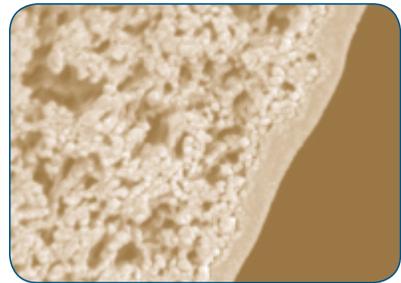
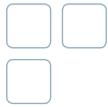


DOE/NETL ADVANCED CARBON DIOXIDE CAPTURE R&D PROGRAM: TECHNOLOGY UPDATE

MAY 2013



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CAPTURE R&D PROGRAM:
TECHNOLOGY UPDATE
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MESSAGE TO STAKEHOLDERS

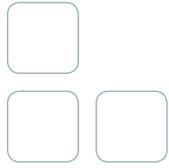
This is the third edition of the *DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update*. The first edition was published in September 2010, and the second in May 2011. This edition of the report includes expanded descriptions of the carbon dioxide (CO₂) capture research and analyses being conducted internally by the National Energy Technology Laboratory's (NETL) Office of Research and Development (ORD) and Office of Program Planning & 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 2 years. The Appendix has also been expanded to include fact sheets for new external projects that were initiated after the May 2011 edition was published. Future editions of this report are planned to be published every other year.

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 CO₂ 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 CO₂ capture technologies. In addition, DOE/NETL is conducting technical-economic analyses to establish the baseline cost and performance for current CO₂ capture technologies and determine the feasibility of advanced capture and compression technologies.

The goals for the Carbon Capture Program call for the development of 2nd-Generation technologies that are ready for large-scale testing in 2020 and Transformational technologies that are ready for large-scale testing in 2030. For capture technologies applied to new power plants, the program goals are to contribute to a capture cost of less than \$40/tonne of CO₂ captured for 2nd-Generation technologies and less than \$10/tonne of CO₂ captured for Transformational technologies. However, post-combustion capture technologies can also be applied to retrofit existing PC power plants.

The competitive advantage for retrofit applications is that they require only the incremental costs associated with CO₂ capture. The base plant is paid off. The program goals for post-combustion retrofits are to develop technologies that achieve less than \$45/tonne of CO₂ captured for 2nd-Generation technologies and less than \$30/tonne of CO₂ captured for retrofit Transformational technologies. Given the significant economic penalties associated with currently available CO₂ capture technologies, significant improvements in both cost and energy efficiency will be required to achieve these goals.

The purpose of this report is to provide an update on the R&D efforts of advanced CO₂ 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 CO₂ 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 CO₂ capture R&D program is included in Chapter 2. A brief discussion of the three basic configurations for CO₂ 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 CO₂ capture technologies and the fundamentals of CO₂ 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 CO₂ capture R&D collaborations. Appendix A contains fact sheets for DOE/NETL's large-scale demonstrations of currently available CO₂ 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 CO₂ capture technology R&D projects being conducted by external researchers.



CHAPTER 1:

INTRODUCTION

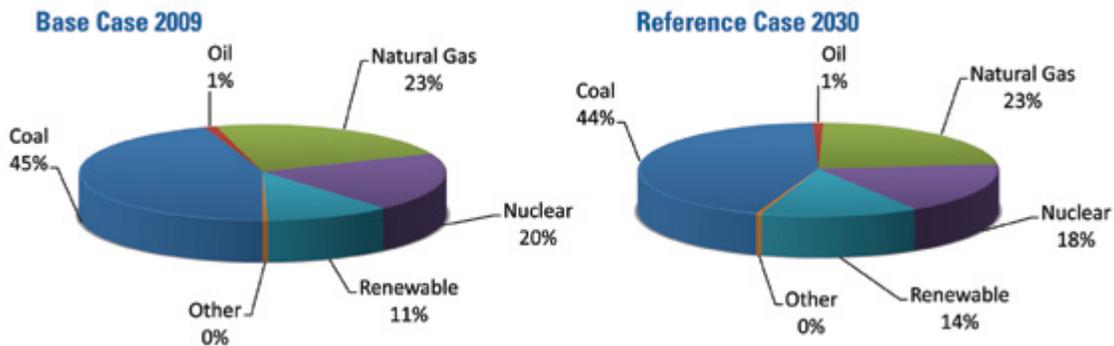


The purpose of this report is to provide an update on the R&D of advanced CO₂ capture technologies for coal-based power systems being conducted by DOE/NETL. While efforts are focused on capturing CO₂ from the flue gas or synthesis gas (syngas) of coal-based power plants, these capture technologies should be applicable to natural-gas and oil-fired power plants and other industrial CO₂ sources. Intended to be updated bi-annually, the report tracks the progress of DOE/NETL's CO₂ capture related technology developments. DOE/NETL's CO₂ 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 CO₂ capture R&D effort is available in companion documents outlining the Program Plans for the Carbon Capture, Advanced Combustion, Gasification, Carbon Storage, Fuel Cells, Turbines, and Crosscutting Research R&D programs that are available for download at:

- **Carbon Capture:**
<http://www.netl.doe.gov/technologies/coalpower/ewr/pubs/Program-Plan-Carbon-Capture-2013.pdf>
- **Advanced Combustion:**
<http://www.netl.doe.gov/File%20Library/Research/Coal/Combustion/Program-Plan-Adv-Comb-Systems-2013.pdf>
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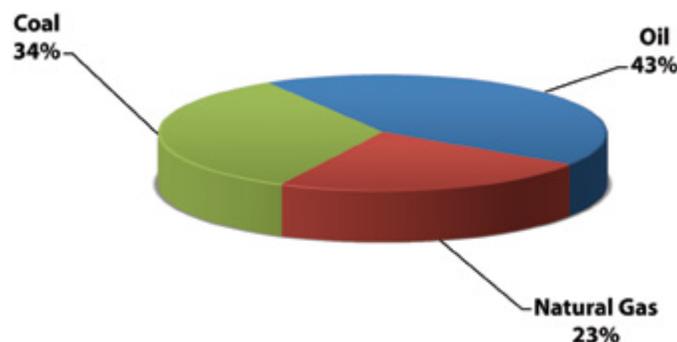


In 2009, coal-based power plants generated approximately 45 percent of the electricity in the United States (see Figure 1-1) and coal is expected to continue to play a critical role in powering the Nation's electricity generation for the foreseeable future. However, electricity production from coal-based power plants is under scrutiny due to concerns that anthropogenic emission of greenhouse gases (GHG), such as CO₂, are contributing to global climate change.

Figure 1-1: U.S. Electricity Generation by Fuel Type¹

Federal legislation and/or regulation could soon be enacted that would limit CO₂ 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 CO₂ emissions in 2009. Coal-based power plants consumed almost 1 billion tons of coal that produced 1.7 billion metric tons of CO₂ emissions, which comprised almost 32 percent of total U.S. anthropogenic CO₂ emissions. Figure 1-2 shows the source of U.S. anthropogenic CO₂ 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 CO₂ emissions projected to be released from today through 2030 will originate from existing coal-based power plants.¹ 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 CO₂ emissions from the power sector.

There are several options available to decrease CO₂ 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 CO₂ emission reductions from fossil-fueled power plants. The CCS process includes three primary steps: CO₂ capture; compression and transport; and storage. The three general categories of CO₂ 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 CO₂ capture will be discussed in more detail in Chapter 3. The captured CO₂ could be transported via pipeline or tanker car to a permanent storage site. The CO₂ 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. CO₂ Emissions by Fuel Type in 2009

There are commercially-available CO₂ 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 CO₂ 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.

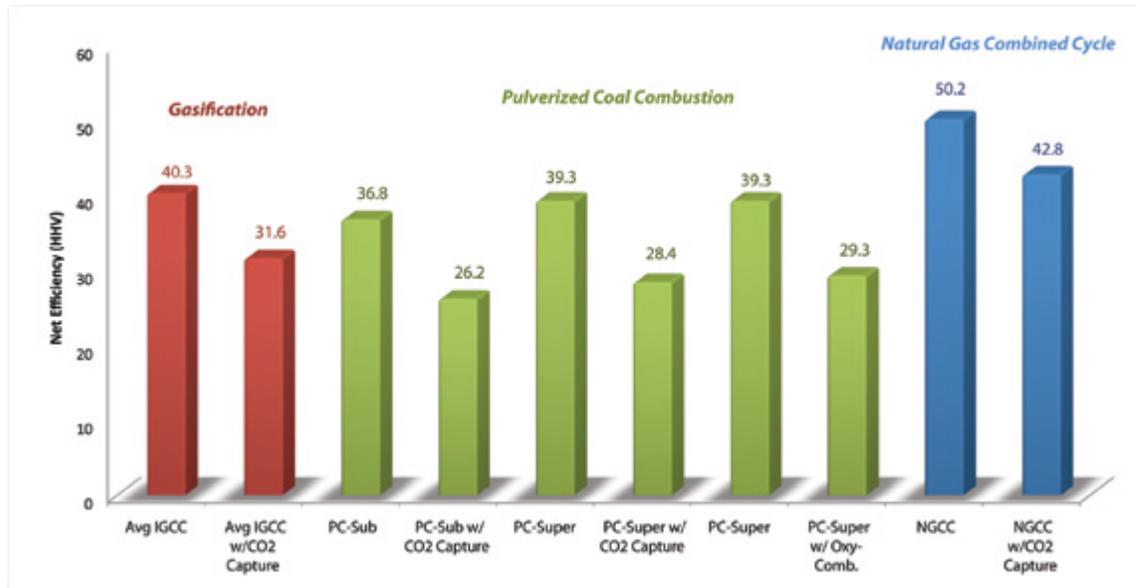


Figure 1-3: Net Plant Efficiency with and without CO₂ Capture and Compression

The net electrical output from a coal-based power plant employing currently available CO₂ 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 CO₂ 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 CO₂ capture and compression technologies on PC, IGCC, and natural gas combined cycle (NGCC) power plants.^{11, 12} Implementation of CO₂ 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 CO₂ capture.^{11, 12} For example, the COE for a new IGCC plant averages \$77/MWh without CO₂ capture, but increases approximately 45 percent to \$112/MWh with pre-combustion CO₂ capture. Likewise, the COE for a new PC plant averages approximately \$59/MWh without CO₂ capture, but increases over 80 percent to \$108/MWh with post-combustion CO₂ capture. Figure 1-4 also shows the cost of CO₂ capture in terms of avoided cost as measured by \$/tonne CO₂. The avoided cost is calculated by dividing the difference in COE, \$/MWh, by the difference in CO₂ emissions with and without CO₂ capture, tonne/MWh. Chapter 12 provides more detailed information on DOE/NETL systems analysis studies on the cost and performance of CO₂ capture technologies.

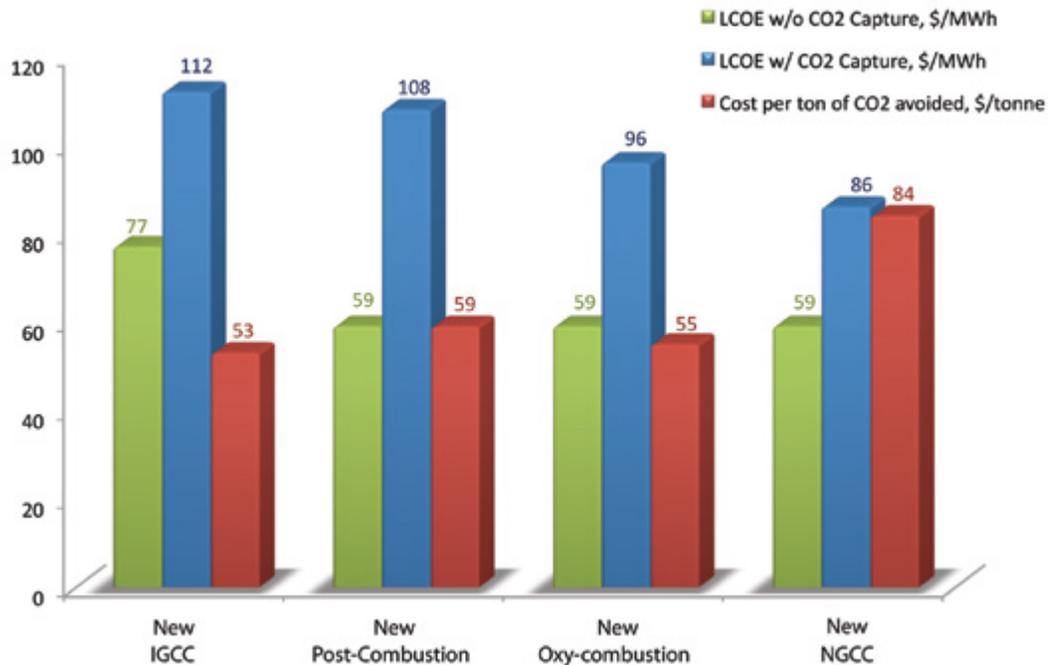


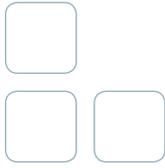
Figure 1-4: CO₂ Capture Costs for Different Types and Configurations of Power Plants

Other major technical challenges associated with the application of currently available CO₂ capture technologies to coal-based power plants include energy and mechanical integration, flue gas contaminants, water use, CO₂ compression, and oxygen (O₂) supply for oxy-combustion systems. Therefore, further R&D of CO₂ 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: CO₂ CAPTURE KEY TECHNICAL CHALLENGES

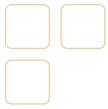
Parameter	Technical Challenge
Scale-Up	While industrial-scale CO ₂ separation processes are now commercially available, they have not been deployed at the scale required for large power plant applications.
Cost	Recent studies conducted by NETL and others show that current technologies are expensive. 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 as part of the CCS and Power Systems program under the overarching Clean Coal Research Program (CCRP). 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 CO₂ 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 CO₂ capture R&D effort.

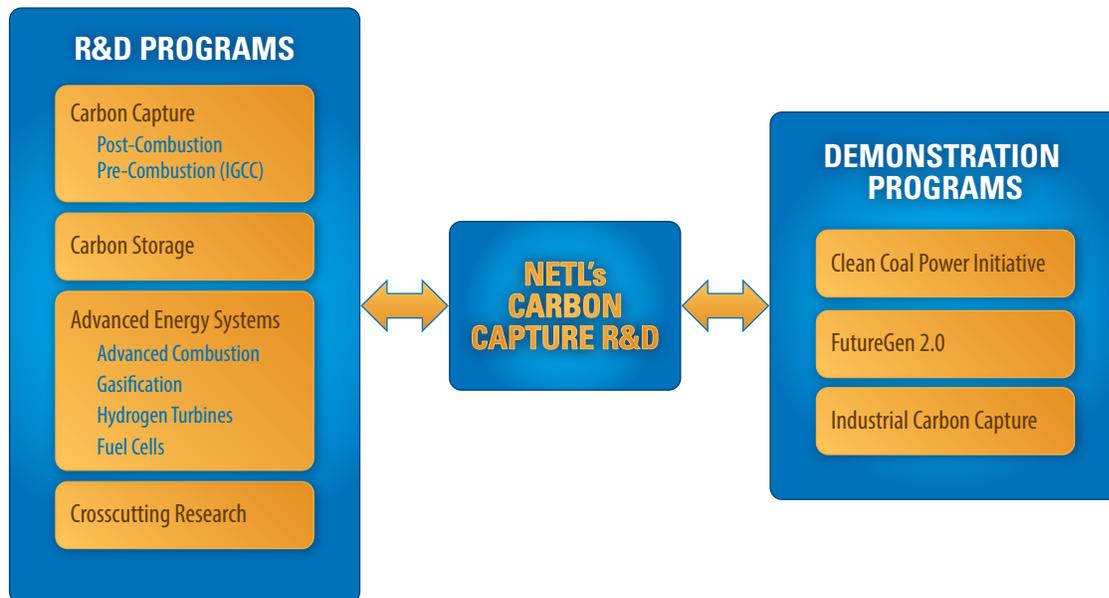


Figure 2-1: NETL Programs Associated with Carbon Capture R&D

The overall CCS and Power Systems program consists of four sub-programs: Carbon Capture; Carbon Storage; Advanced Energy Systems (AES); and Crosscutting Research. These four sub-programs are further divided into numerous elements. In several instances, the individual elements are further sub-divided into activities.

- The *Carbon Capture sub-program* is focused on the development of post-combustion and pre-combustion CO₂ capture technologies for new and existing power. Post-combustion CO₂ capture technology is applicable to conventional combustion-based power plants, while pre-combustion CO₂ capture is applicable to gasification-based systems. In both cases, R&D is underway to develop solvent-, sorbent-, and membrane-based capture technologies.
- The *Carbon Storage sub-program* advances safe, cost effective, permanent geologic storage of CO₂. The technologies developed and large-volume injection tests conducted through this sub-program will be used to benefit the existing and future fleet of fossil fuel power generating facilities by developing tools to increase our understanding of geologic reservoirs appropriate for CO₂ storage and the behavior of CO₂ in the subsurface.
- The *Advanced Energy Systems sub-program* is developing a new generation of clean fossil fuel-based power systems capable of producing affordable electric power while significantly reducing CO₂ emissions. This new generation of technology will essentially be able to overcome potential environmental barriers and meet any projected environmental emission standards. A key aspect of the Advanced Energy Systems sub-program is targeted at improving overall thermal efficiency, including the capture system, which will be reflected in affordable CO₂ capture and reduced cost of electricity (COE). The Advanced Energy Systems sub-program consists of four technology areas:
 - *Gasification Systems* research to convert coal into clean synthesis gas (syngas) that can in-turn be converted into electricity, chemicals, hydrogen, and liquid fuels to suit market needs.
 - *Advanced Turbines* research, focused on developing advanced technology for the integral electricity-generating component in a gasification-based clean energy plant fueled by hydrogen.

- *Advanced Combustion Systems* research that is focused on new high temperature materials and the continued development of oxy-combustion technologies.
- *Solid Oxide Fuel Cells* research, focused on developing large (>100 MW) fuel cell power systems that produce electric power from coal using integrated coal gasification.

The *Crosscutting Research sub-program* serves as a bridge between basic and applied research by fostering the R&D of instrumentation, sensors, and controls targeted at enhancing the availability and reducing the costs of advanced power systems. This sub-program area also develops computation, simulation, and modeling tools focused on optimizing plant design and shortening developmental timelines and other crosscutting issues, including plant optimization technologies, environmental and technical/economic analyses, coal technology export, and integrated program support.

The DOE/NETL programs discussed above primarily direct R&D activities that are conducted externally by other organizations. However, DOE/NETL also conducts internal CO₂ capture research and related studies. DOE/NETL's ORD is developing new breakthrough concepts for CO₂ 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 CO₂ capture technologies; track the cost and performance of new CO₂ 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.

The CCRP is pursuing three categories of CCUS and related technologies referred to as 1st Generation, 2nd Generation, and Transformational. These categories are defined in Figure 2-2.

1st-Generation Technologies—include technology components that are being demonstrated or that are commercially available.

2nd-Generation Technologies—include technology components currently in R&D that will be ready for demonstration in the 2020–2025 timeframe.

Transformational Technologies—include technology components that are in the early stage of development or are conceptual that offer the potential for improvements in cost and performance beyond those expected from 2nd-Generation technologies. The development and scaleup of these “Transformational” technologies are expected to occur in the 2016–2030 timeframe, and demonstration projects are expected to be initiated in the 2030–2035 time period.

Figure 2-2: CCS Technology Definitions

Currently, the CCRP is pursuing the demonstration of 1st-Generation CCS technologies with existing and new power plants and industrial facilities using a range of capture alternatives and storing CO₂ in a variety of geologic formations. In parallel, to drive down the costs of implementing CCS, the CCRP is pursuing RD&D to decrease the COE and capture costs and increase base power-plant efficiency, thereby reducing the amount of CO₂ that has to be captured and stored per unit of electricity generated. A portfolio of technology options is being developed to enable this country to continue to benefit from using our secure and affordable coal resources. The challenge is to help position the economy to remain competitive, while reducing carbon emissions.

There are a number of technical and economic challenges that must be overcome before cost-effective CCS technologies can be implemented. The experience gained from the sponsored demonstration projects focused on state-of-the-art (1st-Generation) CCS systems and technologies will be a critical step toward advancing the technical, economic, and environmental performance of 2nd-Generation and Transformational systems and technologies for future deployment. In addition, the core RD&D projects being pursued leverage public and private partnerships to support the goal of broad, cost-effective CCS deployment. The following long-term performance goals for new coal-fired power generation facilities have been established for the CCRP:

- Develop 2nd-Generation technologies that:
 - Are ready for demonstration in the 2020–2025 timeframe (with commercial deployment beginning in 2025)
 - Cost less than \$40/tonne of CO₂ captured

- Develop Transformational technologies that:
 - Are ready for demonstration in the 2030–2035 timeframe (with commercial deployment beginning in 2035)
 - Cost less than \$10/tonne of CO₂ captured

The goals differ slightly for retrofit applications. The competitive advantage for retrofits is that they require only the incremental costs associated with CO₂ capture. The base plant is paid off. The program goals for post-combustion retrofits are to develop technologies that achieve less than \$45/tonne of CO₂ captured for 2nd-Generation technologies and less than \$30/tonne of CO₂ captured for retrofit Transformational technologies.

THE R&D PROCESS – PROGRESS OVER TIME

The development of an advanced CO₂ 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 CO₂ compression system. Figure 2-3 presents the various R&D components that might be necessary to take a capture technology from concept to commercial reality. Developing a successful CO₂ 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 CO₂ 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 CO₂ capture technology.

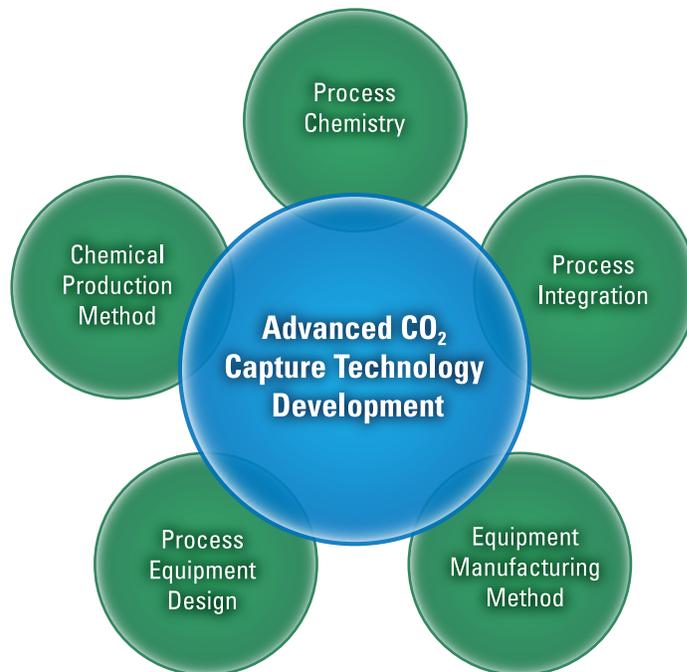


Figure 2-3: Components of CO₂ Capture Technology Development

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 (SO₂) 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 CO₂ Capture Technology Development

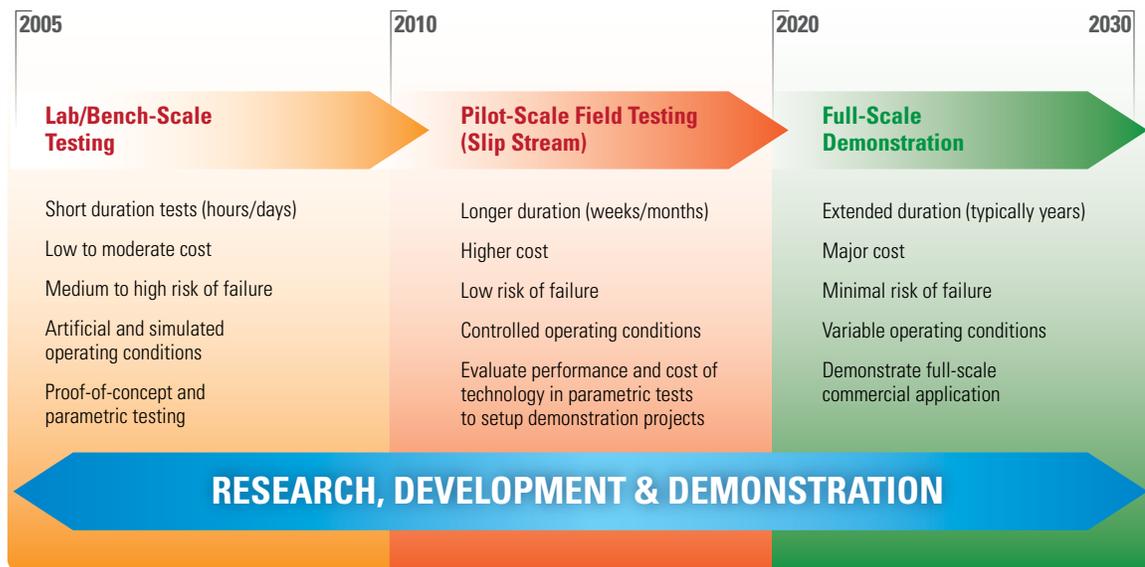


Figure 2-4: Stages of CO₂ Capture Technology R&D

Figure 2-4 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 CO₂ 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 CO₂ 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 CO₂ 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 one post-combustion and three pre-combustion CO₂ capture demonstration projects (see Table 2-1) designed to capture, compress, transport, and store the CO₂ in a saline formation or for beneficial reuse such as enhanced oil recovery. The pre-combustion projects involve CO₂ 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 project will capture CO₂ from a PC plant slipstream representing the equivalent of 240 MW of power production. In August 2010, DOE/NETL announced the selection of an oxy-combustion CO₂ 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				
NRG Energy	Thompsons, TX	Amine	1,400,000	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

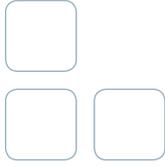
In addition to the demonstrations under the CCPI program, additional CO₂ capture demonstration projects are being conducted under the Industrial Carbon Capture and Storage (ICCS) program (See Table 2-2). Several of the ICCS projects are pursuing capture technologies that are similar to those that are 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

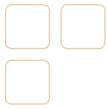
Appendix A includes the DOE/NETL fact sheets for the CCPI and ICCS projects. Additional information on the CCPI and ICCS projects can be found on the NETL website at: <http://www.netl.doe.gov/technologies/coalpower/cctc/index.html>

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



CHAPTER 3:

GENERAL APPROACHES TO CARBON DIOXIDE CAPTURE



There are three general approaches to CO₂ capture for fossil-fuel power plants—pre-, post-, and oxy-combustion. Pre-combustion systems are designed to separate CO₂ from hydrogen (H₂) and other constituents in the syngas stream produced by the gasifier in IGCC power plants. Post-combustion systems separate CO₂ from the flue gas stream produced by conventional PC power plants after fuel combustion in air. In this approach, CO₂ is separated from nitrogen (N₂), which is the primary constituent of the flue gas. Oxy-combustion separates O₂ from the N₂ in air prior to coal combustion, which results in a CO₂ concentrated flue gas stream.

DOE/NETL is investigating a broad portfolio of technology pathways based on all three approaches to CO₂ capture. Research efforts also address critical challenges to cost-effective commercial deployment including key enabling technologies such as O₂ 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 CO₂ 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 O₂. A simplified process schematic for pre-combustion CO₂ capture is shown in Figure 3-1. By carefully controlling the amount of O₂, only a portion of the fuel burns to provide the heat necessary to decompose the remaining fuel and produce syngas, a mixture of H₂ 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 CO₂ while producing additional H₂, thus increasing the CO₂ and H₂ concentrations. An acid gas removal system, such as Selexol™, can then be used to separate the CO₂ from the H₂. Because CO₂ is present at much higher concentrations in syngas (after WGS) than in flue gas, and because the syngas is at higher pressure, CO₂ capture should be easier and less expensive for pre-combustion capture than for post-combustion capture.

In addition, the volume of syngas that requires processing is much lower than the volume of flue gas from a comparable PC power plant, which results in smaller capture equipment sizes and lower capital costs. After CO₂ removal, the H₂ 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 H₂ to power fuel cells with significantly increased overall plant efficiency. The advantage of this type of system is the higher CO₂ 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 CO₂ capture technologies being investigated by DOE/NETL include the use of solvents, sorbents, and membranes. A more detailed description of pre-combustion CO₂ capture processes is provided in Chapter 4.

