



NATIONAL ENERGY TECHNOLOGY LABORATORY



**DOE/NETL
Advanced Carbon Dioxide
Capture R&D Program
Accomplishments**

April 2012



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Program Accomplishments**

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LIST OF ACRONYMS

ABC	Ammonium Bicarbonate
AC	Ammonium Carbonate
ADA	ADA Environmental Solutions
Ar	Argon
ARRA	American Recovery and Reinvestment Act of 2009
ASU	Air Separation Unit
BPSC	Bechtel High Pressure Claus Process
BSF	Boiler Simulation Facility
Btu	British Thermal Unit
CaO	Calcium Oxide
CCS	Carbon Capture and Storage
CFD	Computational Fluid Dynamic
CLC	Chemical Looping Combustion
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
COE	Cost of Electricity
CRADA	Cooperative Research and Development Agreement
DOE	U.S. Department of Energy
EOR	Enhanced Oil Recovery
FGD	Flue Gas Desulfurization
gpm	Gallons per Minute
GPU	Gas Permeation Units
H ₂	Hydrogen
H ₂ O	Water
H ₂ S	Hydrogen Sulfide
H ₂ SO ₄	Sulfuric Acid
Hg	Mercury
HNO ₃	Nitric Acid
hp	Horsepower
IGCC	Integrated Gasification Combined Cycle
ILs	Ionic Liquids
ITM	Ion Transport Membranes
kW	Kilowatts
m ²	Square Meters
MEA	Monoethanolamine
MOF	Metal Organic Framework
MTR	Membrane Technology & Research, Inc.
MW	Megawatt
MWe	Megawatt-Electric
MWh	Megawatt-Hour
MWth	Megawatt-Thermal
N ₂	Nitrogen

NCCC.....	National Carbon Capture Center
NETL.....	National Energy Technology Laboratory
NGCC.....	Natural Gas Combined Cycle
NH ₃	Ammonia
NO.....	Nitric Oxide
NO ₂	Nitrogen Dioxide
NO _x	Nitrogen Oxides
O&M.....	Operation and Maintenance
O ₂	Oxygen
OPPA.....	Office of Program Planning and Analyses
ORD.....	Office of Research and Development
OTM.....	Oxygen Transport Membrane
PC.....	Pulverized Coal
PC4.....	Post-Combustion Carbon Capture Center
PM.....	Particulate Matter
Pox.....	Partial Oxidation
PSA.....	Pressure Swing Adsorption
PSDF.....	Power Systems Development Facility
psi.....	Pounds per Square Inch
psia.....	Pounds per Square Inch Absolute
psig.....	Pounds per Square Inch Gauge
PSTU.....	Pilot Solvent Test Unit
R&D.....	Research and Development
RUA.....	Regional University Alliance
scfd.....	Standard Cubic Feet per Day
scfm.....	Standard Cubic Feet per Minute
SCR.....	Selective Catalytic Reduction
SO ₂	Sulfur Dioxide
SO ₃	Sulfur Trioxide
SO _x	Sulfur Oxides
SRI.....	Southern Research Institute
SwRI.....	Southwest Research Institute
Syngas.....	Synthesis gas
T-Fired.....	Tangentially Fired
TPD.....	Tons per Day
TSA.....	Temperature Swing Adsorption
VPSA.....	Vacuum Pressure Swing Adsorption
WGS.....	Water-Gas Shift

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MESSAGE TO STAKEHOLDERS

The U.S. Department of Energy's (DOE) Fossil Energy Program has adopted a comprehensive, multi-pronged approach to the research and development (R&D) of advanced carbon dioxide (CO₂) capture technologies for coal-based power plants. Under this program, DOE's National Energy Technology Laboratory (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 overall goal of DOE/NETL's CO₂ capture R&D program is to develop advanced technologies that achieve 90 percent CO₂ capture at less than a 10 percent increase in the cost of electricity (COE) of pre-combustion capture for integrated gasification combined cycle (IGCC) power plants and less than a 35 percent increase in COE of post- and oxy-combustion capture for new and existing conventional coal-fired power plants. Given the significant economic penalties associated with currently available CO₂ capture technologies, significant improvements in both cost and energy efficiency will be required to achieve these goals. DOE/NETL CO₂ capture R&D was initiated in the late 1990s, and focused on laboratory-scale research on a broad spectrum of CO₂ capture approaches including advanced second and third generation solvents, sorbents, membranes, oxy-combustion systems, and chemical looping. These laboratory-scale investigations are anticipated to continue through 2017. Testing of promising technologies at the small pilot-scale commenced in 2010 and will continue through 2021. Large pilot-scale testing is scheduled to begin in 2016 and continue through 2025. This schedule will allow for demonstration-scale testing to begin after 2020. It is anticipated that successful progression from laboratory- through demonstration-scale testing will result in several of these advanced technologies being available for commercial deployment after 2030.

The purpose of this report is to provide an overview of some of the significant accomplishments that have been achieved to date through the R&D efforts being conducted by DOE/NETL on advanced second and third generation CO₂ capture technologies for coal-based power systems.

CHAPTER 1: INTRODUCTION

Significant accomplishments have been achieved to date through DOE/NETL R&D efforts on second and third generation advanced CO₂ capture technologies for coal-based power systems. This report provides an overview of some of these accomplishments.

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. In each case, the captured CO₂ would be compressed for transport via pipeline or tanker car to a permanent storage site or for beneficial utilization, such as enhanced oil recovery (EOR).

Although the majority of the CO₂ capture 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 two companion documents: "DOE/NETL Carbon Dioxide Capture and Storage RD&D Roadmap, December 2010" is available for download at:

http://www.netl.doe.gov/technologies/carbon_seq/refshelf/CCSRoadmap.pdf, and "DOE/NETL Advanced Carbon Dioxide Capture R&D Program: Technology Update, May 2011" is available for download at: <http://www.netl.doe.gov/technologies/coalpower/ewr/pubs/CO2Handbook/>.



