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

MAY 2011

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MESSAGE TO STAKEHOLDERS

This is the second edition of the DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update. The first edition was published in September 2010. This edition of the report includes expanded descriptions of the carbon dioxide (CO_2) capture research and analyses being conducted internally by the National Energy Technology Laboratory's (NETL) Office of Research and Development (ORD) and Office of Program Planning and Analysis (OPPA). For projects being conducted by external researchers, the fact sheets located in the Appendix have been updated to reflect changes in the status of technology development that have occurred over the last 8 months. The Appendix has also been expanded to include fact sheets for new external projects that were initiated after the September 2010 edition was published. Future editions of this report are planned to be published annually.

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 CO_2 capture technologies for coal-based power plants. Under this program, 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, first generation technologies, but also the development of second and third generation advanced CO_2 capture technologies. 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 cost of electricity (COE) of pre-combustion capture for integrated gasification combined cycle (IGCC) power plants and less than a 35 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 targets include the completion of laboratory- and small pilot-scale testing of a broad spectrum of CO_2 capture approaches including advanced solvents, sorbents, membranes, oxy-combustion, and chemical looping combustion by 2016; completion of large pilot-scale testing by 2020; and full-scale demonstrations of the most promising technologies beginning by 2020. It is anticipated that successful progression from laboratory- through full-scale demonstration will result in several of these advanced technologies being available for commercial deployment by 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. 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 and the fundamentals of CO_2 compression. Chapters 5 through 10 report on the status of DOE/NETL's external R&D efforts for pre-combustion capture; post-combustion capture; oxy-combustion; oxygen production; chemical looping; and advanced compression, respectively. Chapters 11 and 12 provide a summary of DOE/NETL's internal research efforts and analyses conducted by ORD and OPPA, respectively. Chapter 13 includes a discussion of DOE/NETL's CO_2 capture R&D collaborations. Appendix A contains fact sheets for DOE/NETL's large-scale demonstrations of currently available CO_2 capture technologies being conducted under the Clean Coal Power Initiative and Industrial Carbon Capture and Storage programs. Finally, Appendix B provides detailed information on the status and results of the current portfolio of DOE/NETL's advanced CO_2 capture technology R&D projects being conducted by external researchers.

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. Although the majority of the technology options being considered are still in the laboratory- and bench-scale stages of development, a limited number of small pilot-scale field tests have been initiated. Additional information on DOE/NETL's CO_2 capture R&D effort is available in a companion document, entitled "DOE/NETL Carbon Dioxide Capture and Storage RD&D Roadmap, December 2010" and is available for download at:

http://www.netl.doe.gov/technologies/carbon_seq/refshelf/CCSRoadmap.pdf

In 2009, coal-based power plants generated approximately 45 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 313 gigawatts (GW) of coal-based electricity generating capacity currently in operation will increase to 319 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.
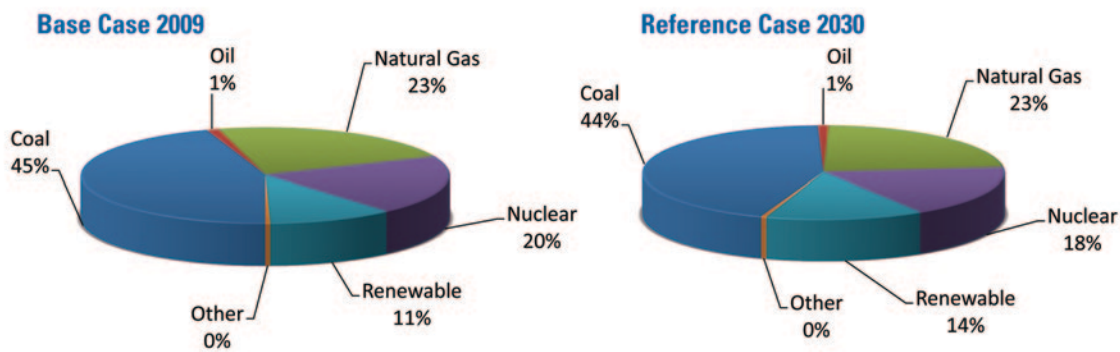
Figure 1-1: U.S. Electricity Generation by Fuel Type[i]

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 69 percent of total U.S. electricity generation and produced almost 40 percent of the 5.4 billion metric tons of total U.S. anthropogenic CO_2 emissions in 2009. Coal-based power plants consumed almost 1 billion tons of coal that produced 1.7 billion metric tons of CO_2 emissions, which comprised almost 32 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 that shows overall coal consumption (electricity and other sectors) contributes 34 percent of the total. 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.
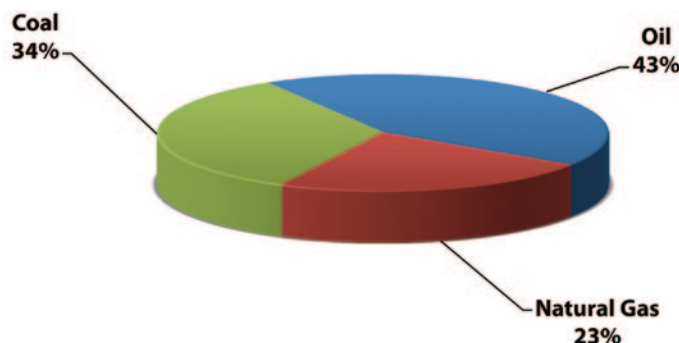
Figure 1-2: Source of U.S. CO_2 Emissions by Fuel Type in 2009

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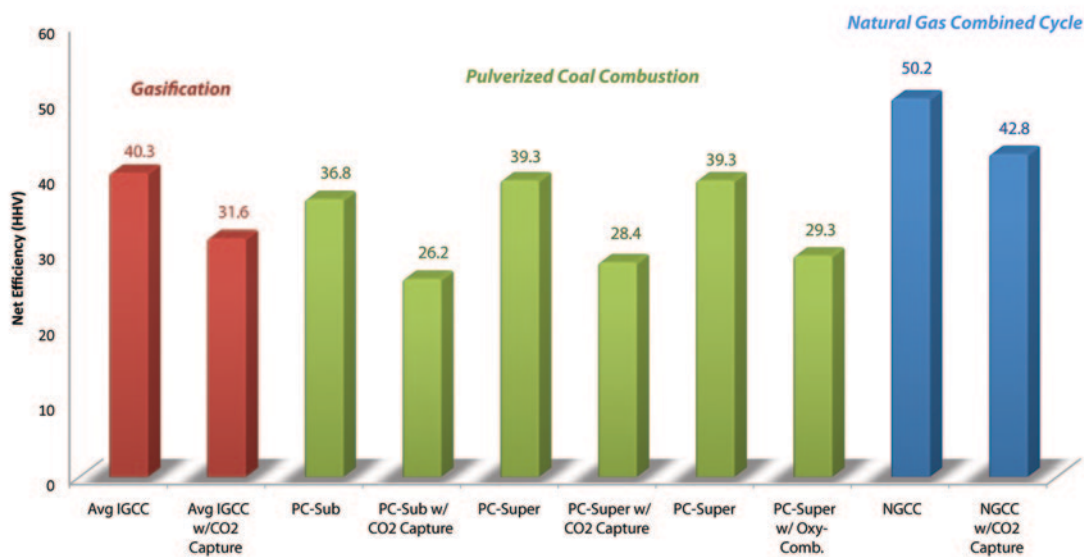
Figure 1-3: Net Plant Efficiency with and without CO_2 Capture and Compression

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 PC, IGCC, and natural gas combined cycle (NGCC) power plants.[ii, iii] Implementation of CO_2 capture results in a 7–10 percentage point decrease in net plant efficiency depending on the type of power generation facility.

Figure 1-4 presents a comparison of the first-year cost of electricity (COE) expressed in 2007 dollars for various power plant configurations both with and without CO_2 capture.[ii, iii] For example, the COE for a new IGCC plant averages $77/MWh without CO_2 capture, but increases approximately 45 percent to $112/MWh with pre-combustion CO_2 capture. Likewise, the COE for a new PC plant averages approximately $59/MWh without CO_2 capture, but increases over 80 percent to $108/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 $/tonne CO_2. The avoided cost is calculated by dividing the difference in COE, $/MWh, by the difference in CO_2 emissions with and without CO_2 capture, tonne/MWh. Chapter 12 provides more detailed information on DOE/NETL systems analysis studies on the cost and performance of CO_2 capture technologies.
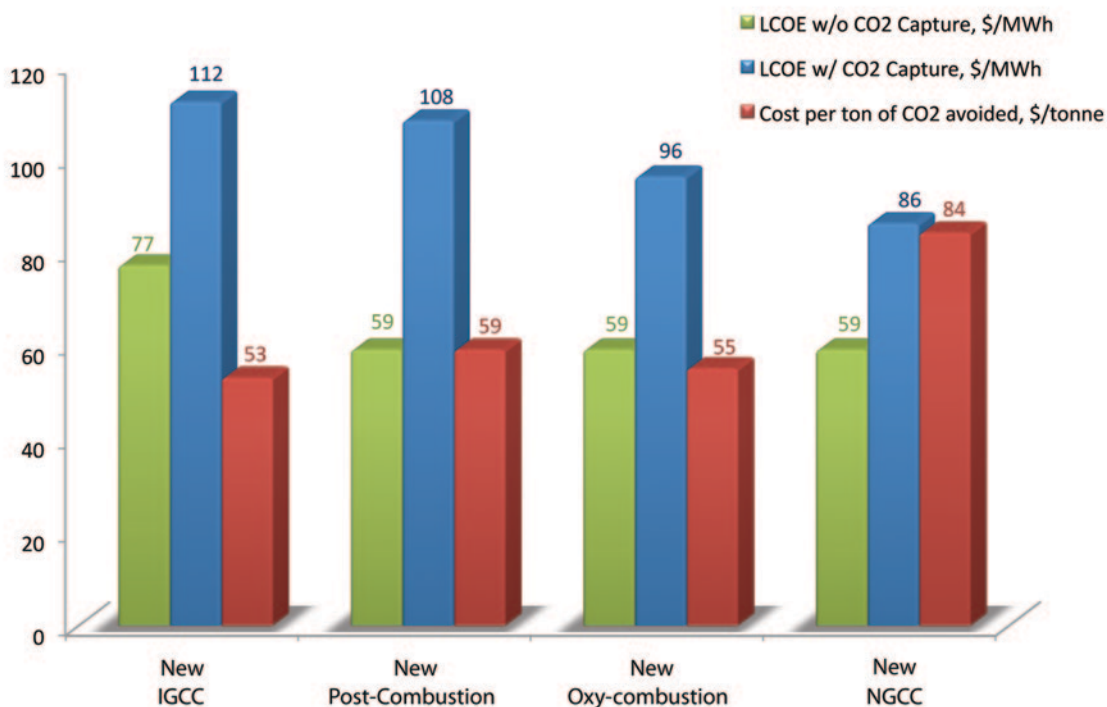
Figure 1-4: CO_2 Capture Costs for Different Types and Configurations of Power Plants

Other major technical challenges associated with the application of currently available CO_2 capture technologies to coal-based power plants include energy and mechanical 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.
Cost	Recent studies conducted by NETL and others show that current technologies are expensive. For example, installing a current state-of-the-art post-combustion CO$_2$ capture technology—chemical absorption with an aqueous amine solution—is estimated to increase the levelized COE by about 75–80 percent.
Auxiliary Power for CO$_2$ Compression	To enable storage, a significant amount of power is required to compress the captured CO$_2$ to typical pipeline levels (1,500–2,200 psia). This auxiliary power decreases the net electrical generation of the power plant and significantly reduces net power plant efficiency.
Auxiliary Power for CO$_2$ Capture	Auxiliary power is also required to operate CO$_2$ capture technologies. This auxiliary power decreases the net electrical generation of the power plant and significantly reduces net power plant efficiency.
Auxiliary Heat for CO$_2$ Capture	A large quantity of heat, typically supplied by steam, is required to regenerate the chemical agents used in many CO$_2$ capture technologies [~1,550 British thermal units (Btu) per pound of CO$_2$ removed for current amine solutions]. Use of steam generated by the plant's boiler decreases the gross electrical generation of the power plant and significantly reduces net power plant efficiency.
Energy Integration	Steam required for regeneration can only be extracted at conditions defined by the power plant's steam cycle. In addition, capture can result in the generation of significant quantities of waste heat. Careful and creative thermal integration of the capture system with the power plant can improve plant efficiency.
Mechanical Integration	Any CO$_2$ capture system must fit within the boundaries of the power plant. This is a significant challenge when dealing with existing plants that have fixed layouts and limited open space.
Flue Gas Contaminants	Constituents in the flue gas, particularly sulfur, can contaminate the chemical agents and other materials used in many CO$_2$ capture technologies, leading to system outages and increased maintenance expenses.
Water Usage	A significant amount of water is used in current technologies for cooling during CO$_2$ capture and compression.
Oxygen Supply	An oxy-combustion power plant will require a supply of high-purity oxygen. Currently available technology—cryogenic air separation unit (ASU)—is energy and capital intensive.

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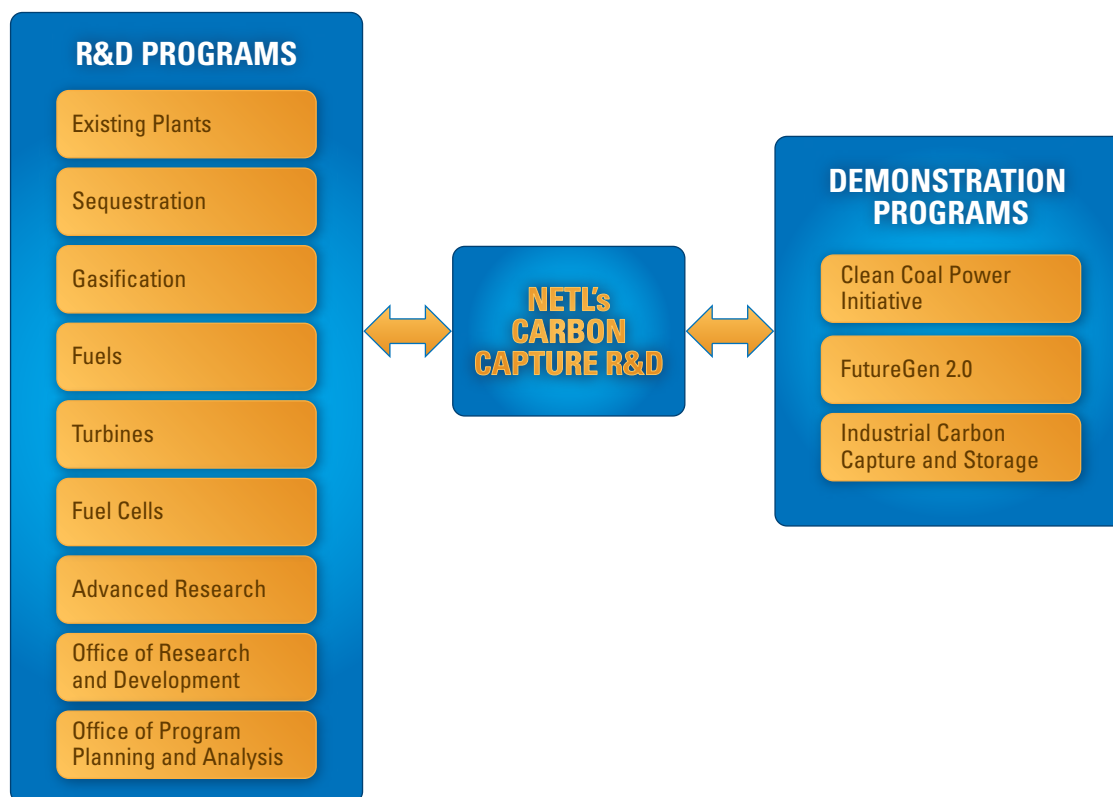
Figure 2-1: NETL Programs Associated with Carbon Capture R&D

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 hydrogen (H_2) and CO_2 in coal-derived syngas.

The DOE/NETL programs discussed above primarily direct R&D activities that are conducted externally by other organizations. However, DOE/NETL also conducts internal CO_2 capture research and related studies. DOE/NETL's 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. A summary of ORD activities is provided in Chapter 11. In addition, DOE/NETL's OPPA 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. A summary of OPPA activities is provided in Chapter 12.

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 35 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.

THE R&D PROCESS – PROGRESS OVER TIME

The development of an advanced CO_2 capture technology includes more than laboratory-scale testing of process chemistry and physics and evaluation of associated operating parameters. The research effort can also involve the development of new chemical production methods; novel process equipment designs; new equipment manufacturing methods; and optimization of the process integration with other power plant systems, e.g., the steam cycle, cooling water system, and CO_2 compression system. Figure 2-2 presents the various R&D components that might be necessary to take a capture technology from concept to commercial reality. Developing a successful CO_2 capture technology requires putting together all these pieces of the puzzle. While some of these developments are unique to a specific process, others could be more generally applicable. For example, a novel process equipment design developed by one research organization could prove vital to optimizing performance of the process chemistry developed by another research organization. While most of the CO_2 capture technology projects encompass the entire range of R&D components, there are some that focus more on a specific component or perhaps are more successful with a specific component, e.g., process chemistry or process equipment design. As a result, it could take the integration of the successful development of multiple components from multiple researchers to eventually arrive at a successful and cost-effective CO_2 capture technology.

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 1 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 10–125 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 1,000–12,000 scfm. For comparison, one megawatt (MW) gross electric generation produces approximately 2,500 scfm of combustion flue gas.

Stages of CO_2 Capture Techology Development

2005	2010	2020	2030
Lab/Bench-Scale Testing	**Pilot-Scale Field Testing (Slip Stream)**	**Full-Scale Demonstration**	
Short duration tests (hours/days)	Longer duration (weeks/months)	Extended duration (typically years)	
Low to moderate cost	Higher cost	Major cost	
Medium to high risk of failure	Low risk of failure	Minimal risk of failure	
Artificial and simulated operating conditions	Controlled operating conditions	Variable operating conditions	
Proof-of-concept and parametric testing	Evaluate performance and cost of technology in parametric tests to setup demonstration projects	Demonstrate full-scale commercial application	

RESEARCH, DEVELOPMENT & DEMONSTRATION

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

Figure 2-3 describes the various stages of R&D scale-up. As the test scale increases, the duration and cost of the projects increase. More importantly, there is a relatively high risk of failure associated with laboratory/bench-scale testing, a lower risk of failure for pilot-scale testing, and a minimal risk of failure for full-scale demonstrations. 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 beginning in October 2008 to conduct a six-month small pilot-scale field test that was conducted in 2010. The approximately 175-scfm small pilot-scale slipstream testing was conducted at Arizona Public Services' coal-fired Cholla Power Plant located in Arizona. In late 2010, DOE/NETL selected MTR to conduct additional scale-up testing of the membrane technology based on a gas flow rate of approximately 2,500 scfm [equivalent to approximately 1.0 MW electric (MW)]. A six-month field test of the membrane system is scheduled to begin in 2013.

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 60–235 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 2.0 Initiative that will repower an existing 200 MW power plant located in Illinois.

Table 2-1: CO₂ Capture Demonstration Projects Being Conducted under CCPI and FutureGen

Performer	Location	Capture Technology	Capture Rate, Tonnes/yr	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	—
NRG Energy	Thompsons, 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

* On 12/17/10, Basin Electric announced an indefinite hold on completing the project.
** This project is not a part of the CCPI program, but has a similar scope and objectives

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 (See Table 2-2). 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/yr	Start Date
Leucadia Energy	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

Appendix A includes the DOE/NETL fact sheets for the CCPI and ICCS projects. Additional information on the CCPI and ICCS projects can be found on the NETL website at: http://www.netl.doe.gov/technologies/coalpower/cctc/index.html

Additional information on FutureGen 2.0 can be found on the NETL website at:
http://www.netl.doe.gov/technologies/coalpower/futuregen/index.html

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CHAPTER 3:
GENERAL APPROACHES TO CARBON DIOXIDE CAPTURE

There are three general approaches to CO_2 capture for fossil-fuel power plants—pre-, post-, and oxy-combustion. Pre-combustion systems are designed to separate CO_2 from hydrogen (H_2) and other constituents in the syngas stream produced by the gasifier in IGCC power plants. Post-combustion systems separate CO_2 from the flue gas stream produced by conventional PC power plants after fuel combustion in air. In this approach, CO_2 is separated from nitrogen (N_2), which is the primary constituent of the flue gas. Oxy-combustion separates O_2 from the N_2 in air prior to coal combustion, which results in a CO_2 concentrated flue gas stream.

DOE/NETL is investigating a broad portfolio of technology pathways based on all three approaches to CO_2 capture. 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. Advanced pre-combustion CO_2 capture technologies being investigated by DOE/NETL include the use of solvents, sorbents, and membranes. A more detailed description of pre-combustion CO_2 capture processes is provided in Chapter 4.
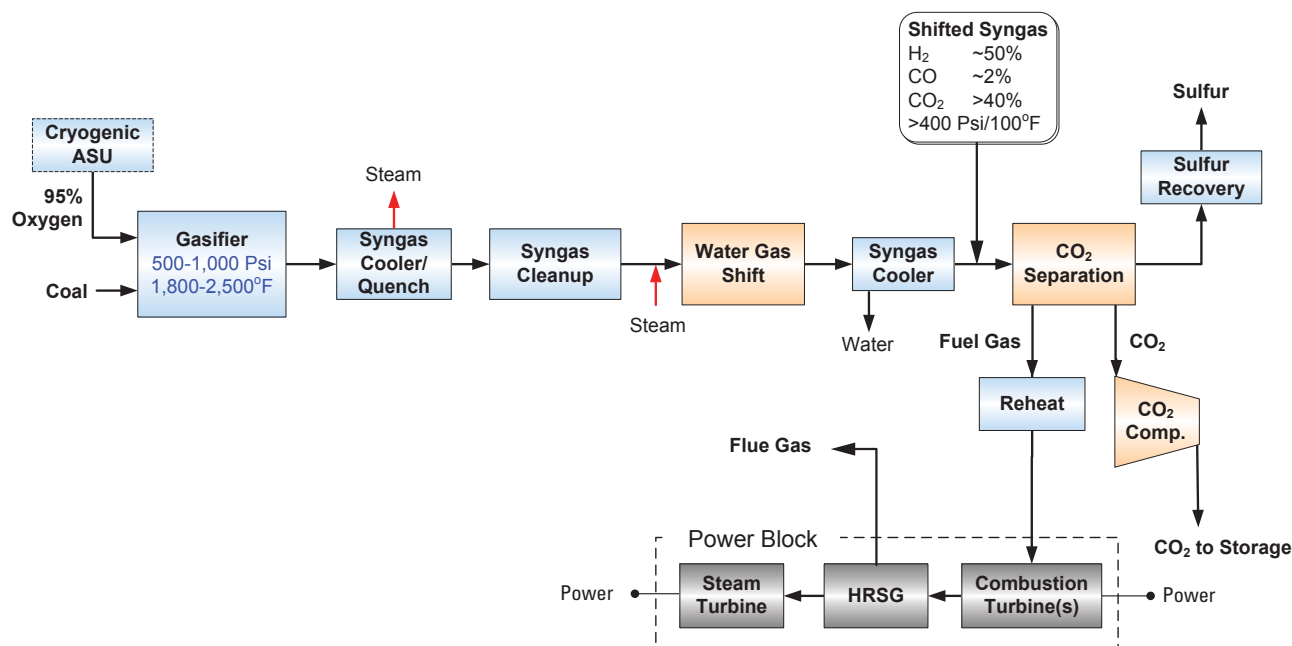
Figure 3-1: Block Diagram Illustrating Pre-Combustion System

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 (13–15 volume percent in coal-fired systems, 3–4 percent in gas-fired turbines); the flue gas is at low pressure [15–25 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. Advanced post-combustion CO_2 capture technologies being investigated by DOE/NETL include the use of solvents, sorbents, and membranes. A more detailed description of post-combustion CO_2 capture processes is provided in Chapter 4.
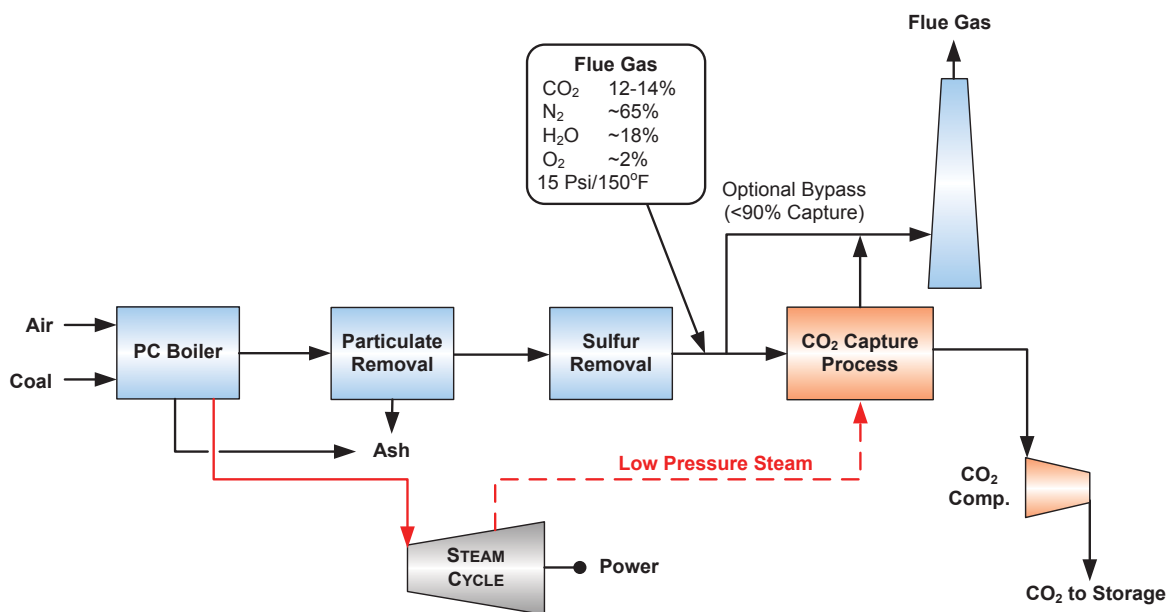
Figure 3-2: Block Diagram Illustrating Post-Combustion System

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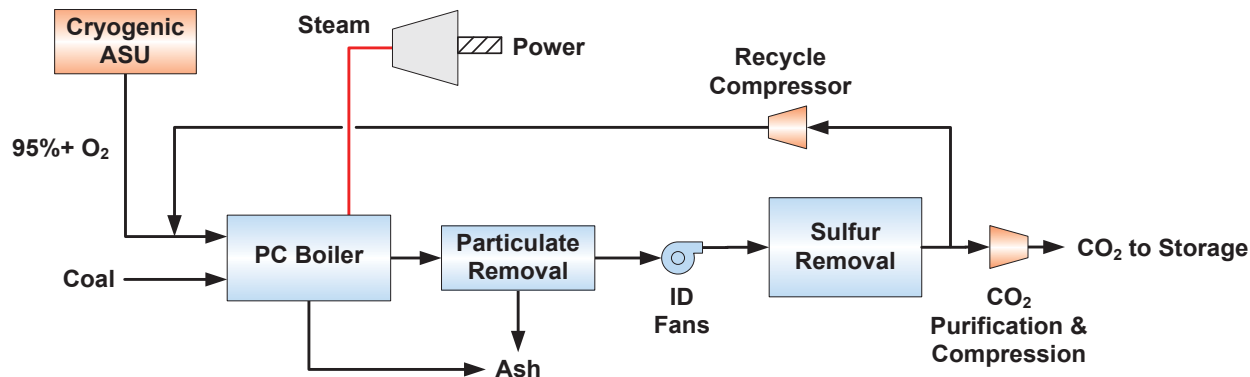
Figure 3-3: Block Diagram Illustrating Oxy-Combustion System

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 AND COMPRESSION

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.
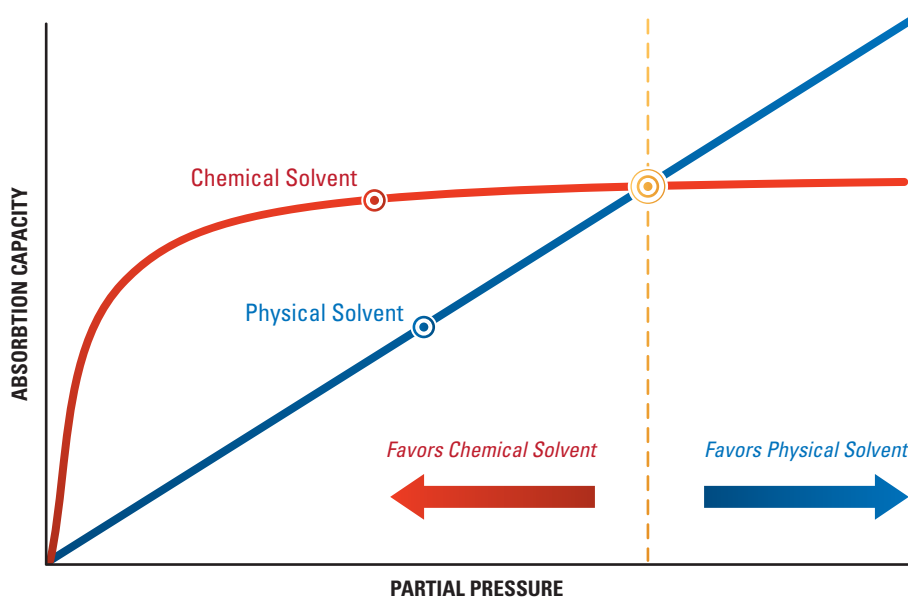
Figure 4-1: Comparison between Chemical and Physical Solvents

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 reac-

tion rates; CO_2 selectivity; co-solvent concentrations; regeneration energy; 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.