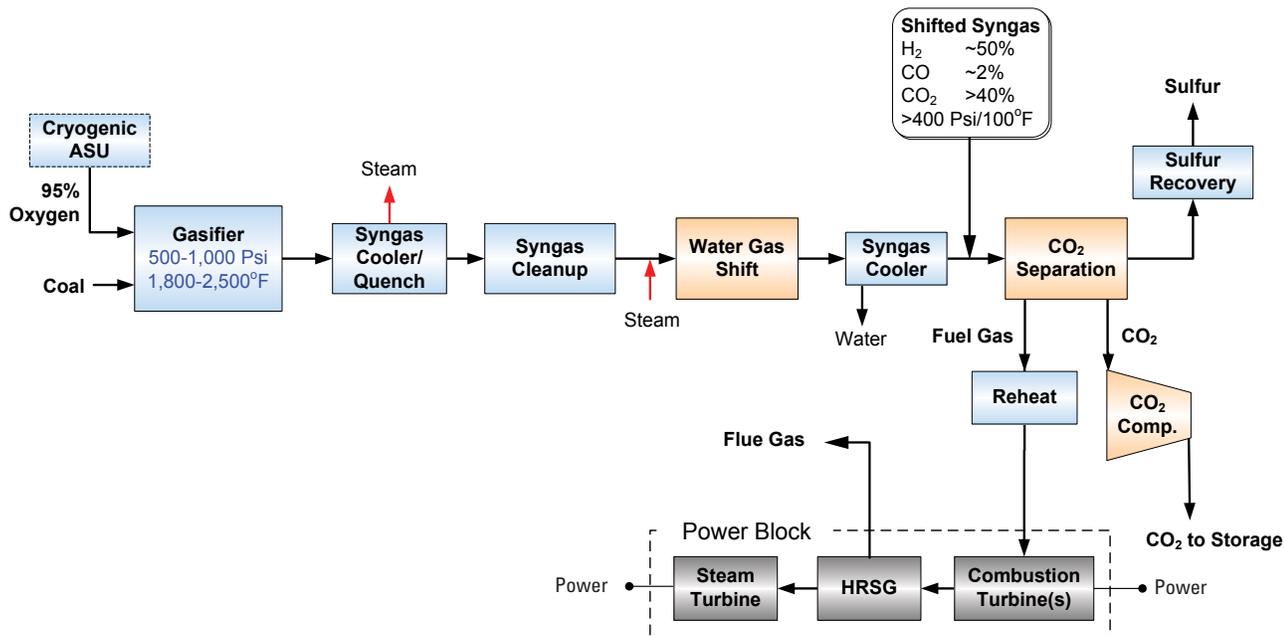


Figure 3-1: Block Diagram Illustrating an IGCC System with Pre-Combustion CO₂ Capture

3.B POST-COMBUSTION CO₂ CAPTURE

Post-combustion CO₂ capture refers to removal of CO₂ from combustion flue gas prior to discharge to the atmosphere. A simplified process schematic of post-combustion CO₂ 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 N₂ and CO₂. The CO₂ 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 CO₂ and regeneration of the solvent. Separating CO₂ from this flue gas is challenging for several reasons: a high volume of gas must be treated because the CO₂ 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 CO₂ capture materials; and compressing captured CO₂ from near atmospheric pressure to pipeline pressure (about 2,200 psia) requires a large auxiliary power load.

Post-combustion CO₂ capture offers the greatest near-term potential for reducing power sector CO₂ emissions because it can be retrofit to existing coal-based power plants and can also be tuned for various levels of CO₂ 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 CO₂ capture technologies being investigated by DOE/NETL include the use of solvents, sorbents, and membranes. A more detailed description of post-combustion CO₂ capture processes is provided in Chapter 4.

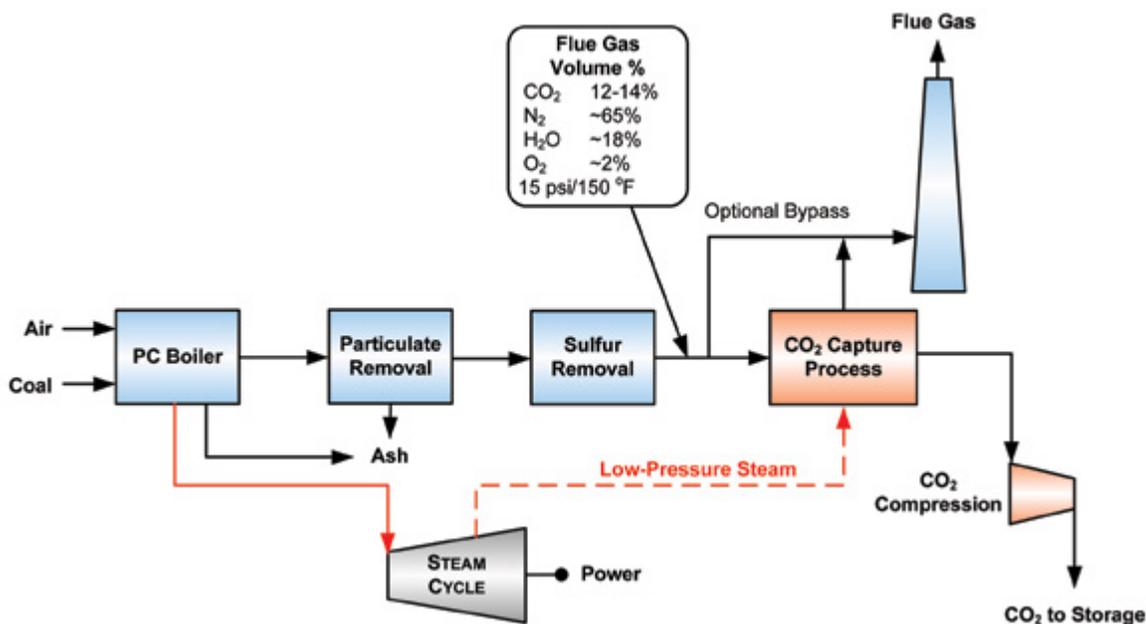


Figure 3-2: Block Diagram Illustrating a PC System with Post-Combustion CO₂ Capture

3.C OXY-COMBUSTION CO₂ CAPTURE

Oxy-combustion systems for CO₂ capture rely on combusting coal with relatively pure O₂ diluted with recycled CO₂ or CO₂/steam mixtures. Under these conditions, the primary products of combustion are water (H₂O) and CO₂ (~60 percent), with the CO₂ separated by condensing the H₂O through cooling and compression (see Figure 3-3).

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 CO₂ flue gas may be necessary to remove other minor gas constituents such as N₂, O₂, and argon in order to produce a CO₂ 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 CO₂

concentration and reduced flue gas volume. A more detailed description of oxy-combustion is provided in Chapter 4.

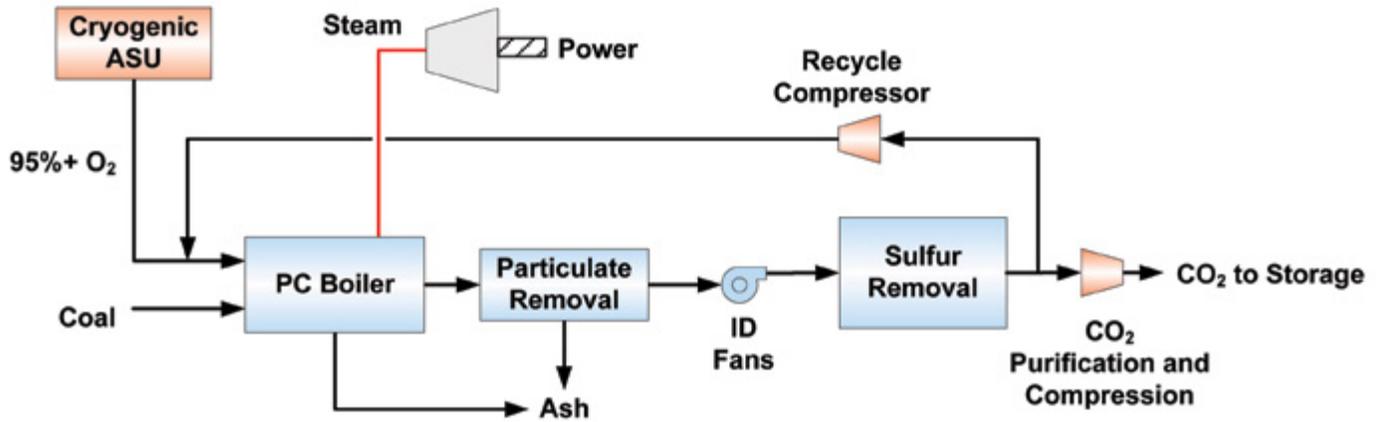


Figure 3-3: Block Diagram Illustrating an Oxy-Combustion System

3.D CHEMICAL LOOPING

Chemical looping is an advanced technology similar to oxy-combustion in that it relies on combustion or gasification of coal in a N₂-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 O₂ from air to the fuel. Figure 3-4 presents a simplified process schematic for chemical looping. Chemical looping splits combustion into separate oxidation and reduction reactions. In the fuel reactor, the oxygen carrier releases the O₂ in a reducing atmosphere and the O₂ reacts with the fuel. The carrier is then recycled back to the oxidation chamber, or air reactor, where it is regenerated by contact with air. Because air is not introduced into the fuel (combustion) reactor, the products of combustion are primarily CO₂ and H₂O. Chemical looping can be applied in either coal combustion or coal gasification processes. A more detailed description of the chemical looping combustion and gasification CO₂ capture processes is provided in Chapter 4.

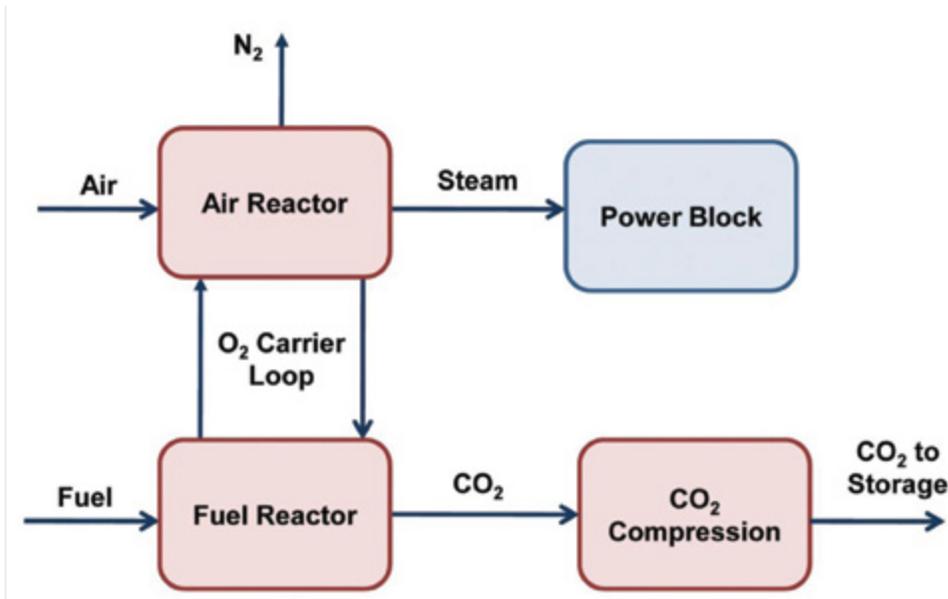
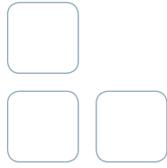
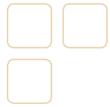


Figure 3-4: Chemical Looping Process



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 CO₂ 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 CO₂ capture. There are two general categories of solvents that can be used for CO₂ absorption—chemical and physical. As the name implies, a chemical solvent relies on the chemical reaction of CO₂ in the solvent to enhance absorption, whereas a physical solvent absorbs molecular CO₂ without a chemical reaction. Physical solvents are well suited for pre-combustion capture of CO₂ from syngas at elevated pressures; whereas, chemical solvents are more attractive for CO₂ 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 CO₂ only weakly interacts with the solvent.

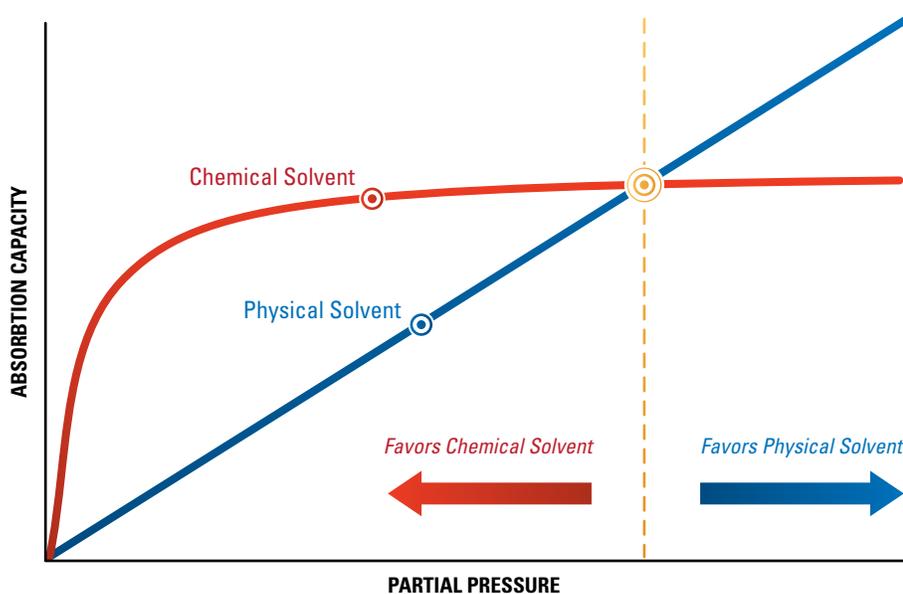


Figure 4-1: Comparison between Chemical and Physical Solvents

Figure 4-1 illustrates the general behavior of chemical and physical solvents. At lower CO₂ 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 CO₂ partial pressure is above about 10 atmospheres (atm). In pre-combustion IGCC applications, the syngas CO₂ partial pressure is typically around 20 atm, therefore a physical solvent is usually preferred over a chemical solvent.

In a CO₂ absorption process, the CO₂ containing gas is contacted with the solvent in an absorber, and CO₂ in the gas is transferred to the solvent. The CO₂-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 CO₂, 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 CO₂-rich gas stream leaving the stripper is condensed, and the high-purity CO₂ 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; CO₂ 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 CO₂ 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 CO₂ 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 CO₂. The heat of reaction is the energy released when the absorbed CO₂ 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 CO₂ from the solvent. A higher energy requirement indicates stronger bonding between CO₂ and the solvent, and often translates to a higher working capacity. Thus, CO₂ working capacity and the heats of absorption and reaction are interrelated.

Depending on the solvent properties, as the CO₂ 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 CO₂ selectivity, the purer the product stream will be. Solvent CO₂ 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 CO₂ 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 CO₂ capture for a post-combustion, MEA-based chemical solvent process applied to a subcritical pressure PC power plant.¹¹ 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 SO₂. 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
<ul style="list-style-type: none"> • CO₂ recovery does not require heat to reverse a chemical reaction. • Common for same solvent to have high H₂S solubility, allowing for combined CO₂/H₂S removal. • System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems. 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery. • Must cool down synthesis gas for CO₂ 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 H₂ may be lost with the CO₂.

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

Advantages	Challenges
<ul style="list-style-type: none"> • Chemical solvents provide fast kinetics to allow capture from streams with low CO₂ 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 CO₂ gas separation using solvent systems in industrial applications. 	<ul style="list-style-type: none"> • 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 CO₂ 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 CO₂ 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 CO₂ will be strongly retained, together with sulfur compounds and hydrocarbons, while “light” components such as N₂, O₂, 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 CO₂ 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 CO₂; 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 CO₂ 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 CO₂ are captured per gram of sorbent. In other words, a CO₂ working capacity of one percent would mean that 1 kg of sorbent would capture 10 g of CO₂ in a given cycle. Reported CO₂ 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 CO₂ working capacity, if it must remain in the adsorption reactor of the cycle for too long, it will result in too little CO₂ 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 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 CO₂ 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
<ul style="list-style-type: none"> • CO₂ recovery is primarily based on pressure swing (versus heat energy). • Common for H₂S to also have high solubility in the same sorbent, meaning CO₂ and H₂S capture can be combined. • System concepts in which CO₂ is recovered with some steam stripping rather than flashed, and delivered at a higher pressure may optimize processes for power systems. 	<ul style="list-style-type: none"> • CO₂ pressure is lost during flash recovery. • Depending on solid sorbent composition and reaction mechanism with CO₂, some sorbents require cooling of the syngas for CO₂ capture. The syngas is then re-heated and humidified prior to firing in the combustion turbine. • Some H₂ may be lost with the CO₂.

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

Advantages	Challenges
<ul style="list-style-type: none"> • Chemical sites provide large capacities and fast kinetics, enabling capture from streams with low CO₂ 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 (CO₂ and heat capacity dependant). 	<ul style="list-style-type: none"> • 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 CO₂ Capture with Sorbents

There is no commercially-available adsorption process for pre-combustion (IGCC) CO₂ capture. The closest application of an adsorption process for CO₂ separation is the PSA process for H₂ purification from syngas. However, H₂ purification is different from a CO₂ removal process. In H₂ purification, the purity of H₂ is the key parameter, whereas the recovery of H₂ is not as critical. For an IGCC power plant with CO₂ capture, H₂ recovery rate and CO₂ purity are both important, but the H₂ purity (above 93 percent) and CO₂ recovery rate (above 90 percent) can be compromised. As a result, an H₂ purification process designed to produce highly pure H₂ would require modification to facilitate the new requirement of CO₂ capture and sequestration.

Due to the high partial pressure of CO₂ in IGCC syngas, a physical sorbent with low heat of adsorption should be sufficient for ambient temperature CO₂ 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 CO₂ 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 CO₂ capture process would provide additional benefit to the IGCC CO₂ capture power plant by accelerating the WGS reaction rate and reducing the excess steam required for the traditional WGS reaction.

4.C MEMBRANE-BASED PROCESSES

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

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

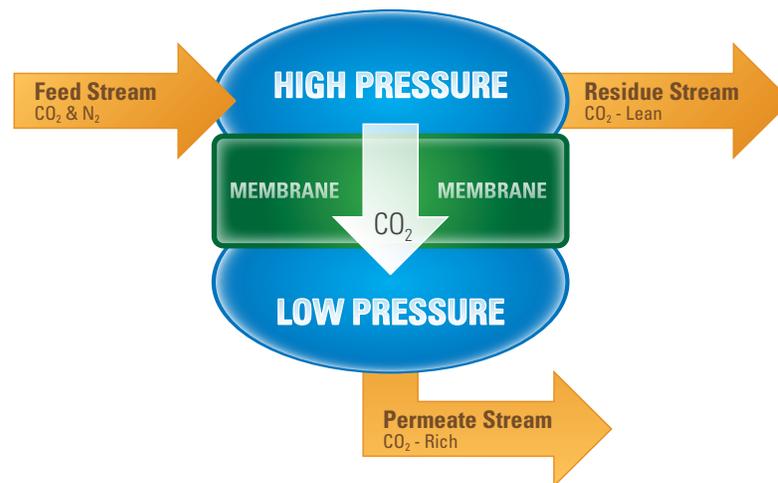


Figure 4-2: Membrane Process Schematic

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

Permeance – A membrane’s design permeance, also known as flux, is an important performance parameter that determines the required membrane surface area, and therefore, the capital cost and footprint of a membrane CO_2 capture system. Increasing CO_2 permeance proportionally decreases the required membrane surface area—a ten-fold increase in permeance results in a ten-fold decrease in area. Permeance is equal to the permeability times the thickness of the membrane. The permeability, P [$\text{cm}^3(\text{STP}) \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$], 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 $10^{-6} \text{ cm}^3(\text{STP}) / \text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$. 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., CO₂ and N₂) is measured as the selectivity, α , which is defined as the ratio of the individual gas permeability or permeance. The highest practical CO₂/N₂ selectivity is about 50 for conventional post-combustion membranes because the CO₂ 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 CO₂ concentration (purity) in the permeate stream. Overall, membrane permeance is the more important design parameter. Membrane selectivity and pressure ratio determine CO₂ 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 CO₂ removal, while pressure ratio and selectivity determine CO₂ purity. By design, membrane CO₂ enrichment (purity divided by feed concentration) will be less than the pressure ratio, regardless of selectivity. Therefore, the pressure ratio determines the maximum CO₂ purity for a given percentage CO₂ 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 CO₂ 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 CO₂ Capture with Membranes

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

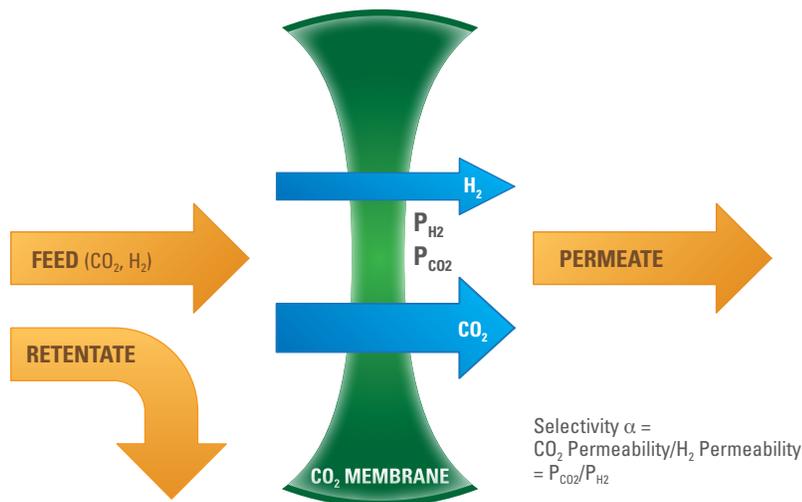


Figure 4-3: Schematic Display of a Pre-Combustion CO₂ Selective Membrane

In an IGCC power plant with CO₂ capture, CO₂ 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 (H₂ or CO₂) so that the chemical equilibrium would be shifted to completion. Membrane reactors, either H₂ or CO₂ 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 CO₂ capture as required in the Selexol process. Membrane reactors have great potential to reduce the COE of an IGCC power plant with CO₂ 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	<p>H₂ or CO₂ Permeable Membrane:</p> <ul style="list-style-type: none"> No steam load or chemical attrition. <p>H₂ Permeable Membrane Only:</p> <ul style="list-style-type: none"> Can deliver CO₂ at high-pressure, greatly reducing compression costs. H₂ permeation can drive the CO shift reaction toward completion—potentially achieving the shift at lower cost/higher temperatures. 	<ul style="list-style-type: none"> Membrane separation of H₂ and CO₂ is more challenging than the difference in molecular weights implies. Due to decreasing partial pressure differentials, some H₂ will be lost with the CO₂. In H₂ selective membranes, H₂ compression is required and offsets the gains of delivering CO₂ at pressure. In CO₂ selective membranes, CO₂ is generated at low pressure requiring compression.
Membrane/Liquid Solvent Hybrids	<ul style="list-style-type: none"> The membrane shields the amine from the contaminants in flue gas, reducing attrition and allowing higher loading differentials between lean and rich amine. 	<ul style="list-style-type: none"> Capital cost associated with the membrane. Membranes may not keep out all unwanted contaminants. Does not address CO₂ compression costs.

Special Considerations for Post-Combustion CO₂ 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 CO₂ 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 CO₂ in the flue gas. Another potential disadvantage of membrane technology for power plant applications is that although 90 percent CO₂ separation is technically achievable in a single-step process, a high level of CO₂ 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 CO₂ 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 CO₂ permeance on the order of 1,000 gpu are needed to make CO₂ 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 CO₂ concentration in the feed stream, CO₂ purity in the permeate stream would be less than 30 percent at a pressure ratio of 2, for CO₂/N₂ selectivity between 20 and 50. If the pressure ratio is increased to 5, CO₂ purity would range from approximately 55 to 65 percent at a CO₂/N₂ selectivity between 20 and 50. Therefore, a multiple-step membrane process with a recycle loop is likely required to

further increase CO₂ purity in the permeate stream.

There is a design trade-off between membrane permeance and selectivity. Figure 4-4 shows a plot of CO₂/N₂ selectivity versus CO₂ permeance for various membranes currently under development by MTR for post-combustion CO₂ capture applications. The plot shows that highly selective membranes generally have low permeance and vice versa. The membranes with the highest CO₂/N₂ selectivity (approximately 50) have the lowest CO₂ 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 CO₂ from natural gas has a permeance of approximately 100 gpu and a CO₂/N₂ 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 CO₂ capture applications.

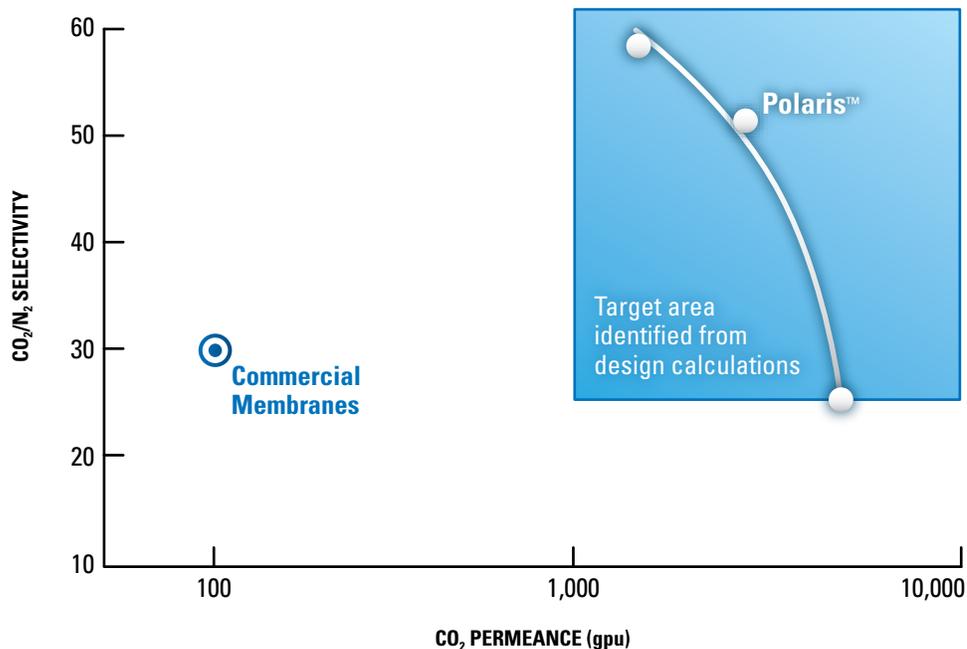


Figure 4-4: Plot of Membrane Selectivity versus Permeance

Pressure Ratio – As discussed above, the pressure ratio determines the maximum CO₂ purity for a given percentage CO₂ concentration in the feed stream. For example, with a CO₂ feed stream concentration of 10 percent and a pressure ratio of 5, the maximum achievable CO₂ 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, CO₂ removal, and CO₂ purity for four pressure ratios between 3 and 15 in a single-step process with membrane design parameters of 100 gpu and 35 CO₂/N₂ 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 CO₂ removal and increases the percentage CO₂ 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.

