# RECENT ADVANCES IN CARBON DIOXIDE CAPTURE AND SEPARATION TECHNIQUES FOR POWER GENERATION POINT SOURCES

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## ABSTRACT

The capture/separation step for carbon dioxide ($CO_2$) from large-point sources is a critical one with respect to the technical feasibility and cost of the overall carbon sequestration scenario. For large-point sources, such as those found in power generation, the carbon dioxide capture techniques being investigated by the in-house research area of the National Energy Technology Laboratory (NETL) possess the potential for improved efficiency and costs as compared to more conventional technologies. The investigated techniques can have wide applications, but the research has focused on capture/separation of carbon dioxide from flue gas (postcombustion from fossil fuel-fired combustors) and from fuel gas (precombustion, such as integrated gasification combined cycle – IGCC). Novel concepts are being developed in wet scrubbing with either chemical or physical absorption; chemical absorption or adsorption with solid sorbents; and separation by membranes. In one concept, a wet scrubbing technique is being investigated that uses an ammonia-based solvent to absorb carbon dioxide from the flue gas of a pulverized coal-fired power plant. In contrast, a physical solvent process to remove $CO_2$ from fuel gas of an IGCC system at elevated temperature and pressure is being developed. Fabrication techniques and mechanistic studies for hybrid membranes separating $CO_2$ from the fuel gas produced by coal gasification are also being performed. Solid, regenerable sorbents that can be employed in either flue gas or fuel gas applications are being investigated. Progress with these sorbents that can be regenerated via a temperature and/or pressure swing has led to a demonstration within the Modular Carbon Dioxide Capture Facility constructed at NETL. An overview of the various novel techniques is presented along with a research progress status of each technology.

## INTRODUCTION

Carbon sequestration is a viable alternative to reduce the emissions of the greenhouse gas, carbon dioxide, from large point sources. It holds the potential to provide deep reductions in greenhouse gas emissions. Additionally, the Carbon Sequestration Program, managed by the U.S. Department of Energy, implements the Global Climate Change Initiative within the United States.[1] Of particular interest are power generation point sources that use fossil fuels. Since nearly one-third of the anthropogenic $CO_2$ emissions are produced by these facilities, conventional coal-burning power plants and advanced power generation plants, such as integrated gasification combined cycle (IGCC), present opportunities where carbon can be removed and then permanently stored. Pulverized coal-fired-base steam cycles have been the predominant electric power generation technology for many years. Coal is burned in a boiler that produces high-pressure steam; the steam then passes through a steam turbine, generating electricity. A generic scheme of a pulverized-coal power generation plant is depicted in Figure 1. Coal is combusted with air that is preheated by the flue gas produced during combustion. Typically, an excess of air is used to ensure total burnout of the coal. The type of combustor, for example wall-fired, tangential, or cyclone, will impact some of the minor components typically found in flue gas, but if the air in-leakage remains low, the concentration of $CO_2$ will not be impacted significantly.

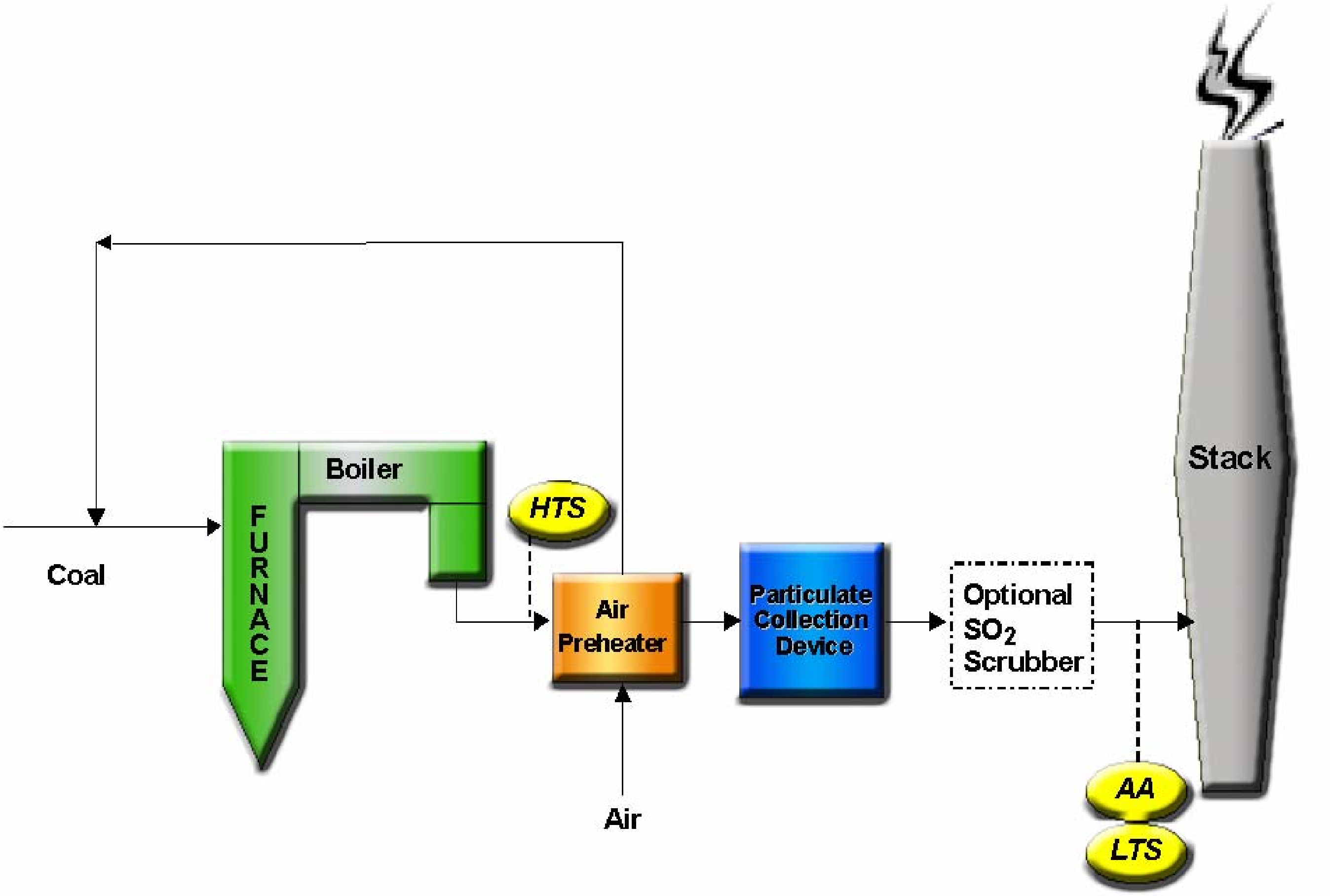

Figure 1: General Case: Conventional Pulverized-Coal Combustion – Flue Gas

After the furnace, the flue gas is cooled in an economizer and its sensible heat is transferred to the combustion air in the preheater. Fly ash would be collected in a particulate collection device, such as an electrostatic precipitator or a baghouse. For a pulverized coal system, approximately 80% of the ash in the coal exits the combustor as flyash, whereas the remaining 20% exits as bottom ash from the furnace, although this loading is dependent on the type of combustor.

