purity for a given percentage CO_2 concentration in the feed stream.

Packing Density – Packing density (membrane area per cubic meter) will impact the footprint of a membrane system. Usually organic (polymeric) membrane has a higher packing density than inorganic membranes. However, inorganic membranes have better thermal stability and can be used at higher temperature.

Contaminants – Membrane stability against contaminants (especially particulates) in the gas stream is also an important design criterion. Lifetime data for CO_2 capture membranes in power plant gas exposure applications are not available. However, it is reported that commercial membrane modules in the petrochemical and natural gas industries have an average lifetime of more than four years. Long-term testing of membranes exposed to actual power plant gas conditions will be necessary to determine the expected service life in order to calculate realistic cost evaluations of the technology.

SPECIAL CONSIDERATIONS FOR PRE-COMBUSTION CO_2 CAPTURE WITH MEMBRANES

In pre-combustion CO_2 separation there are two types of membranes: CO_2 selective membrane and H_2 selective membrane. For a CO_2 selective membrane, CO_2 selectively permeates the membrane and the permeate is a relatively pure CO_2 stream. Figure 4-3 shows the operation of a CO_2 selective membrane. Carbon dioxide has a permeability of P_{CO2} and H_2 has a permeability of P_{H2}. The permeability ratio between two constituents, P_{CO2}/P_{H2}, is known as the membrane selectivity. For an H_2 selective membrane, the permeate is a relatively pure H_2 stream. The advantages of a CO_2 selective membrane are that the hydrogen recovery rate can be high and the CO_2 product is pure. The disadvantages are the H_2 product in the retentate will contain a certain amount of CO_2 and the CO_2 product in the permeate will be at a lower pressure and has to be compressed further to sequestration ready pressure (approximately 2,200 psia). The advantages of an H_2 selective membrane are that CO_2 product in the retentate will be at high pressure (less compression work is required) and pure H_2 in the permeate can be easily achieved. The disadvantages are that it is difficult to achieve a high H_2 recovery rate (some H_2 will remain in retentate) and the CO_2 product in the retentate has to be further purified. Generally speaking, a membrane process has difficulty to achieve both high recovery rate and high purity of the same product in one stage.

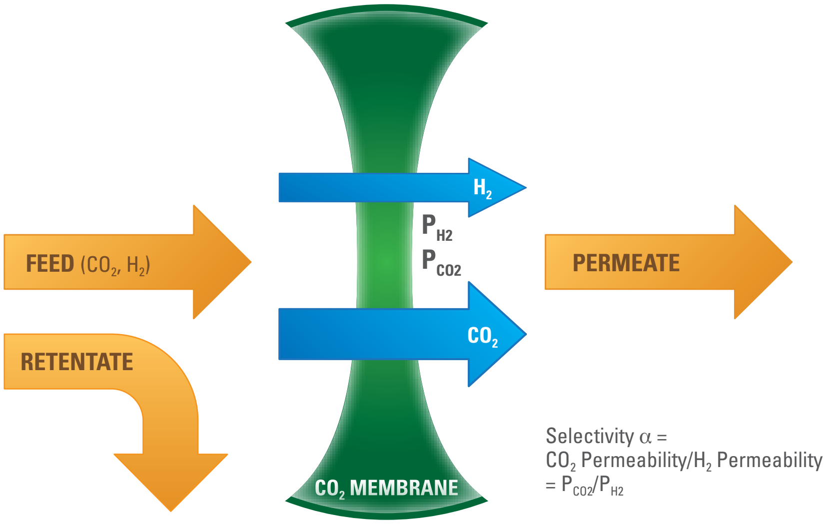


Figure 4-3: Schematic Display of a Pre-Combustion CO_2 Selective Membrane

In an IGCC power plant with CO_2 capture, CO_2 is concentrated through the WGS reaction, which takes place between 200°C and 500°C. However, the WGS reaction is restricted by chemical equilibrium for typical syngas. It is desirable to have a reactor that could constantly remove one of the shift reaction products (H_2 or CO_2) so that the chemical equilibrium would be shifted to completion. Membrane reactors, either H_2 or CO_2 selective, are a perfect candidate for such an application. Since the WGS reaction takes place at a high temperature and high pressure, a high-temperature and high-pressure membrane would be advantageous. A membrane reactor for the WGS reaction will not only improve the WGS reaction, it would also improve the thermal efficiency of the IGCC power plant due to elimination of the heating/cooling of syngas for CO_2 capture as required in the Selexol process. Membrane reactors have great potential to reduce the COE of an IGCC power plant with CO_2 capture.

Table 4-5 presents a summary of the technical advantages and challenges related to pre-combustion membrane-based technologies.

TABLE 4-5: TECHNICAL ADVANTAGES AND CHALLENGES FOR PRE-COMBUSTION MEMBRANE TECHNOLOGIES

Membrane Type	Advantages	Challenges
H_2/CO_2 Membrane	**H_2 or CO_2 Permeable Membrane:** • No steam load or chemical attrition. **H_2 Permeable Membrane Only:** • Can deliver CO_2 at high-pressure, greatly reducing compression costs. • H_2 permeation can drive the CO shift reaction toward completion – potentially achieving the shift at lower cost/higher temperatures.	• Membrane separation of H_2 and CO_2 is more challenging than the difference in molecular weights implies. • Due to decreasing partial pressure differentials, some H_2 will be lost with the CO_2. • In H_2 selective membranes, H_2 compression is required and offsets the gains of delivering CO_2 at pressure. In CO_2 selective membranes, CO_2 is generated at low pressure requiring compression.
Solvent Hybrids	• The membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine.	• Capital cost associated with the membrane. • Membranes may not keep out all unwanted contaminants. • Does not address CO_2 compression costs.

SPECIAL CONSIDERATIONS FOR POST-COMBUSTION CO_2 CAPTURE WITH MEMBRANES

There are two basic membrane module design configurations that can be used for post-combustion application – hollow-fiber and spiral-wound. Hollow-fiber modules are constructed using numerous small diameter (100 to 250 µm), hollow-fiber membranes packed into a module shell. Spiral-wound membrane modules are constructed of large membrane sheets that are wound around a collection pipe. Selection of a membrane module design is a function of cost, packing density, pressure drop, and feasibility of manufacturing the desired membrane polymers as either fiber or sheets.

The major disadvantage in using conventional polymeric membranes for post-combustion CO_2 capture is the potentially large membrane surface area required, because of the large flue gas volume that needs processed coupled with the low concentration and partial pressure of CO_2 in the flue gas. Another potential disadvantage of membrane technology for power plant applications is that although 90 percent CO_2 separation is technically achievable in a single-step process, a high level of CO_2 purity will require a multi-step process. As discussed above, the three important membrane design parameters are permeance, selectivity, and pressure ratio. The following describes the significance of these parameters for post-combustion applications.

Permeance – Increasing CO_2 permeance proportionally decreases the required membrane surface area – a ten-fold increase in permeance results in a ten-fold decrease in area. Some design calculations show that membranes with a CO_2 permeance on the order of 1,000 gpu are needed to make CO_2 removal with membranes cost-effective for post-combustion applications. This value is 10 times higher than current commercial industrial gas separation membranes. Therefore, the major R&D focus is on increasing membrane permeance.

Selectivity – Based on calculations by MTR for a post-combustion membrane application, assuming a 15 percent CO_2 concentration in the feed stream, CO_2 purity in the permeate stream would be less than 30 percent at a pressure ratio of 2, for CO_2/N_2 selectivity between 20 and 50. If the pressure ratio is increased to 5, CO_2 purity would range from approximately 55 to 65 percent at a CO_2/N_2 selectivity between 20 and 50. Therefore, a multiple-step membrane process with a recycle loop is likely required to further increase CO_2 purity in the permeate stream.

There is a design trade-off between membrane permeance and selectivity. Figure 4-4 shows a plot of CO_2/N_2 selectivity versus CO_2 permeance for various membranes currently under development by MTR for post-combustion CO_2 capture applications. The plot shows that highly selective membranes generally have low permeance and vice versa. The membranes with the highest CO_2/N_2 selectivity (approximately 50) have the lowest CO_2 permeance (~1,000 gpu), while the high permeance membranes (~4,000 gpu) have the lowest selectivity (~25). For comparison, a commercially available membrane used for removing CO_2 from natural gas has a permeance of approximately 100 gpu and a CO_2/N_2 selectivity of 30. The shaded region in the upper-right-hand corner of the plot is the membrane performance target area that is thought to be necessary for a cost-effective membrane process for power plant CO_2 capture applications.

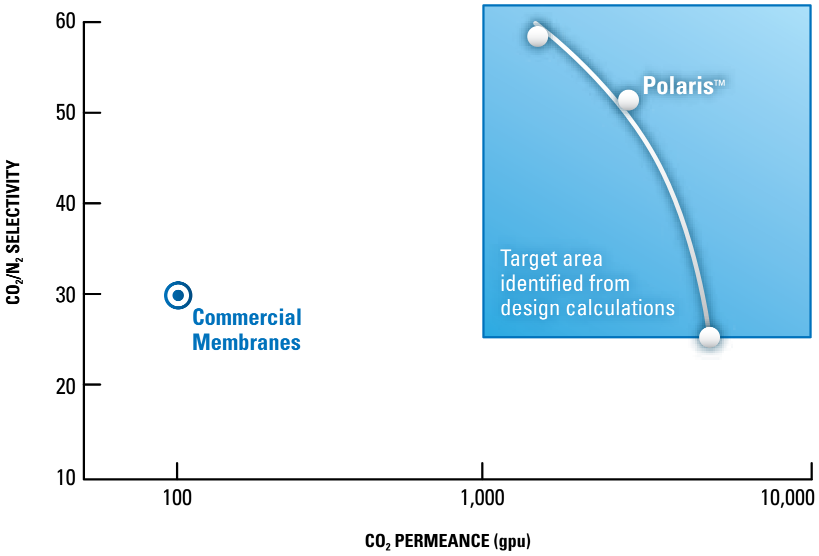


Figure 4-4: Plot of Membrane Selectivity versus Permeance

Pressure Ratio – As discussed above, the pressure ratio determines the maximum CO_2 purity for a given percentage CO_2 concentration in the feed stream. For example, with a CO_2 feed stream concentration of 10 percent and a pressure ratio of 5, the maximum achievable CO_2 purity would be 50 percent. Establishing a pressure differential across the membrane requires either compression of the flue gas on the feed side, or a vacuum on the permeate side. The design trade-off here is the pressure ratio versus total membrane surface area. Figure 4-5 shows the relationship between membrane surface area, CO_2 removal, and CO_2 purity for four pressure ratios between 3 and 15 in a single-step process with membrane design parameters of 100 gpu and 35 CO_2/N_2 selectivity and a design gas flow of 800,000 scfm (approximately equivalent to a 350 MW power plant), as estimated by RTI International. As shown, increasing the pressure ratio decreases the required membrane surface area for a given percentage CO_2 removal and increases the percentage CO_2 purity. The effect of pressure ratio is more pronounced at lower ratios and there can be an order of magnitude difference in required membrane surface area as the pressure ratio is increased.

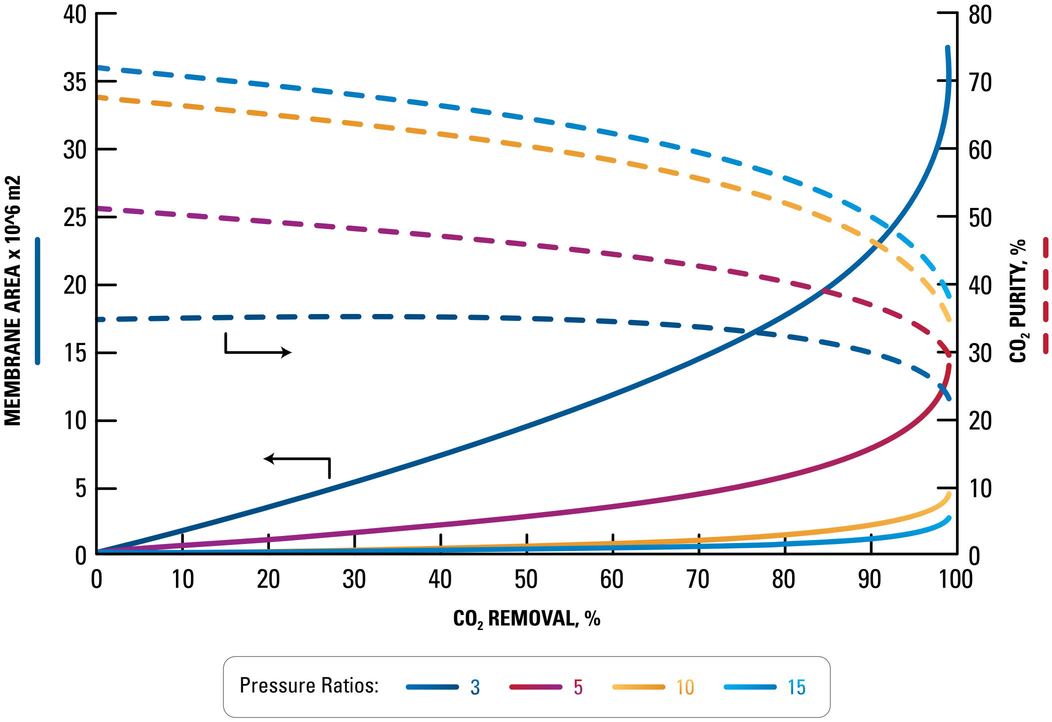


Figure 4-5: Plot of CO_2 Removal, CO_2 Purity, and Membrane Area Versus Pressure Ratio

Stated from an economic point of view, a membrane system design trade-off is primarily the energy costs for compression/vacuum of the flue gas/permeate versus the capital cost for membrane surface area. The energy required for a vacuum-based process should be lower than a compression-based process because the vacuum process only has to manage the small portion of flue gas that permeates the membrane (largely CO_2), while a compression-based process has to compress all of the flue gas (primarily CO_2 and N_2). However, although a vacuum-based process would require less energy than a compression-based process, it would require a larger membrane area because of the lower pressure differential that is achievable across the membrane. As a result of this trade-off, process design is an important component for a cost-effective membrane capture system. As an example, MTR estimated membrane surface area and auxiliary power requirements for a 600 MW power plant equipped with a 1,000 gpu membrane operating at a pressure ratio of 10. It was estimated that a single-step vacuum-based process would require approximately 4.8 million m^2 membrane surface area and 68 MW auxiliary power compared to a compression-based process that would require a membrane surface area of only 590,000 m^2, but 104 MW auxiliary power. Due to practical limitations of membrane design pressure differential and surface area, it appears that a multiple-step membrane process will be required for post-combustion applications.

Table 4-6 provides a summary of the technical advantages and challenges for post-combustion membrane-based technologies.

TABLE 4-6: TECHNICAL ADVANTAGES AND CHALLENGES FOR POST-COMBUSTION MEMBRANE TECHNOLOGIES

Advantages	Challenges
• No steam load. • No chemicals.	• Membranes tend to be more suitable for high-pressure processes such as IGCC. • Trade off between recovery rate and product purity (difficult to meet both high recovery rate and high purity). • Requires high selectivity (due to CO_2 concentration and low pressure ratio). • Good pre-treatment. • Bad economy of scale. • Multiple stages and recycle streams may be required.

4.D LOW TEMPERATURE SEPARATION FOR POST-COMBUSTION

Although there are no current DOE/NETL R&D projects, low-temperature separation is another novel method for post-combustion CO_2 capture that is being investigated by others. Low-temperature separation is also known as anti-sublimation; cold separation; cryogenic separation; freeze separation; and frosting separation.[ii] Low-temperature separation is possible since the flue gas constituents have different freezing temperatures. While low-temperature separation is physically possible, its cost-effectiveness is limited due to the large quantity of energy necessary to accomplish the flue gas cooling.

The required temperature to achieve a desired CO_2 capture rate can be found from the phase diagram of CO_2 (see Figure 4-6). The typical concentration of CO_2 in post-combustion flue gases is between 10 and 14 percent by volume, equivalent to 0.1 to 0.14 atm partial pressure. As shown in the figure, at 0.14 atm the CO_2 will start to anti-sublime (condense out as a solid) at around -100°C (known as the frosting temperature, similar to dew point if condensed as a liquid). However, if 90 percent CO_2 capture is required the flue gas needs to be cooled down to approximately -120°C. The energy consumption of the low-temperature process lies in the flue gas cooling process and the anti-sublimation of CO_2. Different cooling methods will result in not only different energy consumption, but also different capital cost due to the necessary cooling equipment used.

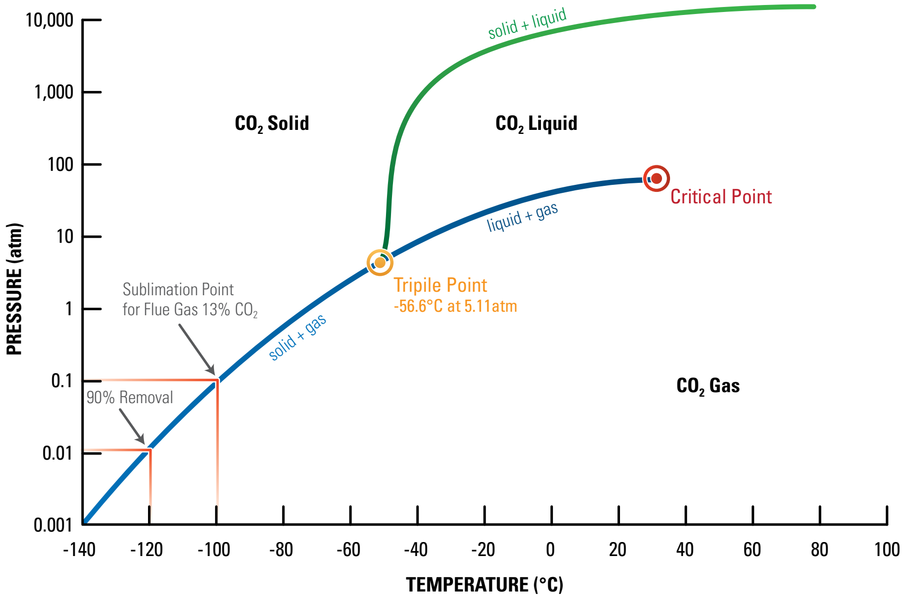


Figure 4-6: Phase Diagram of Carbon Dioxide

One low-temperature separation process has been proposed by the Center for Energy and Processes at Ecole des Mines de Paris in collaboration with ALSTOM. The process uses cascaded refrigeration systems to cool the flue gas. The researchers have performed some experimental work and simulation studies. Another low-temperature separation process has been proposed by Brigham Young University called the cryogenic CO_2 capture (CCC) process. Analogous to cryogenic air separation, the process uses compression/expansion of the flue gas for cooling. In addition, Eindhoven University of Technology and Shell Oil Company are developing a condensed contaminant centrifugal separation process (C3-Sep) for CO_2 separation from natural gas that might be applicable for coal combustion flue gas applications. The C3-Sep process consists of two steps: (1) integral cooling of the gas by expansion to a low temperature, whereby the CO_2 condenses to micron-sized droplets; and (2) removal of these droplets using a rotational particle separator (RPS), which uses centrifugal force to enhance the phase separation of CO_2 from the balance of the gas stream.

4.E OXY-COMBUSTION PROCESSES

In an oxy-combustion process, a pure or enriched O_2 gas stream is used instead of air as the oxidant for combustion (see Figure 4-7). In this process, almost all of the N_2 is removed from the air (sometimes called denitrogenated process), yielding a stream that is approximately 95 – 97.5 percent O_2. Due to N_2 removal from the air, oxy-combustion produces approximately 75 percent less combustion product volume than air-fired combustion and the combustion product consists of approximately 70 percent by volume of CO_2. The lower gas volume also allows for flue gas contaminants (SO_X, NO_X, mercury, particulates) to be more easily removed and at a lower cost. Another benefit is that because N_2 is removed from the air, NO_X production from the boiler is greatly reduced.

Oxy-combustion systems can be configured in either low- or high-temperature boiler designs. In the low-temperature design, flame temperatures approach near that of air-fired combustion (~3,000°F) and in the advanced high-temperature design the flame temperatures are greater than 4,500°F. The low-temperature design uses recycled combustion products to lower the flame temperature to approximate the heat transfer characteristics found in air-fired boilers and is applicable for new or retrofit applications. The high-temperature design uses increased radiant transfer in new construction to reduce the size and capital cost of the boiler.

Oxy-combustion technology involves three major components: air separation unit (ASU), fuel conversion (combustion) unit and CO_2 purification and compression unit. Figure 4-7 shows the three components along with different design options. Based on the different combinations of these three components, oxy-combustion can have several process configurations. These different configurations will have different energy and economic performance.

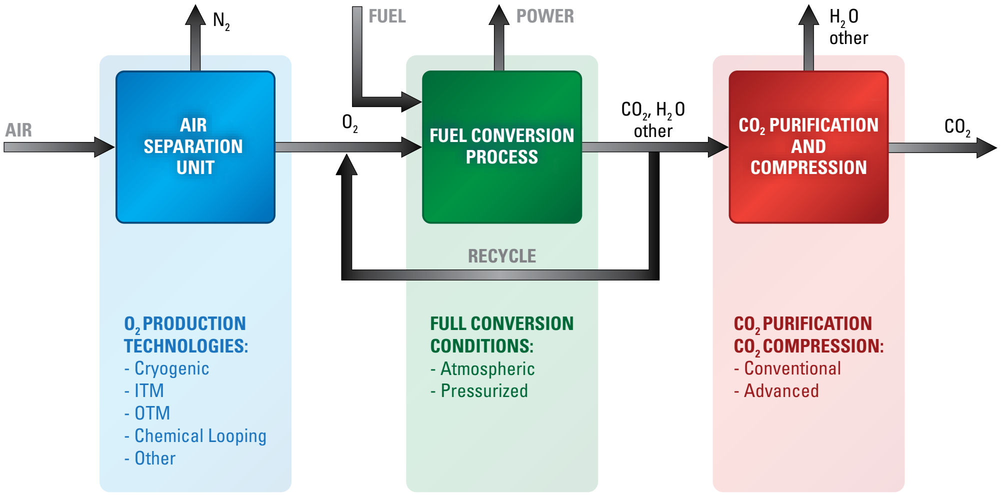


Figure 4-7: Major Components of Oxy-Combustion System

A conventional oxy-combustion technology configuration would use a cryogenic process for O_2 separation, atmospheric combustion for fuel conversion, conventional pollution control technologies (SO_X, NO_X, mercury, particulates), and mechanical compression for CO_2 pressurization. The conventional configuration can be used for retrofitting existing coal-fired power plants without major modification.

In its advanced form, a non-cryogenic O_2 production technology, such as the ion transport membrane (ITM), would be used for O_2 production and a high-pressure combustion system applied for fuel conversion. In an advanced pressurized combustion system, the combustion products are already at elevated pressure so that the CO_2 compression energy requirements can be partially offset. Although, the advanced oxy-combustion configuration, however, is not applicable for retrofitting of existing boilers, there is an option to "repower" the entire boiler. For example, ITM O_2 separation and pressurized combustion would require replacement of the entire boiler system (i.e., a repowering versus a retrofit project). In another advanced oxy-combustion configuration, O_2 is transferred from the air to fuel using an O_2 carrier using a chemical looping process that will be discussed later in this report.

Table 4-7 provides a summary of the technical advantages and challenges for oxy-combustion technologies.

TABLE 4-7: TECHNICAL ADVANTAGES AND CHALLENGES FOR OXY-COMBUSTION TECHNOLOGIES

Advantages	Challenges
• The combustion products are primarily CO_2 and water. • Control of oxygen content provides a new variable for boiler design. • Higher temperature burner flame can produce increased heat flux allowing for design of smaller boilers.	• Low-cost oxygen supply is required. • Reduce cost of CO_2 recycle. • Develop processes to convert existing air-fired furnaces to oxygen-fired. • High heat flux can degrade boiler materials. • Requires careful design of heat flux through the boiler tube walls in new construction. • Requires high temperature materials in new construction. • Increased concentration of acid gases can promote corrosion in the boiler system. • Preventing air in-leakage in retrofit boilers.

4.F CHEMICAL LOOPING PROCESSES

Chemical looping is a breakthrough concept that enables the production of a concentrated CO_2 stream similar to oxy-combustion, but without the need for a separate ASU. The concept of chemical looping can be applied to coal combustion, where it is known as chemical looping combustion (CLC), or to coal gasification, where it is known as chemical looping gasification (CLG). Table 4-8 provides a summary of the technical advantages and challenges for chemical looping technologies.

TABLE 4-8: TECHNICAL ADVANTAGES AND CHALLENGES FOR CHEMICAL LOOPING TECHNOLOGIES

Advantages	Challenges
• CO_2 and H_2O kept separate from the rest of the flue gases. • ASU is not required and CO_2 separation takes place during combustion.	• Undeveloped technology still conceptual and bench scale. • Reliable solids transport system. • Providing efficient heat integration to the process. • Ash separation is problematic. • Attrition-resistant metal oxide carriers required during multiple cycles.

CHEMICAL LOOPING COMBUSTION

Chemical looping splits combustion into separate oxidation and reduction reactions. Subsequently, the products of combustion (CO_2 and H_2O) are kept separate from the rest of the flue gases (primarily N_2). In the CLC process, O_2 is transferred from a gaseous stream (usually air) to a fuel (either gaseous or solid) through a solid chemical. The solid chemical is called the oxygen carrier. In a typical CLC process, the oxidation and reduction of the O_2 carrier are accomplished in two separate reactors. However, O_2 transport may be completed in three or more steps depending on the application and the O_2 carrier used.

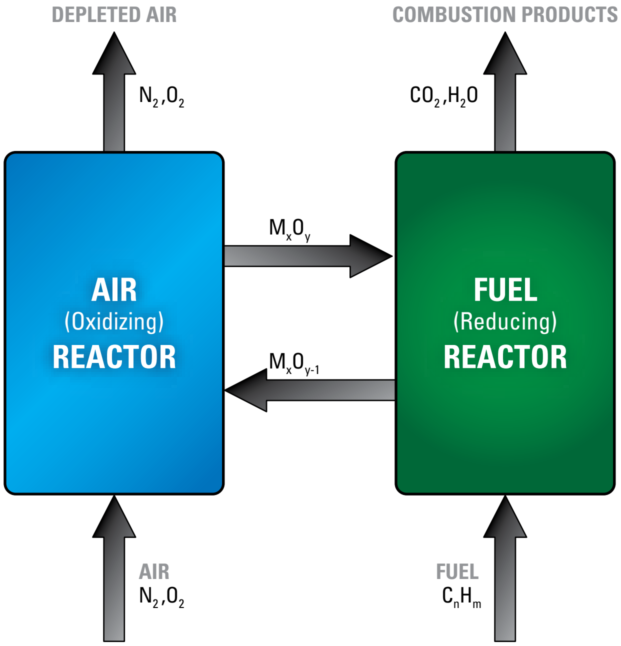


Figure 4-8: Schematic Diagram of a Two Reactor CLC Process

Figure 4-8 is a schematic diagram of a two-reactor CLC process. The O_2 carrier is usually a solid, metal-based compound with chemical composition of M_xO_{y-1}. The solid is oxidized by O_2 in the air to form an oxide of the compound (M_xO_y) and produce a hot flue gas depending on the heat effect of the oxidation reaction. The hot flue gas can be used to produce steam. The metal oxide from the oxidizer enters the fuel reactor and is reduced to its initial state by the fuel. The combustion products from the fuel reactor will be a highly concentrated CO_2 and H_2O stream that can be purified, compressed, and sent to storage.

The overall chemical reactions in the two reactors can be expressed as:

Oxidizer: $$M_xO_{y-1} + 1/2\ O_2 \rightarrow M_xO_y$$

Reducer: $$C_nH_{2m} + (2n+m)\ M_xO_y \rightarrow n\ CO_2 + m\ H_2O + (2n+m)\ M_xO_{y-1}$$

The net reaction of the CLC process is: $$C_nH_m + \tfrac{1}{2}(2n+m)\ O_2 \rightarrow n\ CO_2 + m\ H_2O + \text{heat}$$

CHEMICAL LOOPING GASIFICATION

A chemical looping process can also be integrated into gasification and the WGS reaction. In a CLG system, two or three solid particle loops are utilized to provide the O_2 for gasification and to capture CO_2. A loop, similar to that of CLC, is used to gasify the coal and produce syngas (H_2 and CO). A second solid loop is used in a WGS reactor. In this reactor, steam reacts with CO and converts it to H_2 and CO_2. The circulating solid absorbs the CO_2, thereby providing a greater driving force for the WGS reaction. The CO_2 is then released in a calcination step that produces nearly pure CO_2 for further compression and storage. Figure 4-9 is a schematic diagram of a two-loop CLG process. The operating conditions in the two reactors can be different depending on the application. Considering that the O_2 carrier is a solid (not energy intensive to pressurize) and gaseous fuel is usually already under pressure (syngas, natural gas), it could be advantageous to have the fuel reactor under pressure since it would increase thermodynamic efficiency of the combustion process.

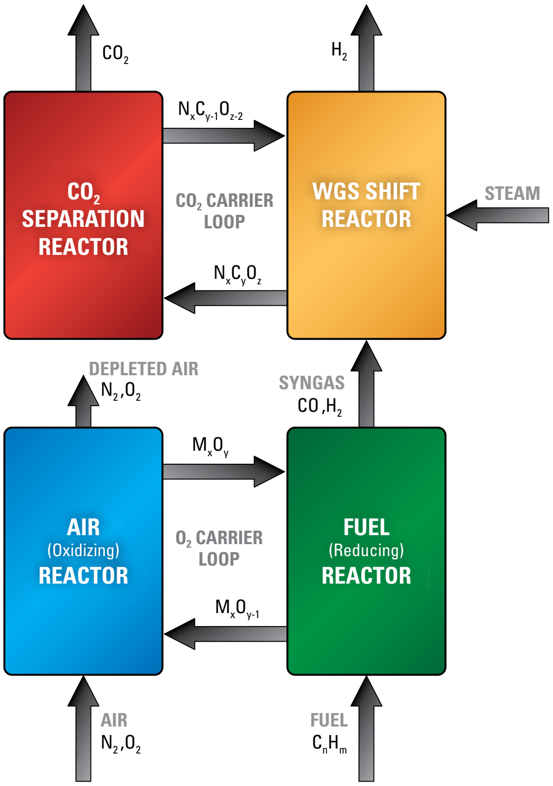


Figure 4-9: Schematic Diagram of a Two Loop CLG Process

For the WGS reaction, the chemical looping process uses a solid CO_2 carrier (instead of O_2 carrier) to separate CO_2 from the WGS reactor, thus improving the WGS reaction. An example is the iron oxide-based syngas chemical looping process, which requires a three-reactor configuration to accomplish the WGS. In the first reactor, syngas is burned by Fe_2O_3:

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$$

In the second reactor, Fe is oxidized by steam to produce H_2:

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

And in the third reactor Fe_3O_4 is further oxidized to Fe_2O_3 to complete the cycle:

$$2Fe_3O_4 + 1/2O_2 \rightarrow 3Fe_2O_3$$

The overall reaction converts syngas (CO and H_2) to H_2 with a small fraction of the syngas lost in the process.

CHAPTER 5:

PRE-COMBUSTION CARBON DIOXIDE CAPTURE R&D EFFORTS

As discussed in Chapters 3 and 4, in pre-combustion capture the CO_2 is recovered from a process gas stream before the fuel is burned to generate power and therefore is primarily applicable to IGCC systems. DOE/NETL is currently funding the development of advanced pre-combustion CO_2 capture technologies that have the potential to provide step-change improvements in both cost and performance as compared to the current state-of-the-art solvent-based processes. The DOE/NETL R&D effort for pre-combustion applications is focused on advanced solvents, solid sorbents, and membrane-based systems for the separation of H_2 and CO_2.

5.A SOLVENTS FOR PRE-COMBUSTION

There are commercially available solvent-based technologies that could be adapted for pre-combustion CO_2 capture on IGCC power plants, but they are not considered to be cost-effective. DOE/NETL R&D activities in this area focus on the development of advanced solvents.

SOLVENT RESEARCH OBJECTIVES

- Increase CO_2 loading capacity
- Reduce regeneration energy
- Improve reaction kinetics
- Decrease solvent corrosivity
- Reduce solvent volatility and degradation
- Lower capital and operating cost

CURRENTLY AVAILABLE SOLVENT TECHNOLOGIES

The current state-of-the-art CO_2 capture technologies that could be applied to IGCC systems (the glycol-based Selexol™ process and the methanol-based Rectisol® process), employ physical solvents that preferentially absorb CO_2 from high pressure syngas streams. The Selexol process operates at around ambient temperature whereas the Rectisol process operates as low as -60 °C. Although these systems are in large scale operation (4,000 ton/day CO_2 separation) today for synthetic natural gas production, petroleum refining and natural gas purification, neither of them is integrated in a coal-based gasification power system.

Recent DOE/NETL systems analysis studies assume a WGS reactor combined with a two-stage Selexol™ process is used for CO_2 capture in IGCC applications. Use of the SelexolTM technology for an IGCC plant leads to a 20 percent energy penalty and an increase in COE of approximately 35 percent (compared to the non-capture IGCC counterpart). The WGS reactor is necessary to convert the CO in the syngas to CO_2. The first-stage Selexol™ process is used for hydrogen sulfide (H_2S) separation, and the second stage for CO_2 separation. Although there are many system types, Figure 5-1 shows an example simplified schematic diagram of a two-stage Selexol™ process used for CO_2 capture.

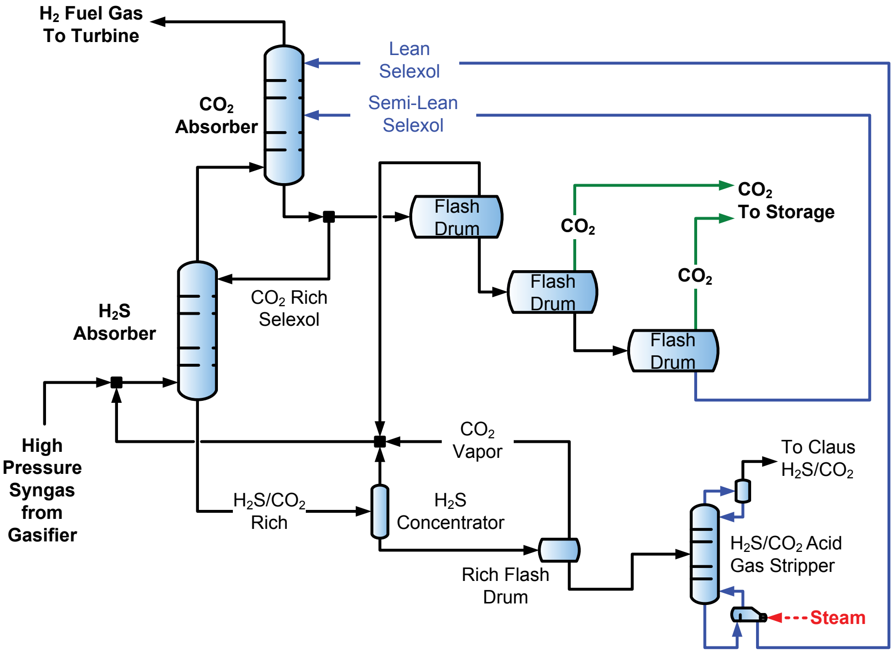


Figure 5-1: Schematic Diagram of the Pre-Combustion Selexol CO_2 Capture Process

Untreated syngas enters the first of two absorbers where H_2S is preferentially removed using CO_2-rich solvent from the CO_2 absorber. The gas exiting the H_2S absorber passes through the second absorber where CO_2 is removed using both semi-lean and lean solvent streams. The treated syngas (now concentrated in H_2) exits the absorber and is sent to the combustion turbine for power generation. The CO_2-rich solvent exits the CO_2 absorber and a portion is sent to the H_2S absorber and the remainder is sent to a series of flash drums for regeneration. The CO_2 product stream is obtained from the flash drums and the semi-lean solvent is returned to the CO_2 absorber. The flash drums operate at progressively lower pressures, ranging from several hundred psia down to near-atmospheric pressure in the final flash drum (e.g. between 300 psia and 22 psia in the DOE systems analysis study). Because a significant fraction of the CO_2 is produced at elevated pressure, the total compression energy requirement is lower than for post-combustion processes that typically generate their entire CO_2 product stream at near-atmospheric pressure. The H_2S/CO_2-rich solvent exiting the H_2S absorber is sent to the acid gas stripper where the absorbed gases are released using a steam heated reboiler. The acid gas from the stripper is sent to a Claus plant for further processing and the lean solvent exiting the stripper is returned to the top of the CO_2 absorber.

DOE/NETL R&D ACTIVITIES

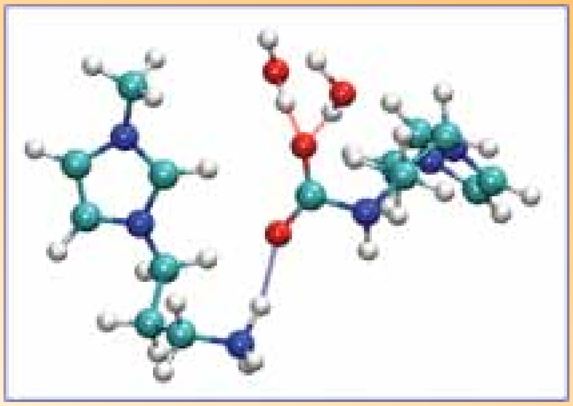
DOE/NETL's pre-combustion solvent R&D activities focus on a number of research objectives that address solvent technology challenges including an increase in CO_2 loading capacity and reaction kinetics coupled with a decrease in regeneration energy. As mentioned in Chapter 2, DOE/NETL's ORD is evaluating the use of ionic liquids as physical solvents for CO_2 capture in IGCC applications. ILs are salts that are liquid at room temperature, have high CO_2 absorption potential, and have low vapor pressure. ILs can absorb CO_2 at elevated temperature, providing a potential option to combine CO_2 capture with warm syngas clean-up. Table 5-1 provides a list of DOE/NETL external R&D projects related to pre-combustion solvent technologies. Currently, there is one pre-combustion solvent CO_2 capture technology being developed by DOE/NETL – Southern Research Institute's (SRI) ammonium carbonate/bicarbonate process. A detailed description of the process is contained in the Appendix.

TABLE 5-1: DOE/NETL R&D PROJECTS FOR PRE-COMBUSTION CO_2 CAPTURE USING SOLVENTS

Project Focus	Participant	Project Number	Performance Period
Ammonium Carbonate	SRI International	0896	9/30/09 – 3/31/12

KEY HIGHLIGHTS OF NETL PRE-COMBUSTION SOLVENT RESEARCH

Ionic liquids developed and tested at NETL have shown a capacity for CO_2 that exceeds existing commercial solvents and can operate at high temperature (more than 200°C), providing a potential option to combine CO_2 capture with warm syngas clean-up for IGCC applications.



Molecular Structure of an Ionic Liquid

5.B SOLID SORBENTS FOR PRE-COMBUSTION

DOE/NETL is exploring the feasibility of employing solid sorbents for pre-combustion CO_2 capture from syngas. The advantage of an adsorption process is that some solid sorbents can be used at a high temperature. In a pre-combustion application this is important since high temperature (above 500°F) CO_2 capture combined with warm/hot gas sulfur cleanup would eliminate syngas reheating and thus improve the overall thermal efficiency of the IGCC power plant. So far, a liquid solvent that could operate at above 500°F temperature has not been identified.

SORBENT RESEARCH OBJECTIVES

- Increase CO_2 loading capacity
- Minimize regeneration energy
- Increase reaction kinetics
- Increase durability
- Improve heat management
- Lower capital and operating cost
- Optimize process design

DOE/NETL R&D ACTIVITIES

DOE/NETL is developing solid sorbents for pre-combustion CO_2 capture from syngas that have potential for a step-change improvement in 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. Table 5-2 provides a list of recent and current DOE/NETL external R&D projects related to pre-combustion sorbent technologies. The Appendix includes summary descriptions and results, if available, for these projects.

TABLE 5-2: DOE/NETL R&D PROJECTS FOR PRE-COMBUSTION CO_2 CAPTURE USING SORBENTS

Project Focus	Participant	Project Number	Performance Period
Warm Gas Cleanup with Sorbents	RTI International	NT42459	6/1/05 – 8/29/10
Evaluation of Sorbents	UNDEERC	NT42465-1.4	6/23/05 – 5/31/09
High-Density Activated Carbon	UNDEERC	NT42465-3.1	6/23/05 – 5/31/09
Sorbent-Enhanced Water-Gas Shift	Lehigh University	NT42455	5/25/05 – 3/30/09
Sorbent-Enhanced Water-Gas Shift	UNDEERC	FT40320	--
High Capacity Regenerable Sorbent	TDA Research, Inc.	0469	10/1/09 – 9/30/11
Sorbent-Enhanced Water-Gas Shift	URS Group	0465	1/1/10 – 1/1/13

KEY HIGHLIGHTS OF NETL PRE-COMBUSTION SORBENT RESEARCH

- Research Triangle Institute has identified lithium orthosilicate ($LiSiO_4$) as the preferred CO_2 sorbent material, as well as several effective methanation promoter catalysts for their substitute natural gas production process. These materials were selected due to their high tolerance to sulfur.
- Research Triangle Institute has completed the technical and economic evaluation of warm CO_2 capture using various sorbents, including lithium magnesium, which has a CO_2 absorption of 4.49 wt% at 250°C.
- Lehigh University has identified potassium carbonate-promoted hydrotalcite and sodium oxide-promoted alumina as CO_2 chemisorbents for use in their Thermal Swing Sorption Enhanced Reaction Process. Thermal stability has been obtained for these chemisorbents and the isotherms and kinetics for CO_2 sorption from N_2 have been characterized.

Sorbent Bed Pressure Drop Testing

5.C MEMBRANES FOR PRE-COMBUSTION

Membranes are a commercially-available technology in the chemical industry for CO_2 removal and H_2 purification. There is, however, no commercial application of membrane processes that aims at CO_2 capture for IGCC syngas. To scale up a membrane process to IGCC power plant scale may not be an issue due to the modular nature of the membrane process. However, the modular design does not exhibit economy of scale – the cost of the system will increase linearly as the plant system scale increases. For a membrane process to be a viable CO_2 capture technology for IGCC applications, a better overall performance is required, including higher permeability, higher selectivity, and lower membrane cost. Gas separation membranes, in comparison to solvent and sorbent separation techniques, function as ‘unit operations’ versus a ‘process’ approach, which simplify the gas separation system complexity, provide increased IGCC power plant integration flexibility and smaller equipment footprint. In addition, gas separation membranes can be designed to produce CO_2 at pressure and, if desired, designed to co-capture CO_2 and H_2S.

MEMBRANE RESEARCH OBJECTIVES

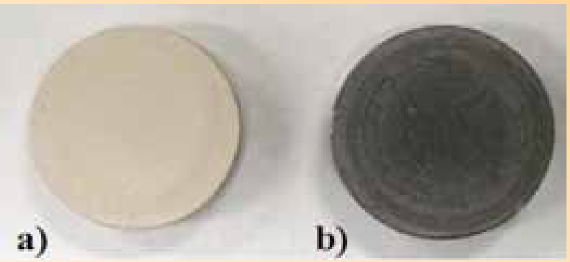
- Increase permeability
- Increase CO_2/H_2 selectivity
- Increase durability (chemical, thermal, physical)
- Optimize membrane process design and integration within the IGCC power cycle
- Lower capital cost

DOE/NETL R&D ACTIVITIES

Several advanced membrane technology options are under development by DOE/NETL to separate CO_2 and H_2 in coal-derived syngas for IGCC applications. Membrane designs include metallic, polymeric, or ceramic materials operating at elevated temperatures, with a variety of chemical and/or physical mechanisms that provide separation. Successful membranes must have high permeability and selectivity at low pressure drop, tolerance to contaminants (e.g., sulfur), and be capable of operation at system temperatures up to 500°C. However, technical and economic barriers exist for viable pre-combustion CO_2 membrane separation such as the development of stable membrane materials, membrane module designs to facilitate optimal surface area, minimize particulate fouling, and low-cost, large-scale membrane manufacturing to provide defect-free membranes. Better methods are also needed to make high-temperature, high-pressure seals using various membrane substrates. Table 5-3 provides a list of recent and current DOE/NETL external R&D projects related to pre-combustion membrane technologies. The Appendix includes summary descriptions and results, if available, for these projects.

KEY HIGHLIGHTS OF NETL PRE-COMBUSTION MEMBRANE RESEARCH

- United Technologies Research Center has achieved an H_2 flux of 61.3 m^3/m^2-s at 100 pounds per square inch gauge (psig) using a palladium-copper (PdCu) alloy membrane.
- Media Process and Technology has successfully combined an H_2 separation membrane with a WGS catalyst (CoS_2/MoS_2) in a single unit to achieve an H_2 yield greater than 90 percent at a CO conversion greater than 97 percent.
- REB Research and Consulting has developed intermetallic alloys that have demonstrated life spans in excess of 15 years (based on accelerated tests) with similar permeability and selectivity properties as palladium at a fraction of the cost ($\$100/ft^2$ compared to $\$3,000/ft^2$).
- Western Research Institute has constructed a 1,000 cm^2, 9 wt% palladium alloy membrane surface that is capable of producing 3,000 ml/min of H_2 at 30 psi H_2 partial pressure.
- Praxair has achieved H_2 flux as high as 318 $scfh/ft^2$ with an H_2/N_2 selectivity of 275 at 300°C and 200 psi using their palladium alloy membrane.
- SRI International has constructed a hollow fiber polybenzimidazole membrane that requires up to 24 times less surface area and approximately 300 times less membrane volume compared to coated tube membranes.



Ceramic Membrane Test Disks

TABLE 5-3: DOE/NETL R&D PROJECTS FOR PRE-COMBUSTION CO_2 CAPTURE USING MEMBRANES

Project Focus	Participant	Project Number	Performance Period
Palladium-Copper Trimetallic Alloy Membranes	United Technologies Research Center	NT43055	6/15/07 – 6/14/09
Carbon Molecular Sieve Membranes	Media Process and Technology, Inc.	NT43057	5/2/07 – 5/1/10
Palladium-Based Membranes	Worcester Polytechnic Institute	NT43058	5/7/07 – 5/6/10
High Flux Metallic Membranes and Reactors	REB Research and Consulting	NT42400	10/1/05 – 3/31/09
Ternary Palladium Alloy Membranes	Southwest Research Institute	NT43056	5/2/07 – 5/1/10
Water-Gas Shift Catalyst with Vanadium Alloy Membrane	Western Research Institute	NT42454	7/1/05 – 12/30/08
Catalysts for Use in Membrane Reactors	Grambling State University	NT43064	12/20/06 – 1/1/10
Dense High Temperature Ceramic Membranes	Argonne National Laboratory	FWP-49601	3/31/98 – 9/30/08
Mixed Matrix Membranes for H_2/CO_2 Separations	University of Texas at Dallas	NT42173	8/26/04-8/31/08
Palladium Alloy Membranes	Praxair, Inc.	NT43054	6/1/07 – 5/31/10
Palladium/Silver Composite Membranes	North Carolina A&T State University	NT42492	9/1/05 – 2/28/09
Palladium-Based Membrane Reactor	Los Alamos National Laboratory	FWP-FE99002-4A24A	10/1/98 – 9/30/08
High-Temperature Polymeric Membranes	SRI International	NT43090	4/1/07 – 2/28/10
Hydrogen Transport Membranes	Eltron Research, Inc.	NT42469	8/16/05 – 9/30/08
Sulfur-Tolerant Palladium Alloy Membranes	Worcester Polytechnic Institute	NT42194	9/28/04 – 9/30/08
H_2/CO_2 Separation Membranes	UNDEERC	NT42465	--
Hydrogen Selective Zeolite Membranes	University Of Minnesota	1322	10/1/09 – 9/30/13
Ternary Palladium-Alloy Hydrogen Separation Membranes	Pall Corporation	1181	10/1/09 – 9/30/12
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	0470	10/1/09 – 9/30/13
Nanoporous, Superhydrophobic Membranes	Gas Technology Institute	0646	10/1/09 – 9/30/11
Polymer Membranes	Membrane Technology Research, Inc.	1124	9/14/09 – 9/10/10
Pressure Swing Absorption with Membrane Contactor	New Jersey Institute of Technology	1123	10/1/09 – 9/30/12

CHAPTER 6:

POST-COMBUSTION CARBON DIOXIDE CAPTURE R&D EFFORTS

DOE/NETL is currently funding the development of advanced post-combustion CO_2 capture technologies that have the potential to provide step-change reductions in both cost and energy demand as compared to currently available amine-based scrubbing technologies. The DOE/NETL R&D projects are focused on solvents, sorbents, and membranes.

6.A SOLVENTS FOR POST-COMBUSTION

As discussed in Chapter 4, solvent-based CO_2 capture involves chemical or physical absorption of CO_2 from combustion flue gas into a liquid carrier. The absorption liquid is regenerated by increasing its temperature or reducing its pressure. DOE/NETL's R&D objectives for post-combustion solvents includes development of low cost, non-corrosive solvents that have a high CO_2 loading capacity; low regeneration energy; improved reaction kinetics; and are resistant to degradation.

SOLVENT RESEARCH OBJECTIVES

- Increase CO_2 loading capacity
- Minimize regeneration energy
- Increase reaction kinetics
- Increase mass transfer
- Reduce solvent corrosivity
- Reduce solvent degradation
- Lower capital and operating cost

CURRENTLY AVAILABLE SOLVENT TECHNOLOGIES

Although CO_2 capture is new to coal-based power generation, removal of CO_2 from industrial gas streams is not a new process. Gas absorption processes using chemical solvents, such as amines, to separate CO_2 from other gases have been in use since the 1930s in the natural gas industry and to produce food and chemical grade CO_2 from gas streams containing 3 to 25 percent CO_2. Starting in the 1940s, physical solvents were developed to absorb CO_2 from gas streams with higher CO_2 concentration (25 to 70 percent) and higher pressure (approximately 10 MPa). In the 1950s and 1960s, gas adsorption processes were developed to remove CO_2 from gas streams associated with hydrogen production (refineries), nitrogen separation, and dehydration. In the 1970s and 1980s, gas separation membranes were developed to capture CO_2 for use in enhanced oil recovery (EOR) and natural gas processing.[iii]

The licensing history of the Econamine FG process (one of a handful of commercially available amine-based chemical solvent CO_2 separation processes) provides a good example of past applications of CO_2 removal technologies.[iv] Prior to 1999, 25 capture facilities were built that captured CO_2 quantities ranging from 700 to 365,000 tons per year using the Econamine FG process. The 10 largest facilities captured more than 22,000 tons of CO_2 per year. Nine of these large facilities captured CO_2 from flue gas generated by the combustion of natural gas. The one exception used flue gas generated by firing a variety of fuels, including heavy fuel oil. The process was also used for pilot-scale testing of three coal-fired applications capturing 700 to 1,600 tons per year. The captured CO_2 from these facilities was used for EOR, urea production, and in the food and beverage industry. The capture rates for these facilities reflect the fact that they were built to serve a specific commercial market for CO_2. Other amine-based solvent processes (e.g., ABB/Lummus) were implemented at similar capture rates during this time period. By comparison, a single 550-megawatt (MW) net output coal-fired power plant capturing 90 percent of the emitted CO_2 will need to separate approximately 5 million tons of CO_2 per year. This large difference in capacity represents a significant barrier to widespread commercial deployment of CO_2 removal technologies for coal-fired power plants.[v]

A 2009 review of commercially available CO_2 capture technologies identified 17 facilities (using both chemical and physical capture solvents) in current operation.[vi] These include four natural gas processing operations and a synthesis gas (syngas) production facility in which more than 1 million tons of CO_2 are captured per year. The largest (a natural gas processing operation in Wyoming) captures 4 million tons per year, which approaches the volume required for capture at electric generating plants. However, it is unclear how transferrable experience with natural gas processing is to separation of power plant flue gases given the significant differences in the chemical make-up of the two gas streams. In addition, integration of these technologies with the power cycle at generating plants presents significant cost and operating issues that must be addressed in order to facilitate widespread, cost-effective deployment of CO_2 capture.

There is limited experience with solvent-based CO_2 capture technologies at the appropriate scale in power plant settings.[vii] AES's coal-fired Warrior Run (Cumberland, Maryland) and Shady Point (Panama, Oklahoma) power plants are equipped with monoethanolamine (MEA) scrubbers developed by ABB/Lummus. They were designed to process a relatively small percentage of the plants' flue gas. At Warrior Run, the MEA system removes CO_2 from approximately three to five percent of the flue gas (approximately 120,000 tons of CO_2 per year). At Shady Point, a small slip stream of the facility's emissions is treated to produce approximately 73,000 tons of CO_2 per year. The CO_2 from both plants is subsequently used in the food processing industry.[vii] At the Searles Valley Minerals soda ash plant in Trona, California, approximately 300,000 tons of CO_2 per year are captured from the flue gas of a coal power plant using an ABB/Lummus MEA capture unit.[vii] This facility has been in operation since 1978. The captured CO_2 is used for the carbonation of brine in the process of producing soda ash.

Figure 6-1 shows a schematic diagram of the MEA process. After conventional air pollutant clean-up, the combustion flue gas enters an absorber reactor and flows counter-currently to a CO_2-lean MEA solution where CO_2 is absorbed into, and chemically reacts with MEA. The treated flue gas (primarily N_2) is discharged to the atmosphere and the CO_2-rich solution is pumped to a stripper reactor for regeneration. In the stripper, the CO_2-rich solution is heated in order to reverse the amine-CO_2 chemical reaction and strip the CO_2 out of solution. A reboiler, supplied with extraction steam from the turbine cycle, provides the heat for regeneration of the MEA solvent in the stripper. Consequently, CO_2 is released, producing a concentrated stream which exits the stripper and is then cooled and dehumidified in preparation for compression, transport, and storage. From the stripper, the CO_2-lean solution is cooled and returned to the absorber for reuse.

Current amine solvents are corrosive; susceptible to degradation by trace flue gas constituents (particularly SO_X); and necessitate significant amounts of energy, in the form of low-pressure steam, for sensible heating, heat of reaction, and stripping for CO_2 regeneration. Installing the current state-of-the-art MEA post-combustion CO_2 capture technology on new conventional PC power plants would increase the COE by about 75 percent. Further, the large quantity of energy required to regenerate the MEA solvent would reduce the net efficiency by approximately ten percentage points.

Amines chemically react with CO_2 via reversible reactions to form water-soluble compounds. Despite the low CO_2 partial pressure in combustion flue gas, amines are capable of achieving high levels of CO_2 capture due to fast kinetics and strong chemical reactions. Depending on the amine type the absorption capacity for some available amines is chemically limited with two moles amine for each mole of CO_2 being required—therefore, having a relatively low CO_2 carrying capacity per mass of solution circulated. In addition, typical amine solution concentrations are limited by viscosity and corrosion. Therefore, most current amine systems are only between 20 and 30 percent amine with the remaining being water. Although the 70 to 80 percent water present in the solution helps control the solvent temperature (as well as viscosity and corrosion) during absorption, which is an exothermic reaction, the water necessitates significant amounts of sensible heating and stripping energy upon CO_2 regeneration. Not every amine system is the same and various vendors offer different designs. In general, depending on the type of solvent mixture, solvent concentration, and amount of process heat integration/optimization, anywhere from 1,200 to greater than 3,000 British thermal units (Btu) per pound of CO_2 in the form of low pressure steam (approximately 45 psia) is required to regenerate the solvent to produce a concentrated CO_2 stream at a pressure of approximately 25 psia.

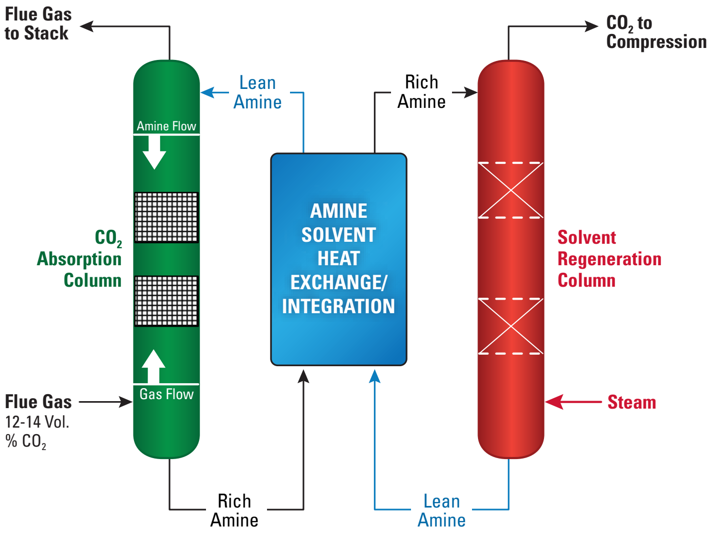


Figure 6-1: Schematic Diagram of the Post-Combustion MEA CO_2 Capture Process

AMINE-BASED SOLVENT PROCESS DEVELOPMENT

With the potential of large-scale power plant CO_2 mitigation on the horizon, technology developers have begun to develop advanced next generation amine solvents. Two leading developers are Fluor Corporation, with the development of the Econamine FG Plus^{SM} technology, and Mitsubishi Heavy Industries (MHI), with the development of a line of hindered amines (KS-1, KS-2, and KS-3) and structured packing (KP-1).[viii, ix, x] The optimizations are focused primarily on extensive thermal integration of the CO_2 capture plant with the power plant and the development of improved solvent formulations with lower stripping steam requirements and lower solvent circulation rates than MEA. The following are some examples of the design improvements:

- Improved solvents for higher reaction rates, higher CO_2 capacity, and lower corrosion and degradation rates
- Split flow configuration for flash regeneration and steam stripping
- Absorber intercooling for higher rich solvent loading
- Structured packing for lower pressure drop, smaller absorber size, and increased gas/liquid mass transfer area

It is important to point out that these technology improvements are still in the development stage and have yet to be demonstrated at power plant scale. To date, no commercial scale Econamine FG Plus^{SM} plants are operating on fossil-based power systems. However, DOE/NETL selected the Fluor Econamine FG Plus^{SM} technology for a CCPI demonstration to be conducted on a 60 MW flue gas slipstream at NRG's W.A. Parish Generating Station beginning in 2015. A commercial 160 ton/day CO_2 capture plant using MHI's KS-1 technology has been in operation since 1999 at the Petronas Fertilizer Corporation in Malaysia, where the CO_2 is captured from reformer flue gas.[iv] MHI is currently conducting pilot-scale, slip-stream testing (~10 ton/day CO_2 capture) at a coal-fired power plant in Matsushima, Japan. MHI's next step is to conduct full-scale testing (~500 ton/day CO_2 capture) demonstration at a coal-fired power plant. Other vendors that offer commercially available amine-based capture processes include ABB/Lummus, HTC Purenergy, Aker Clean Carbon, and Cansolv.[xi]

AQUEOUS AMMONIA-BASED SOLVENT PROCESS DEVELOPMENT

In addition to amines, ammonia-based solvents can be used for CO_2 capture that relies upon a temperature swing to cycle between ammonia carbonate and ammonia bicarbonate. This reaction has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism. Ammonia-based absorption has a number of other advantages over amine-based systems, such as the potential for high CO_2 capacity, lack of degradation during absorption/regeneration, tolerance to O_2 in the flue gas, low cost, and potential for regeneration at high pressure.

Alstom developed the chilled ammonia process (CAP), in which the flue gas is cooled to less than 20°C to optimize the ammonia carbonate reaction with CO_2 and minimize ammonia slip. The resultant ammonia bicarbonate precipitates out of solution as a solid and is subsequently heated to approximately 80°C in the regenerator where the CO_2 is liberated. The ammonia carbonate is then recycled back to the absorber. In 2008, Alstom, EPRI, and We Energies operated a 1.7-MW pilot-scale CAP system at We Energies' Pleasant Prairie Power Plant in Wisconsin.[xii] That relatively small pilot-scale test was followed in late 2009 with a larger pilot-scale test (~20 MW) of CAP at AEP's Mountaineer Power Plant in West Virginia.[xiii] In 2010, DOE/NETL selected the Alstom CAP technology for a CCPI demonstration to be conducted on a 235 MW flue gas slipstream at AEP's Mountaineer Plant beginning in 2015.

DOE/NETL R&D ACTIVITIES

DOE/NETL R&D includes chemical and physical solvents. Although high levels of CO_2 capture are possible, the drawback of a chemical solvent process is that significant amounts of energy are required in the regeneration step, which involves a temperature swing to break the absorbent-CO_2 chemical bond. Advanced chemical solvents that have lower regeneration energy than commercially-available amine systems, and that are also resistant to flue gas impurities, are being developed through DOE/NETL-sponsored research.

While physical solvent-based systems, such as the Selexol™ and Rectisol® processes, are generally viewed as pre-combustion CO_2 capture technologies for high-pressure IGCC power plants, a promising physical solvent-based concept for post-combustion CO_2 control involves ILs. DOE/NETL-sponsored research of ILs is being conducted at the University of Notre Dame and Georgia Tech. ILs includes a broad category of salts that can dissolve gaseous CO_2 and are stable at temperatures up to several hundred degrees Centigrade. Their temperature stability offers the possibility of CO_2 capture without first having to cool the flue gas. Also, since ILs are physical solvents, less energy is required for regeneration compared to today's conventional chemical solvents. The costs for newly synthesized ILs are high, but could be significantly lower when produced on a commercial scale. Some ILs developed by Notre Dame have exhibited CO_2 solubility 40 times greater than prior to the start of the DOE/NETL-sponsored research project, as well as even higher SO_2 solubility, allowing ILs to not only capture CO_2, but also serve as an SO_2 polishing step. However, capacity still needs to be significantly improved to meet cost targets. One possible drawback is that the viscosities of many ILs are relatively high upon CO_2 adsorption compared to conventional solvents, perhaps adversely affecting the energy requirement to pump IL in a conventional adsorption/stripping process.

KEY HIGHLIGHTS OF NETL POST-COMBUSTION SOLVENT RESEARCH

- The University of Notre Dame is developing IL absorbents that have low enthalpy of absorption (~12 KJ/mol), low affinity for O_2 and N_2, and CO_2 absorption capacities up to 0.9 mol-% at 200 mbar and 25°C.
- GE Global Research has discovered that the addition of hydroxyl-containing materials such as triethyleneglycol as co-solvents permit Si-based solvents to capture CO_2 with reduced risk of solids or viscous mixture formation.
- Georgia Tech Research Corporation has successfully synthesized and characterized chemically three precursors for reversible ILs (liquids that react with CO_2 to form an IL, which then dissolve more CO_2 physically). These precursors are (3-aminopropyl) trimethoxysilane, (3-aminopropyl) triethoxysilane, and (3-aminopropyl) triethylsilane.

Oligomer Solvent Screening Test Equipment

Table 6-1 provides a list of recent and current DOE/NETL external R&D projects related to post-combustion solvent technologies. The Appendix includes summary descriptions and results, if available, for these projects.

TABLE 6-1: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO_2 CAPTURE USING SOLVENTS

Project Focus	Participant	Project Number	Performance Period
High-Capacity Oligomers	GE Global Research	NT0005310	10/1/08 – 9/30/10
Integrated Vacuum Carbonate Absorption	Illinois State Geological Survey	NT0005498	10/1/08 – 9/30/11
Phase Transitional Absorption	Hampton University	NT42488	6/15/05 – 6/30/09
Ionic Liquids	University of Notre Dame	NT43091	3/1/07 – 7/21/10
Reversible Ionic Liquids	Georgia Tech Research Corporation	NT0005287	11/1/08 – 10/31/11

6.B SORBENTS FOR POST-COMBUSTION

Solid particle sorbents can be used for post-combustion capture of CO_2 via chemical adsorption, physical adsorption, or a combination of the two. Similar to solvent-based technologies, a temperature swing approach is used forsorbent regeneration. In addition to sorbent development, it is also important to develop an efficient and reliable process configuration. Possible configurations for contacting the flue gas with the solid particles include fixed, moving, and fluidized beds.

SORBENT RESEARCH OBJECTIVES

- Increase CO_2 loading capacity
- Minimize regeneration energy
- Increase reaction kinetics
- Increase mass transfer
- Improve durability
- Improve heat management
- Optimize process design
- Lower cost

DOE/NETL R&D ACTIVITIES

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. There are several DOE/NETL funded projects investigating using solid sorbents to capture post-combustion CO_2 from power plant flue gas. Some potential chemical sorbents are sodium and potassium oxides, carbonates, and amine-enriched sorbents. DOE/NETL is also sponsoring the development of a new class of sorbents known as metal organic frameworks, which are manufactured, micro-porous, thermally stable materials that have the potential for high CO_2 adsorption capacity. MOF represent a class of porous materials that offer several advantages for CO_2 capture, such as ordered structures, high thermal stability, adjustable chemical functionality, extra-high porosity, and the availability of hundreds of crystalline, well-characterized porous structures. Table 6-2 provides a list of recent and current DOE/NETL external R&D projects related to post-combustion sorbent technologies. The Appendix includes summary descriptions and results, if available, for these projects.

KEY HIGHLIGHTS OF NETL POST-COMBUSTION SORBENT RESEARCH

- In 2009, a novel liquid-impregnated clay sorbent developed by ORD captured the prestigious 2009 R&D 100 Award from R&D Magazine. The sorbent can capture up to 99 percent CO_2 in the temperature range of ambient to 60°C for both fixed and fluidized-bed reactor applications and is regenerable at 80°C to 100°C.
- SRI International is developing novel carbon pellet sorbents that are capable of adsorbing up to 0.2 kg of CO_2 per kg of sorbent. These pellets have a low heat of adsorption reaction (25 kJ/mol CO_2) and release CO_2 at atmospheric pressure and low temperature (between 80°C and 100°C).
- The University of Akron has been developing a zeolite amine mixture, impregnated with several additives, that has a CO_2 capture capacity greater than 3,000 μ-mol/g-sorbent, shows less than 5 percent degradation of the amine, and has a heat capacity of only 0.8 kJ/kg-K.
- Research Triangle Institute is developing a low cost (~$200/ton), non-hazardous, dry carbonate process that operates entirely below 120°C with the carbonation process taking place at approximately 50°C to 60°C.
- TDA Research is developing an alkalized alumina sorbent that only loosely bonds CO_2 to the surface of the sorbent permitting rapid, low-energy regeneration at isothermal conditions. Additionally, a novel adsorption and regeneration process utilizing a rotating wheel is being developed.

Sorbent Particles

TABLE 6-2: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO_2 CAPTURE USING SORBENTS

Project Focus	Participant	Project Number	Performance Period
Metal Monolithic Amine-Grafted Zeolites	University of Akron	NT43086	2/21/07 – 2/20/10
Dry Sodium Carbonate	Research Triangle Institute	NT43089	3/7/07 – 3/6/10
Alkalized Alumina	TDA Research, Inc.	NT0005497	11/1/08 – 10/31/11
Metal Organic Frameworks	UOP LLC	NT43092	4/1/07 – 3/31/10
Carbon-Based Sorbents	SRI International	NT0005578	10/1/08 – 9/30/11
Evaluation of Solid Sorbents	ADA-ES, Inc.	NT0005649	9/30/08 – 12/31/10

6.C MEMBRANES FOR POST-COMBUSTION

MEMBRANE RESEARCH OBJECTIVES

- Increase permeability
- Increase CO_2/N_2 selectivity
- Improve durability (chemical, thermal, physical)
- Optimize membrane process design and integration
- Lower cost (capital and energy penalty)

Membrane-based post-combustion CO_2 capture uses permeable or semi-permeable materials that allow for the selective separation of CO_2 from flue gas. While membranes are more advantageous for separating CO_2 in high-pressure applications, such as coal gasification, DOE/NETL is also focused on developing highly-selective and permeable membrane systems designed specifically for CO_2 separation from low partial pressure, post-combustion flue gas streams. Membranes potentially could be a more cost-effective technology option for post-combustion CO_2 capture than solvents or sorbents that require a large amount of regeneration energy to separate the CO_2. Membranes constructed of polymeric materials are currently used in a number of industrial gas separation processes including air separation; hydrogen recovery from ammonia; dehydration of air; and CO_2 separation from natural gas. In general, membrane processes offer several potential advantages compared to other post-combustion CO_2 capture technologies including: (1) simple passive operation with no moving parts; (2) immunity to chemical contaminants; (3) energy-efficient with low operating costs; and (4) a small footprint that is easily expandable due to modular design components.

DOE/NETL R&D ACTIVITIES

DOE/NETL's R&D objectives for post-combustion membranes includes development of low cost, durable membranes that have improved permeability and selectivity, thermal and physical stability, and tolerant of contaminants in combustion flue gas. The major R&D focus is on increasing membrane permeance. However, there is a need for both a high-permeance membrane and an innovative process design for the technology to be cost-effective. In addition, a cost-effective membrane system requires development of commercial-scale membrane modules that can achieve low pressure drop and high packing density. Gas absorption membrane technologies are also under development where the separation is caused by the presence of an absorption liquid on one side of the membrane that selectively removes CO_2 from a gas stream on the other side of the membrane. These membranes are essentially used as a contacting device between the gas flow and liquid flow. An example of this type of membrane would be the membrane-solvent systems that use an amine as the solvent. Table 6-3 provides a list of recent and current DOE/NETL external R&D projects related to post-combustion membrane technologies. The Appendix includes summary descriptions and results, if available, for these projects.

TABLE 6-3: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO_2 CAPTURE USING MEMBRANES

Project Focus	Participant	Project Number	Performance Period
Biomimetic Membrane	Carbozyme, Inc.	NT43084	3/28/07 – 6/27/10
Hollow-Fiber, Polymeric Membranes	RTI International	NT0005313	10/1/08 – 9/30/10
Spiral-Wound, Polymeric Membranes	Membrane Technology & Research, Inc.	NT0005312 & NT43085	4/1/07 – 9/30/10
Dual-Functional, Silica-Based Membranes	University of New Mexico	NT42120	8/23/04 – 4/30/09

KEY HIGHLIGHTS OF NETL POST-COMBUSTION MEMBRANE RESEARCH

- Membrane Technology & Research, Inc. constructed a pilot-scale testing facility that incorporates a membrane with a permeance 10 times greater than existing materials and possesses considerable stability in acid gases.
- The University of New Mexico has been developing a microporus inorganic silica-based matrix membrane with amine functional group additives that enhance the surface diffusion of CO_2. A CO_2 permeance of 0.5 cm^3/cm^2-min-atm and selectivity of ~50 was achieved.

Membrane Modules

6.D RECENTLY SELECTED PROJECTS

In July 2010, DOE/NETL announced the selection of ten new projects that will develop post-combustion CO_2 capture technologies for PC-fired power plant applications. The projects include development of advanced solvents, sorbents, and membranes at bench- and pilot-scale. These projects had not been awarded as of the completion of this report, so detailed information is not yet available. However, the following is a brief summary of the new projects that are expected to get underway in FY2010:

BENCH-SCALE DEVELOPMENT AND TESTING OF POST-COMBUSTION CO_2 CAPTURE

- American Air Liquide, Inc. will develop a cost-effective system for CO_2 capture based on sub-ambient temperature operation of a hollow fiber membrane. The membrane will be coupled with cryogenic processing technology in a closed-loop test system that will verify the effect of possible contaminants, such as SO_X, NO_X and water, on membrane performance. Experimental results will be used to refine the integrated process simulation and to design a slipstream facility.
- Gas Technology Institute is partnering with PoroGen Corporation and Aker Process Systems to develop a cost-effective hybrid technology for CO_2 capture based on a combination of solvent absorption and hollow fiber membrane technologies. The technology could also apply to removal of numerous other gas pollutants such as NO_X and SO_X, separation of CO_2 from hydrogen in refinery streams, and separation of CO_2 from natural gas (natural gas sweetening).
- 3H Company will evaluate the feasibility of its “Self-Concentrating Absorbent CO_2 Capture Process.” The process is based on amines in a non-aqueous solvent, which upon reaction with CO_2, separate into two distinct phases: a CO_2-rich liquid phase and a dilute lean phase. Preliminary experimental data show that the process has the potential of reducing the total regeneration energy by as much as 70 percent. 3H will also develop an engineering design to construct and operate a slipstream demonstration facility at an E-ON power plant in the United States for the next stage of commercialization development.

- Akermin, Inc. is to conduct bench-scale testing to demonstrate the performance of an advanced carbonic anhydrase-potassium carbonate solvent with significantly lower regeneration energy requirements compared to conventional MEA. Akermin will optimize solvent formulation and demonstrate process efficacy during this project.
- ION Engineering, LLC will conduct bench-scale testing of an amine-based solvent that employs an ionic liquid instead of water as the physical solvent, greatly reducing the regeneration energy while lowering process water usage. In addition to a 60 percent reduction in regeneration energy requirement, an ionic liquid-amine solvent mixture offers higher CO_2 working capacity, reduced corrosion, reduced solvent loss, and other benefits when compared to conventional aqueous amine solvents.
- The University of Illinois at Urbana-Champaign and Parsons Corporation will investigate the use of a carbonate salt-based solvent (potassium or sodium carbonate). A preliminary techno-economic evaluation shows that energy use with the Hot Carbonate Absorption Process (Hot-CAP) is about half that of a conventional MEA process. The research team will perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance Hot-CAP technology to the pilot-scale demonstration level.
- URS Group, Inc. will investigate the use of concentrated piperazine (PZ) solvent coupled with two-stage flash regeneration. This process offers several advantages over conventional solvents, including: faster CO_2 absorption rate, higher CO_2 capacity, lower volatility, negligible thermal degradation, negligible oxidative degradation when used with an inhibitor, and production of CO_2 at elevated pressure (resulting in lower compression costs). The project will be conducted initially at a 0.1 MW scale and then scaled to 0.5 MW for testing at DOE's National Carbon Capture Center.

SLIPSTREAM DEVELOPMENT AND TESTING OF POST-COMBUSTION CO_2 CAPTURE

- Membrane Technology and Research (MTR) will conduct a six-month field test at the Arizona Public Service Cholla Power Plant using a 1 MW equivalent membrane skid. Field test data and membrane performance data obtained at the National Carbon Capture Center will allow a thorough techno-economic evaluation of the membrane capture process and will clarify the relative potential of the approach.
- Siemens Energy, Inc. will design, install, and operate a pilot plant for treating a 1 MW equivalent slipstream at the TECO Energy Big Bend Station to demonstrate its POSTCAP technology, which utilizes an amino acid salt formulation as a solvent.
- ADA-ES, Inc. will refine the conceptual design of a commercial solid sorbent-based CO_2 capture technology through slipstream pilot testing and process modeling. A 1 MW equivalent pilot unit will be designed and constructed for operation at a coal-fired power plant to demonstrate the process for at least two continuous months. The pilot tests and process modeling will provide the information necessary to complete a techno-economic analysis of the technology.

CHAPTER 7:

PULVERIZED COAL OXY-COMBUSTION

As discussed in Chapter 4, oxy-combustion involves the separation of N_2 from O_2 prior to fuel combustion (versus N_2/CO_2 separation after fuel combustion). The near term approach involves O_2 production via cryogenic air separation technology followed by mixing with recycled combustion products to serve as the combustion oxidant stream. The amount of combustion products recirculated determines heat transfer mechanisms. The primary products of combustion are CO_2 and H_2O.

EXPERIENCE WITH OXY-COMBUSTION

Unlike pre- and post-combustion CO_2 capture technologies, there is significantly less experience with oxy-combustion with only a few pilot-scale applications in operation worldwide. However, in August 2010, DOE/NETL announced the selection of an oxy-combustion CO_2 capture demonstration project that is being conducted under the FutureGen Initiative that will repower an existing 200 MW power plant located in Illinois and is planned to begin operation in 2015.

DOE/NETL estimates that construction of a new oxy-combustion power plant equipped with a commercially available cryogenic ASU would increase the COE by about 65 percent and reduce the net plant efficiency by approximately 25 percent, as compared to a new air-fired PC power plant without CO_2 capture. A potential alternative to the energy-intensive cryogenic ASU is the ITM, however, ITM/boiler oxy-combustion integration concepts are in very early stages of development and there are currently no planned pilot-scale tests for this configuration.

OXY-COMBUSTION RESEARCH OBJECTIVES

- New oxyfuel-designed boilers
  - Advanced materials and burners
  - Compact designs (FG recycle)
  - Corrosion
- Retrofit existing air boilers
  - Air leakage
  - Heat transfer
  - Corrosion
  - FG recycle
  - Process control/sensors
- Low-cost oxygen
- CO_2 purification
- Co-capture (CO_2 + SO_X, NO_X, O_2)

DOE/NETL R&D ACTIVITIES

Oxy-combustion cannot be simply substituted for air combustion in existing power plants due to differences in combustion characteristics. In a retrofit application, careful engineering design is necessary to approximate the combustion characteristics of air and to maintain the radiant and convective heat transfer design conditions of a particular boiler design. Pulverized coal oxy-combustion has not yet been fully characterized. Oxy-combustion flame characteristics, burner and coal-feed design, and analyses of the interaction of oxy-combustion products with boiler materials are all areas in need of research. As a result, projects in this pathway are conducting laboratory- through pilot-scale research into oxy-combustion boiler characteristics and innovative oxy-burner design.

Although oxy-combustion would produce a flue gas that has a high CO_2 concentration, the flue gas will also include H_2O, excess O_2, N_2 (via ASU carry-over and air in-leakage), SO_2, NO_X, mercury (Hg), and other contaminants. Ongoing research is determining the technical requirements for purification. At the same time, the oxy-combustion technology pathway includes R&D of flue gas purification technologies for various levels of control specific to pulverized coal oxy-combustion power plants.

Table 7-1 provides a list of recent and current DOE/NETL external R&D projects related to oxy-combustion technologies. The Appendix includes summary descriptions and results, if available, for these projects.

KEY HIGHLIGHTS OF NETL OXY-COMBUSTION RESEARCH

- Alstom is conducting oxy-combustion testing using a 5 MW pilot-scale boiler with CO_2 recycle. Detailed data is being collected during the tests on combustion performance, heat transfer distribution, and pollutant formation. Boiler operating and performance differences, as well as changes in design requirements between air- and oxy-firing modes, are being evaluated.
- Air Products is developing an advanced CO_2 purification process that utilizes the reactions of SO_2 and NO_X that occur during compression. After initial compression to approximately 15 bar, the flue gas is cooled and contacted with water in a reactor to convert SO_2 to sulfuric acid and NO_X to nitric acid, which are then bled from the system leaving behind a pressurized, pure stream of CO_2. The process is being tested at small pilot-scale using a flue gas slip-stream at Alstom's 5 MW pilot-scale oxy-combustion boiler.

Alstom's Oxy-Combustion Test Facility

TABLE 7-1: DOE/NETL R&D PROJECTS FOR OXY-COMBUSTION CO_2 CAPTURE

Project Focus	Participant	Project Number	Performance Period
Oxy-Syngas Combustor	Clean Energy Systems, Inc.	NT42645	10/1/05 – 9/30/08
Engineering Assessment of Oxy-Combustion	Argonne National Laboratory	FWP-49539	10/1/97 – 12/31/10
Flue Gas Purification via Compression	Air Products and Chemicals, Inc.	NT0005309	10/1/08 – 9/30/10
NO_x Behavior in Oxy-Combustion	Brigham Young University	NT42530	8/4/05 – 12/31/08
Multi-Pollutant Control	Washington University	NT42531	8/29/05 – 2/28/09
Flue Gas Purification Options	Praxair, Inc.	NT0005341	10/1/08 – 12/31/11
Tangential-Fired Oxy-Combustion Retrofits	Alstom Power	NT0005290	10/1/08 – 9/30/10
Evaluation of Boiler Materials for Oxy-Combustion	Foster Wheeler NA, Corp.	NT0005262	10/1/08 – 9/30/11
Evaluation of Gas Recycle for Oxy-Combustion	Southern Research Institute	NT42430	9/27/05 – 12/30/08
Characterization of Oxy-Combustion Impacts	Reaction Engineering International	NT0005288	10/1/08 – 9/30/11
Oxy-Combustion for Cyclone and Wall-Fired Boilers	Babcock & Wilcox	NT42747	3/31/06 – 9/30/10
Oxy-Combustion and Integrated Pollutant Removal	Jupiter Oxygen Corporation	NT42811	9/28/06 – 9/30/11
Engineering Assessment of Oxy-Combustion	CANMET	IEA-CANMET-CO_2	9/30/99 – 12/31/09

CHAPTER 8:

OXYGEN PRODUCTION

For pulverized coal oxy-combustion and IGCC to be cost-effective power generation options, a low-cost supply of pure O_2 is required. Although a cryogenic ASU can be used to supply high-purity O_2 to the boiler or gasifier, this commercially available technology is both capital and energy intensive. In response, DOE/NETL is funding the development of novel technologies that have the potential to provide step-change reductions in the cost of O_2 production.

Several novel O_2 production technologies currently under development have the potential to reduce the cost of O_2 production including: ion transport membranes (ITM); oxygen transport membranes (OTM); nanofiller-modulated polymeric membranes; a perovskite ceramic sorbent utilizing TSA; and a mixed metal oxide sorbent utilizing PSA. The following is a brief description of the ITM and OTM technologies.

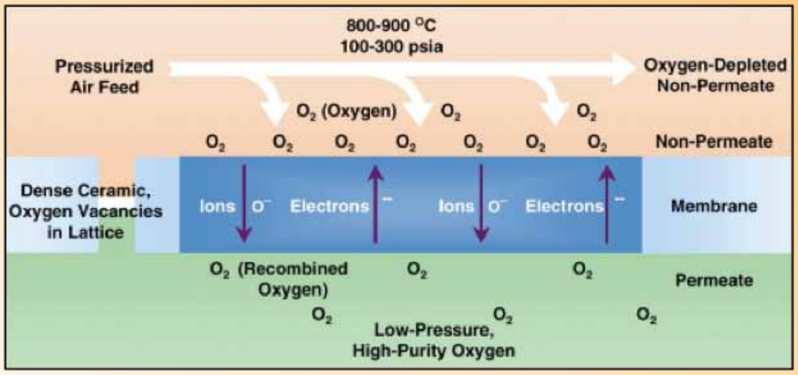
The ITM O_2 production process (being developed by Air Products) uses non-porous, mixed ion and electron conducting materials operating typically at 800 to 900°C. Ion and electron flow paths occur through the membrane counter-currently, and the driving force for O_2 separation is determined by the O_2 partial pressure gradient across the membrane, typically 200 to 300 psig on the feed side and low to sub-atmospheric pressure on the permeate side. The goal of the ITM research is to develop, scale-up, and demonstrate this novel air separation technology for producing O_2 at approximately one-third lower cost and energy requirement compared to conventional cryogenic processes.

