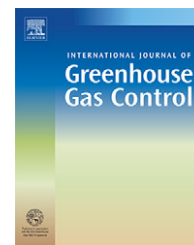


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## Review

# Advances in CO<sub>2</sub> capture technology—The U.S. Department of Energy's Carbon Sequestration Program<sup>☆</sup>

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### ABSTRACT

There is growing concern that anthropogenic carbon dioxide (CO<sub>2</sub>) emissions are contributing to global climate change. Therefore, it is critical to develop technologies to mitigate this problem. One very promising approach to reducing CO<sub>2</sub> emissions is CO<sub>2</sub> capture at a power plant, transport to an injection site, and sequestration for long-term storage in any of a variety of suitable geologic formations. However, if the promise of this approach is to come to fruition, capture costs will have to be reduced. The Department of Energy's Carbon Sequestration Program is actively pursuing this goal. CO<sub>2</sub> capture from coal-derived power generation can be achieved by various approaches: post-combustion capture, pre-combustion capture, and oxy-combustion. All three of these pathways are under investigation, some at an early stage of development. A wide variety of separation techniques is being pursued, including gas phase separation, absorption into a liquid, and adsorption on a solid, as well as hybrid processes, such as adsorption/membrane systems. Current efforts cover not only improvements to state-of-the-art technologies but also development of several innovative concepts, such as metal organic frameworks, ionic liquids, and enzyme-based systems. This paper discusses the current status of the development of CO<sub>2</sub> capture technology.

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## 1. Introduction

Although there is not universal agreement on the cause, there is a growing consensus that global climate change is occurring, and many climate scientists believe that a major cause is the anthropogenic emission of greenhouse gases (GHGs) into the atmosphere. Due to their low cost, availability, existing reliable technology for energy production, and energy density, fossil fuels currently supply over 85% of the energy needs of the United States and a similar percentage of the energy used worldwide (EIA, 2006a,b). The combustion of fossil fuels produces carbon dioxide (CO<sub>2</sub>), a GHG with an increasing potential for by-product end-use in the industrial and energy production sectors. The use of CO<sub>2</sub> as a by-product would not only have economic benefits but would simultaneously mitigate global climate change concerns.

Approximately 83% of the GHG emissions in the U.S. are produced from combustion and nonfuel uses of fossil fuels (EIA, 2006c). The Energy Information Administration (EIA) within the U.S. Department of Energy (DOE) estimates that consumption of fossil fuels (coal, petroleum, and natural gas) will increase by 27% over the next 20 years, thereby increasing U.S. CO<sub>2</sub> emissions from the current 6000 million tonnes per year to 8000 million tonnes per year by 2030. Although U.S. CO<sub>2</sub> emissions are projected to increase, they will decrease from 23% of the world's total in 2003 to 19% in 2030 (EIA, 2006a). Specifically, the EIA estimates that the combined CO<sub>2</sub> emissions from China and India in 2030 from coal use will be three times that of the United States (China, 8286 million tonnes of CO<sub>2</sub>; India, 1371 million tonnes of CO<sub>2</sub>; U.S., 3226 million tonnes of CO<sub>2</sub>) (EIA, 2006b). This illustrates that no single nation can sufficiently reduce GHGs to stabilize their atmospheric concentrations. The effort must be unified and cost effective to sustain domestic and global economic growth while reducing GHG emissions.

One approach that holds great promise for reducing GHG emissions is carbon capture and sequestration (CCS). Under this concept, CO<sub>2</sub> would be captured from large point sources, such as power plants, and injected into geologic formations, such as depleted oil and gas fields, saline formations, and unmineable coal seams (Klara et al., 2003). This approach would lock up (sequester) the CO<sub>2</sub> for thousands of years. The DOE's Office of Fossil Energy (FE) is working to ensure that this can be done at costs and impacts that are economically and

environmentally acceptable. Current state-of-the-art CCS technologies may be used for initial mitigation of GHG emissions, but in the long-term low cost solutions to meet the growing demand for energy will be required, not only to meet environmental standards, but also to increase the standard of living worldwide.

DOE's Carbon Sequestration Program, managed by the National Energy Technology Laboratory (NETL), is pursuing five technological avenues aimed at reducing GHG emissions: CO<sub>2</sub> separation and capture; carbon storage (sequestration); monitoring, mitigation, and verification of stored CO<sub>2</sub>; control of non-CO<sub>2</sub> GHGs; and breakthrough concepts related to CCS. These five avenues encompass a broad spectrum of opportunities for technology development and partnership formation to promote both domestic and international cooperation. This paper deals mainly with the first of these avenues, namely CO<sub>2</sub> separation and capture.

DOE's goal is to have the necessary technology ready for large scale field testing, should it become necessary to impose mandatory limits on CO<sub>2</sub> emissions. The specific goal is to have technologies developed by 2012 that have advanced beyond the pilot scale and are ready for large scale field tests and that can achieve 90% CO<sub>2</sub> capture at an increase in the cost of electricity of less than 20% for post-combustion and oxy-combustion and less than 10% for pre-combustion capture. Capture and separation costs are a significant portion of the cost to sequester CO<sub>2</sub>. Transportation and storage (siting, modeling, drilling, injection, site closure, and monitoring) are generally a minor fraction of the total cost.

### 1.1. GHG emissions resulting from power production

An important component of DOE's Carbon Sequestration Program is directed toward reducing CO<sub>2</sub> emissions from power plants. Roughly one-third of the anthropogenic CO<sub>2</sub> emissions of the U.S. come from power plants (EIA, 2006a). CO<sub>2</sub> emissions in the U.S. from coal combustion (almost entirely used for electric power production) increased over 18% between 1990 and 2003 with a forecasted 54% increase by 2030, if there are no CO<sub>2</sub> controls (EIA, 2006b). Applying current state-of-the-art flue gas CO<sub>2</sub> capture and separation technologies to existing coal-fired power plants that have an average efficiency of 33% would reduce net plant power output by approximately one-third (Figueroa, 2006). Installing CO<sub>2</sub>