The composition of the coal as related to regulations will determine whether various control technologies will be needed in the power generation system. If substantial quantities of sulfur oxides are formed, then a $SO_2$ scrubbing system may need to be incorporated into the system. Additionally, some form of $NO_x$ control may be needed – possibly a combustion modification, for example low-$NO_x$ burners, or selective catalytic reduction. With the issuance of recent EPA regulations in the United States in early 2005, mercury emissions will also need to be controlled in the near future.

With respect to carbon dioxide, capture can occur along the path of the flue gas. A prime process variable will be temperature, whereas in a conventional plant, the pressure throughout is near atmospheric. Another consideration will be the quantity of gas to be removed from the flue gas stream since flue gas flows within power generation facilities can be quite large.

In IGCC power plants, a fossil fuel is reacted with oxygen and steam in a gasifier to produce a fuel gas (also frequently referred to as synthesis gas or syngas) consisting mainly of carbon monoxide and hydrogen. This mixture is then cleaned and burned to generate power in a gas turbine combined cycle. The high efficiency of this process can be exploited by fuels, such as residual oil and coal.[2] The plants consist basically of three main building blocks: coal gasification, gas cleaning, and power generation.[3] A process diagram can be seen in Figure 2. Assuming oxygen-blown gasification with coal, the main products of the gasification process are CO, $H_2$, $CO_2$, $H_2O$, $H_2S$, some gaseous hydrocarbons, and trace amounts of certain pollutants, including mercury. The gas cleanup system of the plant involves particulate removal and acid gas scrubbing. In a typical IGCC plant, the crude fuel gas is first fed to a facility to remove the particulates from the gas stream. The gas leaving the particulates scrubber is then cooled and dewatered and, at this point, consists mainly of CO, $H_2$, and $CO_2$. It also contains the acid gas $H_2S$, which will be removed in the desulfurization system. The acid gas scrubbing process (cold gas cleanup in Figure 2) is generally designed for the removal of sulfur-bearing compounds with very little $CO_2$ removed in the process. However, removal of $CO_2$ at this location is possible. Some designs employ sulfur-tolerant shift catalysts followed by acid gas removal at low temperatures. This approach is preferable when $CO_2$ recovery is desired due to the increase in $CO_2$ partial pressure after the shift reaction.[4] The power generation consists of a gas turbine system followed by a steam turbine bottoming cycle. The desulfurized gas is first injected with steam and partially expanded in gas expanders to recover some work. The partially expanded gas, which is rich in CO and $H_2$, is then burned with air and expanded in a gas turbine to recover more work. The residual thermal energy in the gas turbine exhaust is used to produce steam for the steam turbine bottoming cycle.

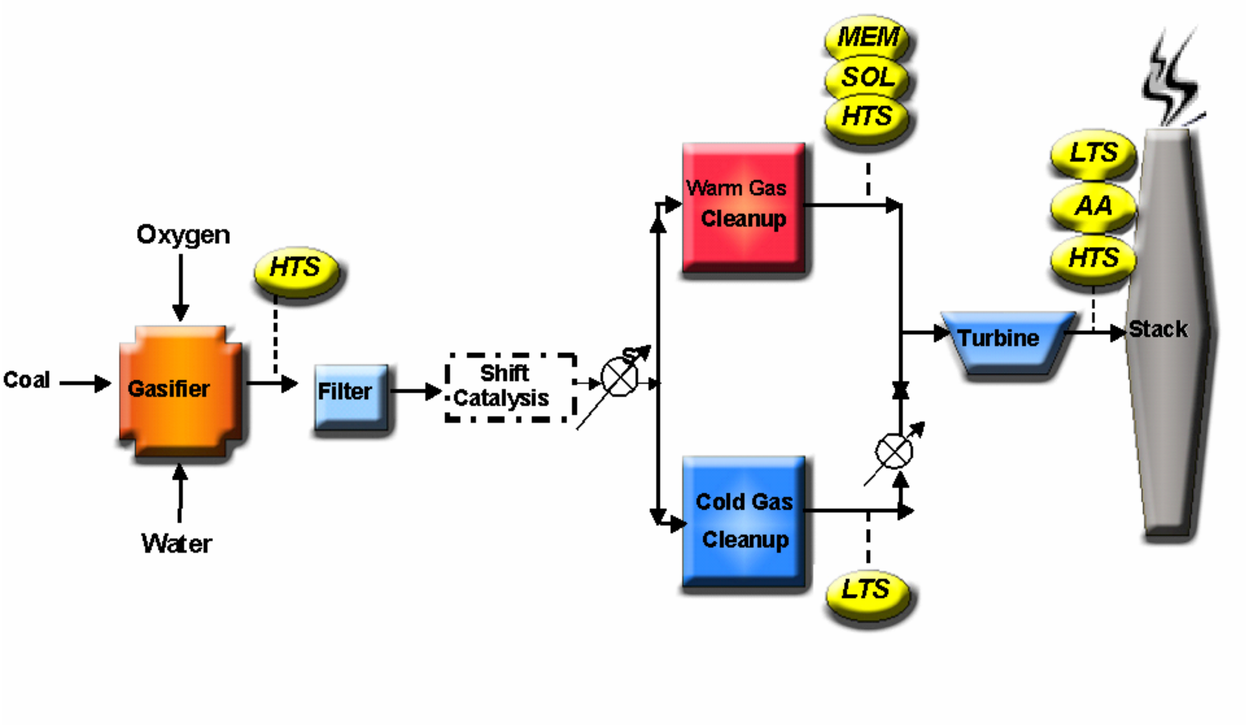

Figure 2: General Case: Advanced Gasification/IGCC – Fuel Gas

The upper flow path in Figure 2 indicates the option where acid gas cleaning occurs within a warm gas cleanup system rather than at the previously described cold (lower) temperatures. The main advantage in cleaning the gas in an IGCC application at higher temperature is that the thermal plant efficiency will be as much as 2-3% greater as compared to the lower temperature acid gas cleaning scenario.[4] The areas of efficiency improvements are that the transfer of heat and latent heat to the more efficient gas turbine cycle are maximized; the capital and operating costs are lowered by reducing the duty on the heat exchangers; and the need for waste water treatment facilities are eliminated.[5]

With respect to $CO_2$ capture in an IGCC system, post-combustion and pre-combustion technologies can be used. With coal utilization and after the gas turbine, about 9% carbon dioxide exists in the flue gas and partial pressure of the carbon dioxide is low. However, precombustion techniques with IGCC offer the opportunity to remove $CO_2$ from the fuel gas before it is combusted in the turbine. The high pressure of the system and the possible shifting of the CO to $CO_2$ produce a high partial pressure of $CO_2$ that could be advantageous with certain removal technologies. Examples of demonstrations of IGCC technology that are currently in operation in the United States are Tampa Electric's Polk Station and PSI Energy's Wabash Station, which have successfully demonstrated the use of coal to produce electricity.