The OTM process (being developed by Praxair) utilizes chemical potential for the O_2 separation driving force instead of pressure. The OTM is designed to integrate directly with the boiler such that the combustion reaction occurs on the fuel side of the membrane, thus creating a low O_2 partial pressure driving force. This chemical potential gradient drives O_2 through the membrane without the need for additional air compression. Recent estimates indicate that OTM can deliver O_2 for oxy-combustion using only 20 to 30 percent of the energy required for a cryogenic ASU.

Table 8-1 provides a list of recent and current DOE/NETL external R&D projects related to O_2 production technologies. The Appendix includes summary descriptions and results, if available, for these projects.

KEY HIGHLIGHTS OF NETL OXYGEN PRODUCTION RESEARCH

- Air Products is developing an ion transport membrane (ITM) for O_2 production based on ceramics that selectively transport O_2 ions when operated at high temperature and pressure. The use of these membranes could reduce the installed capital cost of air separation equipment by more than one-third, while reducing the power requirement for air separation by 35 percent compared to cryogenic methods. Air Products has designed and constructed a prototype facility capable of producing 5 TPD of O_2.
- Praxair is developing an oxygen transport membrane (OTM) that utilizes chemical potential for the O_2 separation driving force instead of pressure. The OTM would be integrated into an advanced oxy-combustion power cycle that uses a combination of OTM and cryogenic ASU to supply the O_2. Test results to date indicate the potential for a 70 percent decrease in auxiliary power consumption for supplying O_2 on a kWh/ton O_2 basis.



Principle of Oxygen Production via ITM

TABLE 8-1: DOE/NETL R&D PROJECTS FOR OXYGEN PRODUCTION

Project Focus	Participant	Project Number	Performance Period
Ceramic Auto-Thermal Recovery	The Linde Group (formerly The BOC Group, Inc.)	NT42748	4/1/06 – 3/31/10
Ion Transport Membrane	Air Products and Chemicals, Inc.	FT40343	10/1/98 – 9/30/10
Nanofiller-Modulated Polymeric Membranes	North Carolina A&T State University	NT42742	2/17/06 – 2/16/09
Materials for Temperature Swing Adsorption Oxygen Separation	Eltron Research, Inc.	ER84600.002	8/8/07 – 8/7/09
Oxygen Transport Membrane-Based Oxy-Combustion	Praxair, Inc.	NT43088	4/1/07 – 3/31/10
Sorbents for Air Separation	TDA Research, Inc.	ER84216	8/7/06 – 8/6/09

CHAPTER 9:

CHEMICAL LOOPING

Chemical looping combustion and chemical looping gasification are in the early stages of process development. Bench- and laboratory-scale experimentation is currently being conducted. Projects in this pathway are advancing the development of chemical looping systems by addressing key issues, such as solids handling and O_2 carrier capacity, reactivity, and attrition. Table 9-1 provides a list of recent and current DOE/NETL external R&D projects related to chemical looping technologies. The Appendix includes summary descriptions and results, if available, for these projects.

TABLE 9-1: DOE/NETL R&D PROJECTS FOR CO_2 CAPTURE USING CHEMICAL LOOPING

Project Focus	Participant	Project Number	Performance Period
Chemical Looping Combustion Prototype	Alstom Power, Inc.	NT0005286 & NT41866	10/1/03 – 9/30/09
Chemical Looping Simulation and Control	Alstom Power, Inc.	NT43095	7/12/07 – 9/30/09
Coal Direct Chemical Looping for Retrofit	Ohio State University	NT0005289	1/1/09 – 12/31/09
Calcium Looping Process for Hydrogen Production	Ohio State University	NT43059	7/5/07 – 7/4/10

KEY HIGHLIGHTS OF NETL CHEMICAL LOOPING RESEARCH

- Alstom Power, Inc. has successfully constructed and tested a pilot-scale (65 kWth) chemical looping facility that incorporates a reactor system that simultaneously produces H_2 or syngas and a separated stream of high purity CO_2. Calcium oxide is used to capture CO_2 and calcium sulfate ($CaSO_4$) is used as the coal oxidizer.
- Ohio State University has constructed a pilot-scale (25 kWth) chemical looping facility that is testing Fe_2O_2 as the oxygen carrier.
- Ohio State University has selected a calcium oxide sorbent to be used in its development of a "one box" system for IGCC applications to combine the WGS with CO_2 removal. The optimum temperature for H_2 production and CO_2 removal was determined to be 600°C.

Chemical Looping Cold Flow Model

CHAPTER 10:

ADVANCED CARBON DIOXIDE COMPRESSION

Once the CO_2 is separated from the flue gas, it must be dehydrated and compressed to a supercritical liquid phase prior to pipeline transport and/or permanent storage in deep geologic formations. DOE/NETL estimates that for a new 661-MW SC coal-fired power plant, CO_2 compression to 2,200 psia would require 44 MW of auxiliary power and increase the COE by 9.6 mills/kWh, including both power consumption and capital costs.[v]

ADVANCED COMPRESSION RESEARCH OBJECTIVES

- Reduce capital costs
- Increase efficiency
- Optimize integration with CO_2 capture process
- Improve heat recovery

To reduce compression costs, DOE/NETL is developing novel concepts for large-scale CO_2 compression. Various compression concepts are being evaluated using computational fluid dynamics and laboratory testing, leading to prototype development and field testing. Research efforts include the feasibility of a supersonic shock wave technology and fundamental thermodynamic studies to determine whether compression in a liquid or gaseous state is preferred. As shown in Table 10-1, DOE/NETL is currently funding two R&D projects in this area. The Appendix includes additional information for these projects.

TABLE 10-1: DOE/NETL R&D PROJECTS FOR ADVANCED CO_2 COMPRESSION

Project Focus	Participant	Project Number	Performance Period
Evaluation of Compression Efficiency Improvements	Southwest Research Institute	NT42650	9/28/05 – 4/15/10
Shock Wave Compression	Ramgen Power Systems	NT42651	5/10/06 – 1/9/11

NOVEL CONCEPTS FOR CO_2 COMPRESSION

Southwest Research Institute (SwRI) is developing two novel concepts that have the potential to reduce CO_2 compression power requirements by 35 percent compared to conventional compressor designs. The first 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. This concept can potentially reduce power requirements since less energy is required to boost the pressure of a cool gas. The second concept involves the use of refrigeration to liquefy the CO_2 so that its pressure can be increased using a pump rather than a compressor. The primary power requirements are the initial compression required to boost the CO_2 to approximately 250 psia and the refrigeration power required to liquefy the gaseous CO_2. Once the CO_2 is liquefied, the pumping power to boost the pressure to pipeline supply pressure is minimal. Prototype testing of each concept is being conducted.

SUPERSONIC SHOCK WAVE COMPRESSION TECHNOLOGY

Ramgen Power Systems is developing a supersonic shock wave compression technology, similar in concept to an aircraft's ramjet engine, for use in a stationary compressor. Ramgen's compressor design, known as a Rampressor, features a rotating disk that operates at high peripheral speeds to generate shock waves that compress the CO_2. Compared to conventional compressor technologies, shock compression offers several potential advantages: high compression efficiency; high, single-stage compression ratios; opportunity for waste heat recovery; and low capital cost. For example, Ramgen's shock compression has the potential to develop compression ratios from 2.0 to 15.0 per stage with an associated adiabatic efficiency of 85 to 90 percent. For CO_2 applications, Ramgen anticipates using a nominal, two-stage 100:1 compression ratio, featuring a matched pair of 10:1 compression stages with an intercooler located between the stages. Recent prototype testing has achieved a 7.8:1 compression ratio.[xiv]

Rampressor Pilot-Scale Test Facility

In August 2009, DOE announced that Ramgen had been awarded $20 million in funding from the American Recovery and Reinvestment Act to further scale up the Rampressor to approximately 13,000 horsepower, which should accelerate commercial deployment of the novel CO_2 compressor.

CHAPTER 11:

CARBON DIOXIDE CAPTURE R&D COLLABORATIONS

The DOE/NETL CO_2 capture project portfolio also includes several overarching R&D projects that are exploring multiple approaches to CO_2 capture for coal-based power plants. These projects include collaborations with the University of North Dakota Energy and Environmental Research Center (UNDEERC), Southern Company, and the CANMET Energy Technology Center.

11.A DOE-EERC FOSSIL ENERGY BASE R&D

The objective of this project is to support the performance of advanced research on new concepts for highly efficient, non-polluting energy systems. As part of this project, the UNDEERC researchers will incorporate a CO_2 sorbent into an H_2 production system in order to enhance the WGS reaction. Testing will involve gasifying coal in a bench-scale continuous fluid-bed reactor and contacting the syngas with pre- and post-shift catalyst sorbent beds for CO_2 removal. This project also includes an examination of available membranes for H_2 and CO_2 separation in coal-derived syngas.

11.B EERC-DOE JOINT PROGRAM ON R&D FOR FOSSIL ENERGY-RELATED RESOURCES

UNDEERC will advance the development of new and improved technologies for the capture and sequestration of CO_2 in order to provide cost-effective options for stabilizing and ultimately reducing concentrations of CO_2 in the atmosphere. As part of this project, researchers will determine the flue gas CO_2 reduction effectiveness of solid adsorbents through the use of a recirculating transport reactor. In addition, UNDEERC will perform pilot-scale tests to demonstrate CO_2 capture technologies, such as solvent scrubbing and oxy-combustion, for fossil fuel and/or biomass-fired energy plants. Further, researchers will fabricate a scrubber system to conduct solvent scrubbing R&D, modify existing pilot-scale units to conduct oxy-combustion tests, and perform system engineering studies to examine efficient and cost-effective integration of CO_2 capture technologies in existing and new power production systems.

11.C NATIONAL CARBON CAPTURE CENTER AT THE POWER SYSTEMS DEVELOPMENT FACILITY

DOE/NETL, EPRI, and Southern Company are responding to the need for developing cost-effective CO_2 capture technology for coal-based power generation with the addition of the National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF). The PSDF is an engineering-scale demonstration site for advanced power system components located adjacent to Alabama Power's coal-fired Plant Gaston in Wilsonville, Alabama. The PSDF is a unique test facility – large enough to produce commercially representative data from the major components required for a commercial plant – while remaining small enough for economic operation. The mission of the PSDF-NCCC is to develop technologies that will lead to the commercialization of cost-effective, advanced coal-based power plants with CO_2 capture. The PSDF-NCCC can test multiple projects in parallel with a wide range of test equipment sizes leading up to pre-commercial equipment sufficient to guide the design of full commercial-scale power plants. The PSDF-NCCC will be capable of testing pre-, post-, and oxy-combustion technologies.

The backbone of the pre-combustion CO_2 capture technology development will be a high-pressure flexible facility designed to test an array of solvents and contactors. Slipstreams will be available with a range of gas flow rates and process conditions using coal-derived syngas for verification and scale up of fundamental R&D capture projects. CO_2 capture technologies under consideration for slipstream testing include advanced solvent, sorbents, and membranes.

For both new and existing power plants, post-combustion capture technology must be made more efficient and cost-effective by developing alternative solvents with lower heats of regeneration and more compact, lower cost equipment. A flexible test module is proposed to provide a site for testing technologies at a wide-range of sizes and process conditions on coal-derived flue gas. The PSDF-NCCC will provide several parallel paths in order to test the candidate processes at the appropriate scale. For R&D projects that have been successfully tested at bench-scale in a research lab, the PSDF-NCCC will provide a 1,000 lb/hr flue gas slipstream for screening tests. For technologies that have been successfully tested at the screening-scale, the PSDF-NCCC will provide a flue gas stream for pilot-scale testing. Two pilot test beds have been designed, a 5,000 lb/hr (0.5-MW equivalent) slipstream and a 10,000 lb/hr (1.0-MW equivalent) slipstream. Advanced solvents, sorbents, and emerging technologies are under considerations for testing in the post-combustion module.

The existing transport reactor for IGCC applications at the PSDF can be operated in a pressurized, oxy-combustion mode, which would result in a flue gas stream that is concentrated with CO_2 at moderate system pressures. System modeling and economic analysis will be used to evaluate the commercial feasibility of operating the transport combustor in oxy-combustion mode.

11.D CANMET ENERGY TECHNOLOGY CENTER

DOE/NETL also provides funding for the Canadian government's CANMET Energy Technology Center through an international agreement with the International Energy Agency's (IEA) Greenhouse Gas Program. The CANMET CO_2 Consortium is conducting research to further the development of oxy-combustion for retrofit to coal-fired power plants. Research activities include: (1) modeling of an advanced, supercritical pressure oxy-coal plant that includes an analysis of the impact of O_2 purity and O_2 partial enrichment, overall process performance, and cost; (2) performance testing of pilot-scale CO_2 capture and compression; (3) experimental investigation of CO_2 phase change at liquid and supercritical states in gas mixtures resulting from oxy-combustion; (4) testing and performance optimization of a novel, multi-function oxy-fuel/steam burner; and (5) development of a mercury removal process and analysis of multi-pollutant control strategies for oxy-combustion power plants.

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APPENDIX

CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

CO_2 Capture Technology Sheets

APPENDIX

PRE-COMBUSTION SOLVENTS

SRI International – Ammonium Carbonate

Project Title:

CO_2 Capture from IGCC Gas Streams Using AC-ABC Process

Technology Area:	**Technology Maturity:**
Pre-Combustion Solvents	Pilot-scale using actual syngas

Primary Project Goal:

SRI International is developing, for integrated gasification combined cycle (IGCC)-based power plants, a carbon dioxide (CO_2) capture technology based on the use of a high-capacity and low-cost aqueous ammoniated solution containing ammonium carbonate (AC), which reacts with CO_2 to form ammonium bicarbonate (ABC).

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 on 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.

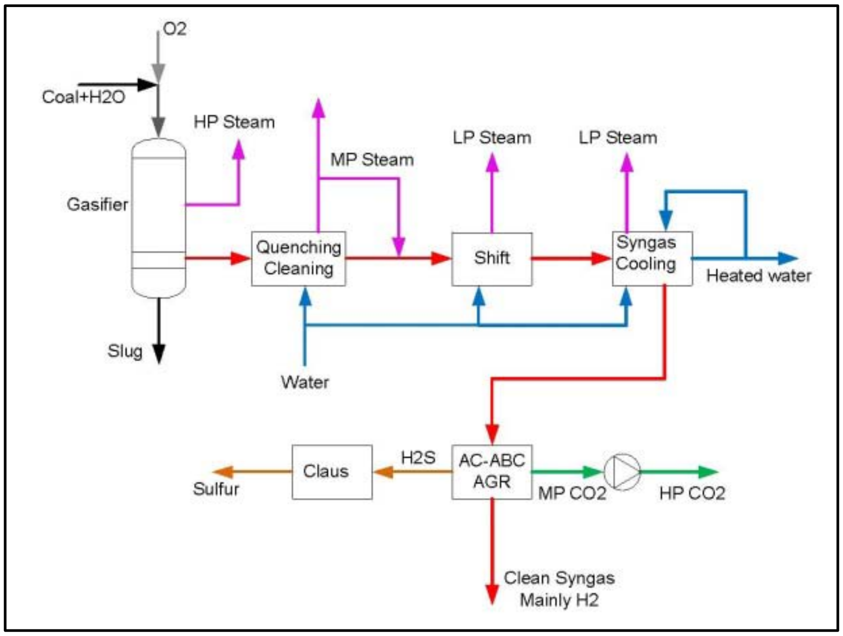

Figure 1: AGR in Gasification System

The concentrated ammoniated solution is used to capture CO_2 and hydrogen sulfide (H_2S) from synthesis gas (syngas) at high pressure. This 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

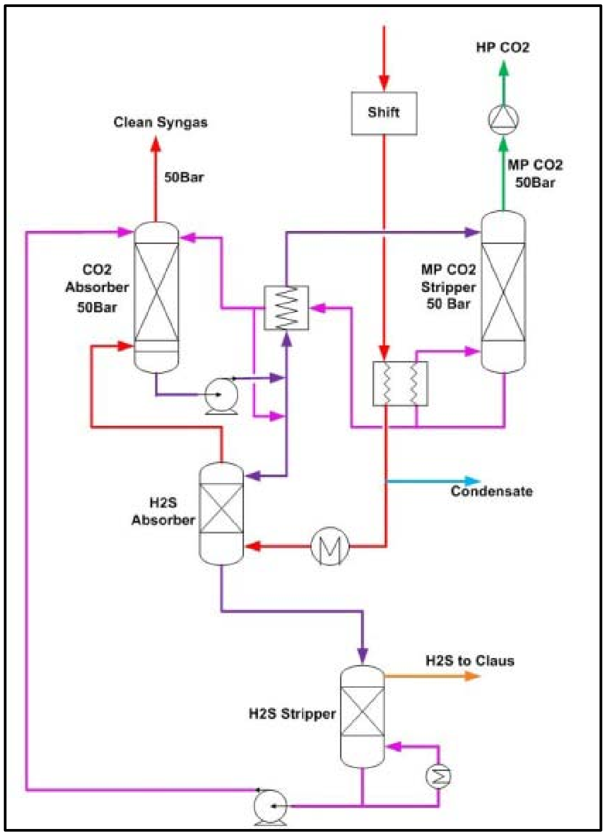

Figure 2: Schematic of the CO_2 and H_2S Capture System

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.

In the first phase of the project, the technology will be tested at bench scale at SRI's facility in California to validate the concept and to determine the optimum operating conditions. SRI will construct a bench-scale batch test reactor unit.

Absorber testing will first determine the solubility of shifted-gas components (H_2, CO, nitrogen [N_2], argon [Ar]), then determine the reactivity of CO_2, H_2S, and carbonyl sulfide (COS), and mixed-gas testing will determine the relative reaction kinetics.

Regenerator testing will 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 carried over into a pilot-scale test.

Pilot-scale testing will be performed on a slip stream of Great Point Energy's 1 ton/day pilot gasifier located at Brayton Point, Massachusetts.

SRI will design and construct a pilot-scale continuous, integrated test system. The pilot-scale test will emphasize stability of integrated operation. The tests will be of longer duration, about six to eight times longer total test time than with the simulated tests at SRI. 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.

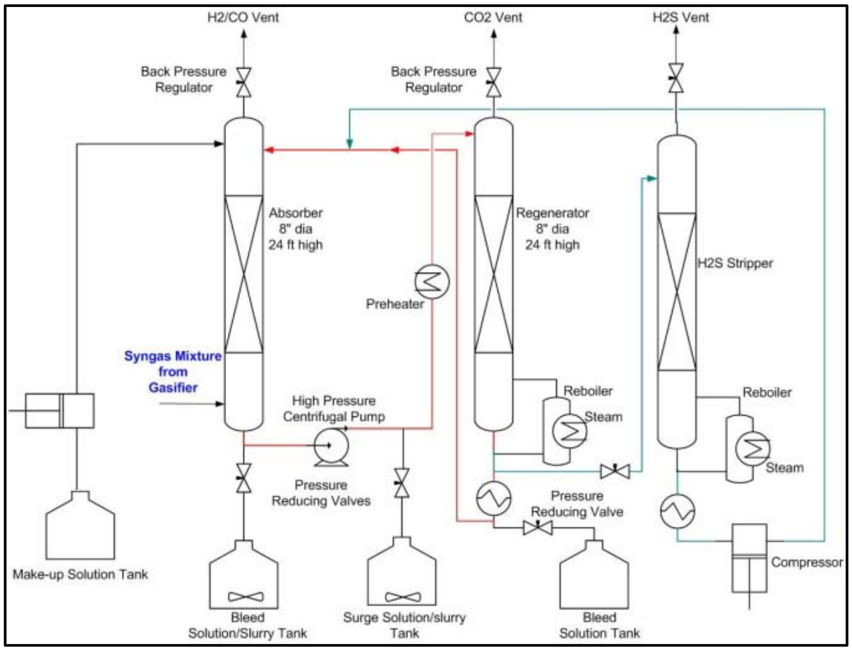

Figure 3: Pilot-Scale Integrated Testing (Preliminary)

A technical and economic analysis will use Aspen modeling to generate the equipment sizing and heat and material flows, DOE cost models, and a base case, 750-MW nominal IGCC plant without CO_2 capture to compare the AC-ABC process with a similar-size plant using CO_2 capture with a Selexol subsystem.

Table 1: Solvent Parameters

	Parameter	Current R&D Value	Target R&D Value
Solvent Properties	Type of solvent	Aqueous ammoniated solution	Aqueous ammoniated solution
	Molecular weight	Nominal 18	Nominal 18
	Boiling point (°C)	Varies with pressure; 100°C at 1 atm	Varies with pressure; 100°C at 1 atm
	Heat of reaction (kJ/mole CO_2)	40 to 60 depending on the NH_3/CO_2 ratio	40 to 60
	CO_2 loading/working capacity*, wt.%	10	20
	Solvent concentration to stripper (mol/liter)	6 M NH_3	8 M NH_3
	Heat capacity of solution (kJ/K/kg)	3.5	3.5
	Viscosity, cP	1	1
Operating Conditions	Absorption temperature, °C	25	25 to 40
	Absorption pressure, atm.	20	50
	CO_2 capture efficiency, %	>90	>90
	Regeneration method	Heating with steam	Heating with steam
	Regeneration temperature, °C	N/A	150
	Regeneration pressure, atm.	N/A	50
Heat Integration	Required regeneration steam temperature, °C	120	170
Miscellaneous	Solvent make-up rate, kg/kgCO_2	N/A	N/A
Product Quality	CO_2 purity, %	>98%	98.1
	N_2 concentration, %	N/A	1.9
	Other contaminants, %	N/A	0.01
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	17.7
	Heat requirement, kJ/kgCO_2	N/A	620.6
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	638.3

*Working capacity is the loading difference CO_2 rich solution before and after it is regenerated.

Equations Describing Chemical Reaction:

$NH_4OH+CO_2 = NH_4HCO_3$

$(NH_4)_2CO_3+CO_2 + H_2O =2NH_4HCO_3$

$NH_4(NH_2CO_2)+CO_2 +2H_2O = 2NH_4HCO_3$

$NH_4HCO_3 = NH_4HCO_3$ (precipitate)

Solvent Reaction Kinetics:

The absorption of CO_2 by the ammoniated solution is proportional (1st order) to the CO_2 partial pressure. Preliminary experiments confirm this behavior. The kinetics of CO_2 absorption is expected to be rapid at the elevated pressures and high CO_2 concentrations expected in the IGCC gas stream downstream of the water gas shift (WGS) reactors.

Solvent Heating/Cooling Method:

During regeneration, the liquid is heated by steam using a reboiler. In the absorber, the liquid is cooled using a heat exchanger and a coolant from a direct contact cooler.

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.

Flue Gas Pretreatment Requirements:

The IGCC gas stream needs to undergo WGS reaction to convert CO to CO_2 and to be cooled to a temperature of 25°C to 50°C.

Waste Streams Generated:

Ammonium sulfate solution from the capture of trace residual NH_3 in the gas.

Technology Advantages:

- Low cost and stable reactive solution.
- Reactive solution has a high CO_2 loading capacity due, in part, to the formation of ABC solids during absorption.
- Optimum operating pressure, including CO_2 output stream, is expected to be between 200 and 700 psi – resulting in lower compression costs than conventional technologies.

R&D Challenges:

- Precipitation of solids could potentially foul packing and heat exchanger surfaces.
- Absorber operation at an elevated temperature could create excessive residual ammonia in the fuel gas stream leaving the absorber.
- Adequate separation of H_2S and CO_2 in the regenerator gas.

Results To Date/Accomplishments:

Results from the project are not yet available.

Next Steps:

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

Available Reports/Technical Papers/Presentations:

CO_2 Capture from IGCC Gas Streams Using the AC-ABC Process; Presentation at the Pre-combustion CO_2 Capture Kick-off Meetings, Pittsburgh, Pennsylvania, November 12-13, 2009; Available at the NETL website.

Contract No.:

DE-FE-0000896

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APPENDIX

PRE-COMBUSTION SORBENTS

Research Triangle Institute – Warm Gas Cleanup with Sorbents

Project Title:

Integrated Warm Gas Multi-Contaminant Cleanup Technologies for Coal-Derived Syngas

Technology Area:

Pre-Combustion

Technology Maturity:

Bench-scale

Primary Project Goal:

Research Triangle Institute (RTI) is developing a modular warm, multi-contaminant synthesis gas (syngas) cleaning system that can be adapted to meet the specifications for both power and chemical/fuels production.

Technical Goals:

- Develop a modular high-temperature (150-370°C or 300-700°F) and high-pressure (up to 83 atm or 1,200 psig) cleanup process that produces an effluent syngas suitable for chemical/fuels production by controlling trace contaminants to the levels shown in Table 1.

Table 1: Targeted Control Levels for Syngas Contaminants

Contaminant	Control Level	Contaminant	Control Level
Sulfur (S)	< 50 ppbw	Selenium (Se)	0.2 ppm
Ammonia (NH_3)	10 ppm	Arsenic (As)	5 ppb
Chlorine (Cl)	10 ppb	Phosphorus (P)	< 20 ppbw
Mercury (Hg)	5 ppbw		

- Utilize a transport reactor and regenerable sorbents to control bulk syngas contaminants, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), ammonia (NH_3), and hydrogen chloride (HCl).
- Evaluate the performance of high-temperature carbon dioxide (CO_2) sorbents and promoters.

Technical Content:

In this project, RTI will develop a sequential process where high-temperature syngas will be cleaned using a transport reactor and a multi-functional fixed-bed system. The system is designed to operate at syngas feed conditions (150 to 370°C [300 to 700°F]) and 28 to 83 atm (400 to 1,200 psig), which will improve plant efficiency by eliminating the need for syngas cooling and re-heating. RTI's novel warm syngas cleaning technology could represent a significant improvement for chemical/fuels production applications due to reduced capital and operating costs; however, development and optimization for trace contaminant removal and warm CO_2 capture is needed to achieve the target syngas specifications for chemical/fuels production.

The bulk contaminant removal system consists of a transport reactor containing regenerable sorbents that target H_2S, COS, NH_3, and HCl. RTI will investigate three sorbents: (1) RTI-3 for sulfur; (2) CBV-712 for NH_3; and (3) a sodium carbonate-based sorbent for chlorine. Syngas leaving the transport reactor is routed to a multi-functional, fixed sorbent bed that reduces contaminants to ppbv levels.

RTI is employing the modified, high-pressure thermal gravimetric analyzer (TGA) shown in Figure 1 and a microreactor system to evaluate the performance of high-temperature CO_2 sorbents. The bench-scale CO_2 sorbent testing campaign includes experiments with lithium orthosilicate (Li_4SiO_4) and magnesium oxide (MgO) sorbents, as well as several promoters and support structures. RTI's Li_4SiO_4 sorbent exhibited a CO_2 adsorption capacity of about 35 wt% at high temperatures, but a technical-economic analysis concluded that the regeneration stage is prohibitively expensive.

Figure 1: Modified TGA for CO_2 Sorbent Testing

Meanwhile, a promoted MgO sorbent has demonstrated a CO_2 capacity of nearly 60 wt% and the ability to be regenerated at a CO_2 partial pressure of about 150 psig. While these initial results are promising, RTI is still developing a knowledge base for the promoted MgO sorbent and on-going research is focused on fundamental issues, including sorbent preparation procedures, sorbent support structures and binders, and syngas pretreatment requirements. As such, the data provided by RTI in Table 2 is preliminary and values for many of the sorbent- and process-related parameters are not available (N/A).

Table 2: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Promoted MgO	
	Heat of adsorption (kJ/mole CO_2)	95-100	~98
	CO_2 loading/working capacity, wt.%	10 -60	30-40
	Surface area, m^2/g	N/A	
	Particle density, cm^3/g	N/A	
	Packing density, cm^3/g	N/A	
	Particle size (mm)	N/A	
	Heat capacity (kJ/K/kg)	N/A	
	Thermal stability, °C	N/A	
	Hydrothermal stability, °C	N/A	
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	
	Cycle time (fixed bed), minutes	N/A	
	Pressure drop (fixed bed), psia	N/A	
Operating Conditions	Adsorption temperature, °C	350 -450	350-450
	Adsorption pressure, atm.	~24	40
	CO_2 capture efficiency, %	> 85	90
	Regeneration method	Thermal	Investigating
	Regeneration temperature, °C	500 - 550	Investigating
	Regeneration pressure, atm.	~24	Investigating
Heat Integration	Required regeneration steam temperature, °C	N/A	Investigating
Miscellaneous	Sorbent make-up rate, $kg/kgCO_2$	N/A	
Product Quality	CO_2 purity, %	N/A	
	N_2 concentration, %	N/A	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, $kJ/kgCO_2$	N/A	Investigating
	Heat requirement, $kJ/kgCO_2$	N/A	Investigating
	Total energy (electricity equivalent), $kJ/kgCO_2$	N/A	Investigating

In parallel with this experimental program, RTI is actively investigating potential process configurations and operating conditions to exploit the attributes of the promoted MgO sorbent. Research is geared toward developing a suitable fluidized version of the sorbent to facilitate sorbent transport between the adsorption and stripping columns, while also improving the heat transfer coefficient of the sorbent bed. RTI is also working to identify the temperature window between adsorption and regeneration that maximizes the sorbent's CO_2 working capacity, while minimizing the sensible heating requirement. In addition, RTI is exploring techniques to reuse the high-quality heat generated during the high-temperature CO_2 adsorption process. For instance, the high-quality heat could be transferred to the steam cycle to generate additional power, or it could be used to replace a portion of the steam generated in the radiant syngas cooler.

Technology Advantages:

Warm syngas cleanup will increase net plant efficiency by eliminating the need for syngas cooling and re-heating, while also producing an effluent syngas suitable for chemical/fuels production and high-purity CO_2 for storage.

R&D Challenges:

Integration and scale up of the bench-scale transport reactor and multi-functional fixed-bed system, as well as startup and standby options for the warm syngas cleanup technologies.

Results To Date/Accomplishments:

- Technical support provided to DOE/NETL researchers has resulted in a computational fluid dynamic (CFD) model that predicts temperature and differential pressure profiles similar to actual pilot plant results.
- Demonstrated that combustion products (CO_2, steam, and carbon monoxide [CO]) do not adversely affect the desulfurization performance of RTI-3.
- Adapted existing bench-scale testing system to support phosphine (in addition to arsine and hydrogen selenide) testing.
- Developing a coconut-based charcoal as a quality control cartridge for supporting mass balance determination during phosphine testing.
- Identified a family of promoters that increased the CO_2 capacity of the MgO sorbent from <2 wt% to 40-60 wt%.
- Completed a technical-economic analysis of warm CO_2 capture using RTI's Li_4SiO_4 sorbent, which concluded that the regeneration stage is prohibitively expensive.
- Independent system analysis by both Nexant and Noblis indicate that RTI's warm syngas cleaning system can yield a three to four point increase in the net HHV thermal efficiency and a 10-15% reduction in capital costs, compared to an integrated gasification combined cycle (IGCC) plant equipped with Selexol™ for acid gas removal.

Next Steps:

RTI will evaluate various regenerator startup heating processes and investigate novel approaches to reduce the syngas sulfur content to <50 ppbw. Further, RTI will continue to optimize promoters and support materials for the MgO-based CO_2 sorbent, while also establishing a baseline economic model for a warm syngas cleaning platform with the Nexant model to include warm CO_2 removal and two cases using the chemical syngas specification (hydrogen [H_2] production and power from H_2). Final test results will not be available until the December 2010 project completion date.

In a follow-on DOE/NETL project (DE-FE0000489), RTI will provide technical support to facilitate successful scale up and demonstration of the warm syngas cleanup process using a large prototype (50 MW) at an IGCC power plant.

Available Reports/Technical Papers/Presentations:

"Development of a Warm Gas Cleanup Technology Platform for Power and Chemicals Production," Pittsburgh Coal Conference, (September 2008).

"High Temperature CO_2 Capture from Syngas for Gasification Applications," Eighth Annual Carbon Capture & Sequestration Conference, (May 2009).

"Warm Syngas Cleanup for Chemical Applications using Regenerable CO_2 Sorbents," Pittsburgh Coal Conference, (September 2009).

Contract No.:

DE-FC26-05NT42459

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UNDEERC – Evaluation of Sorbents

Project Title:

Hydrogen Production and Purification from Coal and Other Heavy Feedstocks

Technology Area:	**Technology Maturity:**
Pre-Combustion Solid Adsorption	Laboratory- and pilot-scale

Primary Project Goal:

The University of North Dakota Energy & Environmental Research Center (UNDEERC) is evaluating the ability of various conventional and high-temperature carbon dioxide (CO_2) sorbents to resist the deleterious effects of hydrogen sulfide (H_2S)-containing (sour) synthesis gas (syngas).

Technical Goals:

- Assess the performance of high-temperature and conventional CO_2 sorbents in simulated and real syngas.
- Evaluate the effect of H_2S on solid sorbents when operating in a fixed-bed under simulated and real syngas conditions.
- Analyze CO_2 sorbents after exposure to real and simulated syngas.

Technical Content:

Gasification of coal and other heavy feedstocks is becoming an attractive approach for power and chemicals production. The solid fuels are transformed into a sour syngas which must be further processed to yield the desired final products (e.g., high-purity hydrogen [H_2] or H_2-rich fuel and a CO_2-rich by-product). Air Products is interested in two types of syngas treatment processes: a high-temperature process (400°C) and an ambient-temperature process. Both require information on the impact of sour gas species on the solid adsorbents and the ability of these adsorbents to reversibly adsorb H_2S and CO_2.

UNDEERC has conducted two major sets of experiments in this program. In Phase 1 of the program, a 10-bed exposure unit was built and operated, and the impact of a synthetic sour syngas on various high- and low-temperature CO_2 adsorbents was determined. Most of the adsorbents showed an increase in sulfur content and subsequent decrease in surface area and CO_2 adsorption capacity with exposure. Two materials were able to maintain their CO_2 capacity at ambient temperature.

In the next phase of work, these two materials were tested in a fixed-bed skid (Figure 1). The unit consisted of two packed beds, with the necessary valves and heating equipment to permit regeneration by pressure swing adsorption (PSA) or temperature swing adsorption (TSA) cycles.

Breakthrough experiments were conducted with 2% H_2S in H_2 feed gas to determine the H_2S adsorption capacity and mass transfer coefficients for the two materials. Hydrogen sulfide adsorption was shown to be reversible and rapid.

Figure 1: Fixed-Bed Reactor Skid

The fixed-bed unit was then connected to the EERC's existing lab-scale circulating fluidized-bed gasifier. The gasifier processed Powder River Basin (PRB) subbituminous coal spiked with elemental sulfur (S) to generate a syngas with an elevated H_2S concentration. The syngas was continuously fed to the fixed bed unit (operating in PSA mode) for more than 1,000 cycles. The adsorbent beds were capable of reducing H_2S in the product stream to less than 50 parts per million (ppm). The H_2S capacity of the adsorbent decreased with initial syngas exposure (first couple hundred cycles), but then remained stable. Post-mortem analysis of the adsorbent showed some deposition of S and chlorine

(Cl) species at the front of the bed and capture of organic tar species.

A new entrained-flow gasifier was built at the EERC's facility in 2009 that will be capable of gasifying solid petcoke. It has been integrated with the fixed-bed unit, and both will be operated in the next quarter.

Technology Advantages:

Sour syngas treatment technologies based on adsorption (high temperature or ambient temperature) have the potential to reduce the capital cost and reduce or eliminate steam consumption for the CO_2/H_2S separation.

R&D Challenges:

The physical/chemical stability of the adsorbents in a sour syngas environment remains a concern, as does the ultimate fate of trace components and the reversibility of heavy component (tars) adsorption.

Results To Date/Accomplishments:

- Identified two promising adsorbents via extended synthetic sour gas exposure tests.
- Demonstrated acceptable adsorption and mass transfer properties of two promising adsorbents for H_2S.
- Successfully operated fixed-bed test unit with coal-based syngas produced in circulating fluidized-bed gasifier.
- Measured stable capacity of H_2S in syngas operation after more than 1,000 cycles of operation.
- Conducted post-mortem analysis of adsorbent to determine progression of Cl, S, and organics into bed.
- Integrated fixed-bed unit and new entrained-flow gasifier at the EERC.

Next Steps:

The EERC will operate the entrained-flow gasifier under oxygen-blown conditions with petcoke feed to generate a second sour syngas feed to the fixed-bed unit. The system will be operated under various conditions (temperature, process flow rates) to determine the impact on separation performance. At the end of the testing, the adsorbent will be systematically removed and analyzed to monitor changes in capacity/integrity. The EERC will also modify the exposure unit to allow injection of low levels of iron carbonyl, carbonyl sulfide, and hydrogen fluoride. Impact of exposure will be determined for the most promising adsorbent to date. Final test results will not be available until the May 2010 project completion date.

Available Reports/Technical Papers/Presentations:

N/A

Contract No.:

DE-FC26-05NT42465-1.4

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UNDEERC – High-Density Activated Carbon

Project Title:

High-Density Activated Carbon for High-Pressure Hydrogen Purification

Technology Area:	**Technology Maturity:**
Pre-Combustion Solid Adsorption	Laboratory-scale

Primary Project Goal:

The University of North Dakota Energy & Environmental Research Center (UNDEERC) is developing high-density, electrically conductive monolithic-activated carbon for use in a high-pressure swing adsorber to produce hydrogen (H_2) and sequestration-ready carbon dioxide (CO_2) from gasification synthesis gas (syngas).

Technical Goals:

- Prepare a high-density, electrically conductive monolithic-activated carbon sorbent for H_2/CO_2 separation.
- Measure adsorptivity, pressure drop, and electrical conductivity (for regeneration) of monolith.
- Determine the feasibility of using activated carbons as CO_2 sorbents in gasification syngas.

Technical Content:

UNDEERC worked with SGL Carbon to produce a monolithic, high-density activated carbon sorbent for use in high-pressure swing adsorbers to separate H_2 and CO_2 in a high-pressure syngas stream, while maintaining the pressure of the H_2 near that of the incoming syngas. By producing and purifying the H_2 from liquid feedstocks at high pressure, the associated cost of compressing the H_2 is reduced. This process, if employed at an integrated gasification combined cycle (IGCC) power plant, could potentially be used to produce high-purity CO_2 for storage.

As syngas passes through the activated carbon adsorbers, CO_2 is adsorbed onto the surface of the material, leaving relatively pure H_2 to pass through. Once saturated, the adsorbers can possibly be regenerated by passing an electrical current through it at constant pressure. Oak Ridge National Laboratory (ORNL) has been developing such a process and has produced a continuous, low-density, porous, fiber-reinforced activated carbon. By being continuous, it can conduct electricity at low voltage and can be sealed in a horizontal container that will not allow gas bypass. However, when used at high pressures, the high pore volume requires significant H_2 for backflushing. The EERC is attempting to significantly increase the density of the carbon monolith in order to reduce the amount of clean H_2 required for backflushing at high pressures and decrease the regeneration interval.

During this project, the EERC attempted to activate four different formulations of high-density carbon fiber/carbon matrix composites. Activation methods included heating to 450°C in static, high-pressure steam or oxygen and the use of chemical activation. However, only butane adsorptivities of 2-3% were able to be obtained for the activated carbon produced from the monolithic carbon fiber composite, whereas commercial granulated activated carbons have butane adsorptivities of up to 18%. In follow-on work, the focus was on pressing mixtures of granular and powdered activated carbon and binder. These results were successful in making conductive monoliths with twice the density of granular beds, or approximately 40% of the theoretical skeletal carbon density. In addition, a method of treatment of the activated carbon granules were developed to reduce the resistivity of the monoliths by a factor of 10 relative to those made from the commercially available granular activated carbon.

Figure 1 shows how well the monolith separates different components from a simulated reformer gas stream. The figure is a plot of gas breakthrough curves for a monolith tested at 200 psig with a simulated reformer gas stream. The horizontal dashed lines show the concentrations of the different gases in the incoming gas stream. The light blue curve on the lower left is oxygen coming out of the monolith that was originally saturated with air. The difference between the sums of the curves and 100% is due to nitrogen, which was not directly detected. The monoliths are being tested at higher pressures in a follow-on U.S. Department of Defense (DoD) project and will be tested for their ability to be regenerated by passing an electric current through the monolith, possibly to disrupt the Vander Waals forces holding the gas molecules to the activated carbon surface or to resistively heat the monolith in a thermal swing adsorption process.

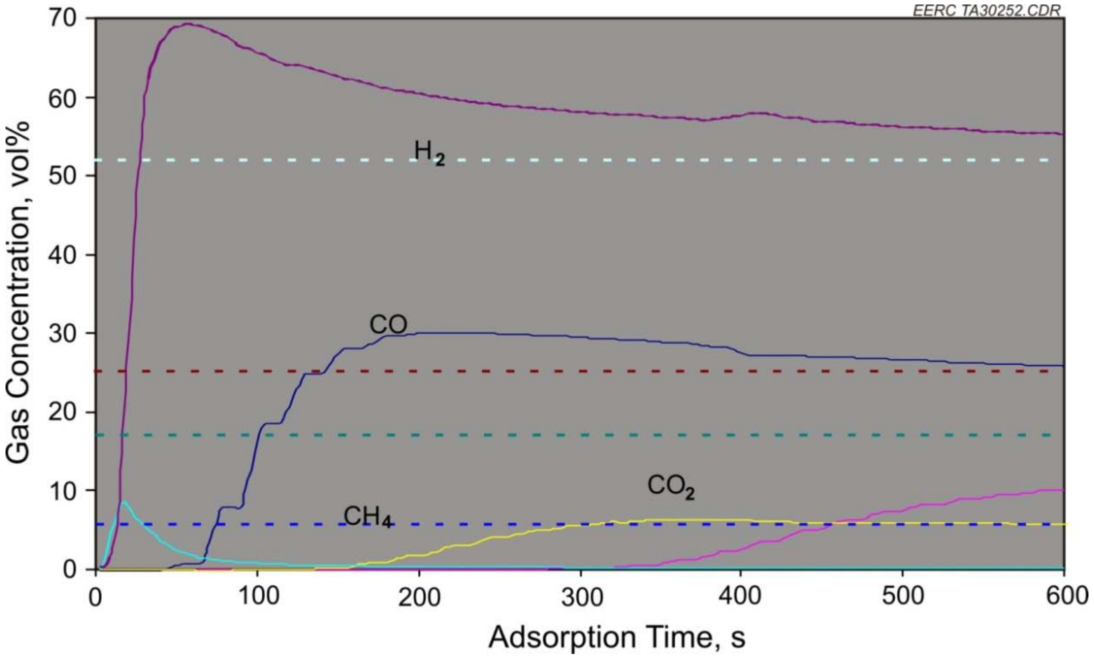

Figure 1: Gas Breakthrough Curves for a Monolith Tested at 200 psig

The following solid sorbent parameter table (Table 1) was completed by the Principal Investigator (PI) with best available data. “N/A” has been used for data that are not available. Data entered in the "Current R&D Value" column are based on test results achieved to date, while data entered in the "Target R&D Value" column are based on anticipated test results.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Activated Carbon	None Provided
	Heat of adsorption (kJ/mole CO_2)	N/A	
	CO_2 loading/working capacity, wt.%	9	
	Surface area, m^2/g	1200	
	Particle density, g/cm^3	N/A	
	Packing density, g/cm^3	0.85	
	Particle size (mm)	monolith	
	Heat capacity (kJ/K/kg)	N/A	
	Thermal stability, °C	75°C	
	Hydrothermal stability, °C	N/A	
Process Configuration	Attrition rate (fluidized bed), %/year	Near 0	
	Cycle time (fixed bed), minutes	N/A	
	Pressure drop (fixed bed), psia	N/A	
Operating Conditions	Adsorption temperature, °C	N/A	
	Adsorption pressure, atm.	N/A	
	CO_2 capture efficiency, %	N/A	
	Regeneration method	Electrical/Thermal	
	Regeneration temperature, °C	N/A	
	Regeneration pressure, atm	N/A	

Heat Integration	Required regeneration steam temperature, °C	N/A	
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	N/A	
Product Quality	CO_2 purity, %	N/A	
	N_2 concentration, %	N/A	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	
	Heat requirement, kJ/kgCO_2	N/A	
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	

Technology Advantages:

High-pressure H_2/CO_2 separation, coupled with isobaric sorbent regeneration using an electrical current, will increase plant efficiency by reducing the parasitic load associated with gas compression. Also, because of the high density of the monolith, the gas adsorption per unit volume is nearly doubled, and the amount of H_2 necessary to flush the intergranular spaces is cut by 25%.

R&D Challenges:

The project team discovered that the carbon sorbents require a long adsorption/desorption cycle time and no activation occurred during exposure to steam for 24 hours, while attempts to activate the material by reaction with an oxidizing gas showed limited results. Further, the introduction of reactive metals had a nominal effect on surface area creation.

Results To Date/Accomplishments:

- Prepared high-density, monolithic-activated carbons for high-pressure H_2/CO_2 separation.
- Measured the surface area, pressure drop, and electrical conductivity of the activated carbon sorbents.

Next Steps:

U.S. Department of Energy (DOE) project completed April 2008, but work is continuing under a DoD program.

Available Reports/Technical Papers/Presentations:

Hurley, J.P. *High-Density Activated Carbon for High-Pressure Hydrogen Purification*; Final Report; U.S. DOE, April 2008.

Contract No.:

DE-FC26-05NT42465-3.1

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Lehigh University – Sorbent-Enhanced Water Gas Shift

Project Title:

Novel Sorption Enhanced Reaction Process for Simultaneous Production of CO_2 & H_2 from Synthesis Gas Produced by Coal Gasification

Technology Area:	**Technology Maturity:**
Pre-Combustion Sorbents	Laboratory-scale

Primary Project Goal:

Lehigh University is evaluating the feasibility of the novel thermal swing sorption enhanced reaction (TSSER) process to simultaneously separate carbon dioxide (CO_2) and carry out the water gas shift (WGS) reaction as a single-unit operation in a sorber-reactor.

Technical Goals:

While evaluating the feasibility of the TSSER process through experiments and process modeling, develop a sorbent that exhibits:

- High selectivity of CO_2 in the presence of steam at 200°C to 500°C.
- Adequate CO_2 working capacity at the reaction temperature.
- Low heat of adsorption for reversible CO_2 sorption and desorption.
- Adequately fast kinetics of CO_2 sorption and desorption.
- Thermal stability.

Technical Content:

The WGS reaction, which converts most of the synthesis gas (syngas) carbon monoxide (CO) to hydrogen (H_2) and CO_2 by reacting the carbon monoxide (CO) with water over a bed of catalyst, can be utilized to enhance H_2 production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2 \text{ kJ/mol}$$

The TSSER process (Figure 1), under development by Lehigh University, simultaneously carries out the WGS reaction and the separation of CO_2 as a single unit operation in a sorber-reactor (Step A). According to this process, the syngas from the coal gasifier (after removal of sulfur impurities) is introduced to a sorber-reactor, which is packed with an admixture of a WGS catalyst and a CO_2 sorbent that can selectively sorb CO_2 in the presence of excess steam. Removal of CO_2 (for geological storage) from the reaction zone drives the reversible reaction to the product side (circumventing equilibrium limits) and enhances the forward reaction rate.

An essentially pure (fuel cell grade) stream of H_2 (dry basis) is produced at feed gas pressure. The sorbed CO_2 is periodically removed (regeneration) by counter-currently purging the reactor with superheated steam at feed gas and near-ambient pressures, as well as at a temperature higher than that of the feed step. An intermediate step of co-current CO_2 rinse at feed gas pressure prior to the regeneration step produces an essentially pure CO_2 stream at high pressure. This significantly reduces CO_2 compression costs.

Two novel CO_2 sorbents have been identified as candidates for the TSSER concept, and key parameters for the optimal CO_2 sorbent are provided in Table 1.

- Potassium carbonate (K_2CO_3) promoted hydrotalcite (400°C to 550°C).
- Sodium oxide (Na_2O) promoted alumina (200°C to 550°C).

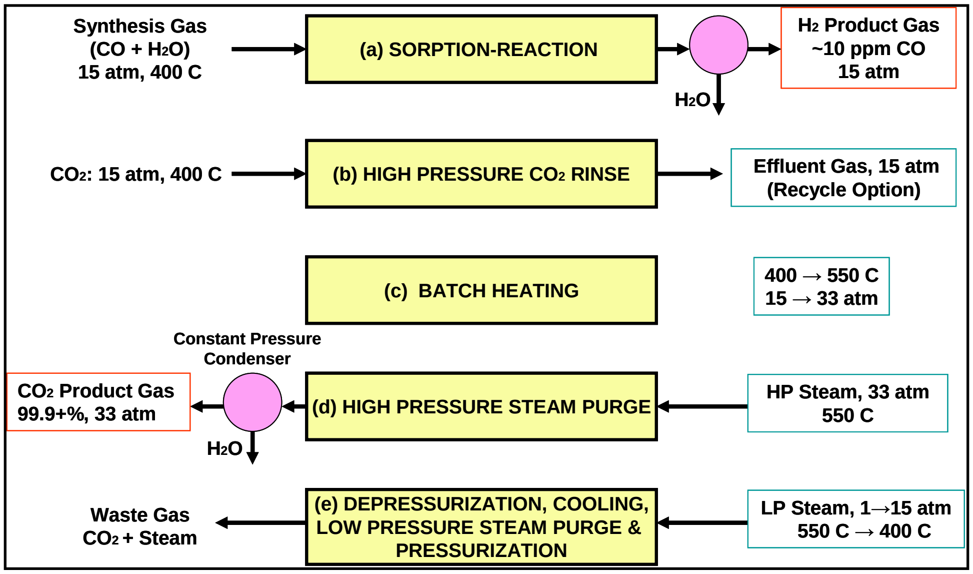

Figure 1: Components of the TSSER Process

This research project includes retrofitting an existing single column sorption apparatus for measurement of high-pressure CO_2 adsorption characteristics; measurement of high-pressure CO_2 adsorption equilibria, kinetics, and sorption/desorption column dynamic characteristics under the conditions of thermal swing operation of the TSSER process; experimental evaluation of the individual steps of the TSSER process; development of a detailed mathematical model for simulating the performance of the individual steps of the TSSER process for optimization, process scaleup, and for guiding future work; simulation and testing of the TSSER concept using a realistic syngas composition; demonstration of the thermal stability of sorbents using a thermogravimetric analysis (TGA) apparatus; and evaluating the effects of sulfur compounds (hydrogen sulfide [H_2S]) present in coal-derived syngas on the CO_2 sorbents.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Na_2O promoted Al_2O_3	New material
	Heat of adsorption (kJ/mole CO_2)	64.9 kJ/mol	Same
	CO_2 loading/working capacity, wt.%	0.65 mol/kg	0.5 mol/kg
	Surface area, m^2/g	N/A	N/A
	Particle density, cm^3/g	2.22 g/cm^3	Same
	Packing density, cm^3/g	0.694 g/cm^3	Same
	Particle size (mm)	1.5 mm	Same
	Heat capacity (kJ/K/kg)	1.05	Same
	Thermal stability, °C	Stable to 600°C	Acceptable
	Hydrothermal stability, °C	Yes to 550°C	
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	Fixed-bed operation
	Cycle time (fixed bed), minutes	20 min	Acceptable
	Pressure drop (fixed bed), psia	<1 psia	<1 psia
Operating Conditions	Adsorption temperature, °C	200-400°C	Same
	Adsorption pressure, atm.	Up to ~25 atm	Same
	CO_2 capture efficiency, %	71%	> 50%
	Regeneration method	Thermal Swing	Novel
	Regeneration temperature, °C	550°C	Same
	Regeneration pressure, atm.	Up to 40 atm	N/A
Heat Integration	Required regeneration steam temperature, °C	550 °C	Acceptable
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	N/A	

Product Quality	CO_2 purity, %	99.9+%	95+%
	N_2 concentration, %	<0.5%	
	Other contaminants, %	<0.5%	
Process Performance	Electricity requirement, kJ/kgCO_2	45.2 kJ/kg CO_2 (for CO_2 compression to 140 atm)	<180 kJ/kg
	Heat requirement, kJ/kgCO_2	6014 kJ/kg CO_2	
	Total energy (electricity equivalent), kJ/kgCO_2	6059 kJ/kg CO_2	

Technology Advantages:

The simultaneous removal of CO_2 drives the WGS reaction to completion, which along with operation at feed conditions (high temperature and pressure), will increase plant efficiency. Regeneration via thermal swing with steam maximizes the CO_2 working capacity of the sorbent, while eliminating H_2 losses that occur during system purging with pressure swing adsorption processes. The TSSER process also produces high-purity H_2 and CO_2 streams.

R&D Challenges:

A considerable amount of time is required to regenerate the sorbents via thermal swing cycling.

Results To Date/Accomplishments:

- Retrofitted and debugged an existing test apparatus for high-pressure operation.
- Characterized the CO_2 sorbents at high pressures, including measurement of isotherms, kinetics, and sorption/desorption column dynamics for CO_2 adsorption from nitrogen (N_2).
- Ascertained the thermal stability of the sorbents.
- Evaluated isothermal and isobaric high-pressure desorption of CO_2 by N_2 purge.
- Developed a CO_2 adsorption isotherm model for use in data analysis and process simulation.
- Developed a process model for data correlation and process simulation.
- Evaluated the performance of each step of the TSSER process.
- Identified Na_2O promoted alumina as the best available CO_2 sorbent for the TSSER process.

Next Steps:

The research team will retrofit the existing apparatus for high-pressure operation to characterize the performance of the CO_2 sorbent, evaluate the effects of H_2S on the chosen sorbent, carry out a detailed heat integration of the TSSER concept and optimize the process plan, and refine the preliminary economic analysis of the TSSER process. Final test results will not be available until the June 2010 project completion date.

Available Reports/Technical Papers/Presentations:

Lee, K. B, A. Verdooren, H. S. Caram, and S. Sircar, “Chemisorption of CO_2 on Potassium Carbonate Promoted Hydrotalcite,” *J. Colloid Interface Sci.*, 308, 30 (2007).

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Chemisorption of CO_2 on Sodium Oxide promoted Alumina,” *AIChE J.*,53, 2824 (2007).

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Effect of Reaction Temperature on the Performance of Thermal Swing Sorption Enhanced Process for Simultaneous Production of Fuel-Cell Grade H_2 and Compressed CO_2 from Synthesis Gas,” *Ind. Eng. Chem. Res.*, In Press (2008).

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Novel Thermal Swing Sorption Enhanced Reaction Process Concept for H_2 Production by Low Temperature Steam-Methane Reforming,” *Ind. Eng. Chem. Res.*, 46, 5003 (2007).

Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Performance of Na_2O Promoted Alumina as CO_2 Chemisorbent in Sorption Enhanced Reaction Process for Simultaneous Production of Fuel-Cell Grade H_2 and Compressed CO_2 from Synthesis Gas,” *J. Power Sources*, 176, 312 (2008).

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Lee, K. B, M. G. Beaver, H. S. Caram, and S. Sircar, “Reversible Chemisorption of Carbon Dioxide: Simultaneous Production of Fuel-Cell Grade H_2 and Compressed CO_2 from Synthesis Gas,” *Adsorption*, 13, 385 (2007).

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Beaver, M.G., Caram, H.S., Sircar, S., “Selection of CO_2 chemisorbent for fuel-cell grade H_2 production by sorption-enhanced water gas shift reaction,” *Int. J. Hydrogen Energy*, 34, 2972 (2009).

Beaver, M. G., Caram, H. S., Sircar, S.,” Sorption Enhanced Reaction Process for Direct Production of Fuel Cell Grade Hydrogen by Low Temperature Catalytic Steam- Methane Reforming,” *J. Power Sources*, 195, 1998-2002, (2009).

“Effect of Reaction Temperature on Performance of Thermal Swing Sorption Enhanced Reaction Process for Simultaneous Production of Fuel-Cell Grade H_2 and Compressed CO_2 from Synthesis Gas,” Presented at 25th International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September 2008 and at AIChE Annual Meeting, Philadelphia, November 2008.

“Utilization of High Temperature CO_2 Chemisorbents in Sorption Enhanced Reaction Concepts for Production of Fuel Cell Grade H_2 from Fossil Fuel Feedstocks,” Presented at 26th International Pittsburgh Coal Conference on September 22, 2009.

“Experimental Demonstration of Sorption Enhanced Reaction (SER) Concepts for Direct Production of Fuel Grade H_2 by SE-Water Gas Shift (WGS) and SE-Steam Methane Reforming (SMR) Reactions”, Presented at the Hydrogen Production and Storage 2009 Meeting held in Washington, DC, Sept. 30-Oct. 2, 2009.

“Selection of CO_2 Chemisorbent for Fuel-Cell Grade H_2 Production by Sorption Enhanced Water-Gas-Shift & Steam- Methane-Reforming Reaction,” Presented at American Institute of Chemical Engineering Annual Meeting, Nashville, Tennessee, November 12, 2009.

Contract No.:

DE-FC26-05NT42455

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UNDEERC – Sorbent-Enhanced Water Gas Shift

Project Title:

Hydrogen Production Using Water Gas Shift Catalyst with CO_2 Sorbents

Technology Area:	**Technology Maturity:**
Pre-Combustion Sorbents	Bench-scale

Primary Project Goal:

The University of North Dakota Energy & Environmental Research Center (UNDEERC) is developing a high-temperature carbon dioxide (CO_2) sorbent to enhance the water gas shift (WGS) reaction and produce a synthesis gas (syngas) stream that is at least 90% hydrogen (H_2) on a nitrogen-free basis.

Technical Goals:

- Develop hydrotalcite sorbent briquettes and determine the optimal chemical composition.
- Test a pressure swing absorber on a continuous fluidized-bed reactor (CFBR) gasification system.
- Test lithium silicate and hydrotalcite sorbents in a bench-scale, heated fixed-bed reactor using a slipstream from the CFBR gasification system.
- Determine the optimum high-temperature CO_2 sorbent.

Technical Content:

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H_2 and CO_2 by reacting the CO with steam over a bed of catalyst, can be utilized to enhance H_2 production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2 \text{ kJ/mol}$$

The sorption-enhanced WGS (SEWGS) process, which combines a high-temperature CO_2 sorbent and a WGS catalyst in a packed-bed reactor that can operate at high temperature and pressure, represents one approach to further promote H_2 production. The SEWGS reactor consists of an initial adsorbent bed to remove inherent CO_2 from the syngas, followed by a second bed wherein the WGS reaction occurs as the CO_2 produced during the reaction is simultaneously captured by the adsorbent bed. Regeneration of the saturated adsorbent bed is accomplished by pressure swing absorption. By incorporating sorbent-based CO_2 removal, not only is a near capture-ready stream of CO_2 produced, but the efficiency of the plant is increased by driving the WGS reaction further to completion.

By routing a slipstream from the CFBR gasification system to the bench-scale, heated fixed-bed reactors shown in Figure 1, UNDEERC evaluated the performance of high-temperature lithium orthosilicate (Li_4SiO_4) and hydrotalcite CO_2 sorbents in the SEWGS process. Hydrotalcites are anionic clays with positively-charged brucitelike ($Mg[OH]_2$) layers and inter layers of anions such as carbonates. Although the hydrotalcite sorbent did exhibit some enhanced WGS properties during bench-scale testing, the sorbent is unlikely to be a cost-effective option for IGCC power plants due to the observed low CO_2 adsorption capacity and the long purge cycles required for regeneration.

UNDEERC also compared the performance of two Li_4SiO_4 sorbents provided by Toshiba and Research Triangle Institute (RTI). Lithium orthosilicate, which reacts with CO_2 via the following reversible reaction, has exhibited a CO_2 adsorption capacity of about 35% (based on sorbent weight) at high temperatures.

$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3 \qquad \Delta H_{rxn} = -142.8 \text{ kJ/mol}$$

As shown in Table 1, the Toshiba sorbent demonstrated superior adsorption at elevated temperatures, whereas the sorbent supplied by RTI showed higher adsorption capacity at relatively lower temperatures. One notable pattern is the sorbent provided by Toshiba demonstrated a reduction in adsorption capacity with decreasing CO_2 concentrations, eventually leading to inferior adsorption at higher temperatures as compared to RTI's sorbent.

Additionally, it was found that RTI's sorbent had slightly better desorption properties with complete desorption taking place at 700°C, whereas Toshiba's sorbent required temperatures as high as 800°C to attain complete desorption in a 100% nitrogen atmosphere.

Figure 1: Heated Fixed-Bed Reactors

Table 1: Comparison of Adsorption Properties of Sorbents Provided by Toshiba and RTI

	100% CO_2		**40% CO_2**		**20% CO_2**	
Temperature (°C)	**Adsorption (wt%)**		**Adsorption (wt%)**		**Adsorption (wt%)**	
	Toshiba	**RTI**	**Toshiba**	**RTI**	**Toshiba**	**RTI**
400	1.32	4.33	0.89	2.48	0.69	1.43
500	19.32	14.10	18.04	12.48	15.89	14.10
600	23.26	15.22	19.87	14.04	18.61	14.39
700	33.32	15.88	31.68	-	2.41	8.97
800	3.46	-	1.45	-	1.31	-

Technology Advantages:

The simultaneous removal of CO_2 drives the WGS reaction to completion, which along with operation at feed conditions (high temperature and pressure), will increase plant efficiency. The Li_4SiO_4 sorbents exhibit high CO_2 adsorption capacity at elevated temperatures and effectiveness across a wide range of CO_2 concentrations.

R&D Challenges:

A considerable amount of time is required to regenerate a Li_4SiO_4 sorbent which, when coupled with the large quantity of sorbent required, imposes significant limitations for industrial use.

Results To Date/Accomplishments:

- Completed testing of a pressure swing absorber on a continuous fluid-bed gasification system.
- Produced 20 wt% potassium carbonate/80 wt% hydrotalcite briquettes.
- Completed testing of Li_4SiO_4 sorbents in heated fixed-bed reactors using a slipstream from the CFBR gasification system, and determined the physical strength in high-moisture atmospheres and the CO_2 adsorption capacity of the sorbents at various operating conditions.

Next Steps:

Project completed March 2009.

Available Reports/Technical Papers/Presentations:

N/A

Contract No.:

DE-FC26-98FT40320-03.13

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TDA Research – High Capacity Regenerable Sorbent

Project Title:

A Low Cost, High Capacity Regenerable Sorbent for Pre-Combustion CO_2 Capture

Technology Area:	**Technology Maturity:**
Pre-Combustion Sorbents	Pilot-scale slipstream using actual syngas

Primary Project Goal:

TDA Research is further developing a low cost, high capacity regenerable carbon dioxide (CO_2) sorbent technology, demonstrating its technical and economic viability for pre-combustion CO_2 capture from coal-derived synthesis gas (syngas) fueling integrated gasification combined cycle (IGCC) power plants.

Technical Goals:

- Optimize chemical and physical properties of an existing sorbent.
- Modify the sorbent to improve capacity and stability.
- Scale up sorbent production using commercially adoptable equipment.
- Demonstrate long-term sorbent performance at bench-scale in the presence of contaminants.
- Design and build a prototype unit to support slipstream demonstration tests using actual syngas.
- Detailed process design and cost analysis to evaluate sorbent's ability to remove CO_2 at a lower cost than current technologies.

Technical Content:

TDA is developing a new pre-combustion CO_2 capture technology that uses a TDA proprietary sorbent modified to remove CO_2 from shifted syngas. The CO_2 capture system uses two (or more) beds that switch positions 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 while the driving force for separation is provided by a swing in CO_2 concentration. The sorbent consists of a carbon support modified with surface functional groups that remove 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 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.

Initially, the researchers will be optimizing the chemical, mechanical, and physical properties of the sorbent to optimize the active material content; assess the impact of key synthesis parameters on surface area, pore volume, and pore size distribution; and determine crush strength, attrition resistance. Cost will be kept to a minimum by evaluating low-cost raw materials and optimizing the production process. Sorbents will be evaluated under simulated syngas, water gas shift (WGS), and simulated contaminant conditions using two TGAs and a 1-inch, 3-inch, and 6-inch bench-scale flow reactor. TDA and the University of California Irvine (UCI) will carry out process design and modeling. Based on that information, UCI will carry out multiple design options and the best option will be selected for detailed simulation.

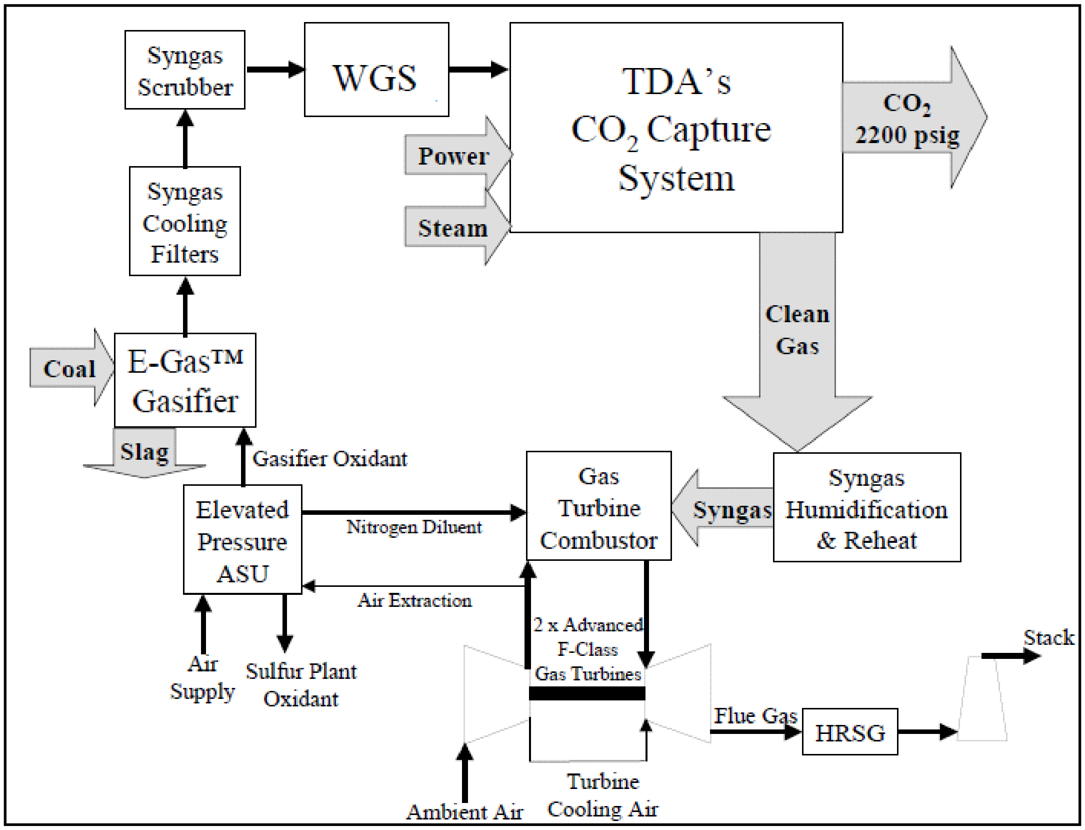

Figure 1: Integrated CO_2 Removal System

The next objective is to scale up sorbent production by a factor of 10 at the end of Year 1 using commercially adoptable equipment. Scale up will explore the use of continuous or semi-continuous preparation approaches, and reduce or optimize the number of processing steps via intensification (co-synthesis, co-firing, etc.). A preparation recipe will be developed in cooperation with MeadWestvaco, who will carry out a detailed analysis to estimate the cost of the sorbent. Long-term tests will be performed to ensure that the sorbent does maintain its CO_2 capacity over many cycles. A minimum of 2,000 cycles are planned in Year 1.

Year 2 of the project focuses on designing, building, and testing a prototype unit using slipstream syngas and analyzing the results. TDA will work with KBR to carry out a detailed design and sizing of sorbent reactors for each of the two gasifier types that will be used for pilot testing.

TDA and UCI will continue to optimize the process design and modeling. The focus of system analysis in Year 2 will be on the integration of the CO_2 capture system with the IGCC plant. TDA will fabricate the test module, which will have a control rack using Labview programming to control, monitor, and log key process parameters. The test module will also have an analyzer rack for continuous analysis of carbon monoxide (CO), CO_2, methane (CH_4), hydrogen (H_2), and water (H_2O) on the adsorption and regeneration sides, and hydrogen sulfide (H_2S) analysis on the adsorption side. TDA will perform all shakedowns and troubleshooting before shipping the test system. Field tests will be performed at ConocoPhillips' Wabash River IGCC Plant with the oxygen (O_2)-blown E-Gas gasifier in Terre Haute and in collaboration with the Southern Company at the National Carbon Capture Center (NCCC) using the syngas generated by an air-blown gasifier at Wilsonville, Alabama. Two, three-week long (500 hours) test campaigns are scheduled with 24 hr/day continuous operation. A majority of testing will be performed under optimum conditions and limited scope testing to assess the impact of operating parameters.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Physical Adsorbent	Physical adsorbent
	Heat of adsorption (kJ/mole CO_2)	20.5	Less than 30
	CO_2 loading/working capacity, wt.%	7	TBD
	Surface area, m^2/g	350-450	TBD
	Particle density, cm^3/g	0.6-0.7	TBD
	Packing density, cm^3/g	0.40-0.45	TBD
	Particle size (mm)	3.2	TBD
	Heat capacity (kJ/K/kg)	TBD	TBD
	Thermal stability, °C	1100	Greater than 400
	Hydrothermal stability, °C	600	Greater than 400
Process Configuration	Attrition rate (fluidized bed), %/year	TBD	Less than 1%
	Cycle time (fixed bed), minutes	TBD	TBD
	Pressure drop (fixed bed), psia	TBD	TBD
Operating Conditions	Adsorption temperature, °C	20-320	200-300
	Adsorption pressure, atm.	1-60	50
	CO_2 capture efficiency, %	99+	90+
	Regeneration method	TBD	TBD
	Regeneration temperature, °C	TBD	TBD
	Regeneration pressure, atm.	TBD	TBD
Heat Integration	Required regeneration steam temperature, °C	TBD	TBD
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	TBD	TBD
Product Quality	CO_2 purity, %	TBD	Pipeline spec
	N_2 concentration, %	TBD	Pipeline spec
	Other contaminants, %	TBD	Pipeline spec
Process Performance	Electricity requirement, kJ/kgCO_2	TBD	TBD
	Heat requirement, kJ/kgCO_2	TBD	TBD
	Total energy (electricity equivalent), kJ/kgCO_2	TBD	TBD

Sorbent Heating/Cooling Method: Isothermal operation is planned.

Heat of Adsorption Handing: The small heat of adsorption will be removed by convective losses (i.e., warming the syngas) and by increasing the sensible heat of the sorbent pellets.

Heat Supply Method for Regeneration: The stored heat in the sorbent pellets and the convective heat input.

Contaminant Resistance: The sorbent will be resistant to syngas contaminants.

Fuel Gas Pretreatment Requirements: Particulate removal, bulk desulfurization, and WGS.

Waste Streams Generated: The spent sorbent will be replaced periodically.

Technology Advantages:

- 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:

- Demonstration to the resistance of syngas contaminants.
- Reducing the use of purge gas during regeneration.

Results To Date/Accomplishments:

Results from the project are not yet available.

Next Steps:

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

”A New Sorbent-Based Pre-combustion CO_2 Capture System,” presented at the International Conference of Energy and Power Generation Systems, Costa Mesa, California, 2010.

Contract No.:

DE-FE-0000469

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KBR
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Southern Company
University of California Irvine

URS Group – Sorbent-Enhanced Water Gas Shift

Project Title:

Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture

Technology Area:	**Technology Maturity:**
Pre-Combustion Sorbents	Bench-scale using simulated syngas

Primary Project Goal:

URS Group, Inc. is investigating and developing a dry sorbent process that combines carbon dioxide (CO_2) capture with the water gas shift (WGS) reaction by developing and optimizing sorbents to perform in synthesis gas (syngas) at high pressure and high temperature.

Technical Goals:

- Determine optimal CO_2 sorbent properties and operating conditions for CO_2 removal and regeneration, and carbon monoxide (CO) conversion in simulated syngas using a combination of computational and experimental methods.
- To develop a sorbent which recovers high-quality heat during CO_2 adsorption; regenerates at elevated pressure; and has minimal deactivation over multiple cycles, high selectivity at high temperatures, high adsorption capacity, and acceptable thermal stability and mechanical integrity. This would result in a sorbent capable of 90% CO_2 removal with high loading capacities and able to operate at the high temperatures and pressures typically encountered upstream of a WGS reactor.
- Determine the process feasibility for sorbing and removing CO_2 as part of the WGS process.
- If successful, the sorbents developed in this program will augment or replace the CO conversion catalysts currently used in WGS reactors and improve overall WGS thermal efficiency.

Technical Content:

URS Group, Inc. will lead an investigative effort for the development of a dry sorbent process configured to combine the WGS reaction with CO_2 removal for coal gasification systems. The result will be a sorption-enhanced water gas shift (SEWGS).

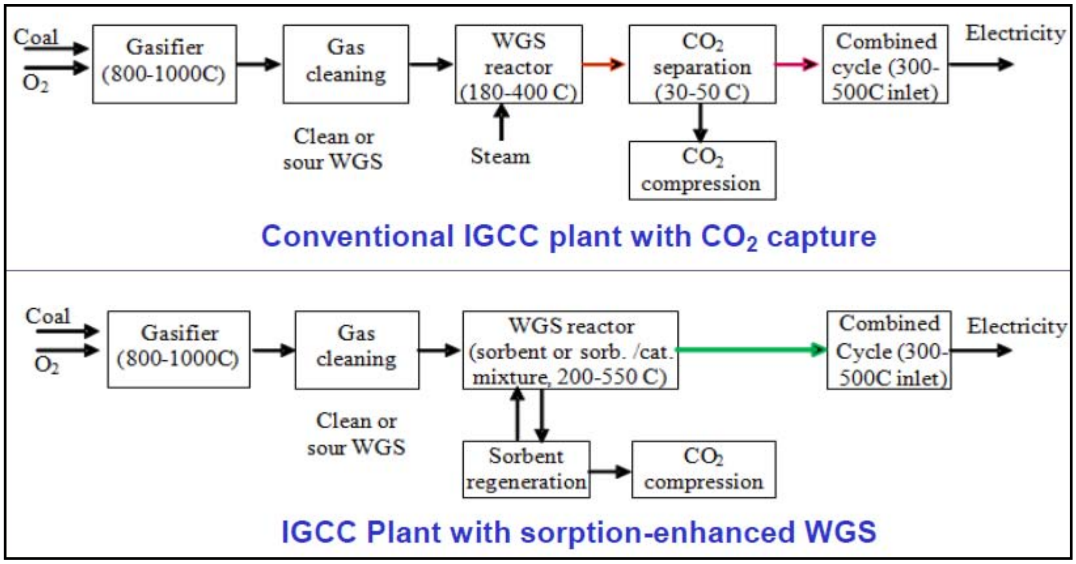

Figure 1: IGCC with SEWGS vs. Conventional IGCC

Process simulation modeling and sorbent molecular and thermodynamic analyses will be performed. These analyses will 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 will include 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 will predict isotherms and properties, predict kinetics and dynamics, and identify sorbents with desired properties using grand canonical Monte Carlo (GCMC) simulation and integrated Kinetic Monte Carlo (KMC) and Molecular Dynamics (MD) simulation. Process simulation analysis will analyze various process scenarios for heat integration between SEWGS and integrated gasification combined cycle (IGCC) and process energy performance for individual sorbents.

Concurrently, the University of Illinois at Urbana-Champaign will perform sorbent development. Sorbents will be synthesized with desired pore structure, surface functionality, and composition guided by the first phase testing and modeling effort. Sorbents will be synthesized using various precursors including calcium and magnesium aluminates, clay-based materials, metal oxides and salts, and adsorbent-shift catalyst hybrid. Sorbent down selection will proceed according to the decision tree shown in Figure 2.

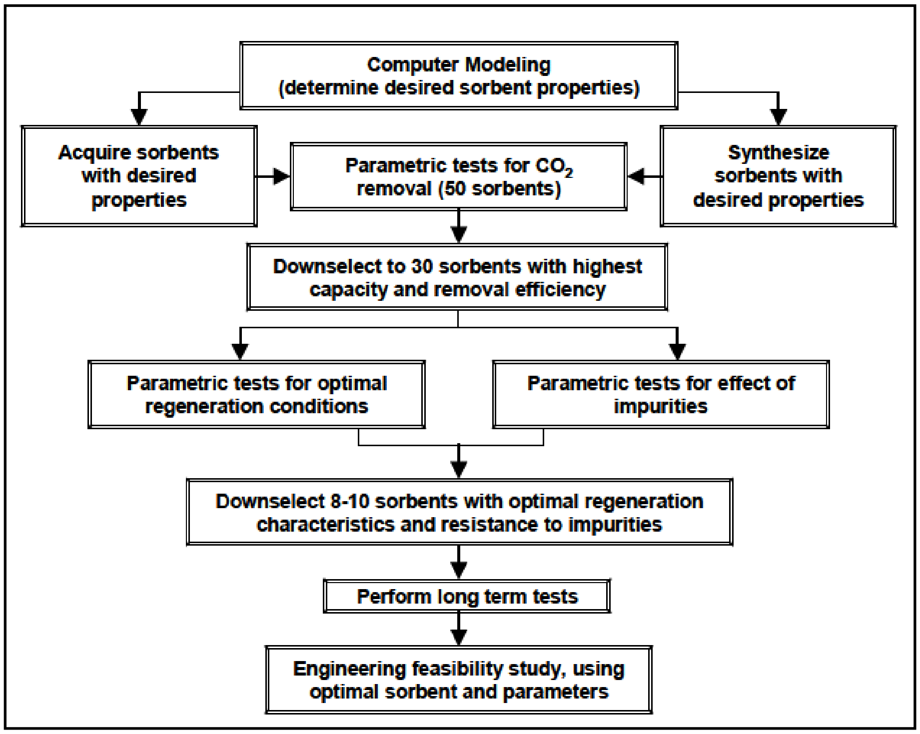

Figure 2: Sorbent Development and Analysis Decision Tree

A high temperature and pressure reactor (HTPR) system at INRS/UIUC capable of 300 psig and 950°C will be used for screening sorbents for CO_2 removal. Also, URS will construct an HTPR to evaluate sorbent adsorption performance in presence of syngas impurities and regeneration performance. Thirty down-selected sorbents will also be tested for sorbent resistance to syngas impurities and determine optimal regeneration parameters. Eight to 10 sorbents will be further down-selected and will be tested on a longer-term basis.

Lab results will be used in a preliminary engineering study of process feasibility for sorbing and removing CO_2 as part of the WGS process with the comparison made to base WGS operation and other CO_2 removal strategies. Parameters include cost of >90% removal (COE, 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

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	1. Calcium based smart sorbents; 2. Calcium & magnesium aluminates; 3. Modified clay-based sorbents; 4. WGS/sorbent hybrid; 5. Others	Program is designed to determine optimal sorbent type(s)
	Heat of adsorption, kJ/mole CO_2	N/A	TBD
	CO_2 loading/working capacity, wt. %	N/A	Optimal loading properties will be impacted by regeneration properties (TBD in program)
	Surface area, m^2/g	N/A	TBD
	Particle density, cm^3/g	N/A	TBD
	Particle size, mm	N/A	TBD
	Heat capacity, kJ/K/kg	N/A	TBD
	Thermal stability, °C	N/A	TBD
	Hydrothermal stability, °C	N/A	TBD
Process Configuration	Attrition rate (fluidized bed), %/year	N/A	Values will be impacted by costs of optimal sorbent type(s)
	Cycle time (fixed bed), minutes	Not applicable to fluidized bed or moving bed configuration	N/A
	Pressure drop (fixed bed), psia	Depending on sorbent properties, to be determined during the project	TBD
Operating Conditions	Adsorption temperature, °C	200-550	550
	Adsorption pressure, atm.	30-40	40
	CO_2 capture efficiency, %	90%	>90%
	Regeneration method	Temperature swing	Temperature swing.
	Regeneration temperature, °C	Depends on sorbent corresponding to highest regeneration pressure achievable	TBD; optimization based on lowest energy input possible
	Regeneration pressure, atm.	Up to 30 atm	Highest possible pressure up to 30 atm
Heat Integration	Required regeneration steam temperature, °C	Steam may not be used; if a steam is used, steam temperature < 1,000°F	TBD
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	N/A	TBD
Product Quality	CO_2 purity, %	>99%	>99%
	N_2 concentration, %	0	0
	Other contaminants, %	Moisture < 600ppm	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	TBD
	Heat requirement, kJ/kgCO_2	N/A	TBD
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	0.1 kWh/kg CO_2 (3,600 kJ/kg)

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 will be 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 far below 1,000°F.

Contamination Resistance:

Sorbents may not be resistant to sulfur species (hydrogen sulfide [H_2S], carbon disulfide [CS_2], etc). Sulfur resistant sorbents will be investigated,

Flue Gas Pretreatment Requirements:

The pretreatment of H_2S/CS_2 is needed for sorbents with no sulfur resistance. Sorbents resistant to sulfur will also be developed to avoid flue gas pretreatment.

Waste Streams Generated:

Desulfurization byproducts.

Technology Advantages:

- No or limited use of a WGS catalyst.
- No gas cooling/reheating for capture.
- No separate CO_2 capture unit required.
- The above three advantages contribute to a decrease in electricity needed.

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

Results To Date/Accomplishments:

Results from the project are not yet available.

Next Steps:

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

Available Reports/Technical Papers/Presentations:

"Evaluation of Dry Sorbent Technology for Pre-Combustion CO_2 Capture," **Pre-combustion CO_2 Capture Kick-off Meetings,** Pittsburgh, Pennsylvania, November 12-13, 2009; http://www.netl.doe.gov/publications/proceedings/09/CO2capture/7-URS%20Dry%20Sorbent%20Kickoff%20Presentatin-111309.pdf.

Contract No.:

DE-FE-0000465

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APPENDIX

PRE-COMBUSTION MEMBRANES

United Technologies Research Center – Palladium-Copper Trimetallic Alloy Membranes

Project Title:

Experimental Demonstration of Advanced Palladium Membrane Separators for Central High-Purity Hydrogen Production

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

United Technologies Reserch Center is developing a palladium copper (PdCu) trimetallic alloy hydrogen (H_2) separator for central H_2 production from coal gasification-derived synthesis gas (syngas).