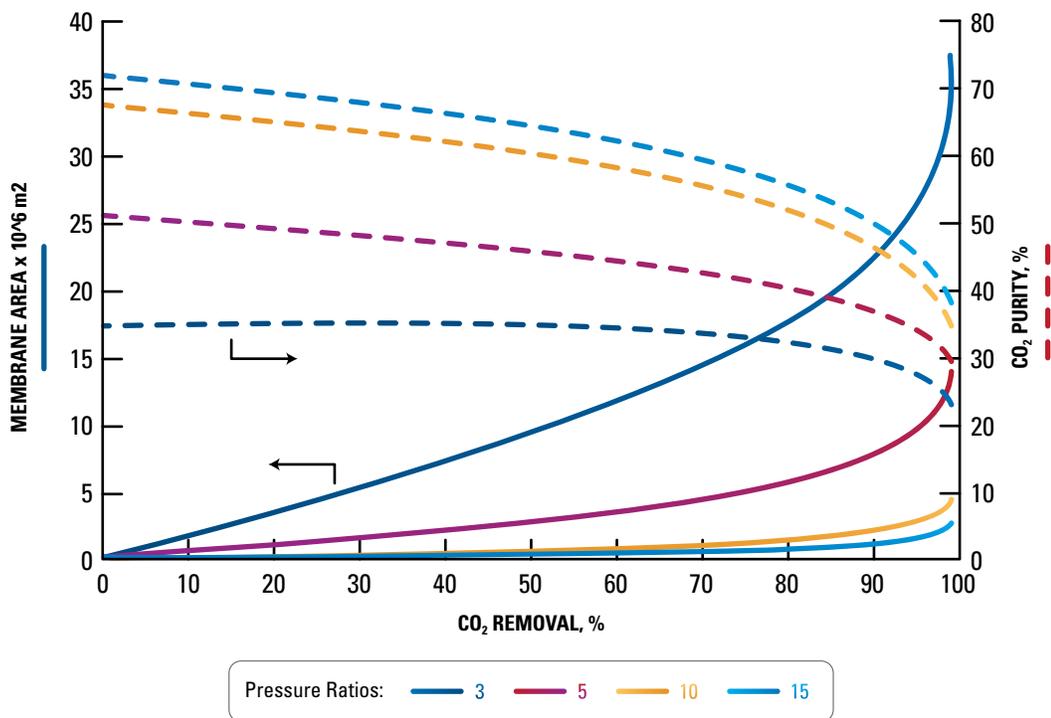


Figure 4-5: Plot of CO₂ Removal, CO₂ Purity, and Membrane Area Versus Pressure Ratio

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 CO₂), while a compression-based process has to compress all of the flue gas (primarily CO₂ and N₂). 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 m² 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 m², 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
<ul style="list-style-type: none"> No steam load. No chemicals. 	<ul style="list-style-type: none"> 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 CO₂ 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 CO₂ 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 CO₂ capture rate can be found from the phase diagram of CO₂ (see Figure 4-6). The typical concentration of CO₂ 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 CO₂ 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 CO₂ 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 CO₂. Different cooling methods will result in not only different energy consumption, but also different capital cost due to the necessary cooling equipment used.

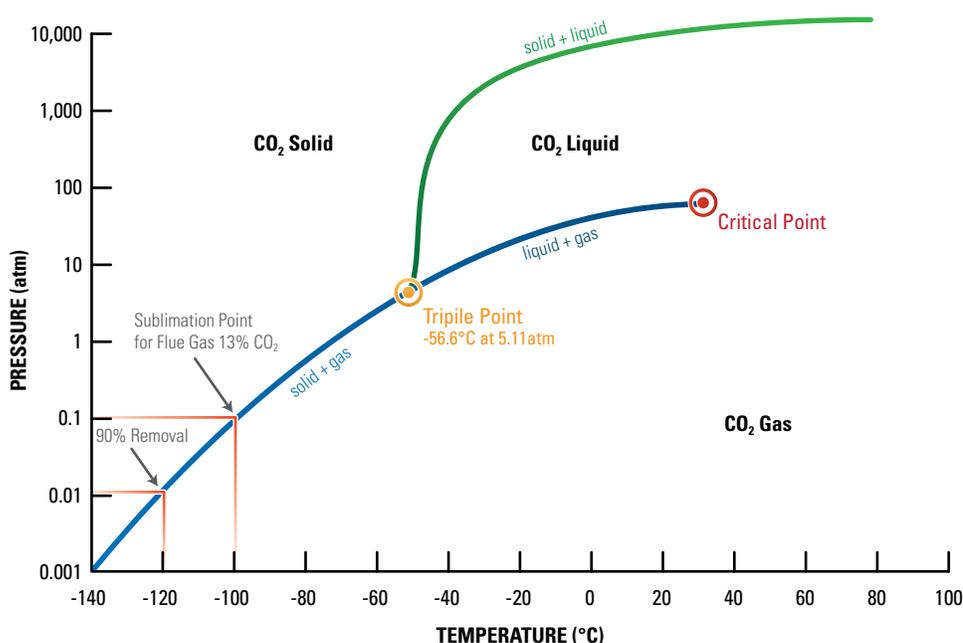


Figure 4-6: Phase Diagram of Carbon Dioxide

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ from the balance of the gas stream.

4.E OXY-COMBUSTION PROCESSES

In an oxy-combustion process, a pure or enriched O₂ gas stream is used instead of air as the oxidant for combustion (see Figure 4-7). In this process, almost all of the N₂ is removed from the air (sometimes called denitrogenated process), yielding a stream that is approximately 95 percent O₂. Due to N₂ 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

CO₂. 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 N₂ 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 approaches 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 CO₂ 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.

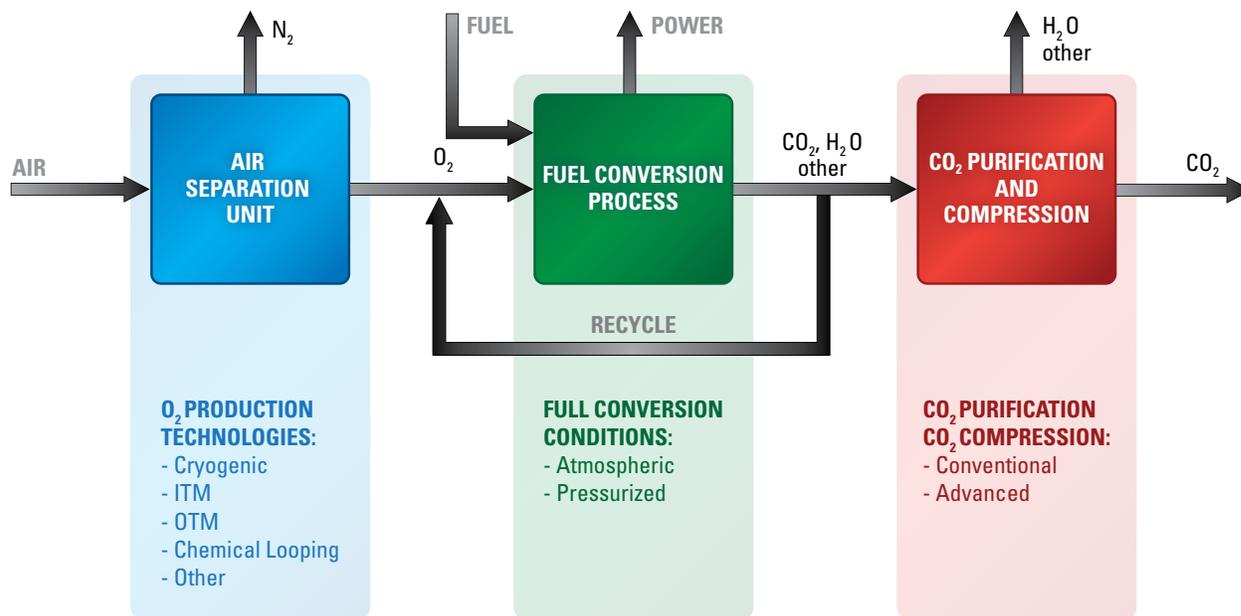


Figure 4-7: Major Components of Oxy-Combustion System

Today's oxy-combustion system configuration would use a cryogenic process for O₂ separation, atmospheric combustion for fuel conversion in a conventional supercritical PC boiler, substantial flue gas recycle, conventional pollution control technologies (SO_x, NO_x, mercury, particulates), and mechanical compression for CO₂ pressurization—equipment that is already available at the scale necessary for power-plant applications. Key process principles, such as air separation and flue gas recycle, have been proven in the past. The conventional configuration can be used for new plants, as well as for retrofitting existing coal-fired power plants without major modification. A simplified process schematic of an oxy-combustion system with CO₂ capture is shown in Figure 4-8.

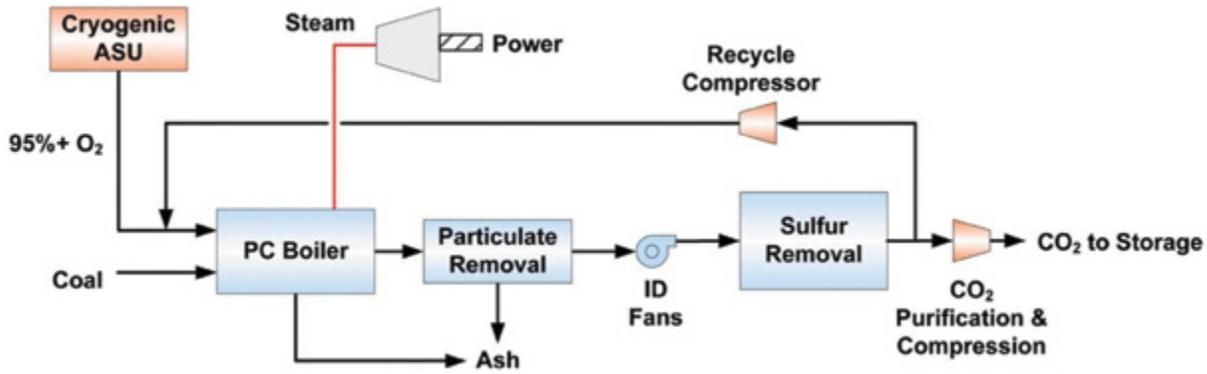


Figure 4-8: Process Schematic of Oxy-Combustion CO₂ Capture

The most significant barrier to the use of 1st-Generation oxy-combustion technology is the high cost. Development of 2nd-Generation and Transformational technologies will be needed to reduce the costs and energy requirements associated with 1st-Generation systems. This involves efforts to develop components of oxy-combustion systems that, when integrated, result in more efficient operations and lower capital costs. The components associated with 1st-Generation, 2nd-Generation, and Transformational oxy-combustion technologies are summarized in Figure 4-9. The technical discussion below describes these components and improvements.

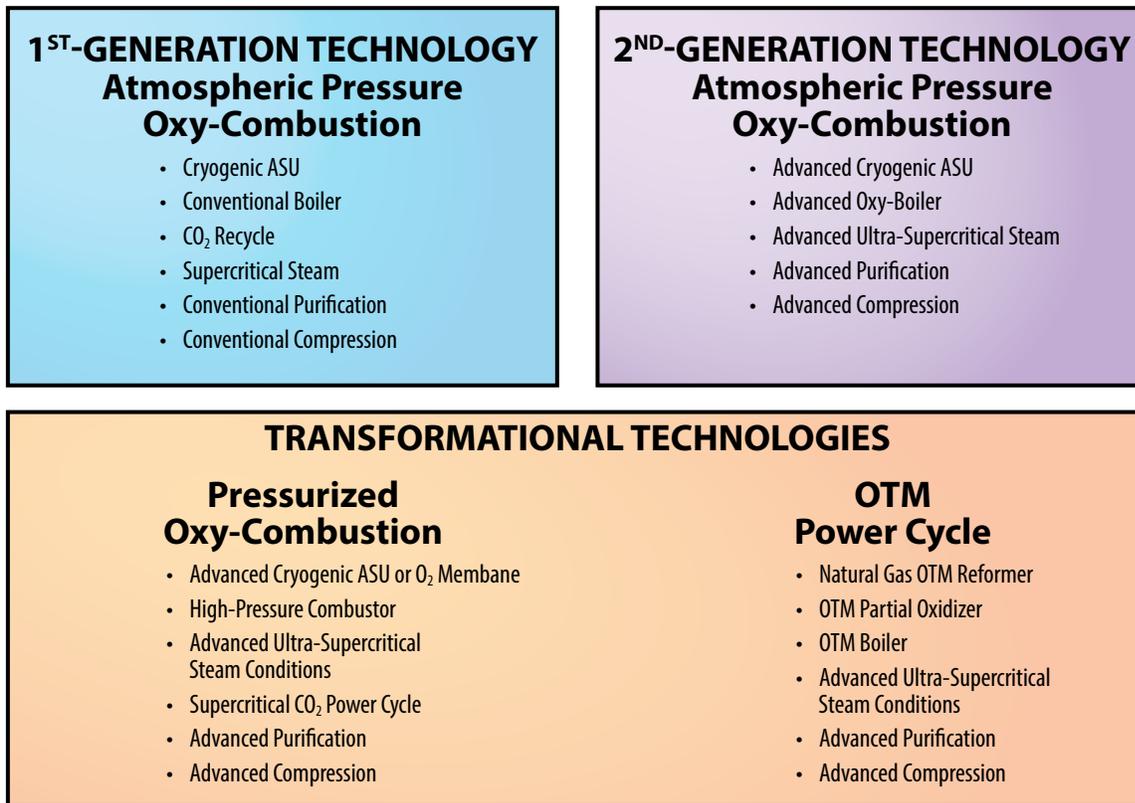


Figure 4-9: Components of Oxy-Combustion Systems

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
<ul style="list-style-type: none"> • The combustion products are primarily CO₂ 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. 	<ul style="list-style-type: none"> • Low-cost oxygen supply is required. • Reduce cost of CO₂ 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.

Oxygen Production

Current oxygen production technology uses cryogenic separation processes that consume over 200 kWh of electricity per ton of O₂ produced. A 500-MW oxygen-fired power plant would require 12,000 tons of oxygen per day; thus, cryogenic oxygen separation represents a significant energy penalty. The energy consumption of current cryogenic technologies is four to five times the theoretical minimum energy required for the process. This indicates that there may be significant room for future improvement. However, due to the nature of the cryogenic distillation process (which involves mostly mechanical processes, such as compression/expansion for refrigeration), the potential efficiency improvement will be relatively limited. Future cryogenic processes will be able to operate around 4.5 bar, which is expected to result in a 10 percent reduction in compression work.

Oxygen production in 2nd-Generation and Transformational oxy-combustion systems will be accomplished by either advanced cryogenic separation or oxygen membrane separation.

Advanced Cryogenic Oxygen Separation – The cryogenic oxygen separation process works by compressing air, cooling via expansion, followed by cryogenic distillation to separate different gases (i.e., oxygen, nitrogen, and argon). One aspect of the cryogenic oxygen separation process that shows promise in terms of cost and performance improvements is reduction of operating pressure of the cryogenic distillation column. Figure 4-10 shows how required compression work will be reduced with respect to the current state-of-the-art cryogenic process when the operating pressure of the distillation column (as indicated by compressor discharge pressure) is reduced.

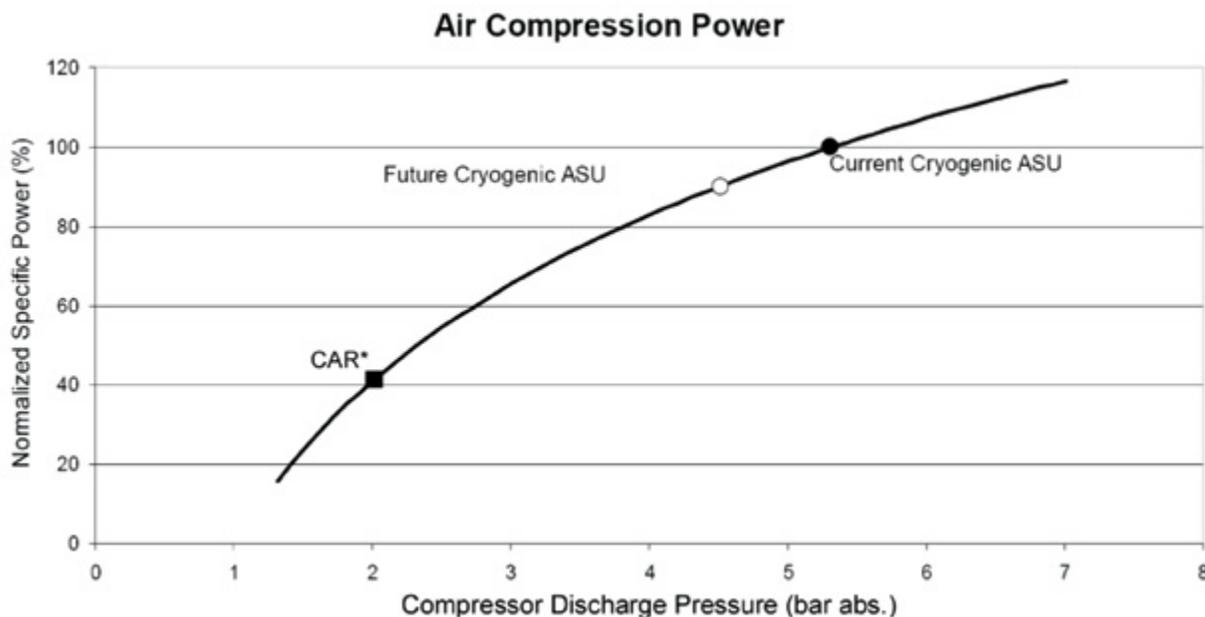


Figure 4 10. Required Compression Power vs. Operating Pressure

Oxygen Separation Membranes – The ITM process is a relatively new oxygen separation technology that has been demonstrated at the pilot scale for gasification-based systems. ITM technology is based on the transport of oxygen ions through the crystal lattice of mixed metal oxides. The ceramic materials used for this application have a high flux and selectivity to oxygen. Oxygen molecules are converted to oxygen ions at the surface of the membrane on the oxygen-rich side and transported through the membrane by an oxygen partial pressure difference. Oxygen molecules then reform on the oxygen-lean side of the membrane. An operating temperature of 800 °C is required in order to activate the ion transport process. The hot oxygen product stream is nearly 100 percent pure. The remaining gas is a pressurized, oxygen-depleted stream from which significant amounts of energy can be recovered. Figure 4-11 is a schematic diagram of an ITM separation process.

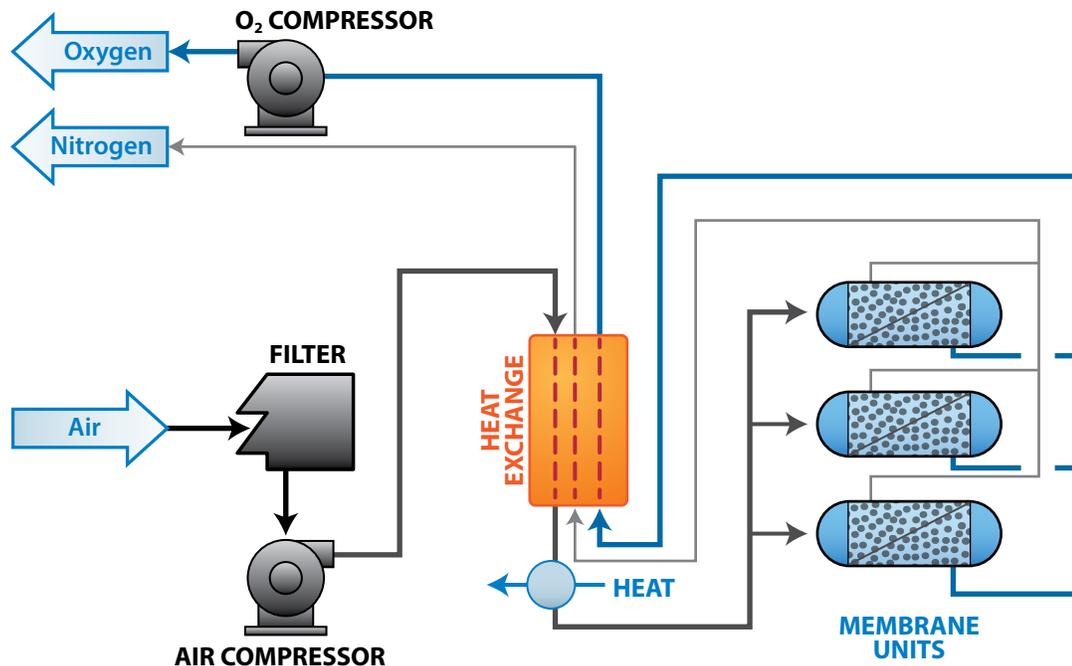


Figure 4-11. Ion Transport Membrane Air Separation Process

Although Figure 4-11 shows the ITM as a stand-alone process, in practice it will be integrated into the power-plant design to minimize energy consumption. Because ITM technology requires a high operating temperature and pressure, the main purpose of power system integration is to recover/reduce compression energy and heat loss.

Boiler Design

Atmospheric Pressure Oxy-Combustion Boilers – Within the definition of 2nd-Generation oxy-combustion technologies, an advanced boiler could include reduced recycle and an advanced recycle system. An advanced recycle system eliminates the flue gas recycle superheating system used for current technology.

An advanced boiler with reduced recycle would be designed to accommodate a smaller flue gas flow and increased temperatures, which results in reduced equipment size. Because of reduced flue gas recycle, an advanced boiler would accommodate a theoretical adiabatic flame temperature of approximately 2,300 °C versus 2,000 °C for current systems. The reduced volumetric flow through the boiler system also allows for a decrease in the size of the associated equipment. Furthermore, fan loads required for flue gas recycle are reduced, increasing system efficiency.

The benefit of smaller oxy-combustion boilers may be limited due to the need for advanced materials that can handle the high temperatures that result with decreasing levels of flue gas recycle. Furthermore, as flue gas recycle is reduced, dilution of sulfur compounds by desulfurized flue gas will be reduced. This will create a demand for sulfur-tolerant materials.

Pressurized Oxy-Combustion Boilers – A number of organizations are investigating the prospect of an oxy-coal power plant in which combustion occurs under pressure. At the center of a pressurized oxy-combustion system is either a PC or circulating fluidized bed boiler operating at elevated pressure, typically in the range of 10–20 bar. Pressurized oxy-combustion has several benefits over atmospheric oxy-combustion:

- Elevated operating pressures offer the potential to reduce latent heat losses from flue gas. In atmospheric pressure oxy-combustion, latent heat can be recovered from flue gas if it is cooled below the dew point of 60–70 °C. Unfortunately, heat at this temperature is of limited value in terms of power production. However, at 10 bar pressure, the dew point rises to 120–140 °C, facilitating heat recovery in the steam cycle. This heat recovery increases boiler efficiency and thus overall plant efficiency.
- Higher pressure operations result in lower gas volumes and corresponding decreases in the volume of process units, including

the boiler. This decrease in size reduces both weight and cost. Reactor wall thicknesses may need to be increased to handle the increased pressure, counterbalancing the total size decrease to some extent, but the net impact should decrease capital cost.

- Operating the boiler at elevated pressure will preclude air in-leakage that is common in atmospheric pressure boilers. This in-leakage increases the concentration of impurities in the flue gas. These impurities must either be removed, increasing costs and process complexity, or co-sequestered with the CO₂, unnecessarily occupying pore space and complicating transport.
- The cost of removing flue gas impurities is reduced at higher pressure.
- Increased gas-side pressure will significantly increase heat transfer rates. Increased gas density at pressure leads to enhanced heat transfer. With pressure increased from 1 to 10 bar, the convective heat transfer coefficient increases by a factor of four, decreasing the needed heat transfer area by a factor of four. The most significant benefit of the reduced heat transfer area will be in superheater bundles. These bundles typically require advanced materials that increase costs. If the heat transfer area is reduced by a factor of four, so too is the capital cost of the heat exchangers.
- Since the boiler operates at elevated pressure, oxygen and coal must be fed to the boiler at elevated pressure. While it requires additional power to pressurize the feed oxygen, this is more than offset by the decrease in power required to compress and purify the CO₂ leaving the plant. The oxygen feed is relatively clean, and the capital cost for the equipment to increase the pressure is much lower than the capital cost of the wet CO₂ compressor required for flue gas pressurization in an atmospheric pressure system.

While several research challenges exist, pressurized steam cycle systems have the potential to increase plant efficiencies by 5 percent or more in comparison to atmospheric steam cycle systems. Critical development needs exist to foster the understanding required to prepare the technology for demonstration-scale testing. These are grouped in two general areas: characteristics specific to the pressurized combustor, and overall system and process design. The list below identifies R&D areas that have been established at this early stage of development:

Pressurized Combustor Design	System/Process Design
Boiler Configuration/Type	Gas Cleaning
Combustion Characteristics	Thermal Integration
Pressure Containment	Power Cycle Integration
Advanced Materials	Process Optimization
Heat Transfer	Advanced Materials
Thermal Integration	
Fuel Feed	
Fuel Conditioning	
Gas Cleaning	
Flue Gas Recycle	

CO₂ Purification and Compression

CO₂ Purification – Although oxy-combustion would produce a flue gas that has a high CO₂ concentration, the flue gas will also include H₂O, as well as excess O₂, N₂, SO₂, NO_x, Hg, and other contaminants. The acidic gases must be removed from the CO₂ stream prior to pipeline transportation to avoid corrosion and to comply with purity requirements for applications such as EOR and geological storage. Therefore, projects in this area focus on the development of flue gas purification technologies. While, commercially available technology exists to remove SO₂ and NO_x from oxy-combustion flue gas streams, advanced purification technologies are being developed that would take advantage of the flue gas conditions to decrease cost and improve performance.

Advanced purification technologies would take advantage of the flue gas makeup to capture SO_x, NO_x, and Hg using higher pressure (≈200–450 psia), hydrolysis, and activated carbon processes with the potential for greater than 90 percent capture and production of saleable acids. In the case of oxy-combustion retrofits with high air ingress, improvements are possible on commercially available cryogenic CO₂ separation technology to push capture rates over 95 percent by using vacuum pressure swing

adsorption. Air Products and Praxair have recently completed advanced CO₂ purification research that is now ready for large pilot- or demonstration-scale testing.

CO₂ Compression – Compression is an integral part of any CO₂ capture system. Since CO₂ separation from the gas stream typically occurs at low pressure, compression is required to reduce the volume flow, making transport more practical. Furthermore, storage sites for geological sequestration and CO₂-EOR require high pressure CO₂ as well. Given the high volume flows, centrifugal compressors are typically employed, especially when the captured CO₂ is produced at near-atmospheric pressure. The physics to compress CO₂ in a centrifugal compressor is the same as that for any other gas. However, CO₂ 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 CO₂ to be liquefied at relatively high temperatures permitting hybrid compression and pumping options.

The CO₂ captured from a power plant will need to be compressed from near-atmospheric pressure to a pressure between 1,500 and 2,200 psia for most applications. However, the compression of CO₂ represents a potentially large auxiliary-power load on the overall power-plant system. For example, in an August 2007 study, CO₂ compression was accomplished using a six-stage centrifugal compressor with inter-stage cooling that required an auxiliary load of approximately 7.5 percent of the gross power output of a subcritical pressure, coal-fired power plant. Conventional compression technology accounts for ≈30 percent of all auxiliary loads in an oxy-combustion system. The capital cost for the compressor and associated equipment is also significant.

To reduce auxiliary power requirements and capital cost, DOE/NETL is developing novel concepts for large-scale CO₂ compression. Various compression concepts are being evaluated using computational fluid dynamics and laboratory testing, leading to prototype development and field testing. Research efforts include development of intrastage versus inter-stage cooling, fundamental thermodynamic studies to determine whether compression in a liquid or gaseous state is more cost-effective, and development of a novel method of compression based on supersonic shock wave technology. DOE/NETL is currently supporting research on two advanced CO₂ compression technologies, a supersonic shockwave compression technology, and a combined interstage cooling and liquefied CO₂ pumping technology.

Supersonic shock wave compressor design features a rotating disk that operates at high peripheral speeds to generate shock waves that compress the CO₂. Compared to conventional compressor technologies, shock compression provides high compression efficiency, high single-stage compression ratios, opportunity for waste heat recovery, and lower capital cost.

The second concept involves initial compression to 250 psia, liquefaction, and pumping. The most energy-intensive components of the process are the initial compression required to boost the CO₂ to approximately 250 psia and the refrigeration power required to liquefy the gas. The pumping power to boost the pressure to pipeline supply pressure (2,200 psia) is minimal after the CO₂ is liquefied. This concept reduces power consumption by 35 percent compared to conventional 10-stage compression.

Compression fundamentals and concepts will be discussed in greater detail in Section 4.G.