In a carbon sequestration scenario, the cost of the capture/separation step is much higher than that of the storage step.[1] Wet scrubbing with an amine solvent, such as monoethanolamine (MEA), to capture $CO_2$ from gas streams is a relatively mature technology. However, for flue gas produced from fossil fuel-fired power generation point sources, the MEA process has certain drawbacks, including a high parasitic energy requirement and high capital and operating costs. For IGCC systems, commercial processes for $CO_2$ removal, such as Selexol, are used as a baseline from which other capture technologies can be compared. The U.S. Department of Energy's National Energy Technology Laboratory (NETL) is conducting in-house research investigating novel techniques to capture/separate $CO_2$ from gases from current or advanced power generation systems. These technologies fall within the process categories of wet scrubbing with either chemical or physical absorption; chemical absorption or adsorption with solid sorbents; and separation by membranes.

In the first category, results from an investigation with an aqueous ammonia scrubbing process to remove $CO_2$ from flue gas have been obtained by testing in a semi-continuous reactor system.[6,7] The process (identified as "AA" in Figures 1 and 2) has an inherent energy savings advantage when compared to MEA scrubbing and has the added capability of removing and converting sulfur dioxide and nitric oxides in flue gas into fertilizer. As can be seen in the figures, it is envisioned that this low temperature process for $CO_2$ removal can be incorporated immediately before the flue gas exits the plant. In another investigation, physical solvents for $CO_2$ removal at high temperatures in IGCC applications are being studied. The higher temperature of operation for these solvents enhances the thermal efficacy of the IGCC power generation system. (See "SOL" in Figure 2.)

The use of solid sorbents is another method to remove $CO_2$ from gas streams. Amine-enriched sorbents[8-10] have been investigated in flue gas streams at temperatures similar to that found after lime/limestone desulfurization scrubbing. The $CO_2$ capture sorbents are prepared by the chemical treatment of high surface oxide materials and other substrates with various amine compounds. The immobilization of amine groups on the high surface area material significantly increases the needed contact area between $CO_2$ and amine. Thus the increase in contact area and less energy consumption during the regeneration step, as compared to conventional MEA scrubbing, potentially improves the efficiency of the process. Additionally, physical adsorbents, such as certain natural and synthetic zeolites, present the opportunity for removal of $CO_2$ from gas streams, such as flue gas.[11-13] The regeneration step is crucial for these types of sorbents and either pressure swing and/or temperature swing can be effectively utilized. Regenerable low temperature sorbents that operate below 300°F are identified as "LTS" in Figures 1 and 2 whereas regenerable high temperature sorbents "HTS" operate above an arbitrary 300°F level. The sorbents can be applied in either power generation scheme. The 300°F cutoff temperature was arbitrary as it reflects one in a range of flue gas temperatures downstream of the air preheater in a conventional coal-fired plant, and in an IGCC application, this temperature typifies the lower end of the warm gas range for obtaining the 2-3% thermal efficiency advantage.

Another method is separation of carbon dioxide from gas by the use of a membrane system. Simplicity, flexibility, the ability to maintain high $CO_2$ pressure, and the potential to perform separations at low energy penalties make membranes interesting for $CO_2$ removal for IGCC applications. In addition to the standard requirement of obtaining high permeability, challenges exist in the development of membranes capable of selectively separating $CO_2$ from the process gas stream. In addition, the reducing conditions and the presence of water and various minor contaminants necessitate the design of membranes with exceptional chemical and physical stability. (See "MEM" in Figure 2 as a potential location for these membranes.) Development of hybrid membranes for the separation of $CO_2$ presents a method that can satisfy the requirements for a durable membrane, especially at elevated temperatures.[14-16]

The research status of the above novel capture technologies that fall within the in-house research area at NETL are described below along with implications of the experimental research on technical direction and costs.

## RESULTS AND DISCUSSION

### ***Ammonia-Based Wet Scrubbing***

The ammonia-based wet scrubbing process is similar to conventional MEA scrubbing in that both are aqueous liquid solutions that chemically react with $CO_2$ to remove it from flue gas. However, the ammonia-based process offers the potential for a reduced parasitic load. If the adsorption/desorption cycle can be controlled so that it is primarily cycling between ammonium bicarbonate and ammonium carbonate, the heat of reaction for $CO_2$ absorption can be reduced to 262 Btu/lb $CO_2$ compared to 825 Btu/lb $CO_2$ for MEA. Laboratory-scale tests indicate that the absorption/desorption process may be controlled in such a manner. Also, because of the temperature of regeneration, the desorption kinetics may be such that regeneration of the rich carbonate/bicarbonate solution will require heat to drive the desorption reaction but with minimal stripping steam. Additionally, the aqueous ammonia system can carry more $CO_2$ per weight of solution so less solution needs to be circulated, resulting in less sensible heat and in a reduction in size and cost of the system.

Another advantage of the ammonia-based process is that aqueous ammonia can be used to control emissions of $SO_2$, $NO_x$, and mercury in addition to $CO_2$. Use of aqueous ammonia for $NO_x$ and $SO_2$ and mercury control is being performed at a 50-$MW_e$ demonstration by Powerspan Corp. at FirstEnergy's Burger coal-fired power plant in Ohio, U.S. The capture of $SO_2$ and $NO_x$ with aqueous ammonia results in the generation of ammonium sulfate and ammonium nitrate, both salable by-products. Mercury is removed from the solution by using a bed of activated carbon.

$CO_2$ absorption and regeneration studies in aqueous ammonia were initially performed in a semi-continuous flow reactor. Simulated flue gas with 15%vol $CO_2$ bubbled through a 3-liter glass container filled with 1500-ml aqueous ammonia solution. Pressure was near atmospheric; total gas flow rate was 7500 sccm; and a mixer operating at 1600 rpm eliminated any mass transfer gradients. The temperature of the absorber was controlled with a cooling/heating coil, through which temperature-controlled water flowed. The baseline condition for the absorption tests was 80°F, utilizing an initial 14% ammonia solution. The exit gas from the absorber was sent to a reflux condenser, where the gas temperature was reduced to 10°F to condense the vapor escaping from the absorber. The condensed vapor continuously drained back to the reactor. The vent gas flow rate was measured by a flow meter. The gas from the flow meter was then analyzed with a continuous emissions monitor for unreacted $CO_2$. The $CO_2$ concentration-versus-time data were used to calculate $CO_2$ absorption rates and to totalize the amount of $CO_2$ absorbed. The same vessel was used as the reactor during the regeneration step. However, in this case no mixing of the solution was conducted. Analytical techniques were developed to identify the forms of the ammonium complexes in solution when carbonation of aqueous ammonium solution occurs. The by-products are mixtures of ammonium bicarbonate, ammonium carbonate, complex salts of carbonate and bicarbonate, ammonium hydroxide, and other compounds. It is desirable to know the compound mix under various absorption or regeneration conditions. A method was developed to determine carbonate, bicarbonate and hydroxide quantitatively using phenolphthalein and total alkalinity titrimetric methods.