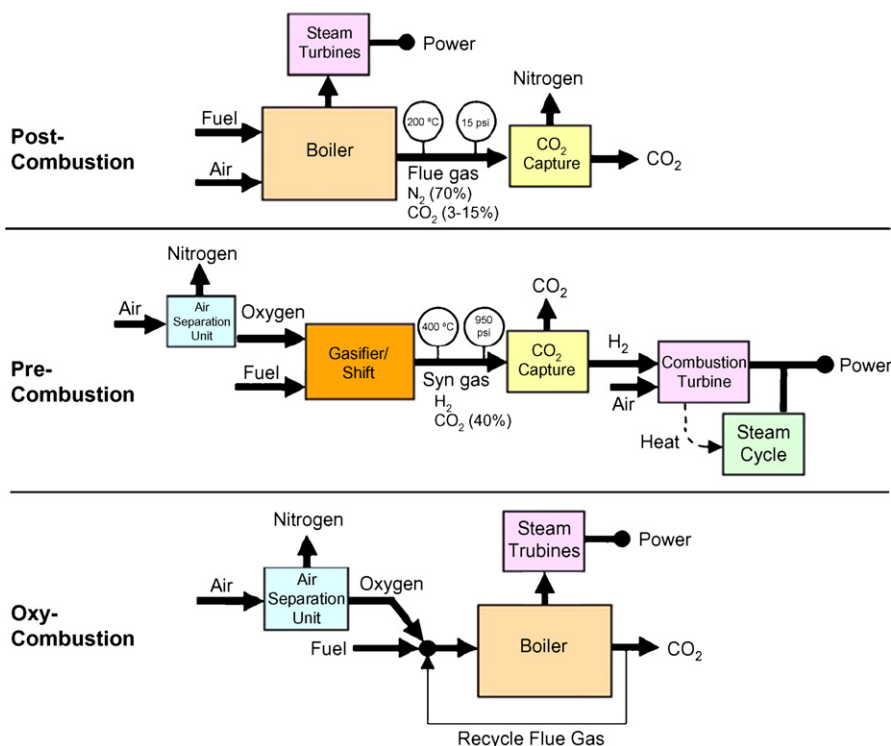


Fig. 1 – Block diagrams illustrating post-combustion, pre-combustion, and oxy-combustion systems.

capture on a state-of-the-art power plant, such as an Integrated Gasification Combined Cycle Unit, would result in a smaller decrease in power output, in the range of 20%, due to inherent process benefits compared to existing PC plants. If CO<sub>2</sub> capture from power plants is to be a mitigation option, then research and development will be critical to achieve wide-scale deployment with acceptable economic and environmental impacts.

As the U.S. and world economies grow, the demand for electric power will continue to increase. The EIA estimates that demand for electricity will increase by 40% in the U.S. over the next 25 years (EIA, 2006a). There are four approaches that can contribute to reducing CO<sub>2</sub> emissions from the large number of new power plants that will be required to meet this growing demand. The first is to reduce carbon intensity. The second is to increase the efficiency of power generation cycles. The third is to develop new power production technologies, such as oxy-combustion and chemical looping. The fourth is to develop innovative and cost effective capture technologies that are scaleable to the size needed by the power and non-power sectors. To maximize abatement of CO<sub>2</sub> in the U.S., all of these approaches will be needed. DOE's Carbon Sequestration Program is focused on the third and fourth approaches to reducing CO<sub>2</sub> emissions.

### 1.2. Importance of capture technology to the implementation of CO<sub>2</sub> sequestration

CO<sub>2</sub> sequestration in geologic formations shows great promise because of the large number of potential geologic sinks. The Carbon Sequestration Regional Partnerships (Litynski et al., 2006, 2007) have estimated that 1120 to 3400 billion tonnes of

CO<sub>2</sub> can be sequestered in the formations identified so far. Also, with higher petroleum prices, there is increased interest in using CO<sub>2</sub> flooding as a means to enhance oil recovery (EOR); and with higher gas prices, there will be growing interest in using CO<sub>2</sub> for enhanced coal bed methane production (ECBM). However, none of these activities will be possible unless CO<sub>2</sub> is first captured. None of the currently available CO<sub>2</sub> capture processes are economically feasible on a national implementation scale to capture CO<sub>2</sub> for sequestration, since they consume large amounts of parasitic power and significantly increase the cost of electricity. Thus, improved CO<sub>2</sub> capture technologies are vital if the promise of geologic sequestration, EOR, and ECBM is to be realized.

## 2. Carbon capture technologies

In consideration of how best to improve CO<sub>2</sub> capture, there are three technological pathways that can be pursued for CO<sub>2</sub> capture from coal-derived power generation: post-combustion capture, pre-combustion capture, and oxy-combustion, as illustrated in Fig. 1. In post-combustion capture, the CO<sub>2</sub> is separated from other flue gas constituents either originally present in the air or produced by combustion. In pre-combustion capture, carbon is removed from the fuel before combustion, and in oxy-combustion, the fuel is burned in an oxygen stream that contains little or no nitrogen.

Table 1 provides a summary of the inherent advantages and disadvantages of each of these pathways. Post-combustion capture applies primarily to coal-fueled power generators that are air fired. Pre-combustion capture applies to gasification plants. Oxy-combustion can be applied to new plants or

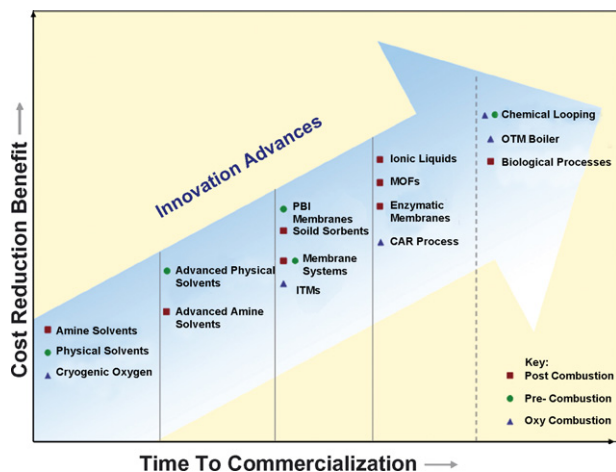
**Table 1 – Advantages and disadvantages of different CO<sub>2</sub> capture approaches**