1.A Pre-Combustion CO₂ Capture

Pre-combustion systems are designed to separate CO₂ from hydrogen (H₂) and other constituents in the synthesis gas (syngas) stream produced by the gasifier in IGCC power plants or other industrial facilities. In a gasifier, fuel is converted into gaseous components by applying heat under pressure in the presence of steam and sub-stoichiometric oxygen (O₂). A simplified process schematic for pre-combustion CO₂ capture is shown in Figure 1-1. 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. A CO₂ capture technology 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 pulverized coal (PC) combustion 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. Advanced pre-combustion CO₂ capture technologies being investigated by DOE/NETL include the use of solvents, sorbents, and membranes.

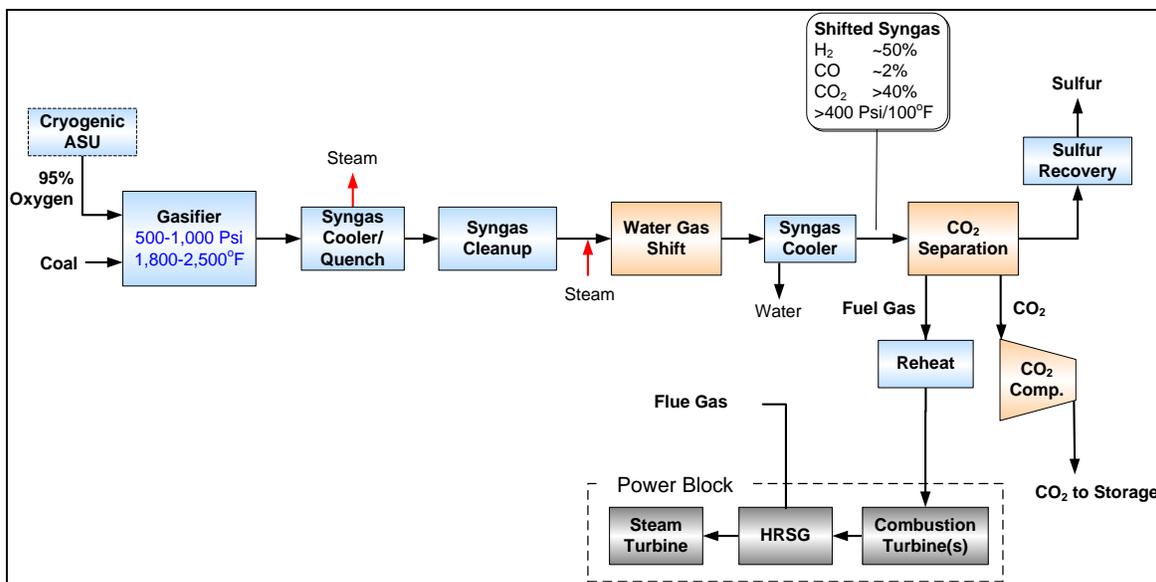


Figure 1-1: Block Diagram Illustrating an IGCC System with Pre-Combustion CO₂ Capture

1.B Post-Combustion CO₂ Capture

Post-combustion CO₂ capture systems are primarily applicable to conventional PC power plants. Post-combustion CO₂ capture refers to removal of CO₂ from combustion flue gas prior to discharge to the atmosphere. In this approach, CO₂ is separated from nitrogen (N₂), which is the primary constituent of the flue gas. A simplified process schematic of post-combustion CO₂ capture is shown in Figure 1-2. 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 to 15 volume percent in coal-fired systems, three to four volume percent in gas-fired turbines); the flue gas is at low pressure (15 to 25 pounds per square inch absolute [psia]); trace impurities (particulate matter [PM], sulfur oxides [SO_x], nitrogen oxides [NO_x], etc.) can degrade the 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.

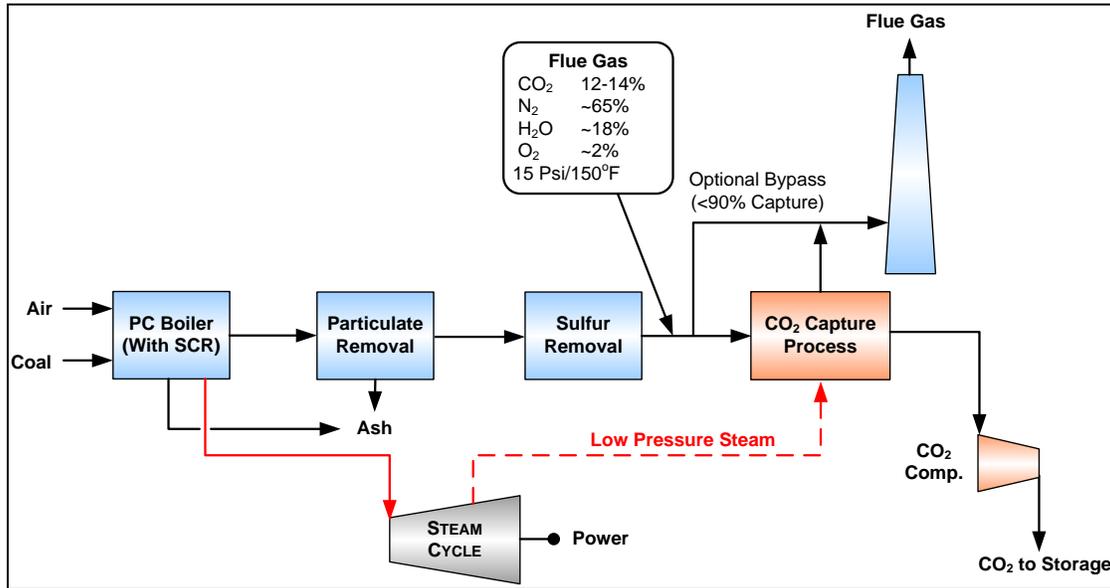


Figure 1-2: Block Diagram Illustrating a PC System with Post-Combustion CO₂ Capture

1.C Oxy-Combustion CO₂ Capture

Oxy-combustion separates O₂ from the N₂ in air prior to coal combustion and is primarily applicable to conventional PC power plants. 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 1-3).