In order to measure $CO_2$ loading capacity change of an aqueous ammonia solution during repeated absorption and regeneration cycles, the following experiments were conducted in the semi-continuous flow reactor. Solutions of 7%, 10.5%, and 14% ammonia were used in cycling tests to determine the potential effective utilization rates available for the aqueous ammonia solutions. Ammonia solutions were made by mixing A.C.S. grade ammonium hydroxide solutions with de-ionized water to provide the desired concentrations. For the cycling tests, the absorption occurred at 80°F followed by thermal regeneration at 180°F. The absorption/regeneration cycle was repeated for a total of three cycles, anticipating that the amount of $CO_2$ absorbed in the absorption step and regenerated in the regeneration step would approach a steady state condition. A plot of the $CO_2$ loading capacity (absorption capacity) versus test cycle number showed that there is a large drop in the loading capacity (g $CO_2$/g solution) between the first and the second cycles, but little change thereafter. These findings indicated that less than 100% regeneration of the initial aqueous ammonia solution was achieved. The loss in capacity was further compounded by the ammonia vapor lost during the test. For each solution, a majority of the ammonia loss occurred in the first cycle absorption step with much lower losses in subsequent cycles. Results from a later five-cycle test are shown in Figure 3 and confirmed the earlier cycling tests.

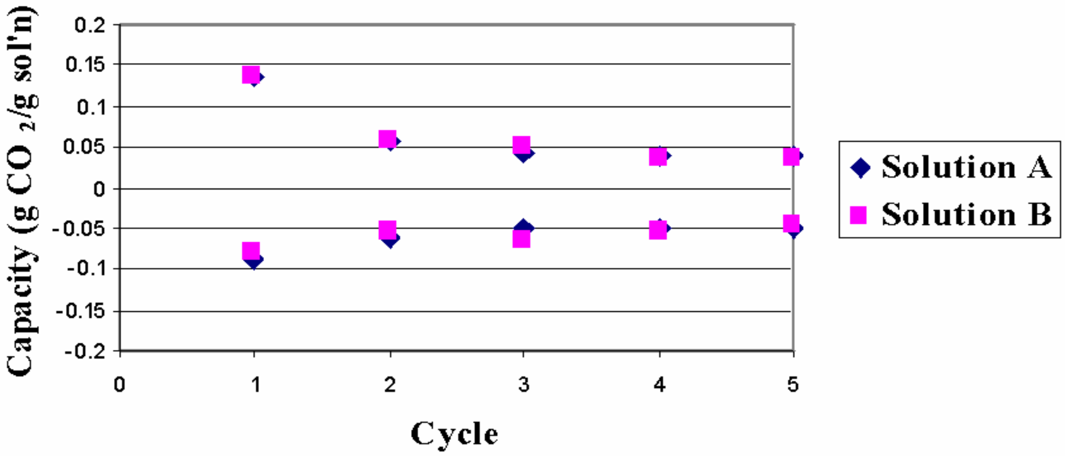

Figure 3: Absorption/Regeneration Capacity of Cycled Solutions (10.5% Initial Ammonia Solution)

The specific absorption capacity of the solutions for each cycle also demonstrated that the experiments appeared to have asymptotically approached a fixed value after the second absorption test. The results with aqueous ammonia are far from optimized with respect to the amount of $CO_2$ regenerated and the ammonia loss. The final measured specific absorption capacity was 0.068, 0.053, and 0.040 g $CO_2$/g solution for the 14%, 10.5%, and 7% initial ammonia solutions, respectively. This compares favorably to current MEA technology that has demonstrated a capacity of 0.054 g $CO_2$/g solution for a 30% MEA solution. The sensible heat of regeneration per mass of $CO_2$ is indirectly proportional to the loading and proportional to the temperature difference between the absorption and regeneration temperatures (131°F to 248°F for MEA, 80°F to 180°F for aqueous ammonia). Using the above absorption capacity data, the sensible heat of regeneration for the aqueous ammonia process may be as little as 45% that of the MEA process. This information, combined with the fact that a contributor to the regeneration heat duty in an MEA process is the heat of vaporization of steam, projects that the aqueous ammonia process can have significant energy savings. The cycling test results demonstrated that a significant reduction in regeneration energy is possible due to the higher loading capacity of the aqueous ammonia-based solution, the lower heat of reaction, and the lower heat of vaporization when compared to standard MEA solutions. From the semi-continuous test results, a systems analysis demonstrating these benefits was conducted through the project management sector at NETL. An EPRI/Parsons 2000 study was used as the basis. The net result indicated that the ammonia process can approach the capture program goal for a technology that results in less than 20% increase in the cost of energy services.

Based on the results from the semi-batch testing, a continuous flow system, similar to a MEA scrubbing system, was designed and constructed. In this system, an absorber to capture $CO_2$ from a simulated flue gas and a regenerator to liberate a concentrated $CO_2$ stream are interconnected by a liquid-to-liquid heat exchanger. The unit utilizes a countercurrent flow packed-bed absorber with structured packing to remove carbon dioxide. Initial ammonia concentrations ranged between 0-28 percent. The column is jacketed with water; the water temperature is controlled by a recirculating heater/chiller. The simulated flue gas can be generated by combining instrument air, nitrogen, nitric oxide or nitrogen dioxide, sulfur dioxide or sulfur trioxide and $CO_2$, metered by mass flow controllers, and heated to temperatures as high as 130°F by a resistance heater with controller before introduction into the bottom of the absorber, which operates at approximately 1 psig. The absorbent, which is initially a solution of aqueous $NH_3$, flows countercurrently to the flue gas in the absorber. The cleaned gas from the absorber is cooled to approximately 45°F utilizing a water-cooled, condensing heat exchanger; the condensate is collected. The gas mass flow after the condenser is measured with a mass flowmeter. A slipstream of the stripped gas is sent to continuous emissions monitors for analysis. The saturated liquid is preheated in a heat exchanger with return liquid from the regenerator to approximately 120°F and pumped to the regenerator, where the temperature can be raised to as high as 200°F, utilizing an imbedded coil that is heated by a recirculating water heater. The $CO_2$-rich gas that evolves from the regenerator is cooled to approximately 60°F in a condenser that is supplied with coolant at 33°F by a recirculating chiller; the flow is measured with a mass flowmeter before being analyzed with a continuous emissions monitor. The precipitate that collects in the condenser is dissolved in water at the completion of each test; the resultant rinsate is weighed and analyzed. The $CO_2$-lean liquid is cooled to the absorber temperature by a chiller and a heat exchanger and circulated back to the absorber for further $CO_2$ removal. Measurements of liquid pH to and from the absorber are continuously made. Liquid samples are taken via syringe through in-line septa at the absorber and regenerator exits and diluted to prevent precipitation of solids. Additional sample locations are below each set of structured packing in the absorber. Titrimetric analysis of the samples is performed to give ammonium hydroxide, ammonium carbonate, and ammonium bicarbonate concentrations, corrected to the undiluted sample concentrations.

Prior to testing, the initial ammonia solution is pretreated to maximize the amount of carbonate/bicarbonate in the starting solution. This is done by flowing a stream of simulated flue gas (15% $CO_2$) through the absorber at 50°F. Analysis of the liquid solution prior to the start of the testing indicates that the hydroxide ion does not exist.

To date, the parameters of absorber temperature, initial $NH_3$ concentration, regenerator temperature, liquid solvent inventory (residence time), and flue gas flow rate are being investigated. All have impacts on the $CO_2$ removal efficiency, efficacy of the solution, and ammonia losses, with the residence time being the most significant out of the parameters investigated thus far. A mathematical model of the process will be initiated. Additionally, a collaborative effort with Powerspan Corp. has utilized the expertise of the industrial organization with respect to ammonia utilization issues.