	Advantages	Barriers to implementation
Post-combustion	<ul style="list-style-type: none"> <li>• Applicable to the majority of existing coal-fired power plants</li> <li>• Retrofit technology option</li> </ul>	Flue gas is ... <ul style="list-style-type: none"> <li>• Dilute in CO<sub>2</sub></li> <li>• At ambient pressure</li> </ul> ... resulting in ... <ul style="list-style-type: none"> <li>• Low CO<sub>2</sub> partial pressure</li> <li>• Significantly higher performance or circulation volume required for high capture levels</li> <li>• CO<sub>2</sub> produced at low pressure compared to sequestration requirements</li> </ul>
Pre-combustion	Synthesis gas is ... <ul style="list-style-type: none"> <li>• Concentrated in CO<sub>2</sub></li> <li>• High pressure</li> </ul> ... resulting in ... <ul style="list-style-type: none"> <li>• High CO<sub>2</sub> partial pressure</li> <li>• Increased driving force for separation</li> <li>• More technologies available for separation</li> <li>• Potential for reduction in compression costs/loads</li> </ul>	<ul style="list-style-type: none"> <li>• Applicable mainly to new plants, as few gasification plants are currently in operation</li> <li>• Barriers to commercial application of gasification are common to pre-combustion capture</li> <li>• Availability</li> <li>• Cost of equipment</li> <li>• Extensive supporting systems requirements</li> </ul>
Oxy-combustion	<ul style="list-style-type: none"> <li>• Very high CO<sub>2</sub> concentration in flue gas</li> <li>• Retrofit and repowering technology option</li> </ul>	<ul style="list-style-type: none"> <li>• Large cryogenic O<sub>2</sub> production requirement may be cost prohibitive</li> <li>• Cooled CO<sub>2</sub> recycle required to maintain temperatures within limits of combustor materials</li> <li>• Decreased process efficiency</li> <li>• Added auxiliary load</li> </ul>

retrofitted to existing plants. Fig. 2 indicates that as innovative CO<sub>2</sub> capture and separation technologies advance significant cost reduction benefits can potentially be realized once they are commercialized. Technologies shown include both those funded by the DOE as well as those that do not receive funding from the DOE's Carbon Sequestration Program.

### 2.1. Post-combustion CO<sub>2</sub> capture

Post-combustion capture involves the removal of CO<sub>2</sub> from the flue gas produced by combustion. Existing power plants use air, which is almost four-fifths nitrogen, for combustion and generate a flue gas that is at atmospheric pressure and typically has a CO<sub>2</sub> concentration of less than 15%. Thus, the



**Fig. 2 – Innovative CO<sub>2</sub> capture technologies—cost reduction benefits versus time to commercialization.**

thermodynamic driving force for CO<sub>2</sub> capture from flue gas is low (CO<sub>2</sub> partial pressure is typically less than 0.15 atm), creating a technical challenge for the development of cost effective advanced capture processes. In spite of this difficulty, post-combustion carbon capture has the greatest near-term potential for reducing GHG emissions, because it can be retrofitted to existing units that generate two-thirds of the CO<sub>2</sub> emissions in the power sector. Some of the options for post-combustion CO<sub>2</sub> capture are discussed below.

#### 2.1.1. State-of-the-art amine-based systems

Amines react with CO<sub>2</sub> to form water soluble compounds. Because of this compound formation, amines are able to capture CO<sub>2</sub> from streams with a low CO<sub>2</sub> partial pressure, but capacity is equilibrium limited. Thus, amine-based systems are able to recover CO<sub>2</sub> from the flue gas of conventional pulverized coal (PC) fired power plants, however only at a significant cost and efficiency penalty. Although amines have been used for many years, particularly in the removal of acid gases from natural gas, there is still room for process improvement. Amines are available in three forms (primary, secondary, and tertiary), each with its advantages and disadvantages as a CO<sub>2</sub> solvent. In addition to options for the amine, additives can be used to modify system performance. Finally, design modifications are possible to decrease capital costs and improve energy integration.

Improvements to amine-based systems for post-combustion CO<sub>2</sub> capture are being pursued by a number of process developers; a few of these are Fluor, Mitsubishi Heavy Industries (MHI), and Cansolv Technologies. Fluor's Econamine FG Plus is a proprietary acid gas removal system that has demonstrated greater than 95% availability with natural gas fired power plants, specifically on a 350 ton/day CO<sub>2</sub> capture

plant in Bellingham, MA. It is currently the state-of-the-art commercial technology baseline and is used in comparing other CO<sub>2</sub> capture technologies. MHI has developed a new absorption process, referred to as KS-1. A key factor in this development is the utilization of a new amine-type solvent for the capture of CO<sub>2</sub> from flue gas (BP America, 2005).

As another example, Cansolv Technologies, Inc. proposes to reduce costs by incorporating CO<sub>2</sub> capture in a single column with processes for capturing pollutants, such as SO<sub>2</sub>, NO<sub>x</sub>, and Hg. Their new DC103<sup>®</sup> tertiary amine solvent has demonstrated fast mass transfer and good chemical stability with high capacity—a net of 0.5 mol of CO<sub>2</sub>/mole of amine per cycle compared to 0.25 mol/mol for monoethanolamine (MEA) (Hakka, 2007).

R&D pathways to improved amine-based systems include modified tower packing to reduce pressure drop and increase contacting, increased heat integration to reduce energy requirements, additives to reduce corrosion and allow higher amine concentrations, and improved regeneration procedures.

### 2.1.2. Emerging technologies

Emerging technologies involve a combination of products and processes that have demonstrated, either in the laboratory or in the field, significant improvements in efficiency and cost over state-of-the-art technologies. Emerging technologies range from major improvements to existing processes to highly novel approaches, as discussed below.

**2.1.2.1. Carbonate-based systems.** Carbonate systems are based on the ability of a soluble carbonate to react with CO<sub>2</sub> to form a bicarbonate, which when heated releases CO<sub>2</sub> and reverts to a carbonate. A major advantage of carbonates over amine-based systems is the significantly lower energy required for regeneration. The University of Texas at Austin has been developing a K<sub>2</sub>CO<sub>3</sub> based system in which the solvent is promoted with catalytic amounts of piperazine (PZ). The K<sub>2</sub>CO<sub>3</sub>/PZ system (5 molar K; 2.5 molar PZ) has an absorption rate 10–30% faster than a 30% solution of MEA and favorable equilibrium characteristics. A benefit is that oxygen is less soluble in K<sup>+</sup>/PZ solvents; however, piperazine is more expensive than MEA, so the economic impact of oxidative degradation will be about the same (Rochelle, 2006). Analysis has indicated that the energy requirement is approximately 5% lower with a higher loading capacity of 40% versus about 30% for MEA. System integration studies indicate that improvements in structured packing can provide an additional 5% energy savings, and multi-pressure stripping can reduce energy use 5–15% (Rochelle et al., 2006).