Regeneration Energy – The total amount of regeneration energy required is a combination of sensible heat, heat of absorption (which includes heats of reaction for chemical solvents), and heat of vaporization. The temperature of the rich solvent must be raised to the stripper temperature (sensible heat), which is a function of the specific heat capacity of the solvent (including water for aqueous solvents). As discussed above, sufficient heat must also be provided to release the CO_2 from the solvent, which is a function of the solvent's heat of absorption/reaction. Finally, for aqueous solvents, the water component of the solvent solution must be vaporized to generate the stripping vapor. The higher the solution's water content, the greater the heat of vaporization energy is required.

A significant amount of energy can be required for regeneration of the solvent in the stripper. For example, DOE/NETL estimates approximately 1,530 Btu per pound of CO_2 capture for a post-combustion, MEA-based chemical solvent process applied to a subcritical pressure PC power plant.[ii] For this study, the energy was provided to the stripper via steam extraction from the turbine cycle, which amounted to approximately 45 percent of the total steam flow from the crossover pipe between the intermediate and low pressure turbines.

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 de-rates 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. • Depending on solid sorbent composition and reaction mechanism with CO_2, some sorbents require cooling of the syngas for CO_2 capture. The syngas is then re-heated and humidified prior to firing in the combustion 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.

A potential advantage of some sorbents—depending on their reaction chemistry—for IGCC applications is they 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.

Feed Stream
CO_2 & N_2

HIGH PRESSURE

Residue Stream
CO_2 - Lean

MEMBRANE   **MEMBRANE**

CO_2

LOW PRESSURE

Permeate Stream
CO_2 - Rich
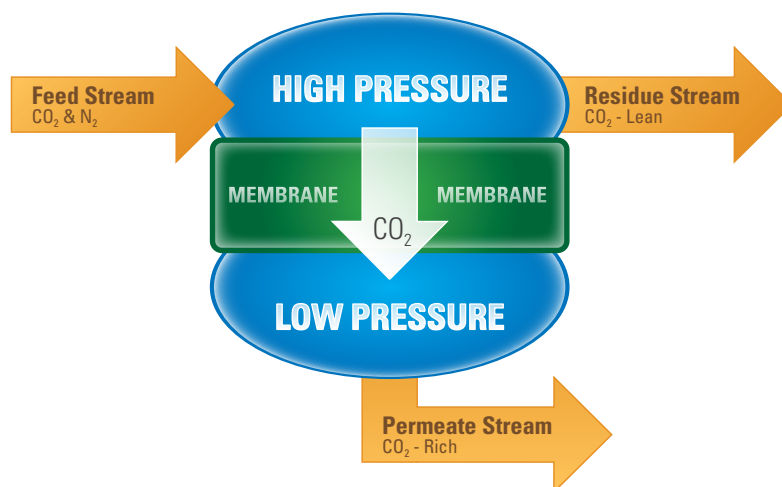
Figure 4-2: Membrane Process Schematic

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 [$cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$], 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 $(STP)/cm^2\cdot s\cdot cmHg$. 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 PH_2. 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.
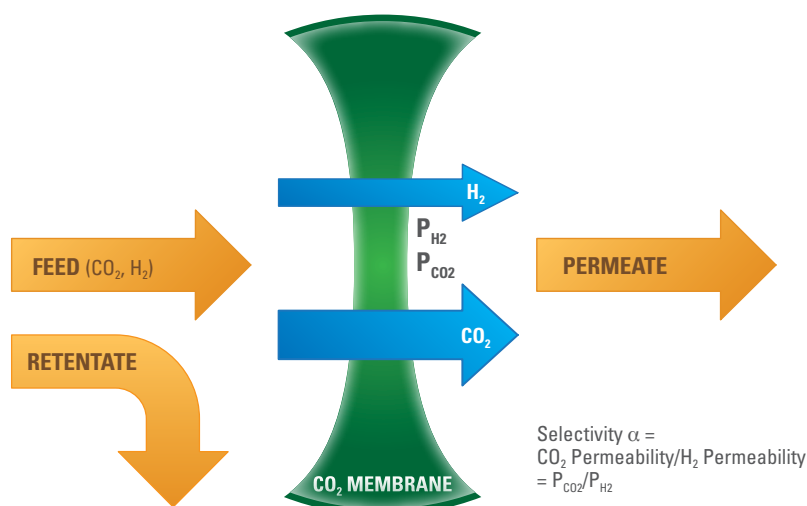
Figure 4-3: Schematic Display of a Pre-Combustion CO_2 Selective Membrane

In an IGCC power plant with CO_2 capture, CO_2 is concentrated through the WGS reaction, which takes place between 200 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.
Membrane/Liquid 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 (100–250 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.
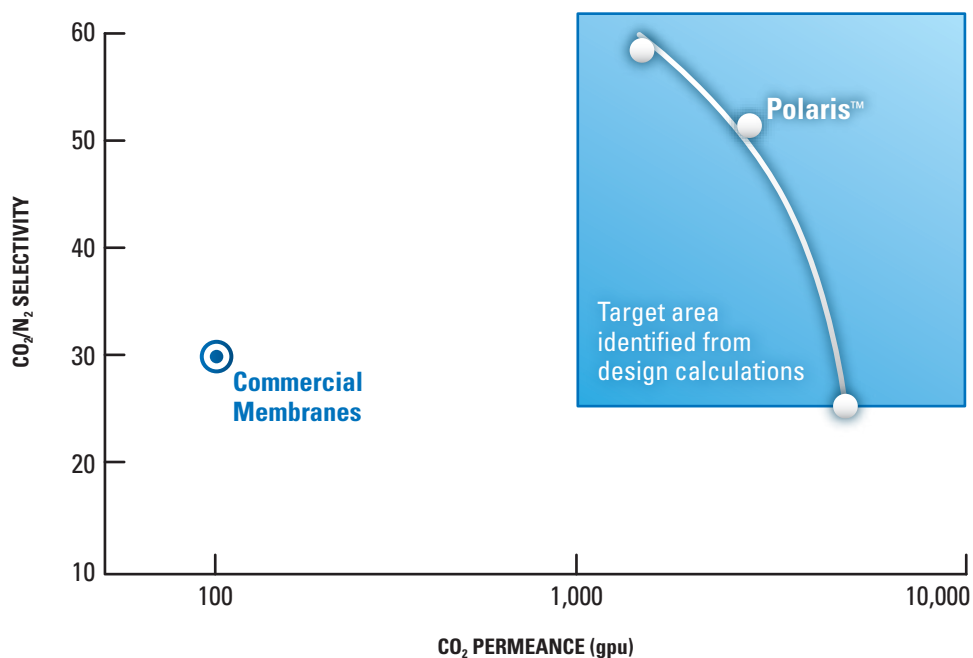
Figure 4-4: Plot of Membrane Selectivity versus Permeance

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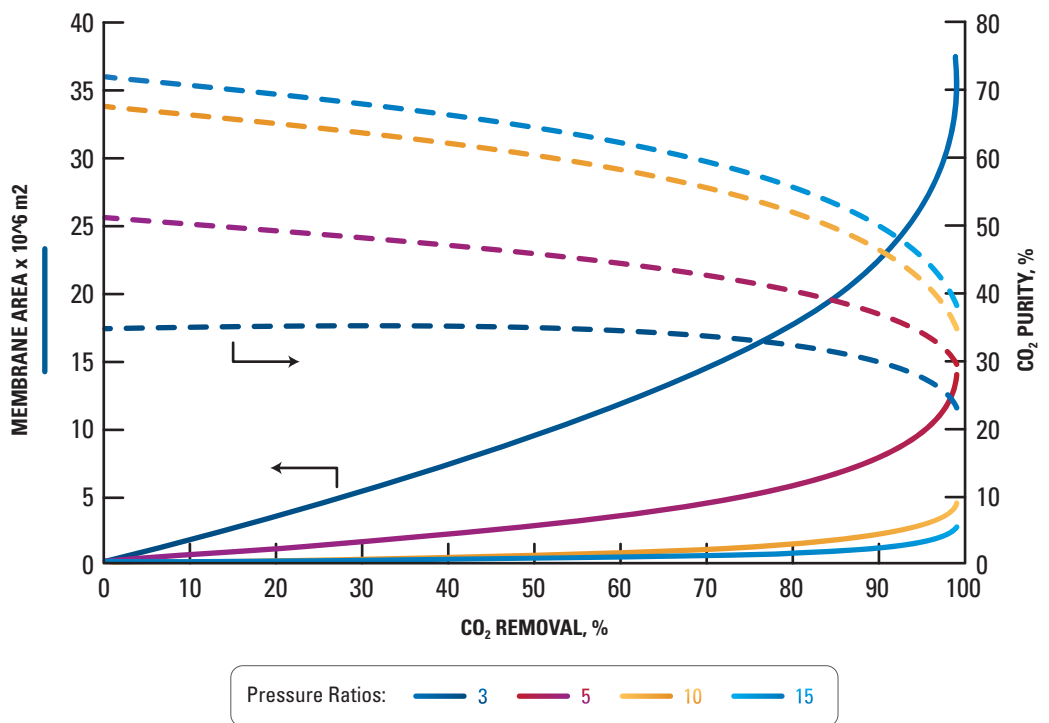
Figure 4-5: Plot of CO_2 Removal, CO_2 Purity, and Membrane Area Versus Pressure Ratio

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.[iv] 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 0.1–0.14 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.
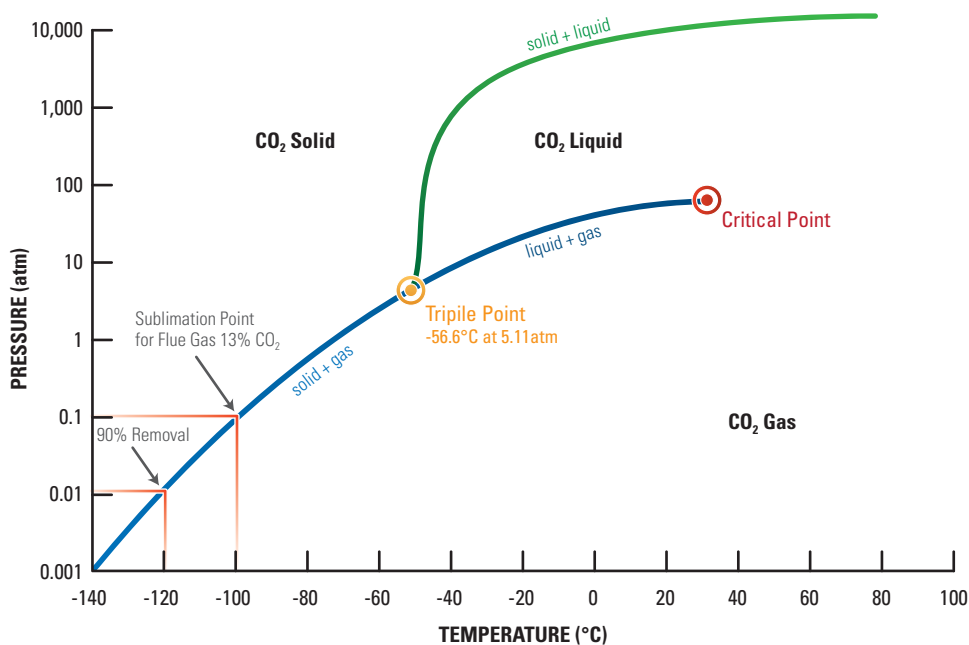
Figure 4-6: Phase Diagram of Carbon Dioxide

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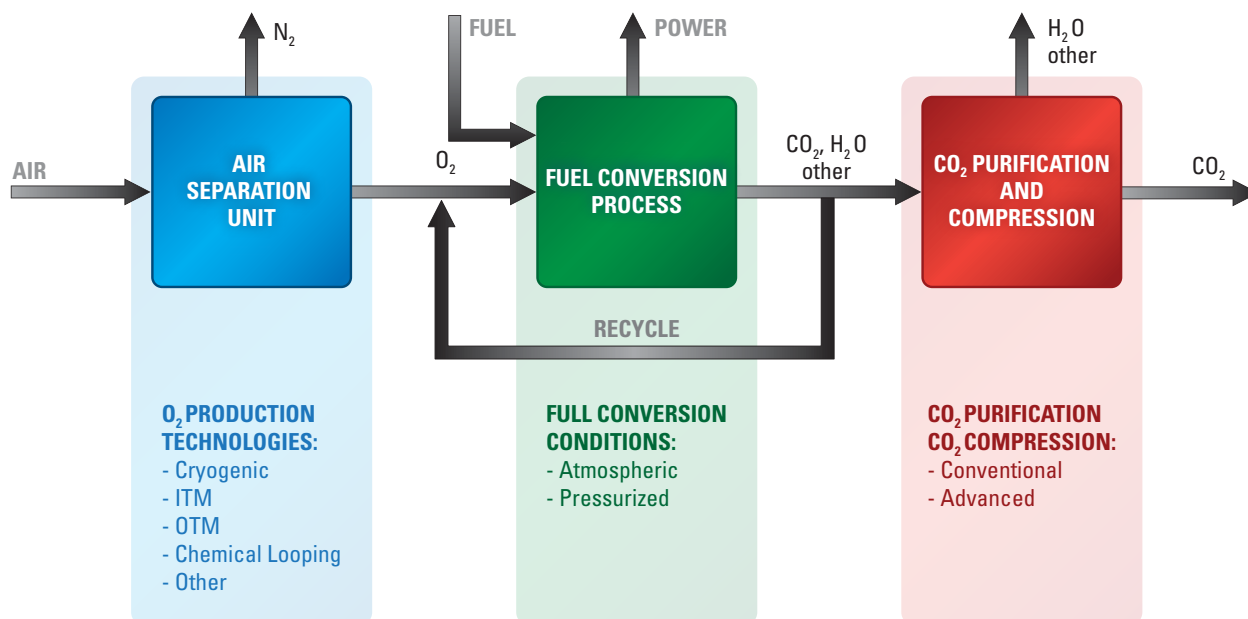
Figure 4-7: Major Components of Oxy-Combustion System

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 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, oxygen 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 oxygen carrier are accomplished in two separate reactors. However, oxygen transport may be completed in three or more steps depending on the application and the oxygen carrier used.
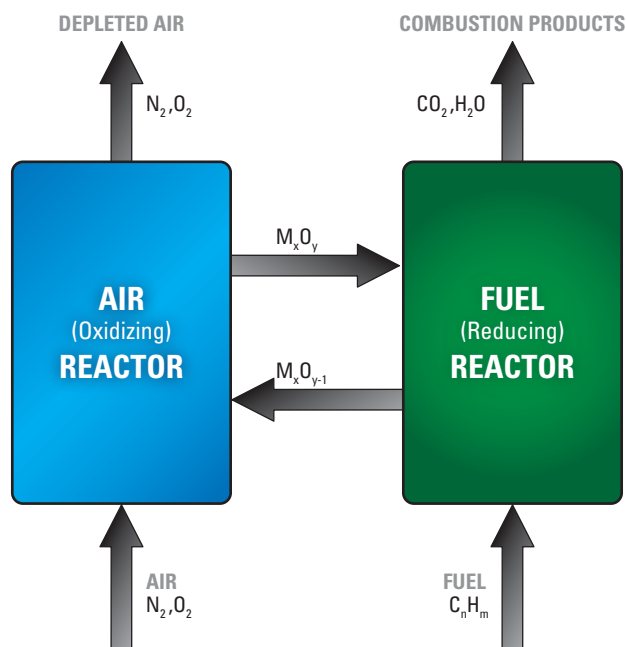
Figure 4-8: Schematic Diagram of a Two Reactor CLC Process

Figure 4-8 is a schematic diagram of a two-reactor CLC process. The oxygen 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:

$$\text{Oxidizer:} \quad M_xO_{y-1} + \tfrac{1}{2}\,O_2 \rightarrow M_xO_y$$

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

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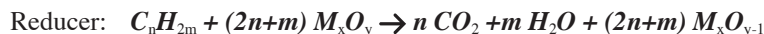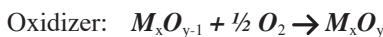
Chemical Looping Gasification

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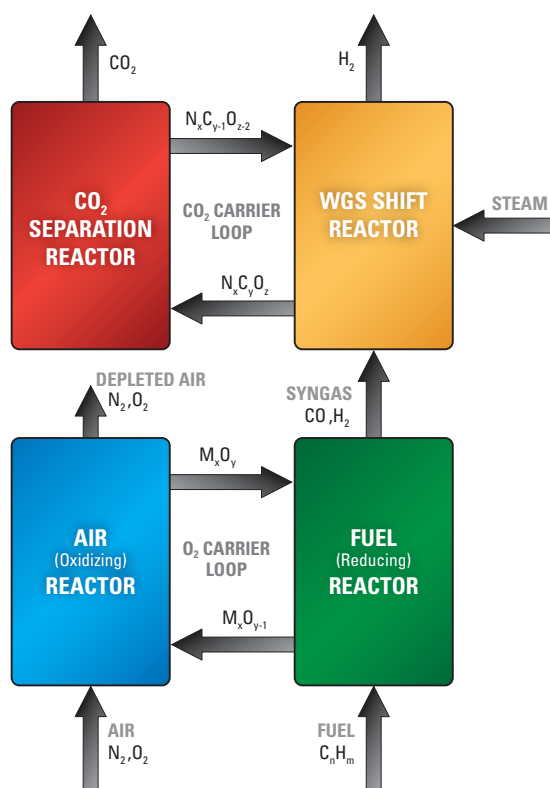
Figure 4-9: Schematic Diagram of a Two Loop CLG Process

For the WGS reaction, the chemical looping process uses a solid carbon carrier (instead of oxygen 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:

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

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$$
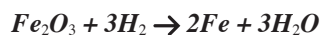
In the second reactor, Fe is oxidized by steam to produce H_2:

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

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

$$2Fe_3O_4 + \tfrac{1}{2} O_2 \rightarrow 3Fe_2O_3$$
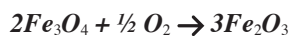
The overall reaction converts syngas (CO and H_2) to H_2 with a small fraction of the syngas lost in the process.

4.G COMPRESSION FUNDAMENTALS

Compression is an integral part of any CO_2 capture system. Since separation typically occurs at low pressure, compression is required to reduce the volume flow making transport more practical. Furthermore, CO_2 storage sites for geological sequestration require high pressure as well. Given the high volume flows, centrifugal compressors are typically employed, especially when the captured CO_2 is produced near atmospheric pressure. The physics to compress CO_2 in a centrifugal compressor is the same as any other gas. However, CO_2 has many unique characteristics compared to other gases that must be considered in the compressor design such as: consideration of real gas effects, high volume reduction, low speed of sound, and avoiding liquid formation. Its high molecular weight allows CO_2 to be liquefied at relatively high temperatures permitting hybrid compression and pumping options.

Figure 4-10 and Figure 4-11 show two types of centrifugal compressors typically used for CO_2 compression service. The first is an integrally geared compressor. It is typically driven by an electric motor that drives a large bull-gear. Driven off this gear are

multiple pinion gears that contain centrifugal compressors on each end. The low pressure stages run at lower speeds, and the speed increases for the higher pressure stages, as will be described in more detail later. The integrally geared design has a separate inlet and exit flange for each stage, permitting intercooling between each stage, which can approach isothermal compression and minimize the power requirement. The drawback of this design is the sheer size and potential reliability issues with the many bearings, seals, and unshrouded impellers.

Figure 4-11 shows a beam-style compressor commonly used in the petrochemical and natural gas industry. It can be configured in a straight-through or back-to-back configuration (as shown). The back-to-back design permits intercooling between the two sections and intercooling between multiple compressor bodies. The beam-style compressor contains only two bearing and seals and has demonstrated reliable service in many applications including large frame sizes in liquefied natural gas (LNG) applications (up to 78-inch impellers) and high pressure (up to 15,000 psi). While some intercooling is possible, the beam-style design will typically consume more power for a given application. New DOE/NETL-sponsored research in internally cooled diaphragms is working to close this gap.[vi]

Figure 4-10: 8 Stage Integrally Geared Compressor
(Courtesy of MAN Turbo[v])
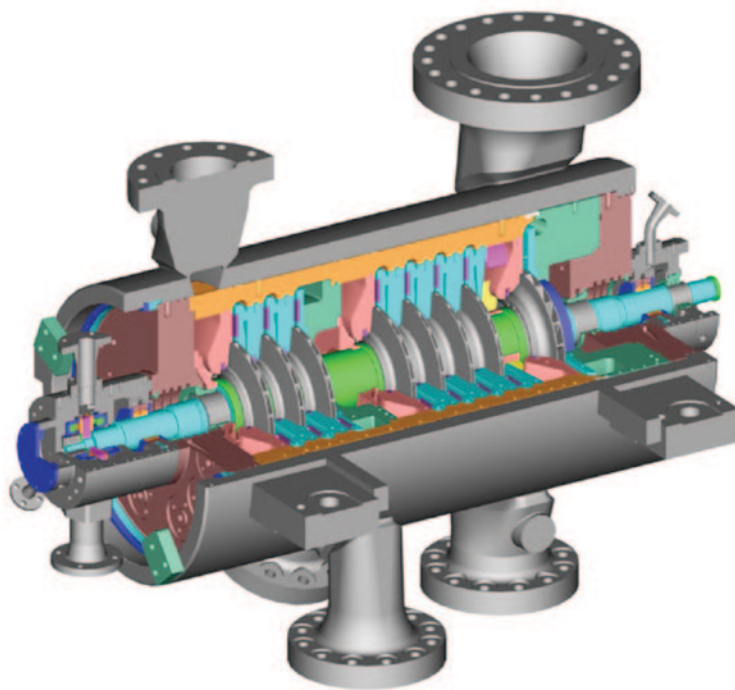
Figure 4-11: Multi-Stage Back-to-Back Centrifugal Compressor
(Courtesy of Dresser-Rand[vii])

Figure 4-12 shows a plot of volume flow versus pressure for CO_2 based on the mass flow from a 400-MW coal-fired power plant. The flow rate at low pressures is high, requiring large compressors. Also, significant reduction in volume flow is predicted using an ideal gas assumption. Furthermore, since CO_2 is a high molecular weight gas, it possesses large deviation from an ideal gas assumption, especially at pressures near and above its critical pressure of 1,071 psia. This plot emphasizes the need for an accurate equation of state to properly predict the correct density (and volume flow) throughout the compressor. Using real gas properties, CO_2 compression from atmospheric to 2,200 psi results in a total pressure ratio of 150:1 and a volume reduction of more than 450:1. This plot also emphasizes the need to separate and capture the CO_2 at the greatest pressure possible due to the volume flow requirement.