### ***Hybrid Membrane***

For the hybrid membrane technology, the membrane is envisioned to separate $CO_2$ within the pre-combustion zone of an IGCC plant. The high pressure of the gasification-based power generation cycle provides an excellent driving force for the membrane and other inherent advantages of membranes exist, i.e. non-moving parts, etc.[15] If the water-gas-shift reaction within the IGCC scheme is performed to increase the hydrogen production for the gas turbine combustor, the $CO_2$ concentration, and thus partial pressure, increases substantially and further enhances the driving force across the membrane. Additionally, if the membrane is fabricated to withstand higher temperatures (300-700°F), an additional benefit with respect to maintaining the higher thermal efficiency of the plant (as compared to cold scrubbing of $CO_2$) is obtained.[4]

One possible means of developing such membranes involves the modification of an inorganic substrate, such as a stable and permeable alumina, with organic groups to increase selectivity towards $CO_2$. The grafting of organosilanes onto the inorganic surface is a well-studied method. Attachment is accomplished when halogen atoms on the silane molecule interact with hydroxyl groups on the inorganic surface, eliminating HCl and forming a covalent attachment. As many as three such interactions can occur per silane molecule, anchoring it to the surface. Since the silane molecule can also contain nearly any organic group, this method provides an extremely flexible tool for surface modification.[21] Membranes useful in $CO_2$ abatement for IGCC have been developed using this method.

Specifically, the hybrid membranes consist of a rigid frame with an organic being the active membrane layer. $CO_2$-philic groups on the ends of the organosilanes enhance the preferential surface diffusion of the $CO_2$ across the membrane. Membranes were prepared by modifying a 2 to 5 μm layer of γ-alumina supported on the inner surface of 2.5 cm long segments of 1 cm diameter α-alumina tubes purchased from Pall Corporation. The nominal pore diameter of the active γ-alumina layer was 5 nm. The initial procedure followed that of McCarley and Way [22] in their silation study of γ-alumina with octadecyltrichlorosilane. After a glaze was applied to aid in mounting, tubes were hydroxylated by refluxing in $H_2O_2$ (Fisher, 31.1%) for 30 min. Afterward, the tubes were treated at 80°C in air to remove residual water before silation. Silation was conducted by reacting the prepared tube in a 3.6% solution of a trichlorosilane in anhydrous toluene (Aldrich, 99.8%) for 6 hours. When silation was complete, the tube was removed, rinsed, and dried at 50°C in ambient air for 24 hours.

Performance testing was conducted in a tube-within-tube continuous flow system. The membrane tubes were mounted in the system using high-temperature Teflon fittings. A flow of He, $CO_2$ or an equal mixture of the two was passed along the tube interior while a roughly equal amount of Ar sweep gas flowed in the annular section surrounding the membrane exterior. Pressure was varied from 0 to 350 kPa on each side of the membrane using a needle valve downstream. Temperature was controlled between ambient and 150$^{o}$C by a clamshell tube furnace with integrated temperature controller. Both the permeate and the retentate were analyzed using an HP 5890 gas chromatograph with twin TCD detectors.

The hybrid membrane work initially progressed through a fabrication phase followed by testing in the previously described membrane test unit.[16] Since a goal of the study was to develop an optimal procedure for the fabrication, characterization, and testing of membranes prepared by modification of tubular alumina composites, careful observation regarding procedures began from the outset. XPS was used to characterize the pretreatment techniques for the membranes. XPS has the ability to aid in determining the elemental composition of the membrane surface as well as within the first 1000 Å below it through sputter profiling. Results of these analyses led to a new technique for depositing the silane within the pores of the membrane substrate. Specifically, an optimized silation procedure was found that is capable of producing a silane monolayer over a larger proportion of the membrane surface.

The unmodified γ-alumina support, having a nominal pore diameter of 5 nm, may be assumed to display Knudsen diffusion. The assumption is confirmed by measurements which show permeance to be 1.87 X $10^{-2}$ and 7.69 X $10^{-2}$ scc/s/Torr/cm$^2$ for $CO_2$ and He, respectively. Those permeances are within the expected range for this type of diffusion. Further evidence of Knudsen diffusion comes from the observed selectivity of 4.1. Theoretical Knudsen selectivity can be calculated as the ratio of the square roots of the molecular weights of the diffusing molecules, 3.3 for He and $CO_2$. The findings are in excellent agreement with those of McCarley and Way [22] who observed permeances in the range of 3.0 X $10^{-2}$ to 1.2 X $10^{-1}$ scc/s/Torr/cm$^2$ for a variety of gases passing through the same unmodified support. The contribution of Knudsen diffusion to mass transfer across the membranes appears to diminish with the addition of the silane group. The initial He selectivity of 4.1 is reduced to 3.3 by silation with n-butyltrichlorosilane and still further to approximately 2 for larger alkyl silanes. This observation could be explained by the gradual plugging of pores with polymer-like clusters of silane molecules which would foster solution diffusion and reduce the contribution of Knudsen diffusion.

The trend in permeance is interesting because of what is not observed. If one assumes steady pore size reduction by addition of longer alkyl chain, it would be expected that permeance would decrease until total pore plugging resulted in the degree of permeance normally observed in solution diffusion. Instead reduction in permeance is observed until the carbon chain length reaches 12 and is stable thereafter. It should be noted that the modified fabrication technique, corresponding to deeper silane penetration, permits a higher permeance as compared to the original technique. McCarley and Way reported the permeance of $CO_2$ through an identical support silated with octadecyltrichlorosilane to be 5.5 X $10^{-5}$ scc/s/Torr/cm$^2$. This value is two orders of magnitude below that observed for an octadecyltrichlorosilane membrane produced by the modified synthesis procedure, but is very similar to the 3.9 X $10^{-5}$ scc/s/Torr/cm$^2$ observed for a membrane produced by silation with n-butyltrichlorosilane using the original procedure based on their work. XPS showed a greater degree of silation in the membrane produced by the modified procedure. It is suggested that regardless of chain length in membranes produced by McCarley and Way's original procedure, the majority of the silane is deposited in a thin layer around the pore openings causing more pores to be plugged and reducing permeance.

To facilitate $CO_2$ selectivity, a membrane was prepared by silation of the supports with 2-acetoxyethyltrichlorosilane (aceto) and which were thought likely to have strong molecular interaction with $CO_2$. The $CO_2$ and He permeances of the aceto membrane did not change significantly with changes in mean pressure indicating a limited contribution from the solution diffusion mechanism. Both He and $CO_2$ permeances for the aceto membrane are on the order of $10^{-3}$ scc/s/Torr/cm$^2$ at 150$^o$C. The temperature trends are of particular interest since not only does the membrane show marked increases in permeance as the temperature increase, but the selectivity for $CO_2$ initially rises in both cases before diminishing at the final temperature of 150$^o$C.

Surface facilitated diffusion, which results from the rapid adsorption and desorption of molecules on a pore surface where one molecule is significantly higher in coverage, is a more reasonable hypothesis. The presence of 2-acetoxyethyl-groups on the pore surface could facilitate adsorption of $CO_2$ at the expense of He. The rise in permeance and selectivity is likely the result of the necessary reversibility of the adsorption in such a process. At room temperature, $CO_2$ could tend to absorb irreversibly, thus blocking adsorption sites and not contributing to diffusion. As the temperature rises, residence time on the surface would decrease, and the surface facilitated mechanism could take over resulting in the observed behavior.