**2.1.2.2. Aqueous ammonia.** Ammonia-based wet scrubbing is similar in operation to amine systems. Ammonia and its derivatives react with CO<sub>2</sub> via various mechanisms, one of which is the reaction of ammonium carbonate (AC), CO<sub>2</sub>, and water to form ammonium bicarbonate (ABC). This reaction has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism. Ammonia-based absorption has a number of other advantages over amine-based systems, such as the potential for high CO<sub>2</sub>

capacity, lack of degradation during absorption/regeneration, tolerance to oxygen in the flue gas, low cost, and potential for regeneration at high pressure. There is also the possibility of reaction with SO<sub>x</sub> and NO<sub>x</sub>—criteria pollutants found in flue gas—to form fertilizer (ammonium sulfate and ammonium nitrate) as a salable by-product.

A few concerns exist related to ammonia's higher volatility compared to that of MEA. One is that the flue gas must be cooled to the 60–80 °F range to enhance the CO<sub>2</sub> absorptivity of the ammonia compounds and to minimize ammonia vapor emissions during the absorption step. Additionally, there is concern over ammonia losses during regeneration, which occurs at elevated temperatures. R&D process improvements include process optimization to increase CO<sub>2</sub> loading and use of various engineering techniques to eliminate ammonia vapor losses from the system during operation (Resnik et al., 2004, 2006; Yeh et al., 2005).

Another ammonia-based system, under development by Alstom, is the chilled ammonia process (CAP), which is scheduled for a 5-MW pilot test in 2007 at We Energies Pleasant Prairie Power Plant. It is also scheduled for a test in mid-2008 on AEP's 1300-MW Mountaineer Plant in New Haven, WV, as a 30-MW (thermal) product validation with up to 100,000 tonnes of CO<sub>2</sub> being captured per year. This process uses the same AC/ABC absorption chemistry as the aqueous system described above, but differs in that no fertilizer is produced and a slurry of aqueous AC and ABC and solid ABC is circulated to capture CO<sub>2</sub> (Black, 2006). The process operates at near freezing temperatures (32–50 °F), and the flue gas is cooled prior to absorption using chilled water and a series of direct contact coolers. Technical hurdles associated with the technology include cooling the flue gas and absorber to maintain operating temperatures below 50 °F (required to reduce ammonia slip, achieve high CO<sub>2</sub> capacities, and for AC/ABC cycling), mitigating the ammonia slip during absorption and regeneration, achieving 90% removal efficiencies in a single stage, and avoiding fouling of heat transfer and other equipment by ABC deposition as a result of absorber operation with a saturated solution. Both the aqueous and chilled ammonia processes have the potential for improved energy efficiency over amine-based systems, if the hurdles can be overcome.

**2.1.2.3. Membranes.** There are a variety of options for using membranes to recover CO<sub>2</sub> from flue gas. In one concept, flue gas would be passed through a bundle of membrane tubes, while an amine solution flowed through the shell side of the bundle. CO<sub>2</sub> would pass through the membrane and be absorbed in the amine, while impurities would be blocked from the amine, thus decreasing the loss of amine as a result of stable salt formation. Also, it should be possible to achieve a higher loading differential between rich amine and lean amine. After leaving the membrane bundle, the amine would be regenerated before being recycled. R&D pathways to an improved system include increased membrane selectivity and permeability and decreased cost (Falk Pederson et al., 2000).

Another concept under development is the use of an inorganic membrane. The University of New Mexico researchers have previously shown the ability to prepare a silica membrane that can selectively separate CO<sub>2</sub> from CH<sub>4</sub> and are

developing a microporous inorganic silica membrane containing amine functional groups for the separation of CO<sub>2</sub> from flue gas. The membrane is produced by sol-gel dip processing. By modifying the membrane, the strong interactions between the permeating CO<sub>2</sub> molecules and the amine functional membrane pores should enhance selective diffusion of CO<sub>2</sub> along the pore wall of the membrane with subsequent blocking of the transport of other gases, such as O<sub>2</sub>, N<sub>2</sub>, and SO<sub>2</sub>. Thus, this novel membrane should have better CO<sub>2</sub> selectivity than a pure siliceous membrane, if the illusive balance between permeance and selectivity can be achieved.

New Mexico Institute of Mining and Technology is looking at zeolite membranes. Zeolites are crystalline aluminosilicate materials with well-defined subnanometer pores and unique surface properties appropriate for molecular separations, such as CO<sub>2</sub> from flue gas. The current work is focusing on the separation of CO<sub>2</sub> from N<sub>2</sub> at high temperatures. The target operational temperature for membrane development is 400 °C (Zhang, 2006).

Innovative use of membranes for CO<sub>2</sub> capture from flue gas is also being investigated. Membrane Technology and Research (MTR) is investigating novel thin-film composite polymer membranes and capture configurations to increase the flux of CO<sub>2</sub> across the membrane, thereby reducing required membrane area. These membranes will be developed based upon thin-film membranes previously developed by MTR utilizing Pebax<sup>®</sup> polyether-polyamide copolymers. This research effort includes studying placement of the membrane modules in the power plant in an optimal configuration so that the driving force across the membrane is maximized.

**2.1.2.4. CO<sub>2</sub> capture sorbents.** A number of solids can be used to react with CO<sub>2</sub> to form stable compounds at one set of operating conditions and then, at another set of conditions, be regenerated to liberate the absorbed CO<sub>2</sub> and reform the original compound. However, solids are inherently more difficult to work with than liquids, and no solid sorbent system for large scale recovery of CO<sub>2</sub> from flue gas has yet been commercialized, although molecular sieve systems are used to remove impurities from a number of streams, such as in the production of pure H<sub>2</sub>.

NETL scientists have developed an amine-enriched sorbent (Gray et al., 2005) that has been investigated with flue gas streams at temperatures similar to those found after lime/limestone desulfurization scrubbing. The CO<sub>2</sub> capture sorbents are prepared by treating high surface area substrates with various amine compounds. The immobilization of amine groups on the high surface area material significantly increases the contact area between CO<sub>2</sub> and amine. This advantage, combined with the elimination of liquid water, has the potential to improve the energy efficiency of the process compared to MEA scrubbing

Research Triangle Institute (RTI) is investigating a dry, inexpensive, regenerable, supported sorbent, sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), which reacts with CO<sub>2</sub> and water to form sodium bicarbonate (NaHCO<sub>3</sub>). A temperature swing is then used to regenerate the sorbent and produce a pure CO<sub>2</sub>/water stream. This process is ideally suited for retrofit application in the non-power and power generation sectors. After condensing the water, the CO<sub>2</sub> is ready for commercial use or

sequestration. Laboratory and pilot plant tests have consistently achieved over 90% CO<sub>2</sub> removal from simulated flue gas. RTI's process has advanced through pilot-scale testing with simulated and coal combustion flue gases. In addition, the reproducibility of their sorbent at a commercial operating facility (Süd Chemie) has been confirmed. The process advantages translate into lower capital costs and power requirements than conventional MEA technology (based on a preliminary economic analysis) (Nelson et al., 2005, 2006a,b).