A centrifugal compressor accommodates changes in volume flow several ways. First, the frame size of the compressor can be adjusted (smaller frame size for smaller volume flows). Therefore, the higher pressure compressors are typically smaller frame sizes. Within a compressor casing, the flow coefficient of each impeller is changed. Typically this is accomplished by simply changing the width of the flow path, though blading changes can alter the flow coefficient as well. Increasing the rotating speed will increase the volume flow and pressure ratio of a given compressor, but operating with impeller inlet relative Mach numbers approaching 1 will reduce the stage efficiency and range. Heavy gases such as CO_2 have a lower speed of sound and higher Mach numbers for a given speed compared with lighter gases. Centrifugal compressors have an optimum flow coefficient typically in the range of 0.05 to 0.12 using Eq. 4-1.
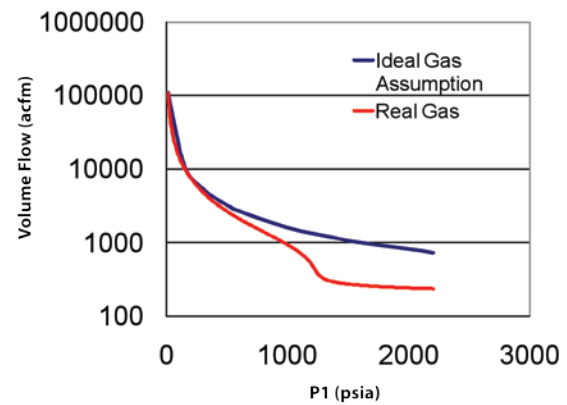
Figure 4-12: Volume Flow versus Pressure for CO_2 at 100 °F

$$\varphi = \frac{700.3\ Q}{N\ D^3}$$
(Eq. 4-1)

where, Q = Volume flow (acfm)
N = Rotation speed (rpm)
D = Diameter (in)

As the CO_2 is compressed, the latter stages will drop in flow coefficient to the point where efficiency will drop to unacceptable levels. Running a smaller impeller faster for the higher pressure stages will increase the flow coefficient and improve the efficiency. This can be accomplished by using a gearbox between compressor bodies or by using an integrally geared compressor where each stage can run at an independent speed.

Design Options for CO_2 Compression

The Southwest Research Institute (SwRI) conducted a thermodynamic analysis that demonstrates how various design options can be used to minimize the horsepower requirement for CO_2 compression.[vi] The analysis is based on an IGCC plant equipped with a Selexol™ pre-combustion chemical solvent process used to capture the CO_2 at three pressures of 22, 160, and 250 psia, and with CO_2 stream inlet temperatures ranging from 50 to 100 °F. The isothermal and semi-isothermal options varied the inter-stage temperature based on the achievable isothermal temperature ranging from 70 to 100 °F. All of the compression options required a final delivery pressure of 2,215 psia. Typical mass flow rates were assumed for the total horsepower calculation. The polytropic efficiency was selected as the basis for efficiency calculations. This allowed the data to be compared to manufacturer-provided data on conventional centrifugal compressors to assure that the assumed process efficiencies were reasonable for the existing state-of-the-art technologies. The Schultz correction factor was used to adjust the polytropic efficiency value.[viii]

Table 4-9 presents a summary of the compression options that were analyzed, which includes conventional multistage centrifugal compression (Options A and B); isothermal and semi-isothermal inter-stage cooling (Options C.1, C.4, and C.7); two-stage, high pressure ratio compression (Options D.3 and D.4); and liquefaction and pumping (Options E.1 and E.2). The table also provides the inlet temperature and polytropic efficiency assumptions and a reference to the thermodynamic equations used for the calculations shown below.

Table 4-9: Process Design Options for CO_2 Compression

Design Option	Compression Technology	Process Parameters	Thermodynamic Equation References
A	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies)	P1 = 22 psia, P2 = 2,215 psia T1 = 50 °F (typical inlet for IGCC) η_p = 70–5% for each stage	Use Eq. 4-2 and 4-3 for polytropic efficiency calculation and Schultz correction factor. Use manufacturer profile as reference for T2.
B	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies) and with additional cooling	Added cooling between MP and HP sections to Option A T1 = 60 °F for interstage suction temp η_p = 70–5% for each stage	
C.1	Isothermal compression at 70 °F and 80% efficiency	Isothermal temp. maintained at 70 °F for same overall inlet/final pressures η_p = 80%	Use Eq. 4-4 (modified isothermal) to include average compressibility.
C.4	Semi-isothermal compression at 70 °F and 1.55 pressure ratio	Set pressure ratio (PR) for stage based on number of stages P1 = 22 psia, P2 = 2,215 psia	Use Eq. 4-2 and 4-3. Iterate to solve for h2/T2 based on 80% polytropic efficiency.
C.7	Semi-isothermal compression at 100 °F and 1.55 pressure ratio	T1 = 70 °F or 100 °F for each stage η_p = 80%	
D.3	High pressure ratio compression at 90% efficiency and no inter-stage cooling	P1 = 22 psia, P2 = 2,215 psia Use conventional process with PR = 10 per stage (requires two stages with interstage P = 220 psia) No interstage cooling. η_p = 90%	Use Eq. 4-2 and 4-3 for polytropic efficiency calculation and Schultz correction factor.
D.4	High pressure ratio compression at 90% efficiency with 1st and 2nd stage cooling	Same as D.3 except with interstage cooling T1 = 50 °F for stage 1 and 100 °F for stage 2 η_p = 90%	
E.1	Centrifugal compression to 250 psia and liquid cryo-pump from 250 to 2,215 psia	Conventional compression from P1 = 22 psia to P2 = 250 psia Refrigerate to 25 °F and pump as liquid to 2,215 psia η_p = 80%	Use Eq. 4-2 and 4-3 for polytropic efficiency calculation and Schultz correction factor. Use Eq. 4-5 and 4-6 for refrigeration and pump calculations.
E.2	Centrifugal compression to 250 psia with semi-isothermal cooling at 100 °F and liquid cryo-pump from 250 to 2,215 psia	Same as E.2 except use semi-isothermal cooling for compression to 250 psia	

Polytropic efficiency is calculated as:

$$\eta_P = \frac{\left(\dfrac{n_p}{n_p-1}\right) \cdot \left(\dfrac{P_2}{P_1}^{\frac{n_p-1}{n_p}} - 1\right) \cdot \dfrac{P_1}{\rho_1} \cdot f}{(h_2 - h_1)}$$

(Eq. 4-2)

where f = Schultz correction factor is calculated as:

$$f = \frac{h_{2s} - h_1}{\frac{k}{k-1} \cdot \left(\frac{P_2}{\rho_{2s}} - \frac{P_1}{\rho_1} \right)}$$

(Eq. 4-3)

Isothermal ideal work is calculated as:

$$\frac{W}{\dot{m}} = \frac{R}{MW} \cdot Z_{avg} \cdot T_o \left(\ln \frac{P_2}{P_1} \right)$$

(Eq. 4-4)

Actual pump work is calculated as:

$$W(act) = h_2 - h_1 = \frac{h_{2s} - h_1}{\eta_{pump}}$$

(Eq. 4-5)

Refrigeration work is calculated as:

$$\dot{W} = (h_1 - h_2) \cdot \dot{m} \cdot \left(RF_{eff} \right)$$

(Eq. 4-6)

Where:

MW	Molecular weight
P_1	Suction gas pressure
P_2	Discharge gas pressure
R	Specific gas constant
RF_{eff}	Effective refrigeration power
T_1	Suction gas temperature
T_2	Discharge gas temperature
T_{2s}	Isentropic gas temperature
T_o	Isothermal gas temperature
W	Work
Z	Compressibility
f	Schultz correction factor
h_1	Suction gas enthalpy
h_2	Discharge gas enthalpy
h_{2s}	Isentropic gas enthalpy
k	Isentropic coefficient
m	Mass flow rate
η_p	Polytropic efficiency
η_{pump}	Pump efficiency
ρ_1	Suction gas density
ρ_2	Discharge gas density
ρ_{2s}	Discharge gas density for isentropic process

The analysis assumes a CO_2 mass flow rate of 1,034,950 lbm/hr is produced from the synthesis gas for a 700-MW IGCC plant. The delivery pressure for pipeline transmission of the CO_2 in a supercritical state is assumed to be 2,215 psia at 70 °F. The Selexol™ pre-combustion capture process provides several higher pressure CO_2 streams, which help to offset some of the large volume reduction that would typically occur over a high pressure ratio. Table 4-10 provides the conditions and volume flow rates assumed for each of the separated CO_2 streams. The inlet volume flow is a strong function of the inlet pressure. Incorporating the higher pressure streams into the compression process helps to reduce the net power requirement because the potential stored energy in the gas is not lost.

Table 4-10: CO_2 Streams from Pre-Combustion Selexol™ Separation Process for 700-MW IGCC Plant

CO_2 Gas Streams	LP	MP	HP1	HP2
Pressure (psia)	21.9	160.0	250.0	299.0
Temperature (°F)	51.0	68.0	90.0	75.0
Density (lbm/ft³)	0.177	1.3	1.87	2.088
Flow Rate (acfm)	33,257	2,158	3,374	1,073

Conventional Multistage Compression – It was assumed that the conventional multistage compression options consist of two parallel trains with a low-pressure (LP) and a high-pressure (HP) compressor driven by either a steam turbine or electric motor. Therefore, the flow through each compression train is one-half the total mass flow, which is equivalent to 517,475 lbm/hr. This mass flow rate is used throughout the thermodynamic analysis to compare the alternative options to the power required for the conventional process.

Options A and B use a conventional approach where the CO_2 is compressed through multiple stages of centrifugal compression using a multistage, back-to-back centrifugal compressor. The Option A analysis provides a baseline estimate for the power required to compress CO_2. The LP stream is compressed and blended with the medium-pressure (MP) stream (which enters the compressor as a side stream). The LP compressor discharge gas is combined with HP1 and HP2 at 250 psia to compress the CO_2 to its final delivery pressure of 2,215 psia in the HP body of the centrifugal compressor. Option B is similar to Option A, except with a 10 °F lower intercooling temperature obtained by utilizing cool waste nitrogen from the air separation process. However, Option B proved to be impractical and was rejected from further consideration.

Based on the selection of the centrifugal compressor design, intercooling of the gas between each compressor body is possible. This requires three intercooling steps in Option A and B. The compression and intercooling steps for Option A and B are shown schematically on a Mollier diagram (pressure vs. enthalpy) in Figure 4-13.
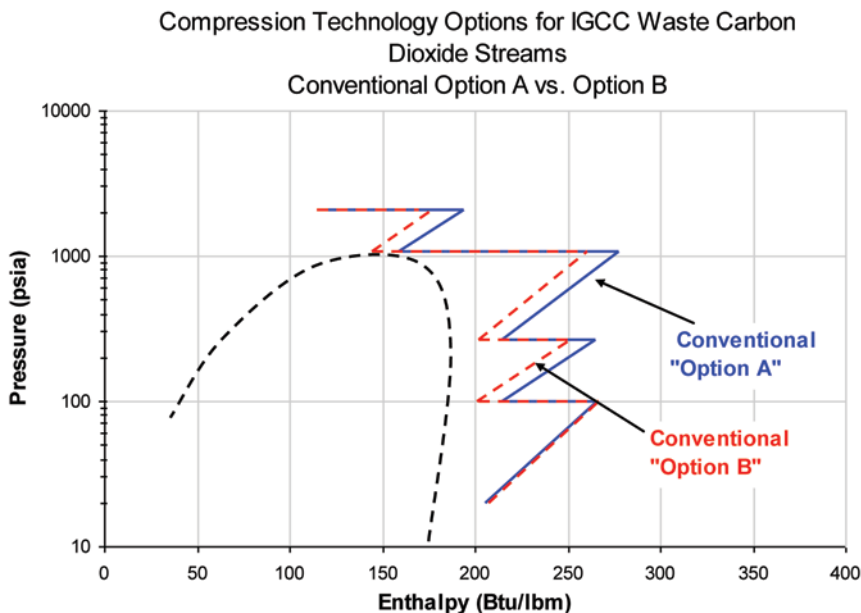
Figure 4-13: Technical Advantages and Challenges for Pre-Combustion Membrane Technologies

Isothermal Compression – The concept of isothermal compression was investigated in Option C due to the known thermodynamic benefit of compressing at lower enthalpy states. The power required for the compression is path dependent. The difference in thermodynamic paths between the conventional compression with intercooling (Options A and B) and isothermal compression (Option C) is shown by comparing the pressure vs. enthalpy curves in Figure 4-13 with Figure 4-14. In Option C, the inlet-cooling concept is applied to each stage, using the same inter-stage pressures as Options A and B. Option C.1 was analyzed as an ideal isothermal compression with an isothermal temperature of 70 °F.

In reality, an isothermal compression process is difficult to achieve because compressing the gas will naturally produce an increase in enthalpy. A compression process which uses fine steps with inter-stage cooling in between each compression stage begins to approach isothermal compression. This practical implementation is termed a semi-isothermal process. To analyze the semi-isothermal process, Option C.4 and Option C.7 use many small compression steps with inter-stage cooling. The inter-stage cooling temperature was varied to determine the amount of cooling required and the effect of the coolant temperature.

The thermodynamic path taken by an isothermal process (Option C.1) and a semi-isothermal process (Option C.3) is shown in Figure 4-14 to illustrate the difference between the two processes. Based on the process variations considered (isothermal temperature and number of compression steps), the analysis shows that the semi-isothermal process begins to approach the isothermal power requirement if small enough compression steps are used. Figure 4-15 plots the compression power versus the number of intercooling steps and demonstrates that isothermal compression can be achieved if intercooling is used between each stage for the 16 total stages.
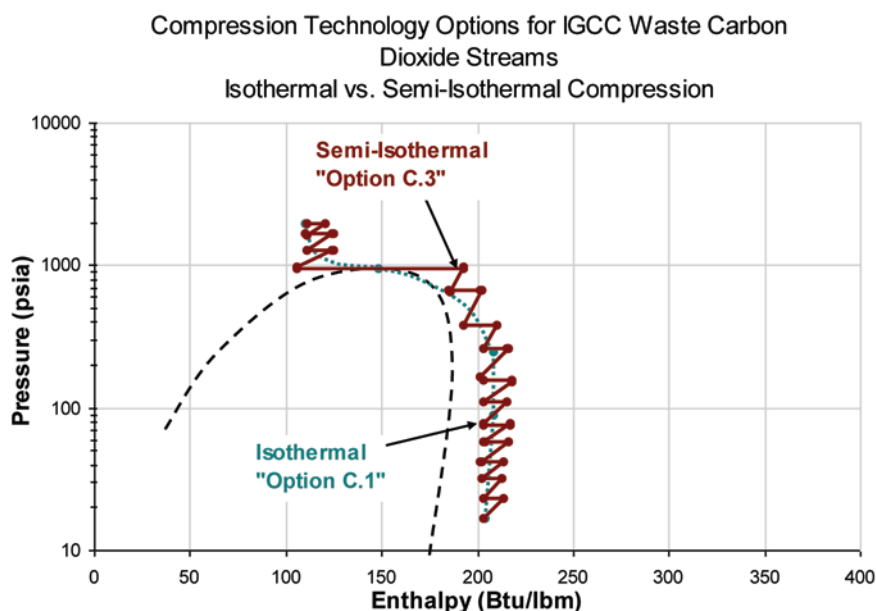
Figure 4-14: Comparison of Isothermal and Semi-Isothermal CO_2 Compression

Thermodynamic Comparison of Compression Process for Carbon Dioxide (22-2215 psia)
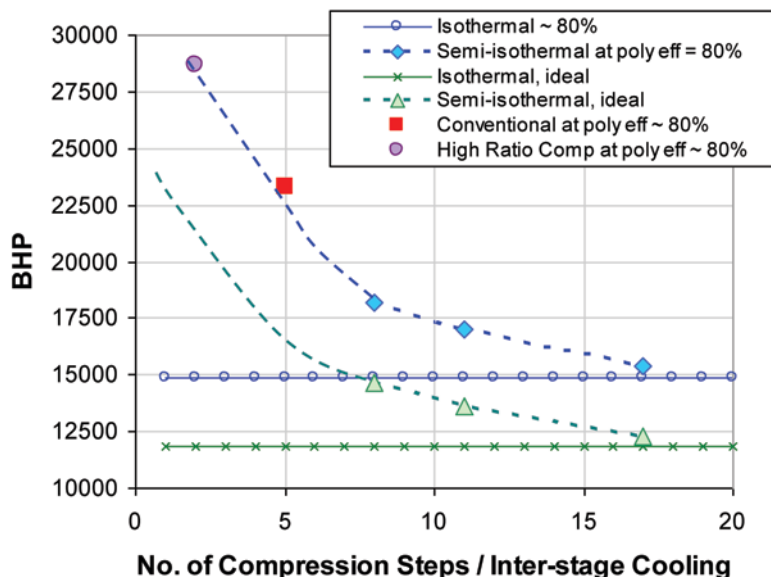
Figure 4-15: Compression Brake Horsepower vs. Number of Intercooling Steps

High-Ratio Compression – A two-stage, high-ratio compression process is also considered in the analysis because of the simplicity and compactness of the compression. Option D utilizes the same thermodynamic calculations for only two stages of compression resulting in a pressure ratio of 10:1—Stage 1 from 22 psia to 220 psia and Stage 2 from 220 psia to 2,215 psia. As a result, only one cooling step is available in between the two stages. It should be noted that it is not possible to introduce the side streams for the MP CO_2 stream shown in Table 4-10 in the high-ratio compression option. As such, all the MP CO_2 gas is assumed to enter the compressor at the inlet pressure of 22 psia. Losing the potential energy in the MP stream and without the added cooling between smaller stages of compression, Option D.3 requires significantly more horsepower than the conventional multistage process. Option D.4 assumes adding inter-stage cooling between Stages 1 and 2 at 220 psia. This improvement reduces the required power for high-ratio compression, but it is still higher than the conventional multistage process. Although not included in this analysis, it is possible to utilize the waste heat from the intercooler and aftercooler with the high-ratio compression concept since the discharge temperature exceeds 500 °F.

Liquefaction and Pumping – The final option in the analysis is to pump the CO_2 in a liquid state at a low temperature. This process (Options E.1 and E.2) is feasible because of the relatively low supercritical point and the high enthalpy values for liquid CO_2. Although pumping liquid CO_2 requires significantly less energy than compression of gaseous CO_2, liquefaction of the CO_2 gas requires large amounts of refrigeration energy. To achieve cryogenic temperatures without forming solid CO_2, it is necessary to first compress the LP and MP streams to 250 psia. The compressed LP and MP streams (after LP compressor) are combined with the HP stream to undergo the liquefaction process. Ambient air cooling is assumed to reduce the temperature of the CO_2 from 255 to 100 °F or lower at no energy penalty. An ammonia absorption cycle refrigeration process is used to further reduce the saturation temperature to -11 °F because of the significant heat transfer required to overcome the latent heat in the gas. Figure 4-16 illustrates the thermodynamic path for Option E compared to Option A.
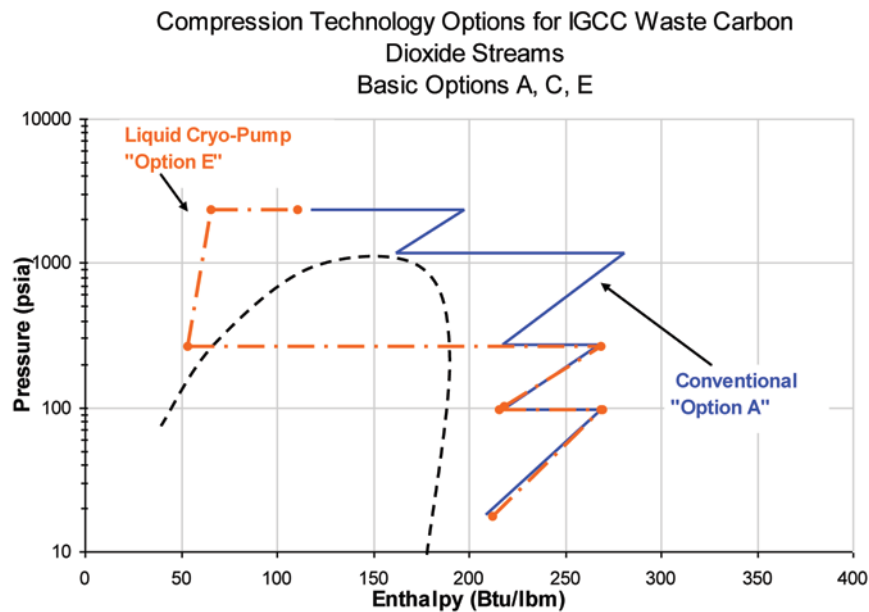
Figure 4-16: Comparison of CO_2 Liquefaction/Pumping to Centrifugal Compression

Power Requirements for Compression Options

Table 4-11 summarizes the power requirements for the compression options considered in the SwRI analysis. Option A, conventional multistage compression, requires a total horsepower of 23,251 BHP (17.3 MW). (Note: This is the required power for each of the two compression trains assumed in the analysis.) As the results show, the amount of horsepower required by each compression option varies significantly according to the thermodynamic path. Option B, additional cooling, provides a small improvement in compression power, but requires that cool waste nitrogen be supplied from the air separation unit to provide the added cooling. While this provides some savings to CO_2 compression, it reduces the efficiency of the air separation unit and thus is discounted as a feasible solution.

Table 4-11: Summary of Power Requirements for Compression Technology Options

Design Option	Compression Technology	Process Parameters	Thermodynamic Equation References
A	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies)	23,251 BHP (17.35 MW)	Base
B	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies) and with additional cooling	21,522 BHP (16.06 MW)	-7.4%
C.1	Isothermal compression at 70 °F and 80% efficiency	14,840 BHP (11.07 MW)	-36.2%
C.4	Semi-isothermal compression at 70 °F and 1.55 pressure ratio	17,025 BHP (12.70 MW)	-26.8%
C.7	Semi-isothermal compression at 100 °F and 1.55 pressure ratio	17,979 BHP (13.41 MW)	-22.7%
D.3	High pressure ratio compression at 90% efficiency and no inter-stage cooling	34,192 BHP (25.51 MW)	+47.1%
D.4	High pressure ratio compression at 90% efficiency with 1st and 2nd stage cooling	24,730 BHP (18.45 MW)	+6.4%

Table 4-11: Summary of Power Requirements for Compression Technology Options

Design Option	Compression Technology	Process Parameters	Thermodynamic Equation References
E.1	Centrifugal compression to 250 psia and liquid cryo-pump from 250 to 2,215 psia	16,198 BHP (12.08 MW) (Includes 7,814 BHP for refrigeration)	-30.3%
E.2	Centrifugal compression to 250 psia with semi-isothermal cooling at 100 °F and liquid cryo-pump from 250 to 2,215 psia	15,145 BHP (11.30 MW) (Includes 7,814 BHP for refrigeration)	-34.9%

Options C.4 and C.7 show that near isothermal conditions can be achieved and result in significant power savings (22.7 to 26.8 percent) over the baseline case. Semi-isothermal compression can be achieved by an integrally geared centrifugal compressor with intercoolers between each stage. While this is a commercially viable approach today, these machines introduce greater size and more complexity than the two-body, in-line barrel compressor assumed in Option A.

Because of the high molecular weight of CO_2, very high-pressure ratios are possible in a single stage, resulting in a compact compression solution. However, Option D shows this approach results in greater power requirements, especially if no intercooling is used; also, this study does not consider the potential waste heat recovery from the inter-stage coolers, which could make Option D more attractive.

Finally, Option E.1 utilizes centrifugal compression followed by liquefaction and pumping. The pump requires only 1,400 BHP (1.04 MW), but the refrigeration system requires almost 8,000 BHP (5.97 MW). Nevertheless, significant power savings can be achieved with this approach. The combination of the semi-isothermal compression with the liquefaction process (Option E.2) results in the greatest energy savings at a 35 percent reduction in compression power over the conventional process. Capital expenditure for this process is greater because of the additional refrigeration system, but some of this cost can be offset by the elimination of two coolers and lower cost of the pump compared to the much larger HP compressor.

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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. In addition, there are a few hybrid technologies that incorporate a solvent with a membrane.

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.

Currently Available Solvent Technologies

> **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

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 Selexol™ technology for an IGCC plant leads to an average nine percentage point decrease in plant efficiency and an increase in COE of approximately 45 percent (compared to the non-capture IGCC counterpart).[ii] 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 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.

Solvent Process Demonstration

RTI International will be conducting a 30–50 MW equivalent demonstration of a pre-combustion MDEA solvent technology for CO_2 capture from a slipstream of syngas at the Tampa Electric Company's Polk Power Station, which is an IGCC facility (DOE/NETL Project DE-FE0000489). The MDEA demonstration is part of a project to scale-up RTI's warm syngas cleaning technology known as the High Temperature Desulfurization Process (HTDP). The demonstration includes the sequestration of up to 300,000 tpy of CO_2 in a deep saline aquifer located beneath the plant site. The project is funded by the American Recovery and Reinvestment Act. The demonstration is to begin operations in FY 2013 and the project is scheduled for completion by September 2015. Additional information on this project is available on the DOE/NETL website at:
http://www.netl.doe.gov/technologies/coalpower/gasification/projects/gas-clean/00489.html

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 later in Chapter 11, DOE/NETL's ORD is evaluating the use of ILs 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 Appendix B.

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	FE0000896	9/30/09 – 3/31/12

PRE-COMBUSTION SOLVENT R&D PROJECT HIGHLIGHT
AMMONIUM CARBONATE
SRI International is developing a pre-combustion chemical solvent CO_2 capture technology based on the use of a high-capacity and low-cost aqueous solution containing ammonium carbonate (AC), which reacts with CO_2 to form ammonium bicarbonate (ABC). The ABC solution is heated to release the CO_2 and regenerate the AC solution. AC has high net CO_2 loading, is a low-cost and readily available reagent, and requires little solvent makeup.