Technical Goals:

- Test the high stability and resistance of a PdCu trimetallic alloy to carbon and carbide formation, sulfur, halides, and ammonia (NH_3).
- Develop a sulfur-, halide-, and NH_3-resistant alloy membrane with a projected H_2 permeance of 25 $m^3m^{-2}atm^{-0.5}h^{-1}$ at 400°C and capable of operating at pressures of 120 atm (12.1 MPa).
- Construct and experimentally validate the performance of PdCu trimetallic alloy membranes operating at a hydrogen (H_2) separation rate of 0.1 kg/day at feed pressures of 20 atm (2 MPa) in the presence of hydrogen sulfide (H_2S), NH_3, and hydrogen chloride (HCl). The performance of the best separator candidate will be demonstrated for a minimum of 2,000 hours of operation.

Technical Content:

Figure 1 depicts one of the membrane separators developed for this project. The purpose of the separators is to house the membrane and receive the flue gas stream from combustion. The membrane allows the H_2 to pass through it, following the H_2 permeate path in the diagram. The remaining gas stream then exits the membrane system for further processing.

Figure 2 illustrates the path of the gas stream through the separation mechanism's structure. The gas stream enters through the PdCu alloy pipes, which allow the H_2 present in the gas stream to permeate through the alloy walls into the secondary level of the structure (shown as the white area within the blue outer-shell), while containing the remaining gases (carbon monoxide [CO], carbon dioxide [CO_2], water [H_2O], and nitrogen [N_2]). The H_2 and other gases can then be separately processed once they exit the separator mechanism.

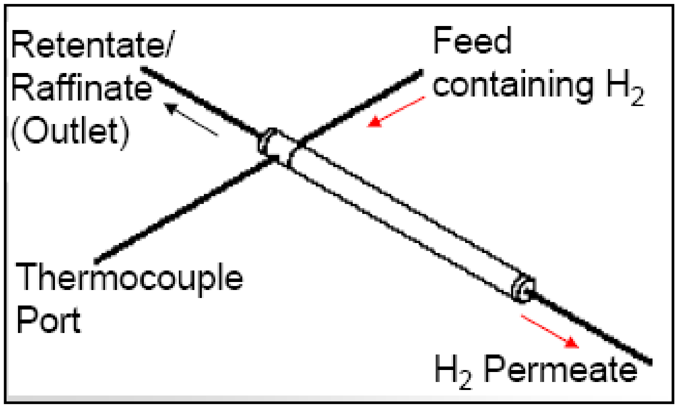

Figure 1: Tubular Membrane Separator

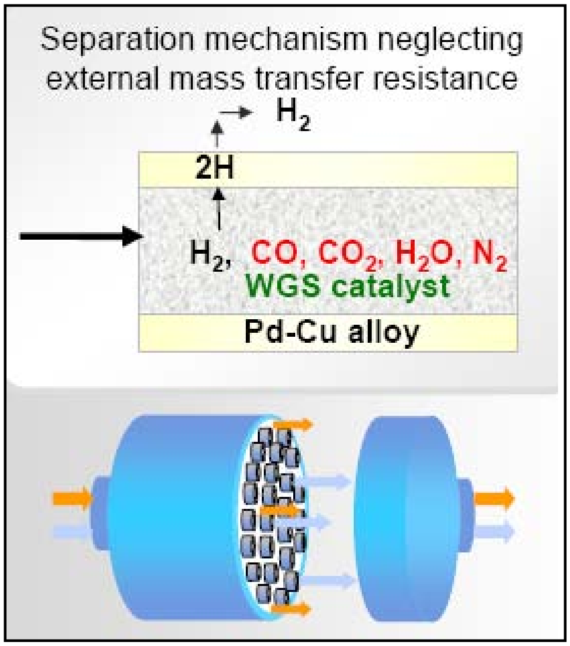

Figure 2: Configuration of Larger Assembly

Table 1: UTRC Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd,Cu	Pd,Cu
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	999999	999999
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	61 $ft^3ft^{-2}h^{-1}$ for a feed containing 100 psig H_2 & 100 psig N_2	200 $ft^3ft^{-2}h^{-1}$
	Temperature, °C	350°C – 600°C	350°C – 600°C
	Bench-scale testing, hours without significant performance degradation	527 h	527 h
	Pilot-scale testing (if applicable), hours without significant performance degradation		
	Maximum pressure differential achieved without significant performance degradation or failure, bar	13.8 bar	13.8 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	157	157
	Pressure drop, bar		
	Estimated cost of manufacturing & installation, $/$m^2$-GPU or equivalent		
Product Quality	CO_2 purity, %		
	N_2 concentration, %		
	Other contaminants, %		
Process Performance	Electricity requirement, kJ/kgCO_2		
	Heat requirement, kJ/kgCO_2		
	Total energy (electricity equivalent), kJ/kgCO_2		

Technology Advantages:

A PdCu alloy-based CO_2 capture membrane is able to better withstand the corrosion and wear associated with membranes constructed of other materials. Less corrosion means the membrane does not need to be replaced as often, resulting in a lower overall operating cost for the power plant. The PdCu alloy also has a stronger resistance to sulfur compared to traditional membranes, resulting in an improved CO_2 capture efficiency.

R&D Challenges:

Tests have shown that the fcc PdCu alloy produced by Power+Energy is capable of meeting all of the program goals except the H_2 flux target. The UTRC ternary alloy tubes tested to date have not been able to exceed the fcc PdCu alloy flux, primarily due to surface compositional variations. Work is in progress to identify ways to change the surface properties of the tubes.

Results To Date/Accomplishments:

The PdCu alloy separators were tested for their H_2 separation performance and the membranes have not yet met all of the DOE 2010 targets. The highest H_2 flux obtained in these experiments was 61.03±0.01 $ft^3h^{-1}ft^{-2}$ at a feed pressure of 7.8 atm (100 psig). The alloy has not yet met the H_2 flux goal of 200 $ft^3h^{-1}ft^{-2}$. Tests also showed that the alloy's sulfur resistance exceeded the project's designated target of 20 parts per million volume (ppmv). The membranes themselves are still costly to make compared to the desired cost of use on the commercial scale. The membranes still do not meet the required average lifespan of three years. Overall, the PdCu alloy testing has successfully met performance requirements for operating temperature (350 to 600°C), sulfur tolerance (20 ppmv), operating pressure (27 atm [400 psi] max.), CO tolerance, and the production of at least 99.5% pure H_2.

In addition:

- Initial technical and economic models are complete.
- Advanced membrane property simulations by atomistic and thermodynamic modeling calculations are complete.
- Hydrogen solubility tests using various alloys for six to 12 separators and H_2 permeability performance tests are complete.

Planned Activities:

- Conduct a durability study on the Pd alloy membrane separators in a high-pressure reformer test rig.
- Continue to work with Power+Energy to develop and test better ternary alloy tubes for use in the new hydrogen separator units.
- Complete revisions to the technical and economic models to better define the feasibility of using these membranes on an industrial scale.

Available Reports/Technical Papers/Presentations:

N/A

Contract No.:

DE-FC26-07NT43055

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Media and Process Technology – Carbon Molecular-Sieve Membranes

Project Title:

Carbon Molecular Sieve Membrane as a True One Box Unit for Large Scale Hydrogen Production

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

Media and Process Technology, Inc. is developing a one-box process for hydrogen (H_2) production based on carbon molecular-sieve (CMS) membranes. Gas cleanup is being combined with a water gas shift membrane reactor (WGS-MR) in a single processing unit.

Technical Goals:

- Develop and test a one-box (gas cleanup and the WGS-MR), H_2 production process that integrates the four major technology components for synthesis gas (syngas) cleanup and conditioning into a single unit.
- Demonstrate the one-box process at bench-scale at the University of Southern California (USC); followed by a single-tube slipstream test at the Power Systems Development Facility (PSDF). Upon successful completion of this testing, a pilot-scale unit will be developed and tested with a stream from a gasifier.
- A mathematical model will be verified with the bench- and pilot-scale test results, and then used to conduct a techno-economic analysis.
- Evaluate the CMS membrane deposited on a ceramic substrate for candidate selection in future full-scale demonstrations.

Technical Content:

The one-box process under investigation combines the gas cleanup and WGS-MR for H_2 production. Figure 1 displays how the one-box process will be incorporated following the gasification of a coal-based feedstock. Syngas cleaning will consist of a water quench, particulate removal, WGS, and CMS membrane to produce an H_2 gas stream and a carbon dioxide (CO_2) stream ready for sequestration. The one-box process will remove the sulfur and other contaminants from the H_2 product stream via the molecular sieving mechanism of the H_2-selective CMS membrane. If a high purity H_2 product is necessary, an optional palladium (Pd) membrane can be installed for post-treatment of this sulfur-removed H_2 product stream. Table 1 compares the one-box process to a conventional H_2 purification processes.

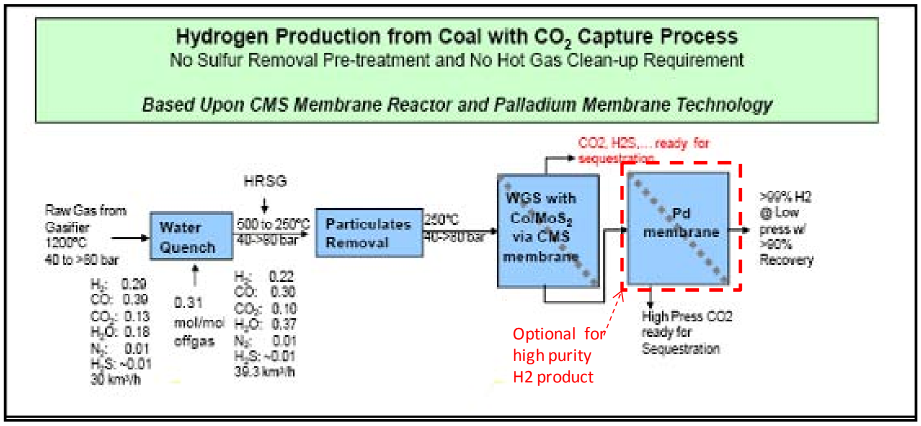

Figure 1: Incorporation of One-Box Process Following the Gasification of a Coal-Based Feedstock

Table 1: One-Box Process Versus a Conventional Hydrogen Purification Processes

Performance Criteria	Conventional WGS with PSA	One-Box Process
H_2 Product Pressure, psig	High pressure, 200 to 400	Low pressure, e.g., 5 to >100 psig
H_2 Product Purity, %	>99.9	>99.9
H_2 Product Yield, %	60 to 80	>90
CO Conversion, %	90 to 97	>97
H_2O/CO Ratio for WGS	3 – 4	~1.5
CO_2 Stream Pressure, psig	Low pressure, 5 to 10	High pressure, i.e., gasifier pressure

Within the one-box unit, a colbalt sulfide (CoS_2)/molybdenum disulfide (MoS_2) catalyst will be used to perform the WGS reaction. As shown in Figure 2, the CMS membrane will incorporate a candle filter configuration that has a high resistance to hydrogen sulfide (H_2S), which allows the H_2 to permeate through the membrane and create an H_2-rich stream. After the H_2 permeates through the CMS membrane, a CO_2-rich stream will remain outside the membrane at a high pressure ready for transportation.

Figure 2: Candle Filter Configuration for CMS Membrane and Module (pilot scale)

Figure 3 shows the permeance of the membrane under investigation for separation of H_2 and CO_2.

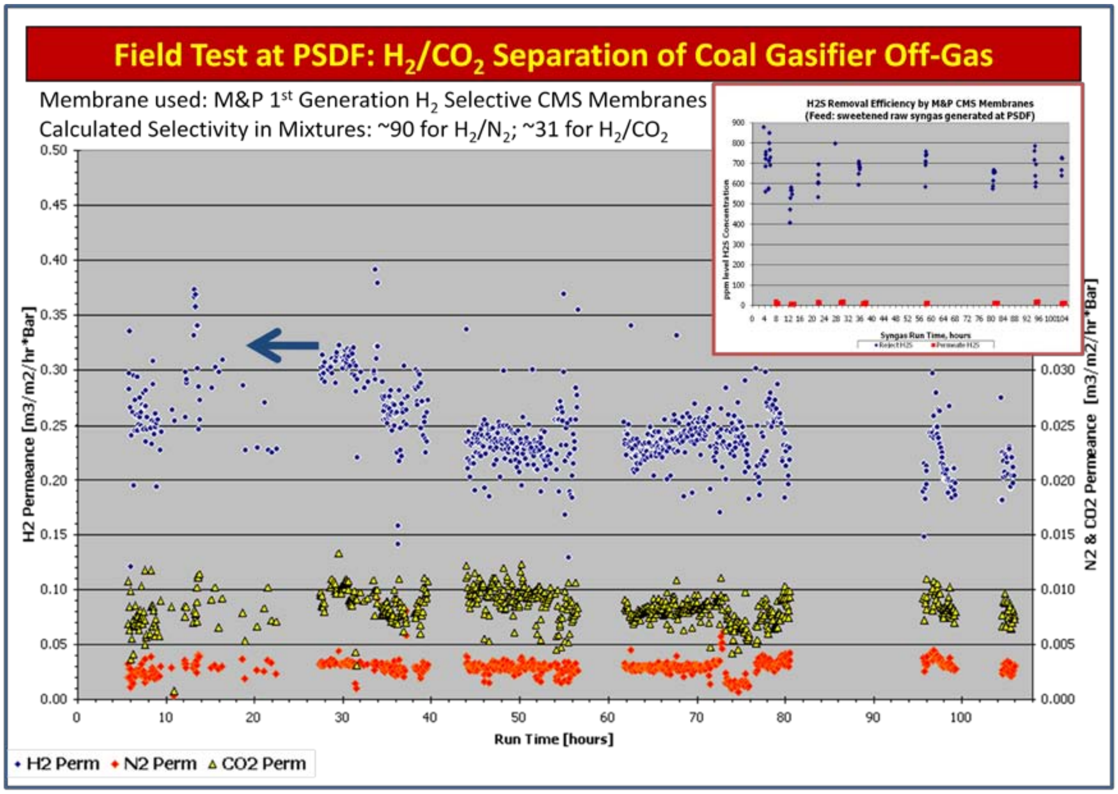

Figure 3: Permeances of Membranes for Separation of H_2 and CO_2 from Coal Gasifier Off-Gas Generated at PSDF

Table 2: Media and Process Technology Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Carbon	Carbon
	Materials of fabrication for support layer (if applicable)	Ceramic	Ceramic
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	25-30 (50->100 for H_2/CO)	25-30 (50->100 for H_2/CO)
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	925 GPU	1,295 FPU
	Temperature, °C	250	>.600
	Bench-scale testing, hours without significant performance degradation	>500	>1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	100	>250
	Maximum pressure differential achieved without significant performance degradation or failure, bar	>50	>50
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube in candle filter configuration	Shell-and-tube in candle filter configuration
	Packing density, m^2/m^3	250	500
	Pressure drop, bar	<0.1	<0.1
	Estimated cost of manufacturing & installation, $\$/m^2$-GPU or equivalent	$\$1,000/m^2$	$<\$500/m^2$
Product Quality	CO_2 purity, %	80	85
	N_2 concentration, %	2	2
	Other contaminants, %	18	13
Process Performance	Electricity requirement, kJ/kgCO_2	Minimal (theoretical 0)	Minimal (theoretical 0)
	Heat requirement, kJ/kgCO_2	Minimal (theoretical 0)	Minimal (theoretical 0)
	Total energy (electricity equivalent), kJ/kgCO_2	Minimal (theoretical 0)	Minimal (theoretical 0)

Technology Advantages:

- Produces a high pressure CO_2 stream for sequestration.
- Achieves nearly complete carbon monoxide (CO) conversion, increases H_2 recovery from the gasification stream.
- Reduces the steam required for the WGS reaction, improving plant efficiency.
- Removes sulfur contaminants and uses an existing Pd membrane to filter >99.9% H_2.

R&D Challenges:

- Scaling the one-box process from laboratory scale to larger scales.
- The one-box process produces a H_2 stream product at a high pressure.
- Increase H_2 recovery rate at a high purity hydrogen.

Results To Date/Accomplishments:

- Performed a membrane performance field test for >100 hours using a slipstream test at the PSDF facility.
- Completed an evaluation of the CoS_2/MoS_2 catalyst for WGS of simulated coal gasifier off-gas.
- Established the separation efficiency of key contaminants in a simulated stream.
- Experimentally determined the performance of the one-box process in a bench-scale unit.

- Evaluated the outside coated CMS membrane and compared its performance with the existing membrane.

Planned Activities:

- Fabricate the ceramic membrane/module for the pilot testing unit and conduct an examination analysis of the ceramic membrane.
- Refine the mathematical model of the one-box H_2 production process from the bench-scale unit.
- Assemble a slipstream testing unit and perform slipstream tests at PSDF.
- Evaluate the performance of the pilot-scale testing unit.
- Complete the simulation, optimization, and economic analysis of the one-box process.
- Assess the ceramic-based, one-box H_2 production unit.

Available Reports/Technical Papers/Presentations:

Hydrogen Production from Syngas, Using a Catalytic Membrane Reactor, Mitra Abdollahi, Hyun Hwang, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, NAMS 2009.

Integrated One Box Process for Hydrogen Production From Syngas, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, AICHE 2009.

Process Intensification in Hydrogen Production From Syngas, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, ISCRE 2010.

Hydrogen Production from Coal-Derived Syngas Using a Catalytic Membrane Reactor-Based Process, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Rich Ciora, Muhammad Sahimi, Theodore T. Tsotsis, Journal of Membrane Science, submitted.

Contract No.:

DE-FC26-07NT43057

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Worcester Polytechnic Institute – Palladium-Based Membranes

Project Title:

Composite Pd and Pd Alloy Porous Stainless Steel Membranes for Hydrogen Production and Process Intensification

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

Worcester Polytechnic Institute (WPI) is developing an advanced synthesis gas (syngas) cleanup system and an integrated, cost-effective, hydrogen (H_2) production and separation process using a unique H_2 separation composite palladium (Pd) and alloy membrane for water gas shift (WGS) reactors. WPI is developing advanced technologies that offer the potential to consolidate two or more unit processes/units such as gas separation processes in one module for process intensification, which would be integrated downstream of a coal gasification system designed to produce a pure stream of H_2 with high-pressure carbon dioxide (CO_2) for sequestration.

Technical Goals:

- Synthesis of composite Pd and Pd/alloy porous Inconel membranes for WGS shift reactors with long-term thermal, chemical, and mechanical stability with special emphasis on the stability of H_2 flux and selectivity.
- Demonstration of the effectiveness and long-term stability of the WGS membrane shift reactor for the production of fuel-cell quality H_2.
- Research and development (R&D) of advanced gas clean-up technologies for sulfur removal to reduce the sulfur compounds to <2 parts per million (ppm) (Sub, ARI).
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost.
- Rigorous analysis and characterization of the behavior of the resulting overall process system, as well as the design of reliable control and supervision/monitoring systems.
- Assessment of the economic viability of the proposed intensification strategy through a comprehensive calculation of the cost of energy output and its determinants (capital cost, operation cost, fuel cost, etc.), followed by comparative studies against other existing pertinent energy technologies.

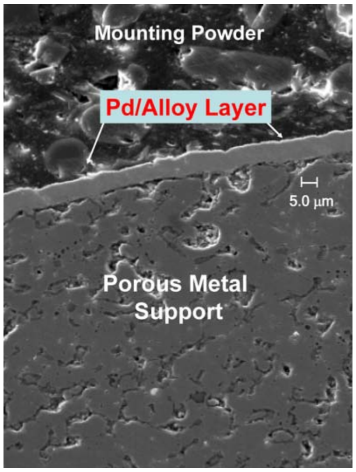

Figure 1: Illustration of WPI's Pd/Alloy Layer

Technical Content:

WPI's unique, patented technology to synthesize robust composite thin Pd and Pd/alloy membranes on porous sintered metal substrates uses an electroless plating process to produce membranes that are stable in the range of 300°C to 450°C. In addition, the novel aspects of the WPI's membrane technology can be summarized as follows:

1. It is made with a patented novel intermetallic diffusion barrier to prevent loss of permeance at high temperatures.
2. It is plated on a porous metal support for mechanical strength at high pressures, low Pd/alloy layer thickness and good chemical resistance to the feed gases.
3. It is made of Pd/alloys that avoid H_2 embrittlement and crack formation during cycling.

4. It is scalable and modular to accommodate small to large diameter and length tubular dimensions by connecting sections with commercial welding techniques.
5. It can be easily integrated into a WGS reactor to effect one-step H_2 production from coal gas at small to large scales.

Further refinement and/or advancement of the aforementioned fabrication approaches and synthesis techniques were successfully reported in the quarterly progress reports submitted to DOE.

Table 1: WPI Membrane Parameters

	Parameter	**Current R&D Value**	**Target R&D Value**
Membrane Properties	Materials of fabrication for selective layer	Pd	Pd/Au
	Materials of fabrication for support layer (if applicable)	PSS-316L, PSS-310, Inconel-625	PSS-316L, PSS-310, Inconel-625
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	∞ N/A	∞ N/A
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units (scfh/ft^2-psi at ΔP=100 psi H_2 partial pressure with P_{Low}=15 psia) *Computed pressure normalized flux. Experiments were conducted at a ΔP=15 psi H_2 partial pressure (P_{Low}=15 psia) due to the large membrane surface area and feed hydrogen demand.	Bench Scale: 3.59 @ 450°C Pilot Scale: *2.91 @ 450°C	DOE 2015 Target: 3
	Temperature, °C	300-450	250-500
	Bench-scale testing, hours without significant performance degradation	3550	N/A
	Pilot-scale testing (if applicable), hours without significant performance degradation	850	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	14	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-Tube	Shell-and-Tube
	Packing density, m^2/m^3 (for 1/2'' OD, 2.5'' L or 1'' OD, 6'' L assemblies)	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %, of the retentate stream (>99.9% hydrogen purity at the permeate side)	**80.3%** (At feed mixed-gas: 37.1% CO_2, 1.2% CO & 61.7% H_2 at 450°C, 212 psia, GHSV of 1069 h^{-1} & 92.6% H_2 Recovery); **83.5%** (At feed mixed-gas: 10% CO_2, 23% CO, 22% H_2 & 45% H_2O at 450°C, 212 psia, GHSV of 4497 h^{-1}, 83.2% H_2 Recovery & 95% CO conversion)	
	N_2 concentration, %	0	N/A
	Other contaminants, % CO (Feed gas: 10% CO_2, 23% CO, 22% H_2 & 45% H_2O at 450°C, 212 psia, GHSV of 4497 h^{-1}, 83.2% H_2 Recovery & 95% CO conversion)	2.9% at the retentate (dry basis) 0% at the permeate	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

Contaminant Resistance: Pd/gold (Au) and Pd/Cu alloy membranes provide some resistance to H_2S and also regenerable.

Flue Gas Pretreatment: PSA for removal of sulfur compounds (Sub, ARI).

Waste Streams Generated: None.

Technology Advantages:

The H_2 separation membrane can deliver CO_2 at high-pressure, significantly reducing compression costs associated with transporting the CO_2 and recompression for sequestration. The membrane also reduces the steam requirement associated with a traditional WGS reactor, thus improving overall plant efficiency. WPI's unique Pd alloy membranes provide high fluxes, proved high selectivity of separation, provide the ability to operate at temperatures around 300-450°C, and allow high-purity H_2 production from the WGS membrane reactor. In addition, by combining reaction, separation, and purification in a single-unit operation, the Pd/alloy-based membrane reactor is markedly more efficient than the conventional technology and also economical by combining the high- and low-temperature shift reactors and preferential oxidation reactor, as well as the H_2 separator (i.e., Pressure Swing Adsorption [PSA]), into a single-unit operation, allowing for process intensification.

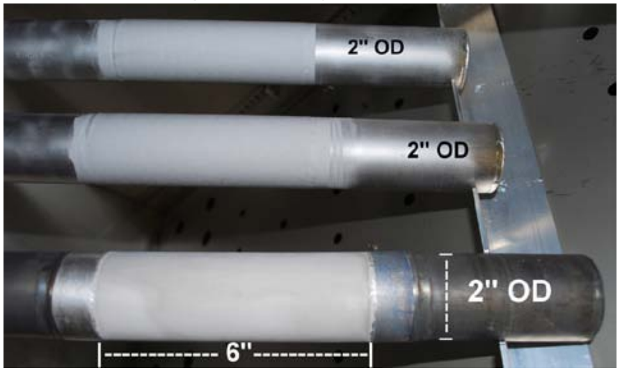

Figure 2: WPI Pd/Inconel H_2 Separation Membranes

R&D Challenges:

- The formulation and synthesis of defect-free membrane materials, which are resistant to sulfur.
- Long-term selectivity stability.
- Support metals with uniform pore size distribution and minimum mass transfer resistance.

Results To Date/Accomplishments:

- Achieved excellent long-term H_2/helium (He) selectivity stability of essentially infinite over a total testing period of ~3,550 hours (>147 days) at 300-450°C & at a ΔP of 15-100 psi (P_{Low}=15 psia).
- At 450°C, achieved re-producible, long-term H_2/He selectivity stability with several membranes with H_2 purity ≥99.99% over a testing period of 30 to 90 days.
- Flux of ~359 scfh/ft^2, which exceeded DOE's 2010 and 2015 H_2 flux targets (T=442°C & ΔP of 100 psi [with P_{Low}=15 psia]).
- Conducted an additional ~3,000 hours of mixed gas permeation experiments (61.7% H_2, 37.1% CO_2 & 1.2% carbon monoxide [CO] w/ and w/o 19% Steam).
- Reduced the number of synthesis steps for the large-scale preparation for potential commercialization of WPI's composite Pd-based membrane production technologies.
- Achieved 99% total CO conversion and 89.9% H_2 recovery in a 12.5 µm-thick Pd-based CMR operated at ~350°C, ΔP=200 psi (P_{Low}=15 psia) H_2O/CO=1.44 and $GHSV_{stp}$=150 h^{-1}, exceeding equilibrium conversion of 93.4% and traditional packed bed conversion of 92.7%.
- Successfully completed steady-state MSR and WGS reaction modeling studies and initiated process intensification analysis.
- Successfully completed unsteady-state WGS reaction modeling studies and implemented process control strategies.
- Completed property and isotherm measurements for the selected adsorbents (Sub, ARI).
- Completed the PSA system construction and initiated PSA testing at 200°C and a feed pressure of 200 psia (with P_{low}=1 atm) (Sub, ARI).

Planned Activities:

- Continue WGS reaction and mixed gas testing studies.
- Complete 2010 technical target screening and qualification tests* Phase 1 and Phase 2.

- Synthesis of thin separation layers to achieve higher H_2 flux using support with minimum mass transfer resistance.
- Continue Pd/Au alloying studies to improve H_2 flux and sulfur resistance.
- Conduct long-term sulfur poisoning and recovery experiments.
- Further refinement and improvement of the unsteady-state CMR model.
- Continue process intensification and performance assessment analyses coupled with process control strategies.
- Initiate economical analysis for the proposed process intensification framework.
- Complete building and testing of a PSA system (sub: ARI).

Available Reports/Technical Papers/Presentations:

JOURNAL ARTICLES:

Ayturk, M. E. and Ma, Y. H., "*Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability," In preparation.*

Chen, C. H. and Ma, Y. H., "The Effect of H_2S on the performance of Pd and Pd/Au composite membrane," Submitted to the Journal of Membrane Science.

Pomerantz, N.; Payzant, E.A. and Ma, Y.H. *"Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication*," AIChE Journal, In press.

Ma, Y. H., Ayturk, M.E., Augustine, A.S. and Kazantzis, N., *"Palladium Membrane Reactor for Water Gas Shift Reaction," Submitted to* Catalysis Today, In press.

Pomerantz, N. and Ma, Y.H. *"Effect of H2S on the performance and long-term stability of Pd/Cu membranes,"* Industrial & Engineering Chemistry Research, 48(8) (2009) 4030 - 4039.

Ayturk, M. E., Kazantzis, N.K. and Ma, Y. H., "*Modeling and Performance Assessment of Pd- and Pd/Au-based Catalytic Membrane Reactors for Hydrogen Production,"* Energy and Environmental Science, *2 (2009) 430-438.*

CONFERENCE PROCEEDINGS:

Ayturk, M. E. and Ma, Y.H. *"Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability."* Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem., 55(1) (2010) xxx.

Chen, C. H. and Ma, Y. H., *"Effect of H_2S concentration on hydrogen permeance of a composite Pd/Au hydrogen separation membrane prepared by galvanic displacement,"* Preprint in the Proceedings of 239th ACS Annual Meeting, March 21st -25th 2010, San Francisco, California, USA.

Pomerantz, N. and Ma, Y.H. "*Effect of mass transfer on Cu plating rate and deposition morphology for Pd/Cu alloy membranes for hydrogen separation," Extended abstract in the* Proceedings of the ACS 239th National Meeting and Exposition, March 21 – 25, 2010, San Francisco, California, USA.

Ma, Y. H., Ayturk, M.E., Augustine, A.S. and Kazantzis, N., *"Palladium Membrane Reactor for Water Gas Shift Reaction," Proceedings of the* 9th International Conference on Catalysis in Membrane Reactors (ICCMR9), June 28th – July 2nd, 2009, Lyon, France.

Chen, C. H. and Ma, Y. H., "Characterization of sulfur resistance of Pd/Au hydrogen separation membranes," Extended abstract in the Proceedings of the 2008 AIChE Annual Meeting, November 16th-November 21st, 2008 Philadelphia, Pennsylvania, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "*The effect of H_2S on the long-term stability of Pd/Cu membranes and the characteristics of H_2S poisoning of electroless deposited Pd," Extended abstract in the* Proceedings of the AIChE Annual Meeting 2008, November 16 – 21, 2008, Philadelphia, Pennsylvania, USA.

Ma, Y. H., Kazantzis, N.,Ayturk, M. E., Pomerantz, N. and Chen, C.-H. Synthesis and Long-Term Characterization of Sulfur Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen Production via Catalytic Membrane Reactor Applications. *Extended abstract in the Proceedings of the 10th Intl. Conf. on Inorganic Membranes (ICIM10)*, (2008) Tokyo, Japan.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement," Preprint in the Proceedings of 234th ACS Annual Meeting, August 19th -23rd, 2007

Boston, Massachusetts, USA.

Pomerantz, N. and Ma, Y.H. *"Effect of H_2S poisoning of Pd/Cu membranes on H_2 permeance and membrane morphology," Extended abstract in the* Proceedings of the ACS 234th National Meeting and Exposition, August 19 – 23, 2007, Boston, Massachusetts, USA.

PRESENTATIONS:

Ayturk, M. E. and Ma, Y.H. *"Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability," To be presented at the* ACS Spring National Meeting and Exposition, March 21st – 25th, 2010, San Francisco, California, USA.

Chen, C. H. and Ma, Y. H., "Effect of H_2S concentration on hydrogen permeance of a composite Pd/Au hydrogen separation membrane prepared by galvanic displacement." *To be presented at the* ACS Spring National Meeting and Exposition, March 21st – 25th, 2010, San Francisco, California, USA.

Pomerantz, N. and Ma, Y.H. *"Effect of mass transfer on Cu plating rate and deposition morphology for Pd/Cu alloy membranes for hydrogen separation," To be presented at the* ACS 239th National Meeting and Exposition, March 21 – 25, 2010, San Francisco, California, USA.

Ayturk, M. E. and Ma, Y.H. *"Long-Term Selectivity Stability and High-Pressure Mixed Gas Hydrogen Permeation Testing of Composite Pd/Inconel Membranes." Presented at the* AIChE Annual Meeting, November 8th – 13th, 2009, Nashville, Tennessee, USA.

Augustine, A. S.; Ayturk, M.E.; Kazantzis, N. and Ma, Y. H. *"Palladium Membrane Reactor for Water Gas Shift Reaction." Presented at the* AIChE Annual Meeting, November 8th – 13th, 2009, Nashville, Tennessee, USA.

Ma, Y. H., Ayturk, M.E., Augustine, A.S. and Kazantzis, N., *"Palladium Membrane Reactor for Water Gas Shift Reaction," Presented at the* 9th International Conference on Catalysis in Membrane Reactors (ICCMR9), June 28th – July 2nd, 2009, Lyon, France.

Ayturk, M. E. and Ma, Y. H., *"Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability," Presented at the* 2008 AIChE Annual Meeting, November 16-21, 2008 Philadelphia, Pennsylvania, USA.

Chen, C. H. and Ma, Y. H., "Characterization of sulfur resistance of Pd/Au hydrogen separation membranes," *Presented at the* 2008 AIChE Annual Meeting, November 16-21, 2008 Philadelphia, Pennsylvania, USA.

Pomerantz, N.; Payzant, E.A. and Ma, Y.H. *"Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication," Presented at the* AIChE Annual Meeting 2009, Nashville, Tennessee, USA, November 8 – 13, 2009.

Pomerantz, N.; Shaw, E. and Ma, Y.H. *"The effect of H_2S on the long-term stability of Pd/Cu membranes and the characteristics of H_2S poisoning of electroless deposited Pd," Presented at the* AIChE Annual Meeting 2008, November 16 – 21, 2008, Philadelphia, Pennsylvania, USA.

Ma, Y. H., Kazantzis, N., Ayturk, M. E., Pomerantz, N. and Chen, C.-H., *"Synthesis and Long-Term Characterization of Sulfur Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen Production via Catalytic Membrane Reactor Applications," Presented at the 10th International Conference on Inorganic Membranes (ICIM10),* August 18-22, 2008, Tokyo, Japan.

Ayturk, M. E., Kazantzis, N.K. and Ma, Y. H., *"Modeling and Performance Assessment of Pd- and Pd/Alloy-based Catalytic Membrane Reactors for Hydrogen Production," Presented at the* International Congress on Membranes and Membrane Processes (ICOM 2008), July 12-18, 2008, Honolulu, Hawaii, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "XPS studies of H_2S poisoned Pd deposits and the implications on Pd membrane performance." *Presented at the* International Congress on Membranes and Membrane Processes (ICOM 2008), July 12-18, 2008, Honolulu, Hawaii, USA.

Ma, Y. H., Kazantzis, N., Ayturk, M. E., Pomerantz, N. and Chen, C.-H., *"Composite Pd and Pd/alloy Porous Stainless Steel Membranes for Hydrogen Production, Process Intensification and CO_2 Sequestration," Presented at the* 2008 NHA Annual Hydrogen Conference & Expo: "Ramping up Commercialization," March 30-April 03, 2008 Sacramento, California, USA.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by

galvanic displacement," *Presented at the* 2007 ACS Annual Meeting, August 19-23, 2007 Boston, Massachusetts, USA.

Pomerantz, N. and Ma, Y.H. "Effect of H_2S poisoning of Pd/Cu membranes on H_2 permeance and membrane morphology." *Presented at the* ACS 234th National Meeting and Exposition, August 19 – 23, 2007, Boston, Massachusetts, USA.

Chen, C. H. and Ma, Y. H., "Preparation of Pd/Au hydrogen separation membrane by galvanic displacement," *Presented at the* 2007 North American Membrane Society Annual Meeting, May 13-16, 2007 Orlando, Florida, USA.

Contract No.:

FC26-07NT43058

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Partners:

Adsorption Research, Inc.

REB Research & Consulting – High-Flux Metallic Membranes and Reactors

Project Title:

High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors

Technology Area:

Pre-Combustion Membranes

Technology Maturity:

Pilot-scale, 8 tonnes CO_2/day

Primary Project Goal:

REB Research & Consulting is developing a carbon dioxide (CO_2)/hydrogen (H_2) separation membrane that utilizes a base metal in place of more expensive palladium (Pd).

Technical Goals:

- Fabricate metallic alloys for coupon testing to determine permeation and inter-diffusion properties along with material embrittlement.
- Conduct more thorough evaluation of most promising membranes in harsher conditions, and evaluate drawability, cladability, and brazability.
- Fabricate an H_2 purifier and membrane reactor units, and perform H_2 permeation, shock resistance, and longevity tests on modules under simulated operating conditions.

Technical Content:

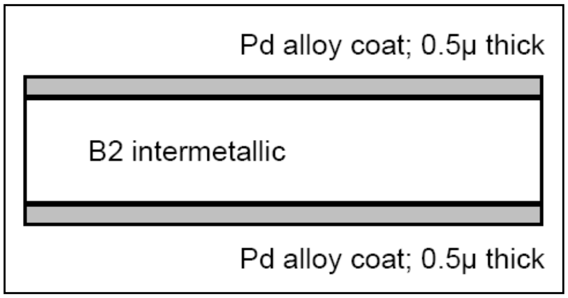

Figure 1: Typical B2 Alloy Coated with Pd-Alloy

The project is investigating a more economic metal to replace Pd for use in an H_2 membrane. The current focus is on B2 alloys. These are similar to the BI alloys (also known as BCC) metals of the 4B and 5B element region (columns) on the periodic table – metals like vanadium (V), niobium (Nb), and tantalum (Ta) that are reasonably good at H_2 purification. These metals have a high H_2 sorption, high H_2 diffusivity, and are flexible enough for membrane fabrication; however, even when alloyed with a moderator, they tend to embrittle. Further, in the B1 form, stress creep and Pd-substrate interdiffusion are a problem. B2 (CP2) metals have similar structure and properties to the B1 metals, but should be much more resistant to creep and interdiffusion. Several membranes of the B2 structure have been developed and tested, and so far as predicted, they have passed H_2 and have been durable. Figure 1 depicts the membrane structure. The B2 intermetallic alloy substrate is coated with a thin layer of Pd alloy for catalytic activity and oxidation protection. These improved membranes so far have been hard to fabricate as tubes.

Figure 2: Hydrogen Permeation Disk

Figure 2 displays the disc configuration that has been developed for use with B2 membrane materials and Figure 3 displays how the B2 alloy discs (H_2 permeation discs) will be assembled into a purifier or membrane reactor.

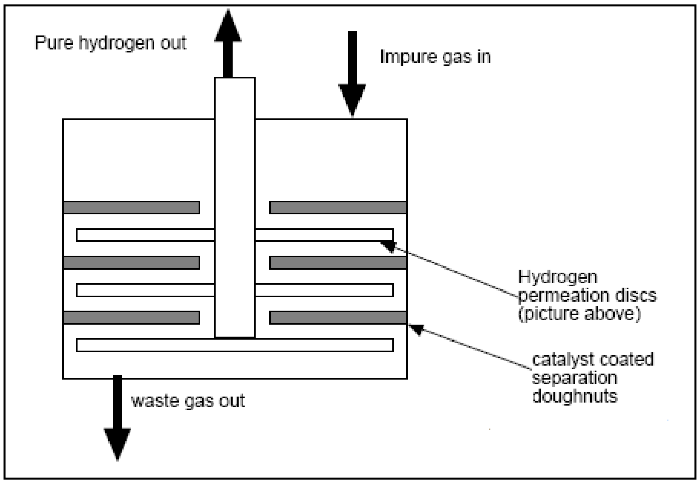

Figure 3: Membrane Reactor Design

A version of this reactor/separator has been tested using a coal gasifier slipstream at the Western Research Institute at Laramie, Wyoming. A device with one catalytic doughnut and two membrane discs produced 2.28 standard cubic feet per hour (scfh) of pure H_2 from a 90 psi slip-stream at 400°C. The total membrane surface area was 0.947 ft^2 and the coal gas had a dry composition of 37% H_2, 27% carbon monoxide (CO), 30% CO_2, 3% methane (CH_4), and 100 parts per million (ppm) hydrogen sulfide (H_2S) (2.41 scfh/ft^2). There was excess steam in the gas. Calculations suggest that a scaled up version of this purifier should allow economical H_2 from coal-gas, where the H_2 permeates through the metal and leaves behind a high-pressure CO_2-rich stream. The high-pressure, CO_2-rich gas stream is sequestration ready.

Table 1: REB Research Membrane Parameters

	Parameter	**Current R&D Value**	**Target R&D Value**
Membrane Properties	Materials of fabrication for selective layer	B2 Alloys	B2 Alloys
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	100% N/A	100% N/A
	Type of selectivity measurement (ideal or mixed gas)	Helium leak	Helium leak, CO /CO_2 in H_2 stream for larger units
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	0.2 mol /m^2s (51 scfh/ft^2) at ΔP= 44 psi	Same. But for gas mixtures
	Temperature, °C	350-400°C	350-400°C
	Bench-scale testing, hours without significant performance degradation	1500	1500
	Pilot-scale testing (if applicable), hours without significant performance degradation	75	200
	Maximum pressure differential achieved without significant performance degradation or failure, bar	6 bar	20 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disc and doughnut	Disc and doughnut
	Packing density, m^2/m^3	135 m^2/m^3	135 m^2/m^3
	Pressure drop, bar	N/A	< 1bar
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	\$1,200/m^2	\$1,200/m^2
Product Quality	CO_2 purity, %	80%	80%
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	0	0
	Heat requirement, kJ/kgCO_2	0	0
	Total energy (electricity equivalent), kJ/kgCO_2	0	0

Membranes, when copper (Cu)-Pd coated, resisted poisoning from 50 hrs with 100 ppm H_2S; better resistance is expected with gold (Au)-Pd coated membranes. Dust from the coal-gas built up at the seals; scaled up operation will require dust filtering. Waste gas was a high-pressure, CO_2-rich stream suitable for sequestration (or perhaps, for sale).

Technology Advantages:

- B2 alloys should extend the life of the separator, effectively making it cost-competitive.
- Membranes have similar selectivity and flux to Pd.
- Projected life of the material to be 15+ years.
- Low embrittlement.
- Base metal costs \$1,080/m^2 (\$100/ft^2), while Pd costs \$32,300/m^2 (\$3,000/ft^2).

R&D Challenges:

There can be difficulty in fabricating membranes to the shapes and tolerances needed. More potential problems can arise, fabricating durable purifiers and membrane reactors with the new alloys (seals). Some alloys are much cheaper than Pd, but exhibit higher embrittlement.

Results To Date/Accomplishments:

- Demonstrated suitable lifespan and flux in accelerated tests at target costs.
- Demonstrated acceptable brazing behavior.
- Lowered the cost/flux of H_2 permeation membranes, thus lowering the cost of H_2.
- Identified several new B2 alloys with potential use in other applications, such as nuclear reactor fabrication.

Planned Activities:

Fabricate and test B2 metal-metal matrix membranes in hopes that these membranes will work as well but will be easier to fabricate.

Conduct disc membrane reactor tests with coal-gas for the new alloy membranes at a higher pressure with revised seals and flow path.

Available Reports/Technical Papers/Presentations:

S. N. Paglieri (AET-3), Y. Wang (MST-8), T. J. Venhaus (AET-3), H. Oona (AET-3), R. E. Buxbaum, K. S. Rothenberger, B. H. Howard, R. P. Killmeyer, "Characterization of V-6Ni- 5Co Membranes for Hydrogen Separation." International Symposium on Metal- Hydrogen Systems (MH-2006) held October 1-6, 2006 in Maui, Hawaii.

Low-cost Coal to Hydrogen for Electricity with CO_2 Sequestration, Dr. Robert E. Buxbaum, Michigan Catalysis Soc. Talk, April 2009.

Development of membranes for hydrogen separation: Pd coated V-10Pd, Paglieri, S.N.[1]; Wermer, J.R.[2]; Buxbaum, R.E.[3]; Ciocco, M.V.[4]; Howard, B.H.[5]; Morreale, B.D.[5], Volume 3, Number 3, September 2008 , pp. 169-176(8).

Development of Group V Based Metal Membranes for Hydrogen Separation, Stephen N. Paglieri, Micheal V. Ciocco, Robert E. Buxbaum, Bryan D. Morreale. AIChE meeting, November 20, 2008, Paper 701f.

Contract No.:

DE-FC26-05NT42400

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Partners:

G&S Titanium Co.
Iowa State University, Ames Lab
Los Alamos National Laboratory (LANL)
Western Research Institute (WRI)

Southwest Research Institute – Ternary Palladium Alloy Membranes

Project Title:

High Permeability Ternary Palladium Alloy Membranes with Improved Sulfide and Halide Tolerance

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

An iterative modeling, rapid fabrication, and testing approach is being employed by Southwest Research Institute (SwRI) to develop and demonstrate an ultra-thin (<5 micron), durable ternary palladium (Pd)-alloy membrane with excellent resistance to sulfur and halogen attacks while meeting or exceeding the hydrogen (H_2) permeability performance established by DOE. A secondary benefit is to support the process of carbon dioxide (CO_2) gas sequestration.

Technical Goals:

- Investigate the performance of a variety of ternary Pd-copper (Cu)-M alloys to identify which experimental alloys show improved H_2 permeance compared to a baseline Pd-Cu alloy.
- Develop the necessary methods for the fabrication of high-performance, thin Pd-alloy membranes using advanced physical vapor deposition methods.
- Experimentally determine the H_2 and nitrogen (N_2) permeation rates of the alloys under a range of pressures 1.3 atm to 11 atm (5 psig to 150 psig feed pressure) and temperatures (200°C to 500°C).
- Characterize the alloy membranes using binary mixture permeation tests, electron microscopy (to observe structure and morphology), X-ray diffraction (for purity of the film and crystal structure), atomic force microscopy (for surface structure), and energy-dispersive X-ray spectroscopy (for alloy composition).
- Test the performance of the alloy membranes in the presence of a single-contaminant and multi-contaminant synthesis gas (syngas).

Technical Content:

A project team consisting of SwRI, Georgia Institute of Technology (GT), the Colorado School of Mines (CSM), TDA Research, and IdaTech LLC is developing a robust, poison-tolerant, H_2-selective, free-standing membrane to produce clean H_2. The project includes three primary tasks: 1) materials modeling and composition selection; 2) fabrication of high-performance ternary alloy membranes; and 3) membrane testing and evaluation; all are operating independently and concurrently. GT has performed extensive DFT calculations for H_2 in the bulk of pure Pd, Pd96Ag4, Pd96Au4, Pd96Cu4, Pd96Ni4, Pd96Pt4, Pd96Rh4, and Pd96Y4. GT has also performed a series of calculations on Pd74Cu26, Pd70Cu30, Pd70Cu¬26Ag4, Pd70Cu¬26Au4, Pd70Cu¬26Ni4, Pd70Cu¬26Pt4, and Pd70Cu¬26Y4. In the last two years, SwRI has deposited and released more than 50 freestanding foils of binary PdCu and ternary PdCuY, PdCuAu, PdCuPt, PdCuAg, PdCuRu, and PdCuNi. The nominal 10-µm thick films were sent to CSM, TDA, and IdaTech. An annealing profile has been developed to reduce stress and facilitate incorporation into a testing apparatus. CSM has conducted several pure gas permeation tests with a SwRI binary and ternary alloy membranes.

To date, the PdCuAu and PdCuPt membranes have exhibited equivalent performance at temperatures in the range of 423-773°C, and their performance correlates well with the predictions from GT. All membranes tested have exhibited no detectable nitrogen leak rate prior to testing, and the H_2 permeability data obtained are consistent with theoretical and literature data. TDA has tested multiple membranes under DOE's National Energy Technology Laboratory (NETL) Test Protocol, with initial promising results from gold (Au) containing foils. IdaTech has received foils and is testing on PdCuAu ternary foils. The program is progressing toward DOE-identified targets, but there have been identified issues with sealing and rupture of the freestanding membranes that have introduced engineering complications that make these membranes challenging for industrial use.

Table 1: SwRI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd Ternary Alloys	Pd Ternary Alloys
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	99.99 N/A	99.99 N/A
	Type of selectivity measurement (ideal or mixed gas)	mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	H_2 - 242 SCFH/ft^2	H_2 - 200 SCFH/ft^2
	Temperature, °C	400	300-600
	Bench-scale testing, hours without significant performance degradation	250	120
	Pilot-scale testing (if applicable), hours without significant performance degradation	24	120
	Maximum pressure differential achieved without significant performance degradation or failure, bar	6.9	6.9
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate & Frame	Plate & Frame
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	4.8	4.8
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	\$16,146/m^2	\$10,764/m^2
Product Quality	CO_2 purity, %	N/A	N/A
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

The technical and patent literature has shown the presence of H_2S in particular reduces or inhibits the H_2 flux for PdCu alloy foil membranes. Consequently, the materials design strategy for the proposed research is to use computational approaches to identify ternary alloys, Pd-Cu-M, that are likely to have increased H_2 permeability and to choose alloying metals so that they will not tend to segregate. There are no flue gas pretreatment requirements, nor is any waste stream generated as a result of using these membranes for H_2 separation.

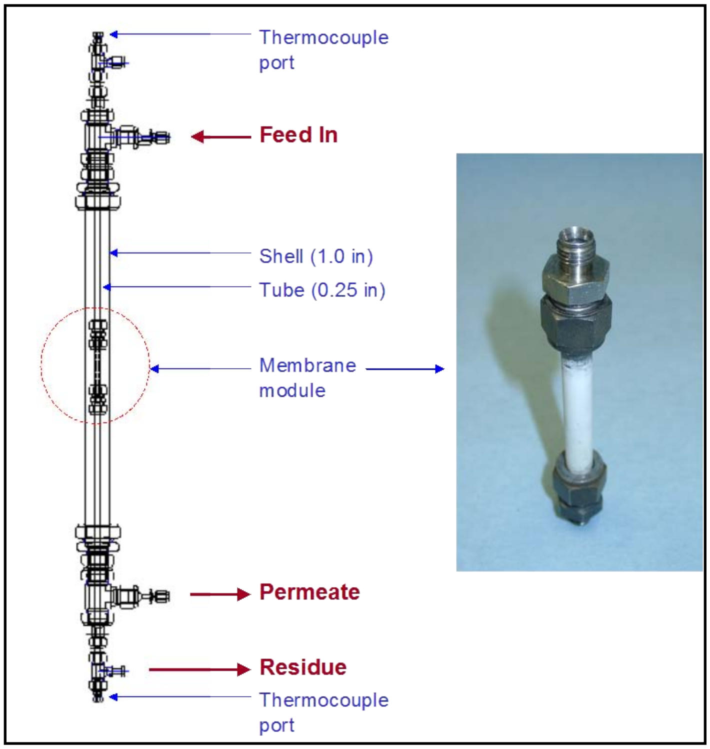

Figure 1: Rig for Testing Membranes in a Syngas Environment

Technology Advantages:

The advanced vapor deposition methods used to construct the Pd-alloy membranes provide unique advantages compared to other membrane manufacturing techniques. The high-power, pulsed magnetron sputtering and plasma-enhanced magnetron deposition methods are able to rapidly produce membranes of almost any alloy composition, providing excellent flexibility in terms of the materials and properties used in a membrane. These methods also generate alloy compositions with good uniformity over areas up to 645 cm^2 (100 in^2).

R&D Challenges:

- New PdCu alloy membranes are not as effective in separating H_2 as pure Pd membranes typically are. Further testing and modification will be needed to combine the flexibility of the new alloys with the performance of the pure Pd membranes.
- A high percentage of Cu (>40%) in the alloy mix significantly reduced the membranes' H_2 solubility.
- Experienced difficulties in generating multiple membranes with a consistent physical surface; defects or unwanted variations occurred in early trials.

Results To Date/Accomplishments:

- Developed a rigorous strategy for predicting H_2 permeability through ternary alloys using complex calculations for use in Pd-Cu-gold (Au), with calculations for Pd-Cu-nickel (Ni) and Pd-Cu-platinum (Pt) still in progress.
- Coated and submitted thin (5-10 micron) membranes of Pd60/Cu40, Pd96M4, and Pd74Cu22Ag4 for structural and composition measurements and permeation testing.
- Determined pure gas H_2 and N_2 permeation rates for a range of pressure differentials (1.3 atm to 11 atm feed pressure [5 psig to 150 psig]) and temperatures ranging from 200°C to 500°C.

Planned Activities:

- Create at least 20 membranes with different Cu concentrations, with the full-scale fabrication of the two to three most promising ternary elements based on their H_2 solubility.
- Preliminary membrane samples at TDA and IdaTech labs using clean syngas and syngas with added impurities.
- Conclude calculations for the development of Pd-Cu-M and Pd-Au-M ternary elements.
- Continue testing thicker ternary foils (10 to 25 µm) for possible use in the membranes.
- Freestanding alloy films of Pd, Pd-Cu, Pd-Au, and Pd-Cu-Ag have been shown to meet the predicted permeability specifications for this project.

Available Reports/Technical Papers/Presentations:

N/A

Contract No.:

DE-FC26-07NT43056

NETL Project Manager:

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Partners:

Colorado School of Mines
The Georgia Institute of Technology
Idatech
TDA Research

Western Research Institute – Water Gas Shift Catalyst with Vanadium Alloy Membrane

Project Title:

Integration of a Structural Water Gas Shift (WGS) Catalyst with a Vanadium Alloy Hydrogen (H_2) Transport Device

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Prototype

Primary Project Goal:

Western Research Institute (WRI) is developing and designing a membrane reactor for processing coal gasification-derived synthesis gas (syngas) that integrates water gas shift (WGS) and hydrogen (H_2) separation functions.

Technical Goals:

- Develop a structural WGS catalyst capable of withstanding high-pressure differentials.
- Develop vanadium alloy H_2 separation membrane.
- Integrate the WGS catalyst and metallic membranes into a device and test under simulated gasifier conditions.
- Fabricate a modular WGS/membrane integrated device capable of producing 10,000 L H_2/day from coal-derived syngas.

Technical Content:

The membrane reactor under development promotes the reaction of carbon monoxide (CO) with water, by use of a WGS catalyst, to produce carbon dioxide (CO_2) and H_2, and then separates the H_2, by use of a metallic membrane. Hydrogen produced can be used for electricity generation. The concentrated stream of CO_2 produced can be further purified and sequestered.

Figure 1 shows a schematic of a possible configuration for the membrane reactor. In this configuration, there are alternating stages of membrane disks and catalyst doughnuts.

By integrating the WGS and the gas separation into one unit, the WGS conversion is increased due to the continuous removal of H_2.

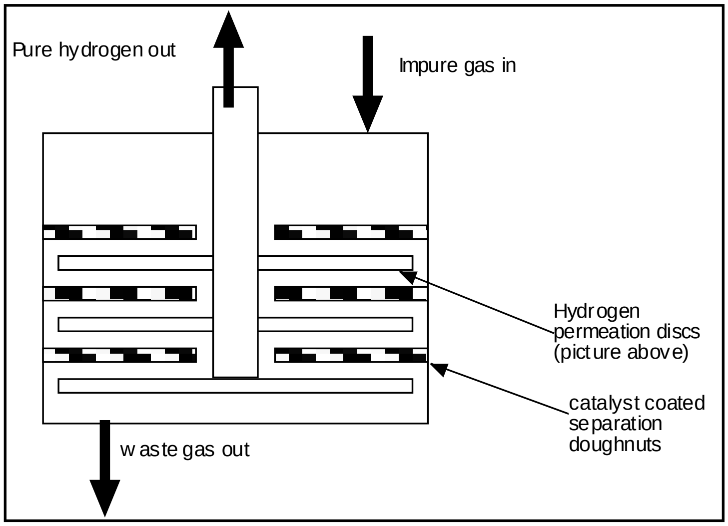

Figure 1: Schematic of Disk and Donut Integrated Device Design

Table 1: WRI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	V-Pd	V-Pd
	Materials of fabrication for support layer (if applicable)	304 SS	304SS
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology CO_2/N_2 for post-combustion technology	100% H_2	100% H_2
	Type of selectivity measurement (ideal or mixed gas)	mixed	mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	52 scfh/ft^2	52 scfh/ft^2
	Temperature, °C	400°C	400°C
	Bench-scale testing, hours without significant performance degradation	100	100
	Pilot-scale testing (if applicable), hours without significant performance degradation	40	40
	Maximum pressure differential achieved without significant performance degradation or failure, bar	200 psig	200 psig
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate	plate
	Packing density, m^2/m^3	10	10
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	\$2,100/m^2	\$2,100/m^2
Product Quality	CO_2 purity, %	N/A	N/A
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

The project is completed so current and target values are identical. The membrane reactor ran at baseline flux levels for 40 hours in a coal-derived syngas mixture with 125 parts per million (ppm) hydrogen sulfide (H_2S) and 30% CO. Other low-level contaminants were not quantified but were also not removed from the gas mixture.

Technology Advantages:

Combining the WGS catalyst with H_2 separating membrane increases production of H_2 by removing from the reaction zone and reduces capital cost of plant by eliminating need for additional gas separation.

R&D Challenges:

Consistent production of vanadium 9 wt% palladium (Pd) alloy is difficult due to persistent cracking of the alloy during rolling.

Results To Date/Accomplishments:

The focus of the chemistry of the WGS catalyst has been on iron (Fe), aluminum (Al), chromium (Cr), copper (Cu), and cerium (Ce) based systems, including:

- Tested catalysts by impregnation into porous mullite substrates and cordierite monoliths.
- Determined highest activity and stability for 75Fe-15Al-8Cr-2Cu.

- Identified among the Fe-Cr-Cu-Ce-oxygen (O) catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Determined that producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures.
- Obtained and tested multiple vanadium alloys for brazing performance with Cu.
- Developed guidelines based on the brazing tests and analysis of the literature to anticipate the performance of vanadium alloys with respect to H_2 transport and fabricability based on alloying elements.
- Determined elements that are potentially positive to both H_2 transport performance and brazing performance include Ce, Cu, Fe, manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn).
- Identified alloying elements that can be sufficiently used to overcome their detrimental effect on brazing.
- Determined that brazing with vanadium and structural alloys, including mild steel, 304 stainless steel, and 9Cr 1Mo steel, were generally excellent.
- Produced an integrated WGS membrane device which produced 10,000 liters per day of H_2 under coal-derived syngas.

Planned Activities:

Project work was recently completed.

Available Reports/Technical Papers/Presentations:

Barton Tom, Morris Argyle. "Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device." http://www.hydrogen.energy.gov/pdfs/review07/pd_18_barton.pdf. (Accessed June 2009).

Barton Tom, Morris Argyle. "The Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device." http://www.hydrogen.energy.gov/pdfs/progress08/ii_g_4_barton.pdf. (Accessed June 2009).

Contract No.:

DE-FC26-05NT42454

NETL Project Manager:

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Grambling State University – Catalysts for Use in Membrane Reactors

Project Title:

Development of Low-Cost Membranes for $H_2/CO_2/CO$ Separation for WGS Reactors

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Laboratory-scale

Primary Project Goal:

Grambling State University is synthesizing low temperature bimetallic nanocatalysts for use in the water gas shift (WGS) reaction for hydrogen (H_2) production from a carbon monoxide (CO) and steam mixture, and is developing low-cost metal/ceramic membranes for H_2/carbon dioxide (CO_2) separation.

Technical Goals:

- Develop micro/mesoporous ceramic membrane disks, composed of tantalum (Ta)/niobium (Nb) alloys, for optimum H_2 separation.
- Examine the effect of alloying the Ta/Nb ceramic membranes with other metals to reduce H_2 embrittlement and promote cathodic protection.
- Develop cellulose acetate interlayers between two micro/mesoporous ceramic disks for optimum H_2 and CO_2 separation.
- Examine the effects of plasticizers on CO_2 permeability.
- Prepare and optimize nano-bimetallic nickel (Ni)/molybdenum (Mo), cobalt (Co)/cerium (Ce), copper (Cu)/Ni, and iron (Fe)/Mo catalysts supported on mesoporus γ-Al_2O_3 and Al_2O_3/SiO_2 granules for the WGS reaction.
- Develop and demonstrate a prototype reactor based on novel low-cost metal (Ta/Nb)/ceramic and cellulose acetate membranes to separate H_2 and CO_2.
- Examine the performance of Ta/Nb and cellulose acetate/ceramic membranes under WGS conditions.

Technical Content:

The WGS will utilize Cu-Ni-Ce/alumina granular nanocatalysts that react CO and steam to produce H_2 and CO_2. Figure 1 represents the chemical reaction inside the WGS as the gas stream is exposed to the catalyst and converts the CO to CO_2. The Cu-Ce catalyst converts approximately 69% of the CO, while Cu-Ce-Ni converts approximately 83% during a 10-hour reaction period.

Table 1 displays different compositions of metal catalysts under investigation for promoting the WGS reaction. Four catalyst compositions (rows 3, 4, 9, and 10 in Table 1) will be evaluated for high temperature shift reactions at a temperature range of 150°C to 450°C and six compositions (1, 2, 5, 6, 7, and 8 in Table 1) for low temperature shift reactions at 150°C to 400°C.

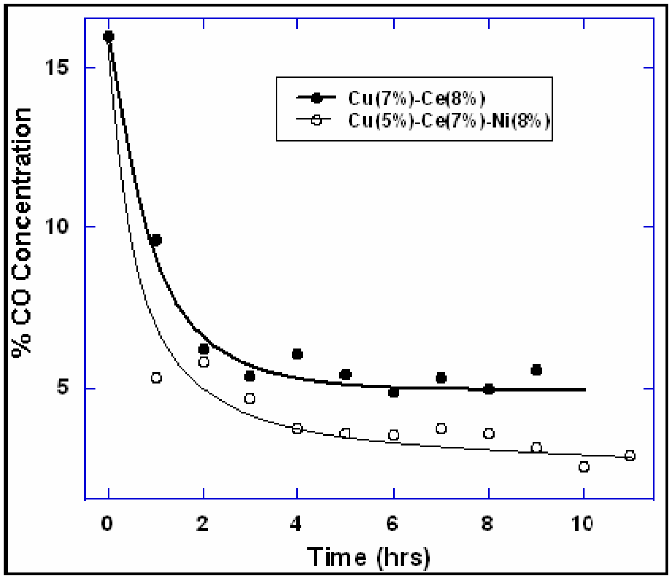

Figure 1: Catalytic Conversion of CO to CO_2

Table 1: Compositions of Metal Catalysts Under Investigation for Promoting WGS Reaction

Catalyst Composition			% Metal	$Ni(NO_3)_2 \cdot 6H_2O$ (g)	Wt. (g)	Wt. CuO (g)	Wt. Cu (g)	Wt. CeO_2 (g)	Wt. Ce (g)	Wt. Fe_2O_3 (g)	Wt. Fe (g)
CU (%)	NI (%)	Ce (%)									
10		11	20.96	0.00	0.00	0.46	0.37	0.52	0.42	0.00	0.00
7	3	11	20.70	0.54	0.11	0.33	0.26	0.48	0.39	0.00	0.00
5	5	11	21.31	0.93	0.19	0.24	0.19	0.49	0.40	0.00	0.00
3	7	11	21.29	1.31	0.26	0.14	0.11	0.48	0.39	0.00	0.000.00
	10	11	21.32	1.86	0.38	0.00	0.00	0.46	0.38	0.00	0.00
	10	9	19.15	1.80	0.36	0.00	0.00	0.37	0.30	0.00	0.00
	10	6	16.09	1.75	0.35	0.00	0.00	0.24	0.19	0.00	0.00
	10	3	13.04	1.69	0.34	0.00	0.00	0.11	0.09	0.00	0.00
	10		10.00	1.64	0.33	0.00	0.00	0.00	0.00	0.00	0.00
7	9	13	28.39	1.93	0.39	0.35	0.28	0.54	0.45	0.00	0.00
Fe(10%) Ce(11%)			21.05	0.00	0.00	0.00	0.00	0.51	0.41	0.54	0.38

After the WGS reaction takes place, the H_2 will be separated from the CO_2 using an outer shell ceramic membrane of Ta/Nb metal that will be used to separate H_2 from the rest of the constituents. The interior of the ceramic membrane will consist of cellulose acetate (CA) with 75% triethyl citrate plasticizer, which will be used to separate the H_2 and CO_2. The CA will be located between two mesoporous ceramic disks. Figure 2 shows a blank ceramic disk on the left (a) and the ceramic disk on the right (b) sputter coated with Nb. The metal film coating the disk is approximately 400 nanometers thick and the coatings will be applied through sputtering (physical) techniques or aluminothermic (chemical) methods.

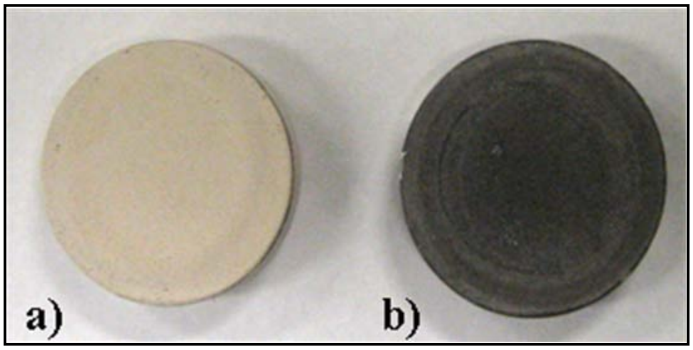

Figure 2: Uncoated and Coated Ceramic Disks

Technology Advantages:

Ceramic membranes incorporating low-cost metals (Ta/Nb) could lower H_2 production costs.

R&D Challenges:

Low Ta/Nb catalytic activity.

The WGS reaction time is longer than desired.

Results To Date/Accomplishments:

- Fabricated cellulose acetate-ceramic membranes and studied CO_2 separation.

- Prepared the bimetallic nanoparticles/sol-gel supported catalysts.
- Fabricated Ta/Nb-ceramic membranes with/without Cu, silver (Ag), and magnesium (Mg) additives and studied H_2 separation.
- Ni(10%)Ce(11%) catalyst was found to be the best WGS catalyst among the low temperature shift catalysts, w$_h$ile Ni(5%)Cu(5%)Ce(11%) was found to be the best among high temperature shift catalysts.

Planned Activities:

- Design a WGS reactor and complete the catalytic studies.
- Integrate system evaluation using the prototype WGS reactor with H_2/CO_2 separation membranes.

Available Reports/Technical Papers/Presentations:

"Bimetallic Nanocatalysts for Water-Gas-Shift Reaction," Naidu V. Seetala, Invited talk at the Inorganic Chemistry Seminar, LSU-Baton Rouge, Louisiana, February 10, 2009.

"Development of Low Cost Membranes for H_2/CO_2 Separation for WGS Reactors," University Coal Research/Contractors Review Conference, Pittsburgh, Pennsylvania, June 10-11, 2008.

"Microreactors for Syngas Conversion to Higher Alkanes: Effect of Ruthenium on Silica-Supported Iron-Cobalt Nanocatalysts," Ind. Eng. Chem. Res., 47 (2008) 1684. *"Preparation and characterization of alumina porous membranes coated with Nb/Ta thin films for the separation of $H_2/CO_2/CO$,"* Ruwantha A. M. Jayasingha, Ramakrishna S. Garudadri, Naidu V. Seethala, and Upali Siriwardane, 235th ACS National Meeting, NewOrleans, Louisiana, April 6-10, 2008.

"*Preparation and characterization of sol-gel alumina supported bimetallic nanocatalysts for WGS reaction,"* J. Bass, N.V. Seetala, A.M.R. Jayasingha, R.K. Garudadri, and U. Siriwardane, Louisiana Academy of Sciences Meeting, Northwestern State University, Natchitoches, Louisiana, March 14, 2008.

"Sol-gel Prepared Cu-Ce-Ni Nanoparticle Alumina Catalysts for WGS Hydrogen Production," Naidu V. Seetala, Johnte Bass, A. M. R. Jayasingha, Rama K. Garudadri, and Upali Siriwardane, *Microscopy & Microanalysis*, Vol. 14, Suppl. 2, (2008) 308.

"*Sol-gel synthesis and characterization of alumina supported Cu-Ni-Ce catalysts for water-gas-shift (WGS) reaction*," Ramakrishna S. Garudadri, Ruwantha A.M. Jayasingha, Naidu V. Seethala and Upali Siriwardane, 235th ACS National Meeting, New Orleans, Louisiana, April 6-10, 2008.

Contract No.:

DE-FG26-07NT43064

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Argonne National Laboratory – Dense High-Temperature Ceramic Membranes

Project Title:

Development of Dense Ceramic Membranes for Hydrogen Separation

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Laboratory- and bench-scale

Primary Project Goal:

Argonne National Laboratory (ANL) is developing a dense ceramic or cermet (ceramic/metallic composite) membrane for separating hydrogen (H_2) from synthesis gas (syngas) generated during coal gasification, resulting in a high concentration carbon dioxide (CO_2) stream.

Technical Goals:

Develop a membrane that is:

- Chemically stable in the presence of steam, carbon monoxide (CO), CO_2, methane (CH_4), hydrogen sulfide (H_2S), ammonia (NH_3), mercury (Hg), and halides.
- Mechanically stable under high pressures, high temperatures, and temperature cycles.
- Capable of providing industrially significant fluxes at desired levels of H_2 selectivity.

Technical Content:

During coal gasification, large volumes of H_2 and CO_2 are produced. Dense ceramic and cermet membranes are being developed for use with coal gasification process to separate H_2 from CO_2. These membranes must be capable of achieving a high flux and selectivity in order to reduce the surface area required to process the high volumes of gas produced. Reducing a membrane thickness can increase H_2 flux; however, to maintain selectivity, the membrane must remain defect free. Dense ceramic and cermet membranes are capable of providing reduced thickness while avoiding the formation of defects.

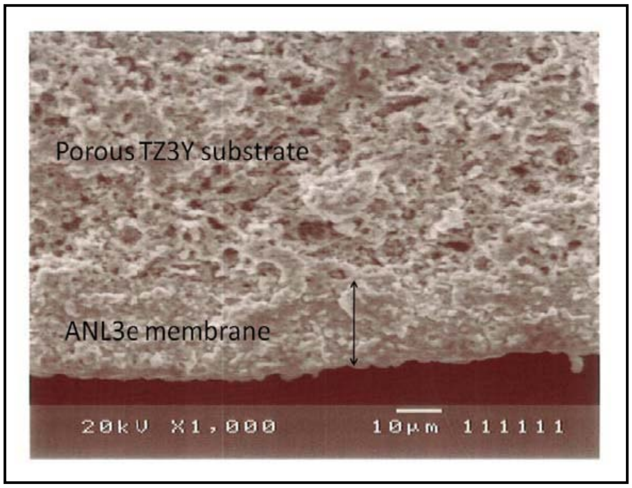

Figure 1: Cross-Sectional View of ANL-3e Thin Film Membrane Sintered at 1,160°C on Porous TZ-3Y Substrate

High density membranes are achieved by sintering the cermet at high temperatures. Sintering aids have been developed that prevent delamination of the cermet from the porous ceramic substrate. Figure 1 shows a cermet membrane with cobalt nitrate as the sintering aid on a TZ-3Y (zirconium dioxide [ZrO_2] partially stabilized with yttrium oxide [Y_2O_3]) substrate.

The chemical stability of the membranes is also important for their use in the corrosive syngas stream produced from coal gasification. Hydrogen sulfide is a particularly corrosive contaminant to membranes containing palladium (Pd). When H_2S reacts with Pd, palladium sulfide (Pd_4S) forms on the surface of the membrane, which greatly reduces H_2 permeation through the membrane. Therefore, it is important to identify the temperatures and pressures at which the membrane is stable. The Pd-containing cermets being developed are stable between about 430°C and 680°C (700 K and 950 K) in stable a gas containing 73% H_2 with between approximately 60-400 parts per million (ppm) H_2S. When the gas contains only 10% H_2, the membrane is stable for H_2S concentrations between approximately 8-50 ppm.

Table 1: ANL Membrane Parameter

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd/TZ-3Y cermet	Pd/TZ-3Y cermet and/or non-precious metal
	Materials of fabrication for support layer (if applicable)	Alumina/Zirconia	Stainless steel
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	150	10,000
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	4.77 scc/min/cm^2 at 400°C with hydrogen feed pressure of 7.17 x 10^5 Pa (7.1 atm) and hydrogen sweep pressure of 4.75 x 10^3 Pa (0.047 atm)	75
	Temperature, °C	400-600	250-500
	Bench-scale testing, hours without significant performance degradation	1,200 hr	1,200 hr
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	180 psi (12.2 bar)	300 psi (20.4 bar)
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disk/short tube	Longer tubes (≈12-in)
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	180 psi (12.2 bar)	300 psi (20.4 bar)
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %	N/A	N/A
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO$_2$	N/A	N/A
	Heat requirement, kJ/kgCO$_2$	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO$_2$	N/A	N/A

Contaminant Resistance: The membrane is tolerant to H_2S between 430°C and 680°C in gas containing 73% H_2 and approximately 60-400 ppm H_2S.

The membrane is tolerant to ≈15 mole %CO and ≈20 mole% steam in the temperature range 400°C and 700°C.

Flue Gas Treatment Requirements: N/A.

Waste Streams Generated: N/A.

Technology Advantages:

- The ceramic phase of the cermet provides 3-D mechanical support that can blunt or deflect crack propagation through the metallic phase.
- ANL's membranes have been tested at high pressure and temperature conditions.
- The ANL membranes are dense with no interconnected porosity; therefore, selectivity for H_2 is high.
- Membrane removes H_2 from H_2 and CO_2 mixture, resulting in a highly concentrated stream of CO_2 ready for sequestration.

R&D Challenges:

- Reducing membrane thickness increases flux, but can lead to pin-holes in the membrane, which reduces H_2 selectivity. Therefore, reducing defects in thinner membrane is desired.
- Developing low-temperature sintering methods to avoid loss of Pd to evaporation during sintering at high temperatures.
- Determining stability restrictions in order to limit the reaction of Pd with H_2S, which forms Pd_4S and reduces H_2 flux.
- Understanding chemical stability in the presence of steam, NH_3, Hg, and halides.
- Increasing the resistance to the effects of particulates impacting the membrane surface.
- Developing leak-proof metal/ceramic seals at high pressures and thermal cycling.
- Reducing the cost of the membrane by investigating non-precious metals/alloys to form the membrane.

Results To Date/Accomplishments:

- Developed dense, cermet membranes that non-galvanically separate H_2 from mixed-gas streams.
- Achieved an H_2 flux of 5_2 cm_3/min-cm_2 measured on an 18-µm thick membrane composed of Pd and TZ-3Y using a feed of 1 atm H_2.
- Achieved H_2 permeation exceeding 150 cm_3/min (0.32 scfh) measured in short, 8-cm long tubular membranes at 600°C and ambient pressures.
- Thin membranes were tested at 400°C as per the test protocol established by NETL.
- Demonstrated durability of membrane during cycling in temperature and H_2 concentration.
- Maintained flux stability for 1,200 hours in feed stream with 400 ppm H_2S at 900°C.
- Observed regeneration of sulfur-poisoned, cermet membrane.

Planned Activities:

- Develop methods for eliminating pin-holes in thinner membranes for high purity and high selectivity for H_2.
- Fabricate and test tubular membranes at high flow rates and changing flow directions to overcome the external transport phenomena that are limiting the H_2 flux at the boundary layer.
- Continue testing of membranes as per the test protocols established by NETL.
- Study the effects of trace contaminants, such as NH_3, Hg, and halides.
- Measure flux at high pressures using simulated syngas streams.
- Perform experiments integrating H_2 separation and shift reaction.
- Make long-term flux measurements and demonstrate reliability and durability of membranes under high-pressure conditions.

Available Reports/Technical Papers/Presentations:

Balachandran, u., et al., "Hydrogen Separation Membranes Annual Report for FY2008," publication date March 17, 2009, http://www.osti.gov/bridge.

Contract No.:

FWP-49601

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University of Texas at Dallas – Mixed-Matrix Membranes for H_2/CO_2 Separations

Project Title:

Mixed Matrix Membranes for CO_2 and H_2 Gas Separations Using Metal-Organic Frameworks and Mesoporous Hybrid Silicas

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

The University of Texas at Dallas is applying metal organic frameworks (MOFs) and mesoporous hybrid silicas in polymer-based mixed-matrix membranes (MMMs) for the separation of hydrogen (H_2) and carbon dioxide (CO_2).

Technical Goals:

The technical goal of this project is to exploit the high surface areas, adsorption capacities, and selectivities of microporous additives for membrane-based separations.

Technical Content:

Matrimid is a widely used polyimide (a polymer) that has both attractive thermal and gas transport properties. When combined with microporous organic-inorganic hybrid nanocrystals for the preparation of polymer-based MMMs, the time and steps required for membrane preparation is reduced compared to inorganic additives.

The following materials have been synthesized and combined with Matrimid to form MMMs: metal organic framework 5 (MOF-5), Copper(II) biphenyldiacetate triethylenediamine metal organic framework (Cu-MOF), metal organic polyhedral 18 (MOP-18), zeolitic imidazolate framework 8 (ZIF-8), zeolite socony mobil 5 (ZSM-5), carbon aerogel, carbon aerogel-zeolite composites, single-walled carbon nanotube (SWNT), Copper(II) bipyridine hexafluorosilicate metal organic framework (Cu-BPY-HFS), and periodic mesoporous organosilicas (PMOs). Experiments have also been conducted to determine the selectivity and permeability of microporous additives with Matrimid MMMs. MOF-5, Cu-MOF, MOP-18, and ZIF-8 were found to be stable up to 350°C, 300°C, 300°C, and 400°C, respectively. Carbon aerogels, carbon aerogel-zeolites, and PMOs showed similar mechanical resistance.

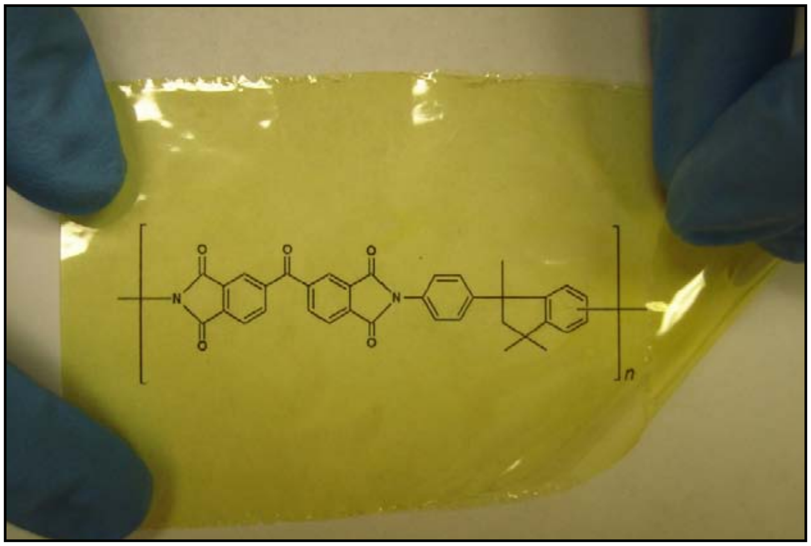

Figure 1: Flat Matrimid Membrane Cast From Chloroform

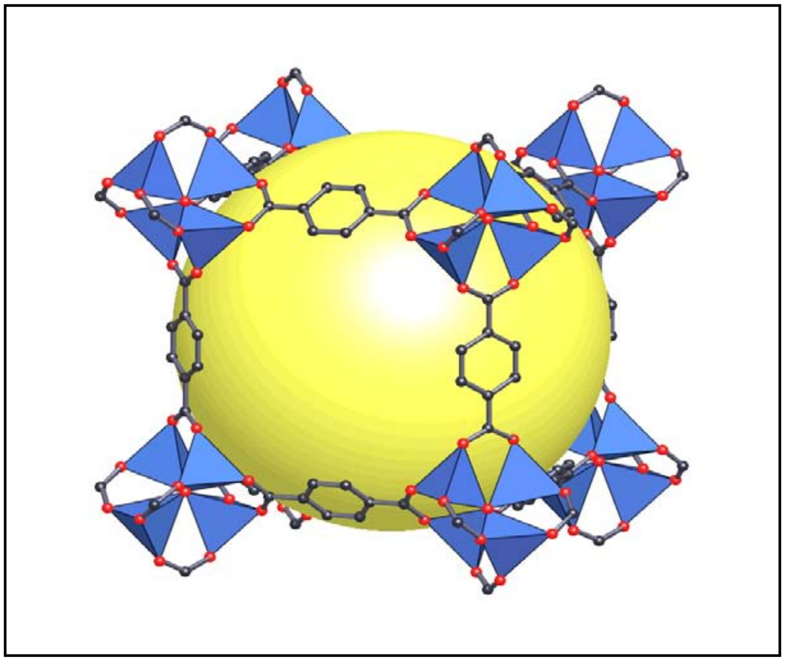

Figure 2: Model of MOF-5

Technology Advantages:

- Addition of substances, such as MOF-5, Cu-MOF, MOP-18, ZIF-8, ZSM-5, carbon aerogel, carbon aerogel-zeolite, functional SWNT and SWNT-short, Cu-BPY-HFS, and PMOs, may provide benefits, such as increased selectivity, permeability, and increased mechanical and thermal stability.
- Incorporation of organic functionalities in frameworks improves dispersion in a polymer matrix.
- Inclusion of these substances reduces time and steps required for membrane preparation. Organic character of the crystals facilitates the dispersion and improves the interfacial contact with the polymer matrix.

R&D Challenges:

- Obtaining selectivities high enough to achieve effective separation.
- Obtaining permeabilities high enough to achieve efficient separation.
- Developing membrane pores resistant to contamination.

Results To Date/Accomplishments:

- Synthesized MOF-5, Cu-MOF, MOP-18, ZIF-8, ZSM-5, carbon aerogel, carbon aerogel-zeolite, functional SWNT and SWNT-short, Cu-BPY-HFS, and PMOs.
- Fabricated all synthesized materials with Matrimid MMMs.
- Completed permeability studies.

Planned Activities:

This project is complete.

Available Reports/Technical Papers/Presentations:

Musselman, Inga H. et al., “Mixed-Matrix Membranes for CO_2 and H_2 Separations Using Metal-Organic Frameworks and Mesoporous Hybrid Silicas.”
http://www.netl.doe.gov/publications/proceedings/05/UCR_HBCU/pdf/papers/Musselman.pdf.

Contract No.:

DE-FG26-04NT42173

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Partners:

Praxair – Palladium Alloy Membranes

Project Title:

Novel Hydrogen Purification Device Integrated with PEM Fuel Cells

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

Praxair is developing a palladium (Pd) alloy membrane capable of concentrating carbon dioxide (CO_2) effluent from technologies, such as coal gasification plants, by efficiently removing high purity hydrogen (H_2) for subsequent use as a fuel.

Technical Goals:

- Develop simulation models to predict H_2 flux based on membrane composition.
- Design a Pd membrane capable of operating at lower than typical temperatures.
- Develop the necessary membranes, seals, and other required components for a cost-effective H_2 purification device.
- Research and select a suitable substrate material that compliments the membrane's thermal expansion properties.
- Develop production practices capable of producing consistently high-quality membrane substrates at low cost.