To address problems associated with pressure drop and heat transfer with solid sorbents, research is being conducted to examine the use of metallic monolith structures coated with a nanostructured hydrophobic zeolite-grafted amine. These systems, currently being researched by the University of Akron, could be tuneable for CO<sub>2</sub> binding strength by altering the alkyl chain of the amine. Also, regenerable SO<sub>2</sub> absorption may be possible through the use of aryl amines.

**2.1.2.5. Metal organic frameworks.** Metal organic frameworks (MOFs) are a new class of hybrid material built from metal ions with well-defined coordination geometry and organic bridging ligands. They are extended structures with carefully sized cavities that can adsorb CO<sub>2</sub>. High storage capacity is possible, and the heat required for recovery of the adsorbed CO<sub>2</sub> is low. Over 600 chemically and structurally diverse MOFs have been developed over the past several years. MOF-177 (Willis et al., 2006) has shown one of the highest surface areas and adsorption capacity for CO<sub>2</sub> at elevated pressure. Additional work is needed to determine stability over thousands of cycles and the effect of impurities at typical flue gas temperature and pressure.

UOP is leading the DOE effort in this area and has developed a virtual high throughput screening (VHTS) model to reduce the number of MOF synthesis experiments to only those that have the highest probability of meeting the DOE sequestration performance and cost metrics. Because there are an unlimited number of possible MOF structures that can be prepared, the VHTS model, which has a high correlation with laboratory measurements on synthesized MOFs, is a valuable screening tool. A team, made up of UOP, the University of Michigan, and Northwestern University, is exploring these materials with the objective of developing a process that can recover CO<sub>2</sub> from the flue gas of a PC-fired power plant. Desirable characteristics of MOFs are low energy requirement for regeneration, good thermal stability, tolerance to contaminants, attrition resistance, and low cost.

**2.1.2.6. Enzyme-based system.** Biologically based capture systems are another potential avenue for improvement in CO<sub>2</sub> capture technology. These systems are based upon naturally occurring reactions of CO<sub>2</sub> in living organisms. One of these possibilities is the use of enzymes. An enzyme-based system, which achieves CO<sub>2</sub> capture and release by mimicking the mechanism of the mammalian respiratory system, is under development by Carbozyme (see Fig. 3). The process, utilizing carbonic anhydrase (CA) in a hollow fiber contained liquid membrane, has demonstrated at laboratory-scale the potential for 90% CO<sub>2</sub> capture followed by regeneration at ambient conditions. This is a significant technical improvement over the MEA temperature swing absorption process. The CA

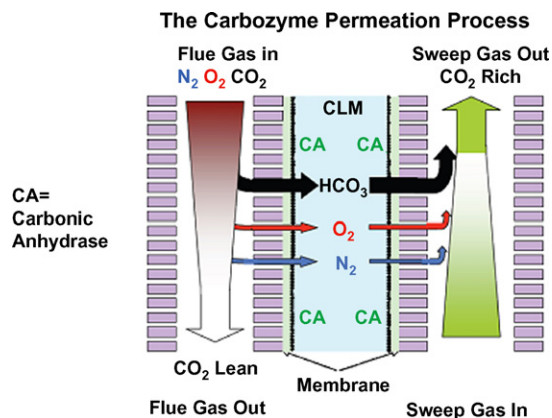


Fig. 3 – Schematic of the Carbozyme permeation process.

process has been shown to have a very low heat of absorption that reduces the energy penalty typically associated with absorption processes.

The rate of CO<sub>2</sub> dissolution in water is limited by the rate of aqueous CO<sub>2</sub> hydration, and the CO<sub>2</sub>-carrying capacity is limited by buffering capacity. Adding the enzyme CA to the solution speeds up the rate of carbonic acid formation; CA has the ability to catalyze the hydration of 600,000 molecules of carbon dioxide per molecule of CA per second compared to a theoretical maximum rate of 1,400,000 (Trachtenberg et al., 1999). This fast turnover rate minimizes the amount of enzyme required. Coupled with a low make-up rate, due to a potential CA life of 6 months based on laboratory testing, this biomimetic membrane approach has the potential for a step change improvement in performance and cost for large scale CO<sub>2</sub> capture in the power sector. Although the reported laboratory and economic results may be optimistic, the “Carbozyme biomimetic process can afford a 17-fold increase in membrane area or a 17 times lower permeance value and still be competitive in cost with MEA technology” (Yang and Ciferno, 2006). The idea behind this process is to use immobilized enzyme at the gas/liquid interface to increase the mass transfer and separation of CO<sub>2</sub> from flue gas. Technical challenges exist before this technology can be pilot tested in the field. These limitations include membrane

boundary layers, pore wetting, surface fouling (Boa and Trachtenberg, 2006), loss of enzyme activity, long-term operation, and scale-up, which are being addressed in a current project.

2.1.2.7. *Ionic liquids*. Ionic liquids (ILs) are a broad category of salts, typically containing an organic cation and either an inorganic or organic anion (Fig. 4) shows the computed electron density for a CO<sub>2</sub> molecule interacting with the ionic liquid [hmim][Tf2N]. The cation [hmim], charge +1, is shown along the top. The anion [Tf2N], charge –1, is along the bottom. A single CO<sub>2</sub> molecule is shown in between the two. This image is from a quantum mechanical calculation that shows the electron density distribution and indicates how CO<sub>2</sub> interacts with the ionic liquid. The blue regions on the surface show areas of relatively large positive charge, while red areas show large negative charge. Green areas are more or less neutral. ILs can dissolve gaseous CO<sub>2</sub> and are stable at temperatures up to several hundred degrees centigrade. Their good temperature stability offers the possibility of recovering CO<sub>2</sub> from flue gas without having to cool it first. Also, since ILs are physical solvents, little heat is required for regeneration. Research at the University of Notre Dame has indicated that, for flue gas application, ILs have demonstrated SO<sub>2</sub> solubility 8 to 25 times that of CO<sub>2</sub> at the same partial pressure (Anderson et al., 2006), thereby allowing this novel solvent to not only remove CO<sub>2</sub> but also serve as an SO<sub>2</sub> polishing step. Collaborative research with NETL scientists has shown that ILs can be used as the separating media for pre-combustion application in supported liquid membranes to separate CO<sub>2</sub> from H<sub>2</sub>.