5.B 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. Appendix B includes summary descriptions and results for these projects.

Table 5-2: DOE/NETL R&D Projects for Pre-Combustion CO₂ Capture Using Sorbents

Project Focus	Participant	Project Number	Performance Period
Sorbent-Enhanced Water Gas Shift	URS Group	FE0000465	1/1/10 – 3/31/13
High Capacity Regenerable Sorbent	TDA Research, Inc.	FE0000469	10/1/09 – 9/30/11
Evaluation of Sorbents	UNDEERC	NT42465-1.4	6/23/05 – 5/31/11
High-Density Activated Carbon	UNDEERC	NT42465-3.1	6/23/05 – 6/22/07
Warm Gas Cleanup with Sorbents	RTI International	NT42459	6/1/05 – 9/30/10
Sorbent-Enhanced Water Gas Shift	Lehigh University	NT42455	5/25/05 – 6/4/10
Sorbent-Enhanced Water Gas Shift	UNDEERC	FT40320	4/1/05 – 3/31/09

PRE-COMBUSTION SORBENT R&D PROJECT HIGHLIGHT
SORBENT-ENHANCED WATER GAS SHIFT

URS Group, Inc. is developing a high-pressure and high-temperature dry sorbent process that combines CO_2 capture with the WGS reaction. 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. The major advantages of this high-temperature sorbent include eliminating or reducing the amount of WGS catalyst required to fully shift the syngas to CO_2 and H_2 and eliminating syngas cooling/reheating that is necessary for current physical solvent CO_2 separation systems.

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. Appendix B includes summary descriptions and results for these projects.

PRE-COMBUSTION MEMBRANE R&D PROJECT HIGHLIGHT
POLYBENZIMIDAZOLE (PBI) MEMBRANE

SRI International is testing a high-temperature PBI polymer membrane developed by Los Alamos National Laboratory (LANL). The membrane 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 membrane for CO_2 capture without requiring additional syngas cooling after the WGS reactor, which would increase plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.
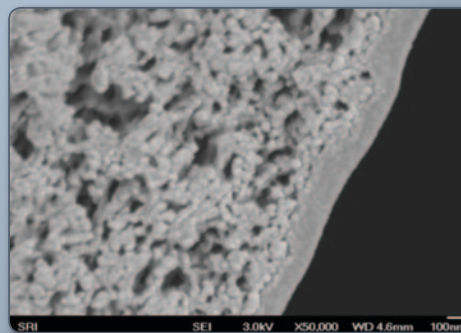
Table 5-3: DOE/NETL R&D Projects for Pre-Combustion CO$_2$ Capture Using Membranes

Project Focus	Participant	Project Number	Performance Period
Integrated WGS Membrane	Western Research Institute	FE0004992	9/24/10 – 12/31/11
Membrane for H$_2$ Separation	Praxair, Inc.	FE0004908	9/29/10 – 12/31/11
Pd-Pd Alloy Composite Membrane for H$_2$ Separation	Worcester Polytechnic Institute	FE0004895	9/20/10 – 12/31/11
Composite Polymer Membrane	University of North Dakota	FE0002196	12/1/09 – 11/30/12
Hydrogen Selective Zeolite Membranes	University Of Minnesota	FE0001322	10/1/09 – 9/30/13
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	FE0000470	10/1/09 – 9/30/13
Ternary Palladium-Alloy Hydrogen Separation Membranes	Pall Corporation	FE0001181	10/1/09 – 9/30/12
Pressure Swing Absorption with Membrane Contactor	New Jersey Institute of Technology	FE0001323	10/1/09 – 9/30/12
High-Temperature Polymer-Based Membrane	Los Alamos National Laboratory	FE13-AC24	10/1/09 – 9/30/12
Ceramic Membrane for H$_2$ Separation	Ceramatec	FE0001045	10/1/09 – 9/30/12
Nanoporous, Superhydrophobic Membranes	Gas Technology Institute	FE0000646	10/1/09 – 9/30/11
Integrated WGS Non-Precious Membrane	University of Texas at Dallas	FE0001293	9/30/09 – 9/29/12
Membrane for H$_2$ Separation	United Technologies Research Center	FE0004967	9/24/10 – 12/31/11
Supported Molten Metal Membrane for H$_2$ Separation	Worcester Polytechnic Institute	FE0001050	9/23/09 – 9/29/11
Nanoporous Metal Carbide Membrane for H$_2$ Separation	Colorado School of Mines	FE0001009	9/23/09 – 9/30/12
Amorphous Alloy Membrane for H$_2$ Separation	Southwest Research Institute	FE0001057	9/23/09 – 9/29/11
Amorphous Alloy Membrane for H$_2$ Separation	University of Nevada	FE0000998	9/22/09 – 9/30/12
Polymer Membranes	Membrane Technology and Research, Inc.	FE0001124	9/14/09 – 9/10/10
Palladium-Copper Trimetallic Alloy Membranes	United Technologies Research Center	NT43055	6/15/07 – 6/14/09
Palladium Alloy Membranes	Praxair, Inc.	NT43054	6/1/07 – 5/31/10
Palladium-Based Membranes	Worcester Polytechnic Institute	NT43058	5/7/07 – 5/6/10
Carbon Molecular Sieve Membranes	Media and Process Technology, Inc.	NT43057	5/2/07 – 5/1/12
Ternary Palladium Alloy Membranes	Southwest Research Institute	NT43056	5/2/07 – 5/1/10
High-Temperature Polymeric Membranes	SRI International	NT43090	3/30/07 – 3/31/12
Catalysts for Use in Membrane Reactors	Grambling State University	NT43064	12/20/06 – 1/1/10
High-Flux Metallic Membranes and Reactors	REB Research and Consulting	NT42400	10/1/05 – 3/31/09

Table 5-3: DOE/NETL R&D Projects for Pre-Combustion CO_2 Capture Using Membranes			
Project Focus	**Participant**	**Project Number**	**Performance Period**
Palladium/Silver Composite Membranes	North Carolina A&T State University	NT42492	9/1/05 – 2/28/09
Hydrogen Transport Membranes	Eltron Research, Inc.	NT42469	8/16/05 – 9/30/08
Water Gas Shift Catalyst with Vanadium Alloy Membrane	Western Research Institute	NT42454	7/1/05 – 12/30/08
Sulfur-Tolerant Palladium Alloy Membranes	Worcester Polytechnic Institute	NT42194	9/28/04 – 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-Based Membrane Reactor	Los Alamos National Laboratory	FWP-FE99002-4A24A	10/1/05 – 6/22/07
Dense High-Temperature Ceramic Membranes	Argonne National Laboratory	FWP-49601	3/31/98 – 9/30/13
H_2/CO_2 Separation Membranes	UNDEERC	NT42465-1.2	6/23/05 – 5/31/11

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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. In addition, there are a few hybrid technologies that incorporate a solvent with a membrane.

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 3–25 percent CO_2. Starting in the 1940s, physical solvents were developed to absorb CO_2 from gas streams with higher CO_2 concentration (25–70 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.[ix]

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.[x] 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 700–1,600 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.[ii] This large difference in capacity represents a significant barrier to widespread commercial deployment of CO_2 removal technologies for coal-fired power plants.

A 2009 review of commercially available CO_2 capture technologies identified 17 facilities (using both chemical and physical capture solvents) in current operation.[xi] 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.[xii] AES's coal-fired Warrior Run (Cumberland, MD) and Shady Point (Panama, OK) 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.[xii] At the Searles Valley Minerals soda ash plant in Trona, CA, 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.[xii] 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 over 80 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 70–80 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.
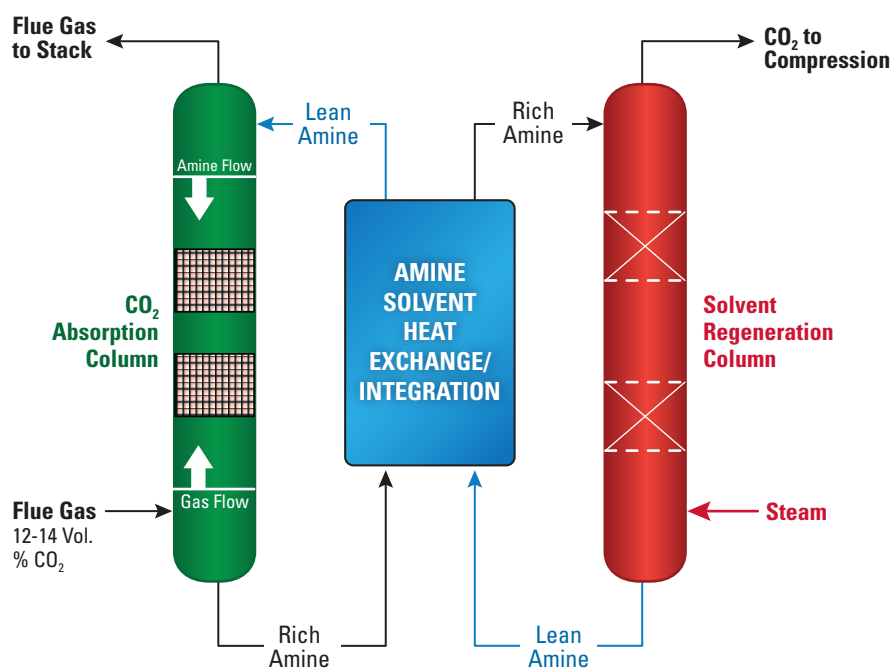
Figure 6-1: Schematic Diagram of the Post-Combustion MEA CO_2 Capture Process

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).[xiii, xiv, xv] 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.[x] MHI conducted pilot-scale, slip-stream testing (~10 ton/day CO_2 capture) at a coal-fired power plant in Matsushima, Japan from 2006 through 2008. In 2010, MHI and Southern Company began small pilot-scale slipstream testing (0.1 MW equivalent) at Georgia Power's Plant Yates using the KS-1 solvent. MHI's next step is to conduct a full-scale demonstration (25 MW equivalent with ~500 ton/day CO_2 capture) of the KS-1 technology at Alabama Power's Plant Barry coal-fired power plant beginning in 2011.[xvi] Other vendors that offer commercially available amine-based capture processes include ABB/Lummus, HTC Purenergy, Aker Clean Carbon, and Cansolv.[xvii]

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.[xviii] 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.[xix] 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.

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

Table 6-1: DOE/NETL R&D Projects for Post-Combustion CO₂ Capture Using Solvents

Project Focus	Participant	Project Number	Performance Period
Hot Carbonate Absorption Process	University of Illinois at Urbana-Champaign	FE0004360	1/1/11 – 12/31/13
Piperazine Solvent with Flash Regeneration	URS Group	FE0005654	9/27/10 – 3/31/14
Amino Acid Salt	Siemens Energy, Inc.	FE0003714	10/1/10 – 10/31/13
Non-Aqueous, Amine-Based Solvent	3H Company, LLC	FE0004274	10/1/10 – 9/30/13
Carbonic Anhydrase-Potassium Carbonate Mixture	Akermin, Inc.	FE0004228	9/30/10 – 9/30/12
Ionic Liquid-Amine Mixture	ION Engineering	FE0005799	10/1/10 – 4/30/12
High-Capacity Oligomers	GE Global Research	NT0005310	10/1/08 – 9/30/10
Integrated Vacuum Carbonate Absorption	Illinois State Geological Survey	NT0005498	9/26/08 – 4/30/12
Ionic Liquids	Georgia Tech Research Corporation	NT0005287	10/1/08 – 9/30/11
Mixed Solvent	Lawrence Berkeley National Laboratory	FWP-ED33EE	6/1/08 – 5/31/13
Ionic Liquids	University of Notre Dame	NT43091	2/28/07 – 2/29/12
Phase Transitional Absorption	Hampton University	NT42488	6/15/05 – 6/30/09

POST-COMBUSTION SOLVENT R&D PROJECT HIGHLIGHT
AMINO ACID SALT
Siemens Energy, Inc. will design, install, and operate a pilot plant for treating a 2.5 MW equivalent slipstream at the TECO Energy Big Bend Station to demonstrate POSTCAP technology for post-combustion CO_2 gas capture. POSTCAP based technology utilizes an amino acid salt (AAS) that can operate in a conventional scrubber system similar to that for MEA, but with negligible solvent volatility, less corrosion, very low degradation and lower regeneration energy. The absorption activity is believed to be similar to MEA, but the capacity of AAS is theoretically double that of MEA. Design capacity is close to this theoretical capacity, which will lead to lower solvent flow rate and inventory for AAS. The solvent is an aqueous solution of approximately 30–40 percent AAS and water.

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 for sorbent 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. Appendix B includes summary descriptions and results for these projects.

POST-COMBUSTION SORBENT R&D PROJECT HIGHLIGHT
METAL ORGANIC FRAMEWORKS

UOP, LLC developed a new class of sorbents known as MOFs, which are manufactured, micro porous, thermally stable materials that have the potential for high CO_2 adsorption capacity. MOFs 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. Based on their properties, MOF-based sorbents would be utilized in a vacuum pressure swing adsorption (VPSA) process for removal of CO_2 from flue gas.

Table 6-2: DOE/NETL R&D Projects for Post-Combustion CO_2 Capture Using Sorbents

Project Focus	Participant	Project Number	Performance Period
Solid Molecular Baskets	Penn State University	FE0000458	9/1/09 – 8/31/11
Alkalized Alumina	TDA Research, Inc.	NT0005497	11/1/08 – 10/31/11
Carbon-Based Sorbents	SRI International	NT0005578 & FE0000896	10/1/08 – 9/30/11
Evaluation of Solid Sorbents	ADA-ES, Inc.	FE0004343 & NT0005649	9/30/08 – 12/31/14
Metal Organic Frameworks	UOP, LLC	NT43092	3/12/07 – 6/30/10
Dry Sodium Carbonate	Research Triangle Institute	NT43089	3/7/07 – 12/31/09
Metal Monolithic Amine-Grafted Zeolites	University of Akron	NT43086	2/21/07 – 3/31/11

6.C MEMBRANES FOR POST-COMBUSTION

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.

> ### 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)

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 devel-

opment 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. Appendix B includes summary descriptions and results for these projects.
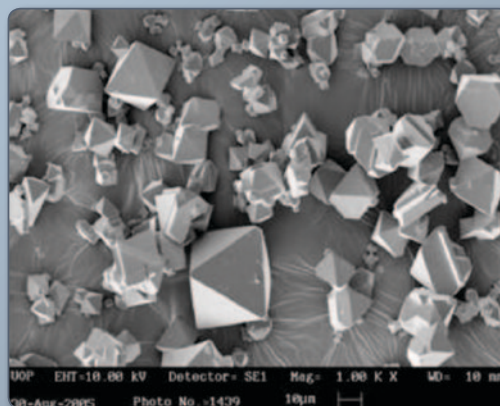
Table 6-3: DOE/NETL R&D Projects for Post-Combustion CO_2 Capture using Membranes

Project Focus	Participant	Project Number	Performance Period
Sub-Ambient Temperature, Hollow-Fiber Membrane	American Air Liquide	FE0004278	10/1/10 – 9/30/12
Hybrid with Solvent and Hollow-Fiber Membrane	Gas Technology Institute	FE0004787	10/1/10 – 9/30/13
Hollow-Fiber, Polymeric Membranes	RTI International	NT0005313	10/1/08 – 3/31/11
Spiral-Wound, Polymeric Membranes	Membrane Technology and Research, Inc.	FE0005795, NT0005312, & NT43085	4/1/07 – 9/30/15
Biomimetic Membrane	Carbozyme, Inc.	NT43084 & NT42824	3/28/07 – 7/31/09
Dual-Functional, Silica-Based Membrane	University of New Mexico	NT42120	8/23/04 – 4/30/09

POST-COMBUSTION MEMBRANE R&D PROJECT HIGHLIGHT
MEMBRANE PROCESS CONFIGURATION

MTR is developing a spiral-wound, polymeric membrane and associated process for CO_2 capture. MTR's process design 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.
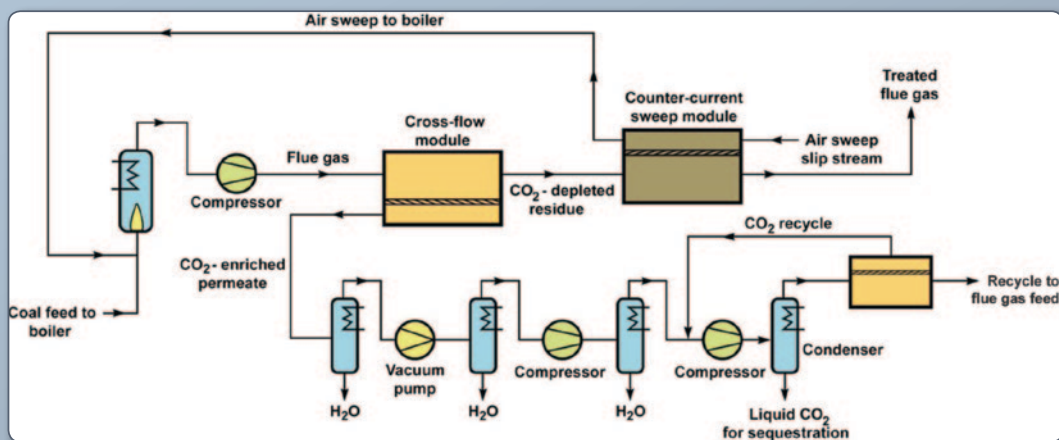
CHAPTER 7:
PULVERIZED COAL OXY-COMBUSTION R&D EFFORTS

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 over 60 percent and reduce the net plant efficiency by approximately 10 percentage points, 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 oxy-combustion boilers
>   - Develop advanced materials and burners
>   - Develop compact boiler designs
>   - Mitigate corrosion
> - Retrofit oxy-combustion boilers
>   - Minimize air leakage
>   - Optimize heat transfer and flue gas recycle
>   - Mitigate corrosion
> - Develop advanced process control/sensors
> - Develop low-cost methods for oxygen production
> - Develop advanced, low-cost methods for CO_2 purification
> - Evaluate potential impacts of co-capture/storage (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. Appendix B includes summary descriptions and results for these projects.

OXY-COMBUSTION R&D PROJECT HIGHLIGHT
OXY-COMBUSTION BOILER DEVELOPMENT

Alstom Power is developing oxy-combustion technology for retrofitting existing tangentially fired boilers. The project includes evaluating the performance of oxy-combustion in pilot-scale tests at their 5 MWe equivalent boiler simulation facility (BSF). The pilot-scale testing includes evaluation of the following variables: three coal types (bituminous, sub-bituminous, and lignite); flue gas recycle at different rates; oxygen injection flow rates and locations; windbox design; and over-fire air compartment design.

Table 7-1: DOE/NETL R&D Projects for Oxy-Combustion CO_2 Capture

Project Focus	Participant	Project Number	Performance Period
Tangential-Fired Oxy-Combustion Retrofits	Alstom Power	NT0005290	9/30/08 – 9/30/13
Evaluation of Boiler Materials for Oxy-Combustion	Foster Wheeler Corporation	NT0005262	10/1/08 – 9/30/11
Characterization of Oxy-Combustion Impacts	Reaction Engineering International	NT0005288	10/1/08 – 9/30/11
Flue Gas Purification Options	Praxair, Inc.	NT0005341	10/1/08 – 12/31/11
Flue Gas Purification via Compression	Air Products and Chemicals, Inc.	NT0005309	10/1/08 – 9/30/10
Oxy-Combustion and Integrated Pollutant Removal	Jupiter Oxygen Corporation	NT42811	9/28/06 – 9/30/11
Oxy-Combustion for Cyclone and Wall-Fired Boilers	Babcock & Wilcox	NT42747	4/1/06 – 12/31/10
Oxy-Syngas Combustor	Clean Energy Systems, Inc.	NT42645	10/1/05 – 9/30/14
Evaluation of Gas Recycle for Oxy-Combustion	Southern Research Institute	NT42430	9/27/05 – 9/25/10
Multi-Pollutant Control	Washington University	NT42531	8/29/05 – 2/28/09
NO_x Behavior in Oxy-Combustion	Brigham Young University	NT42530	8/4/05 – 12/31/08
Engineering Assessment of Oxy-Combustion	CanmetENERGY	IEA-CANMET-CO2	9/30/99 – 12/31/09
Engineering Assessment of Oxy-Combustion	Argonne National Laboratory	FWP-49539	10/1/97 – 12/31/10

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CHAPTER 8:
OXYGEN PRODUCTION R&D EFFORTS

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 800–900 °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 200–300 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 20–30 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. Appendix B includes summary descriptions and results for these projects.

Table 8-1: DOE/NETL R&D Projects for Oxygen Production

Project Focus	Participant	Project Number	Performance Period
Materials for Temperature Swing Adsorption Oxygen Separation	Eltron Research, Inc.	ER84600.002	8/8/07 – 8/7/10
Oxygen Transport Membrane-Based Oxy-Combustion	Praxair, Inc.	NT43088	4/30/07 – 9/30/15
Sorbents for Air Separation	TDA Research, Inc.	ER84216	8/7/06 – 8/6/09
Ceramic Auto-Thermal Recovery	Linde, LLC (formerly The BOC Group, Inc.)	NT42748	4/1/06 – 9/30/08
Nanofiller-Modulated Polymeric Membranes	North Carolina A&T State University	NT42742	2/17/06 – 12/31/10
Ion Transport Membrane	Air Products and Chemicals, Inc.	FT40343	10/1/98 – 9/30/15

OXYGEN-PRODUCTION R&D PROJECT HIGHLIGHT
OXYGEN TRANSPORT MEMBRANE

Praxair is optimizing OTM performance, materials, and process configurations leading to subsequent field testing of OTM technology for both syngas production and oxy-combustion applications. OTM technology creates an entirely new oxygen supply mode to combustion and partial oxidation applications in which oxygen is never actually separated and stored. The use of OTM is expected to reduce the power associated with oxygen production by 70 to 80 percent. One of the current project tasks is the design and construction of a skidded syngas system with O_2 supplied from OTM membranes capable of producing approximately 1 MM scfd of syngas at full capacity.

OTM technology integrates O_2 separation and combustion in one unit. An OTM consists of an inert porous support coated with a dense gas separation layer as illustrated in the figure below. 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 O_2 vacancies in the separation layer using a chemical potential difference as the driving force. Fuel species (CO, H_2, methane [CH4], 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 release electrons which are transported back through the separation layer.
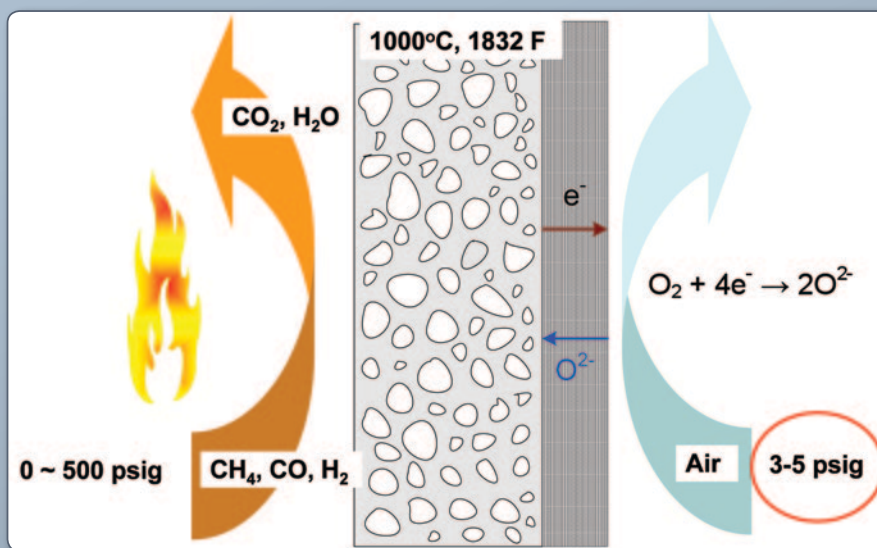
Oxy-Fuel Combustion Wihtout Producing Oxygen

CHAPTER 8: OXYGEN PRODUCTION R&D EFFORTS

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CHAPTER 9:
CHEMICAL LOOPING R&D EFFORTS

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 oxygen 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. Appendix B includes summary descriptions and results for these projects.

CHEMICAL LOOPING RESEARCH OBJECTIVES
- Improve oxygen carrier properties, e.g., capacity, reactivity, and attrition resistance
- Optimize solids handling and process design
- Optimize process heat integration
- Lower capital and operating cost

Table 9-1: DOE/NETL R&D Projects for CO_2 Capture Using Chemical Looping

Project Focus	Participant	Project Number	Performance Period
Chemical Looping for Fluidized Bed Reactor	University of Florida	FE0001321	10/1/09 – 9/28/12
Coal Direct Chemical Looping for Retrofits	Ohio State University	NT0005289	1/1/09 – 12/31/11
Chemical Looping Simulation and Control	Alstom Power	NT43095	7/12/07 – 3/31/11
Calcium Looping Process for Hydrogen Production	Ohio State University	NT43059	7/5/07 – 4/30/11
Chemical Looping Combustion Prototype	Alstom Power	NT0005286 & NT41866	9/30/03 – 9/30/11

CHEMICAL LOOPING R&D PROJECT HIGHLIGHT
LABORATORY-SCALE TESTING

Alstom Power, Inc. has successfully constructed and tested a laboratory-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. In the current phase of the project, Alstom is to design, construct, and operate a 3-MWth CLC prototype that includes process loops to transfer solids and oxygen between the reducing and oxidation reactors.

Chemical Looping Cold Flow Model

CHAPTER 10:
ADVANCED CARBON DIOXIDE COMPRESSION R&D EFFORTS

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 supercritical 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.[ii]

> **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. Appendix B 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
Thermal Integration of CO_2 Compression Processes	Lehigh University	FE0002146	10/1/09 – 6/29/12
Shock Wave Compression	Ramgen Power Systems, LLC	FE0000493 & NT42651	5/10/06 – 12/31/13
Evaluation of Compression Efficiency Improvements	Southwest Research Institute	NT42650	9/28/05 – 12/31/13

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 85–90 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 (Figure 10-1). Recent prototype testing has achieved a 7.8:1 compression ratio.[xx]

Table 10-2 presents a summary of the thermodynamic parameters for the two stages of compression.