Technical Content:

Praxair will develop a Pd alloy membrane capable of operating at lower temperatures to efficiently separate H_2 at low cost from various sources, including synthesis gas (syngas) from coal gasification units. The removal of H_2 from syngas would result in a stream of concentrated CO_2 ready for further purification and sequestration.

A porous ceramic substrate that has graded porosity has been produced. This grading permits the coating of the microporous surface without significant defects while the rest of the tube has open porosity that poses minimal resistance to flow. The Pd alloy coating is achieved by use of the electroless plating method.

Preliminary results have shown that the Pd alloy membranes tested maintain structural integrity after several periods of thermal cycling, which is an important attribute for use in processes where process temperatures are not constant, such as coal gasification.

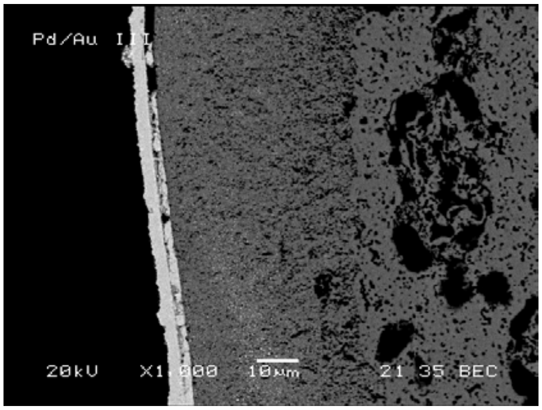

Figure 1: Image of Pd-Au Structure

Several tests have been completed in order to determine H_2 flux through the membrane at various pressures and temperatures. It was found that at 225°C and 0.7 atm (10 psi), the flux is approximately 40 scfh/ft^2, increasing with both temperature and pressure up to 400°C and 4.8 atm (70 psi) where the flux was approximately 300 scfh/ft^2. This demonstrates the membrane's stability at both low and high temperatures, making it a versatile product.

In order to maximize efficiency, a model of H_2 transport through the membrane has been developed. All steps of the entire process are considered in the model, which is used to determine the rate determining step for different membrane compositions and thicknesses. This model will be used to provide guidance for alloy selection and for optimizing membrane properties.

Table 1: Praxair Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd, Pd-Au, Pd-Ru, Pd-Au-Ru, Pd-Ag, Pd-Cu	Pd, Pd-Au, Pd-Ru, Pd-Au-Ru, Pd-Ag, Pd-Cu
	Materials of fabrication for support layer (if applicable)	Modified ZrO_2	Modified ZrO_2
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology CO_2/N_2 for post-combustion technology	>100 N/A	>1,000 N/A
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	965 scfh/ft^2 at 400°C and 200 psi 134 scfh/ft^2 at 400°C and 20 psi	1,000 150
	Temperature, °C	225	200
	Bench-scale testing, hours without significant performance degradation	264 with planned shutdown	250
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	168
	Maximum pressure differential achieved without significant performance degradation or failure, bar	14	14
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell and tube	Shell and tube
	Packing density, m^2/m^3	N/A	3.07
	Pressure drop, bar	N/A	14
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %	N/A	N/A
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

Technology Advantages:

Palladium alloy membranes have:

- High structural stability at both high and low temperatures and through thermal cycling.
- High flux and selectivity.
- Low production costs.

R&D Challenges:

- Structural failure occurs for Pd-gold (Au) membranes at 200°C.
- Ethylenediaminetatraacetic acid (EDTA) has been found to remain in the membrane after completing the plating bath, producing carbon contamination and compromising performance.
- Production of the substrate by protrusion produces defects that are difficult to repair.

Results To Date/Accomplishments:

- Economic analysis based on technical work done in Phase I and Phase II indicates the expected cost for the membrane purifier will be lower than the cost of alternative purification methods.
- A Pd-ruthenium (Ru) membrane had a flux of 965 scfh/ft^2 at 200 psi and 400°C.
- A method to produce substrate tubes by extrusion was developed. Extrusion allows for larger

substrates to be produced and for larger quantities of substrates to be produced.

- A model was developed to determine alloy structures using cluster expansion and a model has been developed to calculate flux based on all steps of the overall process; when combined, the models will assist in finding potential candidate alloys to synthesize and test.
- A multi-tube prototype reactor has been designed and is currently being built with testing scheduled for later this year.

Planned Activities:

- Perform mixed gas permeation tests with H_2, carbon monoxide (CO), CO_2, steam (H_2O), methane (CH_4), and nitrogen (N_2).

Available Reports/Technical Papers/Presentations:

"Novel Hydrogen Purification Device Integrated with PEM Fuel Cells."
http://www.netl.doe.gov/technologies/hydrogen_clean_fuels/refshelf/presentations/2008Reviews/Praxair-NETL%20Review%20080429.pdf.

Contract No.:

DE-FC26-07NT43054

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North Carolina A&T State University – Palladium/Silver Composite Membranes

Project Title:

Development of Palladium (Pd)-Silver (Ag) Composite Membrane for Separation of Hydrogen (H_2) at Elevated Temperature

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Laboratory-scale

Primary Project Goal:

North Carolina A&T State University is designing and developing hydrogen (H_2)-selective, palladium (Pd)-silver (Ag) composite membranes in microporous substrates for use in the production and separation of H_2 and carbon dioxide (CO_2) at elevated temperature.

Technical Goals:

- Fabricate thin film, Pd-Ag alloy composite membranes.
- Evaluate the long-term integrity and stability of the fabricated membranes under thermal cycling.
- Optimize the electroless plating process for co-deposition of Pd-Ag in microporous stainless steel (MPSS) substrate.
- Conduct H_2 permeation studies for disc membranes.
- Fabricate a tubular diffusion cell reactor.
- Conduct H_2 permeation studies for tubular membranes.
- Conduct methanol stream-reforming experiments.

Technical Content:

A reactor-separator is a device that utilizes a catalyst and a membrane. Incorporating a membrane in the reactor permits the removal of H_2 from the reaction zone, which increases the efficiency by allowing a greater conversion rate. Additionally, the removal of H_2 produces a waste stream with high concentrations of CO_2 for subsequent filtration and containment.

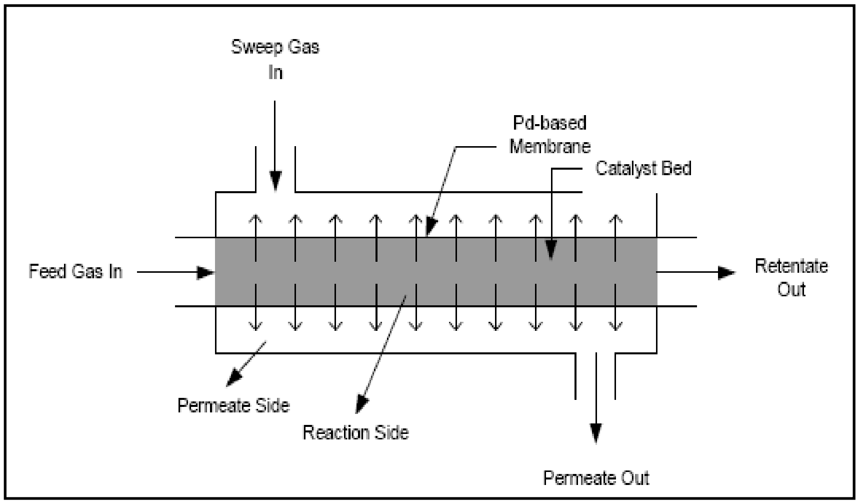

Figure 1: Schematic of Reactor Separator

North Carolina A&T State University has been developing a Pd-Ag alloy thin film composite membrane capable of withstanding high temperatures for use in a reactor-separator; specifically, the reforming of liquid hydrocarbons and methanol by equilibrium shift to produce H_2 for subsequent use as fuel.

Figure 1 is a diagram of a reactor-separator used to convert methanol to H_2. The methanol was fed into the reactor with steam to prevent catalyst degradation and promote additional H_2 production via a water gas shift (WGS) reaction.

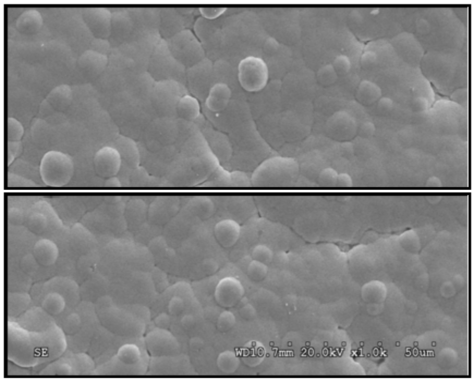

Figure 2: Image of Membrane

Technology Advantages:

Inorganic membrane reactors:

- Have significantly higher H_2 flux (1.791×10^{-6} mol/[m-s-$Pa^{0.56}$]) with high selectivity (~75%) compared to other commercially available membranes.
- Are capable of operating at high temperatures, which allows for the combining of the reaction and separation into a single step.
    - Eliminates the need for additional equipment, which reduces capital costs and lowers energy requirements.
    - Allows for the immediate removal of H_2, which shifts the equilibrium in favor of the desired conversion and consequently increases efficiency.

R&D Challenges:

- Developing an H_2 selective thin solid film that is thermally, chemically, and mechanically stable at high temperatures.
- Designing and fabricating effective seals at high temperature and high pressure.

Results To Date/Accomplishments:

- Installed an electroless plating bath with digital continuous monitoring of temperature.
- Fabricated Pd membranes.
- Conducted permeability measurements of H_2 through Pd membranes.
- Developed a 2-D steady state membrane reactor-separator model to describe the reactive reforming process with effective radial concentration gradients due to H_2 permeation across the membrane cylindrical surface.
- Simultaneous production and separation of H_2 in a Pd-MPSS membrane reactor has been demonstrated using steam methanol reforming (SMR) reactions as an example.

Planned Activities:

This project is complete.

Available Reports/Technical Papers/Presentations:

"Development of Pd-Ag Composite Membrane for Separation of Hydrogen at Elevated Temperature." http://www.netl.doe.gov/publications/proceedings/06/ucr/abstracts/ILIAS.pdf (Accessed 06/04/2009).

Ilias, Shamsuddin. "Development of Pd-Ag Composite Membrane for Separation of Hydrogen at Elevated Temperatures." http://www.netl.doe.gov/publications/proceedings/08/ucr/abstracts/ILIAS2_Abstract.pdf (Accessed June 4, 2009).

Contract No.:

DE-FG26-05NT42492

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Los Alamos National Laboratory – Palladium-Based Membrane Reactor

Project Title:

Membranes for use in Palladium Membrane Reactor Technology for Production of Hydrogen from Coal Gas

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale using simulated syngas

Primary Project Goal:

Los Alamos National Laboratory (LANL) is designing and developing a composite palladium (Pd) membrane reactor (PMR) capable of extracting hydrogen (H_2) from fossil fuels, resulting in near capture-ready concentrations of carbon dioxide (CO_2) in the effluent stream.

Technical Goals:

- Identify and develop sulfur-tolerant water gas shift (WGS) catalysts and membranes.
- Develop methods of fabricating PMRs with thin, active Pd-alloy surfaces on porous substrates.
- Determine the performance of the PMRs at elevated pressures.
- Determine the influence impurities impose on the functionality of PMRs.
- Develop Pd alloys resistant to effects of impurities.
- Determine optimal PMR operating pressure and temperature.

Technical Content:

Current methods of extracting H_2 from hydrocarbons have low efficiency due to limitations imposed by reaction equilibrium. A PMR has been developed that combines the WGS reaction with H_2 separation. By doing so, the H_2 product of the reaction is removed from the reaction zone driving the reaction towards completion, significantly increasing the efficiency of the process. Additionally, the extraction of H_2 leaves behind a near capture-ready concentration of CO_2 in the effluent stream.

Figure 1: Unheated, Broken Pd-Cu/α-Alumina Composite Membrane

The removal of H_2 from the reaction zone increases the reaction rate by freeing up active reaction sites on the catalyst. This results in reaction rates equal to conventional reforming technology at lower temperatures. For instance, conventional methane reforming is carried out at temperatures ranging from 800°C to 1,000°C, whereas equivalent results are obtained in a PMR at temperatures near 450°C.

Additionally, the pressure required to carry out the reaction is reduced by the removal of H_2 from the reaction zone. It is estimated that approximately 60% to 80% of the feed hydrogen (in the form of water and fuel) will be recovered at an inlet pressure of 10 atm. At 20 atm, the anticipated recovery increases to 80% to 95%. However, while higher pressures are not required, the permeation rate decreases significantly with decreasing pressures. Therefore, operating at the optimal operating pressure is important.

Coal gas contains impurities, such as hydrogen sulfate (H_2S), which de-activate and degrade Pd membranes. It is expected that the level of degradation will be proportional to the concentration of H_2S present. However, much of the damage should be reversible and simple to alleviate by methods like exposure to steam or air. Also, by combining Pd with copper (Cu) or gold (Au), the amount of sulfur poisoning is reduced significantly.

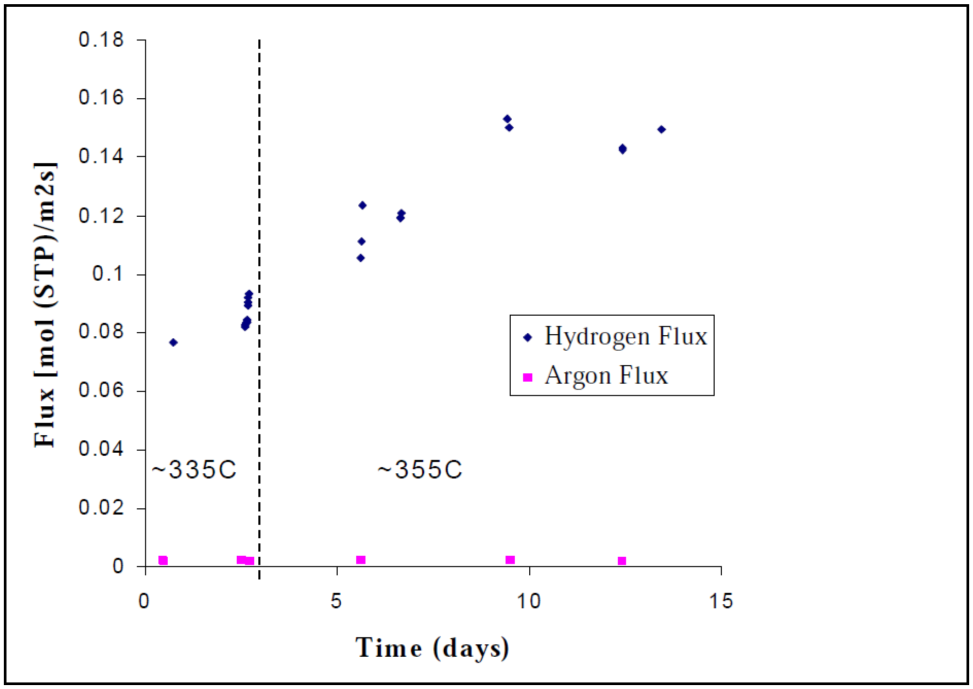

Figure 2: Flux Data for Pd-Cu/α-Alumina Composite Membrane

In order to reduce the cost of membranes and increase the flux of H_2 through the membranes, ultra-thin (<10 microns), Pd-alloy films are applied to H_2-permeable supports to form composite metal membranes. One such membrane has been developed – a vanadium (V) or tantalum (Ta) metal foil coated on both sides with Pd. This membrane has demonstrated fluxes more than 10 times greater than other Pd composite membranes.

Technology Advantages:

In comparison to existing methods of H_2 extraction, PMRs have:

- Nearly 10 times greater flux.
- Reduced capital costs.
- Lower temperatures (450°C), pressures (<20 atm), and amounts of excess water.
- Resistance to hydrogen embrittlement.
- Prolonged physical and chemical stability.

R&D Challenges:

- Thick membranes have fluxes lower than desired that result in higher capital costs and greater space requirements.
- Impurities, such as H_2S, degrade the functionality of Pd consisting apparatus.

Results To Date/Accomplishments:

- Characterized the performance of PMRs with respect to inlet conditions, temperature, geometry, and catalyst type.
- Developed mechanistic model of PMR incorporating information gathered through experimentation.
- Investigated WGS reaction, as well as the reforming of methane, methanol, ethanol, octane, and gasoline with the PMR.
- Fabricated membranes consisting of modified porous supports deposited with thin layers of composite Pd alloys.

Planned Activities:

This project has been completed.

Available Reports/Technical Papers/Presentations:

S. N. Paglieri, D. R. Pesiri, R. C. Dye, and R. C. Snow. Palladium-Coated Vanadium Alloy Membranes for Hydrogen Separation. *Proceedings of the 19th Annual Conf. on Fossil Energy Mater.*, Knoxville, Tennessee; May 9-11, 2005.

S. N. Paglieri, I. E. Anderson, R. L. Terpstra, R. E. Buxbaum, M. V. Ciocco, and B. H. Howard. A Pd_{60}-Cu_{40}/Porous Iron Aluminide Membrane for Hydrogen Separation. *Proceedings of the 21st Annual Conf. on Fossil Energy Mater.*, Knoxville, Tennessee; Apr. 30-May 2, 2007.

S. N. Paglieri, I. E. Anderson, R. L. Terpstra, T. J. Venhaus, Y. Wang, R. E. Buxbaum, K. S. Rothenberger, and B. H. Howard. Metal Membranes for Hydrogen Separation. *Proceedings of the 20th Annual Conf. on Fossil Energy Mater.*, Knoxville, Tennessee, June 12- 14, 2006.

S. N. Paglieri. "Palladium Membranes" in *Nonporous Inorganic Membranes.* Edited by A.F. Sammells and M. V. Mundschau, Miley-VCH, pp. 77-106 (2006).

S. N. Paglieri, Y. Wang, T. J. Venhaus, H. Oona, R. C. Snow, B. P. Nolen, R. E. Buxbaum, K. S. Rothenberger, B. H. Howard, and R. P. Killmeyer. Characterization of V-6Ni-5Co Membranes for Hydrogen Separation. *Proceedings of the 9Th int. Conf. on Inorganic Membranes,* Lillehammer, Norway, June 25-29, 2006.

Contract No.:

FWP-FE99002-4A24A

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SRI International – High-Temperature Polymeric Membranes

Project Title:

Fabrication and Scaleup of Polybenzimidazole (PBI) Membrane Based System for Pre-Combustion Based Capture of Carbon Dioxide

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Prototype, 0.4 tonnes CO_2/day

Primary Project Goal:

SRI International is developing a high-temperature polymer membrane and designing a membrane module for pre-combustion capture of carbon dioxide (CO_2) from integrated gasification combined cycle (IGCC)-derived synthesis gas (syngas).

Technical Goals:

- Design, construct, and test a pre-combustion-based CO_2 capture system (50 kWth) skid using polybenzimidazole (PBI) membranes developed by Los Alamos National Laboratory (LANL).
- Evaluate the effectiveness of the membrane elements for CO_2 separation in relation to permeability and selectivity.
- Perform a techno-economic analysis of an IGCC system employing PBI membranes for carbon capture and sequestration (CCS).

Technical Content:

The membrane under development consists of 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 a PBI membrane without requiring additional cooling after the water gas shift (WGS) section of an IGCC system including carbon capture. Further gas cooling is not required before the PBI membrane, 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 Figure 1, offer a considerable advantage over stainless steel coated tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1 to 0.5 micrometer separation layer.

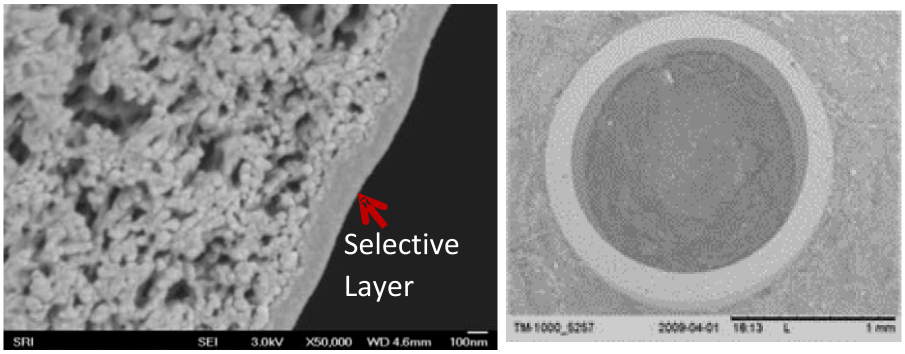

Figure 1: Image of PBI-Based Hollow FIber

The durability of narrow, single-bore, PBI-based hollow fibers has been shown to be considerable, with near constant levels of permeability and selectivity over the course of 330 days while in the presence of hydrogen (H_2), carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250°C.

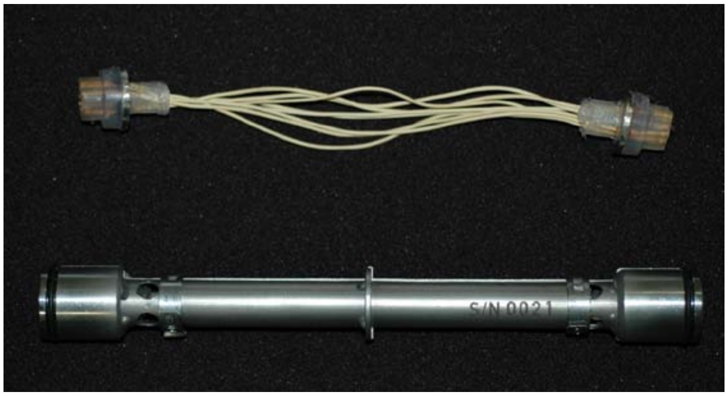

Figure 2: Image of a Bundle of PBI-Based, Asymmetric Hollow Fibers and Fiber Potting

Figure 3: Image of Module Housing

Table 1: LANL PBI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer		
	Materials of fabrication for support layer (if applicable)	PBI	PBI
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	40 N/A	70 N/A
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	100	100
	Temperature, °C	250	250
	Bench-scale testing, hours without significant performance degradation	300	1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	7	20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow-fiber	Hollow-fiber
	Packing density, m^2/m^3	N/A	2,292
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing & installation, $\$/m^2$	N/A	161
Product Quality	CO_2 purity, %	90	90
	N_2 concentration, %	N/A	<1
	Other contaminants, %	N/A	<0.01
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	281
	Heat requirement, kJ/kgCO_2	N/A	0
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	281

Contaminant Resistance: Sulfur tolerance.

Gas Pretreatment Requirements: No pretreatment of the gas stream from WGS is required.

Waste Streams Generated: No waste stream.

Technology Advantages:

- The use of PBI offers several advantages over Selexol and conventional polymeric membranes, including reduced CO_2 compression costs due to the ability to deliver the concentrated CO_2 stream at pressures up to 55 atm (800 psig).
- PBI is thermally stable up to 450°C and sulfur tolerant.
- Highest demonstrated operating temperature (400°C) of a polymer-based membrane with permeabilities and selectivities of interest.

R&D Challenges:

- Designing and synthesizing materials structure and configuration.
- Obtaining desired selectivity, productivity, chemical resistance, and durability at elevated temperatures and pressures by overcoming the limitations of current state-of-the-art technology.
- Understanding and optimizing mass transfer and the interaction with heat transfer.
- Scale up of the technology from laboratory to larger scales.
- Integration and optimization of systems.

Results To Date/Accomplishments:

- Developed an IGCC process simulation model.
- Performed and analyzed several membrane separation scenarios under various temperatures, pressures, and gases, which showed:
    - PBI membrane-based, high-temperature CO_2 separation is competitive with the Selexol system.
    - COE for CO_2 capture may approach the DOE goal under optimized membrane performance.
- Fabricated both single- and multi-bore, hollow-fiber PBI membrane configurations.
- Determined that multi-bore configuration offers increased selective layer area density while single bore provides higher mechanical stability.
- Completed characterization using scanning electron microscope (SEM) and X-ray tomography.
- Identified a sealant for short-term testing.
- Completed permeability measurements with both single- and mixed-gas environments.
- Achieved an H_2 permeability of >100 GPU with an H_2/CO_2 selectivity of 40 at 250°C.
- Determined that the PBI membrane has a high permeability for steam.
- Determined that PBI hollow fiber configuration provides the most compact membrane module.
- Established the fabrication of PBI substrate with interconnected pores.
- Fabricated porous structures with dense walls (not yet optimized).
- Performed risk management analysis to identify several system-level questions pertaining to the PBI technology.
- Developed and refined mitigation strategies that considered all stakeholder needs and requirements.
- Completed successful testing of the polymeric-metallic composite membrane in dry gas environments containing H_2, CO_2, CH_4, N_2, CO, and H_2S from 25°C to 400°C.
- Completed successful testing of the polymer-based membrane on fully hydrated natural gas reformate up to 300°C.

Planned Activities:

- Complete subcomponent design and evaluation.
- Construct membrane modules using the selected hollow fiber substrate and coating.
- Integrate the membrane module with commercially available skids, control systems, and connectors.

- Evaluate the complete system.
- Develop feasible approaches for commercializing the technology in the designated markets and sectors, along with possible routes for technology transfer.

Available Reports/Technical Papers/Presentations:

Krishnan, Gopala et al. "Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane," http://www.sciencedirect.com/science/article/B984K-4W0SFYG-MR/2/a10e288aa794a1a71db6123e6 ddde6c8.

Contract No.:

DE-FC26-07NT43090

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BP
Enerfex
LANL
Visage Energy
Whitefox

Eltron Research – Hydrogen Transport Membranes

Project Title:

Scaleup of Hydrogen Transport Membranes for IGCC and FutureGen Plants

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Pilot-scale, 100 kg/day H_2 production

Primary Project Goal:

Eltron Research is developing an advanced membrane technology for separating and purifying hydrogen (H_2) from carbon dioxide (CO_2).

Technical Goals:

Develop an H_2/CO_2 separation system which:

- Delivers pure H_2 for use in fuel cells, gas turbines, or hydrocarbon processing.
- Retains CO_2 at coal gasifier pressures.
- Operates near water gas shift (WGS) conditions.
- Tolerates coal-derived impurities (e.g., sulfur).

Technical Content:

Hydrogen separation membranes are being developed that will be compatible with high-temperature WGS reactors employed in coal gasification-based H_2 production and combined-cycle power plants. The membranes will operate in the range of approximately 320°C to 440°C. A typical feed gas composition is 41 mol% H_2, 37 % steam (H_2O), 17.8 % CO_2, and 3.3 % carbon monoxide (CO), and will also contain residual impurities from coal gasification that have not been removed upstream of the WGS reactors. The membranes function at pressures set by coal gasifier operations of 30 atm (450 psi) to 70 atm (1,000 psi).

The membranes under investigation will use a dense metal or metal alloy. Metallic membranes have been developed that exhibit high mechanical strength, little distortion in the presence high temperatures and pressures, and resistance to fracture. The membrane unit may be operated solely as an H_2/CO_2 separation device, or be integrated within the WGS reactor and perform the dual function of separation and conversion of CO and H_2O to additional H_2 and CO_2 using surface exchange catalysis.

Figure 1 illustrates Eltron's H_2 membrane. Hydrogen is separated by a multilayer dense membrane, leaving a CO_2-rich stream at high pressure ready for geological storage. The membrane can be operated without a sweep gas for pure H_2 production, or with a nitrogen sweep gas for H_2 turbine power production.

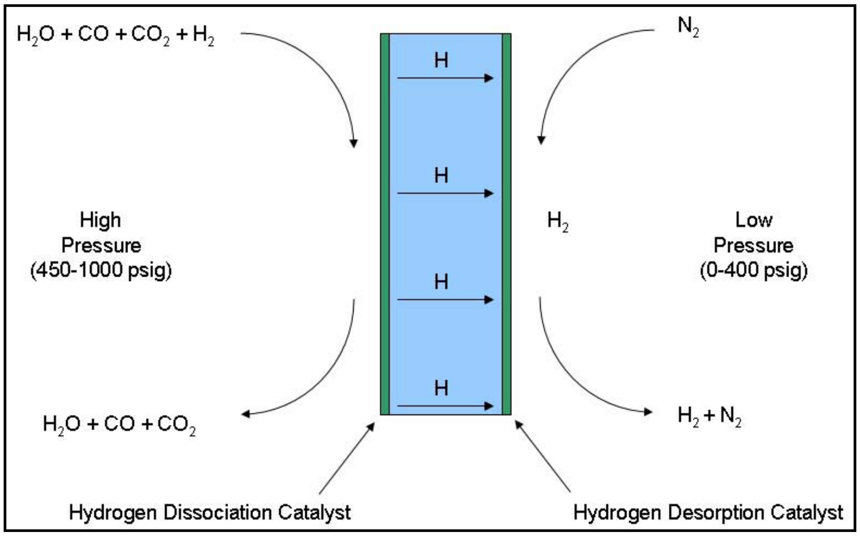

Figure 1: Eltron Hydrogen Membrane

Table 1: Eltron Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Metal Alloy	Metal Alloy
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	100% Selective	100% Selective
	Type of selectivity measurement (ideal or mixed gas)	Mixed Gas	Mixed Gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	4×10^{-4} $mol/m^2/s/Pa^{1/2}$	8×10^{-4} $mol/m^2/s/Pa^{1/2}$
	Temperature, °C	320-440°C	320-440°C
	Bench-scale testing, hours without significant performance degradation	1,000	3,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	69 bar	69 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-Tube	Shell-and-Tube
	Packing density, m^2/m^3	85.2	85.2
	Pressure drop, bar	0.06	0.06
	Estimated cost of manufacturing & installation, $\$/m^2$-GPU or equivalent	6,140	6,140
CO_2 Quality	CO_2 purity, %	95.9	95.9
	N_2 concentration, %	3.2	3.2
	Other contaminants, %	0.9	0.9
H_2 Quality	H_2 Purity	99.99%	99.99%
	H_2 Delivery Pressure (psig)	400	400
Process Performance	H_2 Recovery	65%	95%

The membrane is expected to be contaminant resistant; it also produces H2 product and CO2 at high pressures for efficient carbon capture.

Technology Advantages:

Dense metallic membranes have a high flux and produce essentially pure H_2. They can be operated at the desired application pressures and temperatures, producing a residual CO_2 stream at higher pressures than competing technologies and minimizing CO_2 compression requirements for sequestration.

R&D Challenges:

Major challenges include low membrane tolerance of feed gas impurities, such as hydrogen sulfide (H_2S), and high costs for materials and fabrication of the membrane modules.

Results To Date/Accomplishments:

- Improved composition and properties of the membrane leading to better understanding of fabrication and improved separation performance.
- Demonstrated more stable membrane performance at lower temperatures.
- Developed modeling tools to characterize and design membranes modules and systems.
- Improved membrane-based integrated gasification combined cycle (IGCC) flow sheets, achieving carbon capture greater than 95%, plant efficiencies greater than 6%, and a cost of electricity 10% lower than for conventional technology.

Next Steps:

- Evaluate membrane materials from seven different manufacturers for: H_2 flux, lifetime stability, mechanical strength, scalability, and cost.
- Develop design basis for scale up to 100 kg H_2/day process development unit (PDU).
- Continue to work with commercial suppliers on developing techniques to manufacture full-size alloy membranes.
- Conduct durability tests.
- Conduct further experiments to understand and improve tolerance of contaminants.
- Continue techno-economic analyses relating to process optimization and scale up.

Available Reports/Technical Papers/Presentations:

Advanced Power Systems Peer Review Presentation – July 2007.

Eltron Presentation – June 13, 2008.

Hydrogen Separation Using Dense Composite Membranes, In *Inorganic Membranes for Energy and Fuel Applications*; Arun Bose, Editor; Springer: New York, 2009; 125-172.

Contract No.:

DE-FC26-05NT42469

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Eastman Chemical Co.

Worcester Polytechnic Institute – Sulfur-Tolerant Palladium Alloy Membranes

Project Title:

Sulfur-Tolerant Pd/Cu and Pd/Au Alloy Membranes for H_2 Separation with High Pressure CO_2 for Sequestration

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Laboratory-scale

Primary Project Goal:

Worcester Polytechnic Institute (WPI) is designing and developing sulfur-tolerant composite palladium (Pd)/copper (Cu) and Pd/gold (Au) alloy membranes on porous stainless steel substrates for separating hydrogen (H_2) from coal gases and producing high-pressure, sequestration-ready carbon dioxide (CO_2) streams.

Technical Goals:

- Synthesize a sulfur-tolerant composite Pd/Cu and Pd/Au alloy porous stainless steel membrane with a thin intermediate oxide layer.
- Develop an understanding of the kinetics of Pd/Cu and Pd/Au alloy formations.
- Conduct permeation studies in order to characterize the membrane performance and its relation to the changes in nanostructure properties of the alloy.
- Test the membrane at lab scale using simulated coal gases to develop low-cost, high-flux, ultra-thin, sulfur-tolerant Pd/Cu and Pd/Au membranes for simultaneous H_2 separation from coal gases and production of sequestration-ready CO_2.

Technical Content:

Coal gasification processes with shift reactions, such as integrated gasification combined cycle (IGCC), produce synthesis gas (syngas), a mixture of H_2 and CO_2. WPI is developing a Pd membrane to separate H_2 from syngas at practical rates to produce high-purity H_2 for later use as a combustible, while simultaneously leaving high-pressure, sequestration-ready CO_2 in the waste stream.

However, Pd alone is not sufficient for a membrane intended for use in coal-related processes due to the sulfur composition of coal. Hydrogen sulfide (H_2S), formed during the burning of coal, reacts with Pd to form palladium sulfide (PD_4S), which drastically reduces the membranes permeability and creates small holes, reducing its selectivity. The plating of Pd with Cu or Au has been shown to reduce the reaction with H_2S, therefore increasing the membranes chemical stability.

Palladium/copper membranes were tested for H_2 permeability under 45-55 parts per million (ppm) H_2S. It was found that approximately 80% of the H_2 permeance was lost due to the formation of H_2S. However, exposing the membrane to a stream of pure H_2 recovered some of the H_2 permeance, showing that the reaction is partially reversible. Conversely, the amount of irreversible poisoning increased with the increasing time of H_2S exposure.

Palladium/gold membranes offered even greater permeance than that of Pd/Cu membranes. However, as with Pd/Cu membranes, they exhibited a sharp decline in H_2 permeance when exposed to H_2S. Unlike Pd/Cu membranes, the permeance was nearly fully recovered in pure H_2, indicating that the poisoning was reversible. Also, a longer H_2S exposure time did not increase the permeance decline, as it only slowed the permeance recovery rate.

In both Pd/Cu and Pd/Au membranes, the permeation and chemical resistance to sulfur increased with increasing temperatures, and decreased with decreasing temperatures. Experiments were run at temperatures up to 600°C, demonstrating the thermal stabilities of these membranes.

The damaging effects of H_2S on Pd membranes can be observed by comparing Figure 1 (no exposure) to Figure 2 (exposed to 54.8 ppm H_2S/H_2 gas mixture for 24 hours at 350°C).

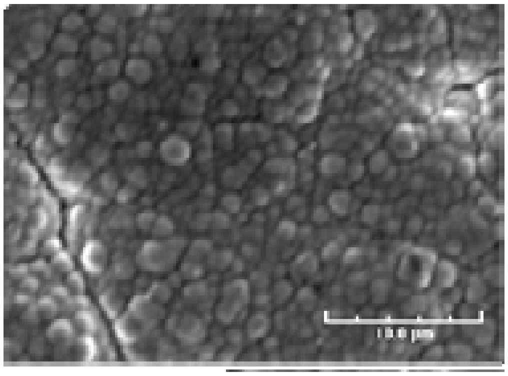

Figure 1: Micrograph of PD as Deposited (No Exposure to H_2S)

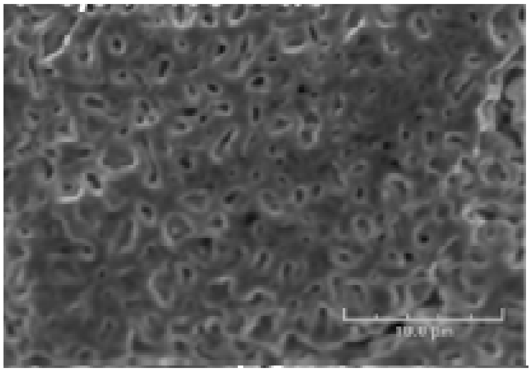

Figure 2: Micrograph of PD Exposed to a 54.8 ppm H_2S/H_2 Gas Mixture for 24 Hours at 350°C

Technology Advantages:

- Permeation lost to the formation of H_2S is recoverable by exposing the Pd/Cu or Pd/Au membrane to a stream of pure H_2.
- Selective properties of Pd/Cu and Pd/Au membranes are retained despite the formation of H_2S.
- Membranes with an oxide and additional Pd/Ag inter-metallic diffusion barrier display additional stability in H_2 permeance.
- Palladium/gold and Pd/Cu membranes show significant gains in chemical stability and sulfur resistance compared to Pd membranes.

R&D Challenges:

- Palladium/gold membranes showed an almost instantaneous sharp decline of the H_2 permeance when exposed to H_2S.
- Palladium/copper membranes showed a permeance decline of approximately 80% when exposed to H_2S.
- With extended exposure to H_2S, the amount of Pd/Cu that was regenerable with pure H_2 decreased.

Results To Date/Accomplishments:

- Synthesized Pd/Cu and Pd/Au alloy porous stainless steel membranes with a thin intermediate oxide layer.
- Conducted permeation studies and observed the membrane performance and its relation to the changes in nanostructure properties of the alloy.
- Conducted studies to determine the effects of H_2S on Pd/Cu and Pd/Au membranes.

Planned Activities:

This project is complete.

Available Reports/Technical Papers/Presentations:

"Sulfur-Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen Separation with High Pressure CO_2 for Sequestration." http://www.netl.doe.gov/publications/proceedings/07/ucr/Poster-Abstract/Ma_Poster_Abstract.pdf.

"Effect of H_2S on the Performance and Long-Term Stability of Pd/Cu Membranes." http://pubs.acs.org/doi/abs/10.1021/ie801947a.

Contract No.:	**NETL Project Manager:**
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Principal Investigator:	**Partners:**
Yi Hua Ma Worcester Polytechnic Institute yhma@wpi.edu	

UNDEERC – H_2/CO_2 Separation Membranes

Project Title:

Gasification of Lignites to Produce Liquid Fuels, Hydrogen, and Power

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale

Primary Project Goal:

The University of North Dakota Energy and Environment Research Center (UNDEERC) is conducting research to determine the effects of lignite coal on gas cleanup processes used for coal gasification; including hydrogen (H_2)/carbon dioxide (CO_2) separation membranes, as well as the removal of condensed vapors, particulates, mercury, and sulfur.

Technical Goals:

- Construct an entrained-flow gasifier (EFG), and perform shakedown on the EFG.
- Demonstrate the gasification lignite, and monitor the composition and concentration of synthesis gas (syngas) produced.
- Perform testing of membranes and other gas cleanup processes.

Technical Content:

Lignite coal is an attractive fuel for gasification because of its calcium and sodium concentrations, which are known to catalyze the gasification reactions. This permits lower operating temperatures with increased carbon conversion efficiency. However, the composition of lignite, mainly sodium and chlorine, causes damaging effects to H_2/CO_2 membrane separators. Research is ongoing on the effectiveness of H_2/CO_2 membrane separators, specifically palladium (Pd)/copper (Cu) membranes, for use in lignite coal-fueled gasification processes.

The gas cleanup configuration can be found in Figure 1, where the syngas is delivered from a transport reactor development unit (TRDU). The waste gas from the separation membrane contains high concentrations of CO_2 that can be further purified and sequestered.

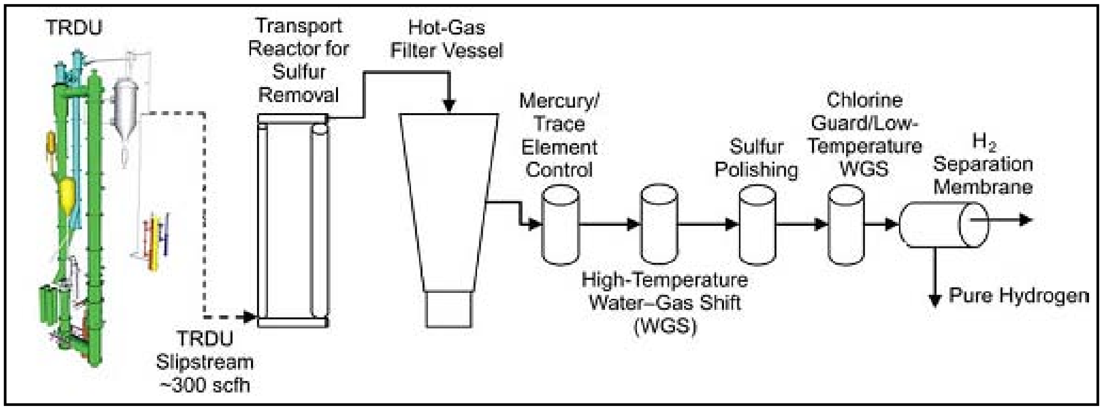

Figure 1: Gas Cleanup Configuration Schematic

Figure 2 is a plot of H_2 flux through the tested membrane over time. The oxygen (O_2)-blown run contained H_2 at higher partial pressures as a result of reduced nitrogen levels, which resulted in higher H_2 flux. This demonstrates that higher-pressure differentials will yield greater quantities of H_2.

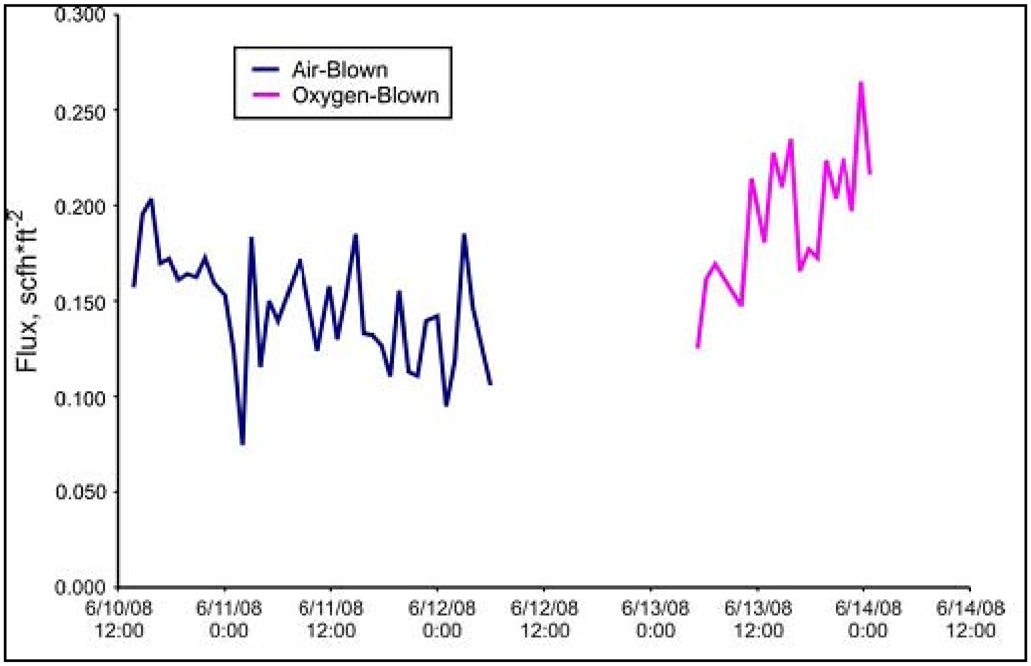

Figure 2: Hydrogen Flux of Air- and Oxygen-Blown Syngas

The permeate stream contained greater than 99.9% H_2, demonstrating the selectivity of the membrane and its ability to be utilized in gasification processes fueled by lignite coal.

To date, Pd-Cu-based membranes developed by Wah-Chang and TDA research have been tested in the EERC's gasification facilities. Both membranes have shown high hydrogen purities, but flux measurements were low because of low partial pressure across the membrane. Additional testing with these and other membranes is planned to occur in 2010. Gasifiers capable of producing syngas at pressures up to 1,000 psi will be used in conjunction with the membranes, resulting in high dP and improved hydrogen flux.

Technology Advantages:

- The calcium and sodium concentrations of lignite coal catalyze the gasification reaction, which permits lower operating temperatures with increased carbon conversion efficiency.
- Pd/Cu membranes produce high purity hydrogen and a separate stream of CO_2 that remains at high pressure and is ready for sequestration.

R&D Challenges:

Lignite's high calcium, sodium, mercury, and chlorine composition cause operation issues, such as bed agglomeration and ash deposition, as well as damage to water gas shift (WGS) catalysts.

Pd/Cu membranes have a low tolerance for sulfur, so gas cleanup systems must remove the hydrogen sulfide (H_2S) and carbonyl sulfide (COS) to subparts per million levels.

Results To Date/Accomplishments:

- Completed feedstock characterization.
- Completed bench-scale testing of gas desulfurization and H_2 and CO_2 purification concepts.
- Completed construction of the EFG.
- Completed gasification test runs on the EFG.
- Conducted testing to determine optimum warm- or hot-gas cleanup to remove impurities, such as condensed vapors and particulates, as well as control trace elements like mercury.

- Conducted testing of high-efficiency sulfur removal techniques.
- Performed testing of H_2/CO_2 separation membranes.

Planned Activities:

- Perform advance characterization analysis of lignites and ash materials.
- Issue final report to project sponsors.
- Continue membrane development work through additional test programs at UNDEERC.

Available Reports/Technical Papers/Presentations:

N/A

Contract No.:

DE-FC26-05NT42465-1.2

NETL Project Manager:

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Partners:

EPRI
Great River Energy
Luminant
North American Coal Corporation
North Dakota Industrial Commission
Porviar Filtration Group
Rio Tinto

University of Minnesota – Hydrogen Selective Zeolite Membranes

Project Title:

Hydrogen Selective Exfoliated Zeolite Membranes

Technology Area:

Pre-Combustion Membranes

Technology Maturity:

Laboratory-scale using syngas

Primary Project Goal:

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.
- Performing 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.

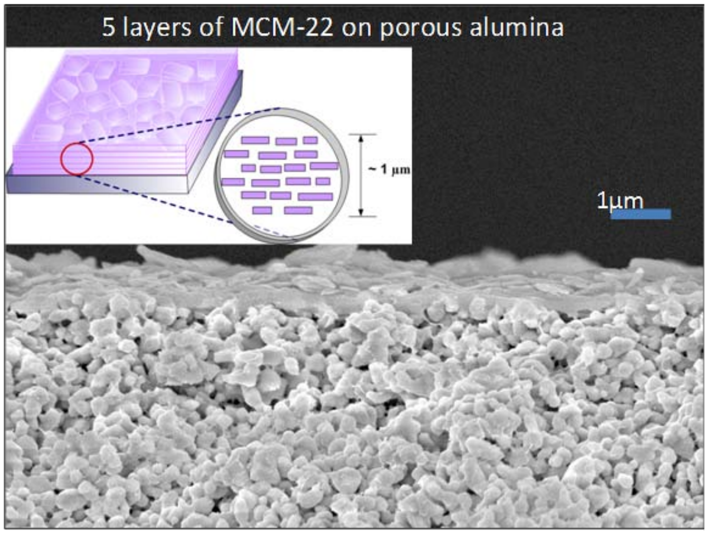

Figure 1: SEM Cross-Section Image of a Five-Layer Membrane Along with its Schematic

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 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).

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.

Contaminant resistance: These materials are crystalline silicates and the main issue is stability to steam. Other contaminants are not expected to create problems.

Flue gas pretreatment requirements: To be determined as project progresses.

Waste streams generated: To be determined as project progresses.

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	MCM-22 plate-like crystals	Exfoliated MCM-22 layers
	Materials of fabrication for support layer (if applicable)	Porous alumina discs (home-made)	Porous stainless steel tubes (commercial)
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology CO_2/N_2 for post-combustion technology	20	80-800
	Type of selectivity measurement (ideal or mixed gas)	ideal	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	0.01 mol/m^2-s-bar	0.1-1 mol/m^2-s-bar
	Temperature, °C	200	500
	Bench-scale testing, hours without significant performance degradation	48	250
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3	10
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	N/A	TBD
	Packing density, m^2/m^3	N/A	TBD
	Pressure drop, bar	1-2 atm	10atm
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	\$3,000/ m^2
Product Quality	CO_2 purity, %	N/A	TBD
	N_2 concentration, %	N/A	TBD
	Other contaminants, %	N/A	TBD
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	TBD
	Heat requirement, kJ/kgCO_2	N/A	TBD
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	TBD

Technology Advantages:

This membrane technology will form the selective film using a coating process and pre-made components, and will have high selectivity, flux, and stability.

R&D Challenges:

- Dispersible exfoliated layers.
- Simple and efficient coatings process.

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:

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.*

Contract No.:

DE-FE-0001322

NETL Project Manager:

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Principal Investigator:

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Partners:

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Pall Corporation – Ternary Palladium-Alloy Hydrogen Separation Membranes

Project Title:

Designing and Validating Ternary Pd Alloys for Optimum Sulfur/Carbon Resistance

Technology Area:

Pre-Combustion Membranes

Technology Maturity:

Pilot-scale using actual syngas

Primary Project Goal:

Pall Corporation is developing an economic, high temperature and pressure, hydrogen (H_2) separation membrane system for carbon dioxide (CO_2) capture, while resisting moderate levels of contaminants using a ternary palladium (Pd)-alloy. A membrane module prototype will be fabricated and will undergo long-term testing in actual coal gasification conditions. The final objective is a pilot-scale membrane system with a product plan for commercialization of the technology.

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 module at a commercial coal gasification facility.
- 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:

Figure 1: A Co-Sputtering Chamber

The project will develop an advanced Pd-alloy for optimum H_2 separation performance and to demonstrate long-term durability under coal synthesis gas (syngas) conditions. Ternary Pd-alloys with potential for favorable performance will be selected based on a literature search. This large set of ternary Pd-alloys will undergo combinatorial alloy spreads on thin film support disks. These disks will be 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 will be compared to baseline tests of traditional Pd-gold (Au) alloy membranes.

The best alloys will be fabricated into 15 cm^2 tubular membranes and tested. As with the combinatorial disks, the 15-cm^2 active area tubes will be exposed to conditions representative of a coal gasifier environment: high temperature and high pressure in the presence of contaminating species. Emphasis will be 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.

Using the best candidate alloys, the 15-cm^2 membranes will be scaled up by a factor of five to 75-cm^2. After a series of performance tests and membrane characterization, a module of 75-cm^2 tubes, made with the best performing alloy, will be assembled. The module will be subjected to 500-hr service tests at a commercial coal gasification facility.

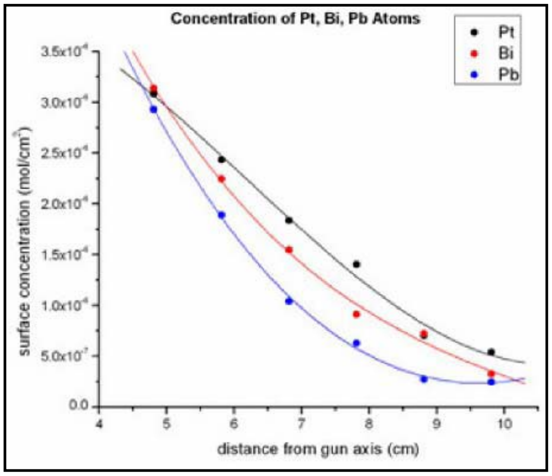

Figure 2: Graph of Atom Concentration as a Function of Distance from the Gun Axis for Pt, Bi, and Pb Targets

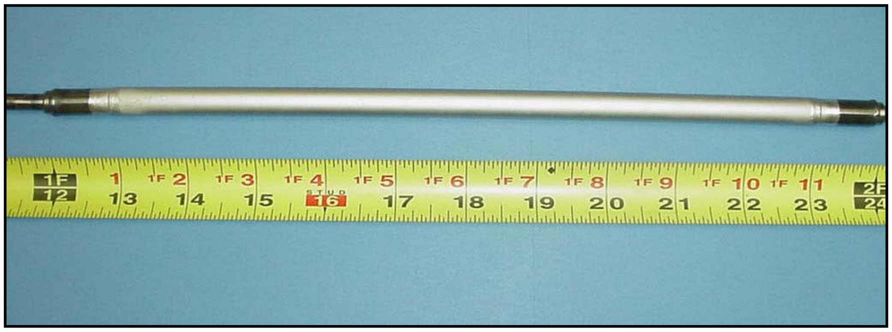

Figure 3: A 75-cm^2 Membrane

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 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%.
- The membrane must be resistant to coking with relatively low steam-to-carbon ratio.
- The system should be stable for a minimum of three years in service.

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Palladium-gold alloys	N/A
	Materials of fabrication for support layer (if applicable)	Zirconia coated porous stainless steel tubes	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology CO_2/N_2 for post-combustion technology	>5,000 of H_2/CO_2	>10,000
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Ideal
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	72 SCFH/ft^2 $psi^{0.5}$	N/A
	Temperature, °C	400	N/A
	Bench-scale testing, hours without significant performance degradation	500 hr with syngas	5,000 hr with syngas
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	300 psi
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %	N/A	N/A
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

Contaminant Resistance: Pd-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 to 20 parts per million volume (ppmv). After a single-stage water gas shift (WGS) reactor, CO can be as low as a few percent.

Flue Gas Pretreatment Requirements: No flue gas pretreatment is required since it is pre-combustion CO_2 capture technology (i.e., coal is converted to syngas by partial combustion/gasification process).

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 will use a proprietary process to create ultrathin, economical, Pd-alloy membranes in virtually any alloy system.
- The project will apply 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 will be 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:

- H_2 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.
- Scaleup of the Pd-alloy surface area from 15 cm^2 to 75 cm^2: Although the membrane fabrication process has been designed for 75 cm^2 on tubular substrates, the actual scaleup has not been attempted.
- 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:

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:

N/A

Contract No.:

DE-FE-0001181

NETL Project Manager:

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Partners:

Cornell University
Georgia Institute of Technology
Oak Ridge National Laboratory
Southern Company

Arizona State University – Dual-Phase Ceramic-Carbonate Membrane Reactor

Project Title:

Pre-Combustion Carbon Dioxide Capture by a New Dual-Phase Ceramic-Carbonate Membrane Reactor

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale using simulated syngas

Primary Project Goal:

Arizona State University is developing a dual-phase, membrane-based separation device which will separate carbon dioxide (CO_2) from typical water gas shift (WGS) mixture feeds and produce hydrogen, 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 permeance and CO_2 selectivity (with respect to hydrogen [H_2], carbon monoxide [CO], or water [H_2O]) larger than 5×10^{-7}mol/m^2.s.Pa and 500.
- 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% purity and CO_2 stream with at least 95% purity.

Technical Content:

A membrane separation device consisting of a porous metal phase and a molten carbonate phase can conduct carbonate ion (CO_3^{2-}) at a high rate. The metal-carbonate membranes only conduct electrons, and 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 can be solved 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 meso-porous 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.

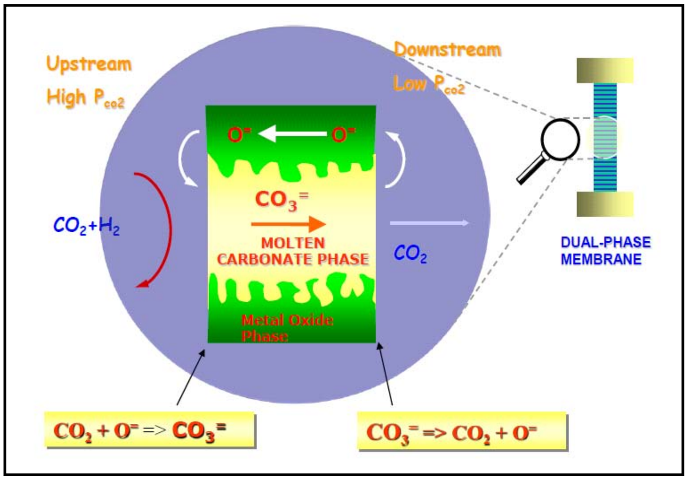

Figure 1: Concept of Dual-Phase Membrane

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.

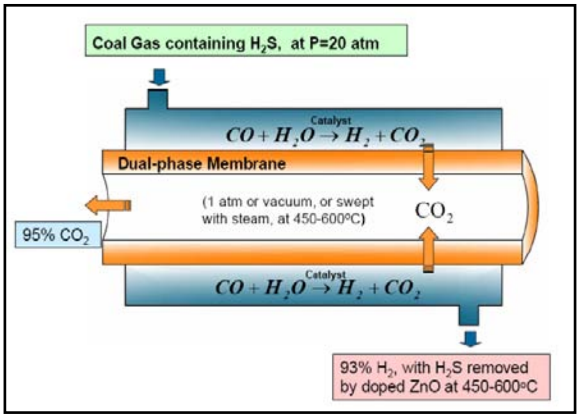

Figure 2: Proposed Membrane Reactor for WGS Reaction

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.

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Li_2/K_2CO_3	Doped Li_2/K_2CO_3
	Materials of fabrication for support layer (if applicable)	Porous stainless steel	Fast-ionic conductors (doped ZrO_2)
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	20	>300
	Type of selectivity measurement (ideal or mixed gas)	Mixed Gas	Mixed Gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	200 GPU	1,500 GPU
	Temperature, °C	800	500
	Bench-scale testing, hours without significant performance degradation	N/A	1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disk	Shell-and-Tube
	Packing density, m^2/m^3	10	60
	Pressure drop, bar	0.2	10
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	N/A	\$1,500-\$3,000m^2
Product Quality	CO_2 purity, %	N/A	95
	N_2 concentration, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	N/A
	Heat requirement, kJ/kgCO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	N/A

Contaminant Resistance: The membrane to be stable in 0.1 -1% atmosphere containing hydrogen sulfide (H_2S).

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: N/A.

Technology Advantages:

- WGS reaction at one temperature (about 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:

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:

N/A

Contract No.:

DE-FE-0000470

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Partners:

None

Gas Technologies Institute – Nanoporous, Superhydrophobic Membranes

Project Title:

Pre-Combustion Carbon Capture by a Nanoporous, Superhydrophobic Membrane Contactor Process

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Bench-scale using simulated syngas

Primary Project Goal:

Gas Technologies Institute (GTI) is developing 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 which minimizes hydrogen loss.
- Tailor highly chemically 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 based on gas/liquid membrane concept. The membrane contactor is an 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 which 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%, and an 800 psi water breakthrough pressure.

The PEEK hollow fiber membrane is nanoporous and can be surface modified to achieve super-hydrophobicity, fiber OD can range from 200µm to 1mm, and fibers can be made with very 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 psig, and a high collapse pressure of greater than 1,000 psig.

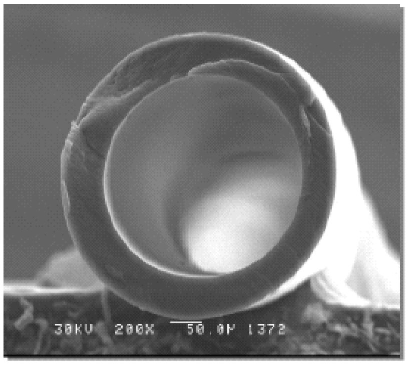

Figure 1: PEEK Hollow Fiber

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 is divided into two phases. The activities of the first phase will be 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.

The focus of the phase two activity is to scale up the process from lab to bench scale. This includes scale up of the membrane module fabrication process so that membrane modules of the size suitable for large-scale application can 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.

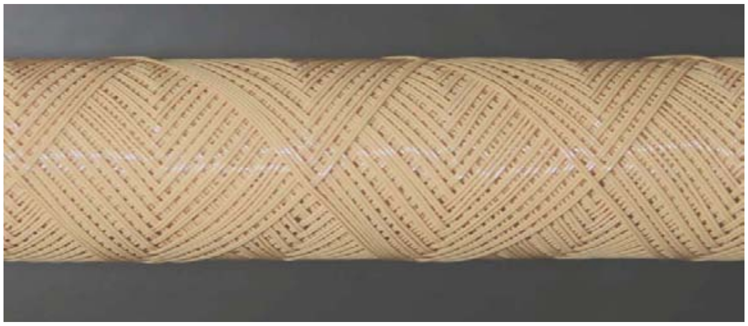

Figure 2: Advanced Hollow Fiber Module Design

Table 1: Major Process Parameter Tables

	Liquid-Sorbent Parameters	**Current R&D Value**	**Target R&D Value**
Liquid Sorbent Properties	Type of sorbent	Physical	Physical
	Molecular weight		
	Boiling point (^{0}C)		
	Heat of absorption (kJ/mole CO_2)	372	400
	CO_2 loading/working capacity*, wt%	10%	20%
	Sorbent concentration to stripper (mol/liter)	10%	20%
	Heat capacity of sorbent (kJ/K/kg)	2	2
	Viscosity, cP	6	10
Operating Conditions	Absorption temperature, °C	25	Maximize
	Absorption pressure, atm.	35	
	CO_2 capture efficiency, %	90	90
	Regeneration method	Flash	Flash
	Regeneration temperature, °C	TBD	TBD
	Regeneration pressure, atm.	Maximize	Maximize
Miscellaneous	Sorbent replacement rate, kg/kgCO_2	TBD	TBD
Product Quality	CO_2 purity, %	99	99
	N_2 concentration, %	TBD	TBD
	Other contaminants, %	TBD	TBD
Process Performance	Electricity requirement, kJ/kgCO_2	TBD	TBD
	Heat requirement, kJ/kgCO_2	TBD	TBD
	Total energy (electricity equivalent), kJ/kgCO_2	TBD	TBD
	Membrane Contactor Parameters	**Current R&D Value**	**Target R&D Value**
Membrane Properties	Materials of fabrication for selective layer	Perfluoro-oligomer	Perfluoro-Oligomer/Polymer
	Materials of fabrication for support layer (if applicable)	PEEK	PEEK
	Selectivity of absorbents for key gas components: H_2/CO_2 for pre-combustion technology	Solvent Dependent	Solvent Dependent
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	300	700
	Temperature, °C	50	Maximize
	Bench-scale testing, hours without significant performance degradation	TBD	TBD
	Pilot-scale testing (if applicable), hours without significant performance degradation	NA	NA
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3.4	Maximize

Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow fiber	Hollow fiber
	Packing density, m^2/m^3	500-1,000	500-1,000
	Pressure drop, bar	0.4	Minimize
	Estimated cost of manufacturing & installation, \$/m^2-GPU or equivalent	\$100	\$40

*Working capacity is the loading difference CO_2-rich solution before and after it is regenerated.

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

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: None.

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 not sufficiently high for gas absorption in the membrane contactor.

Results To Date/Accomplishments:

Results from the project are not yet available.

Next Steps:

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

S. James Zhou, Howard Meyer, Ben Bikson and Yong Ding, "Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture." AIChE Spring Meeting, San Antonio, Texas, March 21-25, 2010.

Contract No.:

DE-FE-0000646

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Membrane Technology and Research – Polymer Membranes

Project Title:

Novel Polymer Membrane Process for Pre-Combustion CO_2 Capture from Coal-Fired Syngas

Technology Area:

Pre-Combustion Membranes

Technology Maturity:

Bench-scale using simulated syngas and membrane stamp field tests using actual syngas slipstream

Primary Project Goal:

Membrane Technology and Research, Inc. (MTR) is developing 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:

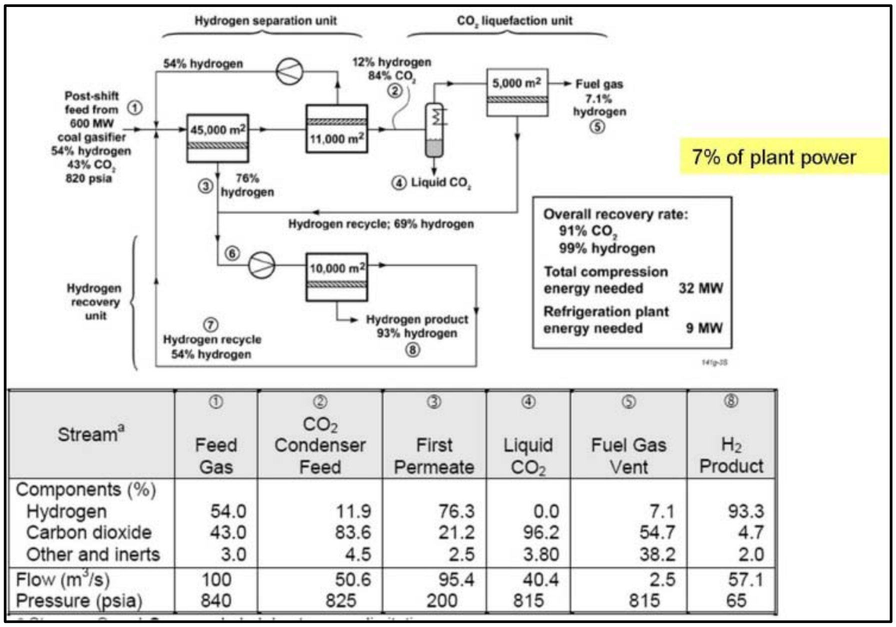
- Investigate novel high-temperature-stable polymers identified by Tetramer for use in hydrogen (H_2)/CO_2 selective membranes.
- Prepare composite polymer membranes and bench-scale modules that have H_2/CO_2 selectivities of 10 or higher and hydrogen permeances of greater than 200 gas permeation units (GPU) at syngas cleanup temperatures of 100-200°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's 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 thrust of this project is development of polymer membranes that currently show mixture H_2 permeances up to 200 GPU and H_2/CO_2 selectivities of 10 at 100-200°C. These membranes can be fabricated into robust, inexpensive modules of the type currently used commercially in the refinery and natural gas industries to separate gas mixtures at high pressures. Experience from these industries shows that membrane selectivity requirements often depend on the process design. Calculations utilizing new polymer membranes and innovative process schemes indicate that membranes with current properties can meet DOE CO_2 capture goals. Further improvements in performance and reductions in energy penalty are possible with membrane optimization.

This program will consist of two 12-month phases. The first phase will focus on materials development with an emphasis on identifying high-temperature polymers with desirable H_2/CO_2 separation properties. Promising polymers will be fabricated into industrial flat-sheet composite membranes and tested with simulated WGS mixtures. Parametric data from these tests will be used in a systems analysis to identify the optimal membrane design for syngas cleanup. Researchers will confirm that composite membranes made from novel membrane selective layers give hydrogen permeances of at least 200 GPU and H_2/CO_2 selectivities of greater than 10 in bench-scale tests using model syngas mixtures. These actual membrane performance data will be used to demonstrate that a membrane process has the potential to meet DOE pre-combustion CO_2 capture program targets.

In the second phase of the project, optimized membrane materials will be down-selected and fabricated into composite membranes on commercial-scale equipment. These membranes will be formed into laboratory-scale, spiral-wound modules, each containing about 1 m^2 of membrane. The modules will be tested with simulated syngas mixtures to provide performance and lifetime data and demonstrate module performance and lifetime consistent with small-scale membrane stamp studies. This information will allow cost estimates of the membrane CO_2 capture process to be prepared to determine the overall technical and economic competitiveness of the proposed process as compared to alternative technologies and the DOE program targets.



Stream[a]	① Feed Gas	② CO_2 Condenser Feed	③ First Permeate	④ Liquid CO_2	⑤ Fuel Gas Vent	⑧ H_2 Product
Components (%)						
Hydrogen	54.0	11.9	76.3	0.0	7.1	93.3
Carbon dioxide	43.0	83.6	21.2	96.2	54.7	4.7
Other and inerts	3.0	4.5	2.5	3.80	38.2	2.0
Flow (m^3/s)	100	50.6	95.4	40.4	2.5	57.1
Pressure (psia)	840	825	200	815	815	65

Figure 1: A Possible Membrane Process Design to Capture 90% CO_2 from Shifted Syngas that Recovers >99% of the Hydrogen in Syngas at >93% Purity

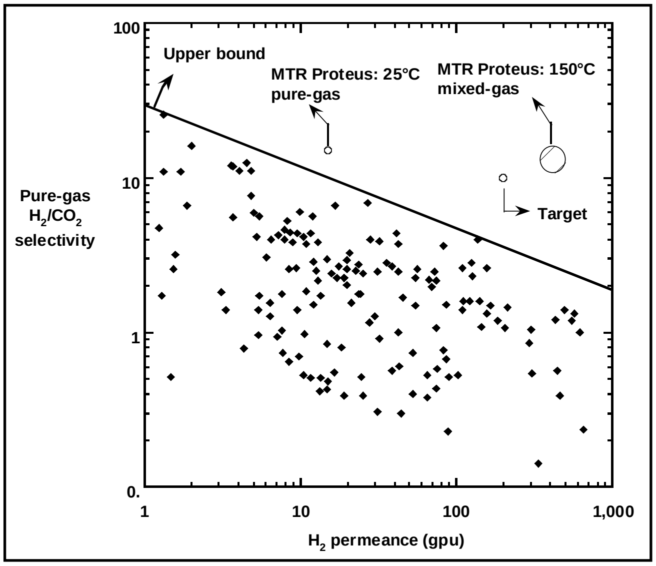


Figure 2: Tradeoff Plot of H_2/CO_2 Selectivity versus H_2 Permeance

An H_2/CO_2 selectivity versus H_2 permeance trade-off curve is presented in Figure 2. All data points below the upper bound are for polymeric membranes from literature and have been translated from pure-gas permeability at 25°C assuming a selective layer thickness of 1 micron. Polymeric composite hydrogen-selective membranes are being developed in this project. The pure- and mixed-gas performance of the membranes is shown in Figure 2. For the mixed-gas measurement, the feed gas is an H_2/CO_2 (50:50 vol%) mixture at 50 psig and 150°C. The mixed-gas performance target set in the proposal (hydrogen permeance = 200 GPU, H_2/CO_2 selectivity = 10 at 150°C) is also included for comparison.

Figure 3 shows a test skid installed by MTR at the National Carbon Capture Center (NCCC) managed by the Southern Company. The skid will be used to test membrane and module candidates with coal-derived syngas throughout this project. Initial tests of both hydrogen-selective and CO_2-selective membranes during November and December of 2009 showed stable performance that exceeded project targets.

Figure 3: MTR Membrane Test Skid at the National Carbon Capture Center

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Polymer	Polymer
	Materials of fabrication for support layer (if applicable)	Polymer	Polymer
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	12-15	>10
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	300-500 GPU	>200 GPU
	Temperature, °C	150	150
	Bench-scale testing at MTR laboratory, hours without significant performance degradation	20 hours	>100
	Pilot-scale testing at field site (if applicable), hours without significant performance degradation	500 hours	500
	Maximum pressure differential achieved without significant performance degradation or failure, bar	15 bar	50 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Spiral-wound	Spiral-wound
	Packing density, m^2/m^3	700	700
	Pressure drop (feed to residue), bar	0.5	0.5
	Estimated cost of manufacturing & installation, $\$/m^2$-GPU or equivalent	1.0	0.5
Product Quality	CO_2 purity, %	N/A	97+
	H_2 concentration, %	N/A	1.0
	Other contaminants (H_2S if it is not removed upstream of the membrane process), %	N/A	1.2
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	<100
	Cooling requirement (electricity equivalent), kJ/kgCO_2	N/A	<150
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	<250

Contaminant Resistance: The greatest concern would be fouling of the membrane surface due to residual particulate matter. 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.

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.

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.
- The process design using hydrogen permeable membranes will create a high pressure CO_2 stream capturing >90% of CO_2 in post-shift syngas and a 93 mol% purity hydrogen stream and could use as little as about 7% of the plant's power output.
- Membranes offer the advantages of simple, passive operation, no use of hazardous chemicals and the subsequent waste handling and disposal issues, no stream 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:

The first project milestone (membrane permeance and selectivity targets) was met ahead of schedule.

Next Steps:

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

A presentation was given at the November 2009 project kickoff meeting.

Another presentation will be given at the spring AIChE national meeting in San Antonio, California, and a journal article is in preparation for *Industrial and Engineering Chemistry* (estimated publication date of Sept 2010).

Contract No.:

DE-FE-0001124

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New Jersey Institute of Technology – Pressure Swing Absorption with Membrane Contactor

Project Title:

Pressure Swing Absorption Device and Process for Separating CO_2 from Shifted Syngas and its Capture for Subsequent Storage

Technology Area:	**Technology Maturity:**
Pre-Combustion Membranes	Laboratory-scale using simulated syngas

Primary Project Goal:

The New Jersey Institute of Technology (NJIT) is developing, via laboratory-scale experiments, a pressure swing absorption-based (PSAB) device using a non-dispersive membrane-based gas-liquid contactor which produces hydrogen at high pressure for integrated gasification combined cycle (IGCC) and a carbon dioxide (CO_2) stream between 1-5 atm containing at least 90% of the CO_2 from a feed gas at ~200°C and 300 psig.

Technical Goals:

- Develop via laboratory experiments an advanced PSAB device and a cyclic process to produce helium (a surrogate for hydrogen) at high pressure from low temperature post-shift reactor synthesis gas and a CO_2 stream containing at least 90% of the CO_2 and suitable for sequestration.
- Provide data and analysis of the cyclic process and device to facilitate subsequent scale up.
- 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 set up will be developed for studying the PSAB process. NJIT will work with Media & Process Technology Inc. and Applied Membrane Technologies (AMT) Inc. to develop ceramic tubule-based and Polytetrafluoroethylene (PTFE) hollow fiber-based absorption devices. The absorption device will be explored on a preliminary basis for performance of PSAB separation of a moist CO_2-helium (He) gas mixture at 150-200°C and 200-300 psig simulating a low temperature post-shift reactor synthesis gas stream.

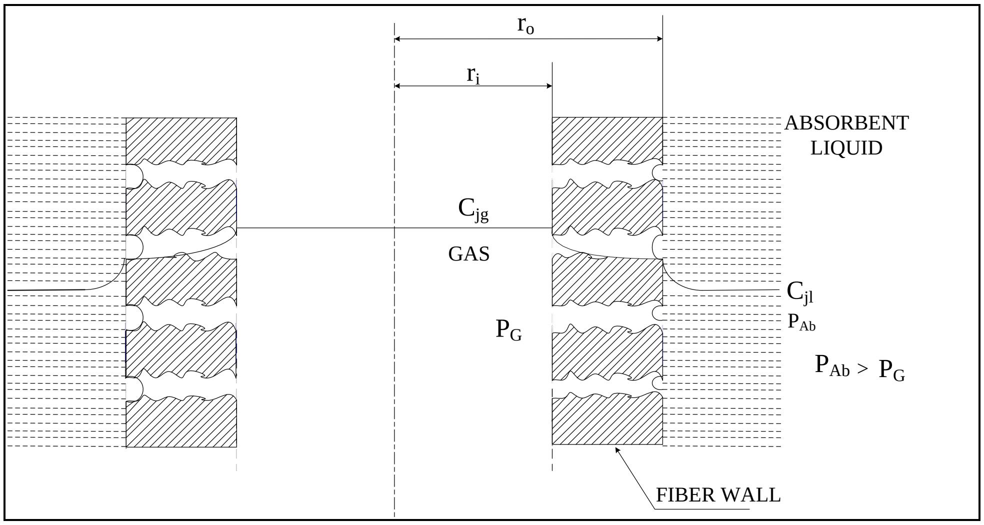

Figure 1: Concentration Profile of Absorbed Species in Gas and Liquid Phases

In phase two, NJIT will explore in detail the purification and separation performance of the PSAB 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. 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 PSAB device and process.

In phase three, 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.

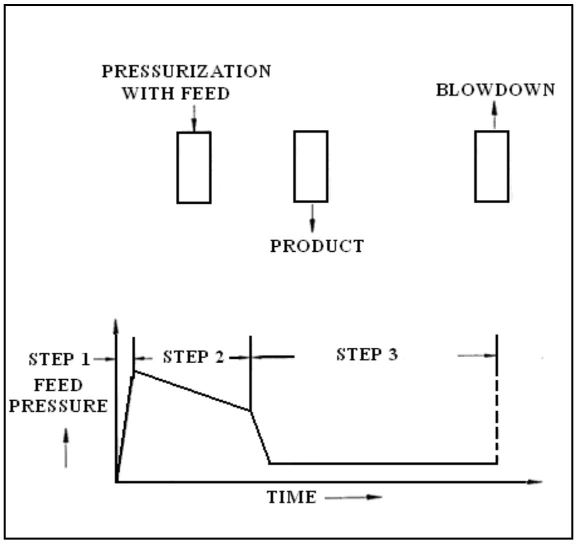

Figure 2: Pressure vs. Time Profile in Bore of Tubule or Hollow Fiber

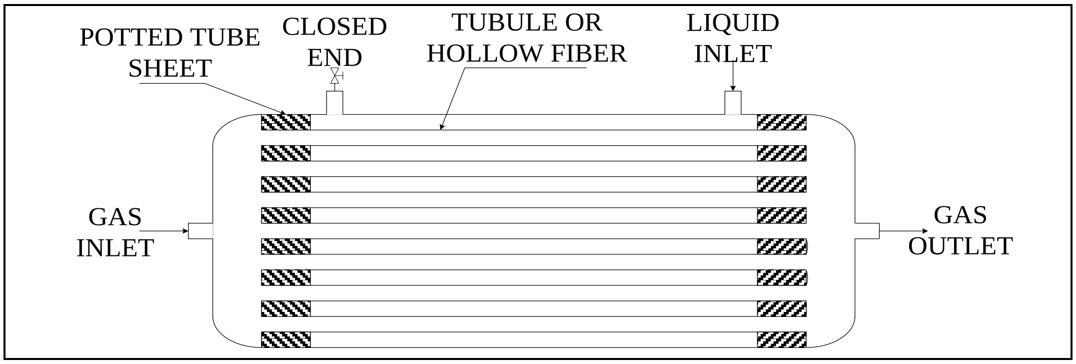

Figure 3: Schematic of Absorber Containing Ceramic Tubules or Hollow Fibers

Table 1: Process Parameters

<table>
<tr><th></th><th>Liquid-Sorbent Bed Parameters</th><th>Current R&D Value</th><th>Target R&D Value</th></tr>
<tr><td rowspan="8">Liquid Sorbent Properties</td><td>Type of sorbent</td><td colspan="2">Ionic Liquid</td></tr>
<tr><td>Molecular weight</td><td colspan="2">200-300</td></tr>
<tr><td>Boiling point (°C)</td><td colspan="2">>500</td></tr>
<tr><td>Viscosity, cP</td><td colspan="2">~33</td></tr>
<tr><td>Heat of absorption (kJ/mole CO_2)</td><td colspan="2">N/A</td></tr>
<tr><td>CO_2 loading/working capacity, wt%</td><td></td><td>N/A</td></tr>
<tr><td>Cycle time (fixed bed), minutes</td><td></td><td>0.4-2 min</td></tr>
<tr><td>Pressure drop (fixed bed), psia</td><td></td><td>1-2</td></tr>
<tr><td rowspan="6">Operating Conditions</td><td>Absorption temperature, °C</td><td></td><td>150-200</td></tr>
<tr><td>Absorption pressure, atm</td><td></td><td>13-20</td></tr>
<tr><td>CO_2 capture efficiency, %</td><td></td><td>>90</td></tr>
<tr><td>H_2 recovery, %</td><td></td><td>N/A</td></tr>
<tr><td>Regeneration method</td><td></td><td>Pressure Swing</td></tr>
<tr><td>Regeneration temperature, °C</td><td></td><td>150-200</td></tr>
</table>

	Regeneration pressure, atm		1-5
Miscellaneous	Sorbent replacement rate, kg/kgCO_2		N/A
Product Quality	CO_2 purity, %		>90
	H_2 purity, %		N/A
Process Performance	Electricity requirement, kJ/kgCO_2		N/A
	Heat requirement, kJ/kgCO_2		N/A
	Total energy (electricity equivalent), kJ/kgCO_2		N/A
	Membrane-Contactor Parameters	**Current R&D Value**	**Target R&D Value**
Membrane Properties	Materials of fabrication for selective layer		Fluoropolymer
	Materials of fabrication for support layer (if applicable)		Ceramic, Teflon, PEEK
	Selectivity of absorbents for key gas components: CO_2/H_2 for pre-combustion		30-100+
	Type of selectivity measurement (ideal or mixed gas)		Mixed Gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units		N/A
	Bench-scale testing, hours without significant performance degradation		100-200
	Pilot-scale testing (if applicable), hours without significant performance degradation		N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar		13-20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other		Hollow Fiber Shell-and-Tube
	Packing density, m^2/m^3		Ceramic, 900 Teflon, 2000 PEEK,5000
	Pressure drop, bar		N/A
	Estimated cost of manufacturing & installation, \$/m^2		100-500 \$/m^2

Contaminant Resistance: Hydrogen Sulfide (H_2S) will not affect the ceramic substrate; it will not affect the fluropolymer coating on ceramic and PEEK materials; the Teflon hollow fibers will remain unaffected also. PEEK material is also unlikely to be affected.

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: Degraded absorption solvent.

Technology Advantages:

- High solubility selectivity of novel selected liquid absorbents, high purification ability of pressure swing adsorption 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 synthesis gas feed.
- Purified CO_2 stream (>90% CO_2) will be available at 1-5 atm.

R&D Challenges:

- Leakage of absorbent through microporous PTFE hollow fibers having a plasma polymerized microporous fluorosilicone coating.

- Capability of the hydrophobic coatings on ceramic tubules to hydrophobize them sufficiently (avoid defects) to eliminate leakage of absorbent into the tube side.
- Effect of module diameter and length on He purification ability.
- Achieve a steady state in the cyclic process by preventing a drift in the composition and amount of two purified product streams obtained.

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:

None.

Contract No.:

DE-FE-0001123

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Partners:

Applied Membrane Technologies
Media and Process Technology
Techverse

APPENDIX

POST-COMBUSTION SOLVENTS

GE Global Research – High Capacity Oligomers

Project Title:

Novel High Capacity Oligomers for Low Cost CO_2 Capture

Technology Area:

Post-Combustion Solvents

Technology Maturity:

Laboratory-scale using simulated flue gas

Primary Project Goal:

GE Global Research is developing a novel oligomeric solvent and process for carbon dioxide (CO_2) 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 CO_2 solubility than current solvents.
- Achieve 25% greater CO_2 capacity than aqueous monoethanolamine (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 two to 20 repeat units) or small molecule species, will be developed. Silicones are known in the literature to be CO_2-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 CO_2 capture sites per molecule, increasing the overall CO_2 capacity. In addition, silicones have a high degree of thermal stability, allowing the system to operate at higher temperatures. Polymer-CO_2 interactions have been extensively studied in the literature and several CO_2-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 CO_2-phillic (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 CO_2 release characteristics.
- Downselect candidate solvents and synthesize.
- Estimate physical, chemical, and thermodynamic properties using modeling to further select candidates.