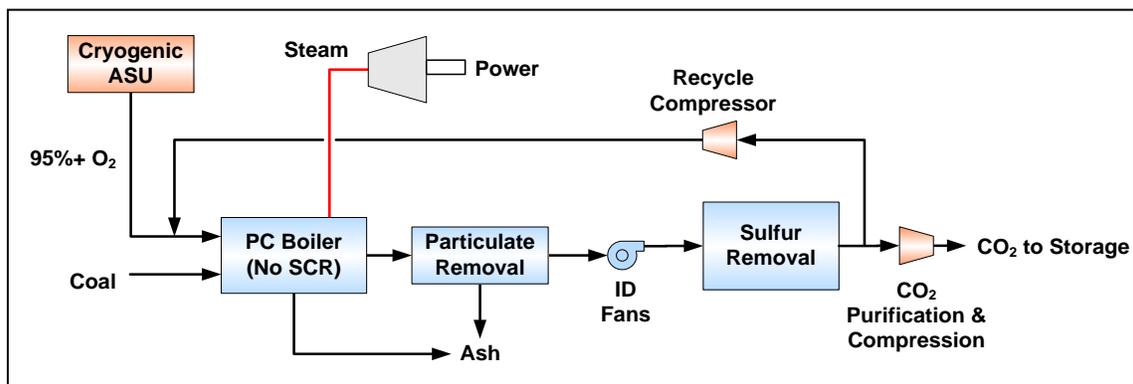


Figure 1-3: Block Diagram Illustrating an Oxy-Combustion System

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 (Ar) 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.

1.D Chemical Looping CO₂ Capture

Chemical looping is an advanced technology similar to oxy-combustion in that it relies on combustion/gasification of coal in a N₂-free environment. Chemical looping can be applied in either coal combustion or coal gasification processes. Chemical looping splits combustion into separate oxidation and reduction reactions. Subsequently, the products of combustion (CO₂ and H₂O) are kept separate from the rest of the flue gases (primarily N₂).

In the CLC process, oxygen is transferred from a gaseous stream (usually air) to a fuel (either gaseous or solid) through a solid. The solid is called the oxygen carrier. In a typical CLC process, the oxidation and reduction of the oxygen carrier are accomplished in two separate reactors. However, oxygen transport may be completed in three or more steps depending on the application and the oxygen carrier used.

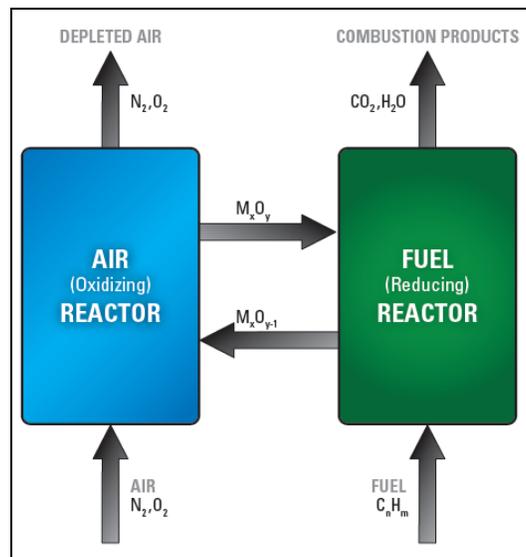


Figure 1-4: Schematic Diagram of a Two-Reactor CLC Process

Figure 1-4 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.

1.E Cost and Performance of First Generation CO₂ Capture Technologies

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.

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. Implementation of CO₂ capture results in a 7 to 10 percentage point decrease in net plant efficiency depending on the type of power generation facility.