Some ionic liquids are commercially available, but the ones most suited for CO<sub>2</sub> separation have only been synthesized in small quantities in academic laboratories. As such, current unit costs are high, but should be significantly lower when produced on a commercial scale for the volumes that would be needed by the power generation sector. The viscosity of many ILs is relatively high compared to conventional solvents. Viscosities for a variety of ILs are reported to range from 66 to 1110 cP at 20 to 25 °C (Kanel, 2003), and high viscosity may be an issue in practical applications. Based on the finding that the anion is critical in determining CO<sub>2</sub> solubility, several ionic

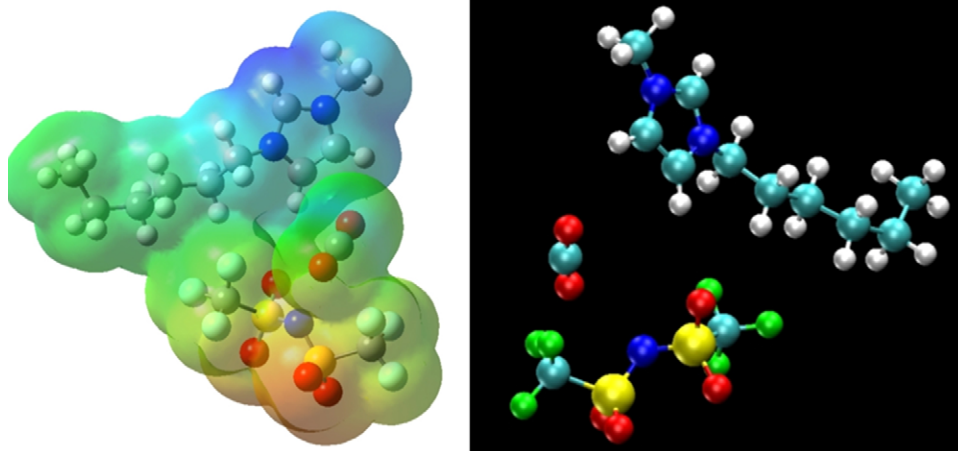


Fig. 4 – Schematic of an ionic liquid interaction with carbon dioxide.

liquids have been developed that have exhibited CO<sub>2</sub> solubilities 40 times greater than achieved prior to the start of the NETL-sponsored research project. Capacity still needs to be significantly improved, however, to meet cost targets. Task specific ILs (TSIL) (Maginn, 2007) that contain amine functionality are being investigated to provide the next step change improvement in CO<sub>2</sub> solubility.

## 2.2. Pre-combustion carbon capture

In pre-combustion CO<sub>2</sub> capture, the CO<sub>2</sub> is recovered from some process stream before the fuel is burned. To the extent that the concentration and pressure of the CO<sub>2</sub> containing stream can be increased, then the size and cost of the capture facilities can be reduced. This has led to efforts to develop combustion technologies that inherently produce concentrated CO<sub>2</sub> streams or CO<sub>2</sub> containing streams at high pressure, for which there are existing capture processes. Some of the developments being pursued related to pre-combustion CO<sub>2</sub> capture are discussed below.

### 2.2.1. Integrated gasification combine cycle

A very promising approach to pre-combustion capture involves IGCC supplemented by shift conversion. With this configuration, coal is first gasified with oxygen to produce synthesis gas (syngas), a mixture of mainly CO and H<sub>2</sub>. The syngas, with added steam, is then sent to a shift converter where the water gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) converts CO to CO<sub>2</sub> and additional H<sub>2</sub>. The CO<sub>2</sub> is separated from the H<sub>2</sub>, which is mixed with steam or nitrogen from the air separation unit and sent to a combustion turbine. The hot exhaust gas from the combustion turbine goes to a heat recovery steam generator (HRSG) to produce steam for the steam turbine that generates additional power and increases the overall power system efficiency. Because of the high CO<sub>2</sub> concentration in the high pressure fuel gas, existing capture processes, such as Rectisol and Selexol, can effectively capture the CO<sub>2</sub>, often in combination with sulfur (H<sub>2</sub>S) removal. Currently, these state-of-the-art capture technologies have not been operated at typical power generation scale, which results in some technical and economic uncertainty.

DOE has sponsored the development of IGCC technology through the funding of two successful IGCC clean coal technology projects: the Wabash River Coal Gasification Repowering Project and the Tampa Electric Polk Station IGCC Project. The Wabash River project involved retrofitting a two-stage, pressurized, oxygen-blown, entrained-flow E-Gas gasifier to produce syngas for a 262 MWe (net) combined cycle. The Tampa Electric project involved installation of a pressurized, oxygen-blown, entrained-flow Texaco gasifier to produce syngas for a 250 MWe (net) combined cycle. Although CO<sub>2</sub> capture was not included in these projects, they demonstrated the production of a high pressure syngas stream amenable to CO<sub>2</sub> recovery.

### 2.2.2. State-of-the-art physical solvent processes

A physical solvent selectively absorbs CO<sub>2</sub> without a chemical reaction. The loading that can be achieved depends upon the solvent being used, the partial pressure of CO<sub>2</sub> in the gas

stream, and the temperature, with higher partial pressures and lower temperatures being more favorable. With physical solvents, capacity is generally proportional to CO<sub>2</sub> partial pressure. R&D pathways to process improvements include modifying regeneration conditions to recover the CO<sub>2</sub> at a higher pressure, improving selectivity to reduce H<sub>2</sub> losses, and developing a solvent that has a high CO<sub>2</sub> loading at a higher temperature. Commercial acid gas removal processes that use physical solvents, such as Selexol and Rectisol, have such properties, but are energy intensive due to their heat transfer requirements. Therefore, their commercial promise is likely to be in the near term until higher performance and less costly technologies are demonstrated.

Another common physical solvent that is commercially used is propylene carbonate (Fluor process). The weaker bonding between CO<sub>2</sub> and this solvent allows the CO<sub>2</sub> to be separated from the solvent in a stripper by reducing the total pressure. However, there is a need for higher efficiency gas-liquid contactors and lower energy requirements for regeneration (MGSC, 2004).