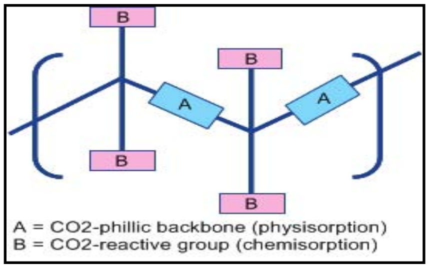
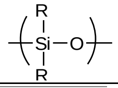
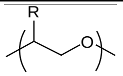
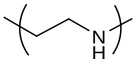
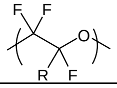
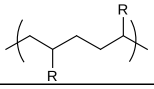
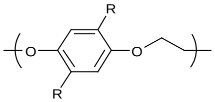
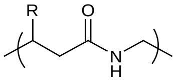
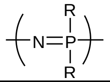
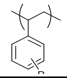


Figure 1: Solvent Concept

- Physically measure solvent properties.
- Conduct degradation and stability tests in the presence of CO_2, water, sulfur dioxide (SO_2), etc.
- Determine minimized cost of energy (COE) and an optimized capture process using power plant models.

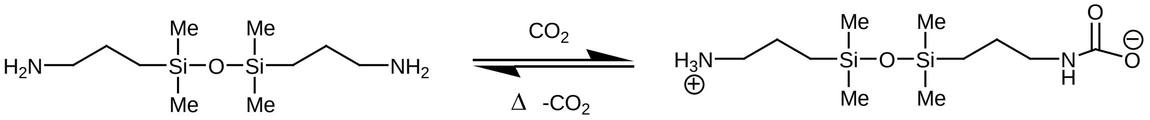
Table 1: Examples of Solvent Backbone Candidates

		Attribute						
Back Bone	**Structure**	**Physical State**	**Cost (Inexpensive)**	**Synthetic Availability**	**Ease of Derivatization**	**CO_2-Philic**	**Stability**	**Total**
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	Must be low viscosity liquid	9 = liquid; 5 = viscous liquid; 1 = solid
Cost (Inexpensive)	Should be <\$10/lb	9 = <\$10/lb; 5 = \$10-2-/lb; 1 = >\$20/lb
Synthetic Availability	Able to be made on large scale	9 = commercial; 5 = small scale; 1 = laboratory
Ease of Derivatization	Must be easily functionalized	9 = easy; 5 = moderate; 1 = difficult
CO_2-Philic	Physisorption	9 = high; 5 = moderate; 1 = low

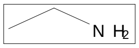
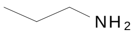
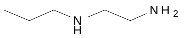
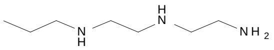
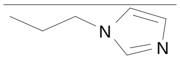
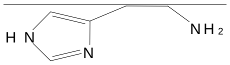
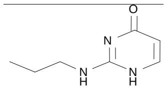
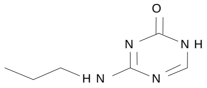
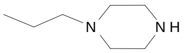
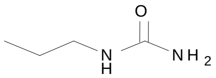
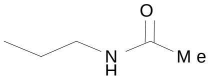
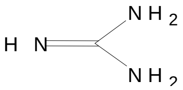
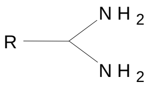
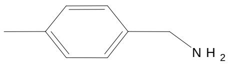
The solvent selection process splits the oligomers into backbones and functional groups so that physisorption and chemisorption are decoupled in the modeling of CO_2 solubility. Higher total scores indicate more promising candidates.

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 CO_2 is shown below:



Currently, the absorption process involves contacting the aminosilicone/glycol solvent system with gas phase CO_2. The viscosity of the system increases as CO_2 reacts until maximum CO_2 absorption is achieved. The solvent system remains a liquid and is transferred to a pressurized desorption chamber where it is heated, the CO_2 is released, and the lean solvent system is regenerated.

Table 2: Examples of Solvent Functional Group Candidates

		Attribute					
Functional Group	**Structure**	**CO_2 Capacity**	**Heat of Reaction**	**Kinetics**	**Ease of Attachment**	**Cost**	**Total**
Aminoethyl		5	5	9	5	9	33
Aminopropyl		5	5	9	9	9	37
Amionoethylaminopropyl		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 9 = high; 5 = moderate; 1 = low
Heat of Reaction 9 = moderate; 5 = low; 1 = high
Kinetics 9 = fast; 5 = moderate; 1 = slow (Reaction with CO_2)
Ease of Attachment 9 = easy; 5 = doable; 1 = difficult

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	None Provided
	Molecular weight	248/150	
	Boiling point (Amino silicone/glycol)	132C@11mm Hg/ 125C@ 0.1mm 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 (Glycol concentration)	@40 C <50(0%) --< 4500 (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/kgCO_2	N/A	
Product Quality	CO_2 purity, %	N/A	
	N_2 concentration, %	N/A	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	
	Heat requirement, kJ/kgCO_2	N/A	
	Total energy (electricity equivalent), kJ/kgCO_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 CO_2 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 CO_2 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 physi-sorption of CO_2 and decreases viscosity.

- Shown thermal regeneration of solvent after CO_2 capture.
- Demonstrated continuous CO_2 absorption by aminosilicone solvent system.
- Discovered aminosilicone solvent systems that show a >25% increase in loading compared to 30% MEA.
- Initial calculations show 48% COE with a path to 35%.

Next Steps:

- Optimize aminosilicone solvent system for maximum capacity.
- Develop methods for synthesizing larger quantities of selected solvents.
- Determine thermal stability and tolerance to impurities of selected solvents.
- Determine thermal stability.
- Construct continuous absorption/desorption unit which will allow determination of reaction rates, mass transfer coefficients, robustness of the solvent system, and any special heating or cooling needs.
- Estimate the impact of the solvent and capture process on the COE production.

Available Reports/Technical Papers/Presentations:

Presentation: Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 24-26, 2009, Pittsburgh, Pennsylvania.

Contract No.:

DE-NT0005310

NETL Project Manager:

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Partners:

GE Energy
University of Pittsburgh

University of Illinois at Urbana-Champaign – Integrated Vacuum Carbonate Absorption

Project Title:

Development and Evaluation of a Novel Integrated Vacuum Carbonate Absorption Process

Technology Area:

Post-Combustion Solvents

Technology Maturity:

Laboratory-scale using simulated flue gas

Primary Project Goal:

The University of Illinois at Urbana-Champaign is proving the novel Integrated Vacuum Carbonate Absorption Process (IVCAP) concept and further improving 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 v acuum 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.

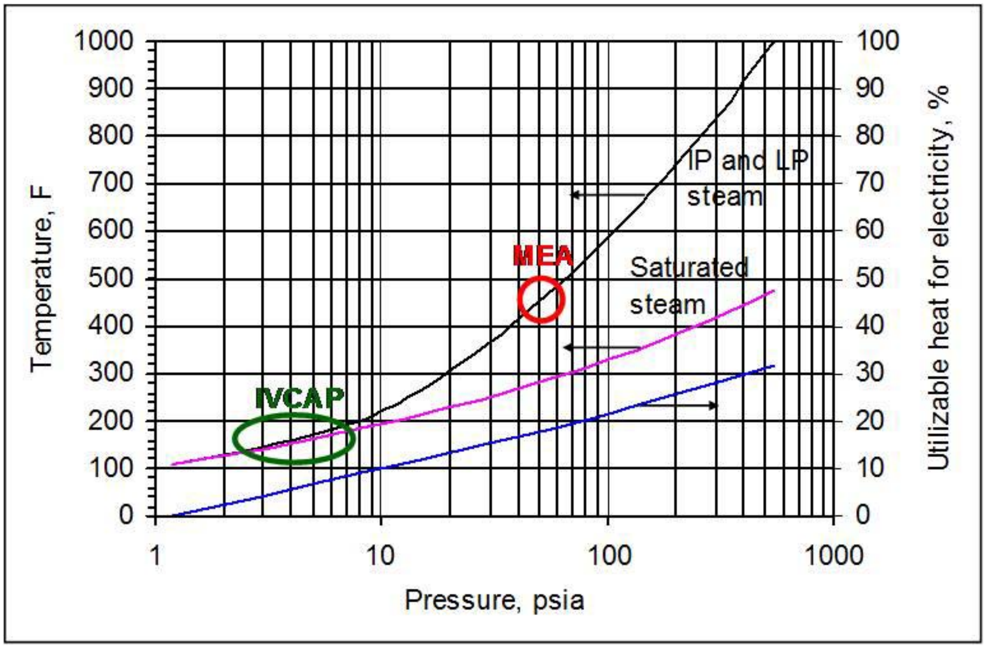

Figure 1: Steam Properties During Expansion in the Intermediate and Low Pressure Turbines

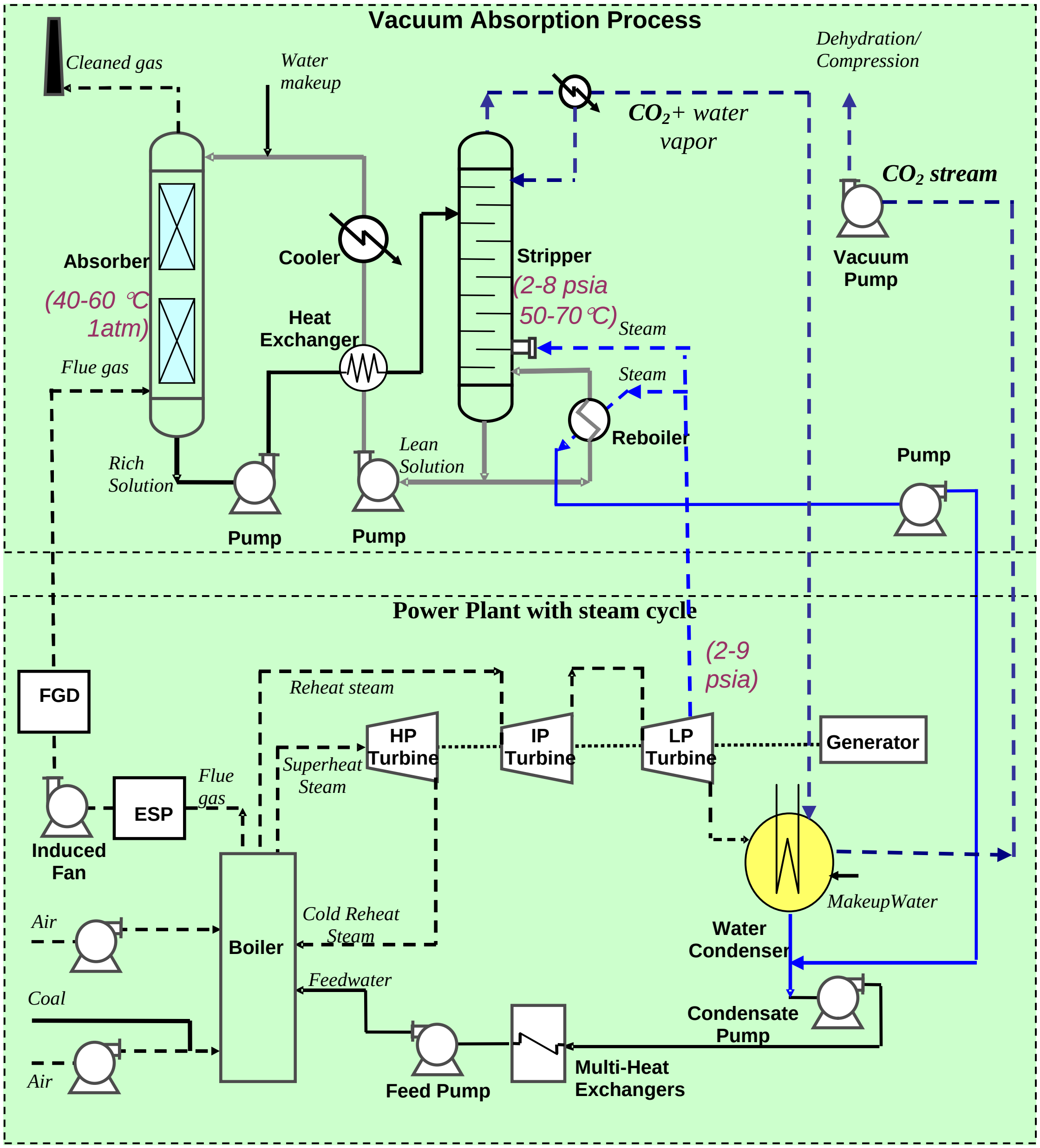

Figure 2: Vacuum Stripping in the IVCAP Allows for Use of Low Quality Steam From the Power Plant

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	$CO_3^{2-} + CO_2 + H_2O = 2\ HCO_3-$	600 kJ/kg

The intrinsic rate of CO_2 absorption into the K_2CO_3 solution is much slower in a monoethanolamine (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 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 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_2CO_3/$KHCO_3$	None Provided
	Molecular weight	138	
	Boiling point (^{0}C)	103	
	Heat of reaction (kJ/mole CO_2)	26.4	
	CO_2 loading/working capacity*, 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^{0}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/kgCO_2	negligible	
Product Quality (based on process simulations)	CO_2 purity, %	>99	
	N_2 concentration, %	negligible	
	Other contaminants, %	0.1%	
Process Performance	Electricity requirement, kJ/kgCO_2 (compress. incl.)	460-580	
	Heat requirement, kJ/kgCO_2	240-550 (Elec. equiv.)	
	Total energy (electricity equivalent), kJ/kgCO_2	800-1130	~800

*Working capacity is the loading difference CO_2-rich solution before and after it is regenerated.

Equation/s Describing Chemical Reaction

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 Reaction Kinetics

Based on the experimental results to date, the overall CO_2 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 CO_2 loading in the solution. The CA enzyme promotes the absorption more significantly when the CO_2 loading in the solution is higher. The CO_2 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 CO_2 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 CO_2-rich solution from the absorber and CO_2-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 SO_2 scrubbing is needed prior to the IVCAP, since SO_2 removal can be combined with CO_2 capture. Therefore, there is also no problem related to SO_2 contamination.

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 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 CO_2.

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 SO_2 without a FGD unit.
- Approximately 25% lower electricity loss.

R&D Challenges:

- Slow kinetics of CO_2 absorption into the K_2CO_3 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 CO_2 absorption into the K_2CO_3 solution. Evaluation on CA enzymes from other sources and enzyme immobilization research is currently underway.

Planned Activities:

- Investigate catalytic methods to enhance the CO_2 absorption rate in the K_2CO_3 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 CO_2-H_2O-K_2CO_3-$KHCO_3$ systems with and without additives at a temperature range of 25°C to 70°C.
    - Inorganic and organic additives to be examined.
- Combine SO_2 removal in the CO_2 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 CO_2 Capture Technology for Existing Plants R&D Meeting, March 2009.

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

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

Contract No.:

DE-NT0005498

NETL Project Manager:

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Partners:

Calgon Carbon Corporation
Illinois Clean Coal Institute
University of Illinois

Hampton University – Phase Transitional Absorption

Project Title:

CO_2 Capture from Flue Gas by Phase Transitional Absorption

Technology Area:	**Technology Maturity:**
Post-Combustion Solvents	Laboratory-scale using simulated flue gas

Primary Project Goal:

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 (CO_2) 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 (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. The absorbent is characterized as phase transitional absorbent due to its ability to separate the concentrated CO_2-rich phase from CO_2-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.

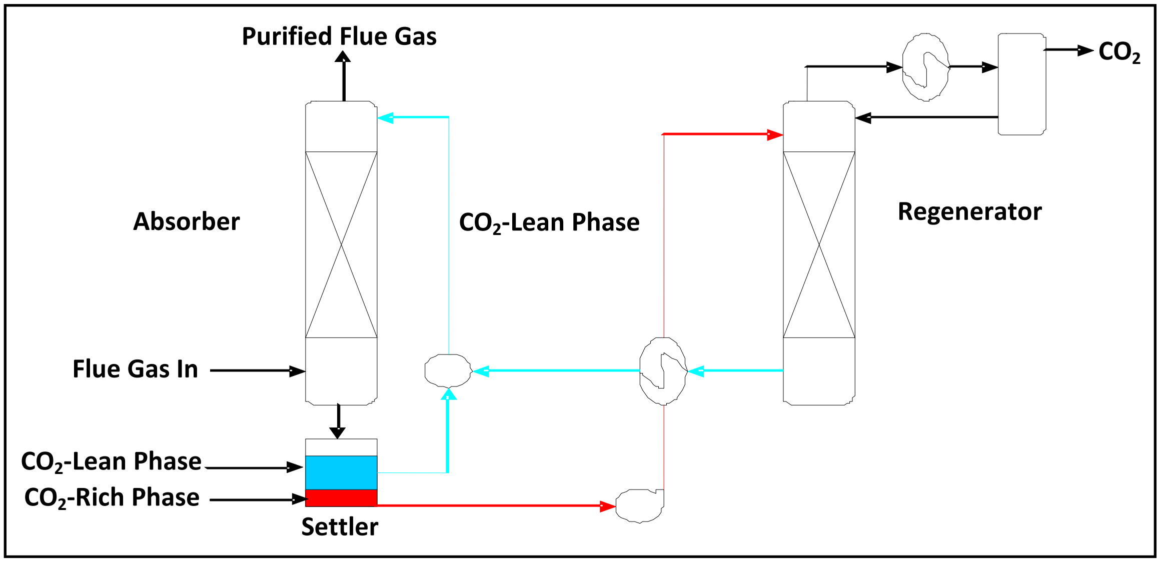

Figure 1: Concept Flow Diagram of Phase Transitional Absorption

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 CO_2-rich phase needs to be regenerated. The CO_2-rich phase is only approximately 20% of the total absorbent. Thus, the pumping and heating requirement 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.

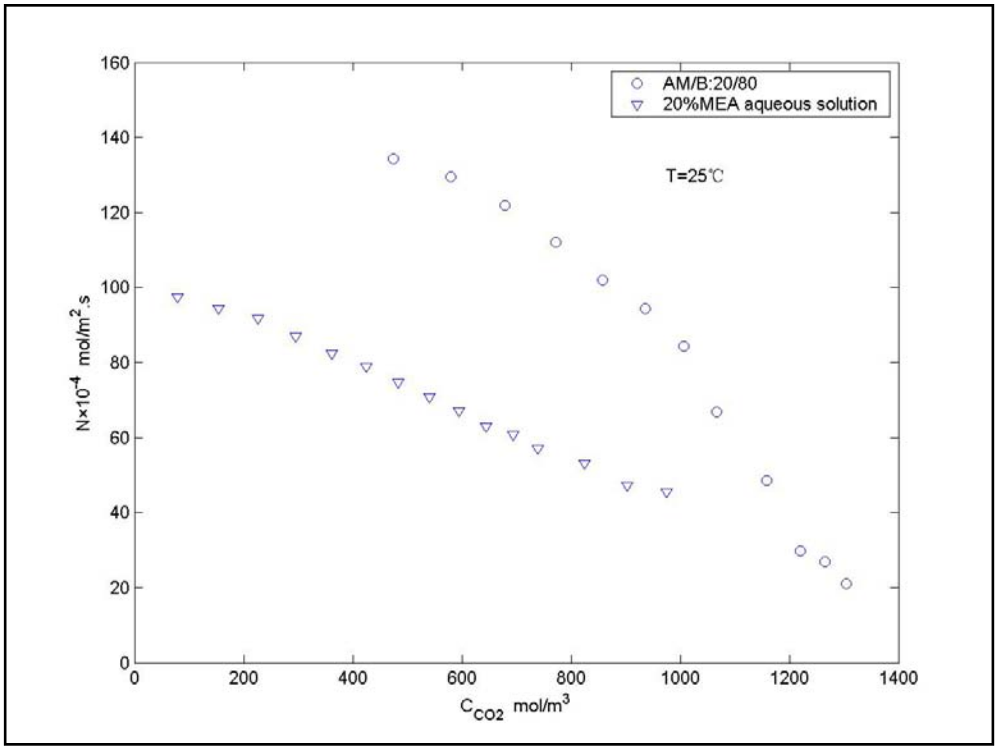

Figure 2: Absorption Rate Comparison(Phase Transitional Absorption vs. MEA Technology)

T = 25 °C; $P_{CO2} = 1$ atm; N=60 rpm; $V_L = 900$ 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% to 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
Solvent Properties	Type of solvent	Non Aqueous amine	
	Molecular weight	Varies	None Provided
	Boiling point (^{0}C)	Varies	
	Heat of reaction (kJ/mole CO_2)		
	CO_2 loading/working capacity*, wt.%	20%	
	Solvent concentration to stripper (mol/liter)		
	Heat capacity of solution (kJ/K/kg)		
	Viscosity, cP		
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/kgCO_2	N/A	
Product Quality	CO_2 purity, %	99.9%	
	N_2 concentration, %		
	Other contaminants, %		
Process Performance	Electricity requirement, kJ/kgCO_2		
	Heat requirement, kJ/kgCO_2	1,000 (heat)	
	Total energy (electricity equivalent), kJ/kgCO_2		

*Working capacity is the loading difference CO_2 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 CO_2 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°C, 25°C, 35°C, 45°C, 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 rpm, 60 rpm, 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:

- Process research data.
- Prepare patent application.
- Prepare for pilot scale.

Available Reports/Technical Papers/Presentations:

Hu, Liang, Monica Wood, Joseph Hoque. "CO_2 Capture from Flue Gas by Phase Transitional Absorption." http://www.netl.doe.gov/publications/proceedings/07/ucr/abstracts/Hu.pdf (Accessed 9/28/2009).

Contract No.:	**NETL Project Manager:**
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Principal Investigator:	**Partners:**
Liang Hu Hampton University lianghu59@yahoo.com	None

University of Notre Dame – Ionic Liquids

Project Title:

Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Solvents	Laboratory-scale using simulated flue gas

Primary Project Goal:

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 (CO_2) over nitrogen (N_2) for the IL will be 50.
- The complexing ratio of CO_2: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 CO_2.
  - 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 CO_2. Examples of ILs are illustrated in Figure 1.

Previous experiments have shown a potential for high CO_2 solubility and low O_2, N_2 solubility (see Figure 2). ILs as CO_2 absorbents are promising for reducing costs by developing a process with higher CO_2 loading in the circulating liquid and lower heat requirements for regeneration. Both of these effects would lower process costs.

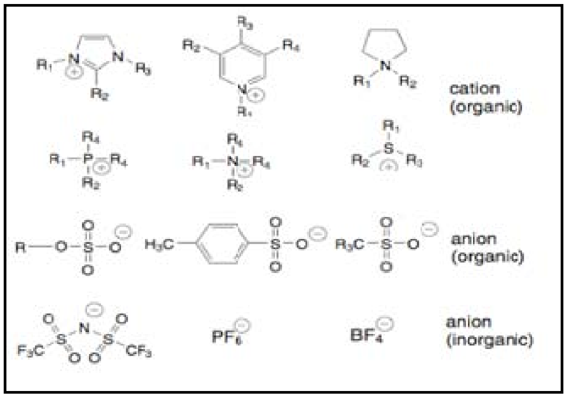

Figure 1: Examples of Ionic Liquids

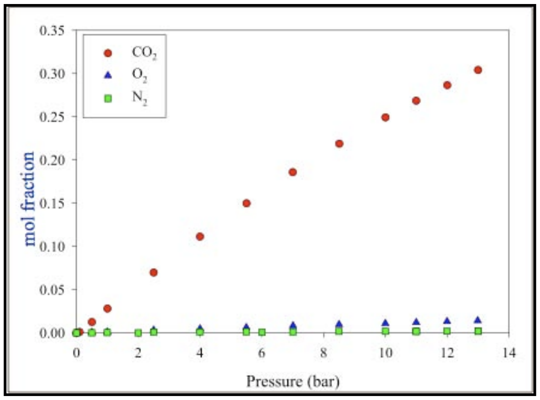

Figure 2: CO_2 Solubility in Ionic Liquids

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 CO_2 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:CO_2) 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 (Keq): Sensitivity includes a range of CO_2 loadings that result from the above enthalpies of reaction.
- Water miscibility: Both partially and fully miscible systems are included. Activities coefficients modeled with NRTL using experimental data.

Preliminary results show much lower parasitic energy compared with a monoethanolamine (MEA) system.

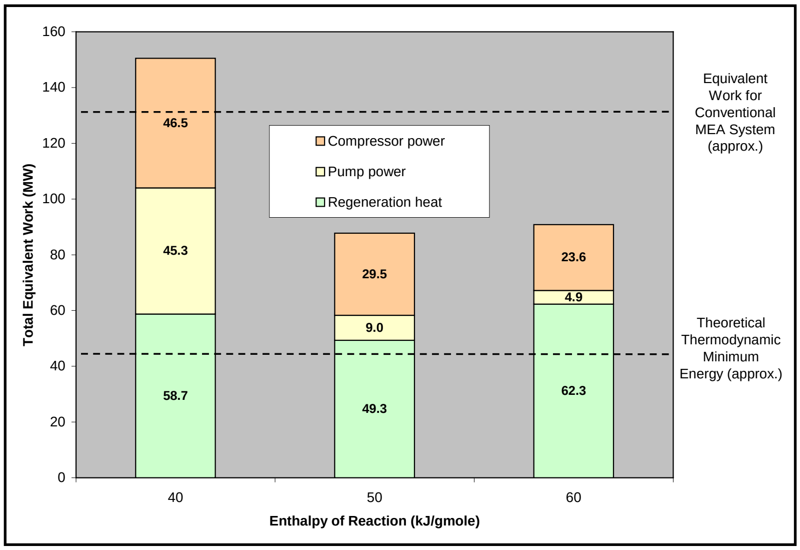

Figure 3: Preliminary Results on the Parasitic Power Requirement of Ionic Liquid Solvents

Table 1: Process Parameters for Ionic Liquid Solvents

	Parameter	Current R&D Value (as of July, 2009)	Target R&D Value
Solvent Properties	Type of solvent	Ionic liquid	Ionic liquid
	Molecular weight	575 g/mol	< 575 g/mol
	Boiling point (^{0}C)	NA – do not boil	NA – do not boil
	Heat of reaction (kJ/mole CO_2)	35-75	35-75
	CO_2 loading/working capacity*, 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
Operating Conditions	Absorption temperature, °C	40-50	40-50
	Absorption pressure, atm.	0.15 of CO2	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/kgCO_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/kgCO_2	390 - 560	Minimize
	Heat requirement, kJ/kgCO_2	1650 - 1850	Minimize
	Total energy (electricity equivalent), kJ/kgCO_2	890 - 950	Minimize

*Working capacity is the loading difference CO_2-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 CO_2 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 CO_2, 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 CO_2, 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 CO_2, unlike the case with “Generation 2” ILs.

Next Steps:

Phase III:

- Continue synthesis and testing of “Generation 3” ILs.
- Select “optimal” IL(s) for lab-scale testing.
- Conduct bench-scale tests to evaluate process design.
- Design a laboratory-scale test system.
- Update economic, engineering, and systems analyses.

Phase IV:

- Construct and operate lab-scale test system using conventional solvent and Phase 3 IL.
- Finalize economic, engineering, and systems analyses.

Available Reports/Technical Papers/Presentations:

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 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 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.

Contract No.:	**NETL Project Manager:**
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Principal Investigator:	**Partners:**
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Georgia Tech Research Corporation – Reversible Ionic Liquids

Project Title:

Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Solvents	Laboratory-scale using simulated flue gas

Primary Project Goal:

Georgia Tech Research Corporation is developing a novel class of solvents for the recovery of carbon dioxide (CO_2) from post-combustion flue gases that will 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.

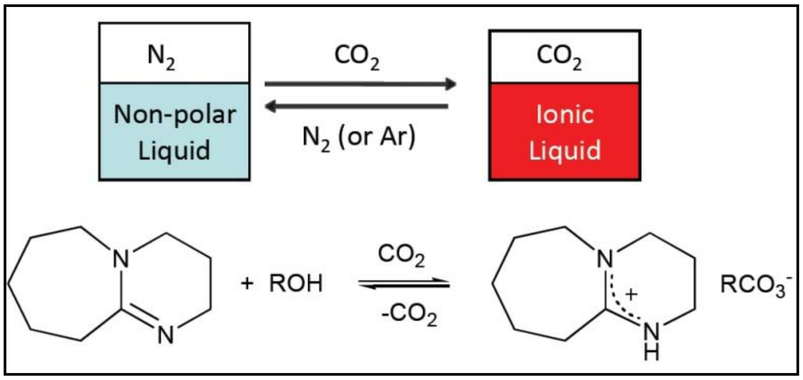

Figure 1: CO_2 Will Switch a Non-Polar Liquid to and Ionic Liquid

In a two-component RevIL, CO_2 at 1 atm acts as a "switch," as shown in Figure 1.

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°C, 25°C, 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.

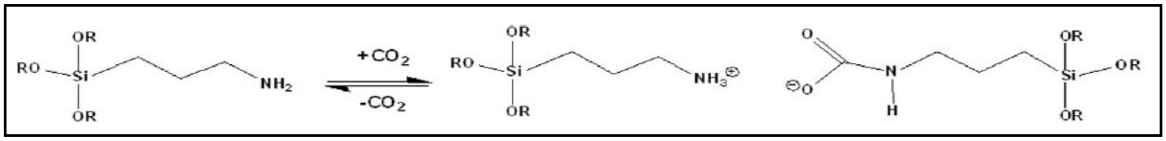

Figure 2: An Example of a Single Component RevIL

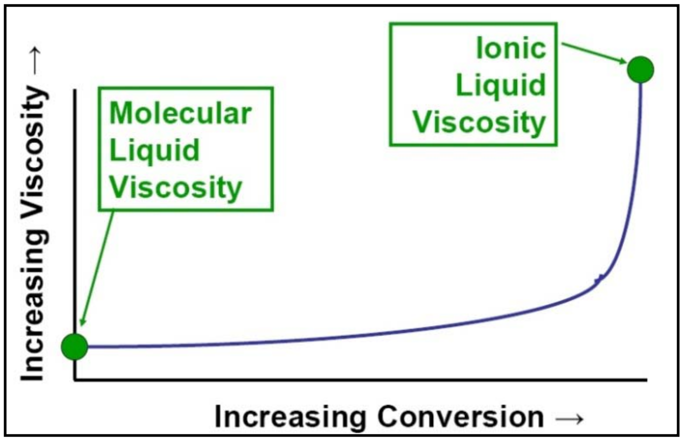

Figure 3: Ionic Liquids are more Viscous Than Their Respective Molecular Liquids

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 (^{0}C)	130	200
	Heat of reaction (kJ/mole CO_2)	Unknown	50
	CO_2 loading/working capacity*, 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/kgCO_2	?	<0.003
Product Quality	CO_2 purity, %	?	>99
	N_2 concentration, %	?	<1
	Other contaminants, %	?	<<1
Process Performance	Electricity requirement, kJ/kgCO_2	?	500
	Heat requirement, kJ/kgCO_2	?	1,500
	Total energy (electricity equivalent), kJ/kgCO_2	?	950

*Working capacity is the loading difference CO_2-rich solution before and after it is regenerated.

Equations Describing Chemical Reaction

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.

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 three precursors for novel RevILs:
  - (3-aminopropyl) trimethoxysilane
  - (3-aminopropyl) triethoxysilane
  - (3-aminopropyl) triethylsilane

Next Steps:

- Successfully synthesize and characterize silylated one-component RevILs.
  - Demonstrate function in presence of water.
- Measure candidate RevILs' thermodynamic properties.
- Measure candidate RevILs' 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 CO_2 Capture Technology for Existing Plants R&D Meeting, March 24-26, 2009, in Pittsburgh, Pennsylvania.

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. Commun. 116-119, 2009.

Vittoria Blasucci, Ryan Hart, Veronica Llopis Mestre, Dominique Julia Hahne, Melissa Burlager, Hillary Huttenhower, Beng Joo Reginald Thio, Charles L. Liotta, and Charles A. Eckert, “Single Component, Reversible Ionic Liquids for Energy Applications,” *Fuel*, in press, 2010.

Contract No.:

NT0005287

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APPENDIX

POST-COMBUSTION SORBENTS

University of Akron – Metal Monolithic Amine-Grafted Zeolites

Project Title:

Metal Monolithic Amine-Grafted Silica for CO_2 Capture

Technology Area:

Post-Combustion Sorbents

Technology Maturity:

Bench-scale using simulated flue gas

Primary Project Goal:

The University of Akron is developing 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 10% 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/tetraethylenepentamine. The adsorption capacity of this novel amine-grated silica was found 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 (i.e., CO_2 capture capacity) can be further fine-tuned and optimized by the sorbent preparation procedures.

The purpose of the metal foil is to fabricate the metal monolithic structure. 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.

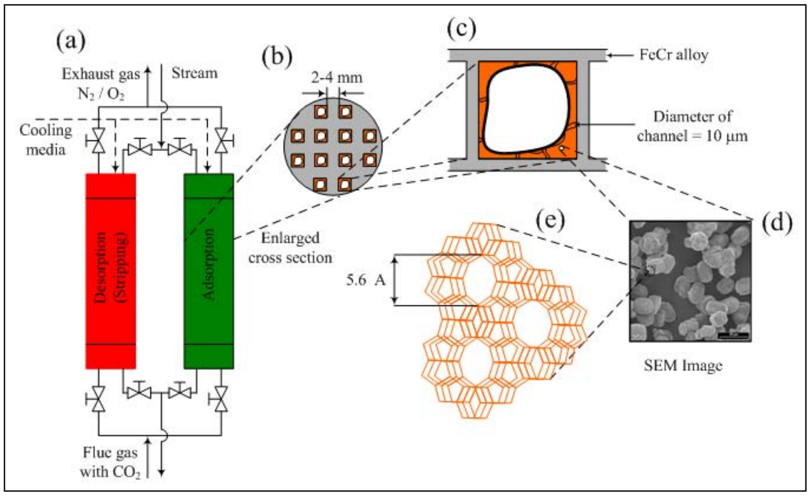

Figure 1: Metal Monolithic Amine-Grafted Silica Sorbents

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 tetraethylene-pentamine. Coal fly ash is being investigated as a support for amine due to its ready availability and low cost.

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 that holds the individual metal (b) tubes with the amine about 2-4 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. The goal is that the CO_2 and SO_2 adsorption capacity of the amine will be greater than 1.5 mmol-CO_2/g-sorbent for CO_2 and 1.0 mmol-CO_2/g-sorbent for SO_2. The regeneration ability of the amine is >500 times, while having <10% degradation of the CO_2 capture 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

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	PEG/TEPA/SiO_2	N/A
	Heat of adsorption (kJ/mole CO_2)	52	50-55
	CO_2 loading/working capacity, wt.%	6.4	6.0
	Surface area, m^2/g		
	Particle density, cm^3/g		
	Packing density, cm^3/g		
	Particle size (mm)	0.05-.3	0.25
	Heat capacity (kJ/K/kg)	1.49	1.3-1.5
	Thermal stability, °C	130°C	130°C
	Hydrothermal stability, °C	Not tested	
Process Configuration	Attrition rate (fluidized bed), %/year		
	Cycle time (fixed bed), minutes	30	
	Pressure drop (fixed bed), psia		
Operating Conditions	Adsorption temperature, °C	50	50
	Adsorption pressure, atm.	1	1
	CO_2 capture efficiency, %		
	Regeneration method	Thermal swing	Thermal swing
	Regeneration temperature, °C	100 - 110	100 - 110
	Regeneration pressure, atm.	1 - 1.05	1 – 1.05
Heat Integration	Required regeneration steam temperature, °C	100-110	100-110
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	Not tested	
Product Quality	CO_2 purity, %	15%	
	N_2 concentration, %	balance	
	Other contaminants, %	N/A	
Process Performance	Electricity requirement, kJ/kgCO_2	N/A	
	Heat requirement, kJ/kgCO_2	N/A	
	Total energy (electricity equivalent), kJ/kgCO_2	N/A	

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 scaleup transition from lab- to bench-scale tests.
- Temperature swing adsorption (TSA) 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

monoethanolamine (MEA) process.
- Currently, the CO_2 capture capacity of the sorbent is too low.

Results To Date/Accomplishments:

Recent results show that the silica-supported amine sorbent with additives is able to capture more than 1.6 mmol CO_2/g-sorbent at 40°C and desorb at 100°C for more than 500 cycles with less 13% degradation. Degradation was found to be due to the overheating of those sorbents which were in contact the tube wall. During heating for CO_2 desorption, the wall temperature is 5°C to 15°C higher than that of the center of packed bed.

Tested three types of sorbent supports for the amines.

- Prepared and determined more than 15 samples of alkyl, amine-grafted zeolite/oxide for CO_2 capture and 10 samples of aryl, amine-grafted oxides for SO_2 capture.
- Conducted DRIFT adsorber studies for CO_2 capture and characterization studies of TEPA/Silica 68.
- Conducted tubular adsorber studies for silicon dioxide (SiO_2) amines in quartz and copper tubes.
- Observed that treating coal fly ash with hydrogen chloride (HCl) followed by sodium hydroxide (NaOH) increased its surface area by an approximate factor of 14.

Next Steps:

- Continue to improve CO_2 and SO_2 capture capacity and stability.
- Determine long-term stability of the sorbents.
- Fine-tune sorbent composition.
- Fabricate CO_2 absorber.
- Test performance of the absorber.
- Conduct economic analysis.

Available Reports/Technical Papers/Presentations:

"Metal Monolithic Immobilized Amine Absorber for Carbon Dioxide Capture," U.S. Patent Applications, Nov. 7, 2008, UA 685.

"Oxide-supported Tetraethylenepentamine for Carbon Dioxide Capture," J. C. Fisher II, J. Tanthana, and S. S. C. Chuang, Environmental Progress & Sust Energy, 28 (4), 589-598, 2009.

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Research Triangle Institute – Dry Sodium Carbonate

Project Title:

Development of a Dry Sorbent-Based Post Combustion CO_2 Capture Technology for Retrofit in Existing Power Plants

Technology Area:	**Technology Maturity:**
Post-Combustion Sorbents	Bench-scale/Small pilot-scale

Primary Project Goal:

Research Triangle Institute (RTI) is developing and testing a commercially viable carbon dioxide (CO_2) capture process from a coal-fired power plant flue gas, with CO_2 and water vapor present, by utilizing a dry sodium carbonate (Na_2CO_3) sorbent.

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.

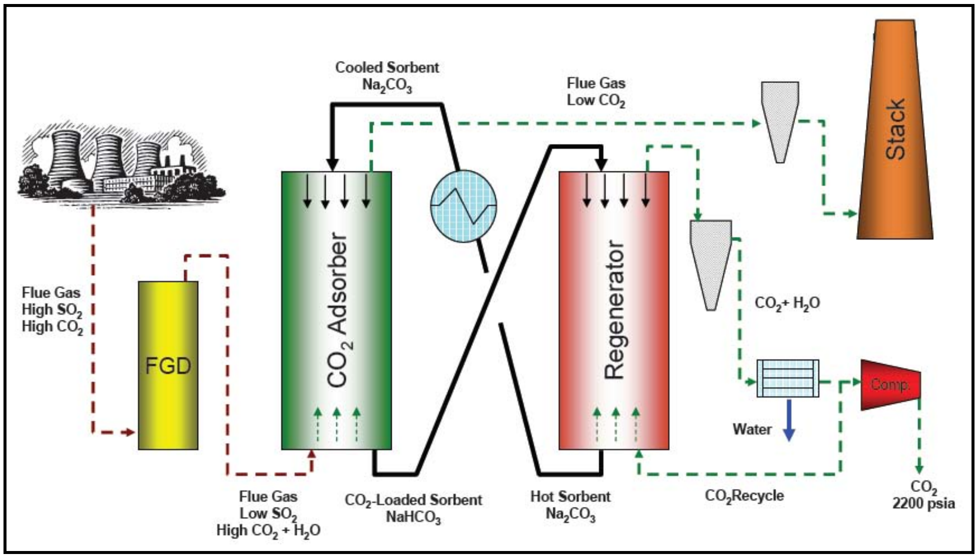

Figure 1: Schematic Diagram of CO_2 Capture Process

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.

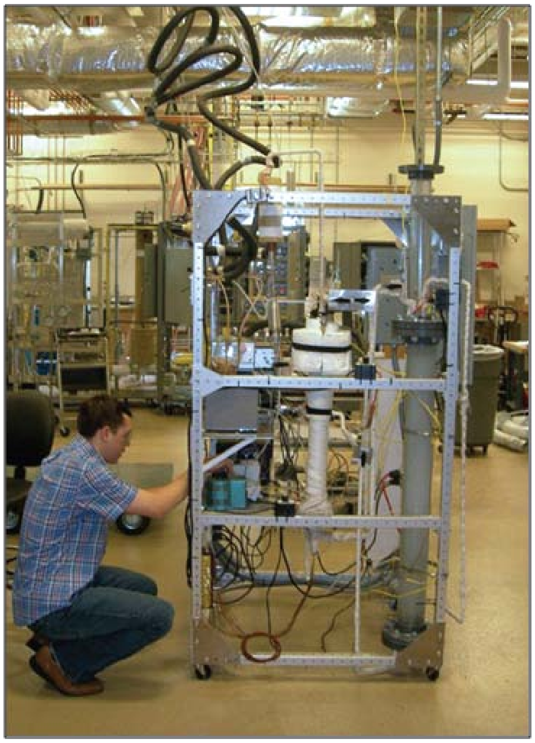

Figure 2: Lab-Scale CO_2 Absorption Reactor Skid

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 to be 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 Particle Size	65 – 75 µm
Surface Area	100 – 120 m^2/g
Physical Strength (AR)	0.77
Na_2CO_3 Content	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 ~20-25%.

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:

- Continue design and construction of the pre-pilot CO_2 capture system.
- Continue sorbent development and identify promising sorbent candidates.
- Conduct process simulation work and preliminary economic analysis of the new dry carbonate process.
- Perform a detailed technical and economic analysis of the dry carbonate process.
- Evaluate the hydrodynamic and heat transfer characteristics of the reactor designs using the heat transfer evaluation system.
- Demonstrate long-term, multi-cycle stability of the engineered sorbent using the packed-bed reactor.

Available Reports/Technical Papers/Presentations:

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents – Final Report – January 2009.

The Dry Carbonate Process: Carbon Dioxide Recovery from Power Plant Flue Gas - CO_2 Capture Technology for Existing Plants R&D Meeting – March 2009.

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.

Carbon Dioxide Capture from Flue Gas Using Dry Regenerable Sorbents Fact Sheet – April 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.

Contract No.:

DE-FC26-07NT43089

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EPA
EPRI
Nexant
Süd-Chemie, Inc.

TDA Research – Alkalized Alumina

Project Title:

Low-Cost Sorbent for Capturing CO_2 Emissions Generated by Existing Coal-Fired Power Plants

Technology Area:

Post-Combustion Sorbents

Technology Maturity:

Bench-scale using simulated flue gas

Primary Project Goal:

TDA Research is designing and developing a low-cost solid sorbent that is capable of cost-effectively and efficiently capturing carbon dioxide (CO_2) from existing coal-fired power plants, as well as an adsorption/regeneration process designed around that material.

Technical Goals:

- Use existing information to select candidates for a low-cost, highly efficient CO_2 sorbent.
- Perform TGA, surface area, and crush strength analyses to characterize the sorbent.
- To determine the effects of sulfur oxides (SO_X), nitrogen oxides (NO_X), and water (H_2O) on the working capacity of the optimum sorbent.
- Construct and demonstrate a novel CO_2 removal system for real flue gas stream.

Technical Content:

A variety of existing materials were selected as sorbent candidates. Each material was characterized by TGA, BET, and crush strength tests. The best sorbents were then selected for further evaluation in a fixed bed to be evaluated under repeated absorption and regeneration cycles and to determine working capacity.

A dry regenerable alkalized alumina material was determined to be the best sorbent available for exhibiting features such as a loading capacity of ~0.7%, little performance reduction in the presence of up to 19% water, and near negligible capacity reduction in the presence of up to 300 parts per million (ppm) SO_X. In addition, alkalized alumina is low cost and easily available.

Figure 1 is a sample excerpt plot of CO_2 concentration over time. This experiment was performed using simulated flue gas that contains 13.6% CO_2, 9% H_2O, and 77.2% nitrogen (N_2). The sorbent was regenerated with steam.

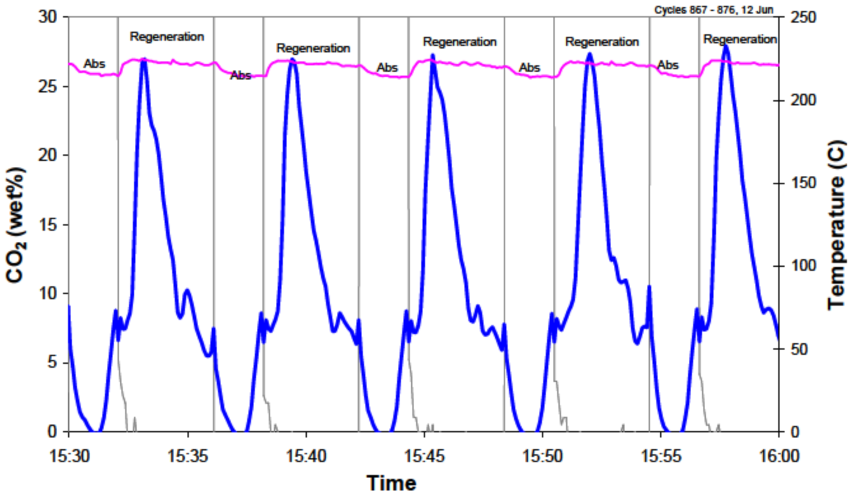

Figure 1: Example of Fixed Bed Screening Test (loading is normalized by the loading under dry conditions)

Figure 2 is an overall schematic of TDA's system, which consists of three primary components: 1) the absorber/regenerator unit; 2) the low-pressure steam generator; and 3) the CO_2 compression and purification unit. The process is designed for the sorbent to pull the dilute CO_2 out of the flue gas at intermediate temperature and near ambient pressure, and then be regenerated with low-pressure superheated steam.

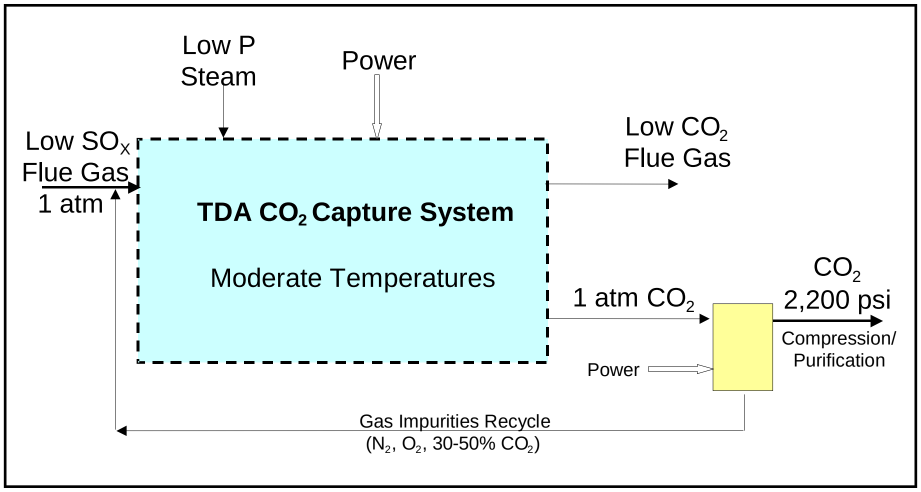

Figure 2: Schematic of TDA's CO_2 Emission Control System

Table 1: Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Adsorbent	Adsorbent
	Heat of adsorption (kJ/mole CO_2)	12 to 25	10 to 20
	CO_2 loading/working capacity, wt.%	0.7	1 to 3
	Surface area, m^2/g	100	100 to 150
	Particle density, cm^3/g	0.63	0.6
	Packing density, cm^3/g	1.05	1
	Particle size (mm)	1.6	9.5
	Heat capacity (kJ/K/kg)	0.8	0.8
	Thermal stability, °C	650	>250
	Hydrothermal stability, °C	110 <T <650	110 <T <650
Process Configuration	Attrition rate (fluidized bed), %/year	TBD	TBD
	Cycle time (fixed bed), minutes	5 to 15	5 to 15
	Pressure drop (fixed bed), psia	2 to 5	0.5
Operating Conditions	Adsorption temperature, °C	110 <T <200	110 <T <650
	Adsorption pressure, atm.	1	1.05
	CO_2 capture efficiency, %	90	90
	Regeneration method	steam	steam
	Regeneration temperature, °C	110 <T <200	110 <T <200
	Regeneration pressure, atm.	1	1.05
Heat Integration	Required regeneration steam temperature, °C	TBD	TBD
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	TBD	Annual

Product Quality	CO_2 purity, %	TBD	99.99998
	N_2 concentration, %	TBD	1.8e-8
	Other contaminants, %	TBD	1.98e-5
Process Performances	Electricity requirement, kJ/kgCO$_2$	Not available	
	Heat requirement, kJ/kgCO$_2$	Not available	
	Total energy (electricity equivalent), kJ/kgCO$_2$	Not available	

Technology Advantages:

- Low regeneration energy.
- Rapid adsorption/regeneration kinetics due to surface-only adsorption.

R&D Challenges:

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

Results To Date/Accomplishments:

- Performed TGA, BET, and crush strength analyses on a variety of sorbent materials.
- Determined alkalized alumina to be the optimum sorbent with a loading capacity of 0.7 wt%.
- Performed extended period testing up to 1,800 cycles and found the sorbent maintained its loading capacity at near constant levels throughout.

Next Steps:

- Optimize the sorbent composition and production process.
- Perform sorbent testing and characterization.
- Create a CO_2 capture process design and ASPEN model that includes steam source, CO_2 compression, and heat sources.
- Perform 1,500-hour sorbent cycling test to evaluate the SO_X and NO_X contamination of the sorbent and to complete wear and service assessments of the sorbent.
- Update ASPEN model with experimental data and perform full system and economic evaluation.
- Construct and install a CO_2 capture bench-scale unit and perform shakedown testing.
- Perform CO_2 capture experiments with the sorbent using real coal-derived flue gas.
- Conduct a final system and economic evaluation of the sorbent.

Available Reports/Technical Papers/Presentations:

TDA Research Presentation – March 2009.

Presentation at Pittsburgh Coal Conference, September 22, 2009.

Contract No.:

DE-NT0005497

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UOP – Metal Organic Frameworks

Project Title:

CO_2 Removal from Flue Gas Using Microporous Metal Organic Frameworks

Technology Area:	**Technology Maturity:**
Post-Combustion Sorbents	Laboratory-scale using simulated flue gas

Primary Project Goal:

UOP is developing and designing 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.

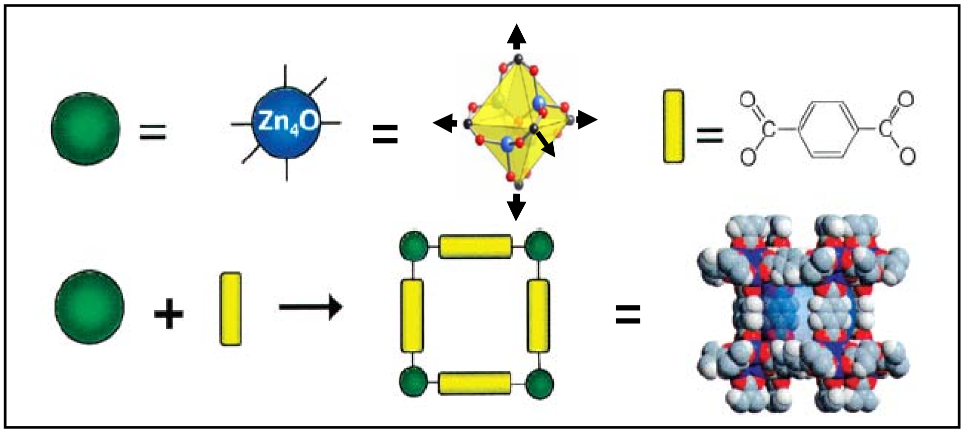


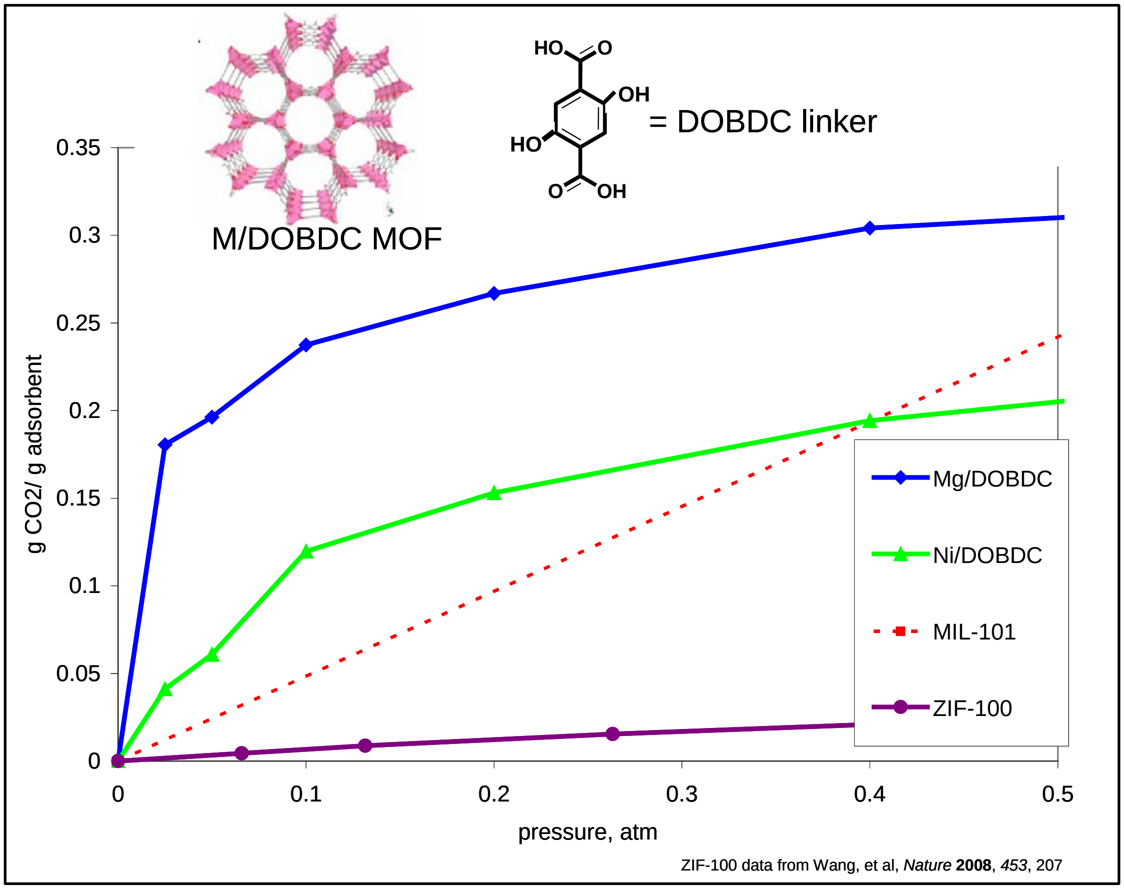
Figure 1: Building Blocks Used to Create Prototypical MOF-5

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 Adsorption (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
Al-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
Al-MIL-53	0.17	0.7	26.0
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

Table 2: Process Parameters for MOF Sorbents

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	MOF	None Provided
	Heat of adsorption (kJ/mole CO_2)	40 – 60	
	CO_2 loading/working capacity, wt.%	10 – 20	
	Surface area, m^2/g	500 – 2000	
	Particle density, g/cm^3		
	Packing density, g/cm^3	0.3 – 0.7	
	Particle size (mm)	0.5 – 2.0	
	Heat capacity (kJ/K/kg)		
	Thermal stability, °C	250 – 400	
	Hydrothermal stability, °C	100 – 200	
Process Configuration	Attrition rate (fluidized bed), %/year		
	Cycle time (fixed bed), minutes	4 – 16	
	Pressure drop (fixed bed), psia	1 – 2	
Operating Conditions	Adsorption temperature, °C	25 – 45	
	Adsorption pressure, atm.	0.1 – 0.15	
	CO_2 capture efficiency, %	90 – 95	
	Regeneration method	VPSA	
	Regeneration temperature, °C		
	Regeneration pressure, atm.	0.01 – 0.05	
Heat Integration	Required regeneration steam temperature, °C		
Miscellaneous	Sorbent make-up rate, $kg/kgCO_2$		
Product Quality	CO_2 purity, %	90 – 98	
	N_2 concentration, %	Balance	
	Other contaminants, %		
Process Performance	Electricity requirement, $kJ/kgCO_2$		
	Heat requirement, $kJ/kgCO_2$		
	Total energy (electricity equivalent), $kJ/kgCO_2$		

Technology Advantages:

- High CO_2 adsorption capacity.
- Good adsorption/desorption rates.
- Good hydrothermal stability.
- Environmentally friendly.

R&D Challenges:

- Effects of sulfur oxides (SO_X), and nitrogen oxides (NO_X) on the MOF material.
- The necessity for separating nitrogen (N_2) from CO_2 before further compression and transport.
- Need for large vacuum pumps to compress the CO_2 from the outlet of the VPSA.
- Pressure drop across the VPSA beds.

Results To Date/Accomplishments:

From the more than 50 MOF materials evaluated, two were selected for further development and testing. The CO_2 capacity for these MOFs was evaluated 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.

Next Steps:

- Collect more CO_2 adsorption data in moisture- and contaminant-containing streams.
- Explore new synthesis space by creating new MOFs.

Available Reports/Technical Papers/Presentations:

UOP MOF Sorbent – March 2009 Presentation, Existing Plants R&D Meeting, Pittsburgh, Pennsylvania.

Contract No.:

DE-FC26-07NT43092

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SRI International – Carbon-Based Sorbent

Project Title:

Development of Novel Carbon Sorbents for CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Sorbents	Bench-scale using simulated flue gas

Primary Project Goal:

SRI International is developing an innovative, low-cost, low-energy, carbon dioxide (CO_2)-consuming capture technology based on adsorption with a high-capacity and low-cost carbon sorbent. The project is validating sorbent performance in a bench-scale system for post-combustion applications and performing parametric testing to determine optimum operating conditions.

Technical Goals:

- Determine properties of the sorbent, such as surface area, heat of absorption and desorption, compressive strength and attrition resistance, and size and shape of sorbent particles.
- Validate the performance of the sorbent in a bench-scale, fixed-bed reactor.
- Perform parametric experiments to determine the optimum operating conditions for the system.
- Evaluate the technical and economic viability of the technology.

Technical Content:

The novel sorbent developed for the project is composed of carbon pellets, as shown in Figure 1. The sorbent was manufactured by ATMI, Inc., and is designated as ACS-1. The characteristics of the sorbent were tested using the BET adsorption technique and thermogravimetric analysis (TGA) under various temperatures, pressures, and gas exposures. These tests occurred in three stages: absorber parametric testing, regenerator parametric testing, and cyclic testing.

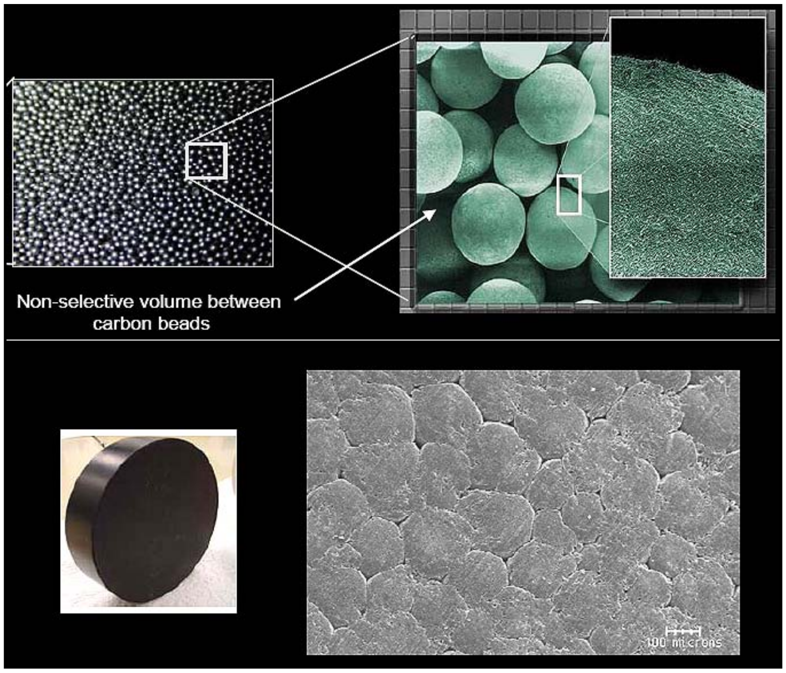

Figure 1: Graphic Displays of the Novel Carbon Pellets Sorbent

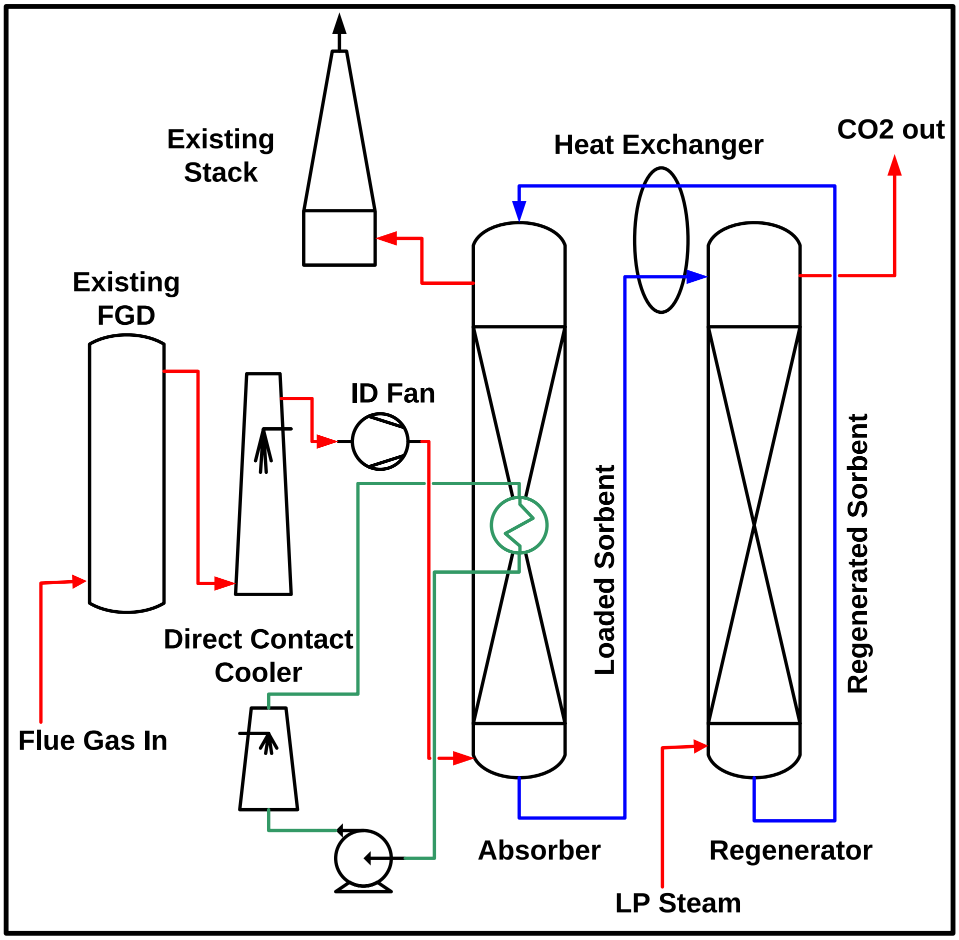

Figure 2: The Proposed Sorbent System

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 moving-bed adsorption reactor, which utilizes a high-capacity carbon sorbent (0.1 to 0.2 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 remaining gas and residues then exit through the existing power plant stack. When the sorbent reaches its capacity, becoming "loaded," it is removed from the adsorption bed and sent through a regeneration reactor. The regeneration reactor uses steam to heat the loaded sorbent to a moderate temperature (~100°C), releasing the trapped CO_2 from the sorbent. The CO_2 is siphoned off to a compressor where it can be prepared for sequestration. The regenerated sorbent is sent back into the adsorption reactor for re-use and the cycle begins again.

Table 1: Process Parameters for Solid Carbon Sorbent

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Carbon	Carbon
	Heat of adsorption (kJ/mole CO_2)	28	28
	CO_2 loading/working capacity, wt.%	5	8
	Surface area, m^2/g	1,600	1,600
	Particle density, cm^3/g	1.1	1.1
	Packing density, cm^3/g	0.7	0.7
	Particle size (mm)	0.2	0.2
	Heat capacity (kJ/K/kg)	1.0	1.0
	Thermal stability, °C	>400	>100
	Hydrothermal stability, °C	>100	>100

Process Configuration	Attrition rate (fluidized bed), %/year	<0.01[1]	<0.05[1]
	Cycle time (fixed bed), minutes	0.25[2]	N/A
	Pressure drop (fixed bed), psia	0.04[3]	N/A
Operating Conditions	Adsorption temperature, °C	15 to 25	25
	Adsorption pressure, atm.	1	1
	CO_2 capture efficiency, %	>95	>90
	Regeneration method	Direct steam	Indirect or direct
	Regeneration temperature, °C	80 to 100	100
	Regeneration pressure, atm.	1	1
Heat Integration	Required regeneration steam temperature, °C	100	100
Miscellaneous	Sorbent make-up rate, kg/kgCO_2	Not known	N/A
Product Quality	CO_2 purity, %	>95	>95
	N_2 concentration, %	<2	<10
	Other contaminants, %	Not available	SO_2, NO_X
Process Performance	Electricity requirement, kJ/kgCO_2	Not available	450[4]
	Heat requirement, kJ/kgCO_2	Not available	680[5]
	Total energy (electricity equivalent), kJ/kgCO_2	Not available	720[6]

Notes:

1. Measured by ASTM D5757 accelerated attrition testing; long-term attrition rate has not been established.
2. 0.25 minutes estimated in a moving bed.
3. At a space velocity corresponding to 95% capture of air-15% CO_2 mixture.
4. Includes electricity for compression of released CO_2 to 150 atm.
5. No heat recovery savings is accounted.
6. Based on simulation of PC-fired boiler from coal to electricity enabling CO_2 capture and compression.

Technology Advantages:

- The sorbent has a low cost and a stable operating range of 20°C to 100°C.
- The sorbent has a high capacity of CO_2 loading with 0.1 to 0.2 kg of CO_2 per kg of sorbent.
- The sorbent features a low heat of adsorption reaction of 25 to 28 kJ/mole of CO_2 and releases CO_2 at atmospheric pressure at a low temperature of 80°C to 100°C.

R&D Challenges:

- Other elements of the flue gas, such as moisture, sulfur oxides (SO_X), and nitrogen oxides (NO_X), may compete with CO_2 in being adsorbed by the sorbent, reducing the amount of CO_2 that gets adsorbed as the gas passes through the reactor.
- A low temperature needs to be maintained for optimal adsorption conditions. Excess heat may have to be removed from the adsorption reactor in addition to the flue gas being cooled prior to treatment by the sorbent.
- The heat exchange between the cold, loaded sorbent and regenerated, hot sorbent will have to be kept to a minimum to maintain optimal temperatures for the adsorption process.

Results To Date/Accomplishments:

- Determined the CO_2 adsorption and desorption characteristics and the heat of adsorption for the carbon sorbent.
- Determined the CO_2 loading on the sorbent as a function of CO_2 partial pressure and temperature.
- The desorption characteristics were tested in a temperature range of 40°C to 100°C using a TGA.
- Evaluated several physical, chemical, and mechanical properties of the sorbent in the context of the CO_2 capture system using a bench-scale, fixed-bed reactor.

- Demonstrated >95% CO_2 capture in a moving bed from air containing 15% CO_2 at ambient temperature.
- Demonstrated regeneration using direct contact steam producing relatively pure CO_2.
- Simulation of CO_2 capture using novel carbon sorbent in a PC-fired boiler from coal to electricity and compressed CO_2.

Next Steps:

- Conduct parametric testing on the absorber and regenerator, including gas velocity, temperature, CO_2 inlet level, sorbent pellet size and geometry, heating method, and the presence of SO_X or NO_X.
- Design and Construct a bench-scale system for testing.
- Conduct 100 cycle tests on select sorbents.
- Conduct a long-term (1,000 cycle) test on the superior sorbent to determine durability.

Available Reports/Technical Papers/Presentations:

Development of Novel Carbon Sorbents for Carbon Dioxide Capture – Hornbostel, Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 2009.

Development of Novel Carbon Sorbents for Carbon Dioxide Capture – Continuation application report submitted to U.S. Department of Energy, August 2009.

Contract No.:

DE-NT0005578

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ATMI, Inc.

ADA-ES – Evaluation of Solid Sorbents

Project Title:

Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture from Coal-Fired Power Plants

Technology Area:

Post-Combustion Sorbents

Technology Maturity:

Pilot-scale using actual flue gas, 1 kW, 0.05 tonnes of CO_2/day

Primary Project Goal:

ADA-ES is assessing the viability and advancing the development of solid sorbent carbon dioxide (CO_2) capture technology for retrofitting coal-based power plants.

Technical Goals:

- Identify and characterize promising sorbents from multiple developers.
- Design, fabricate, and demonstrate a 1-kW slipstream pilot (0.14 m^3/min ≈ 5 [acfm]).
- Complete a technology survey to identify equipment applicable to commercial-scale sorbent processes.
- Complete a preliminary conceptual design and cost estimate for a CO_2 capture process in a 500-MW plant.
- Complete a preliminary design for a 1-MW pilot plant incorporating the new capture process.

Technical Content:

The CO_2 sorbents being investigated can be used in a temperature swing adsorption (TSA) process. Sorbents included in the investigation will be procured from various CO_2 solid sorbent developers. Evaluation of the sorbents will be based on the availability of raw material, manageable disposal costs (low toxicity), CO_2 working capacity, specific heat, temperature change required for regeneration, interaction with flue gas components (sulfur oxides [SO_X] and nitrogen oxides [NO_X]), and adequate strength to minimize wear on the sorbent. Table 1 displays the key properties used to evaluate CO_2 sorbents.

Table 1: Key Properties Used to Evaluate CO_2 Sorbents

Physical Property	Current Range	Goal
Sorbent Particle Size (mm)	Highly varied and controllable	~1 – 10
Sorbent Surface Area (m^2/g)	0.5 – 3,000	0.5 – 1,500
Sorbent Active Component Concentration (wt%)	5 – 100	10 – 100
Shape of Sorbent	Varied	Spherical
Density of Sorbent (g/cm^3 [lb/ft^3])	0.6 – 2.6	Dependant on contractor design
Mechanical Strength	Not reported	Dependant on contractor design
Attrition Fines: Form, Processing, and Fate	Not reported	To be determined

The lab-scale tests consist of <3 grams of the adsorbents exposed to simulated flue gas and then regenerated by a temperature swing. For the adsorption step, the simulated flue gas is 55°C (130°F) with oxygen (O_2) and CO_2 concentrations of 4% and 12%, respectively. The moisture level can be varied (usually 0% or 90% relative humidity). The regeneration temperature is between 65°C to 250°C (150°F to 480°F). After the adsorbents are tested at laboratory scale, the most positively rated adsorbents will be tested at 1-kW pilot scale. Table 2 displays a matrix of the adsorbents tested and the assessment results from the initial laboratory screening.

Table 2: Test Matrix of the Adsorbents and Results from the Initial Laboratory Screening

	Supported Amines	Carbonates	Carbon	Zeolites
Working Capacity	High	High	Low	Low
Thermal Stability	Low	High	High	High
Theoretical Regeneration Energy (vs. aqueous MEA)	Lower	Higher	Similar	Higher
Issues	SO_2	SO_2	Working Capacity	Moisture

After the initial laboratory screening of the sorbents, larger quantities (~90 kg [200 pounds]) of the best materials will then be evaluated in a 1-kW slipstream pilot. Testing is scheduled at three coal-fired power plants burning bituminous, subbituminous, and lignite coals. This flue gas is expected to have temperatures of 60°C (140°F), a CO_2 concentration of 10% to 12%, saturated moisture, oxygen (5% to 6%), NO_X (100 parts per million [ppm] to 120 ppm), SO_2 (50 ppm to 250 ppm). Flue gas pretreatment equipment will allow ADA to control the SO_2, moisture, temperature, and pressure of the flue gas entering the reactor. The 1-kW pilot tests will be parametric in nature to characterize sorbent performance under a range of realistic conditions. In addition, during the parametric tests sufficient process and sorbent performance information will be collected to complete a preliminary, 500-MW conceptual process design and economic evaluation. The following diagram represents the circulating transport reactor that will be employed for the 1-kW pilot tests. A photo of the equipment is also shown.

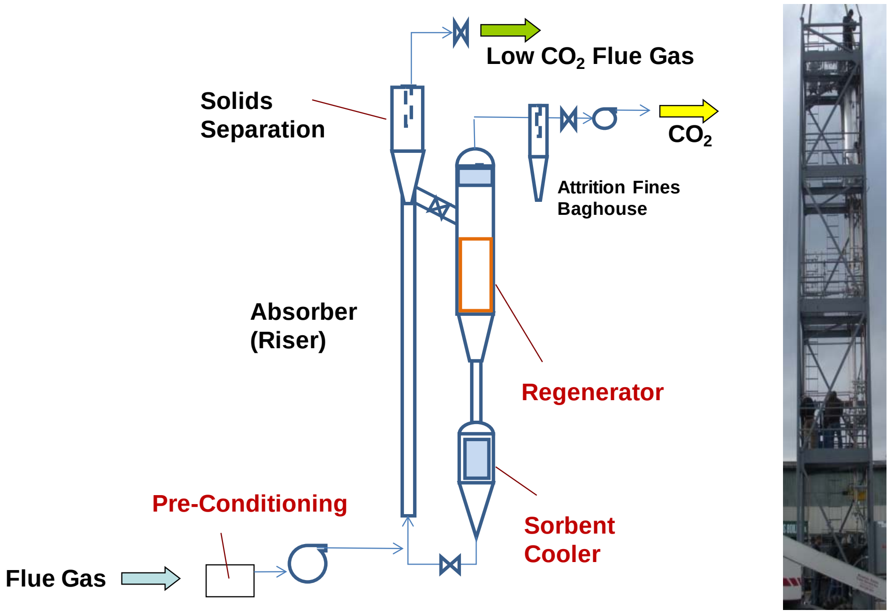

Figure 1: Diagram and Image of Circulating Transport Reactor

Various process concepts will be evaluated for their applicability to post-combustion CO_2 capture using TSA. A preliminary, 500-MW conceptual design will be developed for the process that meets several technical requirements including criteria set for regeneration and solids handling, engineering maturity, and favorable projected capital and operating costs. Only those process concepts that can reasonably meet a commercialization target of 2020 were considered mature enough to progress to the design phase under this project. Preliminary conceptual engineering will include process modeling to determine the cost implications for direct and indirect heating and cooling of the sorbents, capital and operating cost estimates, and preliminary sizing of major equipment.

Many of the research and development targets that will be considered include those listed in Table 3.

Table 3: Process Parameters for Solid Sorbent

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	Supported amine, activated carbon	N/A
	Heat of reaction (kJ/mole CO_2)	~ -60	-60
	CO_2 loading/working capacity, wt.%	14	≥ 15 (stable)
	Surface area, m^2/g	20 – 1,500	TBD
	Particle density, g/cm^3	Pending	TBD
	Bulk density, g/cm^3	0.3 to 0.7	TBD
	Particle size (□m)	30-100	30-100
	Heat capacity (kJ/kg·K)	1.4	0.8 – 1.3
	Thermal stability, °C	100	150
	Hydrothermal stability, °C	Not measured	150
Process Configuration	Attrition rate (fluidized bed), %/year	Not measured	≤ 50
	Cycle time, minutes	Depends on contactor	≤30
	Pressure drop, psia	0.54	0.5
Operating Conditions	Adsorption temperature, °C	55	55
	Adsorption pressure, atm.	1	1
	CO_2 capture efficiency, %	100 (Lab-scale)	90
	Regeneration method	Temperature swing	Temperature swing
	Regeneration temperature, °C	100	100
	Regeneration pressure, atm.	1 (Lab-scale total pressure)	1
Heat Integration	Required regeneration steam temperature, °C	Not measured	120
Miscellaneous	Sorbent make-up rate, kg/kg CO_2	Will be measured for 1 kW pilot	≤0.0005
Product Quality	CO_2 purity, %	20% (Lab-scale with N2 purge)	≥95
	N_2 concentration, %	Not measured	≤5
	Other contaminants, %	Not measured	≤1
Process Performance	Parasitic Electricity requirement[1], kJ/kgCO_2	Not measured	≤20
	Heat requirement, kJ/kgCO_2	Not measured	≤1,500
	Total energy (electricity equivalent)[2], kJ/kgCO_2	Not measured	≤1,800

1. Does not include makeup power or CO_2 compression.

2. Includes compression (estimated at 0.1 MW/ton CO_2).

Technology Advantages:

- Reduction in the regeneration energy requirements by minimizing heat input (no liquid solvent is involved).
- High sorbent working capacities have been demonstrated (lab-scale).
- Fundamental sorbent chemistry is well-know (e.g., amine).
- Components of process equipment are mature (e.g., circulating fluidized bed).

R&D Challenges:

- Minimizing physical attrition.
- Long-term cyclic stability (including the effect of flue gas constituents).
- Minimize equipment footprint.

- Minimize operating and maintenance costs (e.g., minimize moving parts).
- Reduce compression to minimize costs.

Results To Date/Accomplishments:

Lab-Scale Sorbent Screening Results

- Completed laboratory and field tests.
- Completed initial evaluations of the effect of flue gas constituents on sorbent performance.
- Measured working capacity (zero to 14 wt%).
- Measured consistent performance (>260 cycles tested).
- Measured the temperature change required between capture and regeneration (15°C to 195°C).
- Calculated the theoretical regeneration energy (1620 kJ/kg CO_2 to 93,000 kJ/kg CO_2).

1-kW Slipstream Pilot

- Designed and fabricated a 1-kW pilot contactor.
- Installed at Field Site 1.
- Checkout operations underway.
- Procured pilot-scale quantities of three sorbents.
- Produced supported amine sorbents using techniques applicable to commercial-scale manufacturing.

Commercial-Scale Equipment

- Completed a technology survey of equipment and process options.
- Assessed merits of various technologies for this application.
- Completed a high level economic comparison of economic options.
- Completed a final technology selection that will be used for a preliminary 500-MW conceptual design.
- Preliminary assessment of upstream and downstream balance-of-plant impacts.

Next Steps:

- Complete fundamental laboratory analysis of most promising sorbents (e.g., crush strength, heat of adsorption, single and multiple gas isotherms, hydrothermal stability, etc.).
- Conduct parametric field tests at three test sites.
- Assess full-scale equipment design criteria based on lab and 1-kW pilot results.
- Develop capital and operating costs for the selected technology.
- Conduct cursory life cycle CO_2 emissions estimate.
- Develop a preliminary 500-MW conceptual plant design and plant cost estimate.

Available Reports/Technical Papers/Presentations:

Quarterly Technical Reports to the DOE from 4Q08 to 4Q09.

Sjostrom, S.; Krutka, H.; Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture, *Fuel*, accepted for publication, November, 2009.

Sjostrom, S.; Campbell, T.; Krutka, H.; O'Palko, A. *Solid Sorbents as a Retrofit CO2 Capture Technology: Results from Pre-Pilot Field Testing*, Air Quality VII Conference, Arlington, Virginia, October 27, 2009. (Presentation and Paper).

Evaluation of Solid Sorbents as a Retrofit Technology for CO_2 Capture from Coal-Fired Power Plant - Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting - March 2009.

Results from Lab and Field Testing of Novel CO_2 Sorbents for Existing Coal-Fired Power Plants- Power Plant Air Pollutant Control "Mega" Symposium in Baltimore, Maryland - August 2008.

Summary of Post-Combustion CO_2 Capture Technologies for Existing Coal-Fired Power Plants, Air & Waste Management Association Annual Conference, paper #808, Portland, OR, June 24-26, 2008.

Contract No.:

DE-NT0005649

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APPENDIX

POST-COMBUSTION MEMBRANES

Carbozyme – Biomimetic Membranes

Project Title:

Development of Biomimetic Membranes for Near-Zero PC Power Plant Emissions

Technology Area:	**Technology Maturity:**
Post-Combustion Membranes	Pre-pilot scale, 1 tonne of CO_2/day

Primary Project Goal:

Carbozyme is developing an enzyme-based, contained liquid membrane (CLM) to extract carbon dioxide (CO_2) from coal and natural gas combustion flue gas. Carbozyme is also evaluating a state-of-the-art electrodialytic (EDI) method for CO_2 capture and comparing its performance with that of the CLM.

Technical Goals:

- Scaleup the enzyme-catalyzed, CLM permeator design (4 m^2 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:

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 being developed by Carbozyme. 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 promote 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).

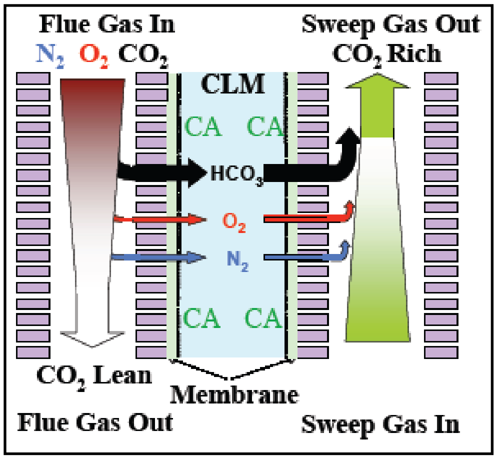

Figure 1: Configuration for Carbozyme-Developed, Enzyme-Based Carbonic Anhydrase Contained Liquid Membrane

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% pure CO_2 stream. The remaining flue gas is sent to the plant stack.