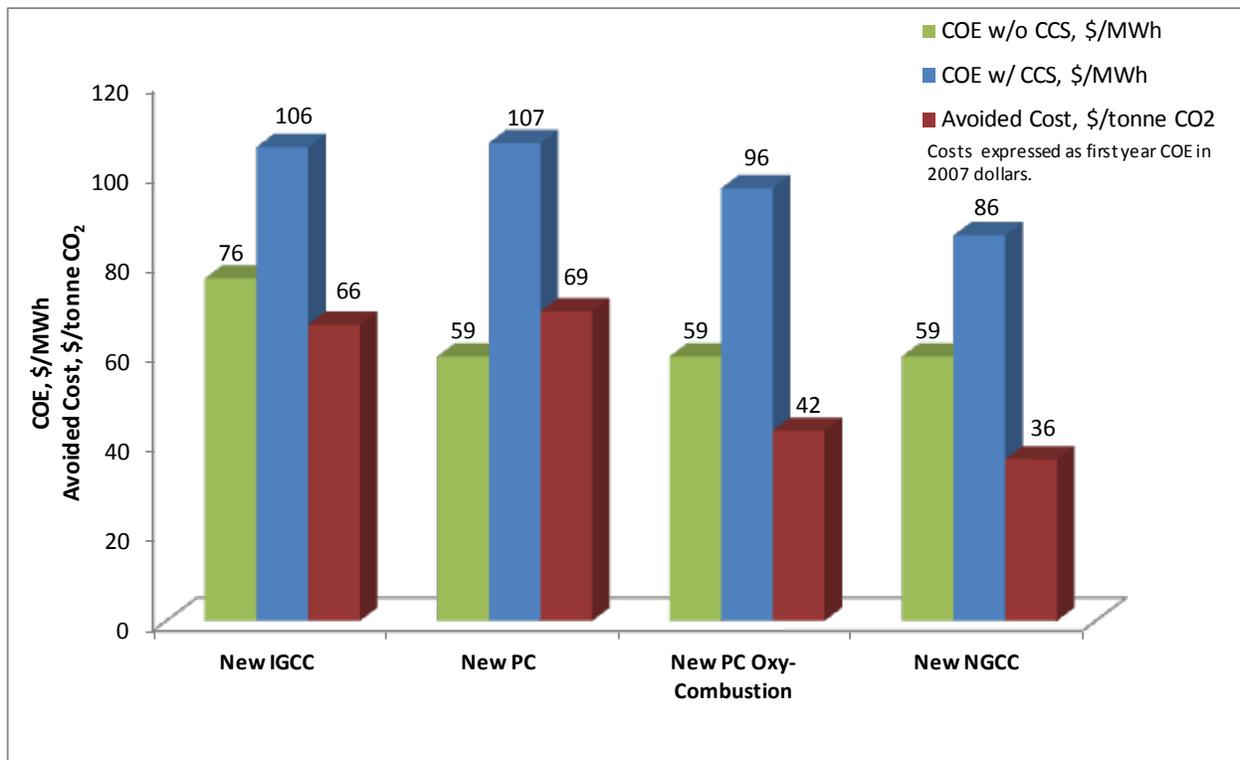


Figure 1-5: CO₂ Capture Costs for Different Types and Configurations of Power Plants

Figure 1-5 presents a comparison of the first-year COE expressed in 2007 dollars for various power plant configurations both with and without CO₂ capture.^{1,2,3} For example, the COE for a new IGCC plant is \$76/megawatt-hour (MWh) without CO₂ capture, but increases approximately 39 percent to \$106/MWh with currently available first generation pre-combustion CO₂ capture. Likewise, the COE for a new PC plant is \$59/MWh without CO₂ capture, but increases more

than 80 percent to \$107/MWh with currently available first generation post-combustion CO₂ capture. Figure 1-5 also shows the cost of CO₂ capture in terms of avoided cost as measured by \$/tonne of 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, where the difference in emissions is referenced to the non-capture PC plant.

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 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 to 80 percent.
Auxiliary Power for CO₂ Compression	To enable storage, a significant amount of power is required to compress the captured CO ₂ to typical pipeline levels (1,500 to 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 CO₂ 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 CO₂ 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.

1.F DOE/NETL CO₂ Capture R&D Program

DOE's CO₂ capture R&D effort is conducted under the Clean Coal Research Program. The program is administered by the DOE Office of Clean Coal and implemented by NETL through contracted research activities, onsite research, and systems analysis studies. Research projects are carried out under various award mechanisms – including partnerships, cooperative agreements, and financial assistance grants – with corporations, small businesses, universities, nonprofit organizations, and other national laboratories and government agencies.

The overall goal of the DOE/NETL CCS and Power Systems Program RD&D effort is to develop advanced fossil fuel conversion systems that achieve at least 90 percent CO₂ capture at costs of less than a 10 percent increase in the total COE for IGCC power plants and less than a 35 percent increase in the total COE for PC power plants compared to those same plants without CCS.

To put that goal in perspective, the utilization of currently available first generation CCS technologies on IGCC and PC power plants would significantly increase their COE compared to those same plants without CCS. DOE/NETL estimates the COE would increase approximately 40 percent for an IGCC power plant equipped with first generation CCS and 80 percent for a PC plant equipped with first generation CCS. (Note: See Section 1.E for additional information on DOE/NETL system analysis studies.) As a result, DOE/NETL is developing a variety of major cost-reduction technology innovations that could help make second and third generation CCS technologies a viable domestic and global option.

In addition to COE, the CCS RD&D goal can also be expressed in terms of dollars per metric ton CO₂ captured (\$/tonne). A \$/tonne metric is more meaningful when discussing the cost of CO₂ capture for purposes of utilization, rather than storage. The cost of CO₂ capture is calculated by dividing the increase in COE (\$/MWh) by the amount of CO₂ captured (tonne/MWh). On that basis, the CCS RD&D goals for IGCC and PC plants are equivalent to approximately \$20/tonne of CO₂ captured (2007 dollars).

Given the significant economic penalties associated with currently available first generation CO₂ capture technologies, step-change improvements in both cost and energy efficiency will be required to achieve these goals. DOE/NETL has adopted a comprehensive, multi-pronged approach to the R&D of advanced second and third generation CO₂ capture technologies for coal-based power plants. The success of this research will enable cost-effective implementation of CO₂ capture 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. While efforts are focused on capturing CO₂ from the flue gas or 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.

DOE/NETL CO₂ capture R&D was initiated in the late 1990s, and focused on laboratory-scale research on a broad spectrum of CO₂ capture approaches including advanced second and third generation solvents, sorbents, membranes, oxy-combustion systems, and chemical looping. These laboratory-scale investigations are anticipated to continue through 2017. Testing of

promising technologies at the small pilot-scale commenced in 2010 and will continue through 2021. Large pilot-scale testing is scheduled to begin in 2016 and continue through 2025. This schedule will allow for demonstration-scale testing to begin after 2020. It is anticipated that successful progression from laboratory- through demonstration-scale testing will result in several of these advanced technologies being available for commercial deployment after 2030.

The following chapters provide a brief overview of the various DOE/NETL CO₂ capture R&D technology areas and include highlights of recent accomplishments for many of the sponsored projects. Additional information on DOE/NETL's CO₂ capture R&D projects is available at: <http://www.netl.doe.gov/technologies/coalpower/ewr/pubs/CO2Handbook/>.

CHAPTER 2: PRE-COMBUSTION CO₂ CAPTURE R&D

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.

2.A Solvents for Pre-Combustion

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. DOE/NETL's ORD is evaluating the use of ionic liquids (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. Another pre-combustion solvent capture technology currently under development is SRI International's ammonium carbonate (AC)/ammonium bicarbonate (ABC) process.