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.
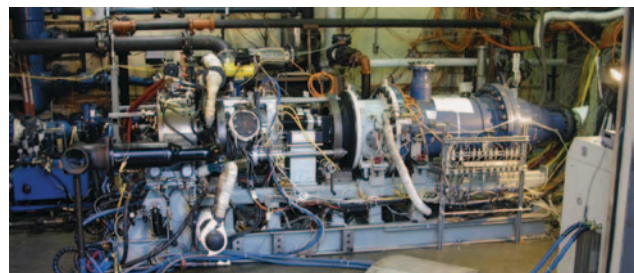
Rampressor Pilot-Scale Test Facility
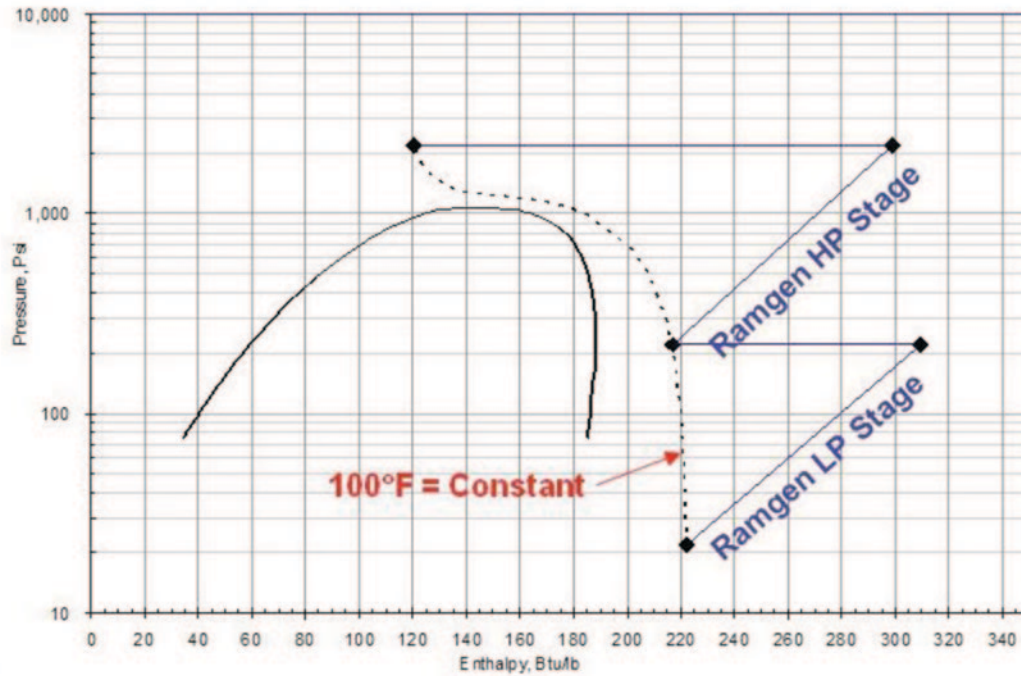
Figure 10-1: Ramgen Two-Stage Shock Wave Compression Pressure-Enthalpy Curve

Table 10-2: Ramgen Two-Stage Shock Wave Compression Parameters

Parameter	Low Pressure Stage	High Pressure Stage
Pressure range	22–220 psia	220–2,200 psia
Compressor shaft work	90.6 Btu/lb	87.0 Btu/lb
Discharge temperature	489 °F	509 °F
Recovery temperature	100 °F	100 °F
Recoverable heat	92.4 Btu/lb	178.8 Btu/lb
Recoverable heat/ compression work	102%	205%

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CHAPTER 11:
DOE/NETL IN-HOUSE R&D EFFORTS

DOE/NETL's ORD is developing new breakthrough concepts for CO_2 capture that could lead to dramatic improvements in cost and performance relative to today's 1st generation technologies. DOE/NETL CO_2 capture technology development is facilitated by the NETL-Regional University Alliance (NETL-RUA), which is a partnership that combines the capabilities of the three ORD research campuses (Albany, OR; Morgantown, WV; and Pittsburgh, PA) along with its regional academic institutions (Carnegie Mellon University, the University of Pittsburgh, West Virginia University, Penn State University, and Virginia Tech).

As shown in Figure 11-1, NETL-RUA's technology development approach includes four focus areas: Energy System Dynamics, Geological and Environmental Systems, Computational and Basic Sciences, and Materials Science and Engineering. With this approach, multi-disciplinary teams of scientists and engineers focus on the development of novel technologies and overcoming the barriers that prevent the widespread acceptance of current technologies.

NETL-RUA utilizes computational and experimental approaches to accelerate the CO_2 capture technology R&D effort. For example, atomistic modeling approaches can be coupled with surface science experiments to understand and optimize the structure and energetics of materials that can be used for CO_2 capture. The resulting molecular-level information can be used as a basis to predict the bulk thermodynamic and kinetic material properties by force-field modeling, Monte Carlo simulation, and molecular dynamics. Validated models are used to predict the performance of these materials, providing a screening tool that focuses experimental resources on only the most promising materials. The materials are fabricated into configurations, including thin-film membranes and sorbent particles, to assess their performance for CO_2 capture applications.
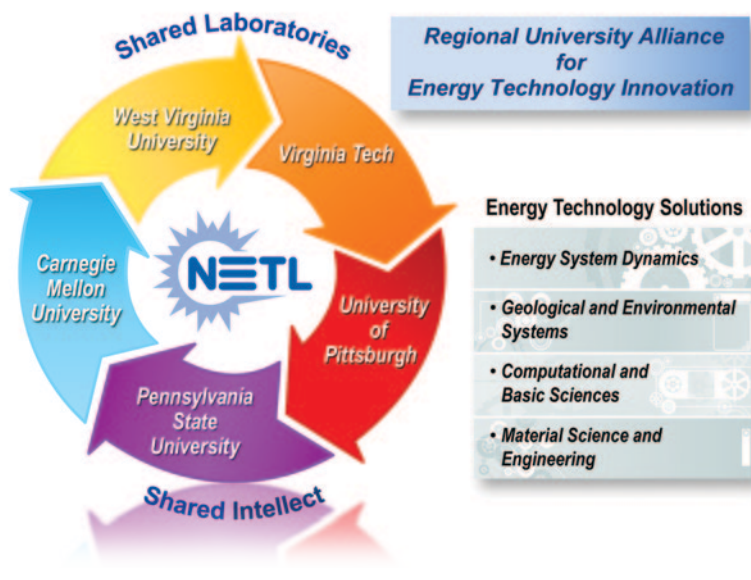
Figure 11-1: NETL-RUA R&D Partnership and Focus Areas
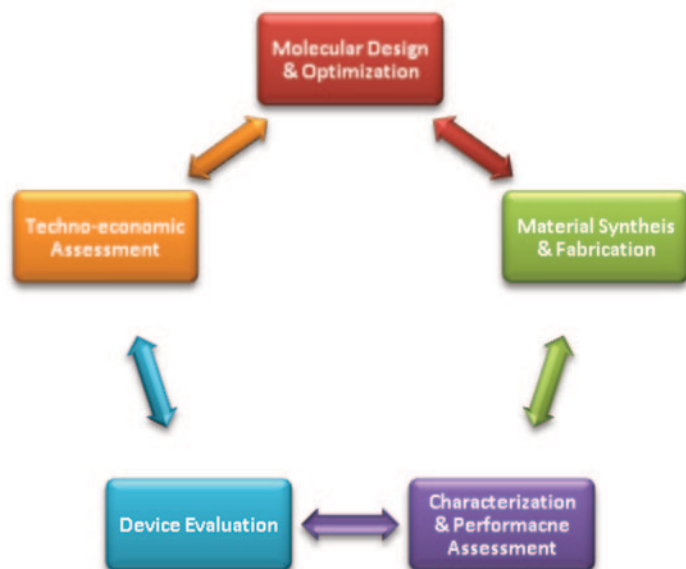
Figure 11-2: NETL-RUA R&D Approach

NETL-RUA works closely with NETL's OPPA to evaluate the technical-economic feasibility of developing these advanced CO_2 capture technologies. NETL-RUA provides the data required for technical-economic assessments in order to minimize the assumptions required to extrapolate laboratory results to plant-scale models. NETL-RUA results are scaled to the device level, such as a membrane module or sorbent bed, using a combined experimental and computational approach. In this approach, computational fluid dynamics (CFD) analyses are combined with small-scale device fabrication and testing to provide insights into the functional performance that can be expected at the plant scale, including performance degradation and heat- and mass-transfer limitations. Figure 11-2 highlights this integrated approach, which can be envisioned as a cyclic process ranging from fundamental science through process evaluation. Furthermore, this process provides insight into the properties that must be improved in future generations of materials, and the scientific limitations bounding such technologies. The following sections provide an overview of NETL-RUA efforts to develop advanced CO_2 capture technologies including: solvents, sorbents, CO_2 and H_2 selective membranes, oxy-combustion, and chemical looping.

11.A SOLVENTS

NETL-RUA is investigating the development of novel solvent-based CO_2 capture technologies for application to both pre- and post-combustion processes. Table 11-1 provides a summary of NETL-RUA's solvent R&D activities. The solvent research efforts focus on tailoring high capacity, low volatility solvents; tailoring the unique properties of "frustrated Lewis acid-base pairs" to produce materials for CO_2 capture (a frustrated Lewis pair is a compound or mixture containing a Lewis acid and a Lewis base that cannot combine because of steric hindrance); and utilizing biological systems, including amino acids, through experimental and computational approaches. For example, NETL-RUA is developing short chain polymer-based chemicals that exhibit capacity similar to conventional solvents, as well as low volatility, low viscosity and improved hydrophobicity. A coordinated effort between NETL-RUA and the National Carbon Capture Center (NCCC) is underway to evaluate the performance of polymer-based solvents through slipstream testing and comprehensive systems analysis.

Table 11-1: NETL-RUA Solvent R&D Activities

CO_2 Capture Technology	NETL-RUA R&D Activities
Solvent Development	• Analyze oligermic solvents at the NCCC. • Develop biological solvents.

11.B SORBENTS

NETL-RUA integrates research efforts from computationally-driven materials development through process development and integration to develop advanced sorbent-based CO_2 capture technologies. Table 11-2 provides a summary of NETL-RUA's sorbent R&D activities. Currently, NETL-RUA is investigating several sorbent materials and strategies for CO_2 capture from coal-derived gas streams, including conventional thermal and pressure swings systems, as well as novel photo-activated processes.

Table 11-2: NETL-RUA Sorbent R&D Activities

CO_2 Capture Technology	NETL-RUA R&D Activities
Sorbent Development	• Investigate basic immobilized amines. • Characterize encapsulated clay-based sorbents. • Improve non-structured molecular baskets. • Optimize $Mg(OH)_2$ sorbents. • Synthesize layer-by-layer IL sorbents.
Reactor and Process Engineering	• Develop a warm, fluid bed, bench scale integrated CO_2 capture sorbent regeneration unit. • Evaluate alternative process concepts and benchmark economics.

NETL-RUA is using state of the art techniques for the synthesis, characterization and performance assessment of sorbent materials, and strategic relationships with industrial partners [e.g., ADA-ES and Research Institute of Innovation Technology for the Earth (RITE)] to evaluate and demonstrate sorbent materials at pilot scale. Current R&D efforts are focused on increasing sorbent capacity, improving regeneration energetics, and minimizing the impact of water, gas contaminants, and attrition. The sorbent R&D effort includes basic immobilized amines; impregnated clays; nano-structured core-shell materials; mixed oxides and hydroxides; and supported solid ionic liquids (ILs).

In addition to conventional sorbent approaches, NETL-RUA is exploring novel materials and concepts that have the potential to dramatically increase the process efficiency of CO_2 capture. For example, NETL-RUA is developing several classes of photo-activated materials that have shown promise for high capacity and efficient utilization of both UV and visible light regions. Materials of interest in these studies include modified titanium oxide (TiO_2)-nanoparticles and dynamic structured MOFs.

Sorbent Reactor and Process Development

NETL-RUA sorbent R&D includes various sorbent reactor development activities in collaboration with industry. Several entrained, fluidized, and moving bed concepts are being evaluated. A bench-scale CO_2 capture unit (C2U) is expected to become operational in 2011 that will provide proof of concept testing for an integrated fluidized bed absorber coupled with a countercurrent self-fluidized bed regenerator (Figure 11-3). The bench-scale testing will evaluate the validity of different kinetic, heat transfer, and gas-solids fluid dynamic models. Test measurements are planned to verify the applicability of the kinetic parameters extracted from sorbent development experiments including the working capacity, the rates of moisture and CO_2 absorption and regeneration, and the system energetics. This work is being conducted in consultation with ADA-ES to support their efforts under DOE/NETL contract (FE0004343) to design and operate a 1 MWe pilot-scale, transport reactor absorber, and fluidized bed regenerator process using solid sorbents.

Research will also be conducted on two novel moving bed concepts developed by NETL-RUA and its industrial partners. The first concept is a rapid cycle rotary process, which is an adaptation of commercial flywheel recuperative heat exchangers. The second concept, developed by Matric, is a patented concept integrating flue gas heat exchange with a moving bed using horizontal perforated plate baffles to control flow, mixing, and heat transfer. The literature and experimental performance characteristics for sorbents tested by NETL-RUA, ADA-ES, and Matric will be compiled, developing a data book for process simulations. Process and economic models will be assembled that will permit evaluation of the separation efficacies of a number of process designs and sorbents. These systems will be developed and benchmarked against the conventional MEA solvent process. The technologies will be optimized for the most suited available sorbents and applications.

Additionally, NETL-RUA and its industrial research partners are using computer-aided process design and optimization tools. One such tool is NETL's Advanced Process Engineering Co-Simulator (APECS) for the design, analysis, and optimization of power plants with CO_2 capture. The APECS software system combines steady-state process simulation with multiphysics-based equipment simulations, such as those based on CFD. These co-simulation capabilities enable the optimization of overall process performance with respect to complex thermal and fluid flow phenomena in key plant equipment components, e.g., combustors, gasifiers, turbines, and CO_2 capture systems.
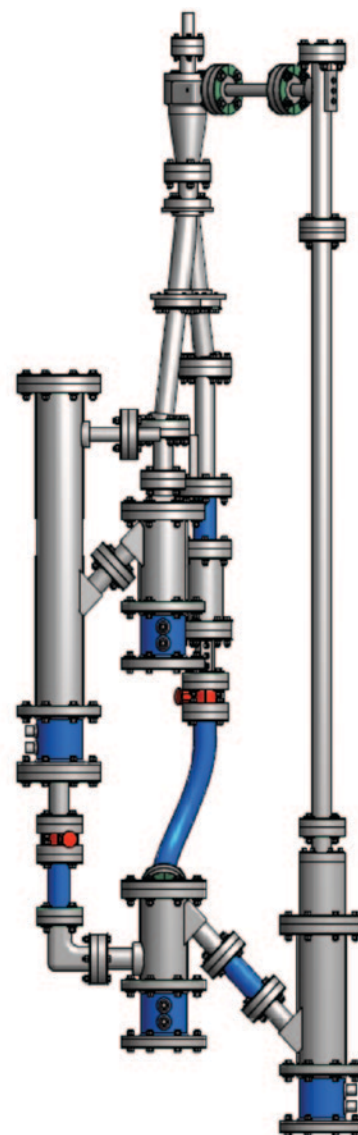
Figure 11-3: Sorbent Test Reactor System

11.C CARBON DIOXIDE SELECTIVE MEMBRANES

NETL-RUA is developing both IL-based membranes and mixed-matrix membranes (MMM) for the selective separation of CO_2 from power plant gas streams. Table 11-3 provides a summary of NETL-RUA's CO_2 selective membrane R&D activities.

Supported liquid membranes, consisting of a liquid transport medium immobilized in a solid support, have the potential to decrease the capital
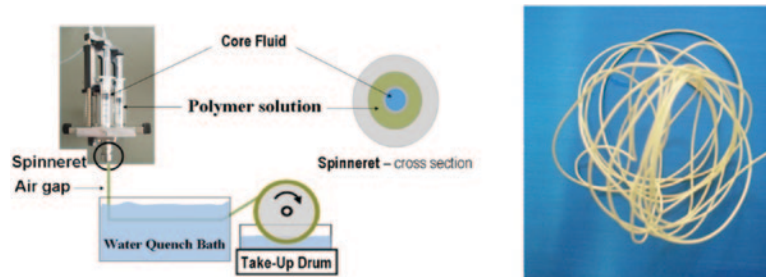
Figure 11-4: Fiber Spinning System and Ionic Liquid Loaded Membrane Fibers

cost of membrane-based gas separations by significantly increasing permeance compared to conventional membrane designs. NETL-RUA researchers are developing ILs encapsulated in polymer fibers to overcome the evaporative and mechanical issues associated with supported liquid membranes. Current research is focused on the development of polymeric supports that retain the IL under typical process pressures and ILs with tailored CO_2 sorption properties.

To solve the membrane stability problem, porous films that retain the IL using capillary force must be replaced with polymer fibers that entirely sequester the IL in their dense active layer or in the small pores immediately beneath that layer. A polymer fiber spinning apparatus has been constructed to fabricate IL-impregnated, polymer hollow fiber membranes (Figure 11-4). The fiber spinning apparatus can also be used to fabricate solid fibers and spheres that contain ILs for use as sorbent materials. NETL-RUA has submitted a patent application for this process and optimization is underway that should result in the production of stable fibers with performance properties that are superior to commercial membranes.

A molecular-level understanding of the absorption behavior of CO_2 is key to the success of supported IL membranes. To better understand basic aspects of absorption, NETL-RUA collaborates with the Center for Gas Separations Relevant to Clean Energy Technologies, an Energy Frontier Research Center based at the University of California, Berkeley and Lawrence Berkeley National Laboratory. Advanced characterization techniques are providing new insight into the interactions between CO_2 and ILs. This knowledge will be used to improve existing Monte Carlo and molecular dynamics simulations, as well as "chemical informatics" methods (computation methods which make use of both computational chemistry and information science techniques), which are currently used to computationally screen ILs. The most promising IL candidates identified using those techniques are synthesized, characterized, and evaluated for membrane performance. Major accomplishments to date include demonstration of the first temperature stable IL membrane, which was tested to 300 °C and development of the first IL-based facilitated transport membrane.

NETL-RUA is also investigating the development of MMMs. MMMs are comprised of porous microcrystals dispersed in a polymer matrix, which are ideal to achieve the selectivity of the porous, crystalline materials and the superior fabrication characteristics of polymers. In an effort to overcome the major limitation with MMMs, incompatibility between polymer and crystalline materials, NETL-RUA is collaborating with the University of California at Berkeley to utilize computational and experimental approaches over a wide range of scales to design and prepare gas-selective MOFs that are compatible with common membrane polymers. Approaches being investigated for the development of MMM include the use of a polymer-MOF "compatibilizer" (a material designed to make two other materials more compatible with one another, e.g. soap is a compatibilizer for oil and water.) and the propagation of polymer growth from the MOF surface. Additionally, NETL-RUA is developing MOFs and polymers with mechanical and chemical stability to overcome particle agglomeration and creating gas transport models for MMM films.

Table 11-3: NETL-RUA CO$_2$ Selective Membrane R&D Activities

CO$_2$ Capture Technology	NETL-RUA R&D Activities
CO$_2$ Selective Membranes	• Develop computational models to accurately predict IL properties. • Implement chemical informatics methods to search possible IL structures. • Probe IL properties using soft X-ray techniques. • Synthesize novel IL with improved properties based on computational guidance. • Optimize fabrication methods for preparation of mechanically robust hollow fiber membranes. • Design and prepare MOFs with enhanced polymer interactions. • Develop techniques for preparing thin, defect free MMM films with engineering structured materials. • Construct a high-throughput screening unit.

11.D HYDROGEN SELECTIVE MEMBRANES

In addition to the development of CO_2 selective membranes, NETL-RUA is investigating membrane systems designed for H_2 removal from mixed gas streams found in IGCC power plant applications. Table 11-4 provides a summary of NETL-RUA's H_2 selective membrane R&D activities. Hydrogen selective membranes have shown promise for the purification of CO_2 from pre-combustion gas streams, where the low-pressure pure H_2 permeate can be directed to an advanced fuel cell or turbine for electricity production, while the high-pressure, CO_2-rich retentate can be processed for sequestration.

Figure 11-5: Syngas Exposure Testing for Palladium Membrane Materials

NETL-RUA is focusing efforts on the development of H_2 selective, contaminant resistant metal membranes, typically high order palladium (Pd)-based alloys. Figure 11-5 shows a micrograph of Pd (left) and Pd-alloy (right) membrane foils after 1,000 hours exposure to raw, coal-derived syngas streams at the NCCC.

Computational and experimental methods are being used to understand how the composition of coal derived syngas influences the catalytic and corrosion behavior of the surface of the membrane; to understand the stability of the underling microstructure of the membrane over time and how this affects bulk transport through the membrane; and to understand issues associated with producing the membrane devices (or reactors) for integration into the gasification system.

Table 11-4: NETL-RUA H$_2$ Selective Membrane R&D Activities

CO$_2$ Capture Technology	NETL-RUA R&D Activities
H$_2$ Selective Membranes	• Design and fabricate Pd-X-Z alloys membranes. • Develop processing techniques for fabrication of metallic membrane by rapid deposition for high throughput screening. • Assess structural and performance of Pd-X-Z membranes. • Examine catalytic and surface stability of membrane materials. • Construct prototype scale composite membrane. • Explore design and processing of non-metallic membranes. • Assess structural stability of metal and non-metal membranes.

11.E OXY-COMBUSTION

NETL-RUA oxy-combustion R&D efforts include: developing the materials required for operational conditions and environments in oxy-combustion systems; understanding the combustion dynamics of various fuel feedstocks; and developing multi-phase combustion models required for boiler retrofit, design, and optimization. Table 11-5 provides a summary of NETL-RUA's oxy-combustion R&D activities.

NETL-RUA is characterizing oxy-combustor flames at all scales, from laboratory combustion tests to pilot-scale demonstrations. The goals of this testing is to quantify the thermal radiation emissions from the flame; determine effective flame temperatures; assess flame stability and spectroscopic properties; and provide the fundamental data required for oxygen injection strategies. Thermal radiation profiles emitted from flames are measured using a series of total radiometers, which are passive thermal devices that are wavelength-independent in their response and are optimized to detect thermal radiation power changes. Two monochromators and a CCD spectrometer are used to measure the spectral emissions of the flame as a function of wavelength from 280 to 5,000 nm. Wien's displacement law is utilized to determine the temperature of the hottest soot or ash emitters as proxies for estimating flame tem-
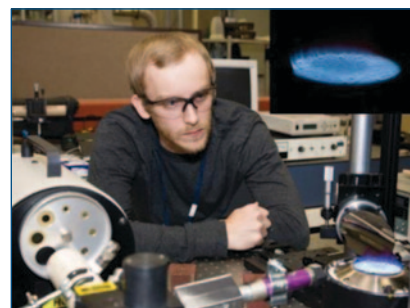
Laboratory Combustion Testing

perature at the location of the measurement. Flame data have been collected during pilot-scale air-firing and oxy-firing of different types of pulverized coal, as well as natural gas, and used to characterize changes in the flame as a function of process parameters, including switching from air to oxy-firing.

The experimental flame characterization tests are complemented by the development of CFD models focused on interpreting and supplementing experimental measurements and investigating the operating regimes to optimize furnace/burner designs for retrofits and new power plants. The experimental approach and models are integrated to better understand the impact of variable feeds and gas recycling on heat flux, gas-solid reactions, and multi-phase flow. Furthermore, the CFD results, along with a literature-based database, are used to define the conditions and environments required for the design and optimization of next generation oxy-combustion materials.

Advanced materials tailored for use in fuel-flexible, oxy-combustion systems are critical to the successful implementation of that technology. NETL-RUA is using experimental and computational methods to understand the impact of oxy-combustion environments on the performance of current boiler materials. Figure 11-6 shows the results of a corrosion evaluation of alloy T92 in air and oxy-combustion environments. These data are used to design new materials tailored for the demanding environments associated with oxy-combustion. Researchers are investigating the corrosion phenomena of several commercial alloys at superheater/reheater (~700 °C) and water-wall conditions (~450 °C), focusing on understanding the impacts of flue gas recycle and ash derived from various fuel feedstocks.
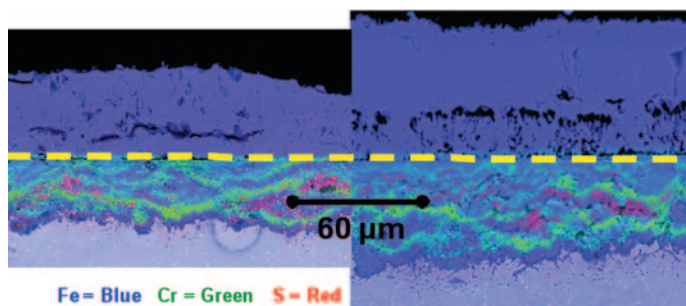
Figure 11-6: Corrosion Evaluation of Alloy T92 in Air and Oxy-Combustion Environments

Table 11-5: NETL-RUA Oxy-Combustion R&D Activities

CO$_2$ Capture Technology	NETL-RUA R&D Activities
Oxy-Combustion	• Develop simulation tools for application to oxy-combustion systems, focused on chemistry, gas flow, and heat transfer. • Generate a database detailing the fundamental and empirical data to validate and verify component models and validation tools. • Identify the effect of oxyfuel environments on conventional boiler materials of construction. • Examine the influence of coal and biomass derived ash on conventional boiler materials of construction.

11.F CHEMICAL LOOPING

The combustion of fossil fuels in the presence of pure oxygen, rather than air, represents an opportunity to facilitate CO_2 capture in both retrofit and new power plant applications. The chemical looping combustion (CLC) process produces pure oxygen via the oxidation-reduction cycling of an oxygen carrier, typically a supported metal. Currently, NETL-RUA is focused on addressing several aspects important to CLC development including: oxygen carrier development; solids handling and separation; and reactor design and optimization. Table 11-6 provides a summary of NETL-RUA's chemical looping R&D activities.