Supercritical CO₂ Power Cycle

Compared to a conventional steam cycle, the supercritical CO₂ cycle has a higher efficiency at the same turbine inlet temperature. In addition, a supercritical CO₂ cycle allows for higher inlet turbine temperatures than a steam cycle using materials that are currently available. A steam cycle turbine inlet temperature limit is approximately 600 °C. A supercritical CO₂ cycle turbine inlet temperature limit is approximately 700 °C, leading to even greater improvements in efficiency. Development of advanced materials that would allow even higher inlet temperatures would lead to more efficiency improvements.

The supercritical CO₂ power cycle operates in a manner similar to other turbine cycles, but it uses CO₂ as the working fluid in the turbomachinery. The cycle is a non-condensing closed-loop Brayton cycle with heat addition and rejection on either side of the expander. Once the system is charged with CO₂, for the most part there is no addition or loss during operation. In this cycle the CO₂ is heated indirectly from a heat source through a heat exchanger—not unlike the way steam would be heated in a conventional boiler. Energy is extracted from the CO₂ as it is expanded in the turbine. Remaining heat is extracted in one or more highly efficient heat recuperators to preheat the CO₂ going back to the boiler. These recuperators help increase the overall efficiency of the cycle by limiting heat rejection from the cycle.

The cycle is operated above the critical point of CO₂ so that it does not change phases (from liquid to gas), but rather undergoes drastic density changes over small ranges of temperature and pressure. This allows a large amount of energy to be extracted from equipment that is relatively small in size. Supercritical CO₂ turbines have a gas path diameter of a few inches compared to a few

feet for utility-scale combustion turbines or steam turbines. The temperature profiles of typical heat sources and the supercritical CO₂ working fluid through the recuperators and heat exchangers can be designed to better match than conventional steam heat exchangers with a phase shift, allowing lower temperature differences between the heat sources and the working fluid (CO₂). In this way irreversible entropy is minimized.

Fossil fuels, particularly coal, can provide an ideal heat source for supercritical CO₂ cycles. The open literature has shown that a supercritical CO₂ closed-loop cycle combined with a coal-fueled oxygen-blown pressurized fluidized bed combustor has the potential to increase efficiency with a lower capital cost than a comparable supercritical steam-based Rankine cycle with the same turbine inlet temperature. Studies suggest that the supercritical CO₂ oxy-fuel pressurized fluidized bed combustor system has the potential to significantly increase efficiency, as much as 9 percentage points over other PC oxy-fuel combustion configurations, with a 20 percent lower COE and the potential for near 100 percent CO₂ capture (from combustion). Water consumption and other emission profiles are also very attractive for this cycle.

The supercritical CO₂ cycle utilizes small turbomachinery, is fuel- and/or heat-source neutral, efficient, and can make use of lower intensity heat sources. These factors make the cycle appealing to a wide range of applications and stakeholders. For instance the supercritical CO₂ cycle can be particularly attractive as a bottoming cycle for simple-cycle gas turbines, providing an improvement of 15–20 additional percentage points, while retaining many of the desirable attributes of the simple cycle configuration. Other bottoming cycle applications will also be attractive. Due to the fuel and heat source neutrality, the cycle is also highly relevant to concentrated solar and nuclear applications, both technology components with a high level of DOE interest. The Department of Defense has also expressed a strong interest for naval propulsion and power due to the compactness and efficiency of this cycle (the U.S. Naval Research Laboratory at Bettis Atomic Power Laboratory has one of three supercritical CO₂ test loops in the United States). In summary, this cycle has significant benefits to a number of power-based applications with multiple stakeholders. This broad range of applications makes the market-based development and deployment of this machinery highly attractive.

Oxygen Transport Membrane (OTM) Advanced Power Cycle

In the oxy-combustion technologies described previously, a pure stream of O₂ is separated in an ASU and then delivered to a boiler for combustion. OTM technology integrates O₂ separation and combustion in one unit.

The basic principle behind the OTM oxy-combustion system is the use of chemical potential instead of pressure as the oxygen separation driving force. Air and fuel are fed to either side of a tubular membrane. As air contacts the membrane, molecular O₂ reacts to form oxygen ions, which are transported through the membrane. Fuel species (carbon monoxide, hydrogen, methane, etc.) react with oxygen ions at the membrane surface to form oxidation products (H₂O, CO₂). The combustion reaction on the fuel side of the membrane creates a very low oxygen partial pressure compared to the air side of the membrane. This difference in chemical potential drives oxygen through the membrane without the need for additional air compression.

The advantage of the OTM oxy-combustion system is that it can provide a highly concentrated, sequestration-ready stream of CO₂ while significantly reducing the need for cryogenic oxygen production or CO₂ separation processes. The use of reactively driven OTMs is expected to reduce the power associated with oxygen production by 70–80 percent. This represents a step change in the cost and related CO₂ emissions, and will enable a variety of oxy-combustion technologies, as well as other combustion applications, where CO₂ capture may be required. Cost and performance simulations of OTM-based power cycles have shown the potential for high net efficiency (>36 percent higher heating value), a major contributing factor that allows the OTM power cycle to meet program cost and performance goals. The development of OTMs will also benefit industrial processes used to produce syngas for subsequent processing into a variety of chemical and/or petrochemical end products by dramatically reducing the power requirements.

The OTM advanced power cycle full-scale plant configuration is illustrated in Figure 4-12. The plant includes a coal gasifier with requisite oxygen production, syngas cleaning, the OTM oxy-combustion system, a conventional steam power cycle, and CO₂ purification and compression.

The OTM oxy-combustion system is composed of two primary components, the OTM boiler and the OTM partial oxidation (POx) unit, circled in red. These components are the focus of the technology R&D in this research focus area. The OTM boiler is the primary steam generator. It houses the OTM tubes that transport oxygen from air into the combustion chamber, steam tubes for the steam cycle, and the combustion chamber where fuel (syngas) is burned with oxygen to generate steam for the power cycle.

The OTM POx units are used to boost the temperature of the syngas to the operating range of the OTM boiler. Like the boiler, they also use OTM tubes to transport oxygen into the reactor for the partial oxidation of the syngas.

As shown in Figure 4-12, the OTM combustion system must be operated using a gaseous fuel. Thus, for a coal-fired OTM system, coal must first be gasified to produce syngas that drives the OTM combustor.

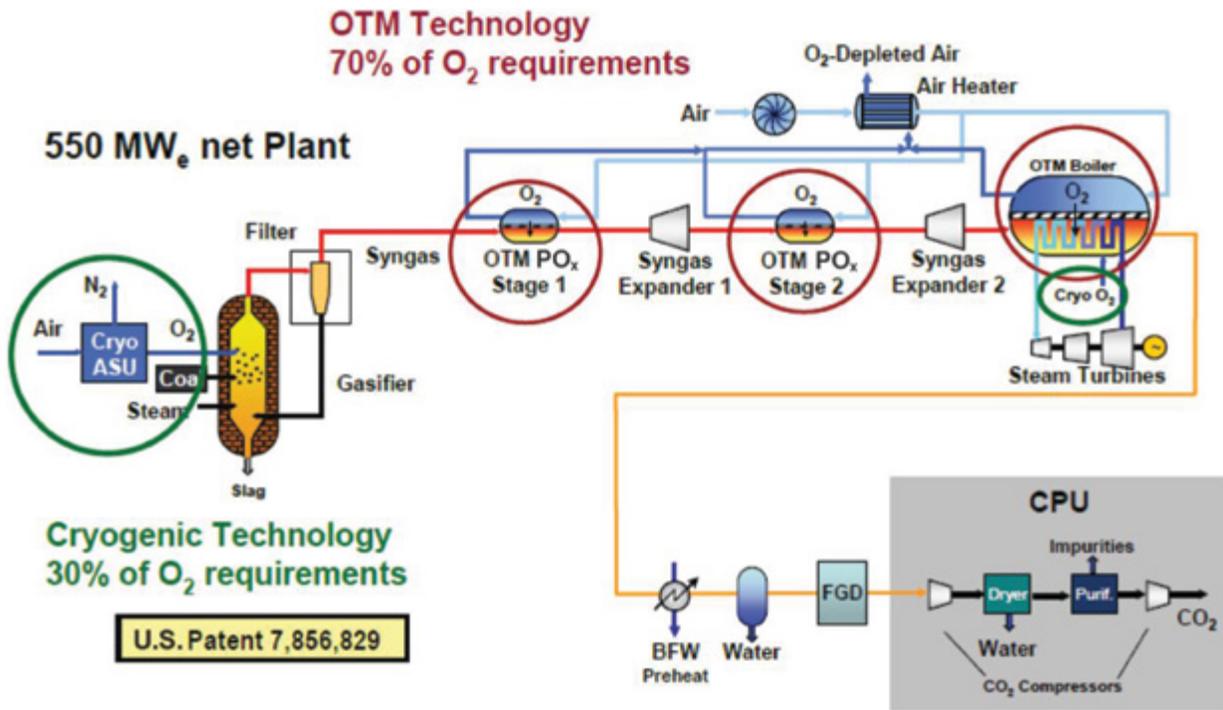


Figure 4-12. OTM Advanced Power Cycle

While the characteristics noted previously show the promise of the OTM system, several aspects of the technology need additional R&D to develop the understanding required to prepare the technology for demonstration-scale testing. These are grouped into three general areas: oxygen membrane characteristics, OTM boiler and POx design, and overall system and process design. The list below identifies areas for continuing R&D:

Oxygen Membrane	Boiler/POx Design	System/Process Design
Oxygen Flux	Module Integration	Gas Cleaning
Membrane Optimization	Heat Transfer	Process Optimization
Modularization	Fluid Dynamics	Thermal Integration
Seals	Thermal Management	
Manufacturability	Operating Conditions	
Contaminant Resistance	Seals	
Operational Stability	Manufacturability	
Reliability	Maintainability	

4.F CHEMICAL LOOPING PROCESSES

Chemical looping is a breakthrough concept that enables the production of a concentrated CO₂ 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
<ul style="list-style-type: none"> • CO₂ and H₂O kept separate from the rest of the flue gases. • ASU is not required and CO₂ separation takes place during combustion. 	<ul style="list-style-type: none"> • 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 combustion (CLC) is a Transformational oxy-combustion technology that involves the use of a metal oxide or other compound as an O₂ carrier to transfer O₂ from the combustion air to the fuel, avoiding direct contact between fuel and combustion air. Figure 4-13 presents a simplified process schematic for chemical looping. The products of combustion (CO₂ and H₂O) are kept separate from the rest of the flue gases. Chemical looping splits combustion into separate oxidation and reduction reactions. The chemical looping process is carried out in two separate reactors. The oxygen carrier releases the O₂ in a reducing atmosphere and the O₂ reacts with the fuel. The oxygen carrier is then recycled back to the oxidation chamber where the carrier is regenerated by contact with air.

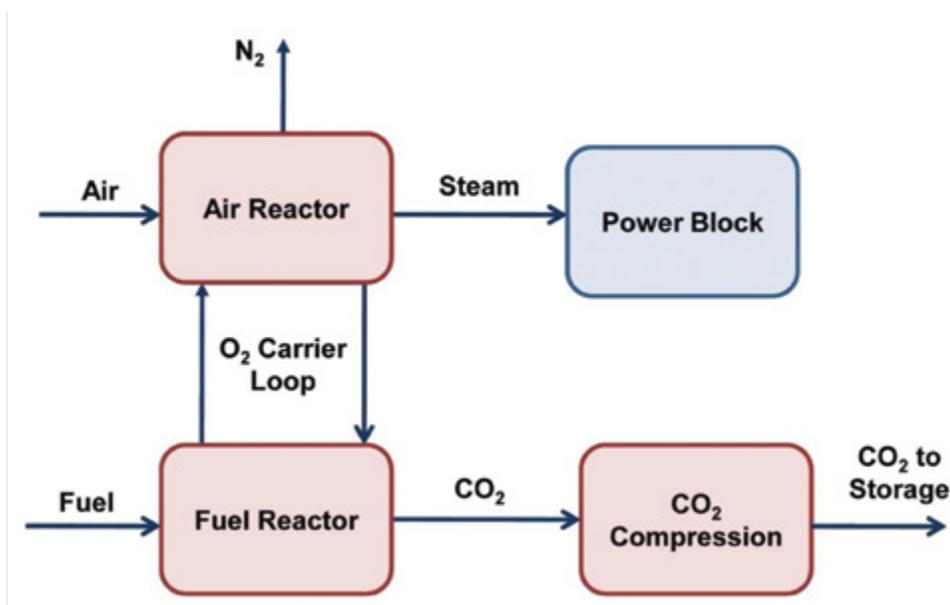


Figure 4-13: Chemical Looping Process

The advantage of using the CLC process is that the CO₂ is concentrated once the H₂O is removed and not diluted with N₂ gas. Another advantage of the CLC process is that no separate ASU is required, and CO₂ separation takes place during combustion. CLC may also be able to take advantage of the supercritical CO₂ power cycle described previously.

The eventual development of CLC offers the potential as a game-changing technology for power generation and CO₂ capture. A recent systems analysis study conducted by Alstom estimates that a power plant equipped with CLC could capture nearly all of the CO₂ generated and have a COE increase of less than 20 percent compared to a conventional coal-fired power plant without CO₂ capture. CLC offers the following advantages:

- Avoids the large investment costs and parasitic power associated with either cryogenic ASUs or ITMs used for oxy-combustion
- Captures CO₂ at high temperature without additional external energy, thus eliminating the thermodynamic penalty normally associated with CO₂ capture
- Involves small equipment and low capital cost (because of fast chemical reactions)
- Requires conventional material of construction and fabrication techniques

Figure 4-14 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 O₂ in the air to form an oxide of the compound (M_xO_y) and produce a hot flue gas. 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 CO₂ and H₂O stream that can be purified, compressed, and sent to storage.

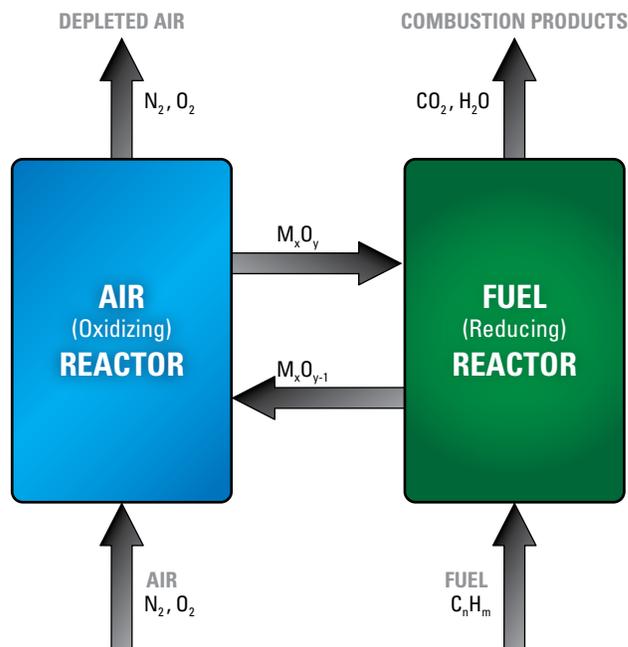
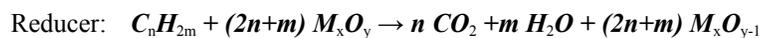
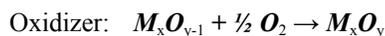


Figure 4-14: Schematic Diagram of a Two Reactor CLC Process

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



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 O₂ for gasification and to capture CO₂. A loop, similar to that of CLC, is used to gasify the coal and produce syngas (H₂ and CO). A second solid loop is used in a WGS reactor. In this reactor, steam reacts with CO and converts it to H₂ and CO₂. The circulating solid absorbs the CO₂, thereby providing a greater driving force for the WGS reaction. The CO₂ is then released in a calcination step that produces nearly pure CO₂ for further compression and storage. Figure 4-15 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.

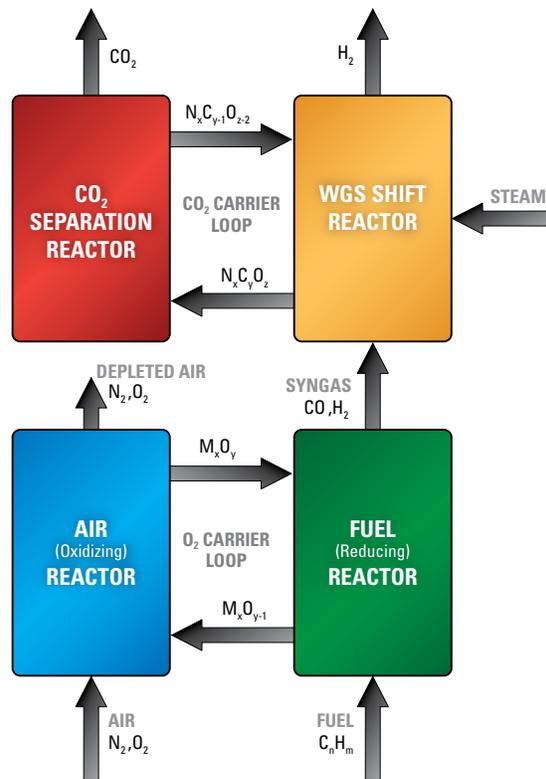
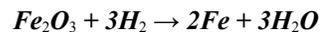
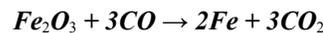
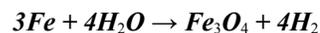


Figure 4-15: Schematic Diagram of a Two Loop CLG Process

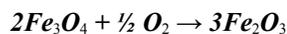
For the WGS reaction, the chemical looping process uses a solid carbon carrier (instead of oxygen carrier) to separate CO₂ from the WGS reactor, thus improving the WGS reaction. An example is the iron oxide-based syngas chemical looping process, which requires a three-reactor configuration to accomplish the WGS. In the first reactor, syngas is burned by Fe₂O₃:



In the second reactor, Fe is oxidized by steam to produce H₂:



And in the third reactor Fe₃O₄ is further oxidized to Fe₂O₃ to complete the cycle:



The overall reaction converts syngas (CO and H₂) to H₂ with a small fraction of the syngas lost in the process.

Chemical Looping R&D

Chemical looping is in the early stages of process development. Bench- and laboratory-scale experimentation is currently being conducted. Projects in this research focus area are advancing the development of chemical looping systems by addressing key issues, such as solids handling and oxygen carrier capacity, reactivity, and attrition. Researchers are investigating several metal oxides for use as the O₂ carrier including calcium, iron, nickel, copper, and manganese. For example, NETL's ORD is conducting laboratory-scale tests using nickel oxide on bentonite and copper oxide on bentonite as O₂ carriers.

While the characteristics noted previously show the promise of CLC, additional technology development is needed to foster the understanding required to prepare the technology for demonstration-scale testing. Development needs are grouped in four general areas: oxygen carrier characteristics, solids circulation strategy, reactor design, and overall system and process design. The list below identifies areas for R&D:

Oxygen Carrier	Solids Circulation	Reactor Design	System/Process Design
Composition	Dilute pneumatic	Gas cleaning	Gas Cleaning
Density	Dense pneumatic	Process optimization	Process Optimization
Reaction kinetics	Mechanical	Thermal integration	Thermal Integration
Oxygen carrying capacity	Flow control		Heat transfer strategy
Fluidization properties	Mechanical valves		
Attrition	Non-mechanical valves		
Agglomeration	Uncontrolled		
Sintering			
Degradation—chemical, thermal, contaminants			

4.G COMPRESSION FUNDAMENTALS

Compression is an integral part of any CO₂ capture system. Since separation typically occurs at low pressure, compression is required to reduce the volume flow making transport more practical. Furthermore, CO₂ storage sites for geological sequestration require high pressure as well. Given the high volume flows, centrifugal compressors are typically employed, especially when the captured CO₂ is produced near atmospheric pressure. The physics to compress CO₂ in a centrifugal compressor is the same as any other gas. However, CO₂ 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 CO₂ to be liquefied at relatively high temperatures permitting hybrid compression and pumping options.

Figure 4-16 and Figure 4-17 show two types of centrifugal compressors typically used for CO₂ 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 4-16: 8 Stage Integrally Geared Compressor (Courtesy of MAN Turbo)

Figure 4-17 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}

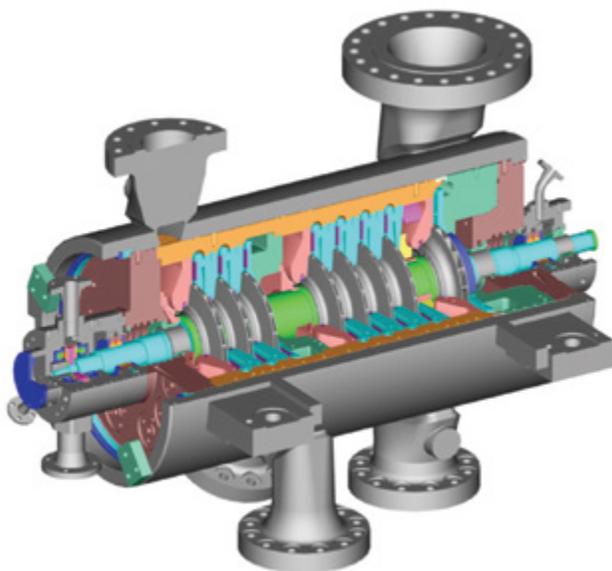


Figure 4-17: Multi-Stage Back-to-Back Centrifugal Compressor (Courtesy of Dresser-Rand®)

Figure 4-18 shows a plot of volume flow versus pressure for CO₂ 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 CO₂ 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, CO₂ 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 CO₂ at the greatest pressure possible due to the volume flow requirement.

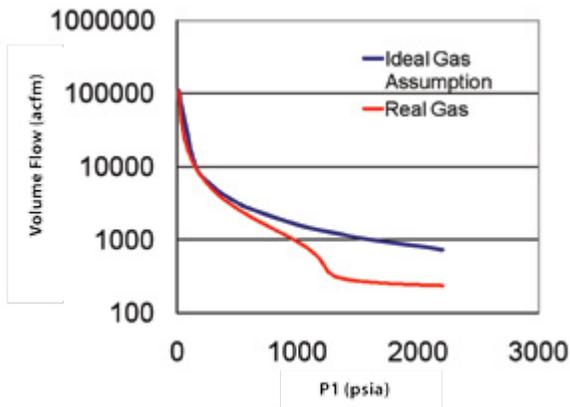


Figure 4-18: Volume Flow versus Pressure for CO₂ at 100 °F

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 CO₂ 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.

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

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

As the CO₂ 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 CO₂ 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 CO₂ compression.^{vii} The analysis is based on an IGCC plant equipped with a Selexol™ pre-combustion chemical solvent process used to capture the CO₂ at three pressures of 22, 160, and 250 psia, and with CO₂ 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 CO₂ 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) $\eta_p = 70\text{--}5\%$ 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 $\eta_p = 70\text{--}5\%$ 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 $\eta_p = 80\%$	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 H ₂ /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 $\eta_p = 80\%$	

TABLE 4-9: PROCESS DESIGN OPTIONS FOR CO₂ COMPRESSION

Design Option	Compression Technology	Process Parameters	Thermodynamic Equation References
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. $\eta_p = 90\%$	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 1 st and 2 nd stage cooling	Same as D.3 except with interstage cooling T1 = 50 °F for stage 1 and 100 °F for stage 2 $\eta_p = 90\%$	
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 $\eta_p = 80\%$	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:

$$\eta_p = \frac{\left(\frac{n_p}{n_p - 1}\right) \cdot \left(\frac{P_2}{P_1}\right)^{\frac{n_p - 1}{n_p}} - 1}{(h_2 - h_1)} \cdot \frac{P_1}{\rho_1} \cdot f \quad (\text{Eq. 4-2})$$

where f = Schultz correction factor is calculated as:

$$f = \frac{h_{2s} - h_1}{\frac{k}{k-1} \cdot \left(\frac{P_2}{\rho_{2s}} - \frac{P_1}{\rho_1}\right)} \quad (\text{Eq. 4-3})$$

Isothermal ideal work is calculated as:

$$\frac{W}{\dot{m}} = \frac{R}{MW} \cdot Z_{avg} \cdot T_o \left(\ln \frac{P_2}{P_1} \right) \quad (\text{Eq. 4-4})$$

Actual pump work is calculated as:

$$W(act) = h_2 - h_1 = \frac{h_{2s} - h_1}{\eta_{pump}} \quad (\text{Eq. 4-5})$$

Refrigeration work is calculated as:

$$\dot{W} = (h_1 - h_2) \cdot \dot{m} \cdot (RF_{eff}) \quad (\text{Eq. 4-6})$$

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 CO₂ 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 CO₂ in a supercritical state is assumed to be 2,215 psia at 70 °F. The Selexol™ pre-combustion capture process provides several higher pressure CO₂ 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 CO₂ 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: CO₂ 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/ft ³)	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 CO₂ 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 CO₂. 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 CO₂ 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 4-19.

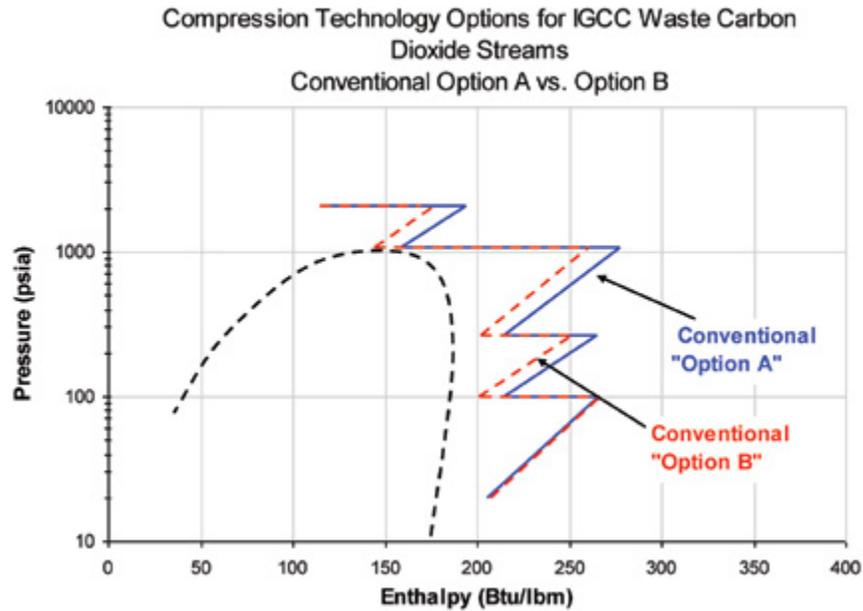


Figure 4-19: Technical Advantages and Challenges for Pre-Combustion Membrane Technologies

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 4-19 with Figure 4-20. 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 4-20 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 4-21 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.