Physical solvents, rather than chemical solvents, can be used in IGCC because of the relatively high partial pressure of CO<sub>2</sub> in the syngas exiting the shift converter. A main benefit of a physical solvent is that it requires less energy for regeneration. Since the main problem with physical solvents is that their capacity is best at low temperatures, it is necessary to cool the syngas before carbon capture. A physical solvent with acceptable capacity at a higher temperature would improve IGCC efficiency.

### 2.2.3. Membranes

Polymer-based membranes, in comparison to other separation techniques, such as pressure swing absorption, are less energy intensive, require no phase change in the process, and typically provide low-maintenance operations (Berchtold, 2006; Zhou and Ho, 2006). A polybenzimidazole (PBI) membrane under development at DOE's Los Alamos National Laboratory (LANL) has demonstrated long-term hydrothermal stability up to 400 °C, sulfur tolerance, and overall durability while operating in simulated industrial coal-derived syngas environments for over 400 days at 250 °C. Membrane thickness has been decreased to less than 3 μm while operating at simulated industrial syngas conditions. In addition, as demonstrated in Fig. 5, the PBI-based membrane exceeds

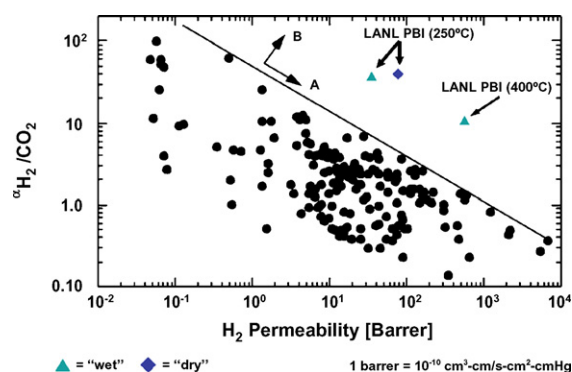


Fig. 5 – Performance of polymer membrane developed by LANL.



the Robeson upper bound for  $H_2/CO_2$  selectivity versus permeability and does so over a broad range of temperatures from 100 to 400 °C (Berchtold, 2006).

NETL researchers have recently fabricated and tested a supported liquid membrane that is  $CO_2$  selective and stable at temperatures exceeding 300 °C. The membrane consists of an advanced polymer substrate and an ionic liquid developed in a collaborative effort with the University of Notre Dame. Supported liquid membranes are of interest because transport takes place through the liquid within the pores rather than through a solid phase. This feature allows the membranes to take advantage of higher liquid phase diffusivities while maintaining the selectivity of the solution diffusion mechanism. NETL researchers were able to fabricate membranes operational at elevated temperatures due to negligible volatility of the ionic liquid and the exceptional resistance to plasticization of the substrate (Ilconich et al., 2007).

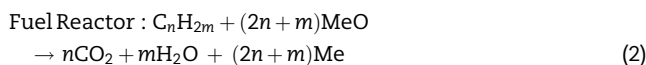
#### 2.2.4. Pre-combustion sorbents

RTI is developing a novel and highly active lithium silicate-based ( $Li_4SiO_4$ ) sorbent material for high temperature  $CO_2$  removal. This material is ideally suited for  $CO_2$  removal from synthesis gas (syngas) derived from gasification of carbonaceous fuels (coal, coke, natural gas, biomass, etc.). Extensive bench-scale testing of this material in both fixed-bed and fluidized bed process configurations has shown the ability to remove more than 90% of the  $CO_2$  from simulated syngas. The lithium silicate-based sorbent is highly effective at temperatures of 250 to 550 °C, pressures of 0 to 20 atm,  $CO_2$  concentrations of 2 to 20%, and in the presence of contaminants such as hydrogen sulfide. In addition, the sorbent has shown excellent regenerability and attrition resistance in thermal cycling tests (Li et al., 2005, 2006). Recent analysis has shown that the lithium silicate-based sorbent has the capability to not only separate  $CO_2$  from syngas, but also to promote the water gas shift reaction.

#### 2.2.5. Chemical looping combustion and gasification

Chemical looping combustion enables the production of a concentrated  $CO_2$  stream without the need for an expensive air separation unit. In this process, oxygen is supplied by a solid oxygen carrier, rather than by air or gaseous oxygen. In one potential configuration, chemical looping is carried out in two fluidized beds. In the first bed, a solid, metal-based compound (Me) is oxidized with air to form an oxide of the compound (MeO) and produce a hot flue gas (reaction (1)), which is used to raise steam for the steam turbine that runs the generator. MeO from the oxidizer flows to the second bed (the reducer). In this fluidized bed reactor, the oxide is reduced to its initial state by the fuel (reaction (2)), while producing a gas with a high concentration of  $CO_2$  that can be captured and sequestered. Limestone may be added for sulfur removal. If  $CaSO_4$  is used as the oxygen carrying compound, sulfur in the coal reacts with limestone to form  $CaS$ , which upon oxidation becomes part of the oxygen carrier stream. A slip stream from the oxidizer removes ash from the system. The ENCAP project consortium is currently investigating chemical looping combustion of both solid and

gaseous fuels.



A related area of research is chemical looping gasification. In this system, two or three solid particle loops are utilized to provide the oxygen for gasification and to capture  $CO_2$ . A loop, similar to that of chemical looping combustion, is used to gasify the coal and produce syngas ( $H_2$  and  $CO$ ). A second solid loop is used in a water gas shift reactor. In this reactor, steam reacts with  $CO$  and converts it to  $H_2$  and  $CO_2$ . The circulating solid absorbs the  $CO_2$ , thereby providing a greater driving force for the water gas shift reaction (as discussed in Section 2.2.1). The  $CO_2$  is then released in a calcination step that produces nearly pure  $CO_2$  for further compression and sequestration. According to an Alstom Power report, their chemical looping gasification system may be able to achieve at least 90%  $CO_2$  capture with an increase of about 16% in the cost of electricity over a traditional air fired circulating fluidized bed (CFB) plant (Nsakala and Liljedahl, 2003). Chemical looping combustion has recently been demonstrated in a 10-kW prototype using interconnected fluidized beds (Lyngfelt et al., 2004).

Both chemical looping combustion and gasification are in the early stages of process development. Bench and laboratory-scale experimentation is currently being conducted. Key hurdles include the handling of multiple solid streams and the development of adequate oxygen carrier materials.