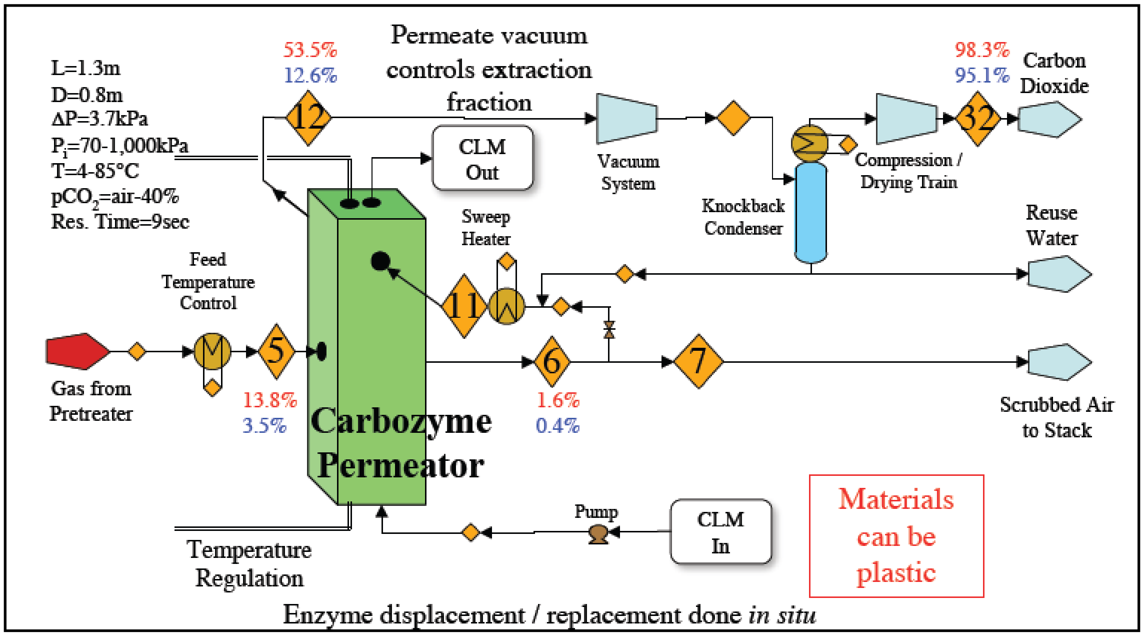

Figure 2: Process Schematic for the Carbonic Anhydrase Contained Liquid Membrane

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 30-50% 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.
- Carbozyme estimates the CA CLM's CO_2 capture cost to be less than $20 per tonne.

R&D Challenges:

- The potential demand for membranes could exceed current manufacturing capacity. The manufacturing capacity for these technologies will have to be expanded before implementation on an industry-wide scale.
- 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.

Results To Date/Accomplishments:

Progress has been made in several categories, such as flue gas stream analysis and conditioning, enzyme selection, enzyme immobilization, membrane module construction, economic analysis, and EDI.

Specific accomplishments include:

- Fabricated a sulfur oxide (SO_X) polisher that exceeds the baseline requirements.
- Secured the CA enzyme from a stable supplier.
- Demonstrated CA enzyme immobilization with a 0.5 m^2 CLM module.

- Constructed and tested a 0.5 m^2 CLM with spiral-wound, hollow-fiber woven array sheets that demonstrated performance close to the program objectives of 90% capture and 95% CO_2 purity.
- Fabricated an 11 m^2 CLM module for scaleup testing.
- Developed a monoethanolamine (MEA) base case engineering and economic analysis that can estimate overall capital costs, levelized cost of electricity (LCOE), and CO_2 removal for a supercritical pulverized coal plant.
- Developed and tested a novel EDI cell for capturing CO_2.

Next Steps:

Project #43084 was completed July 2009. Final report not available.

Available Reports/Technical Papers/Presentations:

"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.

Contract No.:

DE-FC26-07NT43084
DE-FG26-06NT42824

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SRI
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Research Triangle Institute – Hollow-Fiber, Polymeric Membranes

Project Title:

CO_2 Capture Membrane Process for Power Plant Flue Gas

Technology Area:

Post-Combustion Membranes

Technology Maturity:

Pilot-scale using actual flue gas

Primary Project Goal:

Research Triangle Institute (RTI) is developing an advanced hollow-fiber, polymeric membrane-based process that can be cost-effectively retrofitted into current pulverized coal (PC)-fired power plants.

Technical Goals:

- Develop new fluorinated polymer membrane materials that have excellent chemical stability to moisture, sulfur dioxide (SO_2), and nitrogen oxide (NO_X) contaminants present in flue gas; 30 to 50 selectivity for carbon dioxide (CO_2) over nitrogen (N_2); and a 300 to 3,000 gas permeance unit (GPU) permeance for CO_2.
- Identify and develop CO_2 capture membrane process integration strategies.
- Develop and fabricate improved membrane hollow fibers and module designs to handle large flue gas flow rates and a high CO_2 permeance.
- Demonstrate CO_2 capture performance and reliability of membrane modules using actual coal-fired process flue gas.

Technical Content:

RTI's research effort includes membrane materials development, module design, and process design.

RTI is pursuing the development of two hollow-fiber membrane materials. First, RTI is working with Generon to develop a membrane material constructed of polycarbonate-based polymers. Standard polycarbonate is being used as a baseline for comparison to next generation polycarbonates. Lab-scale membrane modules are being studied with simulated flue-gas mixtures with and without flue gas emission contaminants. Two larger-scale polycarbonate membrane module prototypes are being tested with a slipstream of actual flue gas from the U.S. Environmental Protection Agency's (EPA) Multipollutant Combustion Research Facility (MPCRF).

RTI is also working with Arkema to develop the second membrane material constructed of polyvinylidene fluoride (PVDF)-based polymers. A PVDF molecule is comprised of a $[CH_2\text{-}CF_2]_n$ repeat unit, as shown in Figure 1. PVDF is well suited to contact with flue gas, possessing a high resistance to acids and oxidants, a specific affinity to CO_2 and a high CO_2 solubility, and a high thermal stability ($T_d \sim 340°C$). PVDF also features excellent physical and mechanical properties, durability, and longevity suited to the weaving process used for the hollow fiber tube fabrication. Conventional PVDF comes as a homopolymer with semicrystalline properties, a CO_2 permeance of ~5 GPU, and a CO_2/N_2 selectivity of ~23. Arkema is developing advanced PVDF materials to improve its permeance and selectivity parameters.

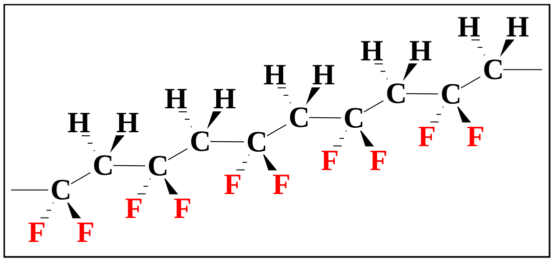

Figure 1: PVDF Molecule

Figure 2 shows a cross-section of a hollow-fiber membrane module. Multiple modules will be utilized in a given CO_2 capture system for power plant applications due to the large quantity of flue gas to be processed. A module consists of numerous small diameter hollow fibers. As the flue gas flows through the fibers, CO_2 preferentially flows across the fiber walls (permeate). The remaining flue gas (retentate) flows out of the membrane module and to the plant stack for discharge to the atmosphere.

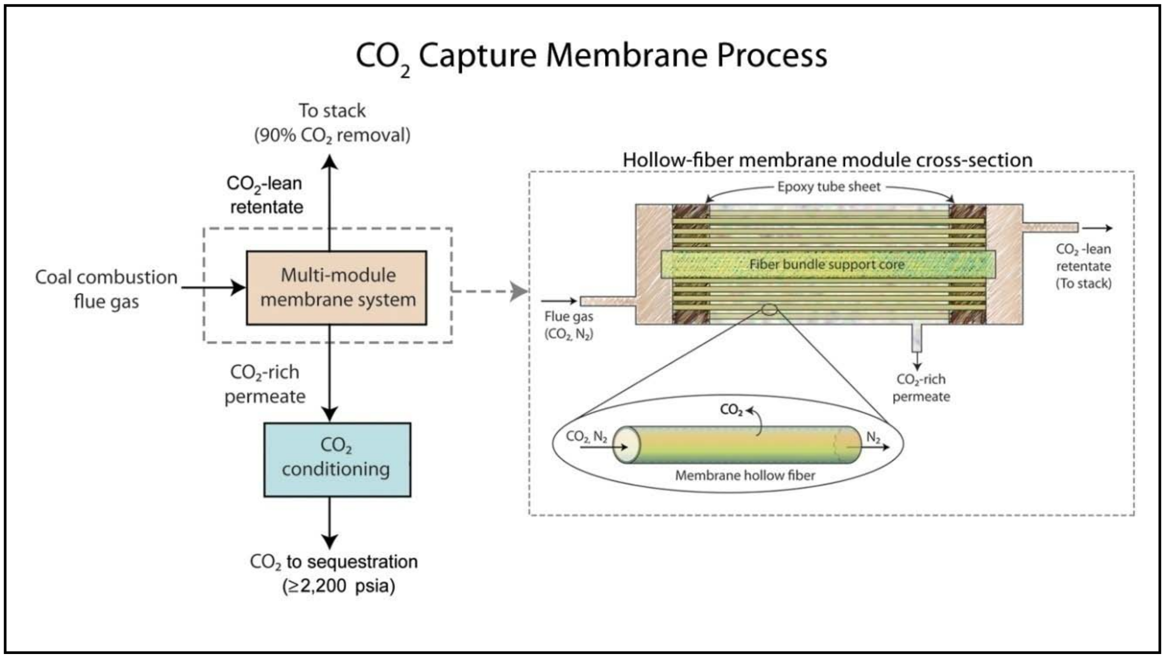

Figure 2: Cross-Section of a Hollow-Fiber Membrane Module

Process simulations for a single-stage membrane process are being conducted to determine the sensitivity of CO_2 removal performance and permeate CO_2 purity on different parameters, including membrane flux, membrane selectivity, membrane fiber dimensions, and membrane pressure driving force.

Technology Advantages:

Membranes could provide PC-fired power plants with a cost-effective method for CO_2 capture. The membrane module system is relatively easy to install within an existing PC-fired plant and does not require any major modifications to the existing equipment and infrastructure. The membrane utilizes passive separation of gases, making it energy efficient because it does not require regeneration energy, as do solvent and sorbent processes. The module's compact design and ability to link with hundreds of modules in tandem makes the hollow fiber membrane system easy to scale and retrofit. The membrane also lacks any moving parts, meaning there is no risk of a mechanical failure.

R&D Challenges:

The flue gas properties may pose certain challenges when using a membrane module. A low CO_2 concentration of 13% to 15%, a low gas pressure of 1 atm, large volumes of gas, and the presence of moisture and contaminants (sulfur oxide [SO_X], NO_X, and particulate matter) can all pose potential challenges to the membrane technology. The compression of the flue gas and CO_2 permeate tends to have a high parasitic energy cost. The fabrication process for the hollow fiber tubes is susceptible to defects and pressure drop issues. The fiber weaving process and module housing design will need to be optimized to achieve the desired flow distribution and other benchmarks.

Results To Date/Accomplishments:

- Four lab-scale modules made from Generon's standard polycarbonate hollow fibers were investigated at 23-25°C and feed pressures up to 200 psig with pure N_2, oxygen (O_2), and CO_2; a mixture of 15% CO_2 in N_2; and a mixture containing 290 parts per million (ppm) SO_2, 15% CO_2, and balance N_2. The two smaller modules (0.75 ft^2 area) showed CO_2 permeance in a range of 70 to 150 GPU, and their CO_2/N_2 selectivity ranged from 20 to 40. However, the two larger modules (100 ft^2 area) gave only a CO_2 permeance of 17 to 24 GPU and CO_2/N_2 selectivity of nine to 12. RTI suspects this result for the larger modules is associated with the significant decrease in pressure driving force for the CO_2 as its permeation occurs down the length of the fibers.

- Arkema's fluoropolymer membrane material has shown improved flux (approximately 700 to 800 GPU) and selectivity, but it has not yet been formed into a hollow fiber.

Next Steps:

- Synthesize novel polymers and membrane films and produce membrane hollow fibers.
- Fabricate lab-scale, hollow fiber membrane modules leading to the construction of a membrane test skid.
- Gather separation performance data on lab-scale membrane modules made from standard polycarbonate membrane hollow fibers to formulate a baseline for future tests.
- Identify the CO_2 capture membrane process system design options and their respective process flow schemes.
- Conduct 300 hours of field testing for the CO_2 capture membrane test skid with real coal-fired flue gas.
- Complete a techno-economic evaluation of the "best" integrated/retrofitted CO_2 capture membrane process package developed during the project.

Final test results will not be available until the December 2010 project completion date.

Available Reports/Technical Papers/Presentations:

"CO_2 Capture Membrane Process for Power Plant Flue Gas," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.

Contract No.:

DE-NT0005313

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Arkema
Arcadis G&M
Generon IGS
U.S. EPA

Membrane Technology and Research – Spiral-Wound, Polymeric Membranes

Project Title:

Membrane Process to Capture Carbon Dioxide from Coal-Fired Power Plant Flue Gas

Technology Area:	**Technology Maturity:**
Post-Combustion Membranes	Pilot-scale slipstream on actual flue gas, 1 tonne of CO_2 per day

Primary Project Goal:

Membrane Technology and Research, Inc. (MTR) is developing a spiral-wound, polymeric membrane and associated process for carbon dioxide (CO_2) capture. The project includes conducting a slipstream field test using full-scale commercial membrane modules to treat combustion flue gas at a coal-fired power plant.

Technical Goals:

- Develop a thin film, composite, polymer-based membrane to increase CO_2 permeance while maintaining CO_2/nitrogen (N_2) selectivity.
- Utilize incoming combustion air in a countercurrent sweep membrane module design to generate separation driving force and reduce the need for vacuum pumps and the associated parasitic energy cost.
- Fabricate commercial-scale membrane modules that meet low pressure drop and high packing density performance targets.
- Conduct a six-month field test of a membrane system at Arizona Public Services' (APS) Cholla Power Plant; the system will process 7,000 standard m^3/day (0.25 MMscfd) of flue gas, separating about one tonne of CO_2/day.
- Analyze the performance of the membrane system, determine how it would be best integrated with a coal-fired power plant, and prepare a comparative study of the membrane-based CO_2 capture process versus other capture technologies.

Technical Content:

MTR is developing composite membranes with high CO_2 permeance and high CO_2/N_2 selectivity for post-combustion flue gas applications. Tests indicate the membrane has 10 times the CO_2 permeance of conventional gas separation membranes. The combination of these membranes with a novel counter-current module design that utilizes incoming combustion air to generate separation driving force greatly reduces the projected cost of CO_2 capture. MTR is developing a commercial-scale membrane module that can meet low pressure-drop and high packing-density performance targets. This thin-film membrane utilizes hydrophilic rubbery polymers and is known by the trade name "Polaris^{TM}."

Spiral-wound membrane modules are the most commonly used design for commercial membrane installations today. Spiral-wound modules are robust, resistant to fouling, and economical; they are used in 95% of the reverse osmosis desalination industry and 30% of the industrial gas separation market. Figure 1 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.

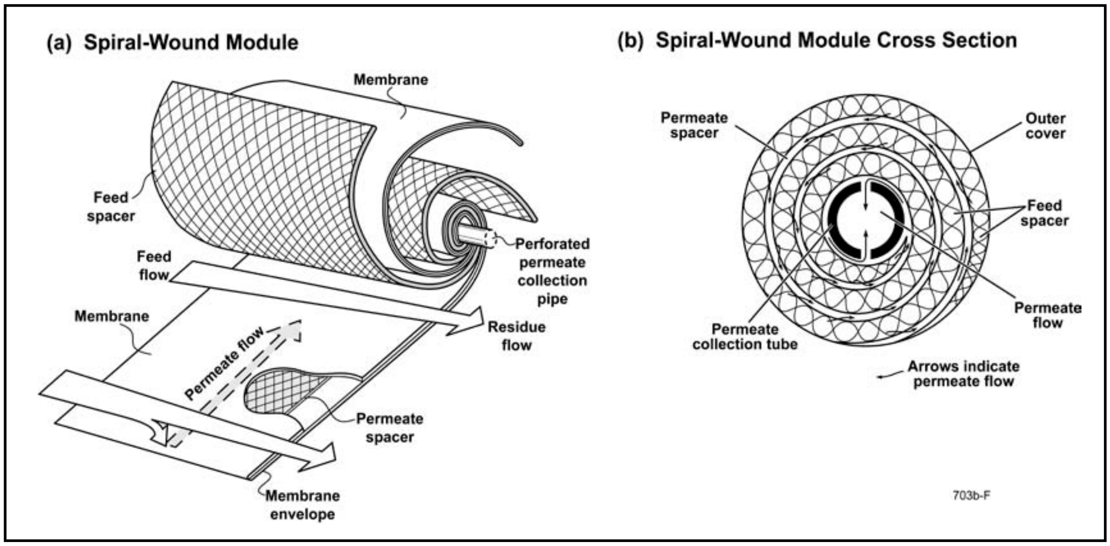

Figure 1: General Design Features of a Spiral-Wound Membrane Module

A schematic comparison of gas flow characteristics for a conventional spiral-wound membrane and the countercurrent sweep module is shown in Figure 2. The countercurrent sweep module is a modified version of the spiral-wound module that utilizes sweep gas on the permeate side and operates in a partial countercurrent pattern. This countercurrent sweep module permits the use of air as a sweep gas, which increases CO_2 flux through the membrane without requiring additional compression energy.

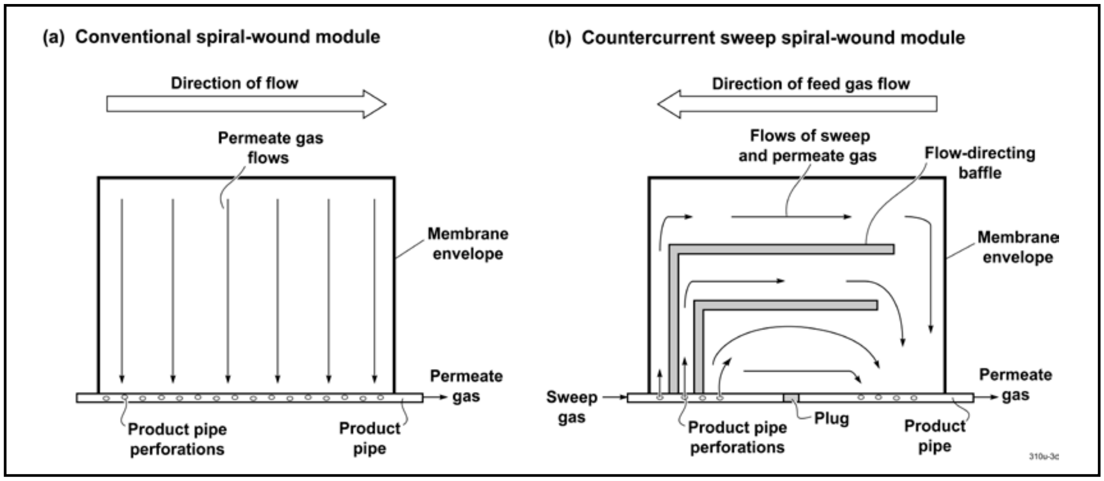

Figure 2: Schematic Comparison of Gas Flow Characteristics for a Conventional Spiral-Wound Membrane and the Countercurrent Sweep Module

Figure 3 shows the process design for the membrane system. The process includes two types of membrane arrangements – a conventional cross-flow module and a novel countercurrent sweep module. First, the combustion flue gas enters a cross-flow module, which removes most of the CO_2. The retentate from the cross-flow module is then fed into a countercurrent sweep module, from which the permeate is recycled back to the boiler via an air sweep, which increases the CO_2 concentration of the flue gas entering the initial cross-flow module. The CO_2-rich permeate from the cross-flow module is then dehydrated and compressed. A second stage cross-flow module is used after compression to further enrich the CO_2 stream by recycle of the permeate back to the inlet of the compressor.

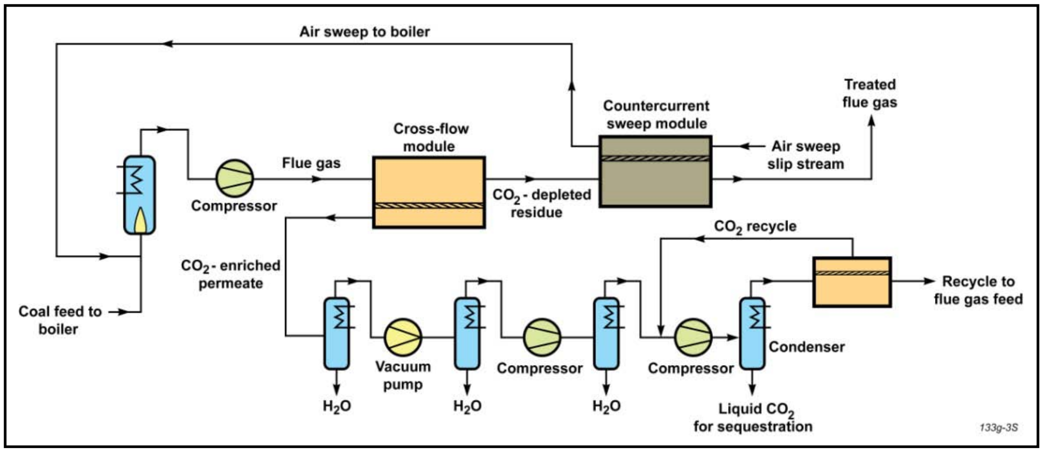

Figure 3: Process Design for the Membrane System

MTR estimates that a 0.5-1.0 million m^2 total membrane area is required to achieve 90% CO_2 capture for a 550-MW plant using this process design and would consume approximately 15- 18% of the plant's gross power output. Figure 4 shows a proposed design for a full-scale membrane system. Each set of modules would be 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 power plant (current RO plants already use similar numbers of modules and module skids.).

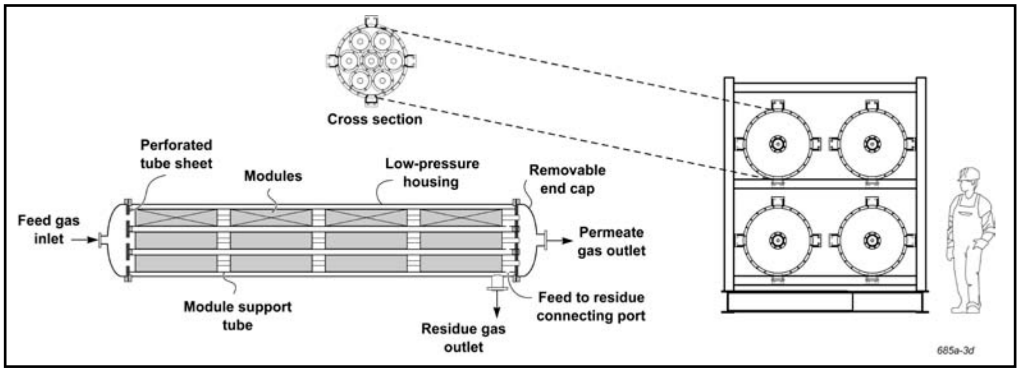

Figure 4: Proposed Design for Full-Scale Membrane System

Figure 5 shows the membrane skid that will be used for the six-month pilot-scale slipstream test being conducted at the coal-fired Cholla Power Plant operated by APS. The skid can hold up to eight (four cross-flow and four countercurrent sweep) eight-inch diameter Polaris^{TM} membrane modules. The membrane skid is designed to capture one tonne of CO_2 per day from a 7,000 standard m^3/day (250,000 scfd) flue gas slipstream. The test will demonstrate membrane operations in commercial-scale modules and determine typical membrane lifetimes under coal combustion flue gas operating conditions.

Figure 5: Membrane Skid Used for Six-Month Pilot-Scale Slipstream Test Conducted at APS's Cholla Power Plant

Table 1: Membrane Process Parameters

	Parameter	**Current R&D Value**	**Target R&D Value**
Membrane Properties	Materials of fabrication for selective layer	polymer	polymer
	Materials of fabrication for support layer (if applicable)	polymer	polymer
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology CO_2/N_2 for post-combustion technology	25	25
	Type of selectivity measurement (ideal or mixed gas)	mixed	mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	1,000	1,500+
	Temperature, °C	50	50
	Bench-scale testing, hours without significant performance degradation	500	500
	Pilot-scale testing (if applicable), hours without significant performance degradation	500+ (natural gas)	5,000 (coal)
	Maximum pressure differential achieved without significant performance degradation or failure, bar	70	70
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	spiral	spiral
	Packing density, m^2/m^3	700	1,000
	Pressure drop, bar	0.1	<0.05
	Estimated cost of manufacturing & installation, $\$/m^2$-GPU or equivalent	0.5	0.1
Product Quality	CO_2 purity, %	No data	98+
	N_2 concentration, %	No data	1
	Other contaminants, %	No data	<0.1
Process Performance	Electricity requirement, kJ/kgCO_2	No data	750
	Cooling requirement, kJ/kgCO_2	No data	150
	Total energy (electricity equivalent), kJ/kgCO_2	No data	900

Other Membrane Parameters:

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 will be examined in the upcoming Cholla field demonstration.

Flue gas pretreatment requirements: Currently, pretreatment requirements are unknown. The upcoming Cholla test will treat post-FGD flue gas and will clarify the need for gas treatment prior to entering the membrane system. Of the species present in flue gas, the greatest concern 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% of the H_2O in flue gas as liquid. The quality of this H_2O, and its potential to be re-used in the plant, will be studied in future work.

Technology Advantages:

- The membranes developed are 10 times more permeable to CO_2 than conventional membranes, which reduces 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 of 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 cross-flow membrane stage, reducing the required membrane area and total system cost.

R&D Challenges:

- The membrane process requires a large membrane surface area to achieve separation due to the low partial pressure of CO_2 in flue gas.
- The countercurrent sweep module design could result in several potential inefficiencies including: sweep-side pressure drop, concentration polarization, poor utilization of the membrane area due to module geometry, and non-countercurrent flow patterns.
- Particulate matter needs to be controlled to reduce its potential impact on the membrane lifetime.
- Feed and permeate side pressure drops may lead to excessive energy losses.
- Cost reductions for the membrane 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 plant.

Results To Date/Accomplishments:

- Scaled up and produced high permeance membrane formulations on commercial casting and coating equipment. Produced more than 500 m^2 of Polaris^{TM} membrane material used to construct 203 mm (eight-inch) diameter commercial-sized conventional cross-flow and novel countercurrent sweep modules.
- Field tested pilot- and commercial-scale membrane modules with various industrial gas streams (raw natural gas, and synthesis gas [syngas] containing sulfur species) for up to three months of continuous operation. The modules showed stable performance throughout these tests.
- Field tests revealed the membrane permeance is 10 times higher than existing materials and the membranes possess good stability in acid gases.
- Provided a membrane system to APS to process 4,250 m^3/day (0.15 MMscfd) of natural-gas fired flue gas to provide concentrated CO_2 for testing at an experimental algae farm.
- Designed and built a membrane system that will process 7,000 m^3/day (0.25 MMscfd) of coal-fired flue gas and capture one tonne CO_2/day from the Cholla power plant operated by APS. The system will begin operation in early 2010.
- MTR estimates the membrane-based CO_2 separation and liquefaction process can capture 90% CO_2 using 15-18% of the plant's energy and cost \$20-\$30 per tonne of CO_2 captured.

Next Steps:

- Conduct a six-month field test at the coal-fired Cholla Power Plant.
- Develop plans for a larger, pilot-scale 20 tonne CO_2 per day membrane capture system.
- Lower the membrane module cost by incorporating low-cost components with a target of $150/m^2.
- Integrate a CO_2 liquefaction section into the overall CO_2 capture system.
- Test options for recycling the air sweep from the countercurrent sweep module to the boiler.

Final test results will be available at the December 2010 project completion date.

Available Reports/Technical Papers/Presentations:

"Power plant post-combustion carbon dioxide capture: An opportunity for membranes," Journal of Membrane Science (2009), doi:10.1016/j.memsci.2009.10.041.

"A Membrane Process to Capture CO_2 from Coal-Fired Power Plant Flue Gas," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.

"The Membrane Solution to Global Warming," 6th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 2007.

Contract No.:

DE-NT0005312 and FC26-07NT43085

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University of New Mexico – Dual Functional, Silica-Based Membranes

Project Title:

Novel Dual Functional Membrane for Controlling Carbon Dioxide Emissions from Fossil-Fueled Power Plants

Technology Area:

Post-Combustion Membranes

Technology Maturity:

Laboratory-scale using simulated flue gas

Primary Project Goal:

The University of New Mexico is developing 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 Ni-doping approach.
- Prepare an ultra-thin silica membrane using a plasma-assisted, atomic layer deposition technique (PA-ALD).

Technical Content:

The dual-functional, silica-based membrane is prepared by a unique sol-gel dip-coating process for depositing a microporous amino-silicate membrane on a porous tubular ceramic support. It consists of a microporous inorganic siliceous matrix, with amine functional groups 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.

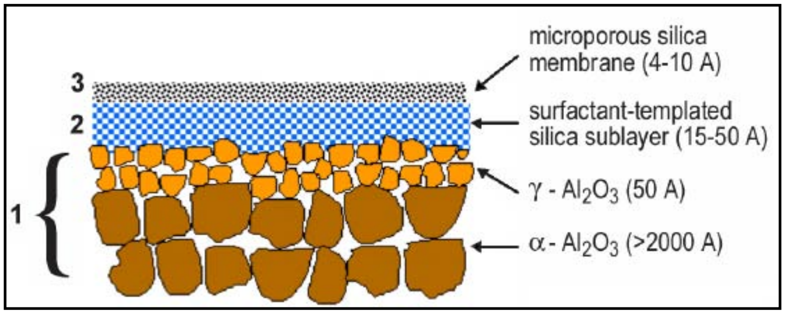

Figure 1: Cross-Section of Membrane

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Aminosilicate/doped-silicate	Aminosilicate/doped silicate
	Materials of fabrication for support layer (if applicable)	Surfactant-templated silica on alumina	Surfactant-templated silica on alumina
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology; CO_2/N_2 for post-combustion technology	CO_2/N_2=80-100 (dry feed); CO_2/N_2 = 50-60 (humidified feed)	CO_2/N_2 = 100
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	CO_2: 400 GPU	CO_2: 1,000 GPU
	Temperature, °C	25-250°C	25-80°C
	Bench-scale testing, hours without significant performance degradation	168 hrs	100 hrs
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3 bar	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Hollow-fiber
	Packing density, m^2/m^3	500	980
	Pressure drop, bar	0.01-0.02	0.01-0.02
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	$0.33-$0.39/m^2-GPU	N/A
Product Quality	CO_2 purity, %	>90%	90%
	N_2 concentration, %	<10%	10%
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kgCO_2	1313 kJ/kgCO_2 or 0.365 kWh/kgCO_2	1333 kJ/kgCO_2 or 0.370 kWh/kgCO_2
	Heat requirement, kJ/kgCO_2	0	0
	Total energy (electricity equivalent), kJ/kgCO_2	1313 kJ/kgCO_2 or 0.365 kWh/kgCO_2	1333 kJ/kgCO_2 or 0.370 kWh/kgCO_2

Note: Values for membrane properties are experimental. Other values are calculated based on membrane properties.

Contaminant Resistance: SO_2 > 10 parts per million (ppm).

Flue Gas Pretreatment Requirements: Particulate removal.

Waste Streams Generated: N/A.

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°C 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:

Project completed April 2009. Final report not yet available.

Available Reports/Technical Papers/Presentations:

"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.

Contract No.:

DE-FG26-04NT42120

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APPENDIX

OXY-COMBUSTION

Clean Energy Systems – Oxy-Syngas Combustor

Project Title:

Coal-Based Oxy-Fuel System Evaluation and Combustor Development

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Pilot-scale using actual flue gas, 163 tons CO_2/day

Primary Project Goal:

Clean Energy Systems (CES) is designing and developing a pre-commercial oxy/synthesis gas (syngas)-fueled combustor to be used in a power generation cycle able to achieve high thermal efficiency with near-zero atmospheric emissions, including carbon dioxide (CO_2).

Technical Goals:

- Evaluate and select a power plant alternative to the Rankine cycle.
- Develop a detailed design of a pre-commercial oxy-fuel combustor.
- Develop an advanced intermediate pressure turbine with oxy-fuel reheat combustors to increase net plant efficiency.

Technical Content:

CES has designed a pre-commercial oxy-fuel combustor that can utilize synthesis gas in an oxy-fuel power cycle to produce electricity from fossil fuel at high thermal efficiency with near-zero emissions. The CES oxy-fuel combustor is capable of producing high-pressure gases over a wide range of high temperatures – from 315°C to 1,760°C (600°F to 3,200°F). To utilize the higher temperatures, and thereby achieve high plant efficiencies, CES is also working with turbine developers to accelerate deployment of advanced oxy-fuel turbines.

The CES cycle involves burning high purity oxygen (O_2) with a gaseous carbonaceous fuel (natural gas, coal syngas, gasified biomass, etc.) in the presence of water to generate a high-pressure, high-temperature drive gas comprised of approximately 90%v steam and 10%v CO_2 (natural gas), or 75%v steam and 25%v CO_2 (syngas). The drive gas drives steam or aero-derivative turbo-generators to produce electricity.

The heart of the oxy-fuel combustor is the main injector, which is used to inject precisely controlled quantities of O_2, fuel, and water into the combustion chamber. Figure 1 shows a schematic view of the syngas main injector, Figure 2 details the fine injection elements of the injector's face, while Figure 3 depicts the assembled syngas combustor.

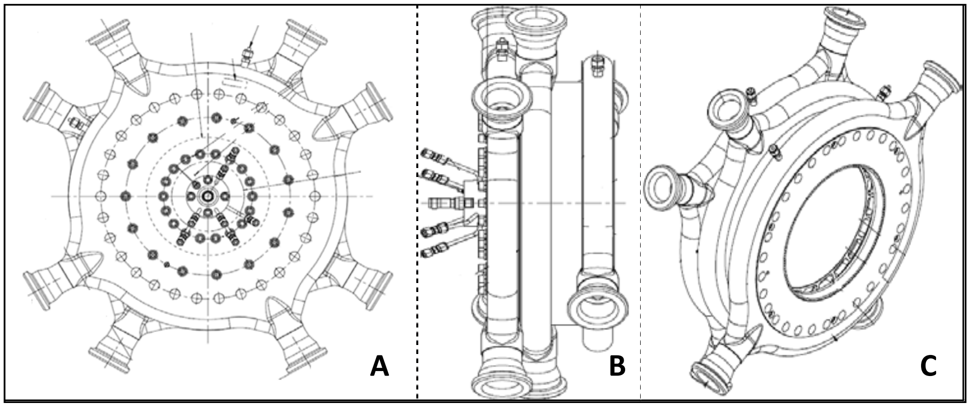

Figure 1: Syngas Main Injector Assembly: A) Front View; B) Side View; C) Rear View

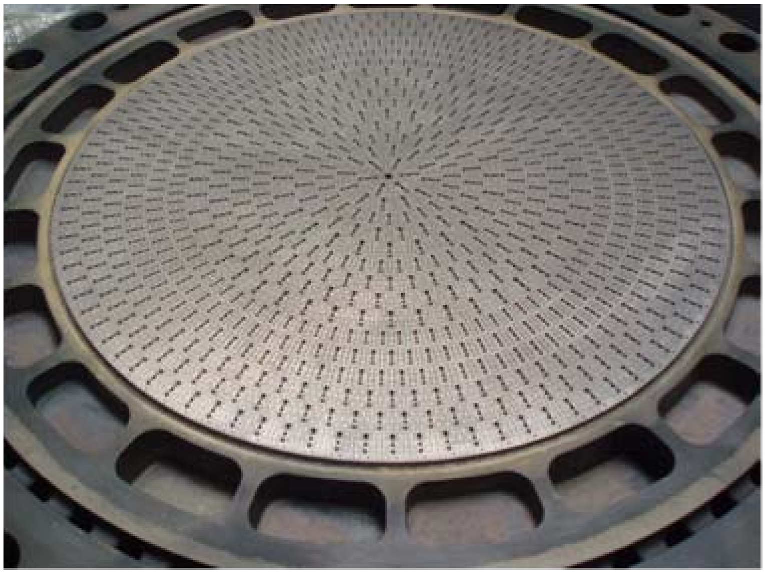

Figure 2: Syngas Main Injector Face

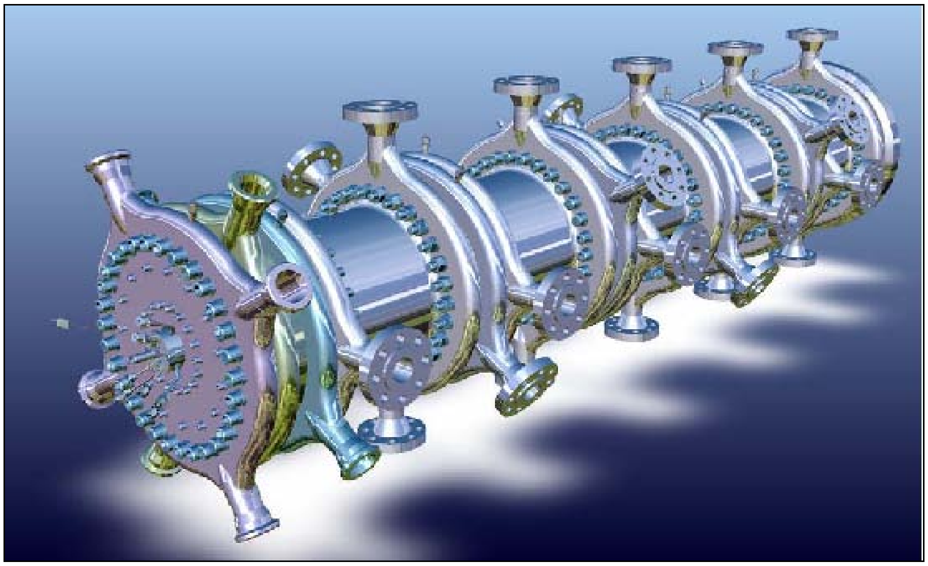

Figure 3: Model Image of Assembled 100 MWt Syngas Combustor

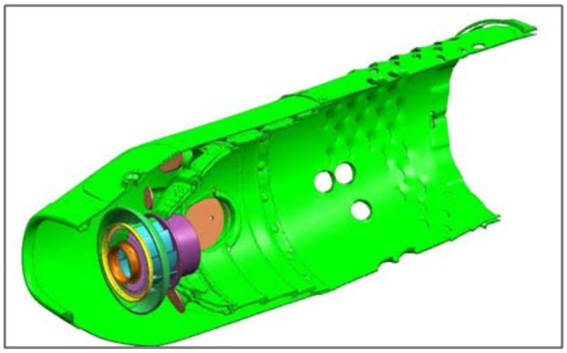

Figure 4: Cutaway Image of J79 Oxy-Fuel Combustor

CES is also developing oxy-fuel intermediate pressure turbines (IPTs), which are derived from existing high-temperature gas turbines. The former air-breathing units are being modified to utilize the steam-CO_2 drive gas from the oxy-fuel combustor. These modified turbines will incorporate unique oxy-fuel reheat combustors to boost the inlet steam/CO_2 temperature, improving overall plant efficiency by up to 10%. Reheating the drive gas exhausting a high-pressure turbine prior to its entry into an IPT significantly increases plant efficiency in oxy-fuel cycles by taking advantage of the higher temperature capabilities inherent in gas turbine-based IPTs. This approach negates the need to develop high-temperature steam turbines by going directly to gas turbines already capable of high inlet temperatures. In a two-pronged approach, CES first modified an aero-derivative aircraft turbine (J79) to accept the steam/CO_2 drive gas by removing its compressor, quadrupling its potential electrical power output. In a joint effort with Florida Turbine Technologies (FTT), the existing J79 turbine “cans” were modified to an oxy-fuel reheat combustor configuration and hot-fired to confirm FTT modeling predictions of temperature and pressure profiles. Figure 4 is a cutaway view of a J79 reheat combustor.

The second prong of oxy-fuel turbine development is the detailed re-engineering of a commercial-scale gas turbine, the 50-MWe Siemens SGT-900 to an oxy-fuel IPT (OFT-900) capable of tripling the original turbine’s power output to 150 MWe. As with the J79, the compressor stage will be removed and modifications will be made to the remainder of the turbine. FTT is under contract by CES to re-engineer the SGT-900 as an oxy-fuel IPT and to provide detailed engineering drawings for the conversion. CES is also developing two reheat combustor prototypes, an aero-derivative designed by FTT and a vane-type reheater designed by CES. Detailed engineering design of the OFT-900 is expected to be completed by 1Qtr/FY11. Figure 5 shows an artist’s conception of the OFT-900.

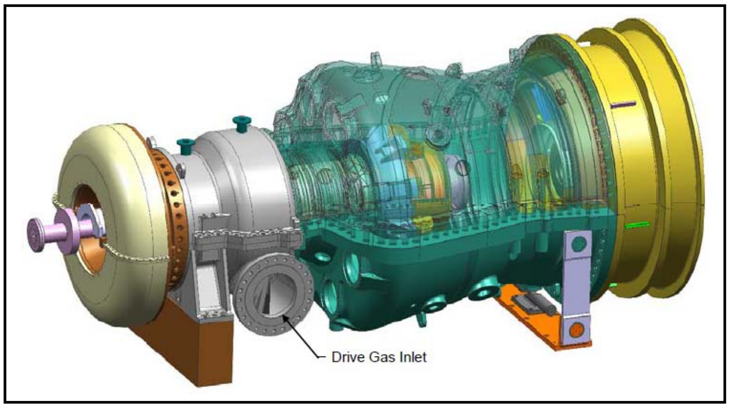

Figure 5: Artist’s Concept of OFT-900

Technology Advantages:

Oxy-Fuel Combustor: An oxy-fuel combustor produces drive gases from fossil fuels, consisting of steam and readily separable CO_2. This process (the CES cycle) produces a base-load power cycle that captures virtually 100% of the greenhouse gases (CO_2). In addition, the oxy-fuel combustor produces high drive gas temperatures, enabling high-efficiency power cycles when coupled with high-temperature steam turbines.

High Temperature Steam Turbines: Utilizing modified gas turbines as oxy-fuel IPTs will significantly reduce development cost and time for high-temperature, oxy-fuel compatible steam turbo-generators. The inherently higher temperature capabilities of these turbines (up to 1,204°C [2,200°F]) permits plant heat rate improvements of 25% compared to conventional steam turbines.

R&D Challenges:

High Temperatures: Equipment is subjected to increased stress, potentially increasing maintenance/ reducing life cycles.

Steam/CO_2 Drive Gas: Condensate from steam/CO_2 drive gases is acidic (carbonic acid), requiring the use of costlier, corrosion-resistant materials. Also, steam/CO_2 transfers heat to metal surfaces more readily than the drive gases from air-fuel combustion, requiring provision for more effective cooling, including use of steam and/or CO_2 as a cooling medium instead of air.

Results To Date/Accomplishments:

- Performed process modeling on coal-based oxy-syngas cycles.
- Modified the Kimberlina combustor for syngas operation and tested at 5 MWth.
- Completed a detailed design of a 100 MWth oxy-syngas combustor and its enclosure.
- Completed hot-fire testing of the J79 oxy-fuel reheat combustor.
- Began detailed engineering redesign of SGT-900 to serve as an oxy-fuel IPT (OFT-900). Includes development of advanced (2nd generation) oxy-fuel reheat combustors for OFT-900.

Next Steps:

- Analyze J79 reheat combustor test results and update FTT combustor model.

- Submit the CES drawing packages for 100 MWth oxy-syngas combustor.
- Complete detailed engineering design of OFT-900.
- Final test results will not be available until September 30, 2010.

Available Reports/Technical Papers/Presentations:

Coal-Based Oxy-Fuel System Evaluation and Combustor Development. http://www.netl.doe.gov/technologies/coalpower/turbines/refshelf/summaries/42645%20CES%20Fact%20Sheet%2016Oct06.pdf.

Viteri, Fermin. *Turbine-Based Zero Emissions Plants*. 2006. http://www.netl.doe.gov/technologies/coalpower/turbines/refshelf/handbook/1.3.1.2.pdf (Accessed 9/2/2009).

Contract No.:

DE-FC26-05NT42645

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Argonne National Laboratory – Engineering Assessment of Oxy-Combustion

Project Title:

Evaluation of CO_2 Capture/Utilization/Disposal Options

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Systems analysis and macroeconomic modeling

Primary Project Goal:

Argonne National Laboratory (ANL) is conducting comparative engineering assessments of carbon dioxide (CO_2) capture retrofit technologies with a focus on oxy-combustion and its possible use as a transitional strategy to integrated gasification combined cycle (IGCC) with carbon capture and storage (CCS).

Technical Goals:

- Develop engineering evaluations for oxy-combustion CO_2 capture from existing pulverized coal-(PC) fired power plants retrofitted for flue gas recirculation (FGR).
- Identify existing power plants that may be retrofit candidates, considering the effects of coal characteristics and the accessibility of a sequestration site.
- Investigate the potential cost-effectiveness of oxy-combustion retrofits with the All-Modular Industry Growth Assessment (AMIGA) model, regarding least-cost investment and ranking, as well as dispatch order and energy use in the economy.

Technical Content:

The project is conducting engineering assessments and economic evaluations on retrofitting PC boilers with oxy-combustion and then eventually repowering the site with IGCC. The engineering assessment for oxy-combustion is being conducted with the ASPEN process model and the economic evaluations with the AMIGA macroeconomic model (see Figure 1). The assessment is investigating the entire life cycle of the plant, which includes 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 is conducting ASPEN modeling for 18 different oxy-combustion and air-fired cases. Three different power production ratings (150 MW, 300 MW, and 450 MW) are being investigated. The model includes a selective catalytic reduction (SCR) system and a flue gas desulfurization (FGD) system for flue gas clean-up.

ANL is also conducting a net present value (NPV) cost assessment for three alternative scenarios for existing PC plants in order to assess the economic feasibility of retrofitting CCS. The three scenarios are:

1. A base case in which an existing PC plant is operated until retirement in year N and then replaced with an IGCC plant with CCS.
2. An alternative case in which a PC plant with N years of remaining life is replaced in year zero with an IGCC plant with CCS.
3. An alternative case in which a PC plant is retrofit in year zero with oxy-combustion and CCS with subsequent replacement of the plant in year N with IGCC, such that the existing oxygen plant and CO_2 recovery system can be used by the IGCC plant.

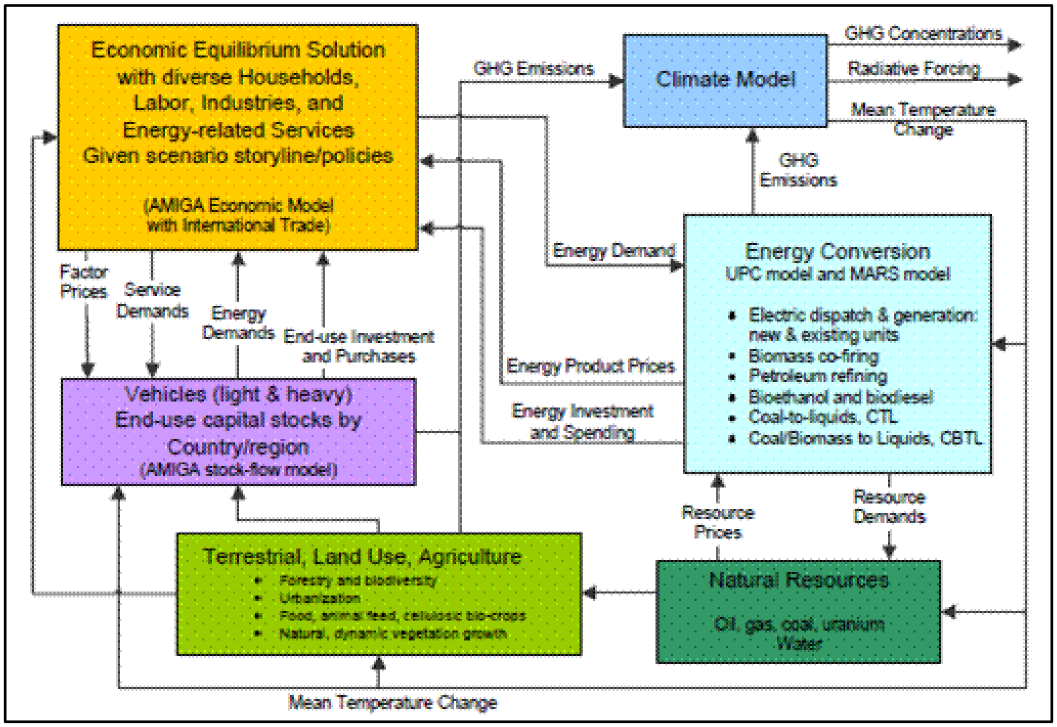

Figure 1: AMIGA Modeling System

Technology Advantages:

- Post-combustion CO_2 capture systems that treat conventional flue gas are critically dependent upon deep levels of sulfur dioxide (SO_2) clean-up to protect solvents. Oxy-combustion does not require that level of SO_2 reduction.
- For plants envisioning repowering, there is an advantage to using oxy-combustion because the air separation unit (ASU) system can be transitioned to the new repowered system.

R&D Challenges:

- Lowering the cost of oxygen production and clean-up.

Results To Date/Accomplishments:

- An FGD model using ASPEN with Electrolyte Wizard was developed to address retrofit details.
- A full energy-cycle was evaluated based on simulation of an oxy-combustion, PC boiler with FGR, and CO_2 capture.
- Process design and economics for 300- to 900-MW PC-fired boilers with low-, medium-, and high-sulfur coals indicate that the oxy-combustion strategy is economic and could be an approach to lower the costs of eventually repowering a site with an IGCC system.
- AMIGA was compared to the Second Generation Model (SGM), which is a competing climate economical model from the U.S. Environmental Protection Agency (EPA).
- AMIGA projects a ramping-up of oxy-combustion retrofits with deployment peaking in 2035.
- AMIGA projects a different investment strategy than some competing macroeconomic models.

Next Steps:

Project to be completed December 2010.

Available Reports/Technical Papers/Presentations:

"Evaluation of CO_2 Capture/Utilization/Disposal Options," NETL Fact Sheet.

"ANNUAL REPORT 2009: Evaluation of CO_2 Capture and Sequestration Using Oxyfuels with AMIGA Economic Modeling," November 23, 2009.

"Economics of CCS Systems – Potential Investment into CCS Technologies Stimulated by a 'Carbon' Market," 8th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania, May 4 - 7, 2009.

"Representing technology in CGE models: a comparison of SGM and AMIGA for electricity sector CO2 mitigation," Int. J. Energy Technology and Policy, 6:*4* (2008) p.323.

"CO_2 capture and sequestration: Technology options for new and retrofit applications," 2nd U.S.-China CO_2 Emissions Control Science & Technology Symposium, Zhejiang University Hangzhou, People's Republic of China, May 29-30,2008.

"High-sulfur Coal Desulfurization for Oxyfuels," 7th Annual Conference on Carbon Capture & Sequestration, Pittsburgh, Pennsylvania, May 5-8, 2008.

Contract No.:

FWP49539

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Air Products – Flue Gas Purification via Compression

Project Title:

Flue Gas Purification Utilizing SO_X/NO_X Reactions During Compression of CO_2 Derived from Oxy-Fuel Combustion

Technology Area:

Oxy-Combustion

Technology Maturity:

Pilot-scale using flue gas, 2.45 tonnes CO_2/day

Primary Project Goal:

Air Products and Chemicals is designing and developing a system for purifying an oxy-combustion derived flue gas by utilizing the reactions of sulfur oxides (SO_X) and nitrogen oxides (NO_X) that occur during compression, leaving behind a pressurized, pure stream of carbon dioxide (CO_2).

Technical Goals:

- Design and construct a 15-atm reactor system for the removal of SO_X and NO_X from actual oxy-combustion derived CO_2-rich flue gas.
- Evaluate reactor performance based on effluents at different pressures and water recycle rates.
- Characterize the reactor effluents to asses any change in performance.
- Develop an engineering model to describe the 15-atm purification reactor performance.

Technical Content:

Acidic gases must be removed from a CO_2 stream prior to pipeline transportation to avoid corrosion and to comply with purity requirements for applications such as enhanced oil recovery (EOR) and geological storage. In order to address this requirement, Air Products and Chemicals is developing a novel approach to remove SO_X and NO_X from the flue gas by converting them to sulfuric acid and nitric acid.

In order to determine the effect of pressure on sulfur dioxide (SO_2) and nitric oxide (NO) conversion, previous experiments were performed where one standard liter per minute (sl/min) of gas was supplied at both 8 atm and 15 atm. The results are shown in the Table 1.

Table 1: Pressure vs. Conversion

	15 atm			**8 atm**		
	Inlet	**After Compressor and Receiver**	**Conversion**	**Inlet**	**After Compressor and Receiver**	**Conversion**
ppm SO_2	900	20	98%	950	150	84%
ppm NO_X	500	50	90%	390	120	68%

Clearly, the conversion rate increases significantly with pressure. Therefore, it is logical to assume that these contaminants can be removed during the compression of CO_2.

The flue gas pilot development unit (PDU) within this project will include three main units, as indicated below: the scrubber/condenser, the compressor, and the reactor. Fine particulate ash and acid mist in the flue gas will need to be removed prior to compression to avoid damage to the compressor.

The compressor will increase the pressure of the gas from near atmospheric to approximately 16 atm in a multistage adiabatic compressor unit. After the initial compression, the flue gas will be cooled prior to entering the reactor. In the reactor, the flue gas will be contacted with water to obtain complete conversion of SO_2 to sulfuric acid and high conversion of NO_X to nitric acid.

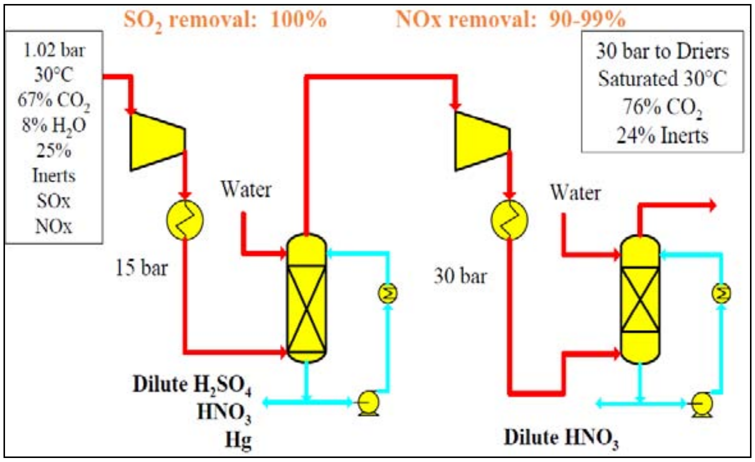

Figure 1: Flue Gas Pilot Development Unit (PDU)

The flue gas will be a 0.3 MWth slip stream supplied by the host site, Alstom Power from a 15 MWth oxy-combustion unit. An estimated composition of the flue gas has been supplied in Table 2.

Table 2: Estimated Flue Gas Composition

Component	% (vol)
CO_2	70 – 80
H_2O	5 – 10
O_2	5 – 8
N_2	7 – 13
Ar	3 – 6
SO_2	2,500 – 5,000 (ppm)
NO_X	1,000 – 2,000 (ppm)

Technology Advantages:

By incorporating an efficient NO_X and SO_X removal system with a compressor, the need for low NO_X burners, flue gas desulfurization (FGD), and $DeNO_X$ systems are greatly reduced or eliminated for oxy-combustion plants. In particular, this system allows for a degree of freedom to optimize any upstream purification needs and target reduction in size or removal of upstream equipment for the retrofit of an existing plant or the construction of a new plant.

R&D Challenges:

The main challenge is to obtain sufficient data for engineering design and to further develop the understanding of the effect of residence time, pressure, and temperature on the unit performance. The prolonged presence of acid gases in the system and the presence of such gases at high pressures in the compressor may lead to the requirement of more advanced materials of construction.

Results To Date/Accomplishments:

- Developed a simulation of the flue gas PDU and modeled the reactions occurring within the reactor.
- Conducted simulations to understand the influence of liquid to vapor flow rates on SO_2 and NO_2 conversions as well as overall residence time in the reactor.
- Developed a design specification for the reactor and auxiliary equipment.
- Selected desired compressors.
- Completed construction and installed reactor system at host site.
- Completed initial test campaign.

Planned Activities:

- Evaluate the performance of reactor-based flue gas.
- Develop an engineering model and perform sensitivity analysis.
- Perform small-scale testing of SO_X/NO_X removal.
- Finalize step up to pilot scale for CO_2 purification and compression.

Final test results will not be available until the September 2010 project completion date.

Available Reports/Technical Papers/Presentations:

Fact Sheet. "Flue Gas Purification Utilizing SO_X/NO_X Reactions During Compression of CO_2 Derived from Oxyfuel Combustion." http://www.fe.doe.gov/fred/factsheet.jsp?doc=6356&projtitle=Flue Gas Purification Utilizing SO_X/NO_X Reactions During Compression of CO_2 Derived from Oxyfuel Combustion. (Accessed 9/16/2009).

Contract No.:

DE-FC26-08NT0005309

NETL Project Manager:

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Partners:

Brigham Young University – NO_X Behavior in Oxy-Combustion

Project Title:

A Mechanistic Investigation of Nitrogen Evolution and Corrosion with Oxy-Combustion

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Pilot-scale using simulated flue gas, 0.05 tonnes CO_2/day

Primary Project Goal:

Brigham Young University (BYU) is investigating the evolution of nitrogen from its origin in coal to emissions in both air- and oxy-combustion. A model of detailed kinetics, devolatilization, and char oxidation in a simple plug flow is also being developed and used to interpret the data.

Technical Goals:

- Modify the flat flame burner (FFB) to run using simulated oxy-fuel combustion.
- Modify the multi-fuel flow reactor (MFR) to run with simulated oxy-fuel combustion.
- Gather data through experimental measurements of gas species in air-fired and oxy-fuel pulverized coal flames.
- Develop a computational model of the combustion process, including fuel devolatilization, gas phase kinetic mechanisms, and char oxidation.

Technical Content:

The experiments were performed at two facilities designed to investigate the evolution of coal nitrogen species, fuel nitrogen oxide (NO_X) formation, and emissions during combustion processes in air and oxygen (O_2)/carbon dioxide (CO_2) mixtures. A model of detailed kinetics, devolatilization, and char oxidation in a plug flow operation was developed and used to interpret the data collected.

In the experiments performed by BYU, the flue gas was not recycled. Rather, bottled CO_2 was used to simulate dry recycled flue gas. While the results are applicable to entrained-flow pulverized coal combustion in general, the absence of turbulence in the laminar flow experiment is a notable difference from any practical combustor.

Pulverized coal was burned in a refractory-lined, laminar flow reactor referred to as the MFR, shown in Figure 1.

The unit at the first facility was a premixed, down-fired staged reactor where the first stage was fuel rich followed by a burnout oxidizer stage. The oxidizer was varied from air (23% O_2 by mass in nitrogen [N_2]) to two different mixtures of O_2 and CO_2 (25% and 30% O_2 by mass). The coals used were Pittsburgh #8, Illinois #6, and Powder River Basin (PRB). Selected coal properties are shown in Table 1.

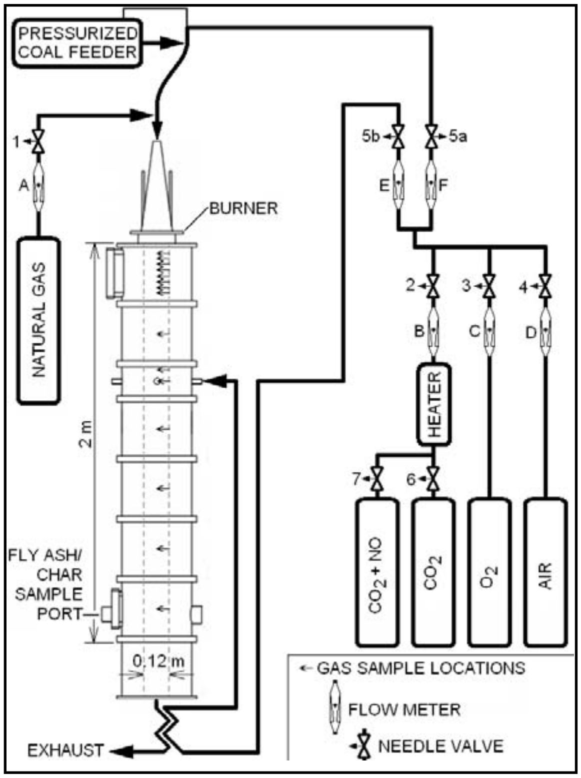

Figure 1: Schematic of the Multi-Fuel Flow Reactor

Table 1: Selected Properties of the Coals

	Sub-Bituminous	Illinois #6	Pittsburgh #8
Proximate Analysis	**DAF wt%**	**DAF wt%**	**DAF wt%**
Volatile Matter	49.72	44.17	41.96
Fixed Carbon	50.28	55.83	58.04
Ash (wt%, dry)	6.42	9.31	10.67
Higher Heating Value (Btu/lb, DAF)	11,981	14,226	14,785
ASTM Rank	Sub-Bituminous A	High-Volatile C Bituminous	High-Volatile A Bituminous
Ultimate Analysis	**DAF wt%**	**DAF wt%**	**DAF wt%**
C	70.56	81.88	85.19
H	4.18	4.37	4.87
O	23.63	7.83	4.70
N	1.04	1.27	1.38
S	0.59	4.64	3.86
	100	100	100

Both the air and mixture cases produced a rapid initial formation of nitric oxide (NO), with a similar amount of total fuel nitrogen converted to NO. In air combustion, NO can be either formed or reduced by thermal equilibrium forces dependent on the local equivalence ratio. At an initial or primary zone stoichiometric ratio (SR) of 0.82, air combustion appeared to produce thermal NO; while at an SR of 0.65, no evidence of thermal NO is seen. In oxy-combustion, initial NO formation produced concentrations above equilibrium, creating a situation where NO was being destroyed by thermal processes at all measured SR.

There is competition between the NO destruction in the fuel-rich region and the NO formation at tertiary air injection, which creates an effluent out of NO minimum for each oxidizer. The magnitude of the minimum was similar for air- and oxy-fuel combustion; however, the SR at the minimum was higher for oxy-fuel combustion, suggesting that oxy-fuel combustion does not require as deep of a staging environment to achieve NO_X reduction and can therefore achieve higher burnout.

The second facility included an FFB with particle and gas sampling. Char particles were sampled after passing through either air- or oxy-flames. In oxy-flames, the normal diluents of N_2 were replaced with CO_2. The ratio of O_2/CO_2 was varied in order to produce different flame temperatures. There was little difference observed between air- and oxy-fuel pyrolysis of coals.

The probe, shown in Figure 2, was used to sample gas in the reactor.

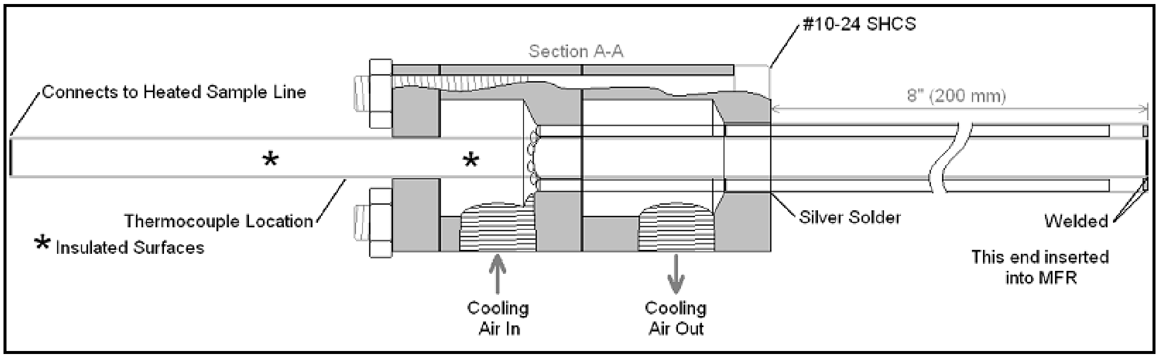

Figure 2: Diagram of the Air-Cooled Gas Sampling Probe

In unstaged, premixed combustion, air- and oxy-fuel combustion produced similar levels of fuel nitrogen conversion to NO_X. Low NO_X emissions from oxy-fuel combustion are therefore not achieved without staged mixing of the oxidizer and fuel as is the case for conventional air combustion.

Technology Advantages:

The research will supply information that will significantly aid in the development of oxy-combustion technology.

R&D Challenges:

Due to the use of bottled CO_2 to simulate dry recycled flue gas, there was an absence of turbulence in the laminar flow experiment, which creates a notable difference from any practical combustor. This could possibly lead to difficulties when scaling to a commercial plant.

Results To Date/Accomplishments:

- Modified the FFB to run using simulated oxy-fuel combustion.
- Modified the MFR to run with simulated oxy-fuel combustion.
- Completed air- and oxy-combustion NO_X profiles with 500 parts per million (ppm) NO added to the reactants to determine the extent of reburning in oxy-combustion.
- Completed a staged combustion experiment of NO_X and major gas species profiles in the MFR reactor.
- Produced a full kinetic mechanism model of oxy-fuel combustion.

Planned Activities:

This project was completed on December 31, 2008.

Available Reports/Technical Papers/Presentations:

Allam, R. J., R. S. Panesar, V. White, D. Dillon (2005) *Optimising the design of an Oxyfuel-Fired Supercritical PF Boiler*, The 30th International Technical Conference on Coal Utilization and Fuel Systems, April 17-21, 2005, Clearwater, Florida.

Andersson, K. (2007) *Combustion Tests and Modeling of the Oxy-fuel Process, An Overview of Research Activities at Chalmers University*, 2nd IEAGHG International Oxy-combustion Workshop, January 25-26, 2007, Windsor, Connecticut.

Asay, B. W. (1982) *Effects of Coal Type and Moisture Content on Burnout and Nitrogeneous Pollutant Formation*, Ph.D. Dissertation, Brigham Young University, Provo, Utah.

Bose, A. C., K. M. Dannecker, J. O. L. Wendt (1988) *Coal Composition Effects on Mechanisms Governing the Destruction of NO and Other Nitrogenous Species during Fuel-Rich Combustion*, Energy and Fuels 2:301-308.

Contract No.:

DE-FG26-05NT42530

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Air Liquide

Washington University – Multi-Pollutant Control

Project Title:

Multi-Pollutant Control Through Novel Approaches to Oxygen Enhanced Combustion

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Laboratory- and pilot-scale, 1.2 tonnes CO_2/day

Primary Project Goal:

Washington University is developing best practices for implementing oxy-fuel combustion with flue gas recirculation (FGR) and sorbent processes to minimize nitrogen oxides (NO_X), sulfur oxides (SO_X), particulate matter ($PM_{2.5}$), and mercury (Hg) emissions, and maximize combustion efficiency and the concentration of carbon dioxide (CO_2) in the flue gas through research and experimentation.

Technical Goals:

- Measure NO_X emissions resulting from air- and oxy-combustion with CO_2 recirculation.
- Determine the effect of CO_2 recirculation on Hg capture, combustion temperature, flame geometry, etc.
- Experimentally determine the optimum approach to mixing coal, oxygen (O_2), CO_2, and sorbents.
- Determine the effect of the steam temperature to identify the optimum preheating conditions for minimized emissions.
- Develop nano-structured sorbent technologies to reduce Hg emissions.

Technical Content:

Oxy-combustion offers several advantages over traditional air-combustion technologies, including higher temperatures and smaller flue gas volume. However, in order to maintain the combustion temperatures at a level that existing, cost-effective materials can handle, the O_2 must be diluted to approximate atmospheric levels. Washington University is researching oxy-combustion that utilizes recirculated flue gas, causing the CO_2 levels in the final flue gas stream to be increased to levels greater than 95%, and controls emissions of NO_X, $PM_{2.5}$, and Hg.

Washington University has also been performing flame types and stability studies for oxy-combustion facilities. The experiments used a 10-25 kW down-fired coal combustor consisting of a non-swirling primary oxidizer (PO) and a swirling secondary oxidizer (SO). The system is run under slight negative pressure and the primary oxidizer preheat temperature was maintained between 300 to 350°C. Table 1 shows the mole fractions of each component in the PO and SO for all flame studies.

Results from these studies showed that 30 mole percent O_2 is required when using CO_2 as the inert gas to obtain stability results similar to conventional coal air-combustion. Also, inert exchange flames were shown to improve flame stability when compared with conventional coal air-combustion despite the O_2 concentration in the PO being substantially reduced.

Table 1: Flame Types for Oxy-Coal Flame Stability Study

	Type	**PO Mole Fraction**			**SO Mole Fraction**			**T_m* (K)**	**T_{NB}** (K)**
	%O_2 in PO/SO*	**O_2**	**N_2**	**CO_2**	**O_2**	**N_2**	**CO_2**	**Fluent Simulation**	
A	6% / 35%	6	94	0	35	65	0	2,420	1,860
B	15% / 25%	15	85	0	25	75	0	2,440	1,860
C	21% / 21%	21	79	0	21	79	0	2,480	1,860
D	21% / 25%	21	79	0	25	75	0	2,600	1,930

E	21% / 35%	21	79	0	35	65	0	2,850	1,950
F	25% / 25%	25	75	0	25	75	0	2,720	1,940
G	35% / 21%	35	65	0	21	79	0		
H	35% / 35%	35	65	0	35	65	0	3,010	2,070
I	21% / 35% (N_2/CO_2)	21	79	0	35	0	65		
J	25% / 25% CO_2^{++}	25	23	52	25	0	75		
K	30% / 30% CO_2^{++}	30	21	49	30	0	70		
L	35% / 21% CO_2^{++}	35	23	42	21	0	79		
M	35% / 35% CO_2^{++}	35	25	40	35	0	65		

Values for component compositions are accurate +/-2%.

$^{+}$ Inert balance in both PO and SO is N_2, unless otherwise indicated.

$^{++}$ Due to eductor, inert balance in PO is not entirely CO_2.

* Maximum temperature in temperature profile, as determined from modeling.

** Maximum flame temperature one inch from downstream from burner exit, as determined from modeling.

Technology Advantages:

Oxy-combustion offers increased temperature, increased thermal efficiency, reduced pollutant emissions, reduced fuel consumption, and improved flame stability. Oxy-combustion alone, and coupled with unique burner designs, can reduce NO_X emissions beyond levels achieved by using overfire air and low-NO_X burners. Also, oxy-combustion with FGR concentrates CO_2 levels, helping to reduce the cost of capture; concentrations up to 95% can be achieved.

R&D Challenges:

It was found that the flame structure of non-premixed systems is changed dramatically when oxy-combustion is used.

Results To Date/Accomplishments:

- Completed modifications to the oxy-coal combustor to minimize air leakage.
- Developed an understanding of flame geometry under oxy-fuel combustion.
- Developed a simple model that explains the presence of appreciable molecular O_2 at the location of peak temperature in high oxy-fuel combustion.
- Obtained NO_X measurements as a function of stoichiometric mixture fractions for a system that maintained a methane flame at both constant temperature and fuel flow rate.
- Examined the effect of replacing nitrogen (N_2) with CO_2 on the jet exit velocity at start-up for non-premixed jet flames of ethylene.
- The performance of titanium dioxide (TiO_2) with UV irradiation for Hg capture was tested in a bench- and pilot-scale system.
- Flame stability in a Type I laboratory-scale pulverized coal combustor was quantified as a function of inert gas type and O_2 concentration in both the primary and secondary oxidizer streams.
- Developed a model of soot inception limits under oxy-fuel combustion conditions and validated with gaseous fuels.
- Completed a study of blow-off limits in oxy-coal combustion.
- Demonstrated that the approach used to mixing the oxy-coal flame can lead to stronger flames even with reduced O_2 in the primary region.

Next Steps:

Project completed February 2009. Final report not yet available.

Available Reports/Technical Papers/Presentations:

C. E. Baukal, *Oxygen Enhanced Combustion*. CRC Press LLC: Boca Raton, 1998; p 490.

C. J. Sung; C. K. Law, Proc. Combust. Inst. 27 (1) (1998) 1411-1418.

F. Chatel-Pelage; R. Varagani; P. Pranda; N. Perrin; H. Farzan; S. J. Vecci; Y. Lu; S. Chen, Thermal Science 10 (3) (2006) 119-142.

L. Bool; H. Kobayashi; D. Thompson; E. Eddings; R. Okerlund; M. Cremer; D. Wang, 19th Annual International Pittsburgh Coal Conference, Pittsburgh, Pennsylvania, September (2002).

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Principal Investigator:	**Partners:**
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Praxair – Flue Gas Purification Options

Project Title:

Near-Zero Emissions Oxy-Combustion Flue Gas Purification

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Bench-scale

Primary Project Goal:

Praxair's project is developing a near-zero emission flue gas purification technology for a retrofitted existing coal-fired power plant with oxy-combustion technology.

Technical Goals:

- Design a contaminant removal system that will produce saleable sulfuric acid and nitric acid without the need for flue gas desulfurization (FGD) or selective catalytic reduction (SCR) units.
- Design a second contaminant removal system that will produce gypsum.
- Achieve greater than 95% carbon dioxide (CO_2) capture by incorporating a vacuum pressure swing adsorption (VPSA) unit in an existing plant with a high air ingress, and reduce sulfur oxide (SO_X) and mercury (Hg) emissions by more than 99% and nitrogen oxide (NO_X) emissions by more than 90% (high and low sulfur coal).
- Perform a techno-economic study and an operability and integration evaluation to assess the commercial viability of retrofitting an existing power plant with the proposed technology.

Technical Content:

Two approaches for SO_X/NO_X/Hg removal are proposed depending on the SO_X levels in the flue gas. By carrying out these unit operations at high pressure, it is envisioned that capital costs would be reduced while achieving very low levels of SO_X and NO_X in the CO_2 stream. For plants with existing FGD and SCR, operating cost savings could be realized by shutting down those units while operating the proposed SO_X/NO_X removal process. For plants burning low sulfur coal, there is no need for investment in separate FGD and SCR equipment for producing high purity CO_2.

High air ingress in existing plants limits the amount of CO_2 that can be recovered from oxy-combustion flue gas using a cold box alone to <65%. The CO_2 recovery limitation is overcome by using a hybrid process that combines a cold box and VPSA (Figure 1). In the proposed hybrid process, up to 90% of CO_2 in the cold box vent stream is recovered by CO_2 VPSA and then recycled and mixed with the flue gas stream upstream of the compressor. The recovery from the process will be >95%.

Pollutant Removal

The high sulfur coal tests will be bench-scale and will utilize a single gas/liquid contact column that operates at up to 17 atm (250 psia) and 150°C (300°F) for testing multiple reactions. Nitric oxide (NO) in the flue gas is converted to nitrogen dioxide (NO_2), which catalyzes sulfur dioxide (SO_2) oxidation to SO_3. The hydrolysis of SO_3 and NO_2 forms sulfuric and nitric acids.

The low sulfur coal experiments will use a single column unit (2.5 cm [1 inch] diameter, 3.8 cm [1.5 inch] long), and operate up to 17 atm (250 psia) and 93°C (200°F). Activated carbon is used as an adsorbent/catalyst for the capture of SO_X and NO_X from the flue gas. The activated carbon oxidizes the SO_2 to SO_3, and a periodic water wash will be used to remove the acid.

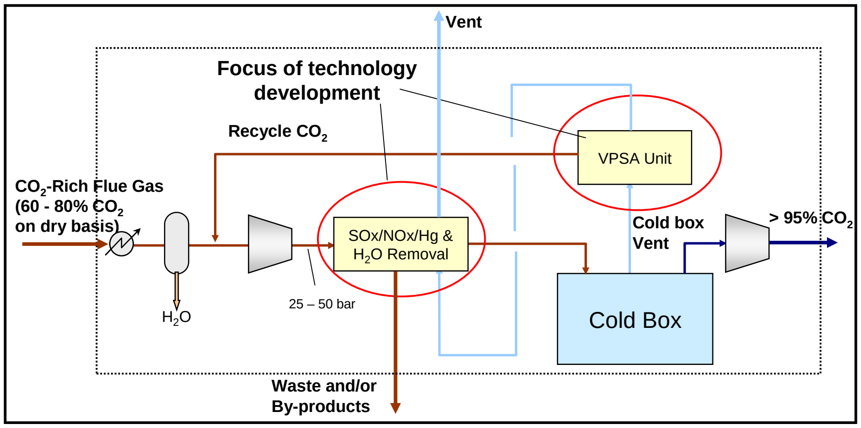

Figure 1: Technology Concept

The chemical reactions for the high and low sulfur coal pollutant removal system are summarized below.

High Sulfur Coal Reactions

$NO_2 + SO_2 \rightarrow NO + SO_3$

$NO + 1/2O_2 \rightarrow NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

$NOx + H_2SO_4 \leftrightarrow H_2SO_4 \bullet NOx$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Figure 2: High Sulfur Coal Pollutant Removal

Low Sulfur Coal Reactions

$SO_2 + 1/2O_2 \rightarrow SO_3$

$NO + 1/2O_2 \rightarrow NO_2$

$SO_3 + H_2O \rightarrow H_2SO_4$

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

Figure 3: Low Sulfur Coal Pollutant Removal

High CO_2 Recovery Using VPSA

The VPSA unit is a multi-bed unit that performs multiple depressurization/re-pressurizations steps. Oxy-combustion flue gas will enter the CO_2 VPSA from the "cold box" (25 to 35 atm and ambient temperature) that will recover additional CO_2 (produce 80% to 95% CO_2 concentration) and recycle the CO_2 back into the CO_2-rich flue gas stream at ambient pressure. The flue gas stream not recycled from the VPSA contains mainly oxygen (O_2), nitrogen (N_2), and argon (Ar) that will be vented to the atmosphere.

Technology Advantages:

Cold box-VPSA hybrid technology achieves >95% CO_2 recovery even for plants with high air ingress. The flue gas purification process for high sulfur coal has lower capital and operating costs than FGD and SCR and it allows for revenue from sale of acids.

R&D Challenges:

- SO_X/NO_X/Hg removal from high sulfur coal:
  - Reactor materials must be able to withstand the operating conditions in the process.
  - Determine an effective NO_X catalyst for producing saleable sulfuric acid.
- SO_X/NO_X/Hg removal from low sulfur coal:
  - Find activated carbon materials that are effective for regeneration based on sorption capacity and ability to maintain performance.
- Identify adsorbents with a tolerance to residual SO_X/NO_X to be used in the VPSA process.

- Determine VPSA cost benefit for recovering additional CO_2.
- Establish proper modifications required for retrofitting existing plants.

Results To Date/Accomplishments:

Bench-scale experimental test systems have been built and commissioned for all three experimental programs.

- SO_X/NO_X/Hg removal from high sulfur coal:
    - Completed preliminary screening tests for NO_X catalyst.
- SO_X/NO_X/Hg removal from low sulfur coal:
    - Identified, through screening tests, three activated carbon materials with potential for SO_X removal and one activated carbon material with potential for both SO_X and NO_X removal.
- High CO_2 Recovery Using VPSA:
    - Identified, through screening tests, six VPSA adsorbents for bench-scale tests.
    - Tested three adsorbents on the bench-scale unit; two of them hold promise.
    - Completed the pilot-scale VPSA unit construction.

Next Steps:

- Perform contaminant (SO_X, NO_X, and Hg) removal tests for high and low sulfur coals.
- Complete bench-scale tests and select two adsorbents for the continuous operation tests.
- Commission pilot VPSA system.
- Conduct commercial viability assessment of the pollutant removal technologies.

Final test results will not be available until the December 2011 project completion date.

Available Reports/Technical Papers/Presentations:

Near-Zero Emissions Oxy-Combustion Flue Gas Purification - March 2009.

Contract No.:

DE-FC26-08NT0005341

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Partners:

AES
Foster Wheeler
WorleyParsons Canada

Alstom Power – Tangential-Fired Oxy-Combustion Retrofits

Project Title:

Oxy-Combustion Boiler Development for Tangential Firing

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Pilot-scale using actual flue gas, 120 tonnes CO_2/day

Primary Project Goal:

Alstom Power is designing and developing a tangentially-fired (T-fired) oxy-fuel technology for retrofitting existing boilers.

Technical Goals:

- Design and develop an innovative oxy-fuel firing system for existing T-fired boilers that minimizes overall capital investment and operating costs.
- Evaluate the performance of oxy-fuel T-fired boilers in pilot-scale tests at Alstom's 15-MWth boiler simulation facility (BSF).
- Determine the boiler design and performance impacts for oxy-combustion.
- Evaluate and improve engineering and computational fluid dynamic (CFD) tools for oxy-combustion.

Technical Content:

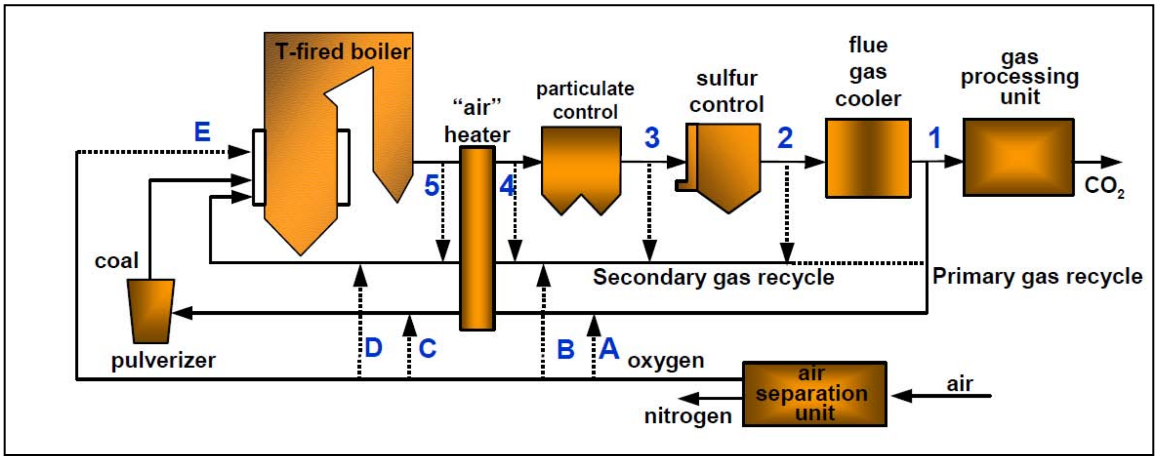

Figure 1: Simplified Oxy-Combustion Process Diagram

Figure 1 is a schematic representation of an oxy-combustion process showing the location of a T-fired boiler and several possible take-off locations for flue gas for recirculation (numbers) and locations for oxygen injection (letters). The different take-off locations will affect variables in the recirculation stream such as water, particulate, and sulfur content for the pilot tests.