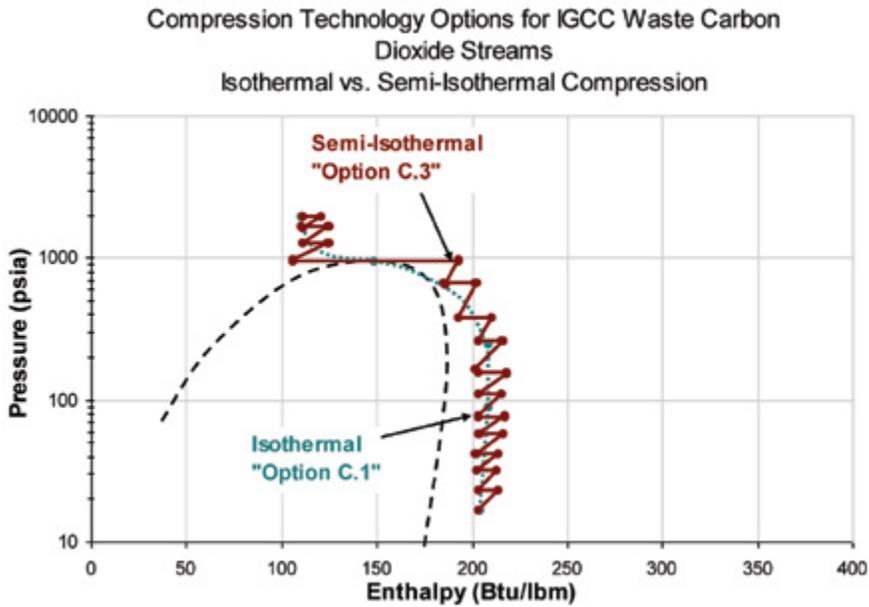


Figure 4-20: Comparison of Isothermal and Semi-Isothermal CO₂ Compression

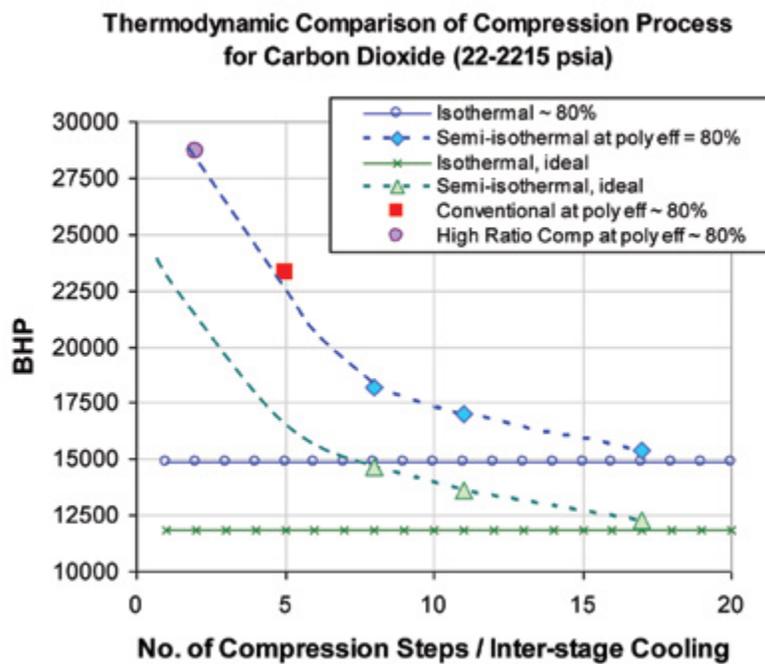


Figure 4-21: Compression Brake Horsepower vs. Number of Intercooling Steps

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 CO₂ stream shown in Table 4-10 in the high-ratio compression option. As such, all the MP CO₂ 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 CO₂ 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 CO₂. Although pumping liquid CO₂ requires significantly less energy than compression of gaseous CO₂, liquefaction of the CO₂ gas requires large amounts of refrigeration energy. To achieve cryogenic temperatures without forming solid CO₂, 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 CO₂ 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 4-22 illustrates the thermodynamic path for Option E compared to Option A.

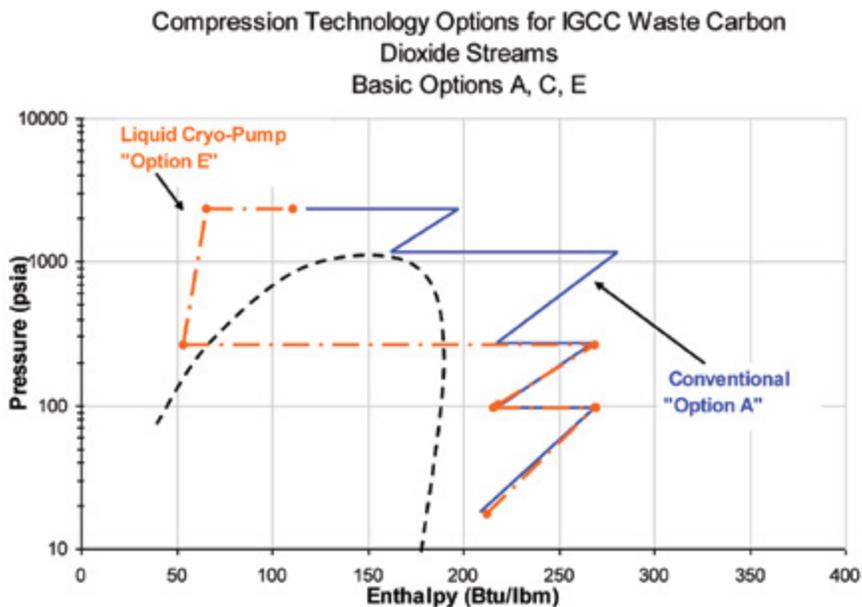


Figure 4-22: Comparison of CO₂ Liquefaction/Pumping to Centrifugal Compression

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 CO₂ 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

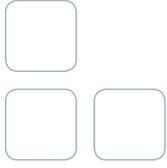
Design Option	Compression Technology	Process Parameters	Thermodynamic Equation References
A	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies)	23,251 BHP (17.35 MW)	Base
B	Conventional Dresser-Rand centrifugal 16-stage compressor (2 bodies) and with additional cooling	21,522 BHP (16.06 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 1 st and 2 nd stage cooling	24,730 BHP (18.45 MW)	+6.4%
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 CO₂, 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.

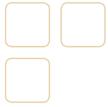
Finally, Option E.1 utilizes centrifugal compression followed by liquefaction and pumping. The pump requires only 1,400 BHP (1.04 MW), but the refrigeration system requires almost 8,000 BHP (5.97 MW). Nevertheless, significant power savings can be achieved with this approach. The combination of the semi-isothermal 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 CO₂ 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 CO₂ 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 R&D effort for pre-combustion applications is focused on advanced solvents, solid sorbents, and membrane-based systems for the separation of H₂ and CO₂. 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 CO₂ 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

The current state-of-the-art CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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).¹¹ The WGS reactor is necessary to convert the CO in the syngas to CO₂. The first-stage Selexol™ process is used for hydrogen sulfide (H₂S) separation, and the second stage for CO₂ separation. Although there are many system types, Figure 5-1 shows an example simplified schematic diagram of a two-stage Selexol™ process used for CO₂ capture.

SOLVENT RESEARCH OBJECTIVES

- Increase CO₂ loading capacity
- Reduce regeneration energy
- Improve reaction kinetics
- Decrease solvent corrosivity
- Reduce solvent volatility and degradation
- Lower capital and operating cost

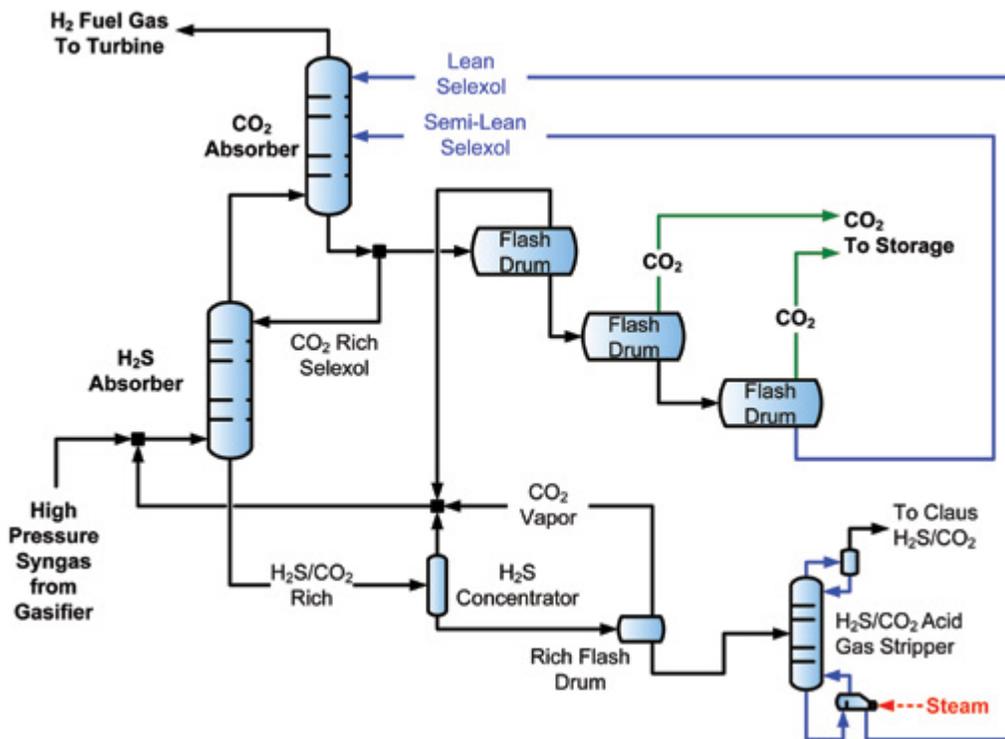


Figure 5-1: Schematic Diagram of the Pre-Combustion Selexol CO₂ Capture Process

Untreated syngas enters the first of two absorbers where H₂S is preferentially removed using CO₂-rich solvent from the CO₂ absorber. The gas exiting the H₂S absorber passes through the second absorber where CO₂ is removed using both semi-lean and lean solvent streams. The treated syngas (now concentrated in H₂) exits the absorber and is sent to the combustion turbine for power generation. The CO₂-rich solvent exits the CO₂ absorber and a portion is sent to the H₂S absorber and the remainder is sent to a series of flash drums for regeneration. The CO₂ product stream is obtained from the flash drums and the semi-lean solvent is returned to the CO₂ 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 CO₂ is produced at elevated pressure, the total compression energy requirement is lower than for post-combustion processes that typically generate their entire CO₂ product stream at near-atmospheric pressure. The H₂S/CO₂-rich solvent exiting the H₂S 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 CO₂ absorber.

Solvent Process Demonstration

RTI International will be conducting a 30–50 MW equivalent demonstration of a pre-combustion MDEA solvent technology for CO₂ 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 CO₂ 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/research/proj?k=FE0000489>

DOE/NETL R&D Activities

Pre-combustion solvent R&D activities focus on a number of research objectives that address solvent technology challenges including increasing CO₂ loading capacity and reaction kinetics coupled with decreasing regeneration energy. As mentioned later in Chapter 11, DOE/NETL's ORD is evaluating the use of ILs as physical solvents for CO₂ capture in IGCC applications. ILs are salts that are liquid at room temperature, have high CO₂ absorption potential, and have low vapor pressure. ILs can absorb CO₂ at elevated temperature, providing a potential option to combine CO₂ 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. One promising pre-combustion solvent capture technology currently under development is SRI International's ammonium carbonate/ammonium bicarbonate process. A detailed description of the process is contained in Appendix B.

TABLE 5-1: DOE/NETL R&D PROJECTS FOR PRE-COMBUSTION CO₂ CAPTURE USING SOLVENTS

Project Focus	Participant	Project Number	Performance Period
CO ₂ Capture Using AC-ABC Process	SRI International	FE0000896	9/30/09 – 12/31/13

PRE-COMBUSTION SOLVENT R&D PROJECT HIGHLIGHT AMMONIUM CARBONATE

SRI International is developing a pre-combustion chemical solvent CO₂ capture technology based on the use of a high-capacity and low-cost aqueous solution containing ammonium carbonate (AC), which reacts with CO₂ to form ammonium bicarbonate (ABC). The ABC solution is heated to release the CO₂ and regenerate the AC solution. AC has high net CO₂ 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 CO₂ 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) CO₂ capture combined with warm/humid 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 a temperature of 500°F has not been identified.

DOE/NETL R&D Activities

DOE/NETL is developing solid sorbents for pre-combustion CO₂ capture that have potential for a step-change improvement in IGCC CO₂ separation. These sorbents must maintain a high adsorption loading capacity, be resistant to attrition over multiple regeneration cycles, and exhibit good performance at the high temperatures encountered in IGCC systems to avoid the need for syngas cooling and reheating. 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
CO ₂ Capture for Low Rank Coal IGCC Systems	TDA Research, Inc.	FE0007966	10/01/2011 - 09/30/2013
Advanced Acid Gas Separation	Air Products	FE0007759	10/01/2011 - 12/31/2012
Sorbent Development for WGS	URS	FE0000465	01/01/2010 - 09/30/2013
High-Capacity Regenerable Sorbent	TDA Research, Inc.	FE0000469	10/01/2009 - 09/30/2012
Hydrogen Production and Purification	UNDEERC	NT42465-1.4	06/23/2005 - 05/31/2011
High-Density Active Carbon	UNDEERC	NT42465-3.1	06/23/2005 - 05/31/2011
Warm Gas Cleanup	RTI	NT42459	06/01/2005 - 09/30/2010
Sorption Enhance Reaction Process	Lehigh University	NT42455	05/25/2005 - 06/04/2010
Sorbent Enhanced Water-Gas Shift	UNDEERC	FT40320-03.13	04/01/2005 - 03/31/2009
Calcium Looping for Hydrogen Production	Ohio State	NT43059	07/05/2007 - 07/31/2011

SORBENT RESEARCH OBJECTIVES

- Increase CO₂ loading capacity
- Minimize regeneration energy
- Increase reaction kinetics
- Increase durability
- Improve heat management
- Lower capital and operating cost
- Optimize process design

PRE-COMBUSTION SORBENT R&D PROJECT HIGHLIGHT
NETL DEVELOPS SORBENT SUITABLE FOR COAL GASIFICATION CO₂ CAPTURE UNDER WARM-GAS CONDITIONS

Objective: The National Energy Technology Laboratory's (NETL) Office of Research and Development (ORD) is developing a regenerable solid sorbent for carbon dioxide (CO₂) capture in coal gasification applications.

Accomplishments: NETL researchers developed and patented a novel magnesium hydroxide (MgOH₂)-based sorbent for CO₂ capture at warm-gas-temperature conditions encountered in coal gasification. The MgOH₂ sorbent exhibits a CO₂ adsorption capacity that is an order of magnitude higher than that of the commercially available Selexol solvent-based process. The MgOH₂ sorbent also possesses a relatively low heat of reaction that reduces regeneration energy requirements compared to other sorbents. In addition, the sorbent can be regenerated at a relatively low temperature (400°C) and high pressure (280 pounds per square inch gauge [psig]). ORD has conducted fixed-bed laboratory-scale and bench-scale flow reactor tests to evaluate the properties and performance of the MgOH₂ sorbent under various operating conditions. This testing demonstrated a 99 percent efficiency of CO₂ removal. NETL has a Cooperative Research and Development Agreement (CRADA) with Air Liquide to apply the MgOH₂ sorbent to a hydrogen production process.



NETL Sorbent Bench-Scale Fixed-Bed Reactor Test System

Benefits: The ability to capture CO₂ at high temperatures avoids the compromise in efficiency caused by other capture methods that require cooling the syngas stream. The MgOH₂ sorbent is not only inexpensive, but also possesses a higher adsorption capacity than other sorbents, which can reduce the process equipment size and cost. The low heat of regeneration and low temperature swing required for the process results in a lower energy requirement compared to other pre-combustion CO₂ capture technologies. In addition, the high-pressure regeneration results in lower compression power and associated costs for preparing the captured CO₂ for transport and storage, or beneficial use.

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 CO₂ 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 CO₂ and H₂ and eliminating syngas cooling/reheating that is necessary for current physical solvent CO₂ separation systems.



5.C MEMBRANES FOR PRE-COMBUSTION

Membranes are a commercially-available technology in the chemical industry for CO₂ removal and H₂ purification. There is, however, no commercial application of membrane processes that aims at CO₂ 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. Gas separation membranes, in comparison to solvent and sorbent separation techniques, function as ‘unit operations’ versus a ‘process’ approach. This decreases the gas separation system complexity and provides increased IGCC power plant integration flexibility and smaller equipment footprint. In addition, gas separation membranes can be designed to produce CO₂ at pressure and, if desired, to co-capture CO₂ and H₂S.

MEMBRANE RESEARCH OBJECTIVES

- Increase permeability
- Increase CO₂/H₂ 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 CO₂ and H₂ in coal-derived syngas. 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°F. However, technical and economic barriers exist for viable pre-combustion CO₂ membrane separation such as the development of stable membrane materials and membrane module designs to facilitate optimal surface area. Processes that minimize particulate fouling and facilitate low-cost, large-scale membrane manufacturing of defect-free membranes are needed. 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

UNIQUE PRE-COMBUSTION CO₂ CAPTURE MEMBRANE TESTED AT THE NATIONAL CARBON CAPTURE CENTER (NCCC)

Objective: Membrane Technology & Research, Inc. (MTR) is developing a new polymer membrane and membrane separation process to capture carbon dioxide (CO₂) from shifted synthesis gas (syngas) generated by a coal-fired integrated gasification combined cycle (IGCC) power plant. MTR's primary research targets are to develop and test a composite polymer membrane that has a hydrogen (H₂)/CO₂ selectivity greater than 10 and H₂ permeance greater than 200 gas permeation units (GPU) at syngas cleanup temperatures of 100 to 200°C. A minimum H₂/CO₂ selectivity of 10 is necessary to achieve 90 percent CO₂ capture.

Accomplishments: The first phase of the project focused on materials development with an emphasis on identifying high-temperature polymers with desirable H₂/CO₂ separation properties. Promising polymers were then fabricated into industrial flat-sheet composite membranes and bench-scale tested with simulated syngas mixtures. In the second phase of the project, optimized membrane materials were down-selected and fabricated into composite membranes, which were formed into laboratory-scale, spiral-wound modules containing about 1 meter squared (m²) of membrane and tested with simulated syngas. The third phase of the project included field testing the membranes at the NCCC using actual syngas. Beginning in late 2009, MTR's Proteus™ membrane was tested for more than 1,700 hours in field tests at the NCCC at a scale equivalent to 50 lb/hr of syngas. The membranes showed stable performance with H₂/CO₂ selectivity of 15 to 25 and H₂ permeance of 200 to 300 GPU, which exceeded project targets. Based on this successful testing, additional scale-up testing to 500 lb/hr of syngas for a full, commercial-scale membrane module was conducted at the NCCC in 2011.

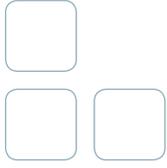
Benefits: Membranes developed in this project are based on polymer materials that show higher H₂ permeance and higher H₂/CO₂ selectivity than conventional polymer materials. Membranes offer the advantages of simple, passive operation; no use of hazardous chemicals and the subsequent waste handling and disposal issues; no water requirements; and a small footprint. Preliminary technical/economic analysis shows that the MTR membrane would increase the cost of electricity (COE) approximately 15 percent, compared to conventional solvent technologies that can increase COE by 25 to 30 percent for the same level of performance.



MTR Membrane Test Skid at the National Carbon Capture Center

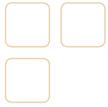
TABLE 5-3: DOE/NETL R&D PROJECTS FOR PRE-COMBUSTION CO₂ CAPTURE USING MEMBRANES

Project Focus	Participant	Project Number	Performance Period
Composite Polymer Membrane	University of North Dakota	FE0002196	12/01/2009 - 05/31/2013
High-Temperature, Polymer-Based Membrane	Los Alamos National Laboratory	04FE13-AC24	10/01/2008 - 09/30/2009
Ceramic Membrane for H ₂ Separation	Ceramatec	FE0001045	09/30/2009 - 12/31/2012
Supported Molten Metal Membranes	Worcester Polytechnic Institute	FE0001050	09/30/2009 - 09/30/2013
Amorphous Alloy Membranes for H ₂ Separation	University of Nevada	FE0000998	10/01/2009 - 05/31/2013
Nanoporous Metal Carbide Membrane for H ₂ Separation	Colorado School of Mines	FE0001009	10/01/2009 - 09/30/2013
Amorphous Alloy Membrane for H ₂ Separation	Southwest Research Institute	FE0001057	09/30/2009 - 09/30/2013
Non-Precious Metal Membranes for Hydrogen Separation	University of Texas-Dallas	FE0001293	10/01/2009 - 12/31/2013
Membrane for H ₂ Separation	Praxair	FE0004908	10/01/2010 - 09/30/2015
Membrane for H ₂ Separation	United Technologies Research Center	FE0004967	09/24/2010 - 10/31/2012
Integrated WGS Membrane	University of Wyoming	FE0004992	09/24/2010 - 06/30/2013
Pd – Pd/Alloy Composite Membrane for H ₂ Separation	Worcester Polytechnic Institute	FE0004895	10/01/2010 - 09/30/2015
Palladium-Based Membrane Reactor	Los Alamos National Laboratory	FE99002-4A24A	10/01/1998 - 09/30/2008
Dense High Temperature Ceramic Membranes	Argonne	FWP-49601	03/31/1998 - 09/30/2011
Mixed-Matrix Membranes for H ₂ /CO ₂ Separations	University of Texas	NT42173	08/26/2004 - 08/31/2008
High Flux Metallic Membranes and Reactors	REB Research	NT42400	10/01/2005 - 06/30/2010
Integrated Structural WGS Catalyst with V-Pd Alloy Membrane	Western Research	NT42454	05/02/2005 - 06/30/2009
Pilot Testing of H ₂ /CO ₂ Separation Membranes	UND EERC	NT42465-1.2	06/23/2005 - 05/31/2010
Hydrogen Transport Metal Alloy Membranes for IGCC-CCS	Eltron	NT42469	08/16/2005 - 09/30/2015
Palladium/Silver Composite Membrane	North Carolina A&T	NT42492	08/05/2005 - 02/28/2009
Palladium-Copper Trimetallic Alloy	United Technologies Research Center	NT43055	06/06/2007 - 06/30/2010
Ternary Palladium Alloy Membranes	Southwest Research	NT43056	05/02/2007 - 12/31/2010
Carbon Molecular-Sieve Membranes	Media Process & Technology	NT43057	05/02/2007 - 05/01/2012
Catalysts for Use in Membrane Reactors	Grambling State	NT43064	01/02/2007 - 06/30/2011
High-Temperature Polymeric Membranes	SRI International	NT43090	03/30/2007 - 03/31/2012
Hydrogen-Selective Zeolite Membranes	University Of Minnesota	FE0001322	10/01/2009 - 09/30/2014
Pd-Alloys for Optimum Sulfur/Carbon Resistance	Pall Corporation	FE0001181	10/01/2009 - 07/31/2014
Dual-Phase Ceramic-Carbonate Membrane Reactor	Arizona State University	FE0000470	10/01/2009 - 09/30/2013
Nanoporous, Superhydrophobic Membrane Contactor Process	Gas Technology Institute	FE0000646	10/01/2009 - 03/31/2012
Polymer Membrane Process Development	Membrane Technology & Research Inc.	FE0001124	09/15/2009 - 09/14/2011
Pressure Swing Absorption Device and Process	New Jersey Institute of Technology	FE0001323	10/01/2009 - 03/31/2013



CHAPTER 6:

POST-COMBUSTION CARBON DIOXIDE CAPTURE R&D EFFORTS



DOE/NETL is currently funding the development of advanced post-combustion CO₂ 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 CO₂ capture involves chemical or physical absorption of CO₂ 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 CO₂ loading capacity; low regeneration energy; improved reaction kinetics; and are resistant to degradation.

SOLVENT RESEARCH OBJECTIVES

- Increase CO₂ 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 CO₂ capture is new to coal-based power generation, removal of CO₂ from industrial gas streams is not a new process as illustrated in Figure 6-1.

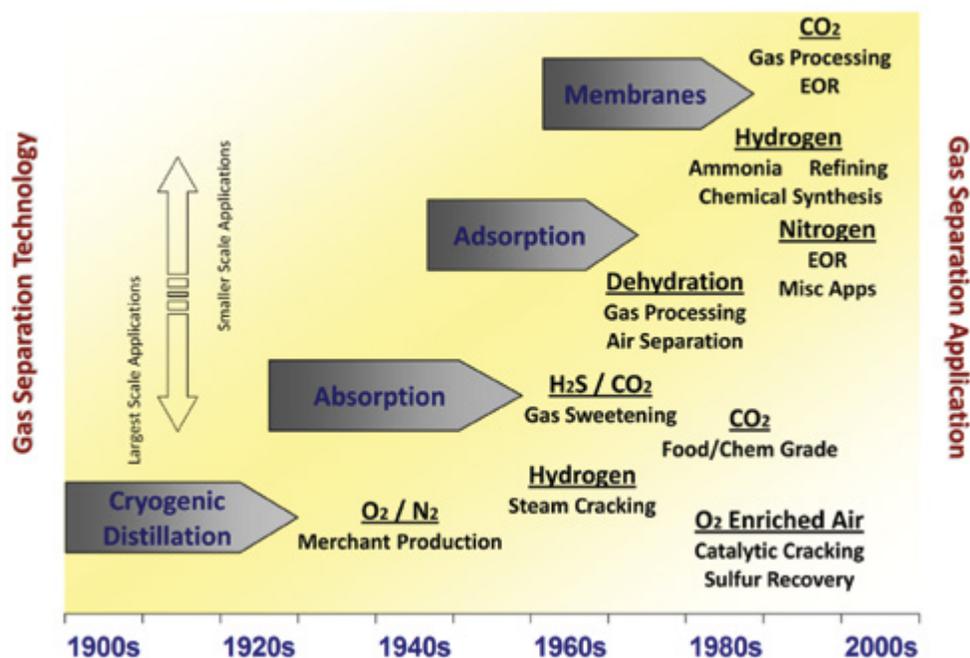


Figure 6-1: History of CO₂ Capture Processes

Gas absorption processes using chemical solvents, such as amines, to separate CO₂ from other gases have been in use since the 1930s in the natural gas industry and to produce food and chemical grade CO₂ from gas streams containing 3–25 percent CO₂. Starting in the 1940s, physical solvents were developed to absorb CO₂ from gas streams with higher CO₂ concentration (25–70 percent) and higher pressure (approximately 10 MPa). In the 1950s and 1960s, gas adsorption processes were developed to remove CO₂ from gas streams associated with hydrogen production (refineries), nitrogen separation, and dehydration. In the 1970s and 1980s, gas separation membranes were developed to capture CO₂ 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 CO₂ separation processes) provides a good example of past applications of CO₂ removal technologies.^x Prior to 1999, 25 capture facilities were built that captured CO₂ quantities ranging from 700 to 365,000 tons per year using the Econamine FG process (Table 6-1). The 10 largest facilities captured more than 22,000 tons of CO₂ per year.

TABLE 6-1. CO₂ CAPTURE PLANTS BUILT PRIOR TO 1999 USING THE ECONAMINE PROCESS

Owner	Location	Fuel	Capture Rate (tons/year)	CO ₂ Use
Carbon Dioxide Technology	Lubbock, TX	Natural Gas	365,000	EOR
Northeast Energy Associates	Bellingham, MA	Natural Gas	111,000	Food Industry
Luzhou Natural Gas	Sechuan, China	Natural Gas	58,000	Urea Plant Feed
Sumitomo Chem/Nippon Oxygen	Chiba, Japan	Heavy Fuel Oil	58,000	Food Industry
Indo Gulf Fertilizer	Uttar Pradesh, India	Natural Gas	55,000	Urea Plant Feed
Prosint	Rio de Janeiro, Brazil	Natural Gas	33,000	Food Industry
N-Ren Southwest	Carlsbad, NM	Natural Gas	33,000	EOR
Messer Greisheim do Brazil	Sao Paulo, Brazil	Natural Gas	29,000	Food Industry
Liquid Air Australia	Altona, Australia	Natural Gas	22,000	Food Industry
Liquid Air Australia	Botany, Australia	Natural Gas	22,000	Food Industry
Messer Greisheim do Brazil	Sao Paulo, Brazil	NR	18,000	Food Industry
San Miguel Corp.	San Fernando, Philippines	NR	16,000	Food Industry
European Drinks	Sudrigiu, Romania	NR	13,000	Food Industry
Cervezaria Bavaria	Barranquilla, Colombia	NR	9,000	Food Industry
Paca	Israel	NR	9,000	Food Industry
Industrial de Gaseoses	Quito, Ecuador	NR	2,200	Food Industry
Pepsi Cola	Manila, Philippines	NR	2,200	Food Industry
Pepsi Cola	Quezon City, Philippines	NR	2,200	Food Industry
Cosmos Bottling	San Fernando, Philippines	NR	2,200	Food Industry
Coca Cola	Cairo, Egypt	NR	2,200	Food Industry
Azucar Liquida	Santo Domingo, Dom. Rep.	NR	2,200	Food Industry
Tokyo Electric Power	Yokosuka, Japan	Coal	1,800	Pilot Plant
Boundary Dam Power Plant	Saskatchewan, Canada	Coal	1,100	Pilot Plant
Kansei Electric Power	Osaka, Japan	Natural Gas	700	Pilot Plant
Sundance Generating	Alberta, Canada	Coal	700	Pilot Plant

NR = Not Reported

Nine of these large facilities captured CO₂ 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 CO₂ 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 CO₂. 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 CO₂ will need to separate approximately 5 million tons of CO₂ per year.^{xi} This large difference in capacity represents a significant barrier to widespread commercial deployment of CO₂ removal technologies for coal-fired power plants.