NETL-RUA is investigating several materials as oxygen carriers specifically tailored for the CLC process with emphasis on improving affordability, oxygen capacity, chemical resistance, and mechanical robustness. NETL-RUA is focused on utilizing both experimental and computational approaches ranging from fundamental science through lab-scale performance assessment to better understand and optimize traditional supported iron (Fe) and copper (Cu) materials, as well as to develop novel carriers such as double perovskites. Additionally, NETL-RUA is utilizing oxidation and combustion kinetic data collected through laboratory tests, along with large-laboratory scale cold-flow experiments, to develop reactive, multi-phase CFD models that can be used to design CLC process reactors.

Table 11-6: NETL-RUA Chemical Looping R&D Activities

CO₂ Capture Technology	NETL-RUA R&D Activities
Chemical Looping Combustion	• Construct and test a lab-scale integrated CLC reactor system. • Characterize synthetic and naturally occurring oxygen carriers for storage, separation and chemical looping.

CHAPTER 12:
DOE/NETL COST AND PERFORMANCE ANALYSES

DOE/NETL's Office of Program Planning and Analysis (OPPA) conducts technical-economic analyses to evaluate the cost and performance of CO_2 capture and compression technologies relative to DOE/NETL's R&D goals, which were presented in Chapter 2. These analyses include baseline studies of current state-of-the-art 1st generation CO_2 capture and compression technologies; screening studies to evaluate the potential feasibility of individual 2nd and 3rd generation advanced CO_2 capture and compression technologies under development by DOE/NETL; and pathway studies to evaluate the progression of cost and performance of 2nd and 3rd generation advanced CO_2 capture and compression technologies that is necessary for DOE/NETL to meet its goals.

The analyses consist of plant-level process and cost engineering studies to assess the potential environmental and economic performance of advanced technologies, and compare them with existing and competing technologies. Analyses can generally be categorized as those assessing conventional energy conversion systems (baseline studies), or advanced technology assessments (screening and pathway studies). Baseline studies are used to compare technologies that can be built now and deployed in the near term. A valid comparison between competing technologies is provided since all systems within a specific study use the same design basis, process assumptions, and economic assumptions. Baseline studies can also include sensitivity analyses for such variables as fuel cost, capacity factor, and financial parameters. Baseline studies also serve as the basis for screening studies and pathway studies that quantify potential improvements in technical-economic performance that could accrue from the development of advanced technologies in the DOE/NETL R&D portfolio. A screening study typically looks at the impact of one technology on plant performance compared to commercially available technologies. A pathway study is developed to quantify the aggregate cost and performance impact of a portfolio of emerging technologies and can be used to guide further R&D efforts. Pathway studies analyze the portfolio of technologies in a stepwise fashion to show a pathway to meet program goals. All of the published OPPA technical-economic analyses are available at: http://www.netl.doe.gov/energy-analyses/refshelf/Default.aspx

An example of results from the technical-economic studies is presented in Figure 12-1, which depicts an overview of first year COE for power plants equipped with 1st and 2nd generation CCS technologies. The COE for the 1st generation technologies are estimates from recently completed baseline studies and the COE for the 2nd generation technologies are estimates on what is achievable based on results of recently completed pathway studies. These cost estimates will be discussed in more detail in the following sections. The COE for the 2nd generation technologies represent levels that meet or exceed the DOE/NETL cost reduction goals for pre-, post-, and oxy-combustion CO_2 capture. For example, the $107/MWh COE for a supercritical PC power plant with 1st generation CCS represents an approximately 80 percent increase over the $59/MWh for a supercritical PC power plant without CCS. Meeting DOE/NETL's cost goal (no more than a 35 percent increase in COE for post-combustion and oxy-combustion CO_2 capture) would require the successful development of 2nd generation CCS with a COE no greater than $80/MWh.
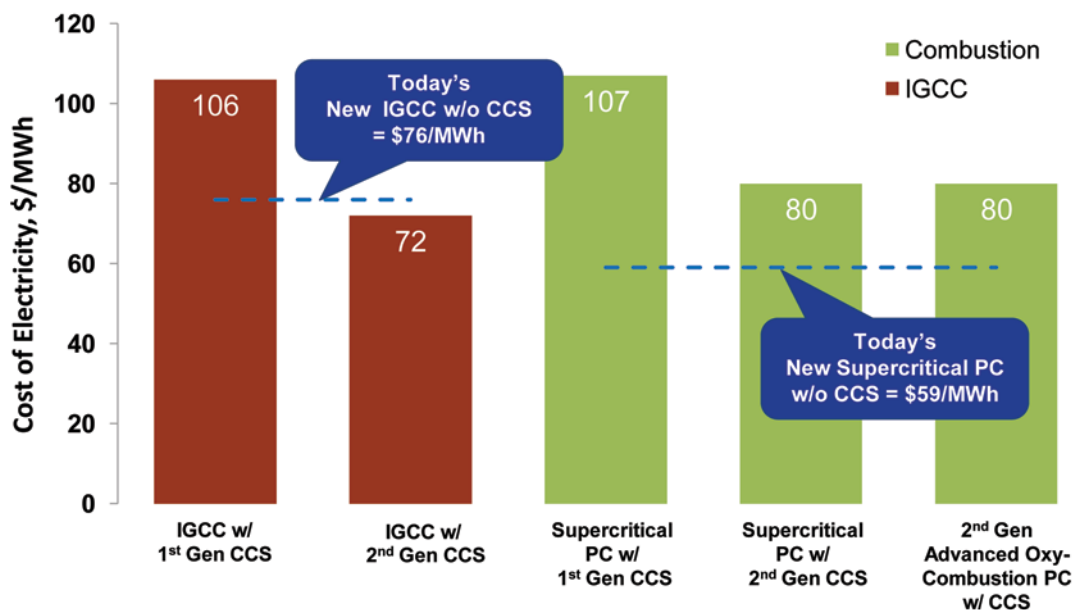
Figure 12-1: First Year COE for Power Plants with 1st and 2nd Generation CO_2 Capture Technologies

12.A GENERAL APPROACH USED TO CONDUCT TECHNICAL-ECONOMIC ANALYSES

OPPA conducts plant-level process and cost engineering analyses to assess the environmental and economic performance of the CO_2 capture and compression technologies. The analyses are designed to:

- Determine cost and performance estimates of the technologies.

- Perform analyses on a consistent design basis so valid comparisons can be made between different technologies.

- Estimate technology performance using a consistent set of process parameter assumptions.

- Estimate system economics using a consistent methodology and set of financial parameters.

The general approach to conducting the technical-economic analyses is outlined in Figure 12-2. Each analysis includes an extensive process simulation and a detailed cost estimate. The plant configuration is simulated using Aspen Plus®, a commercially available process simulator offered by Aspen Technologies, Inc, or another process simulator. Modeling of major processes is based on vendor supplied data, published data, or good engineering judgment as dictated by the availability of data. Mass and energy balances are prepared using the results of the process simulation. Performance calculations are conducted to determine auxiliary power load, net power output, plant efficiency, and other parameters.

Process data (flow rates, pressure, temperature, and compositions) are used in the development of an equipment list for the plant. An engineer, procurement, and construction (EPC) firm is used to estimate the total plant cost (TPC) based on its in-house data base of systems costs. The economic methodology described in the DOE/NETL Quality Guidelines for Energy System Studies is followed to calculate owner's costs and ultimately used to determine the COE and other metrics.[xxi]
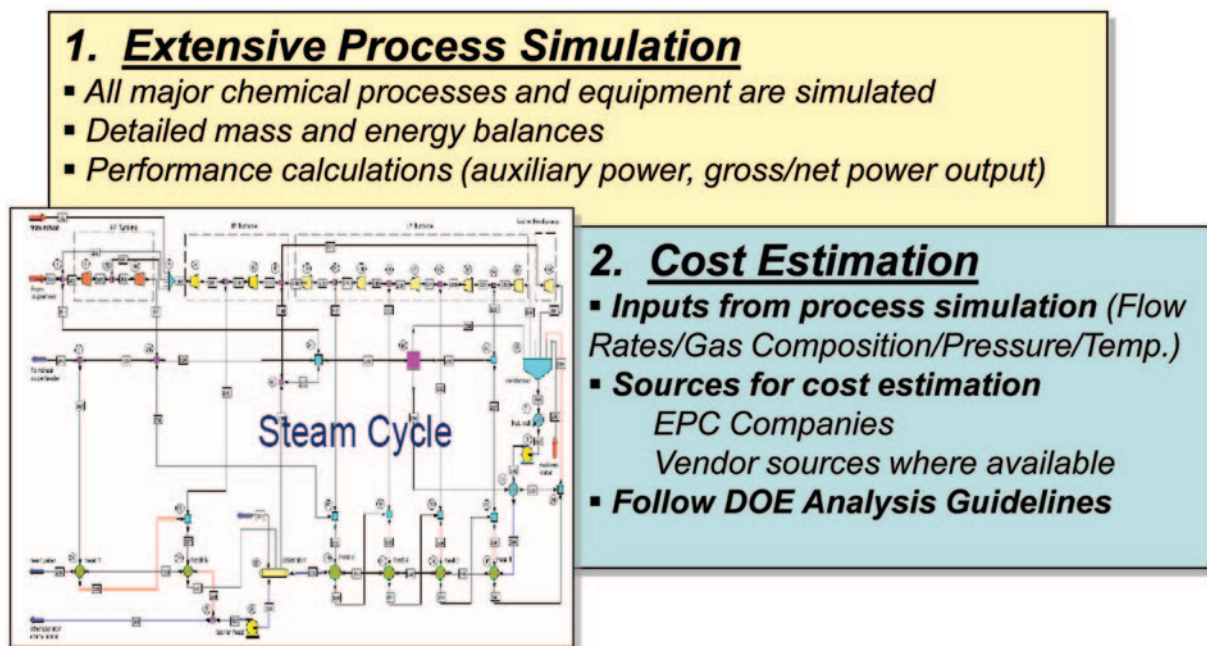
Figure 12-2: Outline of OPPA Approach to Conduct Technical-Economic Analyses

Capital Cost Estimate Accuracy

OPPA capital cost estimates adhere to Recommended Practice 18R-97 of the Association for the Advancement of Cost Engineering International (AACE), which describes a cost estimate classification system as applied in engineering, procurement, and construction for the process industries. Most technical-economic studies conducted by OPPA feature cost estimates intended for the purpose of a "Feasibility Study" (AACE Class 4) and have an expected accuracy range of -15/+30 percent.

Table 12-1 describes the characteristics of an AACE Class 4 cost estimate.

Table 12-1: Characteristics of an AACE Class 4 Capital Cost Estimate

Project Definition	Typical Engineering Completed	Expected Accuracy
1 to 15%	• plant capacity, block schematics, indicated layout, process flow diagrams for main process • systems, and preliminary engineered process and utility • equipment lists	-15% to -30% on the low side, and +20% to +50% on the high side

12.B BASELINE STUDIES

The following is a brief summary of results from OPPA's baseline studies for various power generation cycles and fuel types equipped with and without 1st generation CO_2 capture technologies.

Bituminous Baseline Study

In November 2010, OPPA published an update to its baseline study entitled "Cost and Performance Baseline for Fossil Energy Power Plants Study, Volume 1: Bituminous Coal and Natural Gas to Electricity."[ii] Known as the "Bituminous Baseline Study," it establishes performance and cost data for IGCC, PC, and NGCC power plants equipped with and without CCS. The analyses were performed on a consistent technical and economic basis that accurately reflects current market conditions. Table 12-2 provides a description of the various power plant design cases included in the Bituminous Baseline Study.

Table 12-2: Case Descriptions for Bituminous Baseline Study*

Case	Unit Cycle	Steam Cycle, psig/°F/°F	Combustion Turbine	Gasifier/ Boiler Technology	Oxidant	H_2S Separation/ Removal	Sulfur Removal/ Recovery	CO₂ Separation
1	IGCC	1,800/1,050/1,050	2 × Advanced F Class	GEE Radiant Only	95 mol% O_2	Selexol	Claus Plant	—
2	IGCC	1,800/1,000/1,000	2 × Advanced F Class	GEE Radiant Only	95 mol% O_2	Selexol	Claus Plant	Selexol 2nd stage
3	IGCC	1,800/1,050/1,050	2 × Advanced F Class	CoP E-Gas™	95 mol% O_2	Refrigerated MDEA	Claus Plant	—
4	IGCC	1,800/1,000/1,000	2 × Advanced F Class	CoP E-Gas™	95 mol% O_2	Selexol	Claus Plant	Selexol 2nd stage
5	IGCC	1,800/1,050/1,050	2 × Advanced F Class	Shell	95 mol% O_2	Sulfinol-M	Claus Plant	—
6	IGCC	1,800/1,000/1,000	2 × Advanced F Class	Shell	95 mol% O_2	Selexol	Claus Plant	Selexol 2nd stage
9	PC	2,400/1,050/1,050	—	Subcritical PC	Air	—	Wet flue gas desulfurization (FGD)/Gypsum	—
10	PC	2,400/1,050/1,050	—	Subcritical PC	Air	—	Wet FGD/ Gypsum	Amine Absorber
11	PC	3,500/1,100/1,100	—	Supercritical PC	Air	—	Wet FGD/ Gypsum	—
12	PC	3,500/1,100/1,100	—	Supercritical PC	Air	—	Wet FGD/ Gypsum	Amine Absorber
13	NGCC	2,400/1,050/1,050	2 × Advanced F Class	HRSG	Air	—	—	—
14	NGCC	2,400/1,050/1,050	2 × Advanced F Class	HRSG	Air	—	—	Amine Absorber

* Cases 7 and 8 were removed from the Bituminous Baseline Study prior to final publication and are to be used in a future OPPA study.

The first year COE for the 12 plant configurations is shown in Figure 12-3. The COE is shown by various capital and operating cost components. The most significant component of COE for the IGCC and PC configurations is capital cost recovery, while fuel costs is the dominant component for the NGCC configurations.
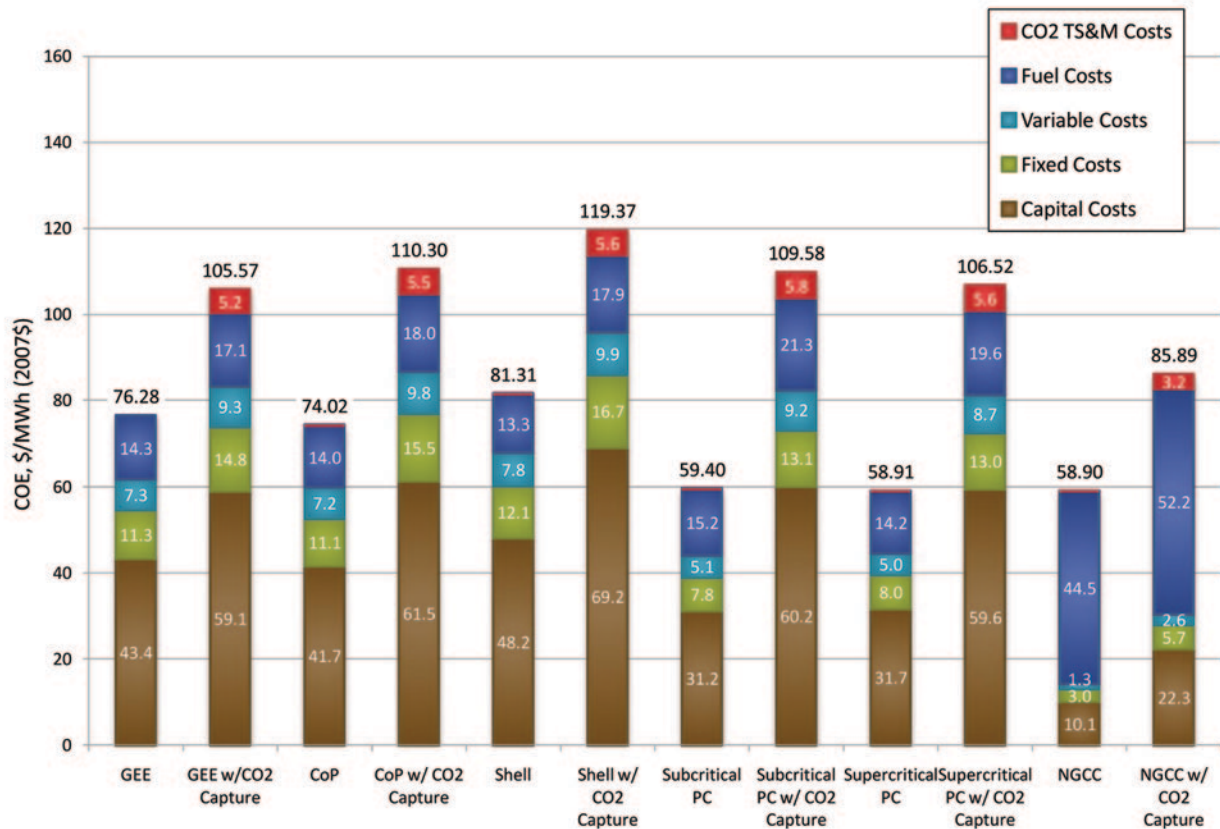
Figure 12-3: First Year COE for Cases in Bituminous Baseline Study

The following are highlights of results from the Bituminous Baseline Study:

- Total overnight cost (TOC) for the non-capture plants are as follows: $718/kW for NGCC; $2,010/kW (average) for PC; and $2,505/kW (average) for IGCC. With CO_2 capture, capital costs are: $1,497/kW for NGCC; $3,590/kW (average) for PC; and $3,568/kW (average) for IGCC.

- At fuel costs of $1.64/MMBtu for coal and $6.55/MMBtu for natural gas, the first year COE for the non-capture plants is: $59/MWh for NGCC; $59/MWh (average) for PC; and $77/MWh (average) for IGCC.

- When 1st generation CCS technology is integrated into these new power plants, the resultant first year COE, including the cost of CO_2 transporting, storing, and monitoring (TS&M), is: $86/MWh for NGCC; $108/MWh (average) for PC; and $112/MWh (average) for IGCC. The cost of transporting CO_2 50 miles for storage in a geologic formation with over 30 years of monitoring is estimated to add about $3–6/MWh. This represents less than 5.5 percent of the COE for each CO_2 capture case.

- A sensitivity study on natural gas price shows that at a coal price of $1.64/MMBtu, the average COE for IGCC with CO_2 capture equals that of NGCC with CO_2 capture at a gas price of $9.80/MMBtu. The average COE for PC with CO_2 capture equals that of NGCC with CO_2 capture at a gas price of $9.25/MMBtu.

Low Rank Baseline Study

The Low Rank Baseline Study (published March 2011) is similar in scope to the Bituminous Baseline Study, but features power plants fueled with Powder River Basin (PRB) coal at a Montana site and North Dakota Lignite at a North Dakota site.[xxii] The study analyzes several power generation configurations with and without CO_2 capture: four IGCC technologies, supercritical and ultra-supercritical PC, supercritical circulating fluidized bed combustion (CFBC), and NGCC.

Bituminous Oxy-Combustion Baseline Study

The Bituminous Oxy-Combustion Baseline Study (published August 2008) included supercritical and ultra-supercritical PC plants with oxy-combustion CO_2 capture and compared the results to non-capture and amine-based post-combustion CO_2 capture systems.[iii] A total of 12 plant configuration cases were analyzed including four conventional air-based combustion cases for reference (with and without CO_2 capture), six oxy-combustion cases with O_2 provided by a cryogenic distillation process, and two oxy-combustion cases with O_2 provided by an ion transport membrane (ITM) process. Both supercritical and ultra-supercritical steam cycles were analyzed and different levels of O_2 purity and CO_2 purity were also considered. The following are a few highlights from the Bituminous Oxy-Combustion Baseline Study:

- For the oxy-combustion cases studied, the increase in levelized COE relative to the air-fired base case ranged from a low of 52 percent for Case 6 to a high of 63 percent for Case 7 (excluding cost of CO_2 TS&M).

- Cryogenic oxy-combustion for supercritical steam conditions has a higher net thermal efficiency (approximately 1 percent) and a lower levelized COE (approximately 0.8 cents/kWh) than an air-fired amine-based post-combustion CO_2 capture system.

- Oxy-combustion with co-sequestration (Cases 5 and 6) has the lowest cost of CO_2 capture.

- One scenario to accomplish the DOE/NETL cost goal is an oxy-combustion ultra-supercritical PC boiler without FGD, without boiler contingency, and with ASU capital and operating costs that are 62 percent of the current market costs of cryogenic ASUs.

Low Rank Oxy-Combustion Baseline Study

The Low Rank Oxy-Combustion Study (published September 2010) analyzed oxy-combustion for supercritical and ultra-supercritical PC plants and supercritical CFBC plants using PRB coal at a Montana site and North Dakota Lignite at a North Dakota site.[xxiii] A total of 17 cases were examined, six of which are air-fired, supercritical power plants, without CO_2 capture taken from the Low Rank Coal Baseline Study and included for reference. The other 11 cases in the study include eight new cases utilizing PRB sub-bituminous coal as a fuel and three additional cases utilizing Buelah-Zap lignite coal. A cryogenic ASU with oxygen purity of 95 percent is assumed in all oxy-combustion cases. The key results of this baseline study are as follows:

- Oxy-combustion as a means of CO_2 capture significantly increases the cost of power production. The 20-year levelized COE for oxy-combustion cases is 58–78 percent higher than its equivalent air-fired case without CO_2 capture.

- The oxy-combustion TPC is the parameter that has the largest impact on levelized COE. The TPC is 69–75 percent of the levelized COE for all cases. For ultra-supercritical and supercritical cases, the TPC is 58–67 percent higher in the oxy-combustion cases. For the CFBC, the TPC is 80–87 percent higher. The higher cost differential in the CFBC cases is attributable to higher process contingencies, which are applied to account for the fact that supercritical CFBC has not been demonstrated at commercial scale. If all contingencies are removed, the cost differential is reduced to 18–25 percent for ultra-supercritical and supercritical cases and 43–70 percent for CFBC cases. This cost differential is primarily the cost of capturing and compressing the CO_2 by adding an ASU, oxy-combustor, and compression and purification unit (CPU) to the conventional air-fired unit design.

- The net plant efficiency is significantly lower in the oxy-combustion cases. On average for all cases, adding CO_2 capture decreases plant energy efficiency by 7–9 absolute percentage points or approximately 21 percent on a relative basis as compared to an air-fired plant. For comparison, the energy efficiency penalty for an air-fired plant using an amine-based post-combustion CO_2 capture system is approximately 11 absolute percentage points or 27 percent on a relative basis.

- Oxy-combustion combined with cosequestration of CO_2 and combustion products offers the potential to be less costly than alternative methods of CO_2 capture.

- Further oxy-combustion R&D programs should focus on demonstrating oxy-combustion at larger scale; developing advanced boiler construction materials; advanced systems to control flue gas recycle; overcoming obstacles to cosequestration; and improving the performance and reducing the cost of ASU and CPU systems.

12.C SCREENING STUDIES

OPPA conducts internal screening studies on pre-, post-, and oxy-combustion technologies with the purpose of making an initial engineering judgment of the subject technology's potential to meet DOE/NETL R&D goals. These studies can also highlight the strengths, weaknesses,s and gaps of technology subcomponents related to their impact on the cost and performance of the entire system. Results from DOE/NETL's screening studies have not been published.

12.D PATHWAY STUDIES

As data becomes available, OPPA conducts a more detailed system study to show the cost and performance benefit of advanced technology components. Frequently, OPPA assesses a group of technologies in a stepwise fashion to show a pathway to meeting DOE/NETL R&D cost and performance goals for CO_2 capture systems. These pathway studies show the progression in COE from 1st generation to 2nd generation CO_2 capture technologies. The following sections provide an overview of three pathway studies on pre-, post-, and oxy-combustion CO_2 capture and the technology steps involved in achieving the improved cost and performance of these 2nd generation CO_2 capture technologies.

Pre-Combustion Capture Pathway Study

OPPA completed a Pre-Combustion Capture Pathway Study in November 2010.[xxiv] Achieving the significant cost reduction for 2nd generation pre-combustion CO_2 capture for IGCC plants shown previously in Figure 12-1 requires technology advancements for the pre-combustion capture system, as well as advances in IGCC gas cleanup, hydrogen-fired turbines, oxygen production, and plant availability. Beginning with the 1st generation pre-combustion CO_2 capture case established in the Bituminous Baseline Study, the Pre-Combustion Capture Pathway Study incorporates technology advancements in a stepwise fashion to determine the potential performance improvements and cost reductions that could result from successful R&D efforts. Table 12-3 shows this study's progression from conventional technologies (reference IGCC) to advanced technologies including: dry coal feed pump; warm gas cleanup (WGCU); high temperature H_2 membranes for CO_2 separation; advanced H_2 turbines (AHT); and ITMs for air separation. Also included are steps to show the impact of overall plant availability and capacity factor improvements that could be achieved in part through improved materials, sensors, and controls.