2.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 a temperature above 500°F has not been identified.

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.

2.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. Scale-up of 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 a smaller equipment footprint. In addition, gas separation membranes

can be designed to produce CO₂ at pressure and, if desired, to co-capture CO₂ and hydrogen sulfide (H₂S).



Wabash IGCC Plant

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.

Pre-Combustion Sorbent R&D Accomplishment

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 Membrane R&D Accomplishment

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

CHAPTER 3: POST-COMBUSTION CO₂ CAPTURE R&D

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 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.

3.A Solvents for Post-Combustion

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.

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.

While physical solvent-based systems, such as the Selexol™ and Rectisol® processes, are generally viewed as pre-combustion CO₂ capture technologies, 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.

3.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.

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” (CACHYS™). 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.

3.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.

DOE/NETL’s R&D objectives for post-combustion membranes include development of low-cost, durable membranes that have improved permeability and selectivity, thermal and physical stability, and are 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.

Post-Combustion Solvent R&D Accomplishment

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

Post-Combustion Sorbent R&D Accomplishment

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

Post-Combustion Membrane R&D Accomplishment

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.

CHAPTER 4: OXY-COMBUSTION AND CHEMICAL LOOPING R&D

Unlike pre- and post-combustion CO₂ 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 CO₂ capture demonstration project that is being conducted under the FutureGen Initiative that will repower an existing 200-megawatt (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 air separation unit (ASU) would increase the COE by more than 60 percent and reduce the net plant efficiency by approximately 10 percentage points, as compared to a new, air-fired PC power plant without CO₂ capture. A potential alternative to the energy-intensive cryogenic ASU is the ion transport membrane (ITM). However, ITM/boiler oxy-combustion integration concepts are in very early stages of development and there are currently no planned pilot-scale tests for this configuration.

Oxy-combustion 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 CO₂ concentration, the flue gas will also include H₂O, excess O₂, N₂ (via ASU carry-over and air in-leakage), SO₂, 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 PC oxy-combustion power plants.

CLC 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. For example, Alstom Power, Inc. is conducting a multiphase R&D program to develop a CLC process utilizing a limestone-based oxygen carrier. The eventual development of chemical looping offers the potential as a game-changing technology for power generation and CO₂ capture.

Oxy-Combustion R&D Accomplishment

Test Evaluates 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.



*Alstom's 15-MWth Boiler
Simulation Facility*

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.

Oxy-Combustion R&D Accomplishment

Pilot-Scale Testing Successfully Demonstrates Compression-Based Flue Gas Purification Process

Objective: Air Products and Chemicals, Inc. is developing a novel, cost-effective, compression-based system for separation and capture of sulfur oxides (SO_x) and nitrogen oxides (NO_x) from the carbon dioxide (CO₂)-rich flue gas stream produced by an oxy-combustion boiler. 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 enhanced oil recovery (EOR) and geological storage. The Air Products purification process results in the conversion of the gas-phase SO_x and NO_x to liquid-phase sulfuric acid (H₂SO₄) and nitric acid (HNO₃) during compression of the flue gas. These constituents are subsequently separated from the pressurized CO₂ stream.

Accomplishments: Air Products successfully designed and constructed a pilot-scale (0.25 to 0.33-megawatt-thermal [MWth] equivalent slipstream) purification system that was used for testing the purification process at Alstom's 15-MWth oxy-combustion Boiler Simulation Facility (BSF) located in Windsor, Connecticut. The pilot-scale system provided flue gas cooling, compression, and acid gas removal. Testing was conducted with two coal types – a low-sulfur West Virginia bituminous and a high-sulfur Illinois bituminous coal. The purification system was operated at 15 bar (~220 pounds per square inch [psi]) and successfully demonstrated the ability to remove nearly 100 percent of the SO_x and up to 90 percent of the NO_x in the oxy-combustion flue gas. Data from the pilot-scale test campaigns are being used to complete development of a reaction model of the system to enable design of larger scale systems for subsequent testing and demonstration. Upon completion of the National Energy Technology Laboratory (NETL) test program, the Air Products purification system was further scaled up to approximately 1 MWth equivalent and is being tested on a flue gas slipstream at Vattenfall's 30-MWth Schwarze Pumpe oxy-combustion demonstration facility in Germany.



Air Products Gas Purification Pilot Development Unit

Benefits: The Air Products purification technology can enable oxy-combustion systems to meet CO₂ purity requirements for geological storage, EOR, and other beneficial uses. In addition, by incorporating an efficient SO_x and NO_x removal system with CO₂ compression, the need for low NO_x burners, flue gas desulfurization (FGD), and post-combustion NO_x control systems are greatly reduced or eliminated for oxy-combustion power plants.

Oxy-Combustion R&D Accomplishment

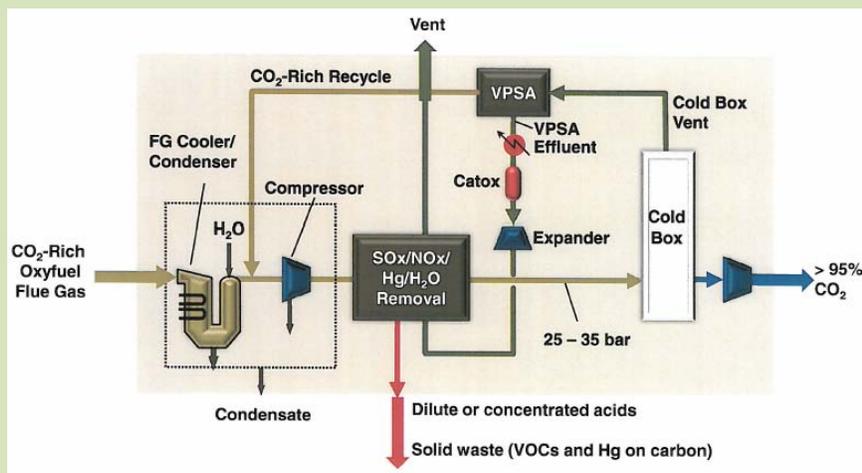
Advanced Flue Gas Purification and CO₂ Recovery Technologies

Objective: Praxair is developing a near-zero emission flue gas purification technology for plants retrofitted with oxy-combustion technology. The project includes development of an activated carbon process for pollutant removal (sulfur dioxide [SO₂], nitrogen oxides [NO_x], and mercury [Hg]) and a vacuum pressure swing adsorption (VPSA) process to enhance overall carbon dioxide (CO₂) recovery.