A 2009 review of commercially available CO₂ capture technologies identified 17 facilities (using both chemical and physical capture solvents) in current operation.^{xii} These include four natural gas processing operations and a synthesis gas (syngas) production facility in which more than 1 million tons of CO₂ 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 CO₂ capture.

There is limited experience with solvent-based CO₂ capture technologies at the appropriate scale in power plant settings.^{xiii} 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 CO₂ from approximately three to five percent of the flue gas (approximately 120,000 tons of CO₂ per year). At Shady Point, a small slip stream of the facility's emissions is treated to produce approximately 73,000 tons of CO₂ per year. The CO₂ from both plants is subsequently used in the food processing industry.^{xi} At the Searles Valley Minerals soda ash plant in Trona, CA, approximately 300,000 tons of CO₂ 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 CO₂ is used for the carbonation of brine in the process of producing soda ash.

Figure 6-2 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 CO₂-lean MEA solution where CO₂ is absorbed into, and chemically reacts with MEA. The treated flue gas (primarily N₂) is discharged to the atmosphere and the CO₂-rich solution is pumped to a stripper reactor for regeneration. In the stripper, the CO₂-rich solution is heated in order to reverse the amine-CO₂ chemical reaction and strip the CO₂ 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, CO₂ 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 CO₂-lean solution is cooled and returned to the absorber for reuse.

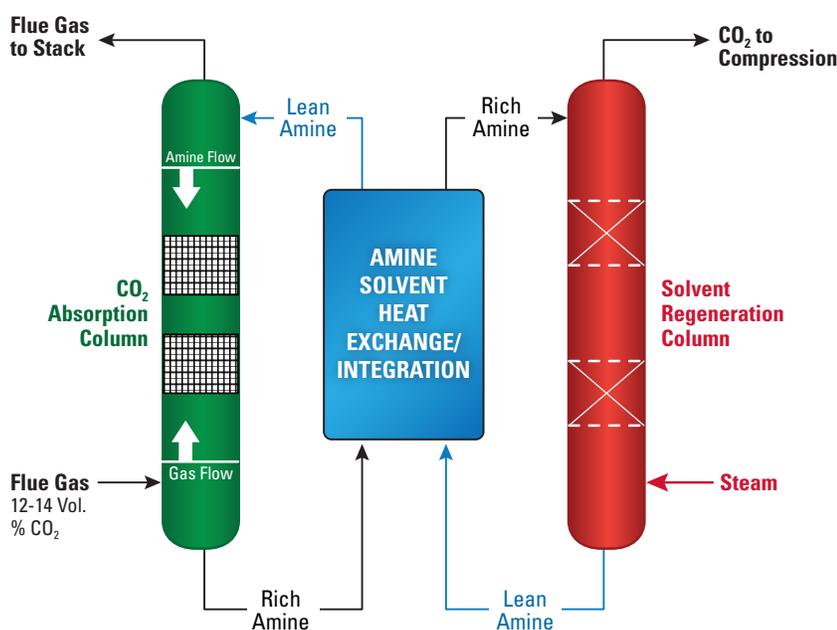


Figure 6-2: Schematic Diagram of the Post-Combustion MEA CO₂ Capture Process

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 CO₂ regeneration. Installing the current state-of-the-art MEA post-combustion CO₂ 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 CO₂ via reversible reactions to form water-soluble compounds. Despite the low CO₂ partial pressure in combustion flue gas, amines are capable of achieving high levels of CO₂ 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 CO₂ being required—therefore, having a relatively low CO₂ 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 CO₂ 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 ther-

mal units (Btu) per pound of CO₂ in the form of low pressure steam (approximately 45 psia) is required to regenerate the solvent to produce a concentrated CO₂ stream at a pressure of approximately 25 psia.

Amine-Based Solvent Process Development

With the potential of large-scale power plant CO₂ 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 PlusSM 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 CO₂ 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 CO₂ 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 PlusSM plants are operating on fossil-based power systems. However, DOE/NETL selected the Fluor Econamine FG PlusSM 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 CO₂ capture plant using MHI's KS-1 technology has been in operation since 1999 at the Petronas Fertilizer Corporation in Malaysia, where the CO₂ is captured from reformer flue gas.^x MHI conducted pilot-scale, slip-stream testing (~10 ton/day CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capacity, lack of degradation during absorption/regeneration, tolerance to O₂ 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 CO₂ 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 CO₂ 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

Although high levels of CO₂ capture are possible with chemical solvent-based systems, these systems also require significant amounts of energy for regeneration, which involves a temperature swing to break the absorbent-CO₂ 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.



A promising physical solvent-based concept for post-combustion CO₂ control involves ILs. DOE/NETL-sponsored research of ILs is being conducted by several organizations including the University of Notre Dame, General Electric, Battelle Pacific Northwest Division, and ION Engineering. ILs includes a broad category of salts that can dissolve gaseous CO₂ and are stable at temperatures up to several hundred degrees Centigrade. Since ILs are physical solvents, less energy is required for regeneration compared to today's conventional chemical solvents. However, the IL working 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 CO₂ adsorption compared to conventional solvents, perhaps adversely affecting the energy requirement to pump IL in a conventional adsorption/stripping process. Although the production cost for newly synthesized ILs is high, the cost could be significantly lower when produced on a commercial scale.

Table 6-2 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 6-2: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO₂ CAPTURE USING SOLVENTS

Project Focus	Participant	Project Number	Performance Period
Chemical Additives for CO ₂ Capture	Lawrence Berkely National Laboratory	FWP-ED33EE	06/01/2008 - 05/31/2015
Novel Aminosilicone Solvent	GE	FE0007502	10/01/2011 - 12/31/2013
CO ₂ BOLs with Polarity-Swing-Assisted Regeneration	Battelle-Pacific NW Division	FE0007466	10/01/2011 - 05/31/2014
Optimized Solvent Formulation	Babcock & Wilcox	FE0007716	10/01/2011 - 01/31/2016
Gas-Pressurized Stripping	Carbon Capture Scientific	FE0007567	10/01/2011 - 09/30/2014
Enzyme and Ultrasonic Combination Technology	Novozymes North America, Inc.	FE0007741	10/01/2011 - 03/31/2015
Waste Heat Integration	Southern Company	FE0007525	10/01/2011 - 03/31/2016
Carbon Absorber Retrofit Equipment	Neumann Systems Group	FE0007528	01/02/2012 - 11/30/2014
Slipstream Novel Amine-Based Post-Combustion Process	Linde	FE0007453	12/01/2011 - 11/30/2015
Slipstream Demonstration Using the Hitachi Advanced Solvent	University of Kentucky	FE0007395	10/01/2011 - 05/31/2016
Hot Carbonate Absorption with Crystallization-Enabled High-Pressure Stripping	University of Illinois at Urbana-Champaign	FE0004360	01/01/2011 - 12/31/2013
Carbonic Anhydrase-Potassium Carbonate Mixture	Akermin, Inc.	FE0004228	10/01/2010 - 6/30/2013
Advanced Solvent	ION Engineering, LLC	FE0005799	10/01/2010 - 09/30/2013
Piperazine Solvent with Flash Regeneration	URS	FE0005654	10/01/2010 - 09/30/2015
Self-concentrating Amine Absorbent	3 H Company, LLC	FE0004274	10/01/2010 - 01/31/2013
POSTCAP Capture and Separation	Siemens Energy Inc.	FE0003714	10/01/2010 - 02/29/2012
Reversible Ionic Liquids	Georgia Tech	NT0005287	10/01/2008 - 9/30/2011
Novel Integrated Vacuum Carbonate Process	Illinois State Geological Survey	NT0005498	10/01/2008 - 04/30/2012
Phase Transitional Absorption	Hampton U.	NT42488	06/15/2005 - 06/30/2009
Ionic Liquids	Notre Dame	NT43091	03/01/2007 - 09/30/2012

PRE-COMBUSTION SOLVENT R&D PROJECT HIGHLIGHT

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

Objective: The University of Notre Dame is developing ionic liquid (IL) solvents that can be used for cost-effective post-combustion carbon dioxide (CO₂) capture. ILs include a broad category of salts that are liquid near ambient temperature. An IL typically contains an organic cation and either an inorganic or organic anion. Due to their chemical diversity, ILs can be tailored to optimize their properties for CO₂ capture. The main advantage of ILs is that less heat is required for regeneration compared to today's conventional chemical solvents.

Accomplishments: University of Notre Dame researchers have successfully synthesized amine-functionalized ILs that possess the necessary properties to optimize the CO₂ capture process. The major research breakthroughs in IL synthesis achieved during this project include: (1) increasing CO₂ capacity; (2) eliminating viscosity increase that occurred upon absorption of CO₂ in earlier versions of the ILs; and (3) tuning reaction enthalpy. Synthesis efforts were based on molecular modeling studies, which revealed that the strategic attachment of the amine group to the IL can lead to an increased CO₂ capacity. This increase in capacity is an important step in the development of IL solvents as a cost-effective post-combustion CO₂ capture process. Researchers also developed an entirely new class of ILs, which exhibit high CO₂ capacities and little or no viscosity increase upon complexation with CO₂.

University of Notre Dame researchers constructed a laboratory-scale test system and are now conducting performance evaluations of the most promising ILs developed to date. ILs are selected for the laboratory-scale testing based on an evaluation of several properties, including: capacity, viscosity, thermal decomposition, reaction enthalpy, and other physical and thermal properties.

Benefits: ILs are promising absorbents for reducing the cost for CO₂ capture as a result of their higher CO₂ loading and lower heat requirements for regeneration compared to conventional aqueous solvents. ILs also have better oxidative and thermal stability.



University of Notre Dame Laboratory-Scale Ionic Liquid Solvent Test System

6.B SORBENTS FOR POST-COMBUSTION

Solid particle sorbents can be used for post-combustion capture of CO₂ 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 CO₂ 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 CO₂ adsorption capacity, and can withstand multiple regeneration cycles. There are several projects investigating using solid sorbents to capture post-combustion CO₂ 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 unique hybrid approaches for using sorbents. In one project, Georgia Tech Research Corporation is developing a process based on rapid temperature swing adsorption using polymer/supported amine composite hollow fibers. Another project is being conducted by the University of North Dakota to develop a process known as "Capture from Existing Coal-Fired Plants by Hybrid Sorption Using Solid Sorbents Capture" (CACHYSTM). The technology uses a regenerable metal carbonate-based sorbent with a high CO₂ loading capacity coupled with a process design that results in a low regeneration energy penalty. Table 6-3 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 SORBENT SCREENING AND PROCESS SCALE UP

Objective: ADA Environmental Solutions (ADA) is assessing the viability and advancing the development of solid sorbent-based carbon dioxide (CO₂) capture technology that can be retrofit to coal-fired power plants.

Accomplishments: Beginning in 2008, ADA initiated a laboratory evaluation of more than 140 potential CO₂ sorbents, which were procured from various sorbent developers worldwide, and included supported amines, carbon-based solids, supported carbonates, zeolites, and hydrotalcites. The CO₂ sorbents were investigated to assess their respective performance in a temperature swing adsorption (TSA) process. Sorbents were evaluated on the basis of cyclic stability, CO₂ working capacity, availability, cost of raw materials, production process, disposal costs, interaction with flue gas constituents, physical strength, and theoretical regeneration energy.

In 2010-2011, ADA conducted slip-stream field testing of four supported amine sorbents, which had performed well during laboratory-scale screening. Two of these sorbents were developed and patented by National Energy Technology Laboratory (NETL) researchers. The 1-kilowatt (kW) pilot-scale testing was conducted at Luminant's Martin Lake Station in Texas and Xcel Energy's Sherburne County Generating Station in Minnesota. The sorbents were evaluated for 50+ adsorption/regeneration temperature swing cycles using a fixed-bed contactor with a flue gas slipstream. Although 90 percent CO₂ removal was achieved when the system was operated in batch mode, the removal rate decreased as the sorbents were circulated during continuous mode operation. This lower level of CO₂ removal was attributed primarily to the system design, which consisted of a co-current transport reactor for adsorption and a fluidized bed for regeneration. Based on these results, ADA plans to utilize a counter-current, staged fluidized-bed design for the adsorption reactor in future testing.

In 2010, ADA was awarded a follow-up project to design and construct a 1-megawatt (MW) pilot-scale plant to demonstrate solid sorbent-based post-combustion CO₂ capture technology to reduce uncertainty of scale up and accelerate the path to commercialization. The field testing is scheduled to be conducted in 2014 at Southern Company's Plant Miller. This project is one of six research and development (R&D) carbon capture projects that were selected by the U.S. Department of Energy (DOE) to receive funding from the American Recovery and Reinvestment Act of 2009 (ARRA). Results of the pilot-scale testing will be used to prepare detailed designs and cost estimates for industrial- and utility-scale CO₂ capture applications.

Benefits: A solid sorbent post-combustion CO₂ capture technology potentially offers several advantages over a conventional aqueous solvent-based process such as monoethanolamine (MEA). Solid sorbents have the potential to significantly reduce the regeneration energy penalty compared to solvents. This energy penalty reduction can be attributed to: (1) the heat capacity of solids is significantly lower than that of water (i.e., by approximately a factor of four), which dramatically reduces the sensible heat input required to accomplish the temperature swing; and (2) the moisture content during regeneration will be significantly lower for solids compared to solvents, so less evaporation will occur.



ADA-ES 1-kW Pilot-Scale Test Equipment

TABLE 6-3: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO₂ CAPTURE USING SORBENTS

Project Focus	Participant	Project Number	Performance Period
Hybrid Sorption Using Solid Sorbents	Univ. of North Dakota	FE0007603	09/28/2011 - 09/30/2014
Low-Cost, High-Capacity Regenerable Sorbent	TDA Research, Inc.	FE0007580	09/28/2011 - 09/30/2014
Rapid-Temperature Swing Adsorption	Georgia Tech Research Corporation	FE0007804	09/29/2011 - 09/30/2014
Rapid Pressure Swing Adsorption	W.R. Grace and Co.	FE0007639	09/30/2011 - 09/30/2014
Advanced Solid Sorbents and Processes for CO ₂ Capture	Research Triangle Institute	FE0007707	09/30/2011 - 12/31/2014
Novel Adsorption Process	InnoSeptra LLC	FE0007948	09/29/2011 - 03/31/2014
Solid Sorbents as Retrofit Technology	ADA-ES	FE0004343	10/01/2010 - 12/31/2014
Low-Cost Solid Sorbent	TDA Research, Inc.	NT0005497	10/01/2011 - 9/30/2014
Hybrid Absorption/Stripper Process	William Marsh Rice University.	FE0007531	11/01/2008 - 08/31/2013
Novel Solid Sorbents	SRI	NT0005578	09/30/2008 - 11/30/2013
Metal Monolithic Amine-Grafted Zeolites	U. of Akron	NT43086	02/21/2007 - 03/31/2011
A Dry Sorbent-Based Post Combustion CO ₂ Capture	RTI	NT43089	03/07/2007 - 12/31/2009
CO ₂ Removal from Flue Gas Using Microporous MOFs	UOP	NT43092	03/12/2007 - 06/30/2010

6.C MEMBRANES FOR POST-COMBUSTION

Membrane-based post-combustion CO₂ capture uses permeable or semi-permeable materials that allow for the selective separation of CO₂ from flue gas. While membranes are more advantageous for separating CO₂ in high-pressure applications, such as coal gasification, DOE/NETL is also focused on developing highly-selective and permeable membrane systems designed specifically for CO₂ separation from low partial pressure, post-combustion flue gas streams. Membranes potentially could be a more cost-effective technology option for post-combustion CO₂ capture than solvents or sorbents that require a large amount of regeneration energy to separate the CO₂. 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 CO₂ separation from natural gas. In general, membrane processes offer several potential advantages compared to other post-combustion CO₂ capture technologies including: (1) simple passive operation with no moving parts; (2) energy-efficient with low operating costs; and (3) a small footprint that is easily expandable due to modular design components.

MEMBRANE RESEARCH OBJECTIVES

- Increase permeability
- Increase CO₂/N₂ 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 development of commercial-scale membrane modules that can achieve low pressure drop and high packing density. Gas absorption membrane technologies are also under development where the separation is caused by the presence of an absorption liquid on one side of the membrane that selectively removes CO₂ 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 a membrane-solvent system that uses an amine as the solvent. Table 6-4 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 6-4: DOE/NETL R&D PROJECTS FOR POST-COMBUSTION CO₂ CAPTURE USING MEMBRANES

Project Focus	Participant	Project Number	Performance Period
Composite Hollow Fiber Membranes	GE	FE0007514	09/29/2011 - 12/31/2014
Inorganic/Polymer Composite Membrane	Ohio State University	FE0007632	09/29/2011 - 05/31/2015
Low-Pressure Membrane Contactors (Mega-Module)	Membrane Technology & Research Inc.	FE0007553	09/30/2011 - 09/30/2014
Electrochemical Membrane	FuelCell Energy	FE0007634	09/29/2011 - 05/31/2015
Hybrid Membrane/Absorption Process	Gas Technology Institute	FE0004787	09/24/2010 - 12/31/2013
Low-Temperature Membrane	American Air Liquide, Inc.	FE0004278	09/27/2010 - 11/30/2012
Polymeric Membranes	Membrane Technology & Research Inc.	FE0005795	09/17/2010 - 09/30/2015
Hollow-Fiber, Polymeric Membrane	RTI	NT0005313	09/26/2008 - 09/30/2011
Dual Functional, Silica-Based Membrane	U. of New Mexico	NT42120	08/23/2004 - 04/30/2009
Biomimetic Membrane	Carbozyme	NT43084	03/27/2007 - 07/31/2009

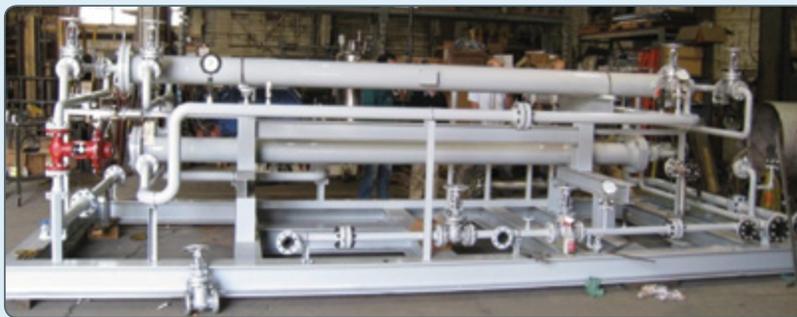
PRE-COMBUSTION MEMBRANE R&D PROJECT HIGHLIGHT

ADVANCEMENTS IN MEMBRANE DEVELOPMENT, PROCESS CONFIGURATION, AND SCALE-UP

Objective: Membrane Technology & Research, Inc. (MTR) is developing a polymeric membrane and associated process for carbon capture (CO₂) capture. The project includes conducting slipstream laboratory-scale (0.05 megawatt-electric [MWe]) and small pilot-scale (1 MWe) tests using full-scale commercial membrane modules.

Accomplishments: MTR has made significant advances in membrane development, process configuration, and scale-up for post-combustion CO₂ capture applications. The use of commercially available membranes for post-combustion CO₂ capture was previously considered impractical due to the large membrane area required for separation because of the low partial pressure of CO₂ in flue gas. However, MTR is using a two-fold approach to address this issue: (1) the development of high-permeance membranes to reduce the required membrane area and associated capital cost, and (2) the use of incoming combustion air in a countercurrent/sweep module design to generate separation driving force and reduce the need for vacuum pumps and the associated parasitic energy cost. In addition to improving membrane performance, improved membrane manufacturing techniques and materials have been developed.

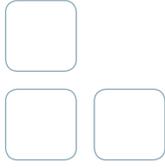
The newly developed membranes have a CO₂ permeance approximately tenfold higher than commercial CO₂-selective membranes. These new membranes – designated Polaris™ – also have a high CO₂/nitrogen (N₂) selectivity. In addition, the membrane permeance has recently been increased from 1,000 to 2,200 gas permeation units (GPU) while maintaining selectivity. This membrane research and development (R&D) program was initiated in 2007. 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 standard cubic feet per minute (scfm). Based on successful bench-scale testing, a follow-up project was initiated in 2008 culminating in a small slip-stream field test that was conducted in 2010. The approximately 175 scfm (equivalent to approximately 1 ton per day [tpd] of CO₂) testing was conducted at Arizona Public Service's coal-fired Cholla Power Plant. MTR now plans to conduct additional small pilot-scale field testing based on a gas flow rate of approximately 2,500 scfm (equivalent to approximately 1 MWe or about 20 tpd of CO₂) as part of a new project with NETL that is scheduled for completion in 2015.



MTR Membrane Test Skid

Benefits: Based on MTR's membrane module performance obtained to date, 90 percent of the CO₂ in flue gas can be separated using about 12 percent of the energy generated by the plant with an additional 8 to 10 percent of the plant's generation required for compression, transport, and geological storage. Preliminary process design simulations suggest a promising CO₂ separation and liquefaction cost of \$30/ton CO₂.

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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.

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 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 ($CO_2 + SO_x, NO_x, O_2$)

OXY-COMBUSTION R&D PROJECT HIGHLIGHT

OXY-COMBUSTION RETROFIT TECHNOLOGY FOR TANGENTIALLY FIRED COAL BOILERS

Objective: Alstom Power, Inc. (Alstom) is developing and testing oxy-combustion technology for tangentially fired (T-fired) boilers in retrofit and new power plant applications.

Accomplishments: Alstom successfully conducted a series of pilot-scale testing (15-megawatt-thermal [MWth] or ~5-megawatt-electric [MWe] equivalent) of a T-fired, oxy-combustion boiler using four different coal types, including sub-bituminous, low-sulfur bituminous, high-sulfur bituminous, and North Dakota lignite. In order to conduct the testing, Alstom modified their T-Fired Boiler Simulation Facility (BSF) located in Windsor, Connecticut, to accommodate firing under both air and oxygen, as well as with several flue gas recycle configurations and oxygen injection methods. Initial screening studies were conducted to assess the impacts of a broad range of process variables and boiler design parameters on oxy-combustion boiler design, performance, and cost. Pilot-scale testing included both oxy- and air-firing tests, which examined the impacts of combustion and oxy-process parameters on boiler design and operation for each of the coals. Test parameters included re-circulated flue gas ratio, effect of oxygen concentration and oxygen distribution into the furnace, re-circulated flue gas take-off location, total excess oxygen, furnace combustion staging, air in-leakage rates, and reduced load operation.

In general, oxy-fired operation of the BSF resulted in stable operation over a broad range of test conditions and produced flue gas with greater than 90 percent carbon dioxide (CO₂) concentration (dry basis). The testing focused on control of furnace heat release rates and heat transfer for boiler thermal performance during oxy-combustion, while obtaining good fuel burnout and control of emissions. By controlling the amount and location of oxygen added, researchers were able to achieve similar heat transfer rates and temperature profiles for both air- and oxy-fired operations. The general operation and combustion performance of oxy-combustion with flue gas recycle presented no significant technical issues.

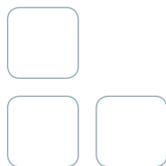
Benefits: Oxy-combustion is a cost-competitive, near-term solution for CO₂ capture that offers a relatively low technical risk due to use of conventional power plant components. The research is providing key data for commercialization of the oxy-combustion process. Results from the 15-MWth testing, along with refined modeling tools (computational fluid dynamics [CFDs] and dynamic simulations), are being applied to develop a basic design for a future full-scale demonstration oxy-boiler. Large, commercial-scale oxy-boiler reference designs are also being developed for industrial and utility applications. In addition to applicability for new power plants, the technology can be readily retrofit to existing T-fired boilers, which represent approximately 41 percent of U.S. coal-fired power plant capacity.



Alstom's 15-MWth Boiler Simulation Facility

TABLE 7-1: DOE/NETL R&D PROJECTS FOR OXY-COMBUSTION CO₂ CAPTURE

Project Focus	Participant	Project Number	Performance Period
Staged, High-Pressure Oxy-Combustion	Washington U.	FE0009702	10/01/2012 - 09/30/2013
Pressurized Oxy-combustion with Flameless Reactor	Unity Power Alliance	FE0009478	10/01/2012 - 09/30/2013
Pressurized Fluidized Bed Combustor Development	Pratt and Whitney Rocketdyne	FE0009448	10/01/2012 - 09/30/2013
Supercritical CO ₂ Power Cycle	Southwest Research Institute	FE0009395	10/01/2012 - 09/30/2013
High Efficiency Molten Bed Oxy-combustion	Gas Technology Institute	FE0009686	10/01/2012 - 09/30/2013
Analysis of CCS Technology Adoption	Argonne	FWP49806	02/01/2011 - 01/31/2014
Engineering Assessment of Oxy-Combustion	Canmet	IEA-CANMET-CO ₂	09/30/1999 - 12/31/2009
Boiler Materials for Oxy-Combustion	Foster Wheeler	NT0005262	09/25/2008 - 01/31/2012
Characterization of Oxy-Combustion Impacts	Reaction Engineering	NT0005288	10/01/2008 - 09/30/2013
Tangentially Fired Oxy-Combustion Boilers	Alstom	NT0005290	09/30/2008 - 04/30/2014
Flue Gas Purification	Air Products	NT0005309	10/01/2008 - 09/30/2010
Near-Zero Emission Flue Gas Purification	Praxair	NT0005341	10/01/2008 - 06/30/2012
Evaluation of Gas Recycle for Oxy-Combustion	SRI	NT42430	09/27/2005 - 09/26/2010
Nitrogen Behavior in Oxy-Combustion	Brigham Young	NT42530	08/04/2005 - 12/31/2008
Multi-Pollutant Control	Washington U.	NT42531	08/29/2005 - 02/28/2009
Oxy-Syngas Combustor & Turbine	Clean Energy Systems	NT42645	09/30/2005 - 03/31/2013
Oxy-Combustion Design for Retrofits	Babcock & Wilcox	NT42747	03/31/2006 - 03/31/2011
Oxy-Combustion & IPR	Jupiter Oxygen	NT42811	09/28/2006 - 09/30/2012
Oxygen Transport Membrane-Based Syngas Production	Praxair	NT43088	03/30/2007 - 09/30/2015



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 O₂ is required. Although a cryogenic ASU can be used to supply high-purity O₂ 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 O₂ production.

The ITM O₂ production process (being developed by Air Products) uses non-porous, mixed ion and electron conducting materials operating typically at 800 to 900° C. Ion and electron flow paths occur through the membrane counter-currently, and the driving force for O₂ separation is determined by the O₂ partial pressure gradient across the membrane, typically 200 to 300 psig on the feed side and low to sub-atmospheric pressure on the permeate side. The goal of the ITM research is to develop, scale-up, and demonstrate this novel air separation technology for producing O₂ at approximately one-third lower cost and energy requirement compared to conventional cryogenic processes.

Table 8-1 provides a list of recent and current DOE/NETL external R&D projects related to O₂ 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
ITM O ₂ Technology	Air Products	FT40343	10/01/1998 - 09/30/2015
Sorbents for Air Separation	TDA Research, Inc.	ER84216	08/07/2006 - 08/06/2010
Materials for Oxygen Separation	Eltron	ER84600.002	08/08/2007 - 08/07/2010
Nanofiller Oxygen Membranes	North Carolina A&T	NT42742	02/17/2006 - 12/31/2010
Low-Cost Oxygen Supply	Linde (BOC)	NT42748	04/01/2006 - 09/30/2008

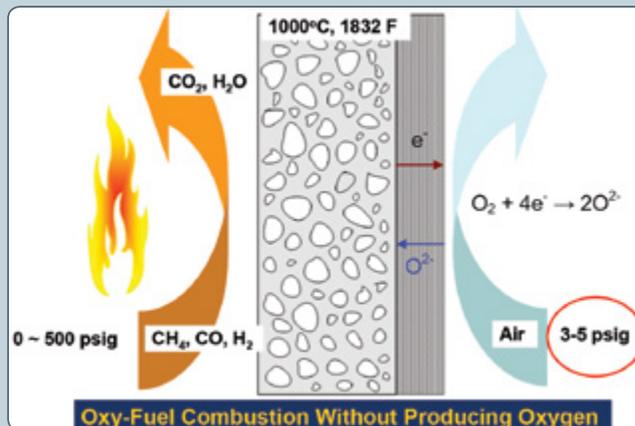
OXY-COMBUSTION R&D PROJECT HIGHLIGHT OXYGEN TRANSPORT MEMBRANE

Objective: Praxair, Inc. is developing the oxygen transport membrane (OTM), which could prove to be a transformational technology based on its potential to drive significant economic benefits in a wide range of industrial processes. In today's conventional design for an oxy-combustion boiler system, the oxygen (O_2) would be separated in a cryogenic-based air separation unit (ASU) and then delivered to the boiler for combustion. OTM technology integrates O_2 separation and combustion in one device.