Table 12-3: Case Descriptions for Pre-Combustion Capture Pathway Study

Case Title	Coal Feed System	Availability	Gas Clean Up	CO₂ Separation	Gas Turbine	Oxygen Production
Reference IGCC	Slurry	80%	2-Stage Selexol	2-Stage Selexol	Adv "F"	Cryogenic Air Separation Unit (ASU)
Coal Pump	Coal Feed Pump	80%	2-Stage Selexol	2-Stage Selexol	Adv "F"	Cryogenic Air Separation Unit (ASU)
85% CF	Coal Feed Pump	85%	2-Stage Selexol	2-Stage Selexol	Adv "F"	Cryogenic Air Separation Unit (ASU)
WGCU/Selexol	Coal Feed Pump	85%	WGCU	2-Stage Selexol	Adv "F"	Cryogenic Air Separation Unit (ASU)
WGCU/H₂Membrane	Coal Feed Pump	85%	WGCU	Hydrogen Membrane	Adv "F"	Cryogenic Air Separation Unit (ASU)
AHT-1	Coal Feed Pump	85%	WGCU	Hydrogen Membrane	AHT-1	Cryogenic Air Separation Unit (ASU)
ITM	Coal Feed Pump	85%	WGCU	Hydrogen Membrane	AHT-1	ITM
AHT-2	Coal Feed Pump	85%	WGCU	Hydrogen Membrane	AHT-2	ITM
90% CF	Coal Feed Pump	90%	WGCU	Hydrogen Membrane	AHT-2	ITM

Figure 12-4 shows the net plant efficiency and COE for each case in the Pre-Combustion Capture Pathway Study assuming individual component R&D cost and performance goals are met. For the pre-combustion CO_2 capture system, successful R&D includes manufacturing of H_2 membranes with consistent high flux properties and long lifetimes and meeting target membrane costs. As shown, significant improvements in efficiency and COE occur for the combination of WGCU and the H_2 membrane and for the AHT. Cost benefits are also achieved through the ITM and availability improvements. Overall, the 2nd generation pre-combustion CO_2 capture and advanced IGCC plant efficiency exceeds that of the 1st generation plant by more than 7 percentage points and provides a greater than 30 percent reduction in COE—dropping below the COE of the baseline IGCC non-capture plant.

Specific to CO_2 capture, the high temperature H_2 membrane paired with WGCU provides an elevated temperature and pressure gas cleanup process that results in a 3 percentage point efficiency improvement and a 12 percent reduction in COE relative to 1st generation solvent-based CO_2 capture. While the H_2 membrane has the capability to produce high purity H_2, in this case it is optimized for power efficiency by using the N_2 from the ASU as a sweep gas, reducing the H_2 partial pressure and producing a mix of H_2 fuel and N_2 diluent for the AHT. The CO_2-rich non-permeate from the H_2 membrane is compressed to a liquid phase and non-condensibles are separated and returned to the topping combustor. The resulting CO_2 stream is produced at elevated pressure.
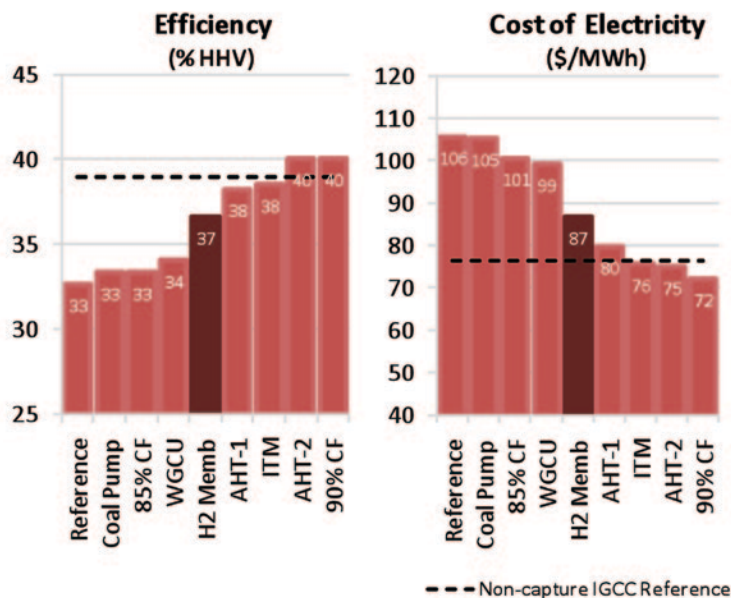
Figure 12-4: Efficiency and First Year COE for Cases in Pre-Combustion Capture Pathway Study

Figure 12-5 highlights the key system performance benefits (reduction in auxiliary power and increase in gross power) of the WGCU and H_2 membrane advancements of the pathway study. The chart shows gross power generation and auxiliary power load normalized by total thermal input for the pathway segment from "2-Stage Selexol" to "WGCU with 2-Stage Selexol" to "WGCU and a H_2 membrane." Overall, the auxiliary power load decreases from 12 percent to 10 percent of total thermal input, while gross power increases from 45 percent to 46 percent of total thermal input. Incorporation of these advanced gas cleanup and CO_2 separation technologies increases the steam turbine output due to elimination of the Selexol reboiler heat duties and the elimination of syngas cooling/reheating and reduces the auxiliary load driven primarily by the reduction in CO_2 compression load.
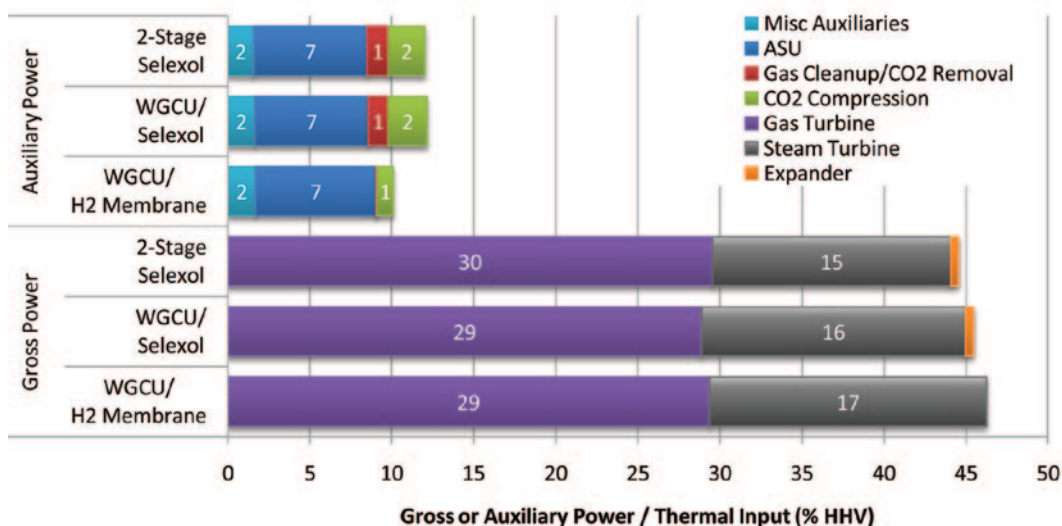
Figure 12-5: Warm Gas Cleanup and H_2 Membrane Performance in Pre-Combustion Pathway Study

The Pre-Combustion Capture Pathway Study assesses just one of many options for 2nd generation CO_2 capture coupled with advanced IGCC designs. The study also highlights the potential significant system benefits for any pre-combustion CO_2 capture system technologies that can achieve the following: produce high pressure CO_2; minimize regeneration steam requirements; operate at elevated syngas temperatures for pairing with WGCU; and provide a capital cost reduction relative to 1st generation capture systems, such as Selexol.

Evaluations of the efficiency, capital cost, and COE benefit of solvents, sorbents, and other membranes for pre-combustion CO_2 capture are ongoing. Through screening and pathway studies, OPPA will continue to evaluate the potential of this suite of technologies to contribute to improvements in efficiency and reduction in the COE for 2nd generation pre-combustion CO_2 capture coupled with advanced IGCC plants.

Post-Combustion Capture Pathway Study

OPPA is also conducting a Post-Combustion Capture Pathway Study which is expected to be completed later in 2011. The cost and performance data presented here are taken from a preliminary draft of the study and are subject to change.

Seven post-combustion CO_2 capture pathway steps are being assessed that represent a possible scenario for the evolution of the PC power plant with post-combustion CO_2 capture. The results quantify the potential improvements in technical-economic performance that could accrue from successful post-combustion CO_2 capture technology development. The results also provide a basis to guide technology development and to measure and prioritize the specific contributions of individual R&D projects.

Table 12-4 lists the progression of design case technologies assessed in the study. Case 1 represents a conventional PC plant, using a supercritical steam cycle without CO_2 capture, while Case 2 includes the Case 1 plant, but equipped with a 1st generation solvent-based CO_2 capture technology (represented by the Fluor Econamine process). Similarly, Case 3 includes the Case 1 PC plant, but equipped with an advanced 1st generation solvent-based technology (represented by the Fluor Econamine process with enhanced solvent performance). These first three cases are reproductions of Cases 11, 12, and 12A reported in the Bituminous Baseline Study.[ii] Cases 4 and 6 include utilization of a further enhanced 1st generation solvent-based technology (represented by the near-commercial MHI KS-1 solvent). While Case 4 assumes the supercritical PC plant design used in Cases 1–3, Case 6 assumes an ultra-supercritical PC plant design.

Table 12-4: Case Descriptions for Post-Combustion Capture Pathway Study

Case	CO$_2$ Removal Technology	Boiler Technology psig/°F/°F	Steam Turbine and Fan Technology	CO$_2$ Compression Technology
1	None	Supercritical 3,500/1,100/1,100	Conventional	None
2	Fluor Econamine	Supercritical 3,500/1,100/1,100	Conventional	Conventional
3	Fluor Econamine with enhanced performance	Supercritical 3,500/1,100/1,100	Conventional	Conventional
4	MHI KS-1 solvent	Supercritical 3,500/1,100/1,100	Conventional	Conventional
6	MHI KS-1 solvent	Ultra-supercritical 5,000/1,350/1,400	Conventional	Conventional
7	Advanced CO$_2$ membrane (MTR)	Ultra-supercritical 5,000/1,350/1,400	Conventional	Enhanced shockwave compression
7A	Plant with reduced membrane cost	Ultra-supercritical 5,000/1,350/1,400	Advanced performance	Enhanced shockwave compression
7A(LR)	Plant with low-risk financing	Ultra-supercritical 5,000/1,350/1,400	Advanced performance	Enhanced shockwave compression
8	Advanced CO$_2$ adsorber (TDA)	Ultra-supercritical 5,000/1,350/1,400	Conventional	Enhanced shockwave compression
8A	Plant with advanced performance	Ultra-supercritical 5,000/1,350/1,400	Advanced performance	Enhanced shockwave compression
8A(LR)	Plant with low-risk financing	Ultra-supercritical 5,000/1,350/1,400	Advanced performance	Enhanced shockwave compression

The last four cases, Cases 7, 7A, 8, and 8A, represent progressions to 2nd generation post-combustion technologies including membranes and sorbents. All of these advanced technology cases are characterized by a number of technology advances and supporting component development needs. All four cases use advanced CO_2 compression (represented by Ramgen's shockwave compression) that is currently under development. Case 7 applies an advanced CO_2 capture membrane process designed for low pressure flue gas conditions (represented by the MTR membrane process). Case 7 applies the basic membrane process concept, but assumes advanced performance and cost capabilities beyond those currently achieved in the membrane development program, but within long-range development goals. Case 7A assumes additional reductions to the membrane cost, as well as applying enhancements to the steam turbine efficiencies and the plant fan efficiencies that represent potential future technology improvements.

Case 8 is analogous to Case 7, but it applies an advanced CO_2 capture sorbent-based process (represented by TDA Research) that assumes advanced performance and cost capabilities beyond the current capabilities demonstrated in the development program. Case 8A is analogous to Case 7A, but it applies the sorbent technology with performance and cost capabilities beyond the current capabilities demonstrated in the development program, as well as applying enhancements to the steam turbine efficiencies and the plant fan efficiencies that represent potential future technology improvements.

The PC power plant net efficiency pathway is displayed in Figure 12-6. The enhanced solvents in Cases 3 and 4 result in increased plant efficiency relative to the baseline 1st generation solvent in Case 2. The use of a ultra-supercritical steam cycle in Case 6 increases the plant efficiency by more than 3 percentage points. The 2nd generation post-combustion technologies used in cases 7, 7A, 8, and 8A yield plant efficiencies that approach the Case 1 baseline supercritical PC power plant without CO_2 capture. The Case 7 membrane technology is estimated to provide the highest net plant efficiency of the advanced technology options. Enhancements to the plant steam turbine and fan efficiencies that might be realized in the future contribute an additional 0.7–0.8 percentage points to the net plant efficiency.

The first-year COE of the advanced post-combustion CO_2 capture technology cases were compared to the COE of an air-fired, supercritical boiler with no CO_2 capture (Case 1), which has a COE of \$58.9/MWh. For comparison, the DOE/NETL goal of no more than a 35 percent increase in COE for CO_2 capture would be equivalent to \$79.5/MWh. The study results represent a pathway progression in technology development toward that goal. The COE for the cases is plotted in Figure 12-7. The advanced 1st generation solvent-based technologies utilized in Cases 3 and 4 show important progressions in power plant performance and cost (almost \$7/MWh reduction in COE relative to the baseline 1st generation solvent technology in Case 2), and are important technology development steps. The ultra-supercritical steam cycle technology introduced in Case 6 provides a step improvement in plant performance and COE, which is reduced by over \$8/MWh relative to the supercritical steam cycle cases in the pathway.
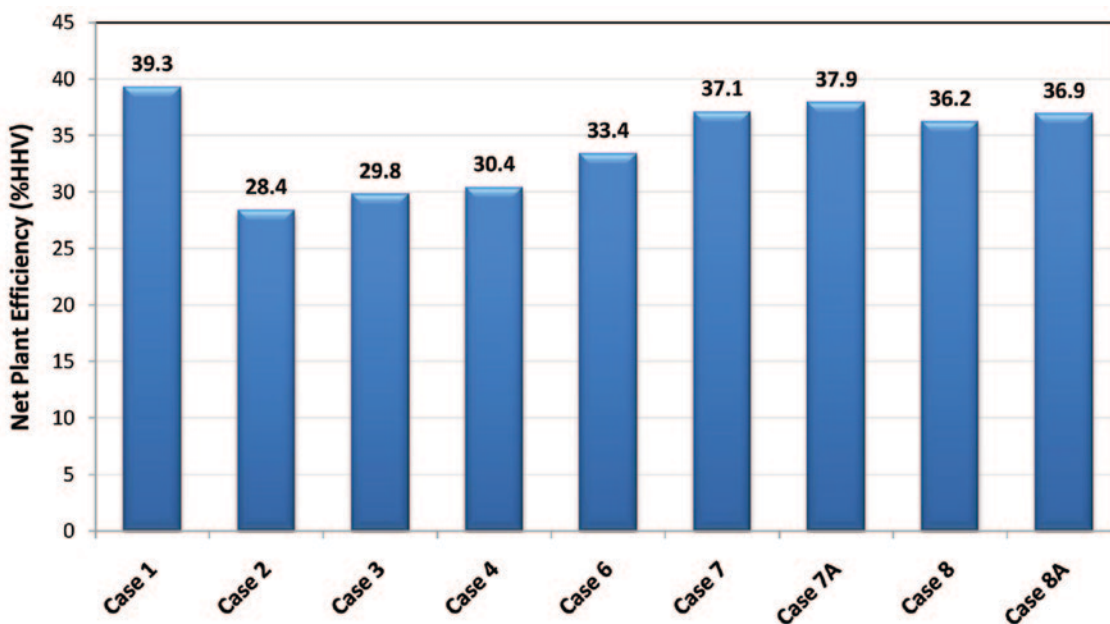

Figure 12-6: Net Plant Efficiency for Cases in Post-Combustion Capture Pathway Study

Case 7A, using the advanced membrane technology, and Case 8A, using the advanced sorbent technology nearly meet the DOE/ NETL goal based on their assumed advanced performance and cost levels. Cases 7A(LR) and 8A(LR) assume that lower risk financing will be available after the reliable performance of an integrated CCS system has been established via multiple demonstrations. This assumption results in a reduction in the assumed capital charge factor (CCF) from 0.124 to 0.117 and results in a COE reduction of approximately $2.7/MWh.

In summary, the Post-Combustion Capture Pathway Study concludes that a PC power plant utilizing advanced 2nd generation CO_2 capture membrane technology (Case 7A), or advanced sorbent technology (Case 8A) coupled with advanced CO_2 compression, could meet the DOE/NETL cost goal if the actual performance and cost factors for these technologies can achieve their assumed enhanced levels and additional enhancements to the power plant steam turbine and/or fan efficiencies can be realized.
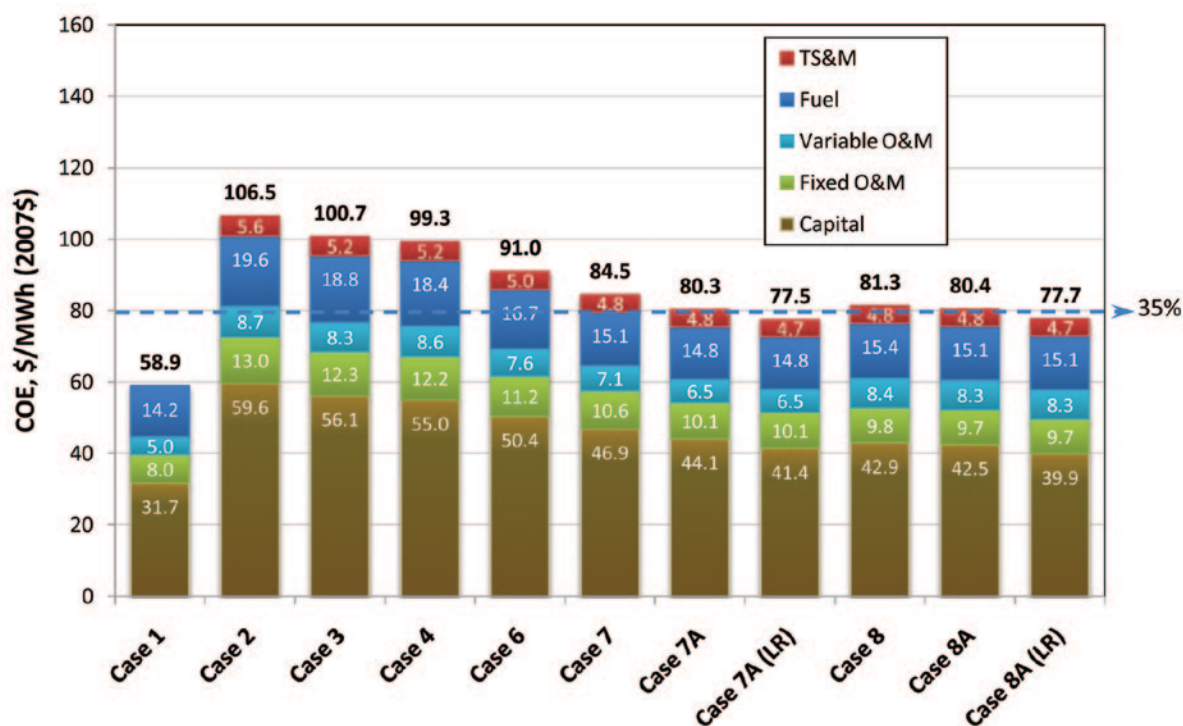
Figure 12-7: First Year COE for Cases in Post-Combustion Capture Pathway Study

Oxy-Combustion Capture Pathway Study

The Oxy-Combustion Capture Pathway Study is expected to be completed later in 2011. The cost and performance data presented here are taken from a preliminary draft of the study and are subject to change. The objective of this pathway study is to guide oxy-combustion R&D in areas that can provide the largest benefits in COE and plant performance. The advanced oxy-combustion technologies evaluated in this study are categorized into four major areas: advanced boiler design; advanced oxygen production; advanced flue gas treatment; and innovative CO_2 compression concepts.

The pathway study includes an analysis of eight advanced technologies that were anticipated to improve oxy-combustion cost and performance. In all, the report covers nine cases: eight cases employing advanced 2nd generation oxy-combustion technologies and a reference case employing what is considered to be current 1st generation oxy-combustion technology. A description of these cases is summarized in Table 12-5.

Each of the advanced oxy-combustion cases are modeled as new, commercial-scale plants projected to be designed and built in the 2030 timeframe. These advances are compared to what is considered to be current technology: a supercritical oxy-combustion boiler equipped with a state-of-the-art cryogenic distillation ASU, a wet FGD unit, and a conventional CO_2 purification/compression system.

Table 12-5: Case Descriptions for Oxy-Combustion Capture Pathway Study

Case	Boiler Technology psig/°F/°F	Advanced PC Concept	Coal Type	Oxidant	Sulfur Removal
Base	Supercritical PC 3,500/1,100/1,100	Current oxy-combustion (1st generation)	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
1	Supercritical PC 3,500/1,100/1,100	ITM with boiler integration	Illinois No. 6	~100% Oxygen/ITM	Wet FGD
1a	Supercritical PC 3,500/1,100/1,100	ITM with natural gas preheater	Illinois No. 6	~100% Oxygen/ITM	Co-capture
2	Chemical looping	Covered in a separate study	—	—	—
3	Ultra-supercritical PC 4,000/1,350/1,400	Advanced materials for ultra-supercritical conditions	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
4	Supercritical PC 3,500/1,100/1,100	Co-sequestration	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
5	Supercritical PC 3,500/1,100/1,100	Advanced recycle	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
6	Supercritical PC 3,500/1,100/1,100	Advanced CO_2 compression	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
7	Supercritical PC 3,500/1,100/1,100	Oxy-combustion boiler	Illinois No. 6	95% Oxygen/ Cryogenic ASU	Wet FGD
Cumulative	Ultra-supercritical PC 4,000/1,350/1,400	Cumulative Case	Illinois No. 6	~100% Oxygen/ITM	Co-capture

The advanced oxy-combustion technologies studied were evaluated to determine if they could meet the DOE/NETL cost goal. The COE of the advanced technology cases were compared to the COE of an air-fired, supercritical boiler with no CO_2 capture. The results are shown in Figure 12-8 and Table 12-6. Although none of the advanced technologies currently meet the DOE/NETL goal individually, the combined effect of including all advanced technologies in the same plant is shown to exceed the DOE/NETL goal.
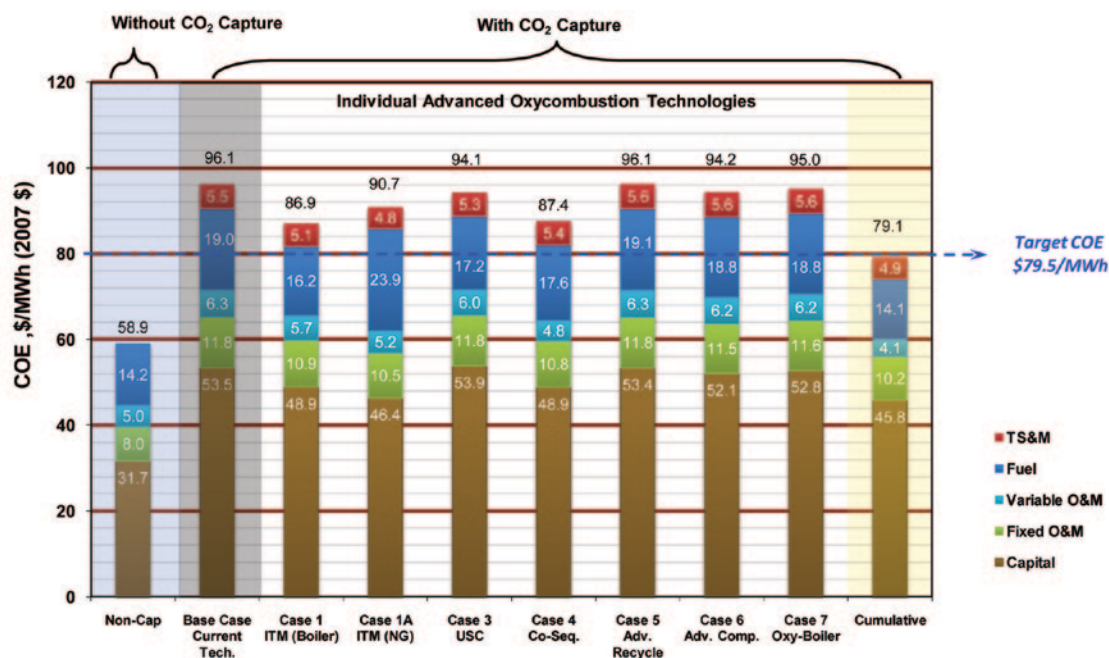

Figure 12-8: First Year COE for Cases in Oxy-Combustion Capture Pathway Study

Table 12-6: Percent Increase in COE for Cases in Oxy-Combustion Capture Pathway Study

Study Case	Cost of Electricity, $/MWh (2007 $)						Increase in COE (%)*
	Capital	Fixed O&M	Variable O&M	Fuel	TS&M	Total	
Non-Capture Reference, Air-fired supercritical w/o CCS	31.68	7.97	5.03	14.22	0.00	58.90	-
Current OF Technology, O₂-fired supercritical w/ASU & CCS	53.45	11.76	6.32	19.05	5.52	96.11	63.2
Case 1, O₂-fired supercritical w/ Boiler ITM &CCS	48.93	10.89	5.73	16.20	5.15	86.90	47.5
Case 1A, O₂-fired supercritical w/NG ITM & CCS	46.38	10.45	5.17	23.90	4.82	90.74	54.1
Case 3, O₂-fired ultra-supercritical w/ASU & CCS	53.88	11.76	5.99	17.20	5.27	94.10	59.8
Case 4, O₂-fired supercritical w/ASU & Co-Sequestration	48.87	10.80	4.77	17.62	5.37	87.42	48.4
Case 5, O₂-fired supercritical w/ASU, Wet Recycle & CCS	53.40	11.75	6.33	19.07	5.60	96.15	63.2
Case 6, O₂-fired supercritical w/ASU & Shock Compression	52.13	11.52	6.20	18.78	5.56	94.19	59.9
Case 7, O₂-fired supercritical w/ASU, Adv. Boiler & CCS	52.83	11.58	6.18	18.83	5.57	94.99	61.3
Cumulative Technology Case	**45.84**	**10.17**	**4.08**	**14.06**	**4.90**	**79.05**	**34.2**

*Relative to non-capture reference case

The major conclusions of this study uncover how future R&D should focus on developing oxy-combustion-specific technologies for the most beneficial improvements in performance and cost. While the Cumulative Case has been shown to meet the DOE/NETL CO_2 capture cost goal, none of the advanced technologies are yet ready for commercial implementation and require substantial RD&D before they can be considered viable solutions for CO_2 capture. The results of this study suggest that both cost and performance improvements need to be made in multiple technologies applicable to the oxy-combustion pathway for CO_2 capture to meet DOE/NETL's CO_2 capture goals. Improvements in the following technologies should have the largest positive impact on oxy-combustion:

- *Oxygen Supply:* Advanced ITM air separation technology shows promise due to its high temperature and high pressure operation, which allows for a relatively large amount of heat and power recovery. ITM system integration, membrane performance enhancements, and capital cost reduction should be the main areas of focus based on the results of this study.