Accomplishments: Bench-scale testing (equivalent to 0.02 ton per day [tpd] of CO₂) of the activated carbon process was conducted and emission reductions of greater than 99 percent and 96 percent were achieved for SO₂ and NO_x, respectively. The pollutant removal process is operated at high pressure (375 to 500 pounds per square inch absolute [psia]) and uses a fixed bed of activated carbon as an adsorbent/catalyst for the capture of sulfur oxides (SO_x) and NO_x from the flue gas. The activated carbon oxidizes the SO₂ to sulfur trioxide (SO₃) and the nitric oxide (NO) to nitrogen dioxide (NO₂), and a periodic water wash is used to remove the acids formed. These results were collaborated with an additional round of higher volume bench-scale testing (equivalent to 0.1 tpd of CO₂) that was successfully conducted in 2011.

In addition, bench-scale testing (equivalent to 0.03 tpd of CO₂) of the VPSA process was conducted to screen and select suitable adsorbents. An additional round of higher volume bench-scale testing (equivalent to 0.3 tpd of CO₂) was conducted in 2011 in order to further demonstrate a scale up of the process. The VPSA process is used in concert with a conventional cold box to enhance CO₂ recovery. High air in-leakage in an existing plant's boiler/ductwork could limit CO₂ recovery to less than 65 percent from oxy-combustion flue gas using a cold box alone. This CO₂ recovery limitation can be overcome by using a hybrid process that combines a cold box and VPSA. In the hybrid process, up to 90 percent of CO₂ in the cold box vent stream is recovered by VPSA and then recycled and mixed with the untreated flue gas stream upstream of the activated carbon pollutant removal process. The next step for development of this technology is to build a small pilot-scale (equivalent to 10 to 50 tpd CO₂) demonstration unit that integrates all the necessary process equipment.

Benefits: Operating the activated carbon process at high pressure should reduce capital costs, while achieving low levels of SO₂ and NO_x in the CO₂ product stream. For existing plants burning low-sulfur coal and not already configured with flue gas desulfurization (FGD) and selective catalytic reduction (SCR) equipment, there is no need for investment in SCR and only 30 percent capacity FGD is needed when using the activated carbon process. Combining VPSA with a cold box results in an overall CO₂ recovery from the process that can exceed 95 percent. For an existing plant with low air in-leakage, the overall CO₂ recovery could exceed 99 percent.



Praxair Flue Gas Purification Process Schematic

CHAPTER 5: OXYGEN PRODUCTION R&D

For PC 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.

Several novel O₂ production technologies currently under development have the potential to reduce the cost of O₂ production, including: ion transport membranes (ITMs); oxygen transport membranes (OTMs); nanofiller-modulated polymeric membranes; a perovskite ceramic sorbent utilizing temperature swing adsorption (TSA); and a mixed metal oxide sorbent utilizing pressure swing adsorption (PSA). The following is a brief description of the ITM and OTM technologies.

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 pounds per square inch gauge (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.

The OTM process (being developed by Praxair) utilizes chemical potential for the O₂ separation driving force instead of pressure. The OTM is designed to integrate directly with the boiler such that the combustion reaction occurs on the fuel side of the membrane, thus creating a low O₂ partial pressure driving force. This chemical potential gradient drives O₂ through the membrane without the need for additional air compression. Recent estimates indicate that OTM can deliver O₂ for oxy-combustion using only 20 to 30 percent of the energy required for a cryogenic ASU.

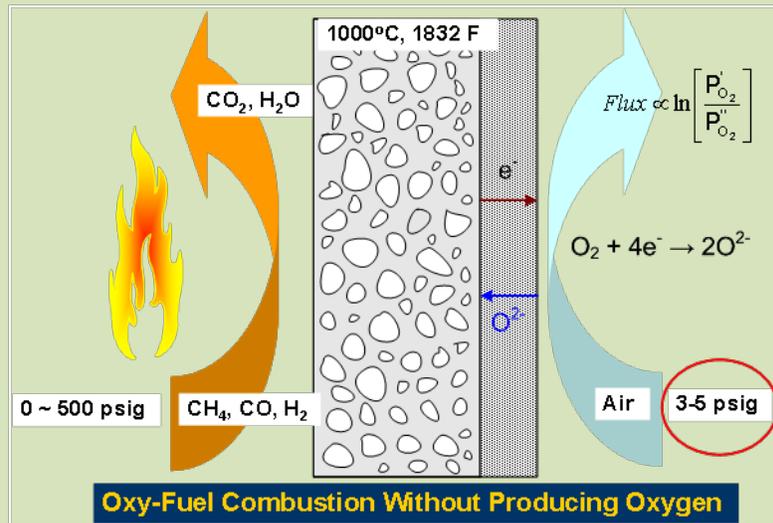
Oxygen Production R&D Accomplishment

Oxygen Transport Membrane – A Transformational Technology for Oxygen Production

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 (O₂) would be separated in a cryogenic-based air separation unit (ASU) and then delivered to the boiler for combustion. OTM technology integrates O₂ 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 (MWth) output. The second phase includes bench-scale testing of an OTM boiler equivalent to approximately 50-kilowatt (kW) thermal output.