To summarize, a survey of available literature helped to determine that hybrid membranes can be a reasonable technique to separate $CO_2$ from various gas streams. The initial study laid the foundation for more ambitious work aimed at developing membranes capable of selective $CO_2$ removal in reducing environments, such as those found in the IGCC process. A pretreatment has been developed and this, combined with a certain silation procedure, allows pore penetration and development of a silane monolayer capable of significantly affecting membrane performance. Procedures have been developed for testing membranes produced by silation. Future testing in the membrane test system will include various combinations of gases as well as tests with membranes with different $CO_2$-selective functional groups. Additionally, a new collaborative effort with the University of Notre Dame will investigate the potential use of ionic liquid-based membranes.

### ***Physical Solvents***

Conventional processes for acid gas ($H_2S$ and $CO_2$) removal from coal-based gasification streams include a chemical/physical process using methyl-diethanolamine (MDEA), a physical solvent process using chilled methanol (Rectisol), and a physical process using mixtures of dimethylethers of polyetheleneglycol (Selexol). The MDEA process requires high thermal energy (heat) for solvent regeneration. The Rectisol process is complex, and refrigeration makes it a very expensive acid gas removal process. The Selexol process is more expensive than the MDEA process, and the chilling option could increase the process costs. However, in an IGCC application, these physical and chemical processes for acid gas removal require cooling and subsequent reheating of the stream before the gas turbine, which decreases the plant thermal efficiency and thusly increases the overall costs. Consequently, there is a need for the development of an alternative process which should be economical and absorb carbon dioxide without significant cooling of the gas streams.[23]

The objective of the physical solvent research is to investigate the potential use of chemically and physically stable compounds as physical solvents for selective $CO_2$ capture from post water-gas-shift reaction streams under elevated pressures and temperatures that are representative of gasification conditions. The first family of candidates that has been studied is perfluorinated compounds (PFCs). After a comprehensive literature review for PFCs, an experimental program was devised to obtain the equilibrium gas solubility and the hydrodynamic and mass transfer parameters (gas holdup, Sauter mean bubble diameter, and volumetric mass transfer coefficient) for $CO_2$ and $N_2$ in three different PFCs, namely perfluoro-perhydrofluorene ($C_{13}F_{22}$), perfluoro-perhydrophenanthrene ($C_{14}F_{24}$), and perfluoro-cyclohexylmethyldecalin ($C_{17}F_{30}$), known as PP10, PP11, and PP25, respectively.

The literature review [23] revealed that the PFCs have high chemical stability due to the high energy of their C-F bonds. They have high boiling points and low vapor pressures because of the strength of the C-F bond and high molecular weight. They also have no dipole and very low molecular interactions due to the repulsive tendency of fluorine atoms. These unique properties lead to high gas solubility, low vapor losses, and low forces required for expelling the gas molecules upon decreasing pressure or increasing temperature. Thus, PFCs show a high potential for selective $CO_2$ capture from post-shift fuel gas streams at elevated pressures and temperatures.

Testing of these physical solvents occurred in an experimental setup that consisted of a reactor, preheater, vacuum system, and data acquisition system. The reactor is a gas-inducing 4-liter ZipperClave reactor with two sight-windows. The reactor is equipped with four symmetrically located baffles, a cooling coil, a specially designed heating jacket, a thermowell, and a six flat-blades impeller with hollow shaft. Holes located at the upper and lower end of the shaft allow the reactor to operate in a gas-inducing or a surface-aeration mode. The transient physical gas absorption technique was employed to measure the volumetric mass transfer coefficient, and the gas solubility was determined when the thermodynamic equilibrium was reached in the reactor. The expanded liquid height method and a photographic method were used to obtain the gas holdup and the Sauter mean bubble diameter, respectively. The experiments were statistically designed for the reactor operating in a gas-inducing mode. A wide range of operating conditions was investigated: pressures (6 - 30 bar), temperatures (27 – 227ºC), mixing speeds (10 - 20 Hz), and liquid heights (0.14 - 0.22 m).

The equilibrium solubilities of $CO_2$ and $N_2$ in PP10, PP11, and PP25, expressed in mole fraction, appeared to increase with pressure at constant temperatures, where the values at infinite dilution were found to follow Henry's law. Figure 4 relates the scrubbing temperature with the constants for the three PFCs and for Selexol data that were obtained from the literature.[35] The solubilities for both gases were greater in PP25 than in the other two PFCs. Under similar operating conditions, the solubility of $CO_2$ in the three PFCs appeared to be about 4 times that of $N_2$, which was attributed to the closeness of the solubility parameter of $CO_2$ to those of the PFCs when compared with that of $N_2$. The results showed that $CO_2$ is more soluble in the Selexol solvent than in the PFCs only at low temperatures (≤ 60ºC). The Selexol process, however, is customarily operated at temperatures of about 39ºC, indicating that the Selexol solvent would not be effective at higher temperatures typifying those at the exit of the gasifier system in a warm gas cleanup application. This study revealed the thermal and chemical stability and the ability of the PFCs to selectively absorb $CO_2$ at temperatures up to 227ºC and pressures as high as 30 bar.[24]