Accomplishments: Praxair is optimizing OTM performance, materials, and process configurations leading to subsequent field testing of OTM technology for both synthesis gas (syngas) production and oxy-combustion applications. This research and development (R&D) effort is providing valuable experience needed to develop commercial OTM technology for both industrial and power generation facilities. To date, Praxair has demonstrated achievement of flux and performance targets with advanced OTM materials; developed a manufacturing protocol for pilot-scale OTM tubes; and completed design and construction of a multi-tube OTM reactor at the University of Utah.

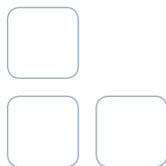
The project includes two phases of technology development testing. The first phase includes design and construction of a small pilot-scale OTM for testing as a syngas production system for industrial applications, which utilizes the OTM partial oxidation (Pox) reactor to generate syngas from a natural gas feedstock. The small pilot-scale OTM Pox reactor testing has a capacity to generate approximately 160,000 standard cubic feet per day (scfd) of syngas, which is equivalent to approximately 0.5-megawatt-thermal (MWh) output. The second phase includes bench-scale testing of an OTM boiler equivalent to approximately 50-kilowatt (kW) thermal output.

Benefits: OTM technology creates an entirely new method of oxygen production for combustion and partial oxidation applications. The main advantage of an OTM is its capability to separate oxygen from air less expensively than conventional cryogenics, while reducing the parasitic power consumption typically associated with cryogenic separation technologies. The use of OTM is expected to reduce the power associated with oxygen production by 70 to 80 percent. In addition to power generation, the development of OTMs will also benefit industrial processes used to produce syngas for subsequent processing into a variety of chemical and/or petrochemical end products. Processes that are under consideration for integration of OTM include gas reformers, Pox reactors, and process heaters. For example, combustion processes in cement plants, chemical plants, refineries, steel and aluminum plants, other manufacturing facilities, and opportunity fueled power plants can benefit using OTM.



Principle of OTM Operation

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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 CO₂ CAPTURE USING CHEMICAL LOOPING

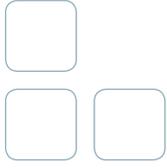
Project Focus	Participant	Project Number	Performance Period
Iron Based Coal Direct Chemical Looping	Babcock & Wilcox	FE0009761	10/01/2012 - 09/30/2013
Solid-Fueled Pressurized Chemical Looping	University of Kentucky	FE0009469	10/01/2012 - 09/30/2013
Chemical Looping Combustion Technology	Alstom	FE0009484	10/01/2012 - 09/30/2013
Coal-Direct Chemical Looping for Retrofits	Ohio State	NT0005289	01/01/2009 - 09/30/2013
Simulation and Modeling for Oxy-Combustion and Chemical Looping	University of Utah	NT0005015	09/10/2008 - 08/31/2013
Magnetically Fluidized Chemical Looping	University of Florida	FE0001321	10/01/2009 - 09/30/2013
Magnetically Fluidized Chemical Looping	Western Kentucky University	FE0001808	12/01/2009 - 11/30/2012
Novel CLC Oxygen Carriers	Alstom	NT43095	07/12/2007 - 07/31/2012

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 H₂ or syngas and a separated stream of high purity CO₂. Calcium oxide is used to capture CO₂ and calcium sulfate (CaSO₄) 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 CO₂ 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, CO₂ 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.^l

ADVANCED COMPRESSION RESEARCH OBJECTIVES

- Reduce capital costs
- Increase efficiency
- Optimize integration with CO₂ capture process
- Improve heat recovery

To reduce compression costs, DOE/NETL is developing novel concepts for large-scale CO₂ 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 CO₂ COMPRESSION

Project Focus	Participant	Project Number	Performance Period
Thermal Integration of CO ₂ Compression	Lehigh University	FE0002146	12/01/2009 - 06/29/2012
Evaluation of Compression Efficiency Improvements	Southwest Research Institute	NT42650	09/28/2005 - 12/31/2013
Shock Wave Compression	Ramgen	FE0000493	05/10/2006 - 06/30/2014

Novel Concepts for CO₂ Compression

Southwest Research Institute (SwRI) is developing two novel concepts that have the potential to reduce CO₂ compression power requirements by 35 percent compared to conventional compressor designs. The first concept is a semi-isothermal compression process where the CO₂ 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 CO₂ 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 CO₂ to approximately 250 psia and the refrigeration power required to liquefy the gaseous CO₂. Once the CO₂ 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 CO₂. 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 CO₂ 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}

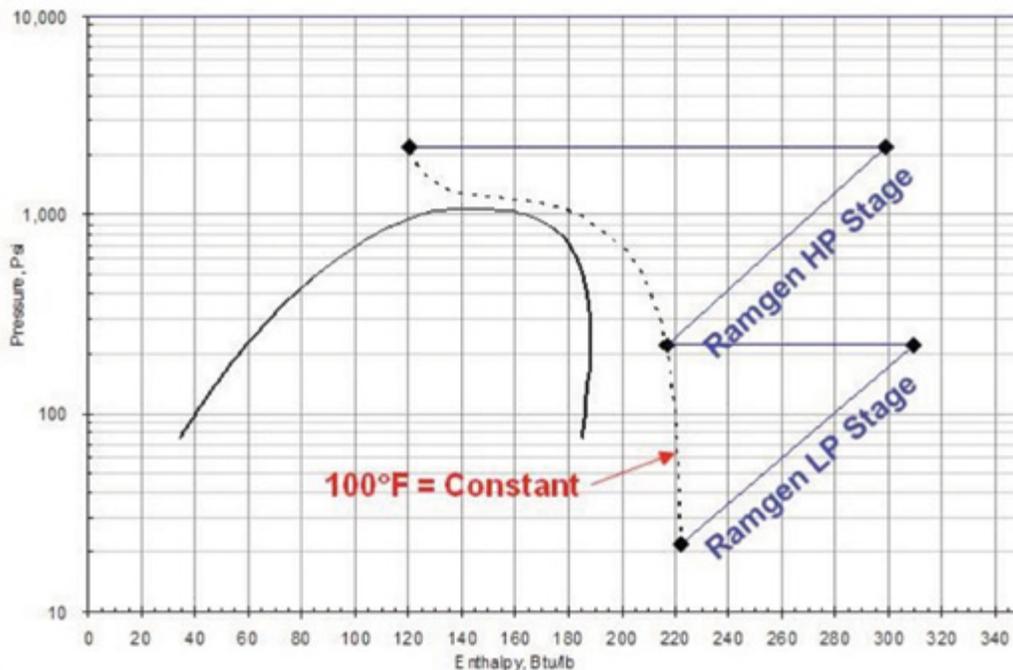


Figure 10-1: Ramgen Two-Stage Shock Wave Compression Pressure-Enthalpy Curve

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

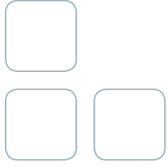
TABLE 10-2: RAMGEN TWO-STAGE SHOCK WAVE COMPRESSION PARAMETERS

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%



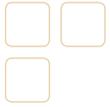
Rampressor Pilot-Scale Test Facility

In August 2009, DOE announced that Ramgen had been awarded \$20 million in funding from the American Recovery and Reinvestment Act to further scale up the Rampressor to approximately 13,000 horsepower, which should accelerate commercial deployment of the novel CO₂ compressor.



CHAPTER 11:

DOE/NETL IN-HOUSE R&D EFFORTS



DOE/NETL’s ORD is developing new breakthrough concepts for CO₂ capture that could lead to dramatic improvements in cost and performance relative to today’s 1st generation technologies. DOE/NETL CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture applications.

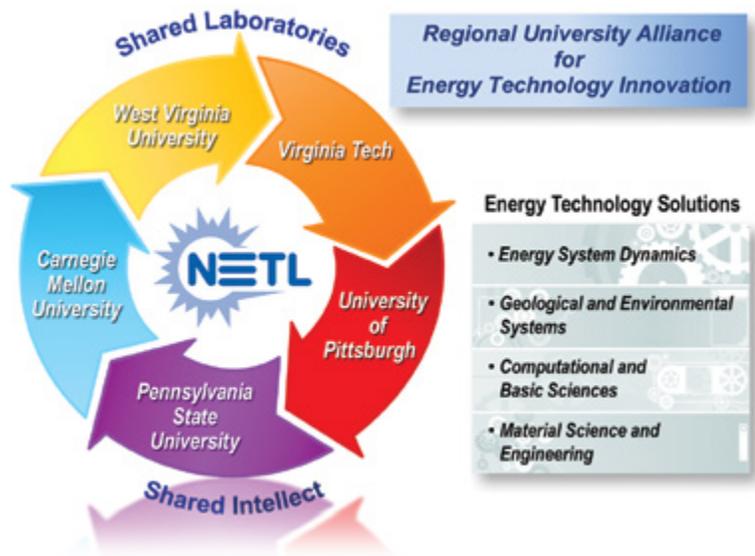


Figure 11-1: NETL-RUA R&D Partnership and Focus Areas



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 CO₂ 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 CO₂ capture technologies including: solvents, sorbents, CO₂ and H₂ selective membranes, oxy-combustion, and chemical looping.

11.A SOLVENTS

NETL-RUA is investigating the development of novel solvent-based CO₂ 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 CO₂ 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	<ul style="list-style-type: none"> Analyze oligomeric 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 CO₂ 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 CO₂ 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	<ul style="list-style-type: none"> 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	<ul style="list-style-type: none"> Develop a warm, fluid bed, bench scale integrated CO₂ 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 CO₂ 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 (TiO₂)-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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture systems.

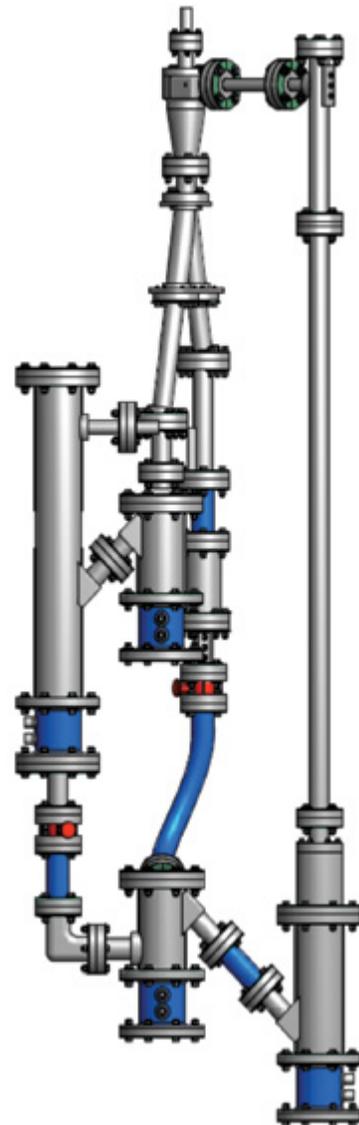


Figure 11-3: Sorbent Test Reactor System

11.C CARBON DIOXIDE SELECTIVE MEMBRANES

NETL-RUA is developing both IL-based membranes and mixed-matrix membranes (MMM) for the selective separation of CO₂ from power plant gas streams. Table 11-3 provides a summary of NETL-RUA's CO₂ 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

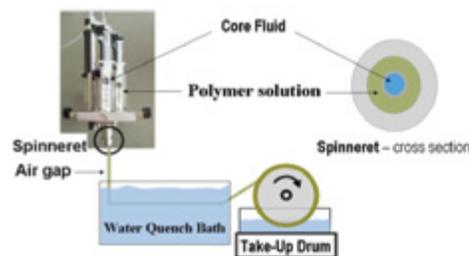


Figure 11-4: Fiber Spinning System and Ionic Liquid Loaded Membrane Fibers

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ SELECTIVE MEMBRANE R&D ACTIVITIES

CO ₂ Capture Technology	NETL-RUA R&D Activities
CO ₂ Selective Membranes	<ul style="list-style-type: none"> • 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 CO₂ selective membranes, NETL-RUA is investigating membrane systems designed for H₂ removal from mixed gas streams found in IGCC power plant applications. Table 11-4 provides a summary of NETL-RUA's H₂ selective membrane R&D activities. Hydrogen selective membranes have shown promise for the purification of CO₂ from pre-combustion gas streams, where the low-pressure pure H₂ permeate can be directed to an advanced fuel cell or turbine for electricity production, while the high-pressure, CO₂-rich retentate can be processed for sequestration.

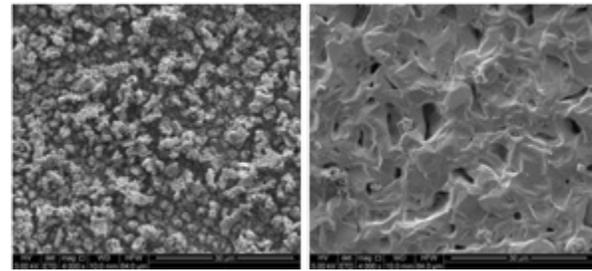


Figure 11-5: Syngas Exposure Testing for Palladium Membrane Materials

NETL-RUA is focusing efforts on the development of H₂ 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 underlining 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.

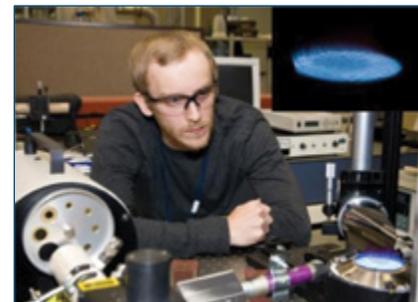
TABLE 11-4: NETL-RUA H₂ SELECTIVE MEMBRANE R&D ACTIVITIES

CO ₂ Capture Technology	NETL-RUA R&D Activities
H ₂ Selective Membranes	<ul style="list-style-type: none"> • 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 temperature 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.



Laboratory Combustion Testing

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.

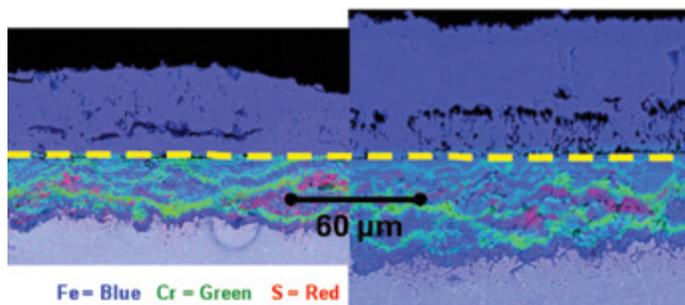


Figure 11-6: Corrosion Evaluation of Alloy T92 in Air and Oxy-Combustion Environments

TABLE 11-5: NETL-RUA OXY-COMBUSTION R&D ACTIVITIES

CO ₂ Capture Technology	NETL-RUA R&D Activities
Oxy-Combustion	<ul style="list-style-type: none"> • 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.

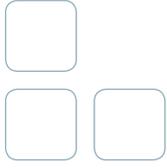
11.F CHEMICAL LOOPING

The combustion of fossil fuels in the presence of pure oxygen, rather than air, represents an opportunity to facilitate CO₂ 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.

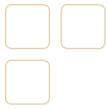
TABLE 11-6: NETL-RUA CHEMICAL LOOPING R&D ACTIVITIES

CO ₂ Capture Technology	NETL-RUA R&D Activities
Chemical Looping Combustion	<ul style="list-style-type: none"> • 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 CO₂ 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 CO₂ capture and compression technologies; screening studies to evaluate the potential feasibility of individual 2nd and 3rd generation advanced CO₂ 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 CO₂ 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/research/energy-analysis/publications/>

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 CO₂ 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 CO₂ capture) would require the successful development of 2nd generation CCS with a COE no greater than \$80/MWh.

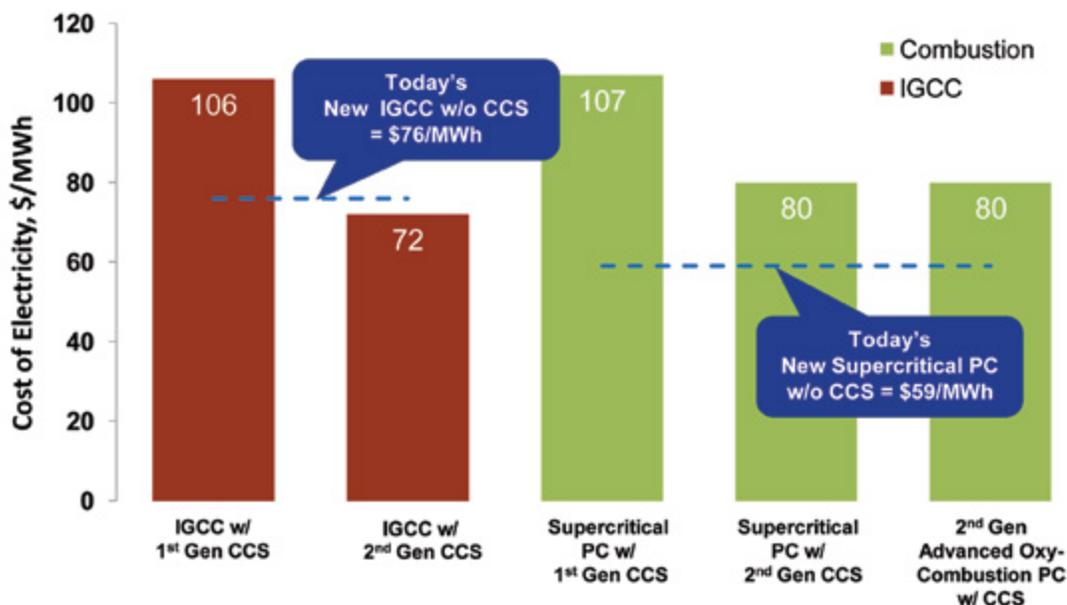


Figure 12-1: First Year COE for Power Plants with 1st and 2nd Generation CO₂ Capture Technologies

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 CO₂ 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.^{xvi}

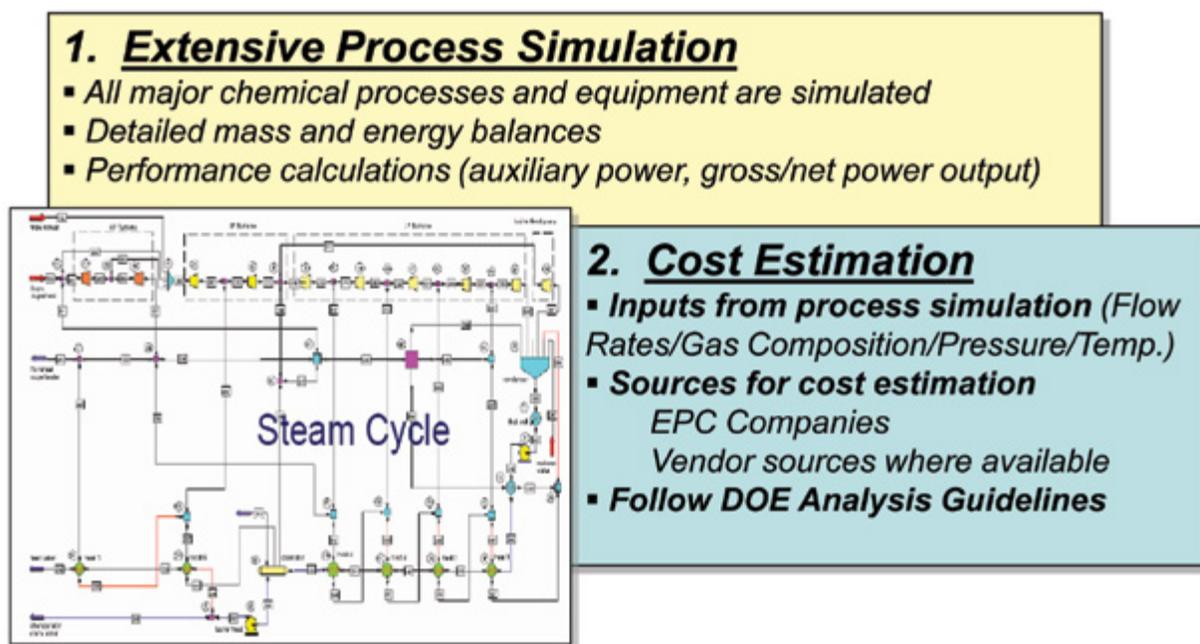


Figure 12-2: Outline of OPPA Approach to Conduct Technical-Economic Analyses

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%	<ul style="list-style-type: none"> 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 CO₂ 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."¹¹ 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 ₂ S Separation/Removal	Sulfur Removal/Recovery	CO ₂ 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 2 nd 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 2 nd 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 2 nd 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.

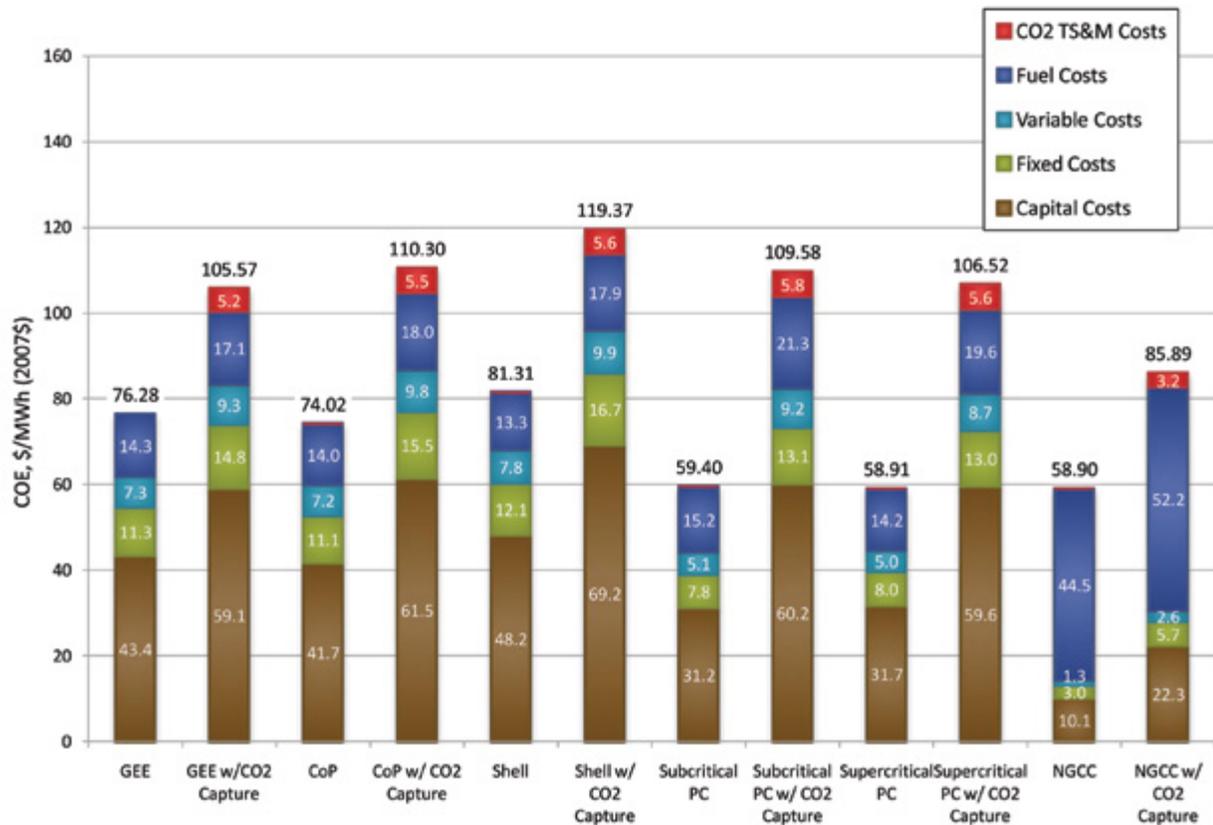


Figure 12-3: First Year COE for Cases in Bituminous Baseline Study

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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture equals that of NGCC with CO₂ capture at a gas price of \$9.80/MMBtu. The average COE for PC with CO₂ capture equals that of NGCC with CO₂ 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.^{xiii} The study analyzes several power generation configurations with and without CO₂ 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 CO₂ capture and compared the results to non-capture and amine-based post-combustion CO₂ capture systems.^{ix} A total of 12 plant configuration cases were analyzed including four conventional air-based combustion cases for reference (with and without CO₂ capture), six oxy-combustion cases with O₂ provided by a cryogenic distillation process, and two oxy-combustion cases with O₂ provided by an ion transport membrane (ITM) process. Both supercritical and ultra-supercritical steam cycles were analyzed and different levels of O₂ purity and CO₂ 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 CO₂ 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 CO₂ capture system.
- Oxy-combustion with co-sequestration (Cases 5 and 6) has the lowest cost of CO₂ 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.^{xiii} A total of 17 cases were examined, six of which are air-fired, supercritical power plants, without CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture system is approximately 11 absolute percentage points or 27 percent on a relative basis.
- Oxy-combustion combined with cosequestration of CO₂ and combustion products offers the potential to be less costly than alternative methods of CO₂ 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, 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 CO₂ capture systems. These pathway studies show the progression in COE from 1st generation to 2nd generation CO₂ capture technologies. The following sections provide an overview of three pathway studies on pre-, post-, and oxy-combustion CO₂ capture and the technology steps involved in achieving the improved cost and performance of these 2nd generation CO₂ capture technologies.

Pre-Combustion Capture Pathway Study

OPPA completed a Pre-Combustion Capture Pathway Study in November 2010.^{xvii} Achieving the significant cost reduction for 2nd generation pre-combustion CO₂ 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 CO₂ 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 H₂ membranes for CO₂ separation; advanced H₂ 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	CO ₂ Separation	Gas Turbine	Oxygen Production
Reference IGCC	Slurry	80%	2-Stage Selexol		Adv “F”	Cryogenic Air Separation Unit (ASU)
Coal Pump	Coal Feed Pump					
85% CF		85%	WGCU	Hydrogen Membrane	AHT-1	
WGCU/Selexol						
WGCU/H ₂ Membrane		90%	AHT-2	ITM		
AHT-1						
ITM		90% CF				
AHT-2						

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 CO₂ capture system, successful R&D includes manufacturing of H₂ 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 H₂ membrane and for the AHT. Cost benefits are also achieved through the ITM and availability improvements. Overall, the 2nd generation pre-combustion CO₂ 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 CO₂ capture, the high temperature H₂ membrane paired with WGPU 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 CO₂ capture. While the H₂ membrane has the capability to produce high purity H₂, in this case it is optimized for power efficiency by using the N₂ from the ASU as a sweep gas, reducing the H₂ partial pressure and producing a mix of H₂ fuel and N₂ diluent for the AHT. The CO₂-rich non-permeate from the H₂ membrane is compressed to a liquid phase and non-condensibles are separated and returned to the topping combustor. The resulting CO₂ stream is produced at elevated pressure.

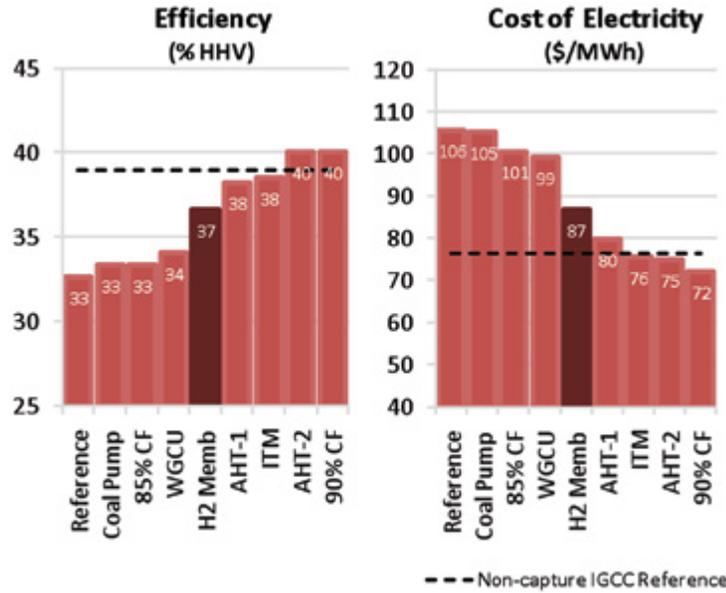


Figure 12-4: Efficiency and First Year COE for Cases in Pre-Combustion Capture Pathway Study

Figure 12-5 highlights the key system performance benefits (reduction in auxiliary power and increase in gross power) of the WGPU and H₂ 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 “WGPU with 2-Stage Selexol” to “WGPU and a H₂ 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 CO₂ 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 CO₂ compression load.