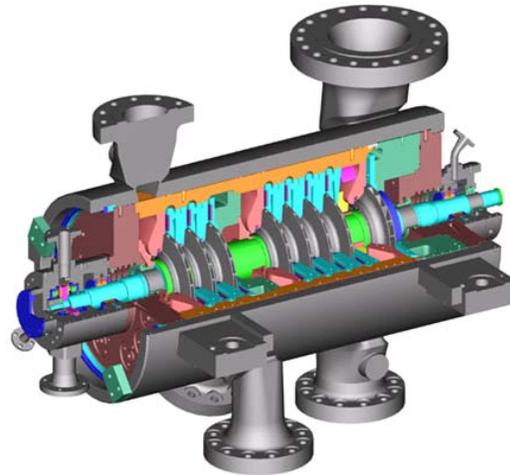
Principle of OTM Operation

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.

CHAPTER 6: ADVANCED CO₂ COMPRESSION R&D

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 flow volume, 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 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 conducted for NETL, 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. The capital cost for the compressor and associated equipment is also significant.



Multistage Back-to-Back Centrifugal Compressor

(Courtesy of Dresser-Rand)

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 (CFDs) and laboratory testing, leading to prototype development and field testing. Research efforts include development of intra-stage 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.

Advanced CO₂ Compression R&D Accomplishment

Semi-Isothermal Compression & Liquefaction Leads to Energy Savings

Objective: Southwest Research Institute (SwRI) is developing novel compression technology concepts to reduce carbon dioxide (CO₂) compression power requirements compared to conventional compressor designs. National Energy Technology Laboratory (NETL) studies have shown that using conventional multi-stage, intercooled compressors for CO₂ compression to typical pipeline supply pressure (approximately 2,200 pounds per square inch absolute [psia]) requires a large amount of auxiliary power – approximately 4.5 percent of gross electrical generation for an integrated gasification combined cycle (IGCC) plant and 7 percent for a pulverized coal (PC) plant.

Accomplishments: SwRI is developing two technology concepts to reduce CO₂ compression power requirements. 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. 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. In this concept, 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 gas. Once the CO₂ is liquefied, the pumping power to boost the pressure to 2,200 psia is minimal. The project includes prototype testing and a full-scale demonstration of each concept.

In order to demonstrate the semi-isothermal compression process, SwRI designed, constructed, and tested an internally cooled compressor diaphragm, which routes cooling fluid through the diaphragm to remove the heat of compression. This prototype was installed into a closed-loop, 700-horsepower (hp) compressor test facility at SwRI and tested for a range of speeds, flows, pressures, and cooling fluid conditions. The testing agreed well with computational fluid dynamics (CFDs) predictions for the heat transfer characteristics. Up to 55 percent of the heat of compression was removed during testing with the cooled diaphragm technology with no additional pressure drop.

In order to demonstrate the pumping process, SwRI also designed and constructed a pilot-scale liquid CO₂ flow loop to evaluate a 100-gallon per minute (gpm) industrial 12-stage vertical turbo-pump. Performance and mechanical testing was performed for a range of speeds, flows, and pressures. The pump met the design conditions with a discharge pressure in excess of 2,200 pounds per square inch gauge (psig) and showed good mechanical behavior.

The next phase of the project includes design, construction, and testing of a 60,000 to 70,000 lb/hr pilot-scale system that combines compression, liquefaction, and pumping technology.

Benefits: SwRI estimates that combining the two novel compression technology concepts can reduce CO₂ compression power requirements by up to 35 percent compared to conventional compressor designs. In addition to benefiting power plants equipped with CO₂ capture systems, these advanced compression technologies are applicable to other large-scale industrial applications with significant compression requirements.



*Liquid CO₂ Pump Loop
Constructed at SwRI*

CHAPTER 7: NATIONAL CARBON CAPTURE CENTER

DOE/NETL and Southern Company established the National Carbon Capture Center (NCCC) in 2009 at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. 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; it is 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. Additional information on the NCCC is available at:

<http://www.nationalcarboncapturecenter.com/>.

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 7-1). 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. Carbon dioxide capture technologies under consideration for slipstream testing include advanced solvent, sorbents, and membranes.