#### 2.2.6. Improved auxiliary processes

The IGCC approach to  $CO_2$  capture outlined above requires several auxiliary processes, including oxygen production, shift conversion, and  $CO_2$  separation. Any improvement to these auxiliary operations will improve IGCC availability and economics in a carbon constrained environment. One approach to improved oxygen production is the use of a membrane system in place of the energy intensive cryogenic system which is currently state-of-the-art. Air Products is developing an ion transport membrane (ITM), in which oxygen diffuses through the membrane as an oxygen ion, for use in  $O_2/N_2$  separation.

Membrane reactors also show promise for improving shift conversion. Since the shift reaction is equilibrium limited, multistage reactors are frequently used. With a membrane reactor, the shift catalyst would be placed inside membrane tubes, which would remove either  $H_2$  or  $CO_2$  from the reaction mixture, depending on the membrane used. This would permit the shift reaction to go to completion in a single stage, avoiding the need for high, intermediate, and low temperature reactors.

### 2.3. Oxy-combustion

An alternative to capturing carbon from fuel gas or flue gas is to modify the combustion process so that the flue gas has a high concentration of  $CO_2$ . A promising technology for accomplishing this is oxy-combustion, in which the fuel is burned with nearly pure oxygen (greater than 95%) mixed with

recycled flue gas. In the most frequently proposed version of this concept, a cryogenic air separation unit (ASU) is used to supply high purity oxygen to a PC-fired boiler. This high purity oxygen is mixed with recycled flue gas prior to combustion or in the boiler to maintain combustion conditions similar to an air fired configuration. This is necessary because currently available materials of construction cannot withstand the high temperatures resulting from coal combustion in pure oxygen. For a new unit, it should be possible to use smaller boiler equipment due to increased efficiency. The main attraction of this process is that it produces a flue gas which is predominantly CO<sub>2</sub> and water. The water is easily removed by condensation, and the remaining CO<sub>2</sub> can be purified relatively inexpensively. Conditioning of the flue gas consists of drying the CO<sub>2</sub>, removal of O<sub>2</sub> to prevent corrosion in the pipeline, and possibly removal of other contaminants and diluents, such as Ar, N<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub>. Babcock & Wilcox is working on cost effective oxy-combustion for retrofitting to coal-fired boilers.

The cost of carbon capture in an oxy-combustion power plant should be lower than for a conventional PC plant, as a result of the decreased flue gas volume and increased concentration of CO<sub>2</sub>, but the cost of air separation and flue gas recirculation significantly reduces the economic benefit. Argonne National Laboratory (ANL) is studying all engineering aspects of retrofitting oxy-combustion to existing boilers, including the effect of impurities and options for CO<sub>2</sub> transportation, use, and sequestration. If the flue gas can be recycled before SO<sub>2</sub> scrubbing, the SO<sub>2</sub> scrubber can be reduced in size, and significant cost savings are possible. Engineering studies are necessary because of the different physical properties of CO<sub>2</sub> compared to N<sub>2</sub>. Among the effects are changes in radiation and the temperature profile in the furnace (Doctor and Molburg, 2005).

Alstom Power is developing an oxygen fired CFB combustor that would produce a concentrated CO<sub>2</sub> flue gas. As CO<sub>2</sub> has different properties than nitrogen, a pressurized fluidized bed combustor would require a redesigned gas turbine. Alstom Power is also conducting modeling studies to better understand and predict the combustion characteristics of oxy-combustion technology. The latest available systems and engineering analysis shows a cost of \$37/ton of CO<sub>2</sub> avoided for a coal-fed circulating fluidized bed supplied with cryogenic oxygen (Nsakala et al., 2004).

To drastically reduce the cost of oxy-combustion, systems will need to be developed to reduce the cost of oxygen production. Praxair, Inc. is investigating an alternative approach to oxy-combustion. Instead of a cryogenic ASU, Praxair is using an oxygen transport membrane within the boiler. At high temperature, oxygen can diffuse across this ceramic membrane. The concept is to pump air through ceramic membrane tubes, allowing pure oxygen to diffuse into the furnace and combust the fuel. After heat recovery, the depleted air is exhausted to the atmosphere. Praxair estimates that their process should improve the thermal efficiency for a natural gas system from 87% to nearly 95% (Shah et al., 2006). Current research is expanding this technology's potential to operate with various coal ranks. A ceramic membrane and seal assembly has been developed for

thermal integration between the high temperature membrane and the combustion process. Prototype single- and multi-tube reactors have been built and operated without membrane failure.

Another technology to reduce the cost of oxygen production for use with oxy-combustion, called ceramic autothermal recovery (CAR), is being developed by The BOC Group. The CAR process uses the oxygen storage properties of perovskites to adsorb oxygen from air in a fixed-bed and then release the adsorbed oxygen into a sweep gas, such as recycled flue gas, that can be sent to the furnace. The process is made continuous by operating multiple beds in a cycle. Early estimates show a cost of electricity increase of approximately 26% for a CAR integrated coal-fired power plant (Acharya et al., 2005).

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### 3. Conclusions

CO<sub>2</sub> capture and separation from large point sources, such as power plants, can be achieved through continued research, development, and demonstration. Worldwide research is being performed to abate global climate change, which a consensus of the scientific community indicates is due, at least in part, to anthropogenic GHG emissions (IPCC, 2007). Research to develop technologies and processes that increase the efficiency of capture systems while reducing overall cost is critical to creating a feasible GHG control implementation plan, covering not only power plants and industrial facilities but also the infrastructure required to support that implementation.

The DOE Carbon Sequestration Program is developing a project portfolio associated with carbon capture and separation technologies that can significantly impact the level of CO<sub>2</sub> emissions from fossil-fueled power generation plants. These technologies, while focused on the power sector due to the volume of its CO<sub>2</sub> emissions, are also applicable to other sectors. The programmatic timeline is to demonstrate a series of cost effective CO<sub>2</sub> capture and separation technologies at pilot scale by 2012, with deployment leading to substantial market penetration beyond 2012. The Sequestration Program has identified performance and cost targets which are necessary to reduce the impact associated with capture and separation of CO<sub>2</sub> not only on the power sector but also on supporting industries.

Research and development is driven by a commercialization focus to satisfy the requirements of identified market segments and to substantially improve performance with a significant cost reduction. Wide deployment of these technologies, in addition to energy efficiency and demand management approaches, is necessary to mitigate GHG emissions and ultimately achieve stabilization.

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