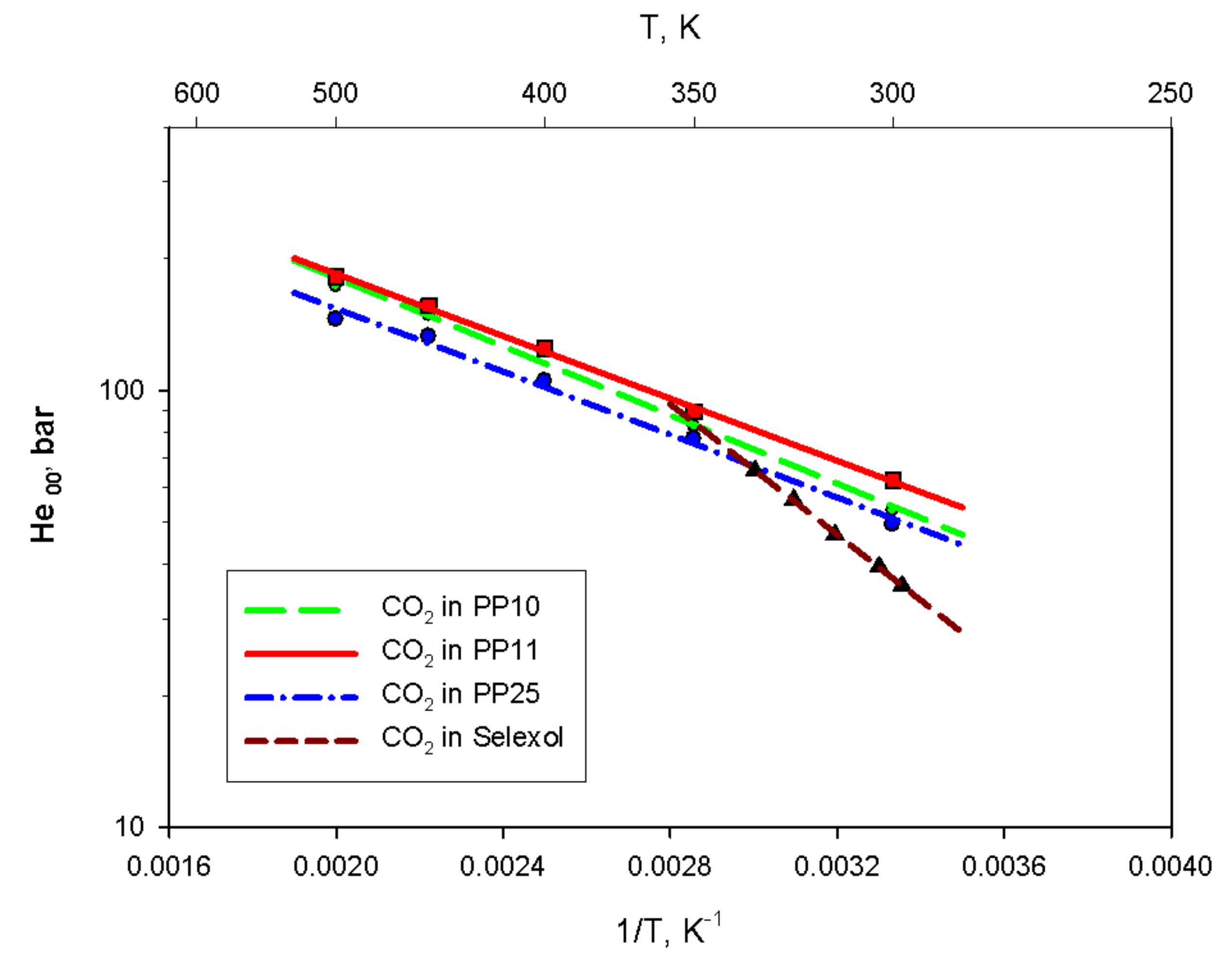

Figure 4: Solubilities of $CO_2$ in Fluorinated Solvents and Selexol

The volumetric mass transfer coefficients ($k_La$) of $CO_2$ and $N_2$ in PP10, PP11, and PP25, increased with increasing mixing speed, pressure, and temperature due to the increase of the gas-liquid interfacial area ($a$) and the liquid-side mass transfer coefficient ($k_L$). The increase of the gas-liquid interfacial area with these operating variables was attributed to the increase of the gas holdup and the decrease of the Sauter mean bubble diameters. The volumetric mass transfer coefficients of $CO_2$ and $N_2$ in the three PFCs, however, decreased with increasing liquid height above the impeller due to the decrease of the gas holdup and increase of the Sauter mean bubble diameter, which led to the decrease of the gas-liquid interfacial area. The volumetric mass transfer coefficients of $CO_2$ in the three PFCs were found to be always smaller than those of $N_2$ due to the smaller gas-liquid interfacial areas (smaller gas holdup and larger Sauter mean bubble diameter) of $CO_2$ when compared with those of $N_2$ under similar operating conditions. The volumetric mass transfer coefficients for $CO_2$ and $N_2$ in PP25 were smaller than those in PP11, and both were smaller than those in PP10, indicating that the volumetric mass transfer coefficients decrease with increasing viscosity of the PFC. Also, under the operating conditions investigated, the gas-liquid interfacial areas of $CO_2$ and $N_2$ in the three PFCs appeared to control the behavior of the volumetric mass transfer coefficients in the gas-inducing reactor.

Testing with mixtures of gases to simulate representative fuel gas mixtures is being completed. Future work will include an in-depth investigation of an ionic liquid used at elevated temperatures as a physical solvent for $CO_2$ removal.

## ***Sorbents***

As previously mentioned, solid sorbents can have applicability in either a conventional power generation scheme or in an IGCC situation. A unique approach for $CO_2$ capture employs dry scrubbing – a process that includes chemical absorption with a sorbent. A dry, regenerable sorbent process is cyclic in the sense that the sorbent can remove the carbon dioxide, be regenerated (and in this step yields a concentrated stream of $CO_2$), and thus be reused. The process can be economically advantageous over commercially available wet scrubbing technologies. Although the process can be used in flue gas separations, it can also be used to capture $CO_2$ from gasification streams at high temperatures. The surroundings of the sorbent, most notably the oxidizing or reducing gas composition and the temperature, have the most significant impact on the performance towards $CO_2$ capture. Depending on the type of sorbent and the bonding of the $CO_2$ to the sorbent, regeneration can be accomplished with a temperature swing, a pressure swing, or a combination of the two. The sorbents can be envisioned within a stationary reactor bed that is periodically switched between the absorption and regeneration modes of operation, such as those found in traditional pressure swing adsorption (PSA). Other reactor configurations, for example entrained reactors, fluidized beds, and moving beds [25], can transport the sorbent between the absorption/regeneration steps.

With respect to an IGCC process, the $CO_2$ absorption reactor could be integrated into one of several IGCC process locations. The site of integration would depend on the nominal operating parameters (i.e., temperature, etc.) required for the particular sorbent of interest. For instance, alkali metal carbonates/bicarbonates ("low temperature") are more suitable for the absorber being placed near the end of the process near the stack. The alkaline-earth oxides/carbonates and some alkali metals ("high temperature") are potentially more adaptable for use in pre-combustion removal where the absorber would be located upstream of the gas combustion turbine. The fuel/synthesis gas location represents a highly-reducing atmosphere whereas the stack gas location represents a more traditional "flue gas" location containing oxygen. These substantial differences in gas surroundings need to be considered when integrating a $CO_2$ capture process into the IGCC system. However, depending on the sorbent, thermodynamic calculations [26] indicate that the dry, regenerable process can be situated at more than one location within the IGCC process.

Some of the initial work in this area investigated calcium oxide.[27] The thermodynamic analysis of carbonation of calcium oxide indicates that the reaction has potential application for systems at relatively high temperature. Based on the calculated equilibrium constants, the forward and reverse reaction rate constants become equal at approximately $860^oC$. Hence the $CO_2$ absorption (forward) reaction appears more favorable between $750\text{-}860^oC$, while thermal regeneration (decomposition or the reverse reaction) is attainable at temperatures higher than $860^oC$ (near $1000^oC$). A CaO reagent thermogravimetric analyzer study revealed ranges of temperature suitable for absorption and regeneration reactions to occur and confirmed the thermodynamic results. The $CO_2$ absorption reaction appears most favorable between $750\text{-}850^oC$, while regeneration (decomposition or the reverse reaction) is attainable at $1000^oC$. The absorption reaction is initially very fast (perhaps 50% conversion after an hour), followed by a much slower rate, due most likely to diffusional limitations from formation of a product layer of $CaCO_3$. By raising the temperature from $850^oC$ to $1000^oC$, the sample can be rapidly regenerated within approximately fifteen minutes. Unfortunately, this work was discontinued since the sorbent's high absorption temperature in an IGCC plant scheme equates to only about 20% capture of the theoretical carbon content that could be removed at the high temperature of operation. More recent work with a sodium-based sorbent at warm gas conditions ($300\text{-}700^oF$) indicates a good $CO_2$ removal capability.