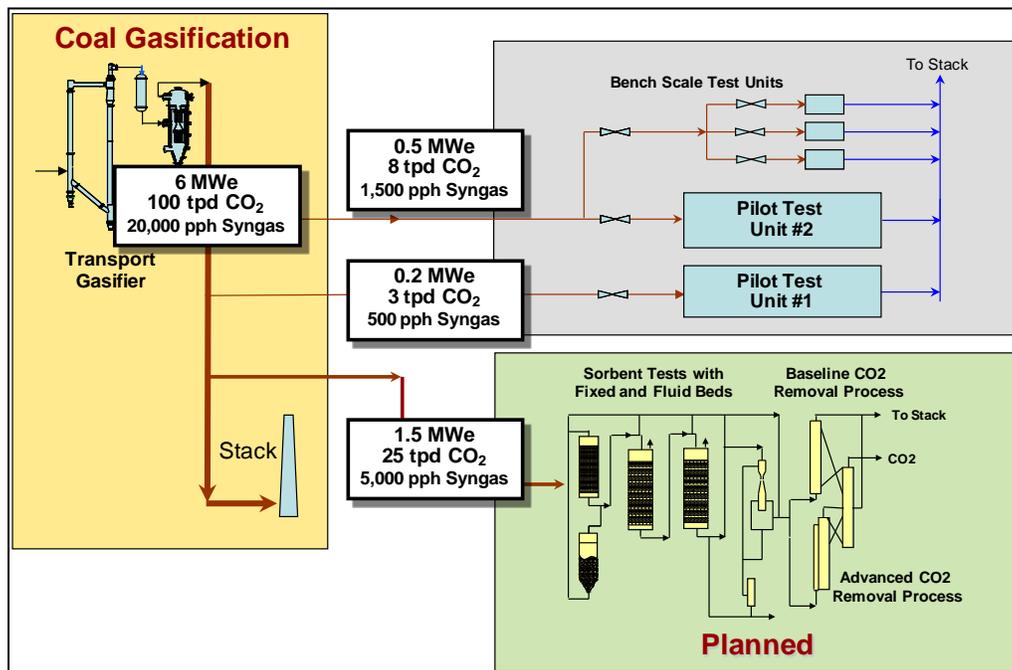


Figure 7-1: NCCC Pre-Combustion CO₂ Capture Slipstream Test Units

Advanced solvents, sorbents, membranes, and other emerging technologies can be tested in the PSDF-NCCC post-combustion module known as the Post-Combustion Carbon Capture Center (PC4) that began operation in 2011. For both new and existing power plants, post-combustion capture technology must be made 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 7-2). 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.

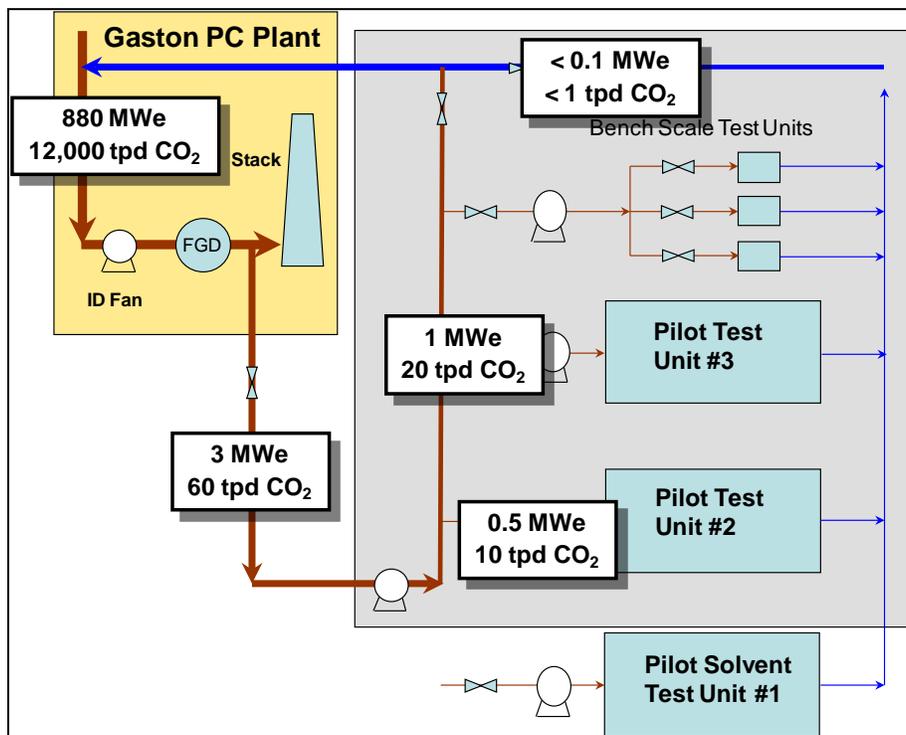


Figure 7-2: NCCC Post-Combustion CO₂ Capture Slipstream Test Units

NCCC R&D Accomplishment

DOE Initiates Post-Combustion CO₂ Capture Testing at NCCC

Objective: The National Carbon Capture Center (NCCC) provides a facility where carbon dioxide (CO₂) capture technologies can be tested on coal-derived gas at various scales. The NCCC sponsors projects from a wide variety of participants and partners to help identify and develop “best-in-class” technologies.

Accomplishments: In cooperation with Southern Company, the U.S. Department of Energy (DOE) established the NCCC in 2009 at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. The NCCC is a unique test facility that now consists of two major sets of infrastructure to support CO₂ capture technology development. One is the pilot-scale coal gasification facility that began operation in 1996 and now produces synthesis gas (syngas) for pre-combustion CO₂ capture technology evaluation. Testing to date on pre-combustion CO₂ capture technologies has included advanced solvents/solutions, solid sorbents, gas separation membrane technologies, and water-gas shift (WGS) catalysts. Infrastructure was also added to increase syngas conditioning capability provided to technology developers including hydrocarbon and sulfur removal equipment.



NCCC Post-Combustion Carbon Capture Center

The other test facility is the Post-Combustion Carbon Capture Center (PC4), which began operation in 2011 and is located at Alabama Power’s E.C. Gaston Plant. The PC4 was designed to provide several parallel paths to test candidate technologies at appropriate scales. The test facility includes three major test areas: (1) a pilot solvent test unit (PSTU) to test developers’ next generation CO₂ absorption solvents; (2) a second test bay to support evaluation of fully integrated test systems supplied by technology developers; and (3) a bench-scale test area to accommodate up to four small test skids of emerging, advanced technologies such as sorbents or membrane systems. The facility has been designed and constructed so that multiple tests can proceed simultaneously.

Initial operations at the PC4 consisted of testing with a monoethanolamine (MEA) solvent to be used as a baseline to evaluate the comparative performance of other advanced CO₂ capture technologies. Testing was also conducted with advanced solvents being developed by Aker Clean Carbon and Babcock & Wilcox Power Generation Group, as well as Membrane Technology Research’s membrane-based technology.

Benefits: The NCCC provides a unique opportunity to provide a testing platform to facilitate the scale-up and development of advanced CO₂ capture technologies in order to accelerate CO₂ capture technology commercialization. In particular, the NCCC provides the following benefits: (1) serves as a centralized research and development (R&D) facility for technology developers; (2) makes available realistic syngas and flue gas to technology developers for performance verification; (3) offers onsite expertise in power plant, process engineering and integration, design, and operation and maintenance (O&M) areas; and (4) provides independent data acquisition and analysis.

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