The pilot-scale tests include the following variables:

- Gas Recycle Take-off Location
- Gas Recycle Flow Rates
- Oxygen Injection Flow Rates and Locations
- Windbox Design
- Over-Fire Air Compartment Design

Additional detailed evaluation of oxy-firing system design variables and their impacts on boiler performance is being conducted using CFD analyses. These models of the BSF were developed and are being used to allow for evaluation of various oxy-fired design options. Key variables evaluated include: gas recycle ratio, gas recycle composition, oxygen injection method and distribution, windbox design, and separate over-fire air design. The models are updated using boundary conditions and data from the BSF test runs to be compared with test measurements and validate predictions.

Figure 2: Photo of BSF with Oxy Modifications

CFD simulations are also being conducted using an 850-MWe supercritical T-fired boiler model to evaluate various oxy-configurations as part of a techno-economic analysis. The economic impacts of these runs are being assessed.

Alstom Power is utilizing its 15 MWth BSF facility, shown in Figure 2, for the pilot tests. The BSF will act as an experimental tool to replicate T-firing conditions in utility boilers and isolate variables to study behavior.

Tangential firing is different from other boiler configurations in that it utilizes air/fuel admission assemblies located at the corners of the boiler furnace, which generate a rotating fireball that fills most of the furnace cross section, as seen in Figure 3. In T-firing, air/fuel mixing is limited until streams are joined together in the furnace cavity, while in wall-firing most of the mixing and flame stabilization occurs at the exit of the burner. Detailed data is being collected during the 15 MWth tests on combustion performance, heat transfer distribution, and pollutant formation. Boiler operating and performance differences, as well as changes in design requirements between air- and oxy-firing modes, are being evaluated.

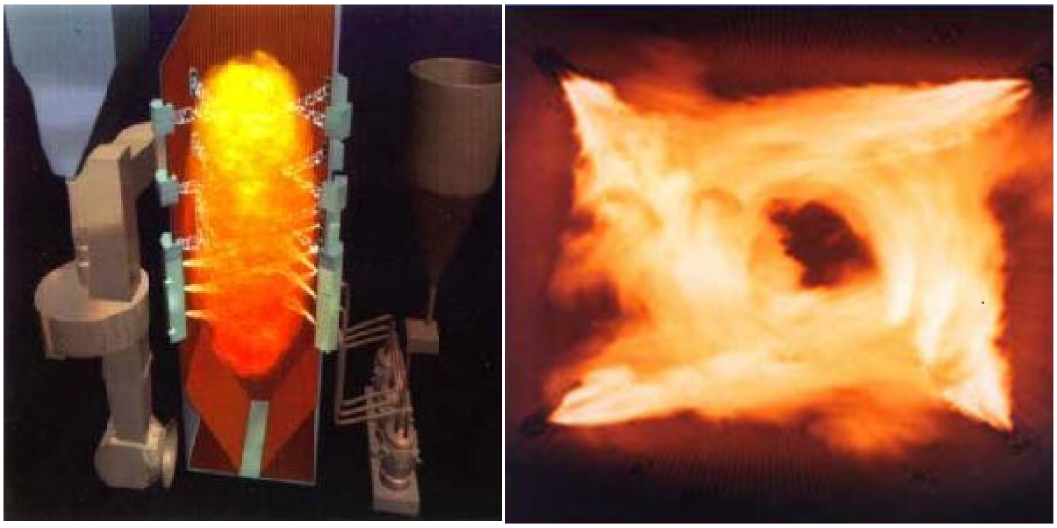

Figure 3: Model of Tangential Firing System Furnace Cavity (left); Top View of Tangential Firing (right)

Technology Advantages:

This project will develop a better understanding of the impacts of oxy-combustion on pollutant formation, ash deposition, fireside corrosion, and heat transfer in a boiler in order to optimize this carbon mitigation technology.

R&D Challenges:

Understanding difference from air firing in pollutant formation, ash deposition, fireside corrosion, and heat transfer rates in an oxy-fired boiler, as well as control of air in-leakage and developing cost-effective designs to address these issues.

Results To Date/Accomplishments:

- Completed the design for BSF modifications.
- Completed CFD screening evaluations.
- Completed modifications to the BSF for oxy-fired operation to permit the firing under both air and oxygen, as well as with several flue gas recirculation (FGR) configurations and oxygen injection methods.
- Completed the two of three large, T-fired, pilot-scale test series over a range of combustion conditions.

Next Steps:

- Conduct an additional large, T-fired, pilot-scale test series over a range of combustion conditions.
- Test a different type of U.S. coal for each test, because coal properties impact the combustion process. Likely candidates include a sub-bituminous coal, a low-sulfur Eastern bituminous coal, and a high-sulfur bituminous coal.
- Examine a matrix of combustion conditions on each of the coals, including the oxygen to re-circulated flue gas ratio, effect of injecting pure oxygen and premixed oxygen and re-circulated flue gas in various configurations, total excess oxygen, furnace staging, various air in-leakage rates, reduced loads, and comparison tests with air firing.
- Test several proposed coal nozzle/windbox designs and compare for flame attachment, uniform heat release, emissions, etc.
- Perform bench-scale ash deposition and corrosion evaluation in order to provide supplemental data to support the evaluation of candidate oxy design options and assist in the analysis of BSF test results.
- Final test results will not be available until the September 30, 2010, project completion date.

Available Reports/Technical Papers/Presentations:

"Oxy-Combustion Boiler Development for Tangential Firing Fact Sheet."
http://www.netl.doe.gov/publications/factsheets/project/Proj609.pdf (Accessed 9/17/2009).

"Alstom's Oxy-Firing Technology Development and Demonstration-Near Term CO_2 Solutions." 34th International Technical Conference on Coal Utilization and Fuel Systems. June 2009.

"Oxy-Combustion Boiler Development for Tangential Firing." Presented at the annual NETL CO_2 capture technology for existing plants R&D meeting.

"Oxyfuel PC and CFB Solutions - A Promising Option for CO_2 Capture." Presented at 8th Annual Conference Carbon Capture & Sequestration, Pittsburgh, Pennsylvania, May 5, 2009.

"Oxy-Firing Technology – Pilot Testing Leading to Large-Scale Demonstration." 11th Annual Electric Power Conference, Chicago, Illinois, 14 May 2009.

Contract No.:	**NETL Project Manager:**
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Great River Energy
LCRA and Austin Energy
Luminant (TXU)
MidWest Generation
NB Power
OG&E
Vattenfall

Foster Wheeler – Evaluation of Boiler Materials for Oxy-Combustion

Project Title:
Oxy-Combustion Boiler Material Development

Technology Area:

Oxy-Combustion

Technology Maturity:

Laboratory-scale using syngas

Primary Project Goal:

Foster Wheeler is conducting a laboratory test program to determine the effect of oxy-combustion on the corrosion and tube life of pulverized coal (PC)-fired boilers.

Technical Goals:

- Conduct computational fluid dynamic (CFD) modeling of air- and oxy-fired PC boilers to determine the flue gas compositions that will exist throughout these units and especially along the furnace waterwalls where highly corrosive micro-climates can exist.
- Use laboratory electric tube furnaces operating at boiler tube temperatures to expose coupons of conventional and advanced boiler tube materials to the CFD flue gas compositions synthesized from gas cylinders for 1,000 hours.
- Conduct post-test macroscopic and microscopic analyses of the material coupons to identify corrosion mechanisms; evaluate the corrosiveness of oxy-fired flue gas relative to air-fired flue gas and identify materials suitable for oxy-combustion.

Technical Content:

Table 1: Waterwall Materials

	Material	Description	Boiler Use	Nominal Composition
1	Tube	SA210-A1	Conventional	0.27% Carbon
2	Tube	SA213-T2	Conventional	1/2 Cr – 1/2 Mo
3	Tube	SA213-T11	Conventional	1-1/4 Cr – 1/2 Mo
4	Weld	T11 to T11	Conventional	1-1/4 Cr – 1/2 Mo
5	Weld Overlay	309L StnStl	Conventional	24 Cr
6	Weld Overlay	Inconel 622	Conventional	21 Cr – 55 Ni
7	Weld Overlay	VDM Alloy 33	Conventional	33 Cr – 31 Ni
8	Thermal Spray	IGS UTE x 5-450	Relatively New	40 Cr – 55 Ni
9	Thermal Spray	IGS UTE x 5-480	Relatively New	25 Cr – 60 Ni
10	Thermal Spray	ISG UTE x 5-500	Relatively New	15 Cr – 80 Fe

Table 2: Superheater/Reheater Materials

	Material	Description	Boiler Use	Nominal Composition
1	Tube	T22	Conventional	2-1/4 Cr – 1 Mo
2	Tube	304H StnStl	Conventional	18 Cr – 8 Ni
3	Tube	347H StnStl	Conventional	18 Cr – 9 Ni
4	Tube	T91/T92	Newer Boilers	9 Cr
5	Tube	NF709	Newer Boilers	20 Cr – 25 Ni
6	Tube	HR3C	Newer Boilers	25 Cr – 20 Ni
7	Weld Overlay	Inconel 622	Conventional	21 Cr – 55 Ni
8	Weld Overlay	VDM Alloy 33	Conventional	33 Cr – 31 Ni
9	Weld Overlay	Inconel 72	Conventional	44 Cr – 55 Ni
10	Welded Coupon	T22 to 304H	Conventional	1-1/4 Cr to 18 Cr

An oxy-combustion boiler retrofit will utilize flue gas recycle (FGR) to maintain the heat absorption of the original air-fired boiler and limit the combustion temperature. Since air nitrogen (N_2) is eliminated, the recycle stream will contain increased levels of the products of combustion including carbon dioxide (CO_2), water vapor (H_2O), and corrosive contaminants (i.e., carbon monoxide [CO], sulfur dioxide [SO_2], hydrogen sulfide [H_2S], and hydrogen chloride [HCl]). As a result, corrosion conditions are expected to increase throughout the boiler. To assess the corrosiveness of oxy-combustion flue gas, coupons of conventional and advanced waterwall and superheater/ reheater materials will be exposed to oxy- and air-fired flue gases in electric tube furnaces. Rectangular shaped coupons, typically 19 mm (3/4 inch) wide by 25 mm (1 inch) high by 3 mm (1/8 inch) thick, will be used to investigate tube materials, tube welds, and tube weld overlays; bullet shaped coupons, typically 19 mm (3/4 inch) in diameter by 38 mm (1-1/2 inch) high, will investigate thermal spray coatings. The conventional and advanced materials to be tested are listed in Table 1 and Table 2.

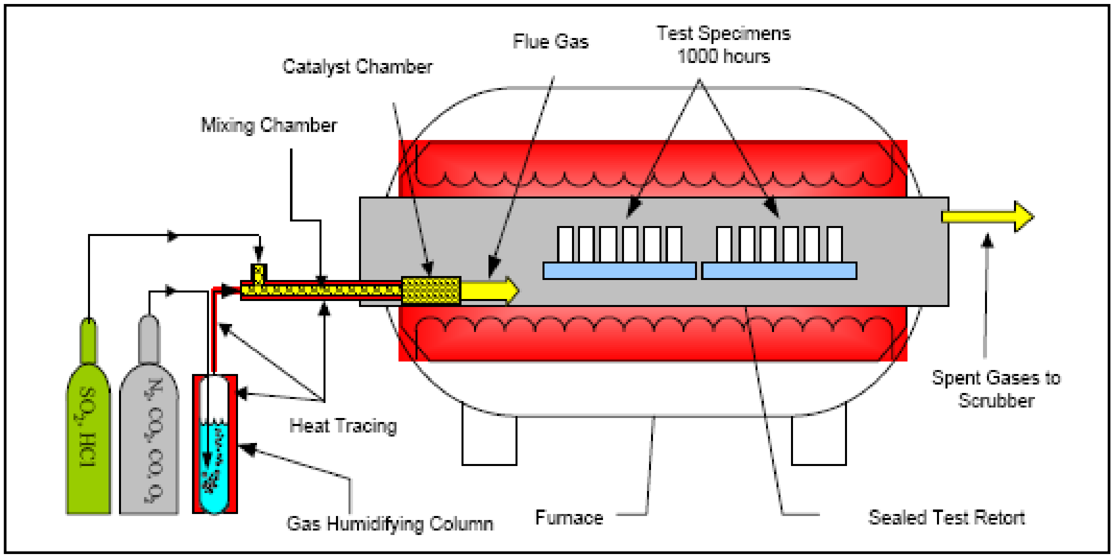

Figure 1: Coupons Mounted in Racks and Inserted in Electric Tube Test Furnaces

The coupons, mounted in racks and inserted in electric tube test furnaces (see Figure 1), will be exposed for 1,000 hours to synthesized air- and oxy-fired flue gases. Foster Wheeler will conduct CFD analyses of nominal 500-MWe air- and oxy-fired boilers to determine FGR rates, bulk flue gas compositions, corrosive wall micro-climates, and gas compositions for the furnace tests. The test gases will be synthesized/blended from gas cylinders and consist of varying concentrations of CO_2, H_2O, N_2, CO, SO_2, H_2S, and HCl.

The material coupons will be coated with three types of synthetic ash deposits representative of high, medium, and low sulfur coals. The deposits will be produced from reagent grade powders that are mixed and applied to the coupons as a paste. The waterwall materials will be tested at three temperatures: 399°C, 468°C, and 538°C (750°F, 875°F, and 1,000°F); the superheater/reheater materials will be tested at: 538°C, 593°C, and 649°C (1,000°F, 1,100°F, and 1,200°F) – temperatures that span the range of boilers operating at subcritical and supercritical pressure. Upon completion of exposure testing, the condition of the coupons will be evaluated macroscopically and microscopically and the materials will be assessed for their suitability for oxy-combustion.

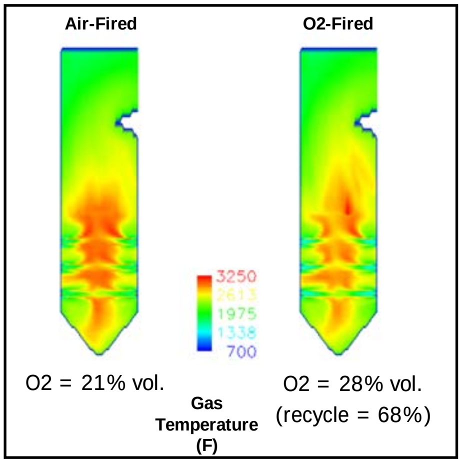

Figure 2: Example of Foster Wheeler CFD Analyses

Technology Advantages:

This project will identify the corrosion mechanisms that occur under oxy-combustion and assess the suitability of conventional and advanced boiler materials for this new combustion environment.

R&D Challenges:

FGR used for the oxy-combustion process could increase corrosion of boiler materials.

Results To Date/Accomplishments:

CFD analyses of nominal 500-MWe PC boilers (wall- and tangential-fired) have identified the bulk flue gas compositions and waterwall micro climates that will exist in these units under air- and oxy-firing. The most corrosive gas compositions together with intermediate levels of corrosiveness for each combustion mode have been selected for use in laboratory electric furnace corrosion studies. Coupons of boiler materials, coated with deposits representative of high to low sulfur coals, have been placed in the furnaces operating at boiler tube temperatures, and exposure to the gases for 1,000 hours has begun.

Next Steps:

- Complete the planned test matrix and conduct macroscopic and microscopic examination of the material coupons to identify corrosion mechanisms and material suitability for oxy-combustion.

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

"Oxy-Combustion Boiler Material Development," Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 2009, Pittsburgh, Pennsylvania.

Contract No.:

DE-NT0005262

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Partners:

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Southern Research – Evaluation of Gas Recycle for Oxy-Combustion

Project Title:

Oxygen-Fired CO_2 Recycle for Application to Direct CO_2 Capture From Coal-Fired Power Plants

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Pilot-scale using actual flue gas, 25 tonnes of CO_2/day

Primary Project Goal:

Southern Research Institute (Southern Research) is designing and developing oxygen (O_2)-fired carbon dioxide (CO_2) recycle technology for retrofit application to coal-fired utility boilers.

Technical Goals:

The technical goals of this project are to:

- Modify the pilot-scale Combustion Research Facility (CRF) to allow O_2-fired and CO_2-recycle operations.
- Design, manufacture, and install an oxy-combustion burner specifically for the CRF.
- Collect data on furnace temperatures, unburned carbon, gas composition, and flow rates into and out of the furnace.
- Evaluate the effect of various parameters, including firing configuration, oxygen purity, CO_2 recycle rate, O_2 concentration, and coal type.

Technical Content:

Southern Research is developing flue-gas recycle for retrofit application to coal-fired utility boilers in order to avoid the excessive flame temperatures that are associated with O_2-firing and to maintain flow and heat-transfer requirements in the furnace and convective sections in existing plants.

Southern Research will conduct the pilot-scale, oxy-combustion experiments using a modified CRF. Figure 1 contains a diagram that represents the CRF with the necessary modifications. These modifications include the addition of an O_2 storage tank and concrete pad; O_2 skid, control, and safety systems; a new burner by MAXON that is designed for O_2 combustion and CO_2 recycle; the additional ducting to allow flue-gas recirculation to the burner; and the decrease in ducting size to account for smaller flue gas flow rate.

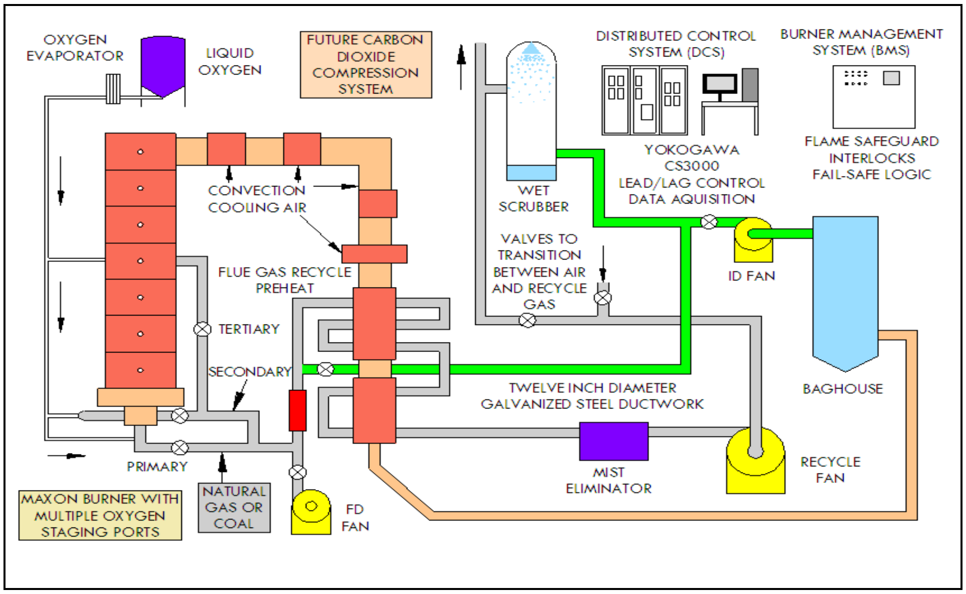

Figure 1: Diagram of the Modified CRF

The CRF will be used to investigate the effects of coal type, firing staging, percentage of flue gas recycled, and O_2 purity on oxy-combustion.

In addition to flue gas recirculation (FGR), an advanced O_2 burner developed by MAXON will be used to allow the flame shape and heat released to be controlled and to provide a stable attached flame. Figure 2 is an image of the oxy-burner being tested by MAXON that is now being used in the CRF at Southern Research.

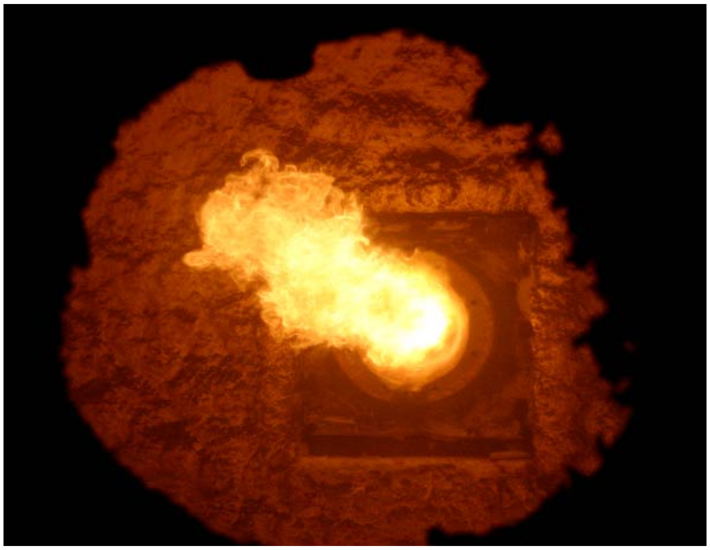

Figure 2: Image of MAXON Oxygen Burner

A preliminary test was performed on the MAXON burner using Illinois Bituminous coal. The test chamber was heated to 2,400ºF with 3% excess O_2. Performance of the burner under air-fired conditions resulted in 0.3 to 0.4 lbs nitrogen oxide (NO_X)/MMBtu. However, oxy-combustion testing resulted in 0.16 to 0.18 lbs NO_X/MMBtu.

Reaction Engineering International (REI), a project team member, also updated a computational fluid dynamic (CFD) model of the CRF facility for oxy-combustion conditions in order to predict oxy-fired burner scenarios. This model will be validated by the CRF oxy-combustion experiments and utilized for any follow on project scaleup preliminary designs.

Technology Advantages:

- Oxy-combustion burner is able to maintain a stable attached flame and can light off without natural-gas assist.
- The reduced volume flue gas produced under oxy-combustion conditions can be less expensive to purify and compress for carbon sequestration than conventional pulverized coal (PC) plants flue gas.
- Recycling dry flue gas through Powder River Basin (PRB) coal pulverizers eliminates concern of

pulverizer fires.

- Burners and recycle rate can be tuned to achieve low-cost operation (i.e., minimize recycle) and maximum heat transfer for a given boiler type and plant configuration.
- With new plants, advanced thermodynamic cycles can recover some of the energy penalty associated with air separation.

R&D Challenges:

- Cost of retrofit for existing plants is significant.
- Energy penalty to produce O_2 is approximately 25%.
- Concern about corrosion of low-temperature ductwork and equipment.

Results To Date/Accomplishments:

- The retrofit has been completed and checked out.
- All of the ductwork, piping, valves, control systems, computers, and safety systems have been installed. The Burner management system has been installed.
- Completed the stand-alone version of the CFD model.
- Manufactured, tested, and installed the oxy-fuel burner in the 1-MW facility.

Next Steps:

- Currently constructing a modification to the system in the form of heat exchangers to cool the recycled flue gas and sulfur dioxide (SO_2) scrubber.
- Conduct FGR and oxy-combustion tests on various coals and firing configurations in the CRF facility, while altering the following factors:
  - Staging (order in which components are deployed in burner).
  - Percentage of FGR.
  - Oxygen purity.
- Compile the data from the testing and the studies done in conjunction with DTE Energy.
- Perform runs of the CFD computer model for each of the test conditions performed or scheduled.
- Final test results will not be available until the June 2010 project completion date.

Available Reports/Technical Papers/Presentations:

Southern Research Oxy-Combustion Presentation – March 2009.

Contract No.:

DE-FC26-05NT42430

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DTE Energy
Maxon Corporation
Reaction Engineering International
Southern Company

Reaction Engineering International – Characterization of Oxy-Combustion Impacts

Project Title:

Characterization of Oxy-Combustion Impacts in Existing Coal-Fired Boilers

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Laboratory-, bench-, and pilot-scale using simulated and actual flue gas, 0.3-8 tonnes of CO_2/day

Primary Project Goal:

Reaction Engineering International (REI) is characterizing and predicting the performance and operational impacts of oxy-combustion retrofit designs on existing coal-fired boilers. Investigations include bench-, laboratory-, and pilot-scale tests, as well as computer simulations.

Technical Goals:

- Collect fundamental data that describes flame characteristics, corrosion rates, and ash deposition properties of coal-fueled air- and oxy-combustion.
- Conduct bench-scale tests for char burnout characterization.
- Conduct laboratory-scale tests for ash characterization with flue gas recirculation (FGR).
- Develop, install, and operate an oxy-fired research burner in a pilot-scale furnace.
- Conduct pilot-scale tests for flame characteristics, heat flux, deposition, and corrosion under different burner firing conditions and multiple coals.
- Develop, validate, refine, and publish sooting, char oxidation, slagging, fouling, and corrosion mechanisms.
- Incorporate validated descriptions of oxy-combustion processes (mechanisms) into computational fluid dynamics (CFD) software to evaluate full-scale oxy-combustion retrofit designs.
- Use CFD software to assess retrofit oxy-firing system and gas recycle designs for an existing pulverized coal-fired utility boiler.

Technical Content:

The primary objective of this program is to develop tools to characterize and predict impacts of carbon dioxide (CO_2) FGR and burner feed design on flame characteristics (burnout, nitrogen oxide [NO_X], sulfur oxide [SO_X] and fine particle emissions, heat transfer), fouling, slagging and corrosion, inherent in the retrofit of existing coal-fired boilers for oxy-coal combustion. This objective will be met by producing multi-scale experimental data focused on burner design, char oxidation, soot evolution, ash characterization and deposition, and corrosion. Mechanisms capable of describing these phenomena under air- and oxy-fired conditions will be developed and validated using the data generated during experimentation and from the literature. The mechanisms will be implemented into a CFD code and an existing coal-fired utility boiler will be modeled under air- and oxy-fired conditions to identify the likely impacts of retrofit.

This project has been tailored to both identify potential impacts of the oxy-combustion retrofit of existing coal-fired utility boilers (through multi-scale experiments) and to develop tools that will allow accurate prediction of these impacts (through mechanism development). Experiments will be performed on three different scales: (1) a bench-scale optical entrained flow reactor will be used to elucidate the impact of oxy-combustion flue gas composition on the rate of char oxidation; (2) a 100-kW lab-scale combustor will be used to characterize the effects of FGR on ash characteristics; and (3) a 1.2-MW pilot-scale combustor will be used to investigate burner and firing system principles, deposition, corrosion, and radiative heat transfer, including soot evolution. The data from these experiments will be used to guide development of mechanisms that may be used to describe char oxidation, deposition (slagging and fouling), corrosion, and soot evolution. The data generated will also be used to produce an overview of firing system principles for oxy-combustion that may help guide design of full-scale firing systems.

Bench-Scale Optical Entrained Flow Reactor Experiments

Bench-scale experimentation will take place at Sandia National labs to further elucidate the behavior of char in an oxygen (O_2)-enriched FGR gas matrix. These experiments will be conducted in Sandia's optical entrained flow reactor and associated particle-sizing pyrometry diagnostics.

100 kW Oxy-Fuel Combustor (OFC) Experiments

Data related to ash characterization and deposition will be collected using experiments conducted in the University of Utah's 100-kW Oxy-Fuel Combustor (OFC), shown in Figure 1. The furnace consists of an OFC chamber and radiant zone in the vertical section, followed by a horizontal convective section where temperature profile is prescribed through adjustment of independently controlled cooling coils to simulate practical furnace temperature profiles.

These air- and oxy-fired experiments will focus primarily on effects of FGR on ash chemistry, under practical time/temperature/particle composition conditions. Multiple modes of gas recycle will be tested to investigate FGR conditions ranging from hot, moist, and particle laden gases to clean CO_2. This information will provide insight into how slagging and fouling may be impacted under oxy-firing conditions. Measurements will include sampling of ash aerosol using low-pressure impactors and isokinetic dilution probes. In addition, mobility particle sizers will determine ultrafine (sub-micron) particle concentrations and particle size distributions, and EDS and CCSEM techniques will be used to identify ash compositions.

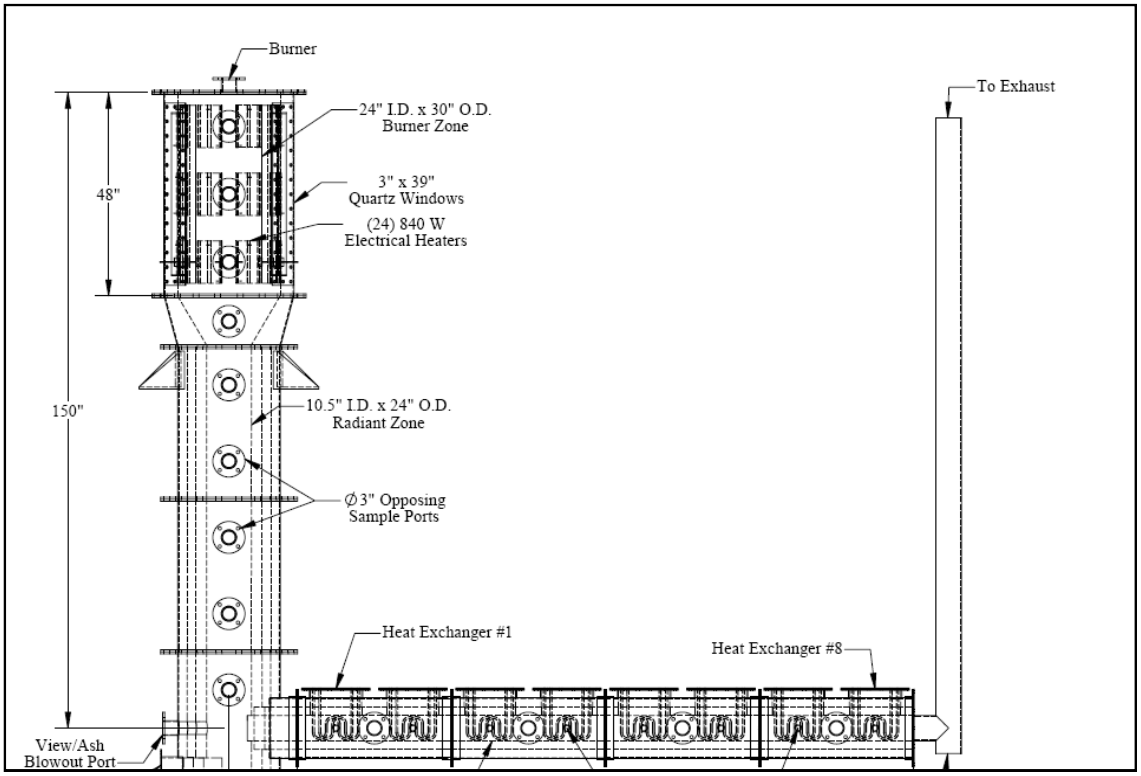

Figure 1: Diagram of 100 kW Oxy-Fuel Combustor (OFC)

Figure 2: Pilot-Scale Combustion Facility (L1500)

1.2 MW Pilot-Scale Furnace (L1500) Experiments

Pilot-scale experiments will be performed in a 1.2-MW pulverized coal furnace (L1500). These experiments will be designed to investigate firing system configuration impact on flame stability and heat transfer, soot evolution and water wall, and superheat material corrosion. A picture of the L1500 is shown in Figure 2. Four weeks of parametric testing will be performed in the L1500 to develop practical guidelines that allow optimized operation of an actual burner under oxy-firing conditions with FGR. The test plan will be developed to meet these goals. Burner operating parameters of interest include:

1. Variable O_2, FGR, and coal distribution in the burner.
2. Variable FGR ratios that produce 27% and 32% O_2 in the O_2/FGR mixture.
3. Variable burner stoichiometric ratio within the range of 0.8 to 1.2.
4. Targeted O_2 injection.
5. Furnace staging of FGR independent of burner conditions.

Six weeks of testing will be performed in the L1500 to characterize corrosion under both air- and oxy-combustion conditions. Results from previous experiments will be used to identify regions in the furnace for installation of the corrosion probes where deposition, heat flux, and flue gas compositions will be favorable for corrosion and relevant for full-scale utility boilers. The parameters of interest in the corrosion test plan will be:

1. Air- and oxy-fired conditions.
2. PRB and bituminous coals.
3. Optimized O_2, FGR, and coal distribution in the burner, from previous experiments.
4. Variable flue gas recirculation ratio, within the limits from previous experiments.
5. Variable burner stoichiometric ratio, within the limits from previous experiments.

Measurements that will be performed in the pilot-scale furnace include:

1. Flue gas composition (O_2, CO_2, carbon monoxide [CO], NO_X, and sulfur dioxide [SO_2]) using existing CEMs.
2. Unburned carbon in ash, using loss on ignition analysis.
3. Flame attachment, using ultraviolet sensors and cameras.
4. Real-time corrosion measurements.

5. Deposition rate and composition at the corrosion locations.
6. Heat flux at the corrosion locations and other locations in the furnace.
7. Local flue gas temperatures, using suction pyrometry.
8. Soot volume fraction using the two-color extinction method.

Technology Advantages:

- Enable the development of validated combustion mechanisms specifically designed for oxy-combustion with FGR for retrofitting existing coal-fired boilers.
- Identify firing system principles that guide oxy-burner design and potential retrofit strategies.
- Quantify impacts of flue-gas recycle properties on ash deposition.
- Develop the capability to assess the performance and optimize the retrofit of oxy-combustion to a full-scale existing boiler to minimize retrofit cost and maximize operability.

R&D Challenges:

- Ability to control and quantify how much air-in leakage occurs inside the oxy-fuel combustor and L1500 furnace during the experiments.
- Development and operation of a coal-fired research burner specifically designed to span a range of coal/ O_2/FGR injection strategies and operating conditions.
- Correlation of experimental data with mechanisms and model predictions in order to provide adequate mechanism/model validation.

Results To Date/Accomplishments:

- Completed baseline ash characterization tests in OFC.
- Completed baseline char oxidation experiments at Sandia.
- Completed design, construction, and delivery of oxy-research burner to University of Utah in preparation for Year 2 pilot-scale testing in L1500 furnace.
- Worked with oxygen supplier and team member Praxair to identify safe operational limits (temperature and oxygen concentration) for oxy-research burner.
- Completed slagging model implementation in CFD code and ran air-fired coal combustion/slagging simulation for 800-MW boiler.
- Completed identification of corrosion correlations for previously identified mechanisms.
- Completed design and acquisition of corrosion probe materials; completed fabrication of probes in preparation for Year 2 tests.
- Completed initial burner parametric testing on L1500 furnace.

Next Steps:

- Test effects of FGR on ash size and composition and determine how this affects fouling and slagging.
- Develop char oxidation mechanism.
- Develop soot formation mechanism.
- Complete burner parametric tests and targeted O_2 injection tests in L1500 furnace.
- Conduct oxy-coal corrosion tests in L1500 furnace.
- Test for the impacts of FGR on soot.
- Use results of L1500 burner tests to develop a full-scale firing system.
- Develop a model of a full-scale oxy-combustion boiler retrofit.
- Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

"Characterization of Oxy-Combustion Impacts in Existing Coal-Fired Boilers," NETL CO_2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, Pennsylvania, March 2009.

Fry, A. and Adams, B., "Characterization and Prediction of Oxy-combustion Impacts in Existing Coal-fired Boilers," 34th International Technical Conference on Clean Coal & Fuel Systems, Clearwater, Florida, June 2009.

Fry, A., Adams, B., Cremer, M., Shan, J., "Development of Oxy-Burner Retrofit Principles for Existing Coal-Fired Utility Boilers," IEA 1st International Oxy-Fuel Combustion Conference, Cottbus, Germany, September 2009.

Adams, B., Fry, A., Senior, C., Wang, D., "Oxy-combustion Impacts on Coal Ash Slagging and Fouling," IEA 1st International Oxy-Fuel Combustion Conference, Cottbus, Germany, September 2009.

Contract No.:

DE-NT0005288

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Sandia National Laboratory
Siemens Energy
Southern Company
University of Utah
Vattenfall AB

Babcock & Wilcox – Oxy-Combustion for Cyclone and Wall-Fired Boilers

Project Title:

Development of Cost-Effective Oxy-Combustion Technology for Retrofitting Coal-Fired Boilers

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Pilot-scale laboratory testing using actual flue gas, equivalent to 13 tons of CO_2/day

Primary Project Goal:

Babcock and Wilcox (B&W) is developing oxy-combustion technology for application to new and existing cyclone and wall-fired boilers. A two-phase research project is being conducted that includes pilot-scale testing and a full-scale engineering and economic analysis.

Technical Goals:

- Conduct pilot-scale testing to evaluate the effect of coal rank (i.e., bituminous, subbituminous, and lignite) on oxy-combustion boiler operation.
- Determine the equipment requirements for the boiler island, flue gas purification, carbon dioxide (CO_2) compression, CO_2 transportation, and CO_2 sequestration for different coal ranks and boiler designs.
- Investigate the potential for multi-pollutant (nitrogen oxides [NO_X], sulfur dioxide [SO_2], and particulate) emissions control.
- Validate an existing three-dimensional computational flow, heat transfer, and combustion model for oxy-combustion scale up to a commercial-size boiler.
- Conduct an engineering and economic assessment of the technology for commercial-scale retrofit and green field application for cyclone and wall-fired boilers.
- Assess CO_2 capture cost reductions via energy integration of the air separation unit (ASU), flue gas purification, and CO_2 compression systems.
- Evaluate the impact of oxy-combustion implementation on net power production and cost of electricity (COE) for cyclone and wall-fired boilers.

Technical Content:

B&W is conducting pilot-scale tests – 14 GJ/hr (6 million Btu/hr) – of oxy-combustion for three coals and two oxy-combustion process configurations at its Barberton, Ohio, test facility. An illustration of the oxy-combustion pilot-scale test facility is shown below (Figure 1). The three types of coal being tested are lignite (North Dakota), sub-bituminous (Decker), and bituminous (Ohio #5). Each of the oxy-combustion tests will run for 100 continuous hours to assess the slagging, fouling, heat transfer, and overall operability characteristics. Data from the pilot-scale testing will be used to validate a computational fluid dynamic (CFD) model of the oxy-combustion process. From the test data, equipment required for flue gas purification, compression, transportation, and sequestration will be determined for the engineering and economic assessment.

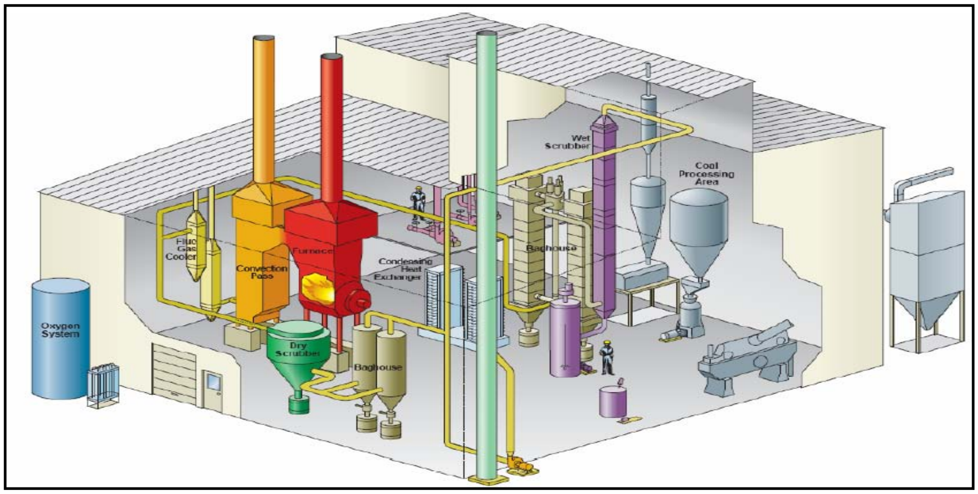

Figure 1: Illustration of B&W's Oxy-Combustion Pilot-Scale Test Facility in Barberton, Ohio

A modeling assessment is being conducted to compare three CO_2 capture purification processes: 1) no purification – only drying to Kinder Morgan pipeline specifications with water (H_2O) at 600 parts per million volume (ppmv); 2) partial condensation at cryogenic conditions (cold box) – 95% CO_2 purity target; and 3) cold box including distillation – 1 parts per million (ppm) oxygen (O_2) target. The purification assessment includes investigation of operating costs, energy requirements, and effects of air infiltration. The following graph (Figure 2) represents a model analysis showing the effect of purification process on CO_2 recovery, purity, and specific energy.

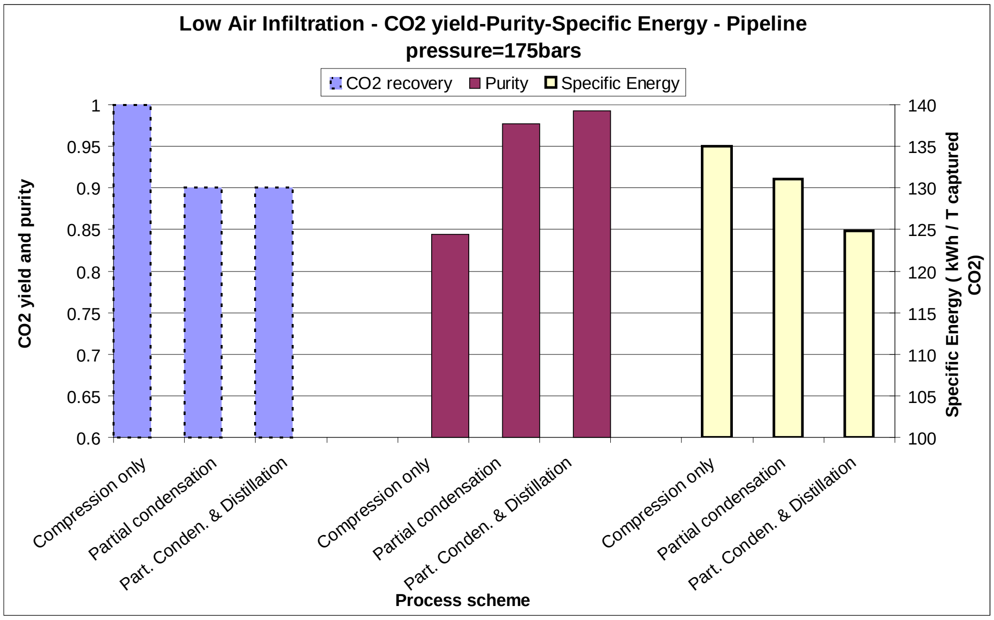

Figure 2: Model Analysis Showing Effect of Purification Process on CO_2 Recovery, Purity, and Specific Energy

Technology Advantages:

- Oxy-combustion has the potential to offer a lower cost solution for CO_2 capture compared to post-combustion CO_2 capture technologies.

R&D Challenges:

The necessary level of flue gas purification remains an issue regarding potential adverse impacts on CO_2 transportation and storage:

- Potential precipitation problems with sulfur dioxide (SO_2) forming sulfate minerals (e.g., anhydrite) if high-sulfur coal is used without scrubbing.
- Non-condensable gases, such as nitrogen (N_2) and O_2, could affect subsurface processes which might require more purification. For example, non-condensable gases could create multi-phase flow which can reduce injectivity or the capacity of the storage site.

Results To Date/Accomplishments:

- Conducted oxy-combustion pilot-scale testing.
- Performed purification and compression studies.
- Determined through sequestration modeling that co-sequestration can be performed with unpurified CO_2 streams (dependent upon geological formations depth, injectivity, and reservoir efficiency).

Next Steps:

- Complete oxy-combustion pilot-scale testing.
- Complete full-scale engineering and economic analysis.
- If the technology is economically viable, a scaleup methodology to full-scale should be determined.

Final test results will not be available until the September 2010 project completion date.

Available Reports/Technical Papers/Presentations:

"Development of Cost Effective Oxy-Combustion for Retrofitting Coal-Fired Boilers," NETL CO_2 Capture Technology for Existing Plants R&D meeting in Pittsburgh, Pennsylvania, March 2009.

"Considerations for Treating Impurities in Oxy-Combustion Flue Gas Prior to Sequestration," 9th International Conference on Greenhouse Gas Control Technologies in Washington, DC, Nov. 2008.

"Developing Oxy-combustion for Retrofitting Coal-fired Boilers," 7th Annual Conference on Carbon Capture and Sequestration in Pittsburgh, Pennsylvania, May 2008.

"Development of Cost Effective Oxy-Combustion Technology for Retrofitting Coal-Fired Boilers," NETL Fact Sheet.

Contract No.:

DE-FC26-06NT42747

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Air Liquide
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Jupiter Oxygen – Oxy-Combustion and Integrated Pollutant Removal

Project Title:

Jupiter Oxy-Combustion and Integrated Pollutant Removal Research and Development Test Facility

Technology Area:	**Technology Maturity:**
Oxy-Combustion	Bench- and pilot-scale

Primary Project Goal:

Jupiter Oxygen is designing, constructing, and operating a 5-MWe, high flame temperature, oxy-combustion test facility with a 20-kWe integrated pollutant removal (IPR) bench-scale system to demonstrate carbon dioxide (CO_2) capture from an oxy-combustion process.

Technical Goals:

- Develop high flame temperature oxy-fuel burners.
- Collect data on burner performance and boiler heat transfer.
- Conduct a study of the ash and slagging characteristics of the process and its impact on boiler materials.
- Capture CO_2 and collect data on impurity removal using the Jupiter Oxygen combustion process along with IPR technology developed by NETL.

Technical Content:

There are two different approaches to oxy-combustion. Jupiter's approach is to use a high temperature flame that is minimally tempered with nitrogen, CO_2, or other inert gases (the only tempering occurs as a result of flue gas recycle (FGR) that is used to motivate coal). High flame temperature oxy-combustion results in improved heat transfer in the boiler's radiant zone. Other oxy-combustion facilities use a low flame temperature approach which uses large amounts of CO_2 recycled through or at the burner to cool the flame to a temperature similar to air firing. The unique combination of the high-temperature approach coupled with the IPR system will allow the evaluation of the impact of using high- and low-temperature approaches and energy recovery on a variety of aspects of power plant operations.

Heating value, mineralogy, and trace element content of the coal will be determined using ASTM procedures, including proximate and ultimate analyses. This information will be used to determine the effect of the coal characteristics on oxy-combustion performance and the effectiveness of emissions capture. Other performance measurements for the test facility include water tube and web temperature, heat transfer rate, flue gas emissions (nitrogen oxides [NO_X], carbon monoxide [CO], CO_2, sulfur dioxide [SO_2], and trace metals), and loss on ignition (LOI) of the ash. The facility will incorporate the following approaches to conduct measurements:

- Flue gas species concentrations will be measured by Fourier Transform Infrared Spectroscopy (FTIR).
- Ash LOI will be measured by laboratory testing.
- Heat transfer in the radiant zone will be determined by spectral flame mapping, furnace gas temperature measurement (at the screen wall and boiler exit), temperature measurements of the flux through the boiler tubes, and optical measurements of the total radiant heat flux from the flame.
- Net heat output from the burner and heat absorbed by the boiler will be calculated based on combustion and steam side energy balances.
- Combustion side mass balances will be calculated by combining species measurements with mass flows.
- Corrosion monitoring probes will be used.

- Gas-phase and particulate-phase trace elements including mercury (Hg) by will be measured by samples from select runs.
- IPR contaminant removal will be measured by laboratory analyses and FTIR.

The IPR system was added to the pilot facility to remove pollutants from the oxy-combustion flue gas re-circulated stream. The current device is used to process 45 to 64 kg/hr (100 to 140 lb/hr) of flue gas from the facility. The IPR system will capture, separate, and produce a dry, supercritical stream of CO_2; a stream of captured pollutants; and a stream of condensed water from the flue gas. Figure 1 shows a representation of the IPR system that is integrated at a pilot-scale facility.

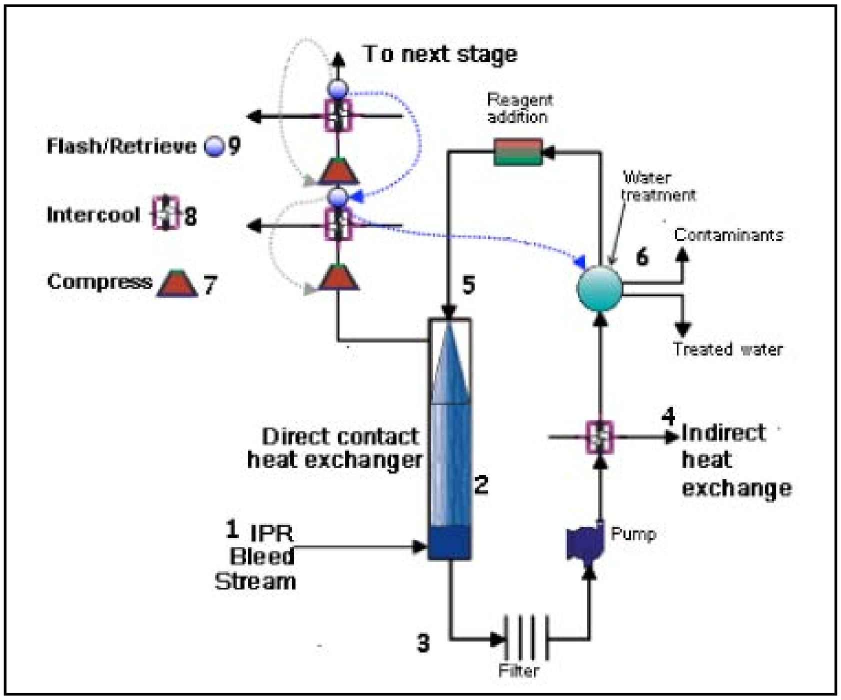

Figure 1: Representation of IPR System Integrated at a Pilot-Scale Facility

The generalized IPR process flow diagram is presented above: a flue gas bleed stream (1) enters the IPR system into a glass-pipe spray tower (2) in which sulfur oxide (SO_X) is removed by a spray stream (reagent addition) as the gas rises. The spray water and combustion condensed water (3) are cooled (4) and partially re-circulated back into the spray tower (5). The water that is not re-circulated back in to the spray tower is treated outside the IPR system (6). As the scrubbed gas leaves the tower, it enters a two-stage reciprocal compressor (7) and a water-cooled, counter flow heat exchanger (8). During the compression stage, separated water can be collected in the collection vessel (9).

Technology Advantages:

The higher flame temperature improves heat transfer in the radiant zone which increases boiler efficiency, lowers the quantity of flue gas, concentrates CO_2 in the flue gas, significantly reduces NO_X emissions and results in fuel savings. For retrofit applications, this technology maintains actual water wall and steam temperatures without altering the boiler design or size. For new construction this technology can use a smaller boiler, which provides the same thermal output as larger existing power plant boilers.

R&D Challenges:

High flame temperature oxy-combustion is still being tested at the pilot scale. Some issues that could arise include increased corrosion, fouling, and slag formation. A better understanding of the interaction of ash, SO_X, and slag on boiler materials is required.

Results To Date/Accomplishments:

- Retrofit and operated a 5-MWe equivalent oxy-coal combustion test facility and the ancillary systems.
- Performed a series of oxy-coal burner development tests which resulted in a modified first generation burner.
- Performed parametric studies with the modified first generation oxy-coal burner.
- Retrofit completed without major boiler modifications.
- No increased fouling and slagging indicated (study continues).
- No damage to boiler materials indicated (study continues).
- Measured performance and species streams in the IPR system.

Next Steps:

Further work with the 5-MWe equivalent oxy-coal combustion test facility and the ancillary support systems will include the following:

- Installation of a larger FGR blower to test at higher recirculation rates.
- Ramp up to the full 50 MMBtu/hr rating of the existing modified first generation burner.
- Develop a second generation high-temperature oxy-coal burner with the aid of computational fluid dynamic (CFD) modeling.
- Develop an air-coal performance base line for the test facility.
- Conducting IPR system performance tests to optimize heat recovery and gas reactions.
- Complete slagging and fouling studies and boiler material corrosion studies.
- Conducting analysis for technical and economic scale up of the technologies.
- Developing data summaries from the studies.

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations:

S. Gerdemann, C. Summers , D. Oryshchyn , B. Patrick , T. Ochs, "Developments in Integrated Pollutant Removal for Low-Emission Oxy-Fuel Combustion."

Jupiter Oxycombustion and Integrated Pollutant Removal of the Existing Coal-Fired Power Generation Fleet – CO_2 Capture Technology for Existing Plants R&D Meeting – March 2009.

Results of initial operation of the Jupiter Oxygen Corporation oxyfuel 15 MWth burner test facility – Paper presented at GHGT-9 Conference – November 2008.

The Jupiter Oxygen Boiler Test Facility: 3rd Generation – Poster presented at GHGT-9 Conference – November 2008.

Project Topical Report [PDF-58KB] (Aug 2009).

Project Status Update [PDF-28KB] (Jan 2009).

Contract No.:
FC26-06NT42811

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EPRI
Maxon Corporation
Michigan State University
Purdue University
University of Wyoming

CanmetENERGY – Engineering Assessment of Oxy-Combustion

Project Title:

CanmetENERGY CO_2 R&D Consortium

Technology Area:	**Technology Maturity:**
Oxy-Combustion and CO_2 Capture	Pilot-scale

Primary Project Goal:

The CanmetENERGY CO_2 R&D Consortium (Consortium) is conducting oxy-fuel combustion research and development (R&D) using a 0.3 MWth (1 million Btu/h) modular pilot-scale facility. The Consortium has completed nine successive phases of R&D that include oxy-fuel combustion, advanced power cycles, integrated multi-pollutant control, and carbon dioxide (CO_2) capture and compression technologies.

Technical Goals

The technical goal of the Consortium is to develop advanced energy conversion technologies with near-zero emissions for improved efficiency and commercial competitiveness for capture of CO_2 and air pollutants resulting from combustion of fossil fuels. One emphasis of the Consortium research program is the oxy-fuel combustion technology. Since, combustion takes place in an oxygen (O_2)-enriched environment, the flue gas comprises mainly CO_2, water, and minor impurities. This CO_2-rich flue gas stream can then be purified, dried, and compressed for pipeline transport and use or permanent storage in geological formations. Oxy-fuel combustion also results in efficiency advances of high flame temperatures and reduced equipment sizes due to lower gas volume.

Technical Content:

The Consortium activities in the past have included experimental investigations using coal; coal slurry; bitumen and natural gas to study the characteristics of oxy-fuel combustion; advanced near-zero emissions Brayton and Rankine cycles; solid oxide fuel cell modeling; multi-pollutant capture research for integrated removal of fine particulates, nitrogen oxide (NO_X), sulfur oxide (SO_X), and mercury (Hg); advanced oxy-fuel combustion processes and co-firing with opportunity fuels such as petroleum coke; system components and prototype design and pilot-scale testing; and modeling and development of new CO_2 capture and compression processes.

The latest completed Phase 9 of the Consortium's program included the development of a CO_2 capture and compression unit. This unit is capable of separating and compressing CO_2 from combustion flue gas streams for pipeline transport and storage. Part of this work involved the development of a CO_2 high-pressure test cell for studying CO_2 phase change, generating vapor-liquid equilibrium (VLE) data, and studying the impact of impurities in the flue gas stream on the capture processes. This has important practical applications relating to the CO_2 pipeline, material selection, and commercial design of these systems. Other ongoing R&D activities include the modeling of advanced supercritical oxy-coal plants with CO_2 capture; cost analysis; the development and testing of multi-pollutant control strategies, as well as testing in oxy-steam mode; and optimization of a novel multi-function oxy-fuel/steam burner.

Figure 1 shows the major process components comprising the 0.3 MWth oxy-fuel Vertical Combustor Research Facility (VCRF) integrated with the CO_2 capture and compression unit (CO_2CCU). The overall pilot-scale research facility is used to develop pollutant control technologies that incorporate a fabric filter or ESP for particulate capture, condensing heat exchangers and/or SO_X scrubbing to remove acid gases and oxidized Hg from the flue gas combustion stream.

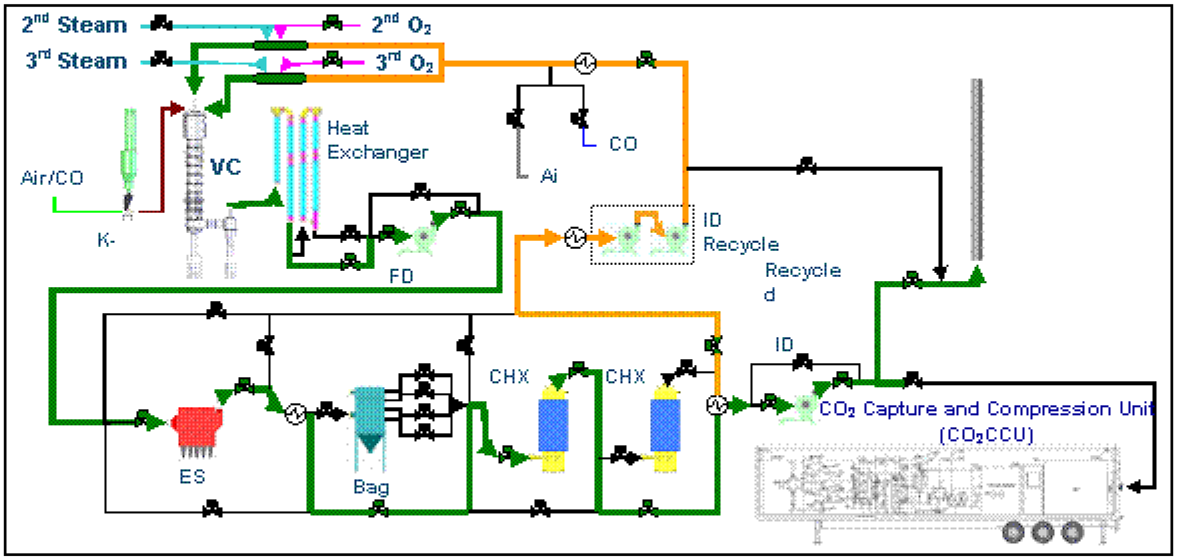

Figure 1: Schematic of the CanmetENERGY's Integrated Oxy-Fuel Vertical Combustor Research Facility

Figure 2 displays the pilot-scale CO_2CCU. The CO_2CCU is capable of processing CO_2 flue gas streams at a maximum rate of 160 Kg/hr with CO_2 concentrations of 50% or higher (in dry volume) to produce a CO_2 product stream with more than 95% purity.

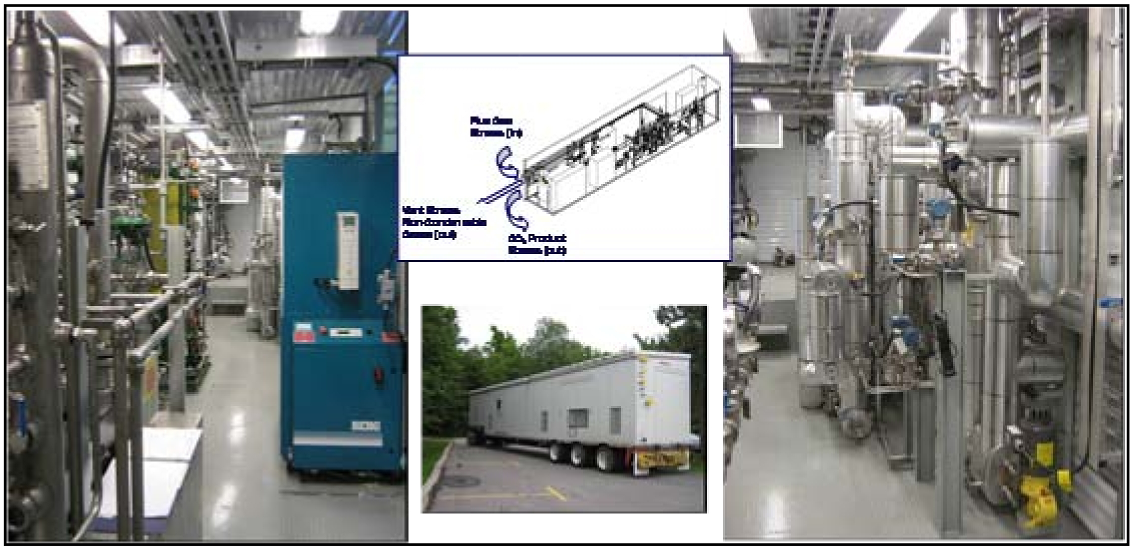

Figure 2: CanmetENERGY's CO_2 Capture and Compression Unit

The high-pressure CO_2 test cell and its high-pressure viewing chamber (HPVC) shown in Figure 3 were used to create supercritical CO_2 and study the CO_2 phase change in a controlled environment. The chamber can handle a maximum pressure of 200 atm and a temperature range of -60°C to 150°C. There are two gas and liquid sample ports located at different heights and optical windows with a CCD camera for observations inside the chamber to study the CO_2 liquid-gas interface.

Figure 3: CanmetENERGY's High-Pressure CO_2 Test Cell and Bench-Scale Facility

Technology Advantages:

- The program allows research to be carried out at a pilot scale small enough to reduce the overall R&D cost, while the experiments scale is sufficiently large enough to provide proof-of-concept before proceeding to a larger and more costly medium-scale pilot technology demonstration.

R&D Challenges:

- Integration and cycle development for O_2/flue gas recirculation (FGR), O_2 combustion, and hydroxy-fuel combustion of fossil fuels in different advanced cycles.
- Improving the understanding of combustion, heat transfer, and emissions in oxy-fuel combustion.
- Development of environmental multi-pollutant controls for NO_X, SO_X, Hg, and particulates.
- Minimizing energy demand for O_2 production while keeping the O_2 purity high.
- Decreasing energy consumption for capture and compression of CO_2.

Results To Date/Accomplishments:

- Developed new, ultra-low NO_X oxy-combustion burner and tested the prototype burners in VCRF with sub-bituminous and lignite coals.
- Determined that FE^{3+} salts were capable of oxidizing Hg and achieved a 75% Hg oxidation with an optimal pH between 1 and 3 on bench-scale tests.
- Increased the computational fluid dynamic (CFD) tools for model simulation of oxy-combustion flame characteristics.
- Created a CO_2 capture and compression process simulator and implemented a pilot-scale CO_2 capture research facility that has enhanced the program's CO_2 research capabilities.
- Developed new advanced gas turbine and high-efficiency fuel cell-based power generation cycles.
- Developed models of advanced supercritical oxy-coal plants with CO_2 capture and cost models for economic analysis.
- Developed and tested multi-pollutant control strategies and processes.
- Conducted testing in oxy-steam mode for pulverized coal and performed optimization of a novel multi-function oxy-fuel/steam burner.

Next Steps:

Phase 10 program work under consideration will include projects in areas related to the modeling and economic analysis of supercritical coal-fired plants with CO_2 capture; performance testing of an advanced CO_2 recovery module; development of global control strategies for the CO_2CCU; development of multi-pollutant control processes for removal of SO_X, NO_X, and Hg emissions using the CO_2CCU; testing of a novel hot sieving electrostatic precipitator; development of process models for advanced post-combustion capture of CO_2; development of models and optimization tools for mitigating greenhouse gas (GHG) emissions from oil sands and upgrading facilities; and oxy-firing of bio-based fuels with CO_2 capture.

Available Reports/Technical Papers/Presentations:

“Novel Oxy-Steam Burner for Zero-Emission Power Plants,” 1st International Oxy-Fuel Combustion Conference, Cottbus, Germany, September 2009.

“Performance of an Advanced Pilot-Scale CO_2 Capture and Compression Unit,” 1st International Oxyfuel Combustion Conference, Cottbus, Germany, September 2009.

"An Integrated Approach for Oxy-fuel Combustion with CO_2 Capture and Compression," 7th Annual Conference on CCS – May 5-8, 2008.

Contract No.:

IEA-CANMET-CO2

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The CO_2 Capture Project (CCP2)
U.S. Dept. of Energy
Governments of Canada and Alberta
Ontario Power Generation
SaskPower

APPENDIX

OXYGEN PRODUCTION

Linde – Ceramic Auto-Thermal Recovery

Project Title:

Pilot-Scale Demonstration of a Novel, Low-Cost Oxygen Supply Process and its Integration with Oxy-Fuel Coal-Fired Boilers

Technology Area:	**Technology Maturity:**
Oxygen Supply	Pilot-scale, 0.7 tonnes O_2/day

Primary Project Goal:

Linde, LLC, formerly The BOC Group, is conducting pilot-scale tests of its Ceramic Auto-Thermal Recovery (CAR) oxygen (O_2) generation process, integrated with a coal-fired combustor, to produce a carbon dioxide (CO_2)-rich flue gas.

Technical Goals:

Phase I:

- Evaluate the performance of a 0.7-tonne/day, O_2 pilot-scale CAR system (long- and short-duration), when fully integrated with a pilot-scale coal combustor, and determine the optimum operating conditions of this unit.
- Perform a techno-economic evaluation of a commercial-scale, O_2-fired power plant that utilizes a CAR system to provide the O_2.

Phase II:

- Design and construct a nine-tonne/day, O_2 pilot-scale CAR unit.

Technical Content:

In the CAR process, O_2 is separated from an air stream using a perovskite ceramic oxide adsorbent (composed of lanthanum, strontium, cobalt, and iron) at high temperature (800°C to 900°C). As shown in Figure 1, the process involves two separate beds that are cycled to deliver the O_2 flow (one bed is adsorbing the oxygen, while the other is desorbing). The O_2 is desorbed from the catalyst by a partial pressure swing using a purge gas containing low levels of O_2 in standard runs; CO_2 is used for this purpose. Half cycle times are varied for most efficient operational parameters, but fall in the range of 30 seconds to one minute. Multiple temperatures are monitored in the catalytic bed and are spatially placed to give an accurate representation of the bulk temperatures in the ceramic bed.

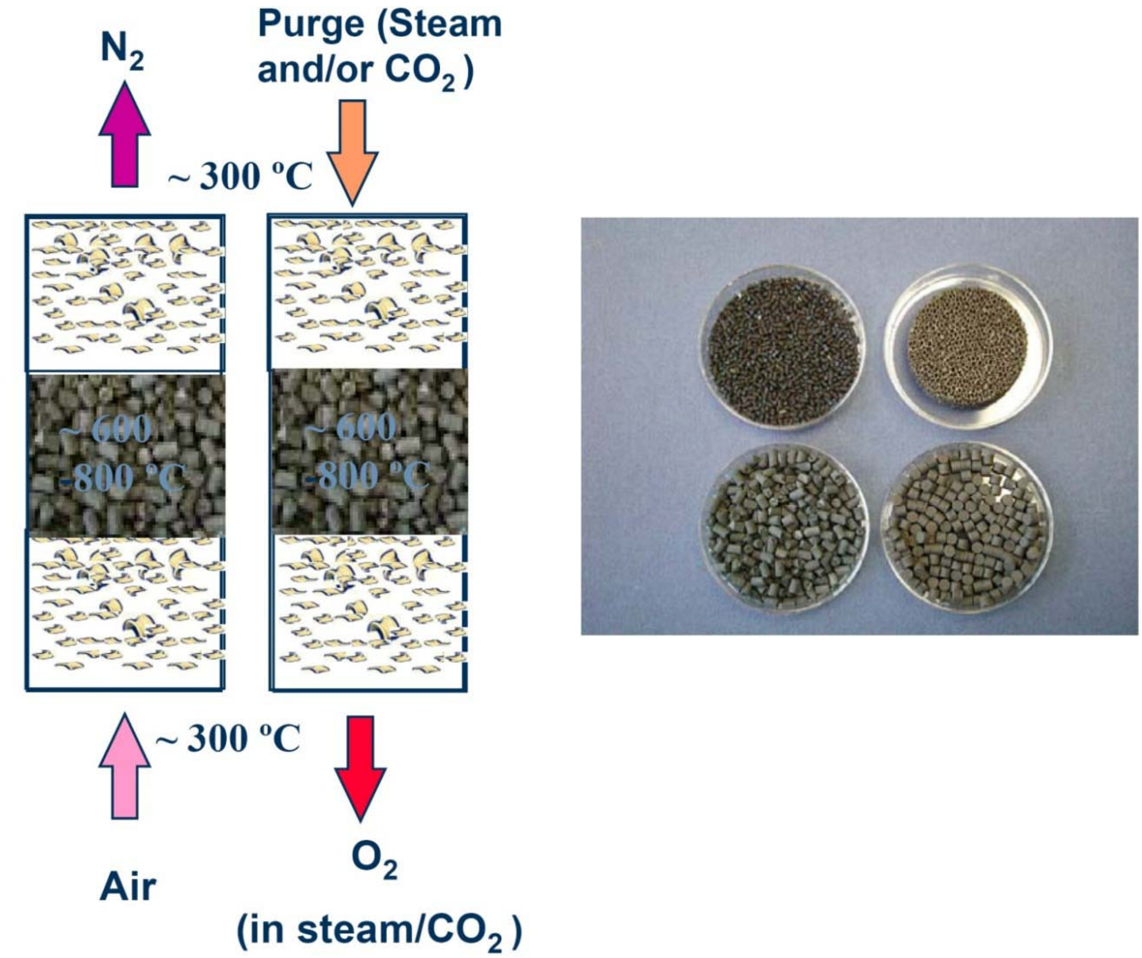

Figure 1: Ceramic Auto-Thermal Recovery (CAR) Two-Bed Oxygen Separation Process

Technology Advantages:

The O_2 production process has shown a clear advantage in performance and cost compared to an air separation unit (ASU).

R&D Challenges:

Although the CAR process alone compares favorably to an ASU, the techno-economic analysis has shown that overall capital costs, heat losses, and fuel consumption make the CAR process unfavorable compared to an ASU unless the working oxygen capacity of the CAR adsorbent can be increased from the current level of approximately 0.5 wt% to approximately 1.0 wt%. In addition, long duration tests have shown that the perovskite adsorbent experiences substantial mechanical breakdown and decline in performance when exposed to sulfur dioxide (SO_2).

Results To Date/Accomplishments:

Completed Phase I activities include:

- Evaluated the performance of the 0.7-tonne/day, O_2 pilot-scale CAR system (long- and short-duration) and determined the optimum operating conditions of the unit.
- Performed a techno-economic evaluation of a commercial-scale, O_2-fired power plant that utilizes a CAR system to provide the O_2.

Next Steps:

Phase I results led to cancellation of Phase II activities; project completed September 2008.

Available Reports/Technical Papers/Presentations:

May 2007 Presentation, 6th Annual Conference on Carbon Capture and Sequestration, Pittsburgh, Pennsylvania.

Contract No.:

DE-FC26-06NT42748

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Partners:

Alstom Power Plant Laboratories
Western Research Institute

Air Products – Ion Transport Membrane

Project Title:

ITM Oxygen Technology for Integration in IGCC and Other Advanced Power Generation Systems

Technology Area:	**Technology Maturity:**
Oxygen Supply	Prototype, 5 tons O_2/day

Primary Project Goal:

Air Products and Chemicals is designing and developing an ion transport membrane (ITM) based on ceramics that selectively transport oxygen (O_2) ions when operated at high temperature. This high temperature process may be integrated with advanced power generation processes that require O_2 as a feedstock, such as integrated gasification combined cycle (IGCC) and other clean energy and industrial applications.

Technical Goals:

- Design, construct, and operate a .1-ton/day (TPD) technology development unit (TDU) to validate the ITM technology concept, verify the technology prospects for stand-alone O_2 production plants, and integrate with IGCC and other advanced power generation systems.
- Design and construct a 5-TPD prototype facility and produce greater than 95% O_2 purity.
- Increase the scale of the engineering test facility from 5 TPD O_2 to 150 TPD O_2 in an intermediate scale test unit (ISTU).

Technical Content:

Air Products and Chemicals is designing a ceramic ITM that, under high temperatures, separates O_2 from nitrogen (N_2). These non-porous, multi-component metallic oxides have high O_2 flux and selectivity (100%), resulting in high capacity production of high purity O_2 at low cost. Figure 1 illustrates the concept of the ITM.

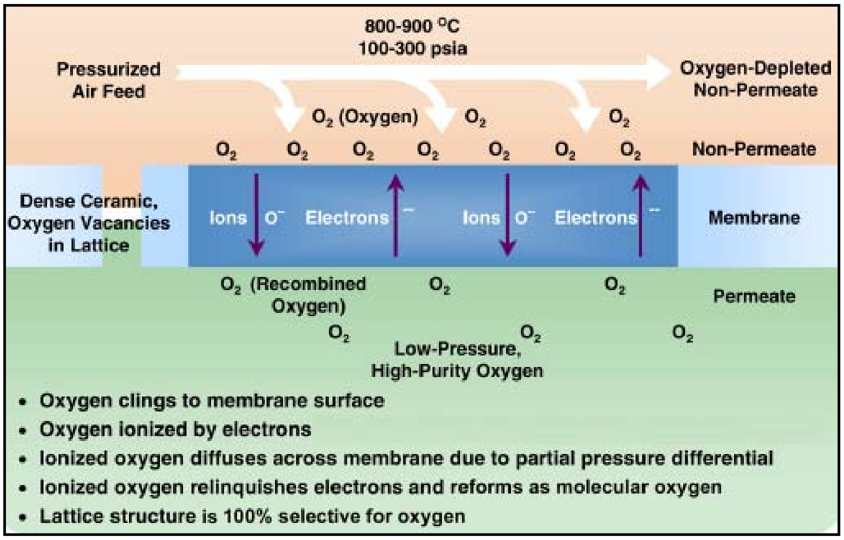

Figure 1: Conceptual Schematic of ITM O_2 Technology

The membrane structure incorporates a non-porous ITM on supporting porous and slotted layers that typically operate between 800°C and 900°C. The driving force for O_2 separation is determined by the relative O_2 partial pressure gradient across the membrane. Therefore, air is typically supplied at pressures of 7 atm to 20 atm, while the product O_2 pressure is typically below ambient (~1 atm).

Figure 2 shows a schematic diagram of an ITM O_2 production plant that includes both indirect and direct heating of the pressurized feed air, in order to satisfy the heating requirement of the thermally activated transport mechanism. While not shown in the schematic, the resulting hot, pressurized, non-permeate stream can be recovered if combined with a gas turbine power generation system.

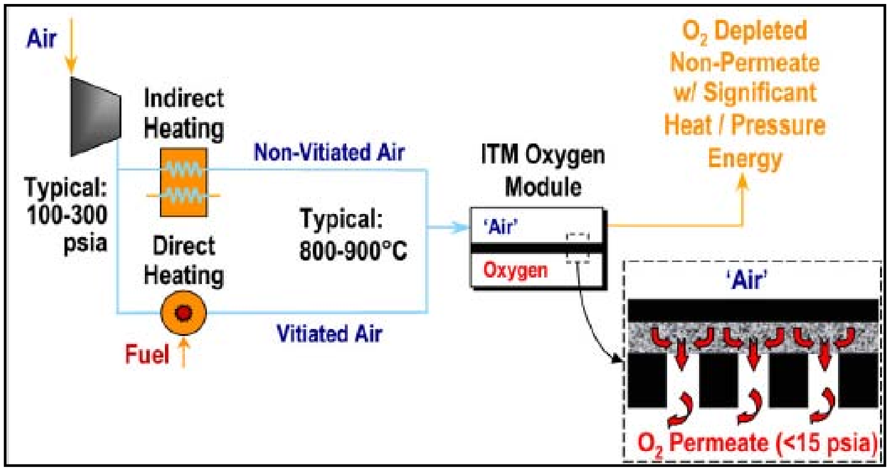

Figure 2: Diagram of O_2 Production Plant

An ITM O_2 plant is projected to decrease the installed capital cost of air separation equipment by more than one-third and the installed capital cost of an IGCC facility by 7%, while improving efficiency and reducing the power requirement for air separation by approximately 35%. These increases in efficiency and reductions in cost, along with the near-capture ready concentrations of CO_2 in the waste stream, make ITM a technology that may be capable of making CO_2 capture more economically feasible.

Technology Advantages:

This technology is capable of producing 90+% O_2 at high flux rates. It is resistant to structural damage and provides consistent performance during thermal and hydraulic cycling. It offers low capital and operating costs, improves efficiency and reduces the power requirement for air separation by approximately 35% relative to cryogenic separation, and reduces capital cost of an IGCC facility by 7%.

R&D Challenges:

Scale up from 5 TPD to 150 TPD and obtaining flux rates competitive to other available technologies.

Results To Date/Accomplishments:

- Established the feasibility of the ceramic membrane approach.
- Designed and constructed commercial-scale membrane modules.
- Designed and constructed a prototype facility capable of producing 5 TPD of O_2.
- Developed five vessel design concepts for the ISTU.
- Developed a method based on scanning acoustic microscopy (SAM) to view the inside of wafers and other module components non-destructively.

Next Steps:

- Select one of the proposed designs for a scaleup plant and perform a detailed design.
- Construct an ISTU that co-produces electrical power and up to 150 TPD O_2.

Final test results will not be available until the September 2010 project completion date.

Available Reports/Technical Papers/Presentations:

B. C. H. Steele, *C. R. Acad. Sci. Paris*, t.1, Series II, 533 (1998).

D. Wright and R. J. Copeland, Report No. TDA-GRI-90/0303 *prepared for the Gas Research Institute*, September 1990.

ITM Oxygen for Gasification. International Thermal Operations and Heavy Oil Symposium 1-3 November 2005, Calgary, Alberta. Canada SPE/PS-CIM/CHOA 97801: PS2005-XXX. P.N. Dyer, R.E. Richards, S.L. Russek, and D.M.Taylor, "Ion Transport Membrane Technology for Oxygen Separation and Syngas Production," *Solid State Ionics*, 134 (2000) 21-33.

Contract No.:

DE-FC26-98FT40343

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Pennsylvania State University
Siemens Power Group
SofCo

NC A&T State – Nanofiller-Modulated Polymeric Membrane

Project Title:

Development of Nanofiller-Modulated Polymeric Oxygen Enrichment Membranes for Reduction of Nitrogen Oxides in Coal Combustion

Technology Area:	**Technology Maturity:**
Oxy-Combustion Membranes	Laboratory-scale

Primary Project Goal:

North Carolina A&T State University (NCATSU) is designing and developing a nanofiller-modulated polymer membrane for the oxygen (O_2)-enrichment of coal combustion and gasification applications. This will reduce the volume of waste gas and increase the concentration of near-capture ready carbon dioxide (CO_2) within the waste gas to simplify capture and reduce related costs.

Technical Goals:

- Research and select polymer candidates as well as functional nanofillers.
- Experiment with the selected nanofiller-modulated polymers and document the fundamental microstructure-property relationships.
- Develop models for selected membranes using Material Studio 4.0 and Groningen Machine for Chemical Simulation (GROMACS) 3.3.

Technical Content:

NCATSU is researching membrane technology capable of separating O_2 from nitrogen (N_2). The selected membranes must be capable of producing a sufficient volume of high purity O_2 at reasonable operational and capital costs. The primary method of research used to develop a membrane with the required traits has been to vary the amount and type of filler, the type of polymer backbone, and the method of distribution and casting used. The results are used to develop computational models to further study and develop the technology. The membranes evaluated thus far include single-walled carbon nanotube, nanofumed silica polydimethylsiloxane (PDMS), and zeolite-modulated polyimide (a polymer) membranes.

The polyimide selected was Matrimid 5218 – chosen for its high glass transition temperature, high structural and thermal stability, low cost, and high porosity. For example, a mixed matrix membrane utilizing Matrimid 5218 as the polyimide backbone and a zeolite as the filler was fabricated on a porous stainless steel substrate. This membrane was exposed to pure N_2 and pure O_2 at 3.4 atm (50 psi) for two hours. The resulting permeability was 0.114 Barrer and 0.380 Barrer, respectively, with a selectivity for O_2 of 3.33. After 12 hours, the results improved to a permeability of 0.093 for N_2 and 0.460 for O_2, with a selectivity for O_2 of 4.95. While the results are still below required values, they show considerable potential that a mixed matrix polyimide membrane with zeolite nanofiller could meet the requirements necessary for commercial application in the future.

As for nanofumed silica PDMS membranes, the fumed silica chosen was CAB-O-SIL TS-530. The hydrophobic silica was chosen because it had greater potential for proper mixing with the elastomer. However, the fumed silica did not produce good dispersion in the polymer, resulting in limited success. The O_2 selectivity observed for 1% and 2.5% fumed-silica at 4.1 atm (60 psi) was 2.72 and 2.81, respectively. When compared to an O_2 selectivity of 2.54 for pure PDMS, it is apparent that little improvement was achieved through the use of the fumed silica.

Lastly, molecular dynamics simulations have been conducted to calculate the theoretical O_2 molecular diffusion coefficient and N_2 molecular coefficient inside single-walled carbon nanotube PDMS membranes, in order to predict the effect of the nanotubes on the gas-separation permeability. A simulated model of these membranes is shown in Figure 1.

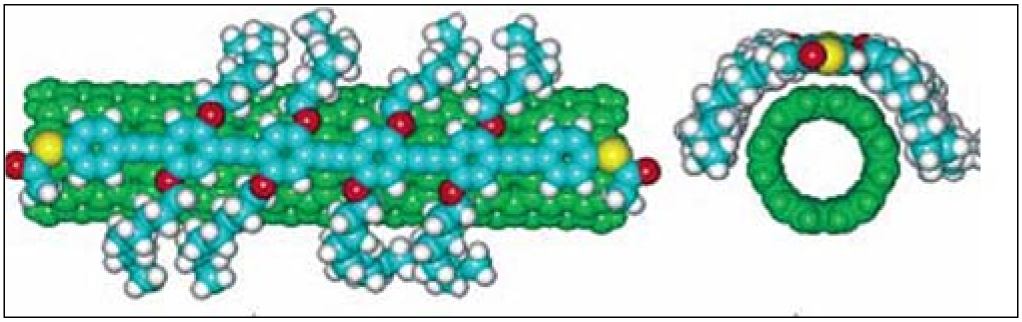

Figure 1: Model of Single-Walled Carbon Nanotube PDMS Membranes

The selectivity achieved from experimentation is 0.86 for PDMS filled with single-walled carbon nanotubes. When compared to pure PDMS, with a selectivity of 1.97, it is apparent that this filler is not appropriate for the purpose of this project.

Technology Advantages:

The membranes being researched have several desirable properties, including high glass transition temperatures, high thermal and structural stability, high selectivity (0.460 Barrers), and high permeability (4.95). In addition, capital costs are low, due to the absence of precious metals found in many other membrane technologies.