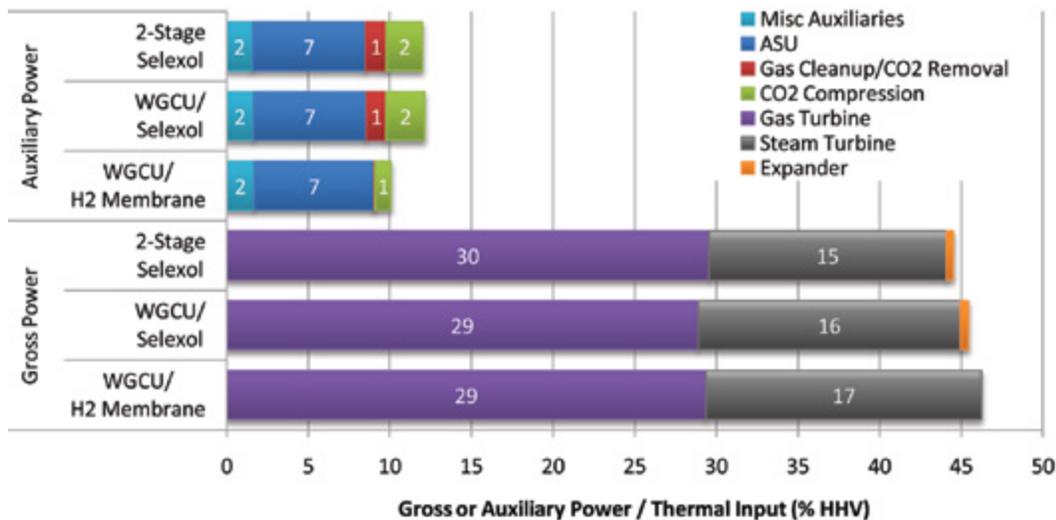


Figure 12-5: Warm Gas Cleanup and H₂ Membrane Performance in Pre-Combustion Pathway Study

The Pre-Combustion Capture Pathway Study assesses just one of many options for 2nd generation CO₂ capture coupled with advanced IGCC designs. The study also highlights the potential significant system benefits for any pre-combustion CO₂ capture system technologies that can achieve the following: produce high pressure CO₂; minimize regeneration steam requirements; operate at elevated syngas temperatures for pairing with WGPU; 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 CO₂ 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 CO₂ 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 CO₂ capture pathway steps are being assessed that represent a possible scenario for the evolution of the PC power plant with post-combustion CO₂ capture. The results quantify the potential improvements in technical-economic performance that could accrue from successful post-combustion CO₂ 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 CO₂ capture, while Case 2 includes the Case 1 plant, but equipped with a 1st generation solvent-based CO₂ 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.³ 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 CO₂ compression (represented by Ramgen's shockwave compression) that is currently under development. Case 7 applies an advanced CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture technology cases were compared to the COE of an air-fired, supercritical boiler with no CO₂ 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 CO₂ 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.

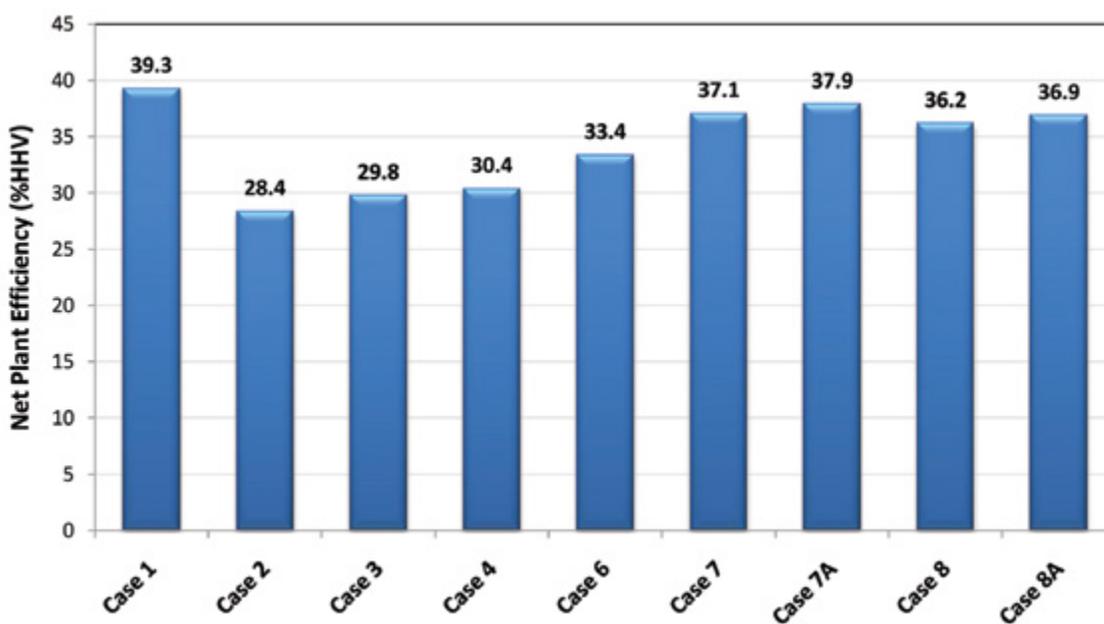


Figure 12-6: Net Plant Efficiency for Cases in Post-Combustion Capture Pathway Study

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 CO₂ capture membrane technology (Case 7A), or advanced sorbent technology (Case 8A) coupled with advanced CO₂ 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.

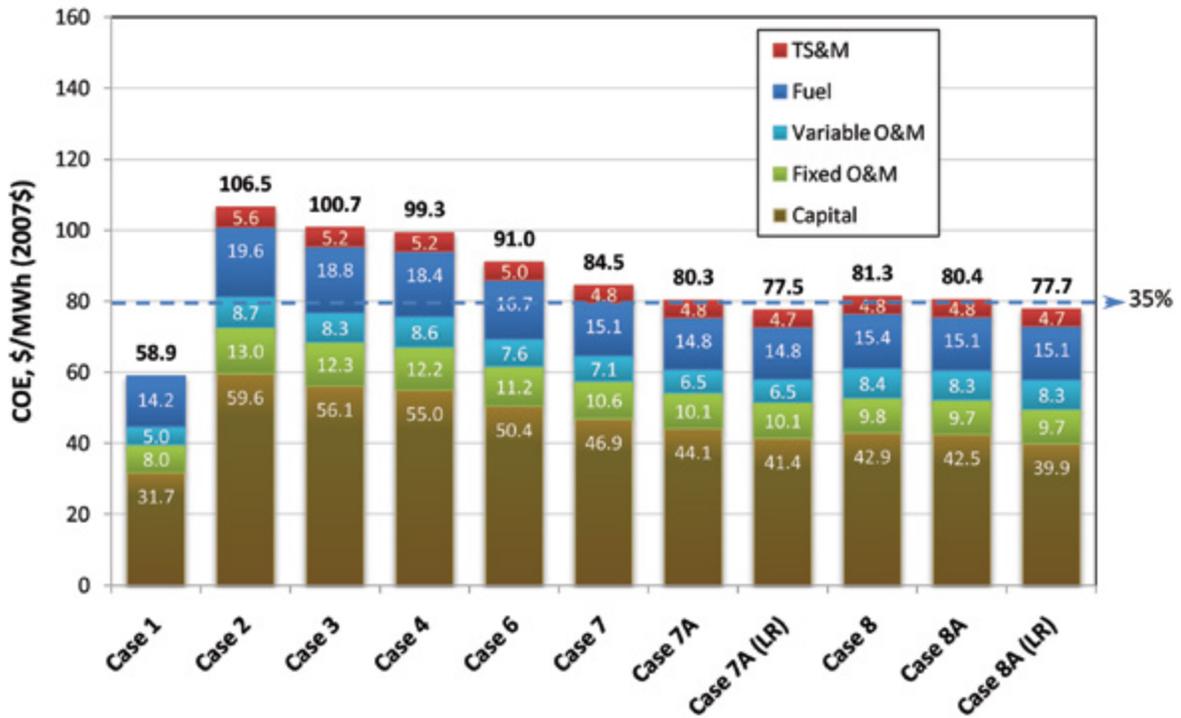


Figure 12-7: First Year COE for Cases in Post-Combustion Capture Pathway Study

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 CO₂ 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 CO₂ 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 (1 st 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 CO₂ 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.

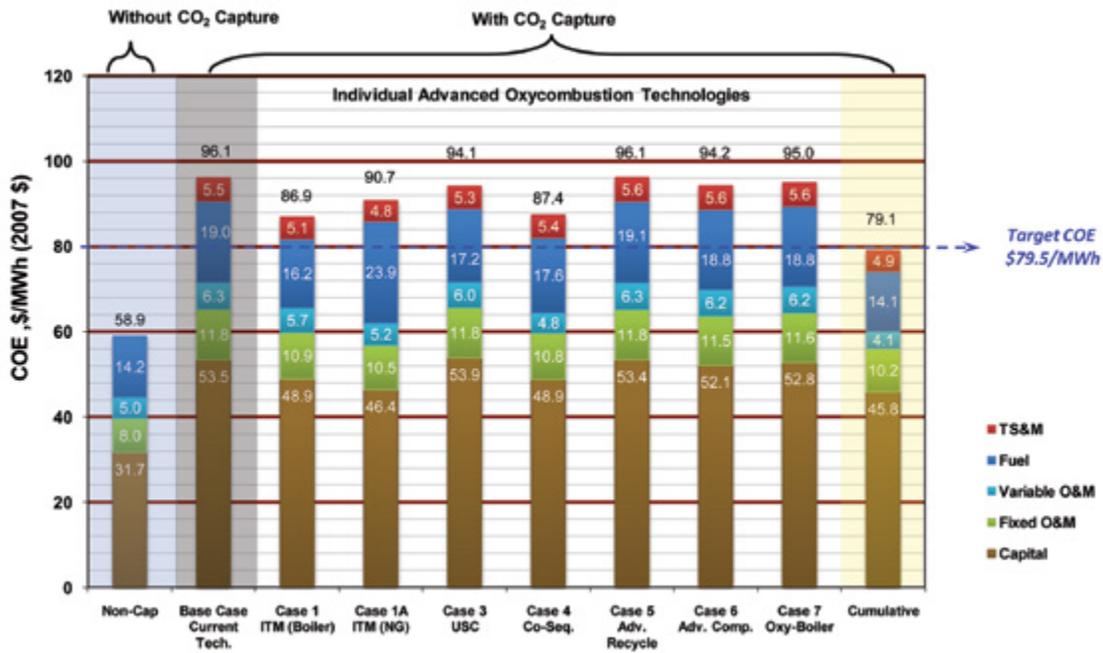


Figure 12-8: First Year COE for Cases in Oxy-Combustion Capture Pathway Study

TABLE 12-6: PERCENT INCREASE IN COE FOR CASES IN OXY-COMBUSTION CAPTURE PATHWAY STUDY

Study Case	Cost of Electricity, \$/MWh (2007 \$)					Total	Increase in COE (%)*
	Capital	Fixed O&M	Variable O&M	Fuel	TS&M		
Non-Capture Reference, Air-fired supercritical w/o CCS	31.68	7.97	5.03	14.22	0.00	58.90	-
Current OF Technology, O ₂ -fired supercritical w/ASU & CCS	53.45	11.76	6.32	19.05	5.52	96.11	63.2
Case 1, O ₂ -fired supercritical w/ Boiler ITM & CCS	48.93	10.89	5.73	16.20	5.15	86.90	47.5
Case 1A, O ₂ -fired supercritical w/NG ITM & CCS	46.38	10.45	5.17	23.90	4.82	90.74	54.1
Case 3, O ₂ -fired ultra-supercritical w/ASU & CCS	53.88	11.76	5.99	17.20	5.27	94.10	59.8
Case 4, O ₂ -fired supercritical w/ASU & Co-Sequestration	48.87	10.80	4.77	17.62	5.37	87.42	48.4
Case 5, O ₂ -fired supercritical w/ASU, Wet Recycle & CCS	53.40	11.75	6.33	19.07	5.60	96.15	63.2
Case 6, O ₂ -fired supercritical w/ASU & Shock Compression	52.13	11.52	6.20	18.78	5.56	94.19	59.9
Case 7, O ₂ -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 CO₂ 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 CO₂ 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 CO₂ capture to meet DOE/NETL's CO₂ 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 CO₂ 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 SO₂, NO_x, PM, Hg, and CO₂. The model can be used as a screening model for evaluating advanced process designs for CO₂ 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 CO₂ 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 CO₂ stream using oxygen rather than air for combustion in a PC plant, with recycle of the CO₂-rich flue gas. Additional options under development include advanced power system components and CO₂ capture technologies promising lower costs. To simulate a complete CCS system, the costs of CO₂ 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>

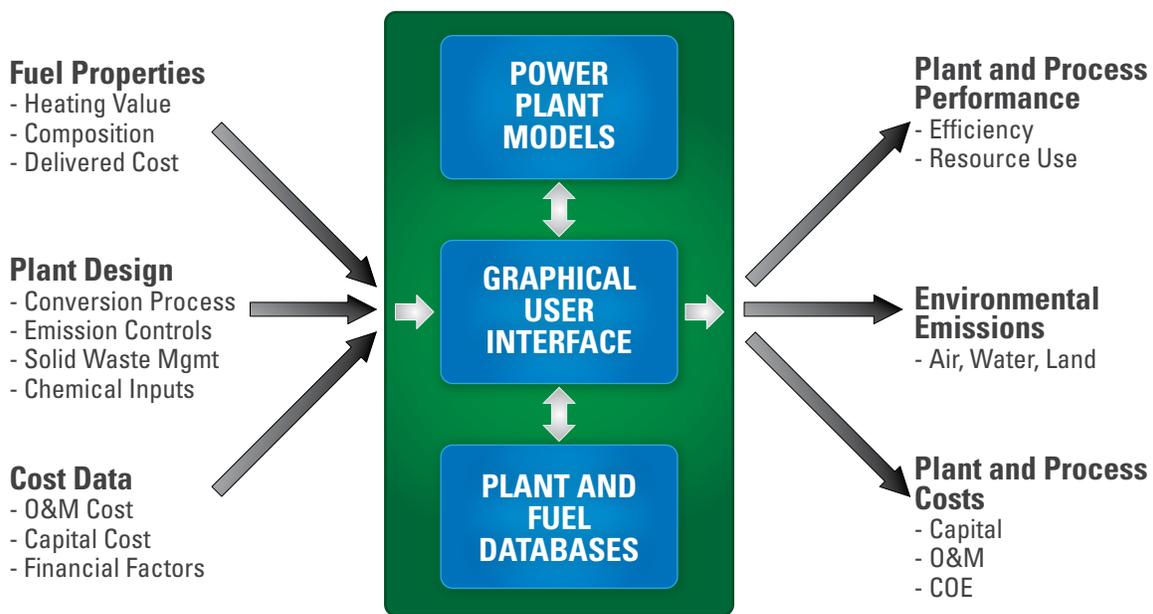
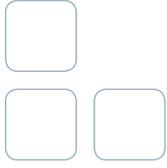


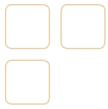
Figure 12-9: Structure of the IECM Modeling Environment

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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 CO₂ 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 CO₂ 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 CO₂ sorbent into an H₂ 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 CO₂ removal. This project also includes an examination of available membranes for H₂ and CO₂ 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 CO₂ in order to provide cost-effective options for stabilizing and ultimately reducing concentrations of CO₂ in the atmosphere. As part of this project, researchers will determine the flue gas CO₂ reduction effectiveness of solid adsorbents through the use of a recirculating transport reactor. In addition, UNDEERC will perform pilot-scale tests to demonstrate CO₂ 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 CO₂ 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 CO₂ capture technology for coal-based power generation with the addition of the National Carbon Capture Center (NCCC) at the Power Systems Development Facility (PSDF). The PSDF is an engineering-scale demonstration site for advanced power system components located adjacent to Alabama Power's coal-fired Plant Gaston in Wilsonville, Alabama. The PSDF is a unique test facility – large enough to produce commercially representative data from the major components required for a commercial plant – while remaining small enough for economic operation. The mission of the PSDF-NCCC is to develop technologies that will lead to the commercialization of cost-effective, advanced coal-based power plants with CO₂ 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 CO₂ 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. CO₂ 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 CO₂ 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.

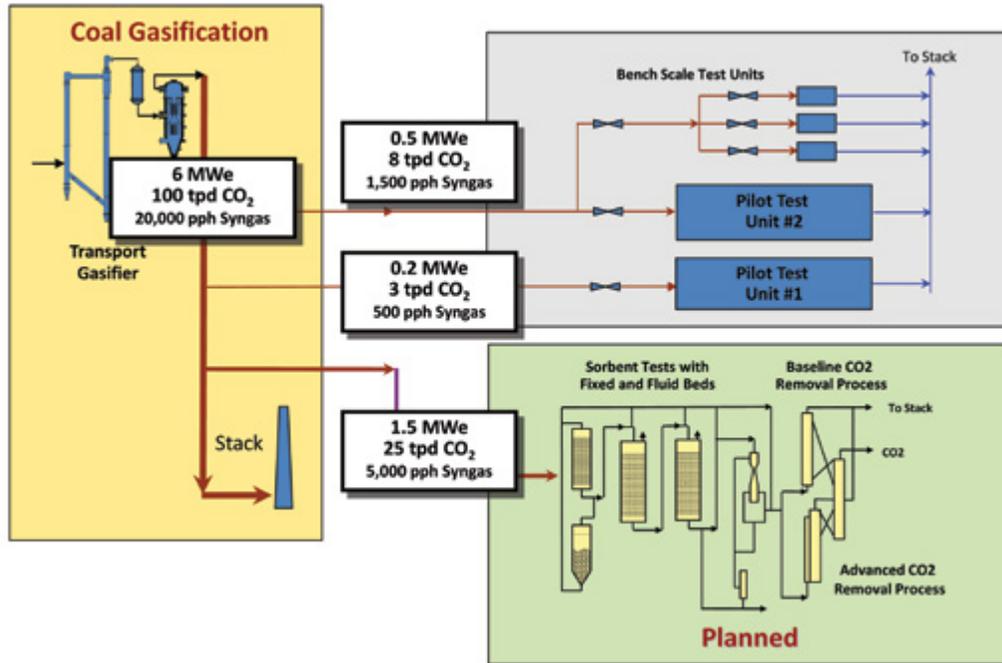


Figure 13-1: NCCC Pre-Combustion CO₂ Capture Slipstream Test Units

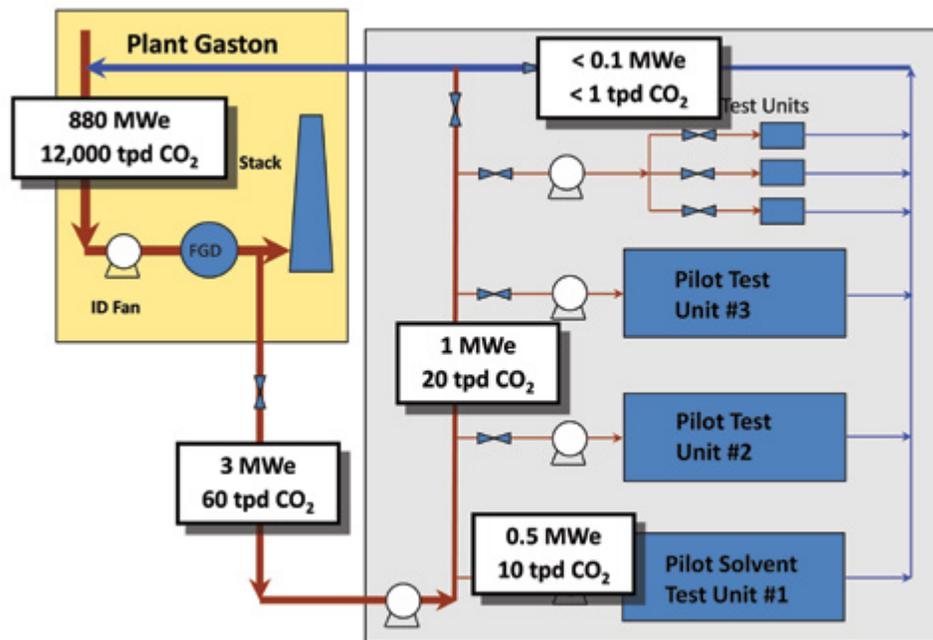


Figure 13-2: NCCC Post-Combustion CO₂ Capture Slipstream Test Units

Other Pilot-Scale Testing Facilities

In addition to the DOE/NETL/Southern Companies testing facility at NCCC, there are some privately-held facilities where pilot-scale testing is being conducted. These include a Babcock and Wilcox (B&W) facility in Ohio and an Alstom facility in Connecticut.

The B&W testing center is called the Regenerable Solvent Absorption Technology facility. It consists of a 7,500-square-foot, seven story building containing absorption and regeneration equipment for the testing of solvent capture technologies (Figure 13-3). It can treat approximately 3,100 pounds per hour of flue gas from B&W's coal-fired Small Boiler Simulator facility - equating to about 7 tons per day of captured CO₂ (approximately 0.5 MWe). Testing operations at the facility were initiated in 2009, and since that time, numerous solvents have been successfully tested.

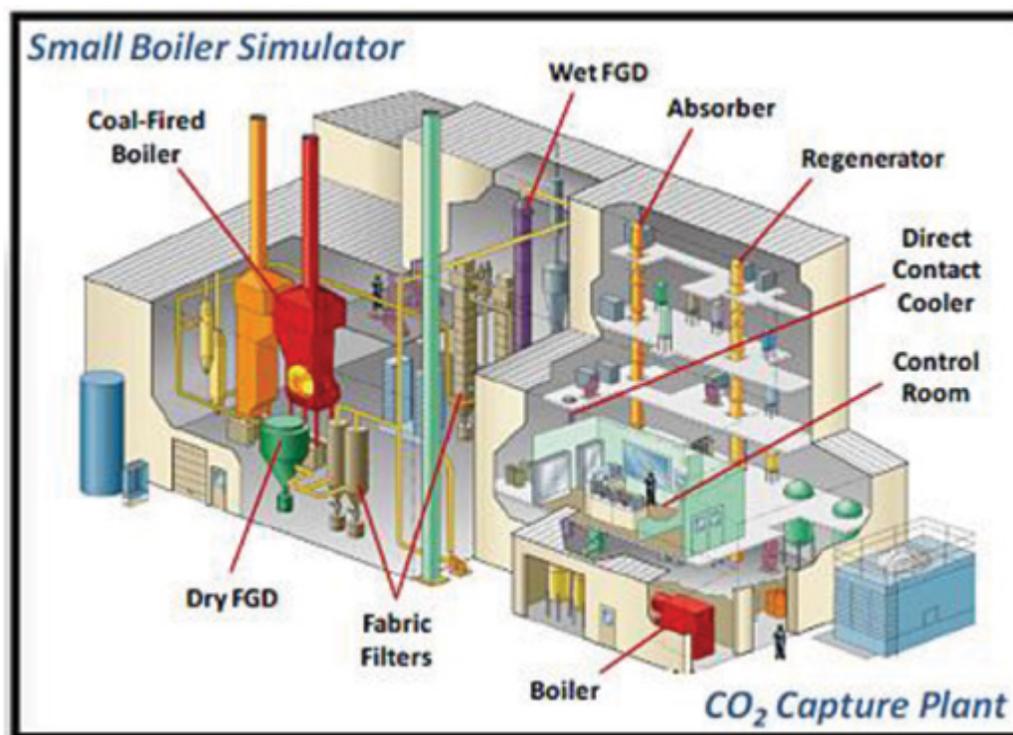


Figure 13-3: B&W Regenerable Solvent Absorption Technology Facility

The Alstom facility is known as the Boiler Simulation Facility (BSF). Testing here includes a comprehensive evaluation program focusing on development of a 5 MWe tangentially fired, atmospheric pressure oxy-combustion system (Figure 13-4). Design options including gas recycle configurations and oxygen injection schemes are being evaluated. BSF testing can cover a range of oxy-combustion configurations and include a number of coal types. Coals tested have included PRB subbituminous, low sulfur Eastern bituminous, Illinois high sulfur bituminous, and lignite. Key measurements from past BSF test campaigns include:

- Operating conditions - flows, temperatures, pressures
- Heat transfer characteristics
- Gas composition at various locations (CO₂, O₂, H₂O, NO_x, SO₂, total hydrocarbons)
- Furnace and convection pass gas temperature distributions
- Mercury, trace metals, and SO₃ measurements
- Deposition and Corrosion Probes
- Detailed furnace mapping – temperature, gas composition, particulate sampling



Figure 13-4. Alstom 5 MWe Boiler Simulation Facility

As indicated above, these are private facilities and thus not open to the public. However, it is possible that teaming arrangements could be made to foster the technology development process.

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 CO₂ 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 O₂ purity and O₂ partial enrichment, overall process performance, and cost; (2) performance testing of pilot-scale CO₂ capture and compression; (3) experimental investigation of CO₂ 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 CO₂ 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 CO₂ 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 CO₂ capture-related R&D projects.

TABLE 13-1: ARPA-E IMPACCT PROGRAM CO₂ 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/>

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 CO₂ 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://science.energy.gov/bes/efrc/> 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 CO₂ 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.

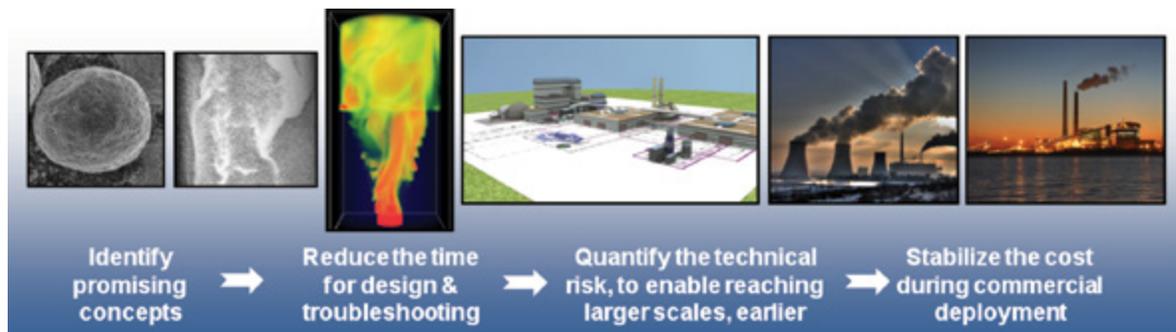


Figure 13-5: Carbon Capture Simulation Initiative

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 CO₂ 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 CO₂ 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 CO₂ capture technologies of most relevance to industry.

13.H SMALL BUSINESS AND UNIVERSITY CO₂ CAPTURE R&D EFFORTS

In addition to the relatively larger contracted and on-site CO₂ 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 CO₂ capture technology development. Table 13-2 provides a summary of some of the recent and current CO₂ 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://science.energy.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://energy.gov/fe/science-innovation/clean-coal-research/crosscutting-research/university-coal-research>

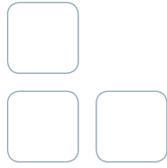
Historically Black Colleges and Universities and Other Minority Institutions Program

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://energy.gov/fe/science-innovation/clean-coal-research/crosscutting-research/university-coal-research>

TABLE 13-2: SMALL BUSINESS AND UNIVERSITY CO₂ 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 Capture 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	Envergen, 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 Advanced 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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