- *Sulfur-Tolerant Materials:* Research should be conducted to develop sulfur-tolerant materials to handle the recycled flue gas in systems with reduced FGD. It is understood that completely eliminating the FGD may not be possible in the near-term because of materials constraints, however if continual progress is made in this area, system efficiency will continue to increase in proportion.

- *Oxy-Combustion Boilers:* As sulfur-tolerant materials are developed, smaller oxy-combustion-based boiler designs with enhanced heat transfer may become more effective. Sulfur-tolerant materials will allow less recycle, less FGD requirements, and therefore higher efficiencies all while decreasing the boiler size, and potentially cost depending on the premium for exotic material.

- *Advanced Steam Conditions:* While not specific to oxy-combustion, raising steam conditions in the Rankine cycle also has a beneficial effect on oxy-combustion systems, as might be expected. The oxy-combustion cycle appears to impose no direct limitations on the steam conditions that can be applied. However, advanced steam conditions should be taken into consideration when designing advanced oxy-combustion-specific boiler designs.

In summary, the Oxy-Combustion Capture Pathway Study suggests that a diverse portfolio of oxy-combustion-based technologies should be included in RD&D plans for government, industrial, and academic entities as a means to drive down costs and improve the performance of CO_2 capture.

12.E INTEGRATED ENVIRONMENTAL CONTROL MODEL

The Integrated Environmental Control Model (IECM) provides electric utility companies, equipment suppliers, government agencies, researchers, and policy analysts with an easy-to-use tool for estimating the performance, emissions, and cost of alternative fossil fuel power plant configurations and emission control technology scenarios. IECM is a user-friendly desktop/laptop modeling tool developed by Carnegie Mellon University (CMU) with support from DOE/NETL to provide fast, reliable estimates of the performance, emissions, and cost of a variety of conventional and advanced fossil fuel power plants (PC, IGCC, and NGCC) whose design is specified by the model user drawing from a large menu of technology options for controlling emissions of SO_2, NO_X, PM, Hg, and CO_2. The model can be used as a screening model for evaluating advanced process designs for CO_2 capture to provide systematic estimates of the plant-level performance, costs, and environmental emissions.

IECM incorporates a variety of technology options for pre-, post-, and oxy-combustion CO_2 capture. Carbon dioxide capture process options incorporated in IECM include an amine-based chemical absorption system for post-combustion capture on PC and NGCC plants and a sorbent-based physical absorption system for pre-combustion capture at IGCC plants. The oxy-combustion plant option produces a concentrated CO_2 stream using oxygen rather than air for combustion in a PC plant, with recycle of the CO_2-rich flue gas. Additional options under development include advanced power system components and CO_2 capture technologies promising lower costs. To simulate a complete CCS system, the costs of CO_2 transport and storage also are included in the modeling framework.

Figure 12-9 shows a schematic of the IECM inputs, outputs, and internal structure. A graphical user interface allows the model to be easily used to configure a plant design of interest, set values for key parameters, and get results in tabular or graphical form. Input parameters can be adjusted to represent either current technology or advanced, high-performance designs. The probabilistic capability of IECM allows uncertainties in performance and cost results to be quantified, enabling more rigorous assessments of technological risks and benefits. IECM is fully supported, documented, updated periodically, and available free online at: http://www.cmu.edu/epp/iecm/index.html
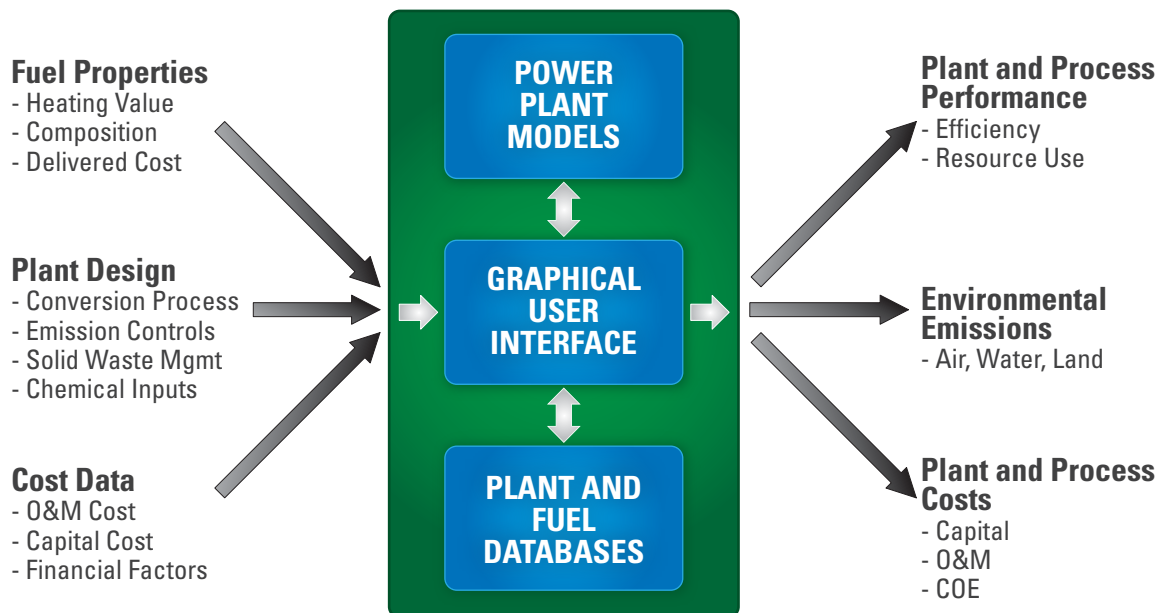

Figure 12-9: Structure of the IECM Modeling Environment

CHAPTER 13:
CARBON DIOXIDE CAPTURE R&D COLLABORATIONS

DOE/NETL also participates in collaborations with other organizations that include R&D projects that are exploring multiple approaches to CO_2 capture for coal-based power plants. These R&D collaborations include the University of North Dakota Energy and Environmental Research Center (UNDEERC), Southern Company, CANMET Energy Technology Center, DOE's Advanced Research Projects Agency-Energy, and DOE's Energy Frontier Research Centers. In addition, DOE/NETL also provides grants to small businesses and universities through programs that support fossil energy research, including advanced CO_2 capture technology development. The following is a brief summary of each of these R&D programs.

13.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.

13.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.

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

DOE/NETL 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, AL. 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 is capable of testing pre-, post-, and oxy-combustion technologies.

The backbone of the pre-combustion CO_2 capture technology development is a high-pressure flexible facility designed to test an array of solvents and contactors (Figure 13-1). Slipstreams are 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.

The existing transport reactor for IGCC applications at the PSDF can also 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 are being used to evaluate the commercial feasibility of operating the transport combustor in oxy-combustion mode.

Advanced solvents, sorbents, membranes and other emerging technologies can be tested in the PSDF-NCCC post-combustion module. For both new and existing power plants, post-combustion capture technology must be made

Power Systems Development

more efficient and cost-effective, e.g., by developing alternative solvents with lower heats of regeneration and more compact, lower cost equipment. A flexible test module provides a site for testing technologies at a wide-range of sizes and process conditions on coal-derived flue gas. The PSDF-NCCC provides several parallel paths in order to test the candidate processes at the appropriate scale (Figure 13-2). For R&D projects that have been successfully tested at bench-scale in a research lab, the PSDF-NCCC provides 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 provides 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.
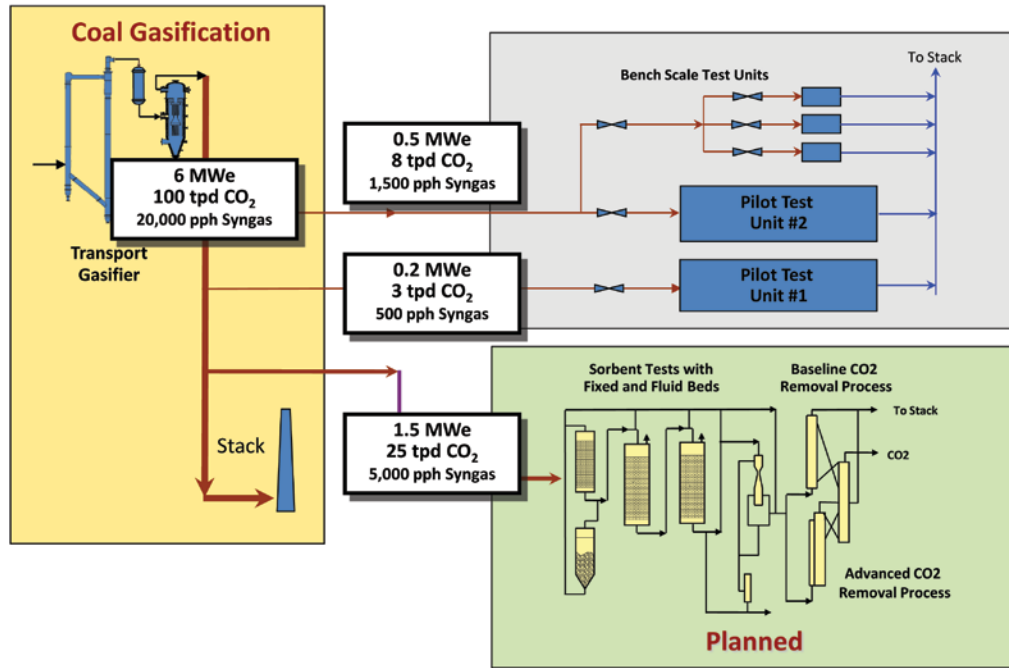

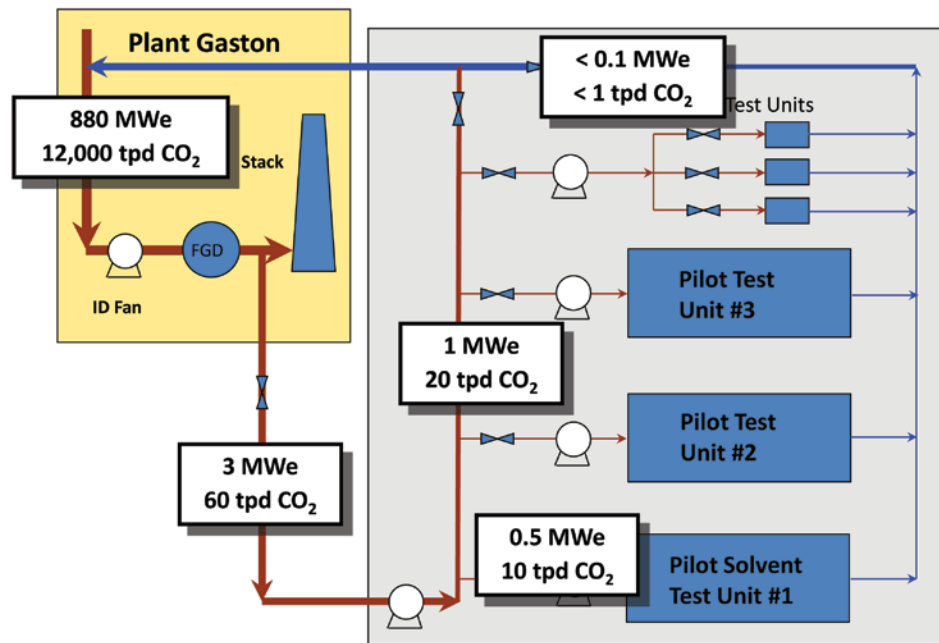Figure 13-1: NCCC Pre-Combustion CO_2 Capture Slipstream Test Units

Figure 13-2: NCCC Post-Combustion CO_2 Capture Slipstream Test Units

13.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.

13.E ADVANCED RESEARCH PROJECTS AGENCY-ENERGY

NETL has been collaborating with DOE's Advanced Research Projects Agency-Energy (ARPA-E) that provides high risk, high reward research on CO_2 capture technology under its Innovative Materials and Processes for Advanced Carbon Capture Technologies (IMPACCT) Program. ARPA-E was organized in 2007 as the energy equivalent to the Department of Defense's Defense Advanced Research Projects Agency (DARPA). One of ARPA-E's objectives is to advance creative "out-of-the-box" transformational energy research that industry by itself cannot or will not support due to its high risk, but where success would provide dramatic benefits for the Nation.

ARPA-E complements existing DOE/NETL efforts by accelerating promising ideas early in the technology development pipeline. The IMPACCT program seeks to significantly reduce the cost of CO_2 capture through a combination of new materials, improvements to existing processes, and demonstration of new capture processes. Areas of interest include: catalysts/solvents, chemical looping, membranes, phase change materials, and sorbents. Table 13-1 provides a summary of ARPA-E's current CO_2 capture-related R&D projects.

Table 13-1: ARPA-E IMPACCT Program CO_2 Capture R&D Projects

Project Focus	Participant	Project Focus	Participant
Biocatalyst for Acceleration of Solvents	Codexis, Inc.	Bio-Mimetic Catalysts	Lawrence Livermore National Laboratory
Solvent/Membrane Hybrid	University of Kentucky, Center for Applied Energy Research	MOF Polymer Composite Membranes	Georgia Tech
Metal-Organic Frameworks	Lawrence Berkeley National Laboratory	Gelled Ionic Liquid-Based Membranes	University of Colorado, Boulder
Ionic Liquids Involving Phase Change	University of Notre Dame	Inertial CO_2 Extraction System (ICES)	ATK
Cryogenic Carbon Capture	Sustainable Energy Solutions	Carbon Nanotube Membranes	Porifera, Inc.
Chemical and Biological Catalytic Enhancement of Weathering of Silicate Minerals	Columbia University	Enzyme Synthetic Analogue	United Technologies Research Center
Organic Liquids	RTI International	Resin Wafer Electrodeionization	Nalco Company
Metal-Organic Frameworks	Texas A&M University	Electric Field Swing Adsorption (EFSA)	Lehigh University
Electrochemically Mediated Separation	Massachusetts Institute of Technology	Syngas Chemical Looping Process	Ohio State University
Phase Changing Absorbents	GE Global Research	Ionic Liquid-Impregnated Hollow Fibers	Oak Ridge National Laboratory

Additional information on ARPA-E can be found at:
http://arpa-e.energy.gov/ and http://arpa-e.energy.gov/ProgramsProjects/IMPACCT.aspx

13.F DOE ENERGY FRONTIER RESEARCH CENTERS

In August 2009, DOE's Office of Basic Energy Sciences established 46 Energy Frontier Research Centers (EFRC). These Centers involve universities, national laboratories, nonprofit organizations, and for-profit firms, singly or in partnerships, and were selected by scientific peer review and funded at $2–5 million per year per Center for a 5-year initial award period. The Centers are conducting fundamental research in technical areas identified in major strategic planning efforts by the scientific community. The purpose of the EFRC is to integrate the talents and expertise of leading scientists in a setting designed to accelerate research toward meeting critical U.S. energy challenges.

The University of California, Berkeley is the lead institution for the Center for Gas Separations Relevant to Clean Energy Technologies, which is conducting research on CO_2 capture. The research focus is developing new strategies and materials for selective gas capture and separation based on molecule-specific chemical interactions in the following areas:

Materials Synthesis – The synthesis of new gas-permeable materials with control over the molecular functionalities that have contact with gas molecules is essential. The focus here is on: (1) generating metal-organic frameworks exhibiting high internal surface areas (up to 4,800 m²/g), and surfaces lined with robust and tailorable chemical groups; and (2) self-assembled polymer films with synthetic or biomimetic functional units.

Materials Characterization – Detailed atomic-level structural characterization of the new materials is necessary both before and after exposure to gas samples in order to probe hypotheses on interaction mechanisms. In addition, accurate means of assessing the selectivity, kinetics, and thermodynamics of gas adsorbate binding is needed to demonstrate efficacy and test computational models.

Computational Separations – A strong computational component to the research is essential for understanding the chemical interactions at a molecular level, as well as for guiding the synthetic efforts toward materials exhibiting high specificity and tunable interaction energies.

Additional information on EFRC can be found at:
http://www.er.doe.gov/bes/EFRC/index.html and http://www.cchem.berkeley.edu/co2efrc/

13.G CARBON CAPTURE SIMULATION INITIATIVE

The DOE's Carbon Capture Simulation Initiative (CCSI) is a partnership among national laboratories, industry and academic institutions that will develop and deploy state-of-the-art computational modeling and simulation tools to accelerate the commercialization of CO_2 capture technologies. The CCSI will provide end users in industry with a comprehensive, integrated suite of scientifically validated models, with uncertainty quantification, optimization, risk analysis and decision making capabilities. The CCSI will incorporate commercial and open-source software currently in use by industry and will also develop new software tools as necessary to fill technology gaps identified during the project. The goals of the CCSI R&D effort include:

- Enable promising concepts to be more quickly identified through rapid computational screening of devices and processes.
- Reduce the time to design and troubleshoot new devices and processes.
- Quantify the technical risk in taking technology from laboratory-scale to commercial-scale.
- Stabilize deployment costs more quickly by replacing some of the physical operational tests with virtual power plant simulations.
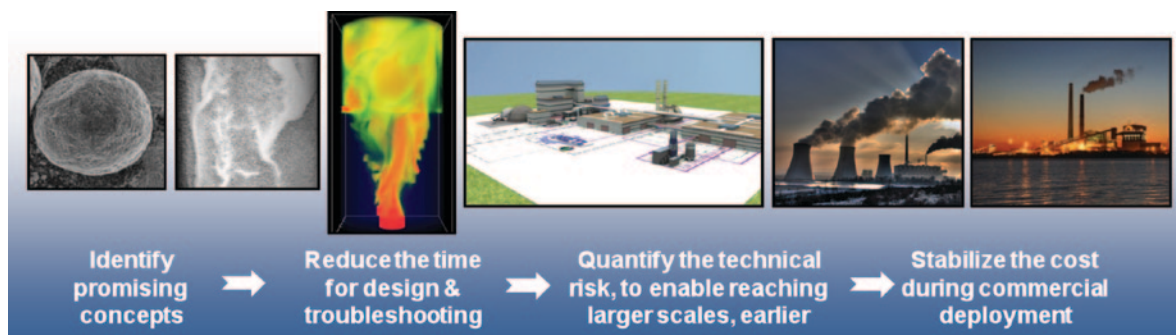

Figure 13-3: Carbon Capture Simulation Initiative

CCSI brings together expertise from NETL, Los Alamos National Laboratory (LANL), Lawrence Berkeley National Laboratory (LBNL), Lawrence Livermore National Laboratory (LLNL), and Pacific Northwest National Laboratory (PNNL) and is organized into 10 task sets that fall under three focus areas. The first focus area—Physicochemical Models and Data—addresses the steps necessary to model and simulate the various technologies and processes needed to bring a new CO_2 capture technology into production. The second focus area—Analysis and Software—is developing the software infrastructure to integrate the various components and implement the tools that are needed to make quantifiable decisions regarding the viability of new CO_2 technologies. The final focus area—Industrial Applications—ensures the strength of the industry partnerships. By working closely with industry from the inception of the project to identify industrial challenges, CCSI ensures that the simulation tools are developed for the CO_2 capture technologies of most relevance to industry.

13.H SMALL BUSINESS AND UNIVERSITY CO$_2$ CAPTURE R&D EFFORTS

In addition to the relatively larger contracted and on-site CO_2 capture R&D efforts highlighted in this report, DOE/NETL also provides grants to small businesses and universities through three programs that support fossil energy research, including advanced CO_2 capture technology development. Table 13-2 provides a summary of some of the recent and current CO_2 capture-related projects conducted under these programs.

Small Business Innovation Research and Small Business Technology Transfer Programs

Small Business Innovation Research (SBIR) and Small Business Technology Transfer (STTR) are U.S. Government programs in which Federal agencies with large R&D budgets set aside a small fraction of their funding for competitions among small businesses only. Small businesses that win awards in these programs keep the rights to any technology developed and are encouraged to commercialize the technology. The SBIR program was established to provide funding to stimulate technological innovation in small businesses to meet Federal agency R&D needs. STTR projects must involve cooperative research collaboration between the small business and a non-profit research institution. SBIR and STTR have three distinct phases. Phase I explores the feasibility of innovative concepts with awards up to $100,000 for about 9 months. Only Phase I award winners may compete for Phase II, the principal R&D effort, with awards up to $750,000 over a two-year period. There is also a Phase III, in which non-Federal funding is used by the small business to pursue commercial applications of the R&D. Also under Phase III, Federal agencies may award non-SBIR/STTR-funded, follow-on grants or contracts to continue the R&D effort. Additional information on DOE's participation with the SBIR/STTR programs can be found at: http://www.sc.doe.gov/sbir/

University Coal Research Program

DOE encourages greater university participation in its fossil energy R&D effort through the University Coal Research (UCR) program. DOE sets aside funding for a special university-only competition that requires professors to conduct cutting-edge research alongside students who are pursuing advanced degrees in engineering, chemistry and other technical disciplines. Through the UCR program, not only do new discoveries in energy science and technology emerge from the universities, but also a new generation of scientists and engineers with hands-on experience in coal-related research enter the workforce. The number of grants awarded varies depending on the size of each award and the amount of the year's appropriation. Typically between $2.4 million and $5 million is available annually under the entire UCR program. Private companies also provide funding to help leverage Federal dollars in some of these projects. Additional information on DOE/NETL's participation with the UCR program can be found at: http://fossil.energy.gov/programs/powersystems/advresearch/advresearch-university.html

Historically Black Colleges and Universities and Other Minority Institutions Program

DOE also provides R&D grants through the Historically Black Colleges and Universities and Other Minority Institutions (HBCU/OMI) program to expand learning opportunities for university students and increase collaborative efforts between minority students and the fossil fuel industry. The goal of the HBCU/OMI program is to enhance research methods and capabilities of minority institutions that can help expand diversity for future generations of energy scientists and engineers. Annual competitions are held with about $1 million made available each year for research and training at these institutions under the entire HBCU/OMI program. Research proposals can span virtually the entire spectrum of fossil fuel topics. Recently, the focus has been on sensors and controls; computational energy sciences; and advanced materials for power generation and for hydrogen separation and storage. Additional information on DOE/NETL's participation with the HBCU/OMI program can be found at: http://fossil.energy.gov/programs/powersystems/advresearch/advresearch-university.html

Table 13-2: Small Business and University CO$_2$ Capture R&D Efforts

Grant Program	CO$_2$ Capture R&D Area	Project Title	Participant	Project Number
SBIR	Pre-Combustion Solvent	Field Demonstration of CO$_2$ Capture from Coal-Derived Syngas	Membrane Technology and Research, Inc.	FE0006138
SBIR	Pre-Combustion Membrane	Molecular Separations Using Micro-Defect Free Ultra Thin Films	Eltron Research, Inc.	ER85353
SBIR	Pre-Combustion Novel	A High Efficiency Integrated Syngas Purification and Hydrogen Separation and Storage System	ACENT Laboratories, LLC	ER85249
SBIR	Post-Combustion Solvent	Regeneration Study of Phase Transitional Absorption for CO$_2$ Cpature from Post Combustion Flue Gas	3H Company, LLC	SC0001440
SBIR	Post-Combustion Solvent	Advanced Amine Solvent Formulation and Process Integration for Near-Term CO$_2$ Capture Success	Trimeric Corporation	ER84625
SBIR	Post-Combustion Solvent	A Low-Energy, Low-Cost Process for Stripping Carbon Dioxide from Absorbents	AIL Systems, Inc.	ER84592
SBIR	Post-Combustion Sorbent	Superhydrophobic Aerogel as Sorbent Material for CO$_2$ Capture	Aspen Aerogels, Inc.	SC0004289
SBIR	Post-Combustion Sorbent	Development of Nobel Sorbent for CO$_2$ Capture	Shakti Technologies	SC0002427
SBIR	Post-Combustion Sorbent	Carbon Dioxide Recovery from Flue Gas Using Carbon-Supported Amine Sorbents	Advanced Fuel Research, Inc.	ER83885
SBIR	Post-Combustion Membrane	Carbon Dioxide Capture from Large Point Sources	Compact Membrane Systems, Inc.	ER83925
SBIR	Oxygen Production	A Novel Oxygen Separation Membrane for Oxygen Production	Enogetek, Inc.	ER84667
SBIR	Oxygen Production	Novel Air Separation for Oxy-Combustion Process	TDA Research, Inc.	ER84677
SBIR	Oxygen Production	Sorbents for Air Separation	TDA Research, Inc.	ER84216
SBIR	Oxygen Production	Novel Supports and Materials for Oxygen Separation and Supply	Eltron Research, Inc.	ER84600.002
STTR	Post-Combustion Sorbent	Capture of CO$_2$ by Hybrid Sorption (CACHYS) for Existing Coal-Fired Plants	Envergex, LLC and University of North Dakota	SC0004476
STTR	Post-Combustion Membrane	Ceramic Membranes for CO$_2$ Capture from Existing Coal-Fired Power Plants	NexTech Materials, Ltd. and The Ohio State University Research Foundation	SC0004228
UCR	Pre-Combustion Sorbent	Computational Fluid Dynamic Simulations of a Regenerative Process for CO$_2$ Capture in Advacned Gasification Based Power Systems	Illinois Institute of Technology	FE0003997
UCR	Pre-Combustion Membrane	Novel Zeolitic Imidazolate Framework/Polymer Membranes for Hydrogen Separations in Coal Processing	University of Texas at Dallas	NT0007636
UCR	Post-Combustion Membrane	Dual-Phase Inorganic Membranes for High Temperature Carbon Dioxide Separation	Arizona State University	NT41555
UCR	Chemical Looping	Process/Equipment Co-Simulation on Syngas Chemical Looping Process	Ohio State University Research Foundation	NT0007428
HBCU	Post-Combustion Solvent	CO$_2$ Capture From Flue Gas by Phase Transitional Absorption	Hampton University	NT42488
HBCU	Oxygen Production	Development of Nanofiller-Modulated Polymeric Oxygen Enrichment Membranes	North Carolina A&T State University	NT42742

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