R&D Challenges:

- The experiments performed thus far have shown that the nanofillers and polymers used have unstable properties over extended periods of time.
- It was found that fumed silica did not produce good dispersion in the polymers tested.
- Insufficient permeability and selectivity for O_2.

Results To Date/Accomplishments:

- Performed permeation and diffusion experiments using polymers with nanosilica particles, nanotubes, and zeolites as fillers.
- Studied the influence of nanofillers on the self diffusion, free volume, glass transition, O_2 diffusion and solubility, and perm-selectivity of O_2 in polymer membranes.
- Developed molecular models of single-walled carbon nanotube and nanofumed silica PDMS membranes, and zeolites-modulated polyimide membranes.

Next Steps:

- Optimize the gas selectivity of polymer membranes by studying the effects of different nanofillers and zeolites on polymer membrane behavior.
- Research glassy polymers to determine their gas-separation behavior.

Final test results not yet available.

Available Reports/Technical Papers/Presentations:

J. Zhang, J. Lou**,** S. Ilias, P. Krishnamachari, J. Yan. “Thermal properties of poly(lacticacid) fumed silica nanocomposites: Experiments and molecular dynamics simulations,” Polymer, **2008,** 49, 2381-2386.

J. Zhang,Y. Liang, J. Yan, J. Lou, “Study of molecular weight dependence of glass transition temperature for amorphous poly(l-lactide) by molecular dynamics simulation,” Polymer, **2007,** 48, 4900-4905.

Vu, D. Q.; Koros, W. J.; Miller, S. J., Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results. *Journal of Membrane Science* **2003,** *211* (2), 311-334.

Vu, D. Q.; Koros, W. J.; Miller, S. J., Mixed matrix membranes using carbon molecular sieves: II. Modeling permeation behavior. *Journal of Membrane Science* **2003,** *211* (2), 335-348.

Contract No.:

DE-FG26-06NT42742

NETL Project Manager:

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Eltron Research – Materials for Temperature Swing Adsorption Oxygen Separation

Project Title:

Novel Supports and Materials for Oxygen Separation and Supply

Technology Area:

Oxygen Production

Technology Maturity:

Laboratory-scale, 5-10 lb O_2/day

Primary Project Goal:

Eltron Research is designing and developing a temperature swing adsorption (TSA) system capable of producing high purity (>99%) oxygen (O_2) for use as an air substitute in power plants, reducing waste gas volume and simplifying carbon dioxide (CO_2) capture and containment.

Technical Goals:

- Produce materials which provide more O_2/m^3*hr than the zeolites currently used in small to mid-size TSA O_2 separation technologies (23 kg O_2/m^3*hr).
- Develop materials capable of producing an O_2 with purity comparable to cryogenic O_2 separation (99%).

Technical Content:

Eltron Research is developing a TSA system that is capable of producing O_2 at purities comparable to those produced by cryogenic methods but at reduced cost.

This program initially focused on the coating of sintered metal fiber filters (SMFFs) with cerium oxide (CeO_2), silicon oxide (SiO_2), and/or aluminum oxide (Al_2O_3). These base-coated fibers were then separately impregnated using the chosen mixed metal oxide nitrate. The SMFFs used were chosen for their high porosity (80%) and permeability (1,500 L/dm*min), which provided a near-negligible post-reactor pressure drop. Also, due to their high thermal conductivity, the chosen SMFFs had significantly reduced thermal irregularities compared to ceramic monoliths. This feature resulted in near isothermal reactor beds. Cerium- (Ce), silicon- (Si), and aluminum- (Al) based oxides were chosen as base-coating materials for their ability to increase surface area and provide a more ideal binding surface on the SMFFs. Additionally, they also prevent or dramatically decrease agglomeration and its impact on the overall O_2 storage and release capability of the materials. However, based upon an economic analysis, it was determined that the volume needed for the SMFFs was too large, and so the program was then re- focused strictly on fixed beds with no SMFF supports. In addition, the focus was changed from co-precipitated mixed metal oxide materials to perovskite materials produced using ceramic processing methods.

Twelve combinations of materials were selected and produced via ceramic processing methods and calcined at high temperatures (>900°C). Upon testing, results showed that one of the selected materials (K-12), a perovskite, was capable of producing >132 kg O_2/m^3*hr, far surpassing the original mixed metal oxide primary material produced via co-precipitation from nitrate solutions..

Figure 1 compares the O_2 production rates of several leading technologies, including Eltron's primary materials. Figure 2 compares the required reactor volume, based on a 5 ton/day O_2 system. As indicated, the K-12 sorbent offers significantly improved O_2 production over existing PSA zeolite-based sorbents. Utilizing a sorbent capable of such high production rates may significantly reduce the required reactor volume, leading to reduced capital and operational costs.

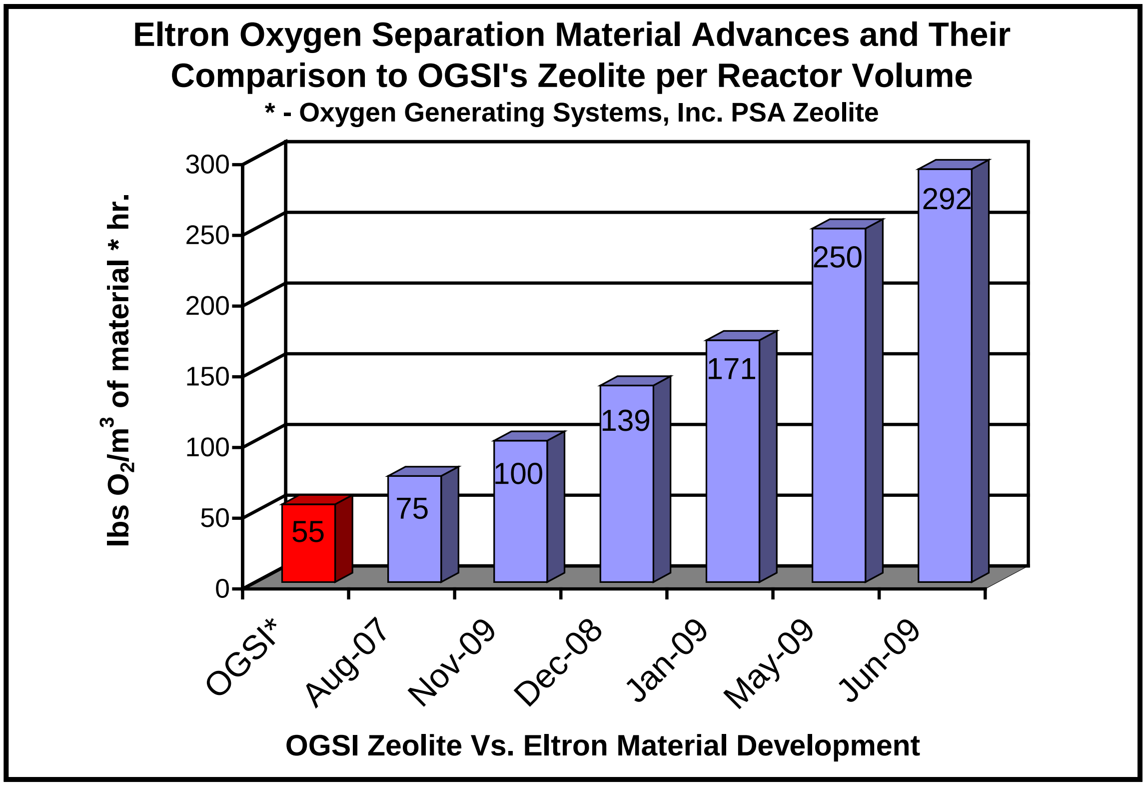

Figure 1: Oxygen Production Comparison

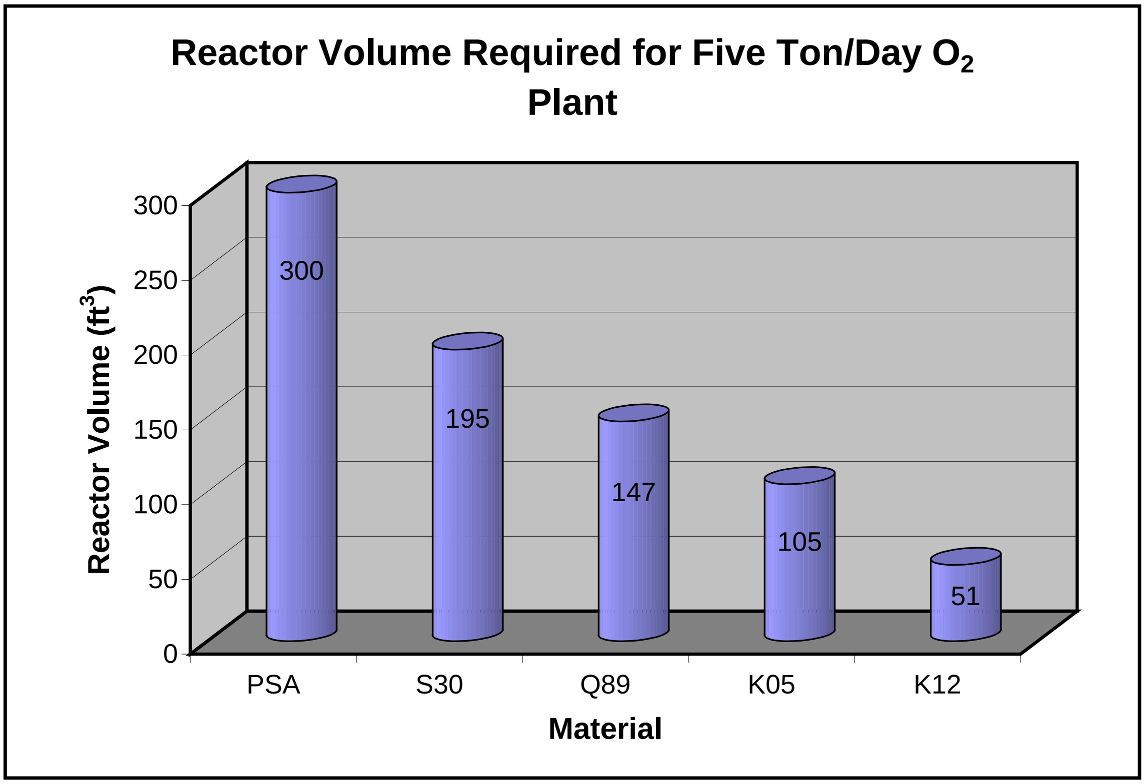

Figure 2: Required Reactor Volume Comparison

Technology Advantages:

Materials being researched have superior mechanical strength, durability, and thermal resistance when compared to current TSA materials. They have the capability of producing O_2 at >99% purity, industrially relevant volumes, and at significantly reduced cost in comparison to cryogenic methods.

R&D Challenges:

Heating issues (i.e., how to most effectively heat large amounts of material; how to heat and cool a large amount of material fast; how to make sure heating is even; etc.).

Results To Date/Accomplishments:

- Developed a new primary material (K-12) which yields >132 kg O_2/m^3*hr.
- Observed that air flow during calcination is crucial to phase formation.
- Adding polyvinyl butyral (PVB) binder to calcined K-12, pelletizing, and re-firing at calcination temperatures yields a material which produced >130 kg O_2/m^3*hr with no drop-off in performance (16,000+ cycles).

Next Steps:

- Complete fabrication of scaleup reactor capable of producing 2.3 kg (5 lb) of O_2/day.
- Complete initial testing and optimization of reactor system.

Final test results will not be available until the August 2010 project completion date.

Available Reports/Technical Papers/Presentations:

A.R. Smith and J. Klosek, "A review of air separation technologies and their integration with energy conversion processes," Elsevier, 2001, http://www.airproducts.com/NR/rdonlyres/D29B6AF0-A218-415D-B692-20537B197E7D/0/2_ReviewOfAirSeparationTechnologiesAndTheirIntegrationWithEnergyConversionProcesses2001p.pdf.

"Oxygen," Madehow.com, http://www.madehow.com/Volume-4/Oxygen.html (accessed September 18, 2007).

"Technology: SeprOx," Trans Ionics Corporation, http://www.transionics.com/tech_seprOx.html.

"Vision Fossil Fuel Options for the Future," National Research Council, 2005.

Contract No.:

DE-FG02-07ER84600.002

NETL Project Manager:

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Praxair – Oxygen Transport Membrane-Based Oxy-Combustion

Project Title:

OTM-Based Oxy-Combustion for CO_2 Capture from Coal Power Plants

Technology Area:	**Technology Maturity:**
Oxygen Supply	Laboratory-scale

Primary Project Goal:

Praxair is developing membrane hardware and assessing the technical and economic feasibility of an advanced oxy-combustion power cycle that uses a combination of ceramic oxygen transport membranes (OTM) and a cryogenic air separation unit (ASU) to supply the oxygen (O_2) required for combustion.

Technical Goals:

Phase I:

- Develop more detailed OTM cost and performance estimates based on experiments.
- Develop a preliminary conceptual design and cost models for a pilot plant utilizing OTM technology.
- Identify the rate limiting steps for O_2 separation through the OTM and address kinetic or mass transport limitations by appropriate materials selection and membrane architecture.
- Develop procedures to manufacture ⅓ pilot-size OTM tubes; test them for O_2 flux and durability in carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), and water (H_2O) fuel streams with the presence of sulfur impurities.
- Test OTM membranes in a coal gas OTM reactor.

Phase II (many Phase I tasks will be repeated at pilot-scale):

- Scale up the physical size of the membranes to that required for pilot-scale demonstration.
- Deliver a plan for pilot-testing of the technology that includes the basic engineering design and cost of key components of OTM-based equipment, as well as an update to the system and economic analysis of the proposed cycle.

Technical Content:

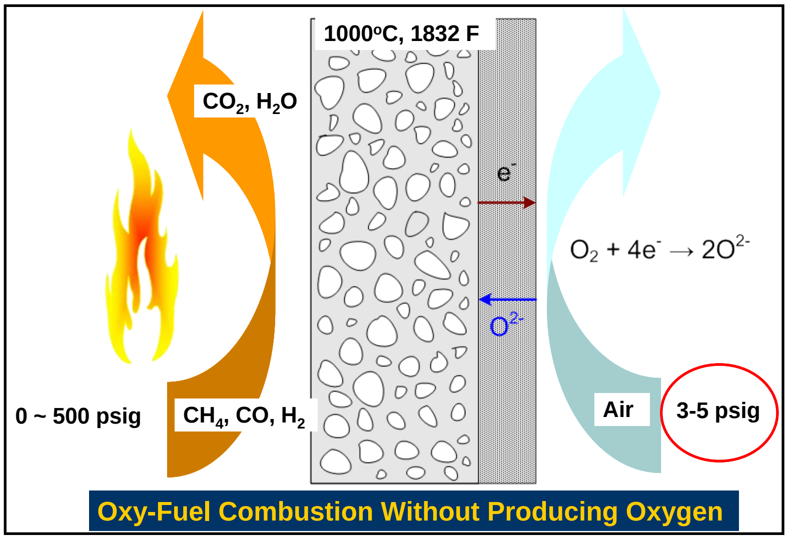

Figure 1: Schematic of Ceramic OTM

As oxy-combustion is currently practiced, a pure stream of O_2 is separated out in an ASU and then delivered to a boiler for combustion. OTM technology integrates O_2 separation and combustion in one unit. An OTM consists of an inert porous support coated with an internal dense gas separation layer, as illustrated in Figure 1. Air contacts the separation layer where molecular O_2 reacts with O_2 vacancies and electrons on the membrane surface to form O_2 ions, which are transported through the separation layer using a chemical potential difference as the driving force. Fuel species (CO, H_2, methane [CH_4] etc.) located on the porous support side diffuse through the support and react with O_2 ions at the membrane surface to form oxidation products (H_2O, CO_2) and O_2 vacancies and electrons in the crystalline lattice structure of the separation layer.

Several process concepts incorporating ceramic OTM are being explored to understand their impact on process economics. One process concept under development is shown in Figure 2. In this process, coal is first gasified in an O_2-blown gasifier to generate synthesis gas (syngas). The syngas is optionally reacted in an OTM partial oxidation reactor to raise its temperature.

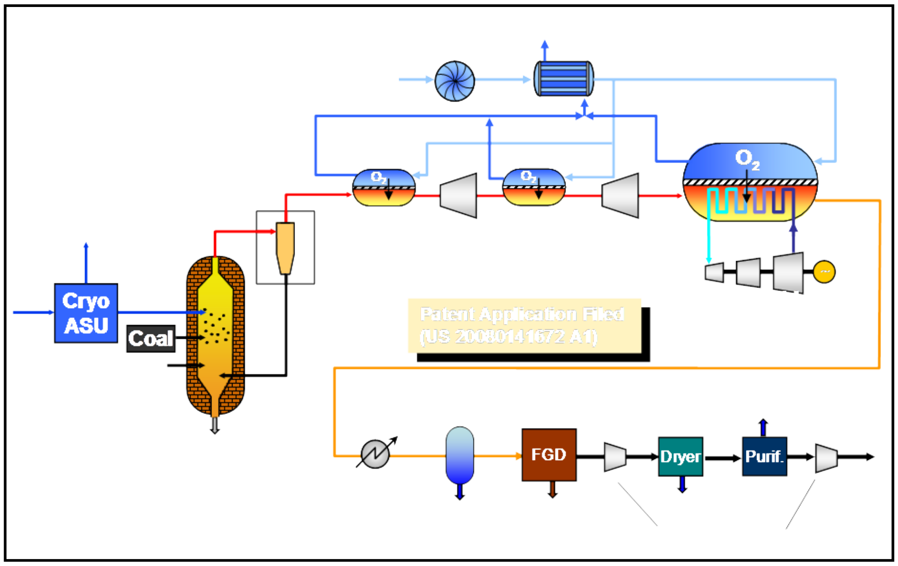

Figure 2: OTM-Based Process for Power Generation with CO_2 Capture

The hot syngas is expanded to recover power. After the syngas is expanded to slightly above the ambient pressure, it is sent to the OTM boiler. Within the OTM boiler, syngas is first passed over an array of OTM tubes. Air is preheated by heat exchange with the O_2-depleted air and then passed on to the inside of the OTM tubes. Oxygen from the air transports across the membrane and reacts with the syngas. Since the rate of O_2 transport is limited by the availability of the membrane area, the oxidation of syngas will take place over a large area (the OTM zone) within the boiler. As the syngas gets oxidized, the driving force for O_2 transport will decrease and the required membrane area will increase. For practical reasons, the OTM will be used to supply O_2 to the fuel side until 80-90% fuel utilization is achieved. The remainder of fuel will be combusted using O_2 supplied from the cryogenic ASU.

The thermal energy released within the boiler is used for steam generation. In the OTM zone, steam tubes will be interspersed with the OTM tubes such that the temperature is maintained at the optimum level for membrane performance. After the fuel is completely oxidized with externally supplied O_2, the flue gas will pass through a convective section of the boiler for further steam generation and boiler feed water preheating. The flue gas exiting the boiler is processed according to a purification process proposed for a conventional oxy-fuel technology.

A number of OTM-based power cycles have been simulated for comparison against the DOE Cost of Electricity (COE) targets. Table 1 illustrates two of these cases, “OTM Case 2” and “OTM Case 5.” Included in the table for comparison purposes are two DOE reference cases. The base case for comparison is a DOE pulverized coal air-combustion power cycle (without CO_2 capture). A second DOE case including post-combustion capture (PCC) is also included for comparison with the OTM cases.

Table 1 includes data regarding the net efficiency, plant cost, and COE for three different coal prices. The COE increase over the DOE base case (column one) is calculated and those cases meeting the DOE target of <35% increase in COE are highlighted in green. Note that all OTM cases show substantial improvement over DOE’s projections for air-coal power plants with PCC (column two). The high net efficiency, >37% HHV, seen in the OTM cases is a major contributing factor which keeps the COE low in comparison to the PCC case.

Table 1: COE Comparison of Standard DOE Air-Coal Power Cycles with OTM Power Cycles (OTM Case 2 and Case 5 differ in their treatment of coal impurities)

Case		DOE Base SC	DOE PCC SC	OTM Case 2	OTM Case 5
Net Efficiency (HHV)		39.7	27.2	37.15	37.4
Cost Basis (Year)		3/2008	3/2008	3/2008	3/2008
Plant Cost ($/kW)		$1,908	$3,488	$2,858	$2,834
	Coal Price ($/MMBtu)				
COE ($/MWh)	1.8	$70.5	$115.2	$97.0	$94.6
	3	$82.9	$133.2	$110.2	$107.7
	4	$93.2	$148.3	$121.3	$118.7
COE % Increase Over Base	1.8		63.4%	37.6%	34.2%
	3		60.7%	32.9%	29.9%
	4		59.1%	30.2%	27.4%

Technology Advantages:

Unit power consumption for supplying O_2 (kWh/ton of O_2) to the oxy-fuel combustion process is reduced by more than 70%. This results in a step change in efficiency improvement and decrease in COE for a power plant that enables CO_2 capture.

In a conventional oxy-fuel process, the efficiency of the power plant will drop by 9-10%. Due to such a large efficiency penalty, the cost of CO_2 avoided will be 25-30% higher than the cost of CO_2 captured. In comparison, the efficiency drop for the OTM-based power cycle will be only 2-3%. As a result, the cost of CO_2 avoided would be within 10% of the cost of CO_2 captured.

R&D Challenges:

- Reliability of the OTM tubes at high pressure.
- Achieving membrane cost and performance targets.
- Engineering design of OTM equipment.

Results To Date/Accomplishments:

- Improved OTM performance by a factor of two to three.
- Observed stable OTM performance in the presence of hydrogen sulfide (H_2S) and carbonyl sulfide (COS).
- Power cycle process economics meet or exceed DOE goals of <35% increase of COE for coal power plant with CCS.

Next Steps:

- Demonstrate stable operation of the coal-fueled OTM reactor.
- Cost estimates for a pilot-scale demonstration and cost projections for a commercial-scale OTM.
- Target O_2 flux and reliability for pilot-scale OTM.

Final test results will not be available until the December 2010 project completion date.

Available Reports/Technical Papers/Presentations:

March 2009 Presentation at the CO_2 Capture Technology for Existing Plants Conference in Pittsburgh, Pennsylvania.

Contract No.:

DE-FC26-07NT43088

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Partners:

ENrG Inc.
The University of Utah

TDA Research – Sorbents for Air Separation

Project Title:

Sorbents for Air Separation

Technology Area:	**Technology Maturity:**
Oxygen Production, Chemical Looping	Bench-scale

Primary Project Goal:

TDA Research is designing and developing a new regenerable chemical sorbent to selectively remove oxygen (O_2) from air.

Technical Goals:

- Optimize and screen sorbent formulations.
- Scale up sorbent production.
- Perform long-term testing of the sorbent to demonstrate its durability through a minimum of 5,000 absorption/regeneration cycles.
- Design and size a conceptual air separation system based on experimental results.

Technical Content:

Air separation units (ASUs) are one of the most expensive components of the integrated gasification combined cycle (IGCC) plant, accounting for approximately 18% of the overall plant cost and more than 14% of the cost of electricity (COE). TDA Research is developing a new, highly efficient, sorbent-based air separation technology that can produce high purity O_2 from air at high temperatures (approximately 800°C).

By performing the air separation at high temperatures, much of the COE increase is avoided, because much of the energy penalty associated with separating air by cryogenic methods is in cooling the gas to temperatures as low as 80 K. Additionally, some of the capital cost is reduced due to the faster kinetics which permits the use of less material.

TDA's sorbent, a mixed metal oxide, has been found to achieve up to 4% wt O_2 capacity and maintain its capacity for more than 300 cycles. This sorbent can be regenerated under near isothermal and isobaric conditions by changing O_2 partial pressure between the absorption and regeneration bed. This then demands the use of a minimum of two separate reactors, one for absorption and the other for regeneration. A solid circulation system is being developed to eliminate the use of high temperature valves. Figure 1 is a schematic depiction of this process.

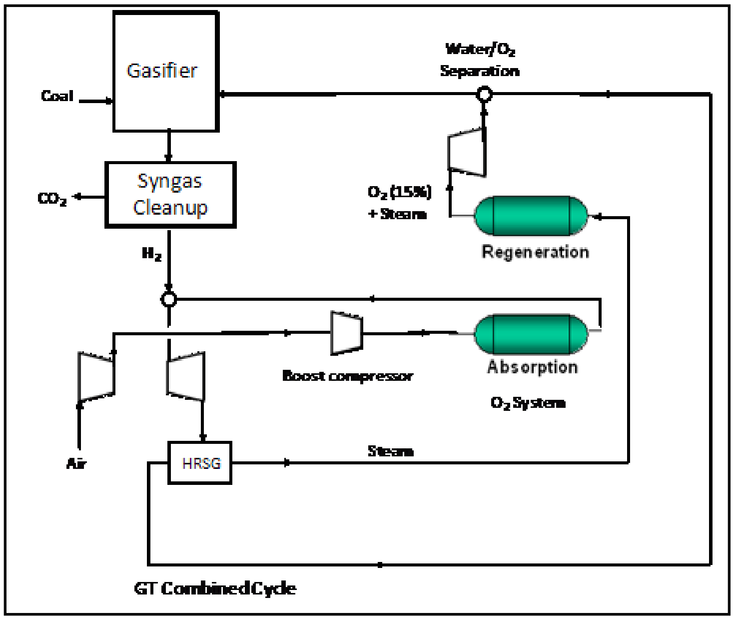

Figure 1: Schematic of Two Reactor Air Separation Unit

It is estimated that the cost of O_2 could be as low as $18.5/tonne ($16.8/ton), which is a significant savings compared to cryogenic methods ($31-35/tonne) and is below the U.S. Department of Energy's (DOE) target of $22/tonne. Also, capital cost is estimated to be $85-104/kWe, which again is well below cryogenic plants ($360/tonne) and achieves DOE's target of $82-110/ton.

Technology Advantages:

The process temperature is maintained at 600-800°C to increase the reaction kinetics. The sorbent is regenerated under an inert gas (e.g., steam) at the same temperature and pressure, eliminating time required for temperature and/or pressure transitions. The oxidized phase is meta-stable and a small change in chemical potential leads to its reduction.

R&D Challenges:

- Scale up from batch to prototype.

Results To Date/Accomplishments:

- Optimized sorbent formulations and screened them under representative IGCC plant conditions.
- Scaled up sorbent production.

Next Steps:

Project completed August 2010. Final report not yet available.

Available Reports/Technical Papers/Presentations:

PCC Oxy-combustion Alptekin, Presentation at the Pittsburgh Coal Conference, September 30, 2008.

Contract No.:

DE-FG02-08ER84216

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Partners:

APPENDIX

CHEMICAL LOOPING

Alstom – Chemical Looping Combustion Prototype

Project Title:

Alstom's Chemical Looping Combustion Prototype for CO_2 Capture from Existing Pulverized Coal-Fired Power Plants

Technology Area:	**Technology Maturity:**
Chemical Looping	Prototype-scale, 3-MWt, 1,000 lb of coal/hr

Primary Project Goal:

Alstom is designing, building, and testing a 3-MWth limestone-based chemical looping combustion (CLC) prototype facility.

Technical Goals:

- Design a CLC prototype that consumes approximately 454 kg/hr (1,000 lb/hr) of coal and uses calcium sulfate ($CaSO_4$) as an oxygen (O_2) carrier.
- Test cold flow solids transport.
- Characterize the environmental performance of the CLC prototype facility.
- Develop design information for a larger-scale CLC commercial demonstration plant.

Technical Content:

In this project, Alstom will scale up the limestone-based CLC process from a 65-kW_{th} pilot, which was successfully demonstrated in an earlier project, to a 3-MWth prototype facility that is expected to be operational in 2010 and 2011. CLC utilizes a metal oxide or other compound, in this case $CaSO_4$, as an O_2 carrier to transfer O_2 from the combustion air to the fuel. Since direct contact between fuel and combustion air is avoided (Figure 1), the products from combustion (carbon dioxide [CO_2] and water) will be kept separate from the rest of the flue gases (primarily nitrogen). CLC splits combustion into separate oxidation and reduction reactions. The O_2 carrier releases O_2 in a reducing atmosphere to react with the fuel. The carrier is then recycled back to the oxidation chamber to be regenerated by contact with air. Calcination of hot solids produced in the oxidation reactor will produce a concentrated stream of CO_2 in lieu of the dilute CO_2 stream typically found in flue gas from coal-fired power plants. This will enhance the ability to capture CO_2 at coal-fired power plants.

Located at Alstom's Power Plant Laboratory in Windsor, Connecticut, the prototype will include process loops to transfer solids and O_2 between the reducing and oxidation reactors. The facility will have the ability to combust coal, gasify coal, or produce hydrogen; however, hydrogen is not expected to be produced during this particular project. After installation and startup of the prototype, Alstom plans to conduct seven weeks of cold flow and hot flow testing, with CO_2 vented to the atmosphere. Information gleaned from prototype testing will be used to develop a technical plan and cost estimate for a subsequent larger-scale commercial demonstration project at a full-scale power plant.

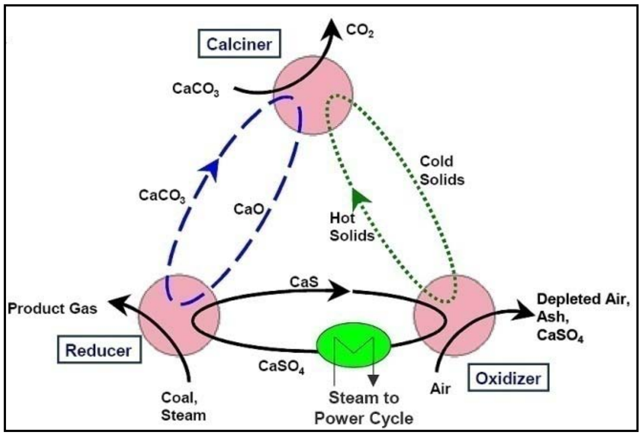

Figure 1: Limestone-Based CLC Process

Technology Advantages:

An air separation unit (ASU) is not required for O_2 production and CO_2 separation takes place during combustion. Additionally, the versatile technology can produce power, synthesis gas (syngas), or hydrogen, while offering fuel flexibility.

R&D Challenges:

In addition to scaleup issues, challenges associated with the CLC process include solids handling and transport; O_2 carrier capacity, reactivity, and attrition; and ash management.

Results To Date/Accomplishments:

In an earlier project (NT41866), Alstom completed the following:

- Successful construction and testing of a 65-kW_{th} pilot-scale CLC facility.
- Completion of 4.6-m (15-foot) Cold Flow Model testing.
- Successful scale up to a 12.2-m (40-foot) Cold Flow Model.
- Successful completion of internal and ASME/DOE peer reviews.

Next Steps:

Alstom will design and test a prototype CLC facility that consumes approximately 454 kg/hr (1,000 lb/hr) of coal and uses $CaSO_4$ as an O_2 carrier. While offering the flexibility to conduct testing in combustion and gasification modes, the facility will be used to test cold flow solids transport. Final test results will not be available until the March 2011 project completion date.

Available Reports/Technical Papers/Presentations:

Presentation: Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 24-26, 2009, in Pittsburgh, Pennsylvania.

Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase 1 Final Report, U.S. DOE, December, 29, 2004.

Andrus, H. E., Jr., et. al., Hybrid Combustion-Gasification Chemical Looping Coal Power Technology Development – Phase II Final Report, U.S. DOE, June, 9, 2006.

Andrus, H.E., Thibeault, P. R., Chemical Looping Spec Gate review and Peer Review Report, 22 August, 2005.

Johnson, K, et. al., Sorption-Enhanced Steam Reforming of Methane in a Fluidized Bed Reactor.

Nsakala, N. Y. and Liljedahl, G. N., Greenhouse Gas Emissions Control by Oxygen Firing in Circulating Fluidized Bed Boilers, Alstom Power – U.S. DOE Report, PPL Report No, PPL-03-CT-09, 15 May 2003.

Contract No.:

DE-NT0005286

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Partners:

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PEMM Corporation
University of British Columbia

Alstom – Chemical Looping Simulation and Control

Project Title:

Development of Computational Approaches for Simulation and Advanced Controls for Hybrid Combustion-Gasification Chemical Looping

Technology Area:

Chemical Looping

Technology Maturity:

Laboratory-scale

Primary Project Goal:

Alstom is developing advanced computational models and optimizing control systems for chemical looping processes.

Technical Goals:

- Identify sensor and control needs for chemical looping processes.
- Develop process simulation models with dynamic capability to evaluate control methods.
- Incorporate advanced process controls into the chemical looping plant design process.
- Investigate advanced process controls for complex solids flow and gas pressure control.
- Develop a control system (i.e., flow, temperature, pressure, etc.) design concept for the chemical looping prototype facility.

Technical Content:

Alstom is developing advanced computational models and optimizing control systems for chemical looping processes, such as the hybrid combustion-gasification process shown in Figure 1. The process is based on the oxidation, reduction, carbonation, and calcination of calcium-based compounds to chemically react with coal in three riser reactors: an oxidizer, a reducer, and a calciner. The calcium compounds serve as oxygen (O_2) carriers that also transport heat between the various reaction loops.

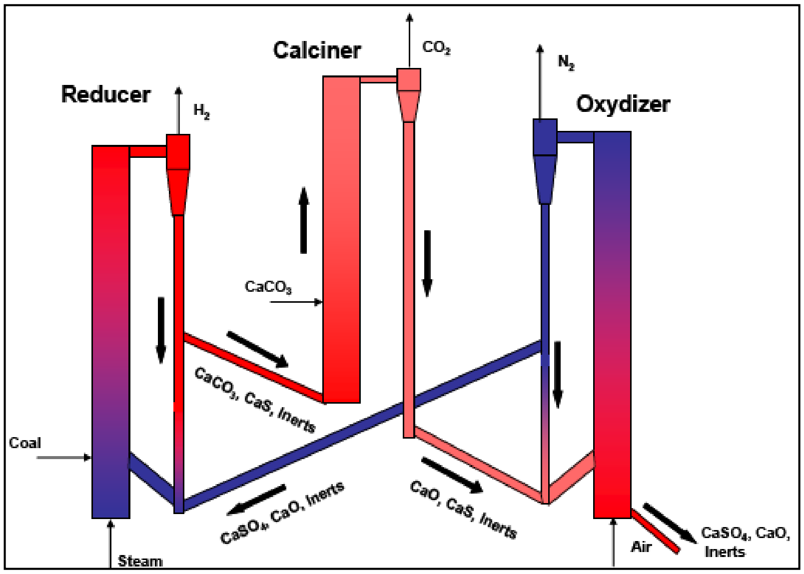

Figure 1: Alstom's Hybrid Combustion-Gasification Process

Chemical looping is a complicated process with multiple material and energy streams between the three reactors. In order to obtain and maintain optimal conditions for maximum combustion and reduced waste stream volume with minimum required energy, advanced and sophisticated control systems are required. As such, process control development is needed to operate the system in a safe, integrated, and optimized fashion and is viewed as critical for meeting the performance goals of the innovative chemical looping system. This project is developing model-based controls that can be used to operate the system. Approaches to model development and control algorithms are being developed by researchers at Alstom Power Plant

Laboratories and at the University of Illinois Urbana-Champaign (UIUC).

Alstom is developing computational models to gain a better understanding of chemical looping process behavior and to develop control strategies, including: a two-loop cold flow model, a hot loop model (without reactions), and a real-time dual loop cold flow simulator. The dual loop simulation platform can be configured to test conceptual control designs. For example, it can evaluate control strategies with different sensors and actuators. In addition to developing process models, Alstom is developing advanced sensors, such as the ultrasonic-time of flight, and the image-based laser-light spot and triangulation prototype level sensors.

Utilizing advanced computational models to enable continuous operation and control of the process, coupled with implementing state-of-the-art sensors, will directly impact the overall performance of the system including operational costs and efficiencies associated with coal-fired power production processes such as chemical looping. Also, doing so will ultimately lead to significant reductions in CO_2 emissions and waste stream volume, simplifying CO_2 capture and containment.

Technology Advantages:

Advanced control systems for chemical looping will provide for stable and continuous operation of the process, thus enabling high efficiency, high reliability, low environmental impact, and reduced costs for plants that are capturing CO_2. Experimental work at the bench-scale has shown that traditional controls are unable to maintain stable loop control when compared to model-based control of the same system, suggesting that this approach may be essential for operating the loops together in a continuous manner.

R&D Challenges:

Challenges include the development of real-time, fast response models for dynamic control of the loops followed by the inclusion of reliable instrumentation as input into the model-based control. Additional challenges will be to integrate these controls with the scaleup of the process and to include the appropriate dynamics, reactions and externalities so the control can account for a large number of variables that impact stable loop control.

Results To Date/Accomplishments:

- Developed process and control performance benchmarks.
- Completed process characterization by developing an understanding of the operation and control issues at the cold flow and chemical looping test facilities.
- Completed process modeling and simulation.
- Validated chemical looping process models.

Planned Activities:

Alstom will evaluate a nonlinear model predictive controller (MPC), formulate MPC design for hot flow mode, and modify the cold flow test facility to support advanced sensors and control tests. Final test results will not be available until the March 2011 project completion date.

Available Reports/Technical Papers/Presentations:

The 33rd International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, Florida, USA, June 1- 5, 2008, "Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

51st ISA Power Industry Division Symposium & 18th Annual Joint ISA POWID/EPRI, Controls & Instrumentation Conference, Scottsdale, Arizona, USA, June 8-13, 2008, "Simulation and Advanced Controls for Hybrid Combustion-Gasification Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

International Pittsburgh Coal Conference, Pittsburgh, PA, USA, September 21-24, 2009 (To be submitted by Alstom), "Dynamic Simulation and Advanced Controls for Alstom's Chemical Looping Process," Xinsheng Lou, Carl Neuschaefer, and Hao Lei.

Modelling, Controller Design, and Computational Tools for the Closed-Loop Control of the Cold Flow Fluidized Bed Rise, submitted to the journal of Nonlinear Phenomena in Complex Systems by UIUC Dong Ye, Shu Zhang, Vivek Natarajan, Bryan Petrus, and Joseph Bentsman, (subcontractor to Alstom under the DOE/Alstom contract on chemical looping simulation and controls).

An invited presentation on this project was given by Mr. Carl Neuschaefer at the workshop on advanced controls organized by DOE/NETL (Ms. Susan Maley) aligned with 2008 ISA Power Conference in Scottsdale, Arizona, USA.

Contract No.:

DE-FC26-07NT43095

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University of Illinois Urbana-Champaign

Ohio State University – Coal Direct Chemical Looping for Retrofit

Project Title:

Coal Direct Chemical Looping Retrofit to Pulverized Coal Power Plants for In-Situ CO_2 Capture

Technology Area:

Chemical Looping

Technology Maturity:

Laboratory-scale

Primary Project Goal:

Ohio State University is designing, building, and testing a sub-pilot scale (25-kWth) coal direct chemical looping (CDCL) facility.

Technical Goals:

- Evaluate the reactivity, recyclability, and physical strength of different iron oxide (Fe_2O_3)-based oxygen (O_2) carrier particle compositions.
- Determine optimum fuel reactor operating conditions to gasify coal char using O_2 carrier particle.
- Operate integrated sub-pilot system for a minimum of 50 continuous hours with the optimal O_2 carrier.
- Determine the fate of nitrogen oxide (NO_X) and sulfur via integrated system testing.
- Conduct techno-economic analysis of the CDCL process.

Technical Content:

Researchers at Ohio State University (OSU) are developing a one-step CDCL process to produce electric power and high-purity carbon dioxide (CO_2) in retrofit power plant applications. While preliminary tests with the bench-scale reactor have shown 90 to 95% coal char conversion and >99% volatile conversion, the primary focus of this project is to identify the optimal O_2 carrier chemical composition and conduct integrated, continuous CDCL testing at the sub-pilot (25-kWth) scale.

As shown in Figure 1, the CDCL system consists of a fuel reactor and a combustor. The moving-bed fuel reactor utilizes a countercurrent gas-solid contacting pattern to maximize the conversion of the Fe_2O_3-based O_2 carrier, as it releases O_2 to facilitate the conversion of pulverized coal to CO_2 and water. The combustor, an entrained-flow reactor, uses air to pneumatically transport the O_2 carrier back to the fuel reactor, while re-oxidizing the O_2 carrier and generating a significant amount of heat. A portion of the heat generated in the combustor is used for steam generation via the high-temperature exhaust gas, while the remainder is carried to the fuel reactor by the hot regenerated particles to supply the heat required for coal conversion.

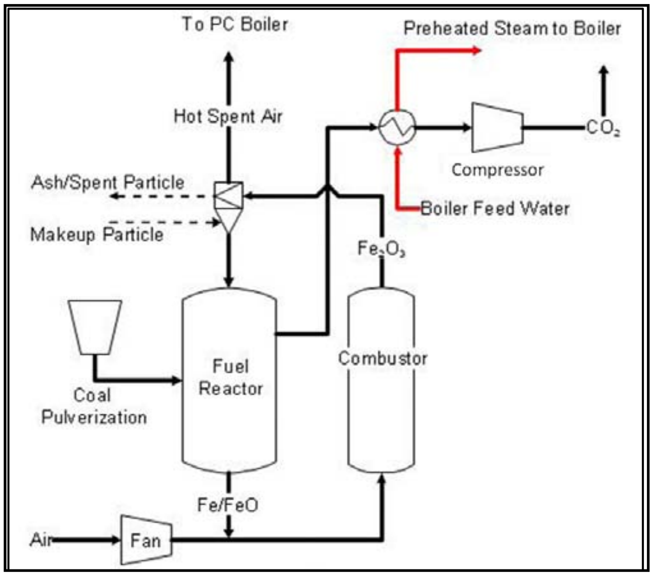

Figure 1: CDCL Process Flow Diagram

The O_2 carrier consists primarily of Fe_2O_3 based on earlier tests that showed an acceptable O_2 capacity and no loss of activity during more than 100 redox cycles in a thermogravimetric analyzer (TGA) test. To optimize the reactivity, recyclability, and physical strength of the Fe_2O_3-based O_2

carrier for the CDCL process, OSU researchers evaluated the performance of six support materials (aluminum oxide [Al_2O_3], titanium dioxide [TiO_2], magnesium oxide [MgO], silicon dioxide [SiO_2], bentonite, and kaoline) and two promoters (cerium oxide [CeO_2] and zirconium oxide [ZrO_2]) using a TGA and a fixed-bed reactor. These initial screening experiments were used to select the 10 most reactive and recyclable particle compositions, which were subjected to additional reactivity and physical strength tests. These 10 particles were tested to measure their reactivity with coal char in an inert environment and their tolerance to carbon deposition using TGA. The particles were then pelletized for further evaluations, such as pellet strength and reactivity, using a fixed-bed. After eliminating pellets with unacceptable strength and reactivity, the five most promising Fe_2O_3-based composite O_2 carrier particles were identified.

Bench-scale (2.5-kWth) testing of the five most promising O_2 carrier particle compositions in a moving-bed reactor will be used to determine the optimal O_2 carrier particle composition for the CDCL process. Continuous bench-scale tests will be conducted for at least 15 hours.

Using the sub-pilot scale (25-kWth) testing unit shown in Figure 2, the integrated CDCL process will be evaluated during a minimum of 50 hours of continuous operation with the optimal O_2 carrier particle composition. During testing, OSU researchers will monitor the composition of outlet gases (including CO_2, sulfur dioxide [SO_2], and [NO_X]), attrition of the O_2 carrier, and the ash separation effectiveness of the cyclone system.

To quantify the performance and potential benefits of the CDCL process, detailed modeling and a techno-economic analysis of the system will be conducted by CONSOL Energy.

Figure 2: Sub-Pilot Scale (25-kWth) CDCL Unit

Technology Advantages:

An air separation unit is not required for O_2 production and CO_2 separation simultaneously takes place with the coal conversion. Additionally, the CDCL process is a versatile technology that can produce power, synthesis gas (syngas), or hydrogen (H_2), while offering fuel flexibility.

R&D Challenges:

In addition to scaleup issues, challenges associated with the CDCL process include solids handling and transport; O_2 carrier capacity, reactivity, and attrition; slow reaction rates between the O_2 carrier and coal char; and ash management.

Results To Date/Accomplishments:

- Tested the base O_2 carrier particle with the standard protocol.
- Identified initial five O_2 carrier particles.
- Constructed the bench-scale reactor system for additional O_2 carrier optimization tests.
- Initiated construction of the sub-pilot scale system.
- Developed a cold model for the CDCL fuel reactor to study the contacting patterns of O_2 carrier and pulverized coal.

Next Steps:

OSU will complete moving-bed testing of the candidate O_2 carriers, conduct continuous bench-scale testing for at least 15 hours, perform integrated CDCL testing at the sub-pilot scale for at least 50 continuous hours, and complete a techno-economic analysis. Final test results will not be available until the December 2011 project completion date.

Available Reports/Technical Papers/Presentations:

Presentation: Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting, March 24-26, 2009, in Pittsburgh, Pennsylvania.

Contract No.:

DE-NT0005289

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Clear Skies Consulting
CONSOL Energy Inc.
Shell/CRI/Criterion Inc.

Ohio State University – Calcium Looping Process for Hydrogen Production

Project Title:

Enhanced Hydrogen Production Integrated with CO_2 Separation in a Single-Stage Reactor

Technology Area:

Chemical Looping

Technology Maturity:

Laboratory-scale

Primary Project Goal:

Ohio State University is developing the Calcium Looping Process (CLP) to enhance hydrogen (H_2) production by integrating the water gas shift (WGS) reaction with high-temperature carbon dioxide (CO_2), sulfur, and hydrogen (H_2) halides removal from synthesis gas (syngas) in a single-stage reactor.

Technical Goals:

- Reduce steam requirement and operate at near-stoichiometric steam consumption.
- Evaluate the regenerability of the calcium oxide (CaO) sorbent by repeated in-situ carbonation and regeneration for 10-100 cycles.
- Demonstrate simultaneous removal of CO_2, sulfur, and halides using a CaO sorbent in the bench-scale, fixed-bed unit.
- Produce either a 90 to 95% H_2 stream without WGS catalyst, or a 99+% high-purity H_2 stream with WGS catalyst at high temperatures and pressures.
- Demonstrate H_2 production with the sub-pilot scale testing unit.
- Perform a techno-economic feasibility study for different integrated process scenarios using Aspen.

Technical Content:

The WGS reaction, which converts most of the syngas carbon monoxide (CO) to H_2 and CO_2 by reacting the CO with water over a bed of catalyst, can be utilized to enhance H_2 production at an integrated gasification combined cycle (IGCC) plant. The excess steam serves to drive the shift equilibrium toward the products. The reaction is exothermic and, due to equilibrium constraints, typically consists of two stages: (1) high-temperature shift that benefits from high reaction rates at elevated temperatures; and (2) low-temperature shift that yields more favorable reaction equilibrium.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{rxn} = -41.2 \text{ kJ/mol}$$

Researchers at the Ohio State University (OSU) are developing the CLP that combines the WGS reaction and high-temperature, sorbent-based acid gas removal in a single-stage reactor, as shown in Figure 1. By implementing the CLP near the high-temperature reaction zone, syngas cooling and re-heating is no longer required, and the process may eliminate the need for the WGS catalyst. A CaO sorbent is used as the circulating material for in-situ removal of CO_2, sulfur, and H_2 halides. By incorporating sorbent-based CO_2 removal, not only is a near capture-ready stream of CO_2 produced, but plant efficiency and H_2 production are increased by driving the WGS reaction further to completion.

As shown in Figure 2, the CLP is comprised of three reactors: (1) the carbonator where high-purity H_2 is produced and contaminant removal takes place; (2) the calciner where the CaO sorbent is regenerated and a sequestration-ready CO_2 stream is produced; and (3) the hydrator, which reactivates the CaO sorbent. The carbonator (either a fixed, fluidized bed or an entrained flow reactor) operates at high pressures ranging from 20 to 30 atm and temperatures of 550°C to 650°C. The thermodynamic constraint of the WGS reaction is overcome in the carbonation reactor by the incessant removal of the CO_2 product from the reaction mixture, which enhances H_2 production. This is achieved by concurrent WGS reaction and carbonation reaction of CaO to form calcium carbonate ($CaCO_3$), thereby removing the CO_2 product from the reaction mixture and obviating the need for a WGS catalyst and excess steam addition. The CLP does not require syngas pretreatment, because the CaO sorbent also controls hydrogen sulfide (H_2S), hydrogen chloride (HCl), and carbonyl sulfide (COS) to ppb levels. Key parameters for the CaO sorbent are provided in Table 1.

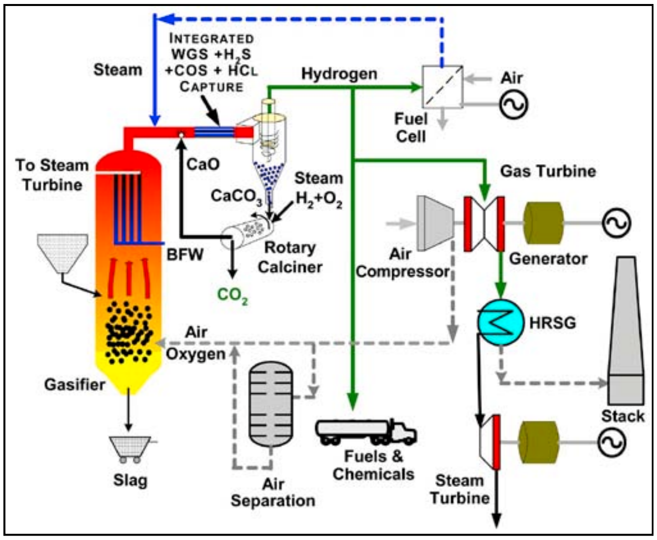

Figure 1: Calcium Looping Process for Enhanced Hydrogen Production with In-Site CO_2 and Sulfur Capture in a Single-Stage Reactor

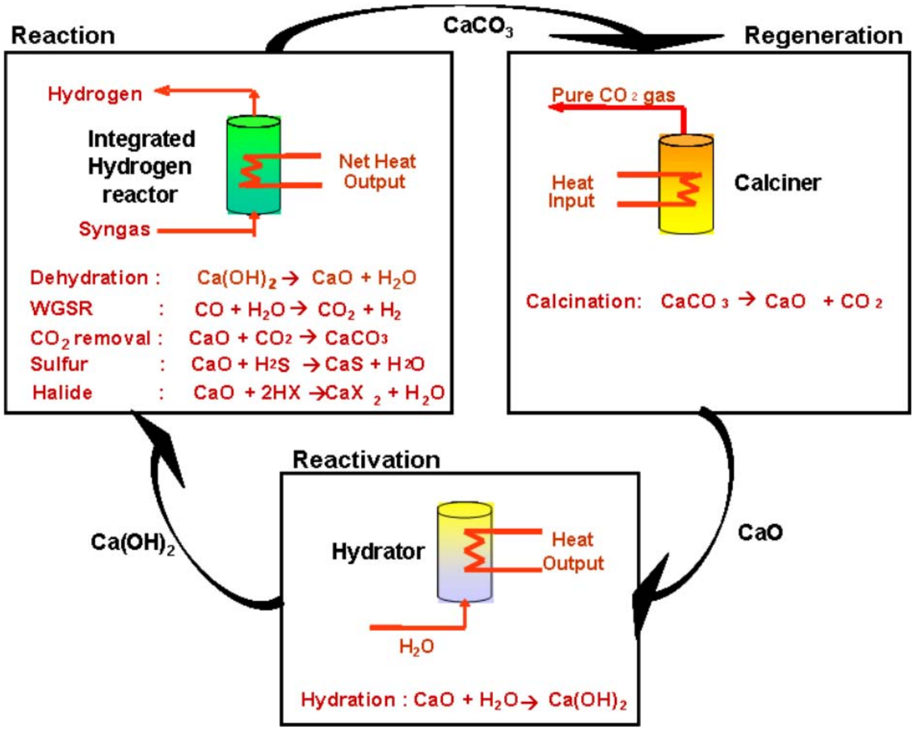

Figure 2: Illustration of the Reaction Schemes in the Calcium Looping Process

The spent sorbent, consisting mainly of $CaCO_3$, is regenerated back to CaO in the calciner, which operates at atmospheric pressure in a rotary, or a fluidized bed system. Calcination occurs at temperatures above 900°C in the presence of 1 atm CO_2, but CO_2 dilution via steam addition or syngas combustion in a direct-fired calciner permits calcination at lower temperatures. The regenerated CaO sorbent is then conveyed to the hydrator.

The hot solids from the calciner are then cooled to 500°C to 600°C and hydrated via contact with low-temperature steam in the hydrator. The calcination process causes sorbent sintering, which reduces the sorbent's reactivity; the hydration process reverses this affect by increasing the pore volume and surface area available for reaction with the gas mixture. The calcium hydroxide reacts in the H_2 reactor to produce CaO and steam. The steam obtained from the dehydration reaction is used for the WGS reaction. Hence, no excess steam is required in the CLP as the WGS steam is supplied to the hydrator.

Table 1: Solid Sorbent Parameters

	Parameter	Current R&D Value	Target R&D Value
Sorbent Properties	Type of sorbent	CaO powder	CaO powder
	Heat of adsorption (kJ/mole CO_2)	-178.3	-178.3
	CO_2 loading/working capacity, wt.%	45-55%	55%
	Surface area, m^2/g	14-32	14-32
	Particle density, cm^3/g	1.150 g/cm^3	1.150 g/cm^3
	Packing density, cm^3/g	1.289 g/cm^3	1.289 g/cm^3
	Particle size (mm)	0.01-0.05	0.01-0.05
	Heat capacity (kJ/K/kg)	0.96(CaO)-1.23($CaCO_3$)	0.96(CaO)-1.23($CaCO_3$)
	Thermal stability, °C	Much higher than the temperature of operation	Much higher than the temperature of operation
	Hydrothermal stability, °C	N/A	N/A
Process Configuration	Attrition rate (fluidized bed), %/year	NA since micron sized particles are used	NA since micron sized particles are used
	Cycle time (fixed bed), minutes	N/A	N/A
	Pressure drop (fixed bed), psia	N/A	N/A
Operating Conditions	Adsorption temperature, °C	600	600
	Adsorption pressure, atm.	1-30 atms	1-30 atms
	CO_2 capture efficiency, %	>99%	>99%
	Regeneration method	Calcination in N_2, or pure CO_2	Calcination in CO_2
	Regeneration temperature, °C	700-950	700-950
	Regeneration pressure, atm.	1	1
Heat Integration	Required regeneration steam temperature, °C	External steam not required for regeneration	External steam not required for regeneration
Miscellaneous	Sorbent make-up rate, $kg/kgCO_2$	N/A	
Product Quality	CO_2 purity, %	N/A	>99%
	N_2 concentration, %	N/A	<1%
	Other contaminants, %	N/A	-
Process Performance	Electricity requirement, $kJ/kgCO_2$	N/A	N/A
	Heat requirement, $kJ/kgCO_2$	N/A	N/A
	Total energy (electricity equivalent), $kJ/kgCO_2$	N/A	N/A

Technology Advantages:

The simultaneous removal of CO_2 drives the WGS reaction to completion, which along with operation at feed conditions (high temperature and pressure), will increase plant efficiency. The process also eliminates the need for a WGS catalyst.

R&D Challenges:

In addition to scaleup issues, challenges associated with the process include solids handling and transport, as well as ash management.

Results To Date/Accomplishments:

- Determined optimum temperature (600°C) for H_2 production and impurity removal.
- Identified temperature range for CO_2 capture while reducing excess steam requirements.
- Identified process conditions for H_2S and halide capture.
- Combined WGS, carbonation, and sulfidation reactions in the absence of a catalyst.
- Designed and fabricated a cold model for the chemical looping reducer.
- Developed the sorbent reactivation process by hydration and achieved sustained reactivity for multiple cycles.

Next Steps:

OSU will complete an Aspen simulation and techno-economic analysis of the CLP, conduct sub-pilot scale testing to evaluate process feasibility, and design a 1-5 MWe pilot-scale plant. Final test results will not be available until the September 2010 project completion date.

Available Reports/Technical Papers/Presentations:

Balasubramanian, B., Lopez-Ortiz, A., Kaytakoglu, S. and Harrison D. P., "Hydrogen from Methane in a Single-Step Process," *Chem. Engng. Sci.*, **54**, 3543-3552 (1999).

Christopher Higman, Maarten van der Burgt, "*Gasification,*" 2003 Elsevier, New York, U.S.A.

Department of Chemical and Biomolecular Engineering. February 12, 2009.

Dr. Liang-Shih Fan, Fanxing Li, Shwetha Ramkumar, Liang Zeng, Andrew Tong. *Process/equipment Co-Simulation on Syngas Chemical Looping Process.* Ohio State University Department of Chemical and Biomolecular Engineering.

Gerhartz W., "Ullmann's Encyclopedia of Industrial Chemistry," A12, 5th edition, VCH, New York pp. 179-242 (1993).

Liang-Shih Fan, *Syngas Chemical Looping Sub-Pilot and Pilot Scale Demonstrations*, Ohio State University.

"*Steam, Its Generation and Use,"* 40th edition, by Babcock & Wilcox Company.

Contract No.:

DE-FC26-07NT43059

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Partners:

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Consol Energy Inc.

APPENDIX

ADVANCED COMPRESSION

Southwest Research Institute – Evaluation of Compression Efficiency Improvements

Project Title:

Novel Concepts for the Compression of Large Volumes of CO_2

Technology Area:	**Technology Maturity:**
Compression	Pilot-scale, 90 tonnes/hr

Primary Project Goal:

Southwest Research Institute (SwRI) is examining methods of boosting the pressure of carbon dioxide (CO_2) from pulverized coal (PC), oxy-combustion, and integrated gasification combined cycle (IGCC) plants to pipeline pressures with minimum parasitic energy expended.

Technical Goals:

- Conduct thermodynamic and economic analysis to determine the preferred CO_2 state for compression.
- Identify and evaluate intercooling concepts.
- Develop preliminary intercooling design.
- Calculate total potential energy savings.
- Complete a comprehensive thermodynamic and cost analysis of an IGCC plant incorporating the new compression technology.
- Design a two-stage compressor test rig based on the analyses and design studies.
- Design, fabricate, and test a multi-stage pump test rig based on the analyses and design studies.
- The tests include:
    - Power requirements.
    - Vibrations.
    - Temperatures.
    - Seal flows.
    - Incidences of cavitation.
    - Net positive suction head test.

Technical Content:

Like work, power is path dependant, meaning that how a compressor operates will determine the total power that it consumes. Figure 1 shows how two compression processes can achieve the same pressure, but still consume different quantities of power. The isothermal compression, even at 60% efficiency, is preferable to isentropic compression at 100% efficiency.

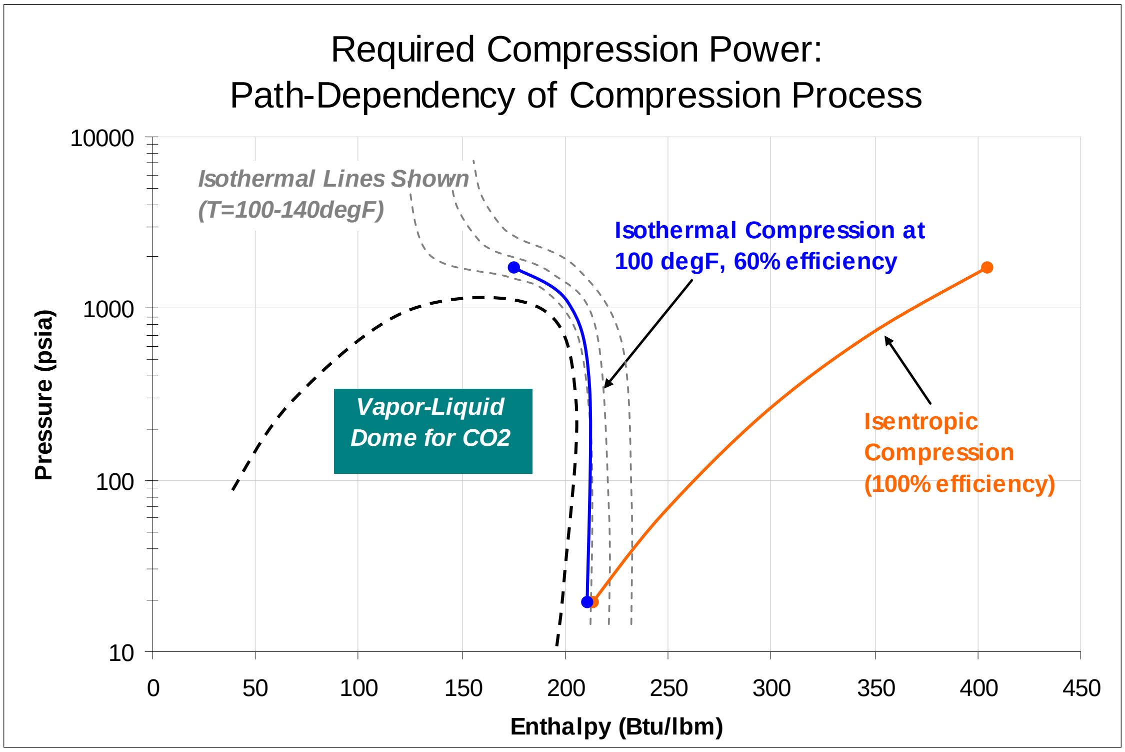

Figure 1: The Path Dependency of Compression Power

SwRI has examined a number of different compression options to find the ones that would consume the least amount of power. It was found that compressing CO_2 while simultaneously cooling it to approximate isothermal compression would lower power consumption. Following liquefaction, the pressure of the liquid CO_2 could then be further increased using a pump for total low power consumption.

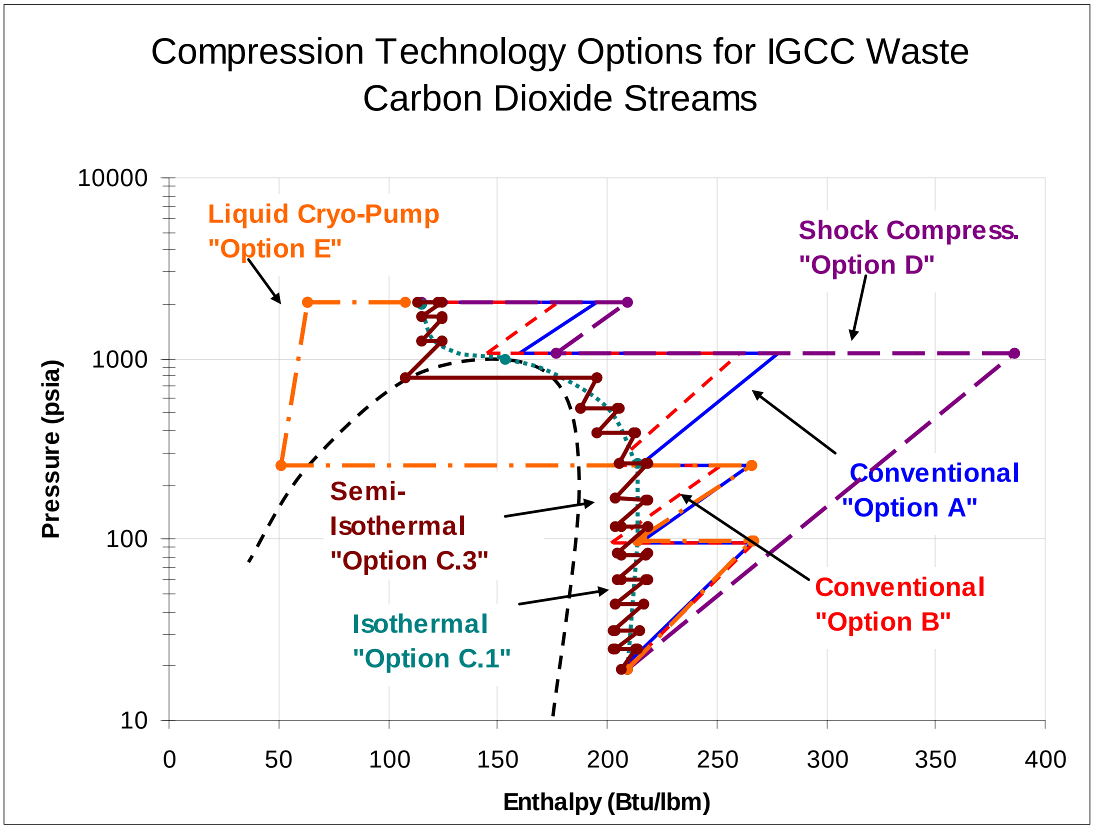

Figure 2: Required Compression Power for the Investigated Technology Options

Table 1: Comparison of Compression Technologies

Option	Compression Technology	Power Requirements	% Diff from Option A	Cooling Technology
A	Conventional Dresser-Rand Centrifugal 10-stage Compression	23,251 BHP	0.00%	Air-cool streams between separate stages
B	Conventional Dresser-Rand Centrifugal 10-stage Compression with additional cooling	21,522 BHP	-7.44%	Air-cool streams between separate stages using ASU cool N2 stream
C.1	Isothermal compression at 70 degF and 80% efficiency	14,840 BHP	-36.17%	Tc = 70 degF inlet temp throughout
C.4	Semi-isothermal compression at 70 degF, Pressure Ratio ~ 1.55	17,025 BHP (Required Cooling Power TBD)	-26.78%	Tc = 70degF in between each stage.
C.7	Semi-isothermal compression at 100 degF, Pressure Ratio ~ 1.55	17,979 BHP (Required Cooling Power TBD)	-22.67%	Tc = 100degF in between each stage.

Option	Compression Technology	Power Requirements	% Diff from Option A	Cooling Technology
D.3	High ratio compression at 90% efficiency - no inter-stage cooling	34,192 BHP	47.06%	Air cool at 2215 psia only
D.4	High ratio compression at 90% efficiency - intercooling on final compression stage	24,730 BHP	6.36%	Air cool at 220 and 2215 psia
E.1	Centrifugal compression to 250 psia, Liquid cryo-pump from 250-2215 psia	16,198 BHP (Includes 7,814 BHP for Refrigeration) [1]	-30.33%	Air cool up to 250 psia, Refrigeration to reduce CO2 to -25degF to liquify
E.2	Centrifugal compression to 250 psia with semi-isothermal cooling at 100 degF, Liquid cryo-pump from 250-2215 psia	15,145 BHP (Includes 7,814 BHP for Refrigeration) [1]	-34.86%	Air cool up to 250 psia between centrifugal stages, Refrigeration to reduce CO2 to -25degF to liquify

Option E.2 was selected as the most desirable.

Figure 3 shows a design for an internally cooled compressor. The flow of the CO_2 is shown in red, while the cooling liquid is shown in blue.

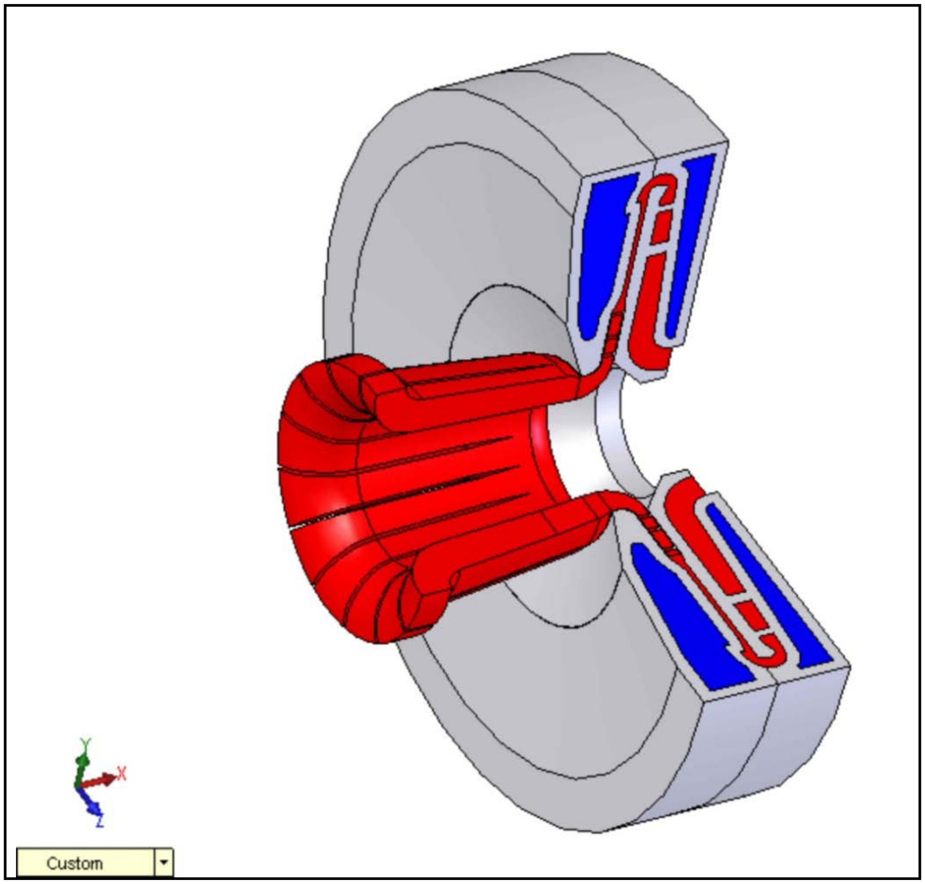

Figure 3: Design for an Internally Cooled Compressor

Technology Advantages:

- New compression process could use up to 35% less power.
- Applicable to all types of power plants.
- Could result in significant capital savings compared to an integrally geared compressor.
- Pump operating costs will be lower than high-pressure compressor operating costs.

R&D Challenges:

- There will be a wide range of CO_2 output from the power plant based on required electrical output.
- CO_2 compression technology must have high reliability.
- IGCC plants contain multiple CO_2 streams at different pressures.

Results To Date/Accomplishments:

- Conducted a thermodynamic and economic analysis to determine the preferred CO_2 state for compression.
- Calculated total potential energy savings.
- Created detailed designs for compressor and pump.

Next Steps:

- Optimize and verify the compressor and pump designs.
- Fabricate and assemble the prototype compressor and pump.
- Conduct functional tests of prototypes.

Final test results will not be available until the April 2010 project completion date

Available Reports/Technical Papers/Presentations:

Presentation at Annual NETL CO_2 Capture Technology for Existing Plants R&D Meeting in March 2009 in Pittsburgh, Pennsylvania.

Contract No.:

DE-FC26-05NT42650

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Partners:

Dresser-Rand, BP

Ramgen Power Systems – Shockwave Compression

Project Title:

High-Efficiency, Low-Cost CO_2 Compression Using Super-Sonic Shock Wave Technology

Technology Area:	**Technology Maturity:**
Compression	Pilot-scale, 1,680 tonnes/day CO_2

Primary Project Goal:

Ramgen Power Systems is designing and developing a unique compressor technology based upon aerospace shock wave compression theory for use as a land-based carbon dioxide (CO_2) compressor.

Technical Goals:

Phase I

- Complete testing of a high-pressure ratio (10:1) air compressor rotor for the Ram 2 program.
- Demonstrate the feasibility of high-pressure shock wave compression.
- Develop and detail a viable commercialization path.

Phase II

- Perform critical success factors risk reduction validation and test program to identify and reduce technical risk areas.
- Complete general assessment, preliminary, and final design of a demonstration CO_2 supersonic shock compressor approximately 13,000 hp in size.

Technical Content:

When shock waves pass through a gas they cause a localized compression. Ramgen is developing a compressor that creates and utilizes this effect to accomplish efficient CO_2 compression.

Figure 1 shows that the rotating rotor rim has small, shallow angles which, when rotating at high speeds, will produce supersonic shock waves both prior to and post-peak. These shock waves, modeled in the 3-D Euler Computational Fluid Dynamics (CFD) image shown, are first oblique, then normal. Additionally, strakes (ridges) are incorporated into the design of the rotor to form sidewalls. The strakes are utilized as shock compression ducts, as well as to separate high-pressure discharge 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 and therefore higher quality heat of compression that combine to deliver significant installed and operational cost savings versus existing turbo-compressors.

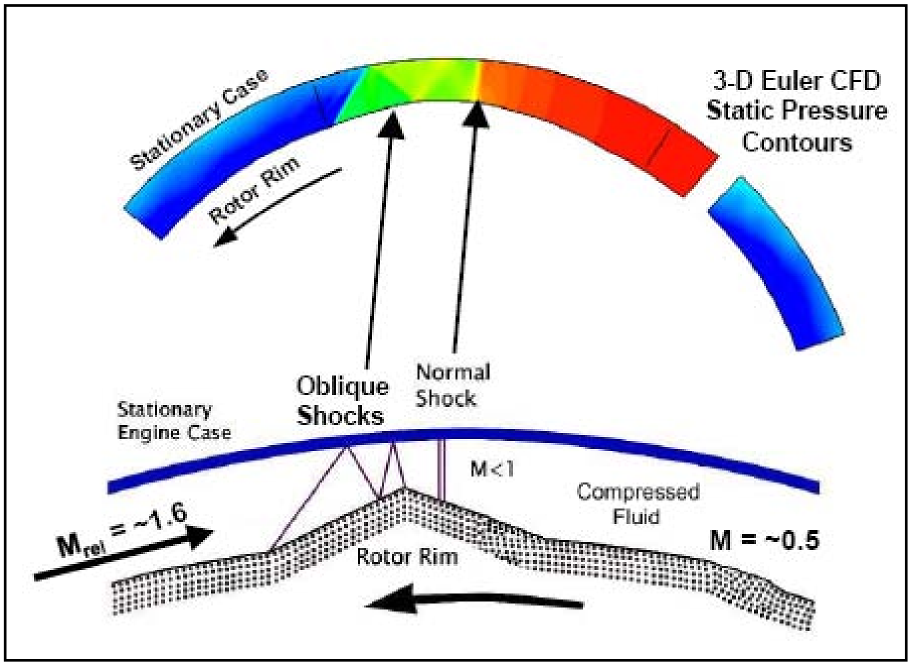

Figure 1: Schematic of Rotor Rim and Engine Case and 3-D Euler CFD Image Depicting Shock Wave Behavior

Two stages of compression are used with an intercooler located between the stages to optimize the efficiency of the compression process. Figure 2 shows the energy required as shaft work and the thermal energy lost to the cooling stream. The numbers found in the figure represent a stage in the process; each stage is driven independently through an external gearbox.

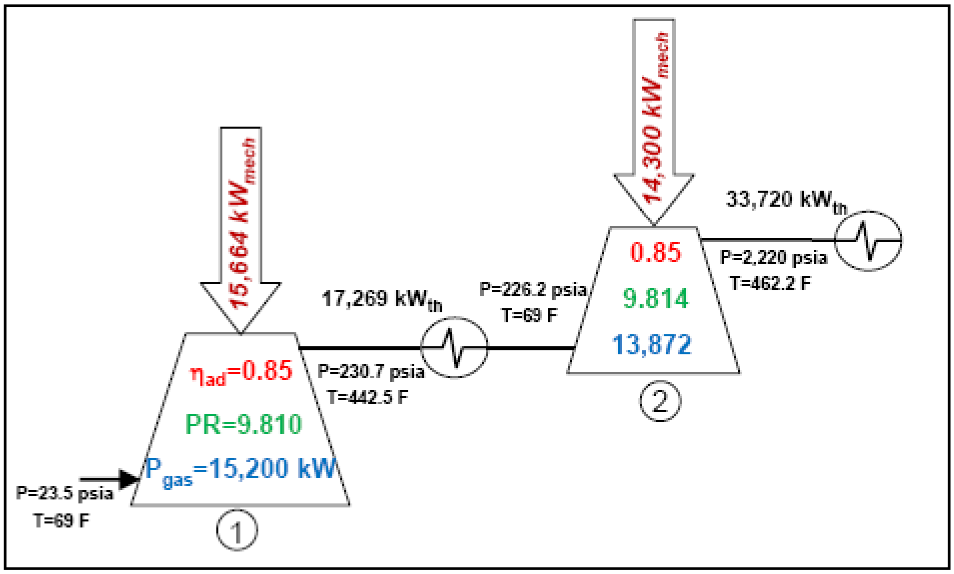

Figure 2: Series Process Schematic

As seen in Figure 2, the total shaft power is 29,964 kW_{mech}, which corresponds to a heat of compression of 50,989 kWth. Approximately 28,986 kWth of the heat of compression lost is recoverable down to 93°C (200°F).

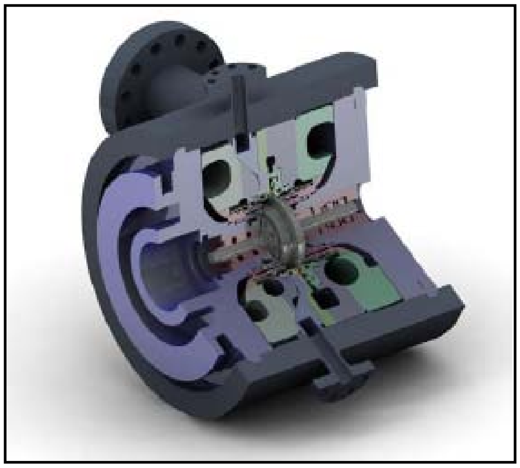

Figure 3: Cross Sectional Model of a 1/10th Scale Single Stage Supersonic Shock Wave Compressor

Technology Advantages:

- Competitive operating efficiency and reduced installed capital cost (approximately 50%) over multi-stage bladed turbo compressors.
- High stage discharge temperature enables cost-effective recovery of heat of compression.
  - Improves carbon capture and sequestration (CCS) efficiency.
  - Reduces power plant de-rate.

R&D Challenges:

- Complicated shock wave aerodynamics on the 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.

Results To Date/Accomplishments:

- Completed flow path validation test conceptual design review.
- Completed demonstration unit feasibility study.
- Prepared a detailed systems analysis of the technology.
- Prepared a rigorous comparative economic analysis based on the systems analysis.
- Achieved breakthrough rotor pressure ratio of approximately 7.9:1 in air.
- Demonstrated tip speeds up to ~2,200 ft/s and M_{rels} up to ~2.7.
- Successfully modeled full flow path 3-D viscous CFD.
- Matched performance prediction/design tools to test.
- Obtained benign surge characteristics.
- Gathered data for preliminary compressor maps.
- Developed and demonstrated bearing designs suitable for product application.

Next Steps:

Develop high speed performance computing capability at Oak Ridge National Laboratory.

Final test results will not be available until the December 2010 project completion date.

Available Reports/Technical Papers/Presentations:

Presentation in March 2009 at NETL CO_2 Capture Technology for Existing Plants R&D Meeting, http://www.netl.doe.gov/technologies/coalpower/ewr/co2/co2compression/supersonic.html (May 2009).

Presentation at 2008 Seventh Annual Conference on Carbon Capture and Sequestration, http://www.netl.doe.gov/technologies/coalpower/ewr/co2/co2compression/supersonic.html (May 2009).

Contract No.:

DE-FC26-06NT42651

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APPENDIX

RD&D COLLABORATIONS

UNDEERC – Partnership for CO_2 Capture

Project Title:

Partnership for CO_2 Capture

Technology Area:	**Technology Maturity:**
Oxy- and Post-Combustion	Pilot-scale

Primary Project Goal:

The University of North Dakota Energy and Environmental Research Center (UNDEERC) is conducting pilot-scale testing to demonstrate and evaluate 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 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.
- Perform systems engineering modeling to examine efficient and cost-effective integration of CO_2 capture technologies in existing and new systems.

Technical Content:

UNDEERC is constructing two pilot-scale systems with the intention of performing experiments on several advanced CO_2 capture technologies and comparing them to one another, as well as to monoethanolamine (MEA), which is considered to be the current state-of-the-art technology.

Baseline testing will be conducted using MEA to gather information to characterize each of the units. The results obtained by using MEA in the CO_2 absorption system will be used as a standard by which all other solvents will be compared. Data to be collected includes CO_2 removal, CO_2 purity, required regeneration heat, and effects of sulfur oxide (SO_X), nitrogen oxide (NO_X), particulate matter, and trace metals.

Figure 4: UNDEERC Post-Combustion CO_2 Capture Test Facility

Baseline testing of the oxy-combustion system will follow similar procedures as the absorption system. The data collected will 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.

Once CO_2 capture technologies have been selected, testing will begin. Some of the technologies under consideration include other solvents (monodiethanolamine [MDEA], tailored amines, designer amines, ammonia, and potassium bicarbonate), membranes (metal membranes and carbozyme), and solid sorbents (zeolites, metal-organic frameworks, solid amines, and C-Quest). In addition to testing these technologies, different fuels will be used to evaluate their impact on the performance of the fabricated test units. Factors to be examined will include the effects of SO_X, NO_X, and other gas components; effects of ash deposition along with corrosion of refractory; and alloy components.

UNDEERC has completed the construction of the oxy-combustion system and has begun shakedown testing of the units. UNDEERC has also completed an Aspen model of the solvent absorption and stripping column (SASC) system.

Technology Advantages:

UNDEERC will be capable of providing experimental data for a variety of advanced CO_2 capture technologies and oxy-combustion systems. This information will not only provide needed information for further advancement, but will provide a clear comparison of various approaches.

R&D Challenges:

Retrieving enough information on existing technologies to make appropriate selections for testing.

Results To Date/Accomplishments:

- Completed design and construction of the post-combustion test system.
- Completed the oxy-combustion retrofit.
- Performed shakedown and preliminary baseline testing on oxy-combustion system.
- Modeled the combustion test facility (CTF) system in Aspen with and without the oxygen-fired retrofit modifications.

Next Steps:

- Perform several weeks of operation of the CTF unit equipped with the various control technologies selected.

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

Available Reports/Technical Papers/Presentations:

Chen, S.G.; Lu, Y.; Rostam-Abadi, M. *Carbon Dioxide Capture and Transportation Options in the Illinois Basin*; Topical Report Oct 1, 2003–Sept 30, 2004 for U.S. Department of Energy Contract No. DE-FC26-03NT41994.

Metz, B.; Davidson, O.; Coninik, H.; Loos, M.; Meyer, L. *IPCC Special Report Carbon Dioxide Capture and Storage Technical Summary*; ISBN 92-9169-119-4, Sept 2005.Narula, R.; Wen, H.; Himes, K. Economics of Greenhouse Gas Reduction – The Power Generating Technology Options. Presented at the World Energy Congress, Buenos Aires, Brazil, October 2001.

U.S. Environmental Protection Agency. Greenhouse Gas Inventory Sector Analysis. www.yosemite.epa.gov (accessed June 2006).

Contract No.:

DE-FC26-08NT43291-02.5

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