Low temperature sorbents can be used in flue gas or fuel (IGCC) gas applications. Two categories of these type sorbents are amine-enriched sorbents and zeolites. Pertaining to the former, the capture of $CO_2$ from flue gas produced from coal combustion using a MEA scrubbing system will involve a large energy penalty [28], and the absorption step is influenced by the availability of gas/liquid interaction surfaces and the concentration of the amine in the aqueous solution.[29] The regenerative step of the MEA process is, in general, energy intensive. The high energy requirement of this process is related partly to low capacity ($CO_2$ absorbed per unit mass) and high water fraction, such that a large body of liquid must be heated upon regeneration to release a small amount of gas. Energy savings can be achieved if a sorbent that has high absorption capacity at moderate temperatures and pressures can be developed. The higher the absorption capacity, the less quantity of sorbent required to handle a given gas stream, and the less sensible and latent energy is required in the regeneration step.

Novel $CO_2$ capture sorbents are being prepared by the chemical treatment of high surface materials with various amine compounds. The implanting of amine groups on the high surface area material increases the contact area between $CO_2$ and amine by several orders of magnitude. Furthermore, the mass and heat-transfer problems are reduced due to the novel concept of gas-amine-enriched solid reactions for $CO_2$ capture versus that of gas-liquid reactions. Therefore, only a small amount of sorbent is needed for capturing the same amount of $CO_2$ as compared to that of the typical MEA process. Thus, a significant improvement in the efficiency of the process is accomplished due to the increased contact area and decreased energy consumption for regenerating the absorbents.

High-surface area inorganic (mesoporous) surface materials were modified with amine groups and the $CO_2$ capture capacity of these sorbents were studied with pure $CO_2$ and simulated flue gas mixtures. In addition, exploratory work with immobilized amine-enriched sorbents for the capture of $CO_2$ are being conducted.[8-10] A variety of solid materials, including silica-based and polymeric substrates were enriched with amine and tested as sorbents for capture of $CO_2$. Tests were conducted in a laboratory-scale packed bed reactor that contained 1-2 grams of sorbent and that had simulated flue gas as a feed. Absorption occurred in the presence of moisture at temperatures of 25–30$^{o}$C and the study for $CO_2$ desorption was conducted over the temperature range of 30–120$^{o}$C. Findings indicated that this amine treatment can be successfully applied to a variety of solid substrates resulting in excellent absorptivity and regeneration. The $CO_2$ capture capacities were improved for all of the solid substrates and the amine-treated sorbents have demonstrated the ability to capture $CO_2$ from gas streams in a moist environment.

Pertaining to the other category of low temperature sorbents, zeolites can be used in either a pressure swing adsorption (PSA) or temperature swing adsorption (TSA) operational mode that are identified as viable methods to remove $CO_2$ from high pressure gas streams, such as those encountered in IGCC systems. PSA processes are based on preferential adsorption of the desired $CO_2$ gas on porous materials at a high pressure. When the pressure is decreased, the gas is desorbed from the porous sorbent and the sorbent can be reused for subsequent adsorption. Two large scale PSA processes for separation of $CO_2$ were developed by Japanese firms.[30] Molecular sieves and activated carbons have been the preferred sorbents for the process. It is also reported that higher energy penalties are associated with the utilization of molecular sieves than with the amine process.[31] However, during the last decade several new PSA process concepts have been reported in the literature to improve the performance of the process. While it is important to consider the improved process design of the PSA systems to enhance the recovery rate, it is equally important to utilize sorbents with high $CO_2$ adsorption capacity, high selectivity for $CO_2$, high diffusivity, high rates of adsorption, and high regenerability.

Recovery rates can also be enhanced if PSA systems are utilized in high pressure gas streams, since some PSA sorbents have shown superior adsorption capacity at higher pressures. According to an IEA coal research report [32], the PSA/TSA processes may be more suitable for $CO_2$ capture from gasification process. It should be possible to make the PSA/TSA technique superior to the existing $CO_2$ capture techniques by utilizing proper system designs and sorbents with high capacity.

An objective of the low-temperature sorbent study is to develop regenerable sorbents that have high selectivity, high regenerability, and high adsorption capacity for $CO_2$. These properties are critical for the success of the PSA/TSA process. Past findings [11-13] indicate that molecular sieves, natural and synthetic zeolites, and activated carbons preferentially adsorb carbon dioxide in volumetric adsorption/desorption isotherms from simulated fuel gas or flue gas mixtures. Similarly, high pressure micro reactor studies were conducted to understand the competitive adsorption of $CO_2$ from a gas mixture containing 15% $CO_2$, 82% $N_2$, and 3% $O_2$ saturated with water vapor at ambient temperature. Excellent separation of $CO_2$ from gas mixtures was observed for the sorbents mentioned above, although the presence of water vapor appears to affect the sorbent performance. Sorbent capacities were equal to or better than those obtained from $CO_2$ commercial processes. The sorbent tests conducted have also shown that the amount of $CO_2$ adsorbed on some synthetic and natural zeolites can be increased substantially by increasing the pressure from 1 atm to 20 atm. Investigation of sorbents for $CO_2$ capture is an ongoing effort.

NETL conducted a $CO_2$ capture workshop in 2003 that inaugurated the new modular carbon dioxide capture facility (MCCF). A goal for the MCCF is to make it available to others for partnering purposes where experimental testing would be performed to further advance the particular technology. An earlier NETL process developmental unit that was used in the study of dry, regenerable sorbents for flue gas desulfurization [33] was the basis in the formulation of the MCCF. Key components of that system, including the furnace and ancillary piping, were incorporated into the MCCF. Additional modifications were made to the system to facilitate evaluation of $CO_2$ capture technologies at relatively lower process temperatures than previously encountered.

In the flue gas mode, the MCCF can mimic coal-fired combustion processes that produce electricity.[34] The combustor can be fired with natural gas, coal, or a combination of the two; burning at approximately 40 pounds of pulverized coal per hour results in a flue gas (110-scfm) laden with various pollutants. The versatility of a “black-box” design permits the incorporation of a particular capture/separation technology anywhere along the flue gas path. If regeneration of the capture medium is required as part of the capture/separation process, this step can be readily integrated into the system.

The MCCF was commissioned recently and a physical adsorbent (zeolite 13X, a molecular sieve composed mainly of sodium aluminosilicate) was the first candidate to be evaluated in the MCCF. Since the adsorption temperature (approximately $100^oF$) is below the typical dewpoint of flue gas, drying equipment was designed for the MCCF. (See Figure 5.) A condensing shell-and-tube heat exchanger was placed in the flue gas line to remove water from the flue gas. A refrigeration unit, using chilled water (near $40^oF$) circulated on the shell side of the condenser, lowered the moisture level in the flue gas to about 1%. An electric gas heater was installed downstream of the chiller to reheat the flue gas back to the desired adsorption temperature (near $100^oF$). The MCCF adsorber was filled with a stationary bed of zeolite with no sorbent transport. The bed cross section measured 8 ft high by 1 ft wide, with a horizontal bed depth of 5 inches in the direction of gas flow. The bed inventory was approximately 150 lb of zeolite when the vessel was completely filled.

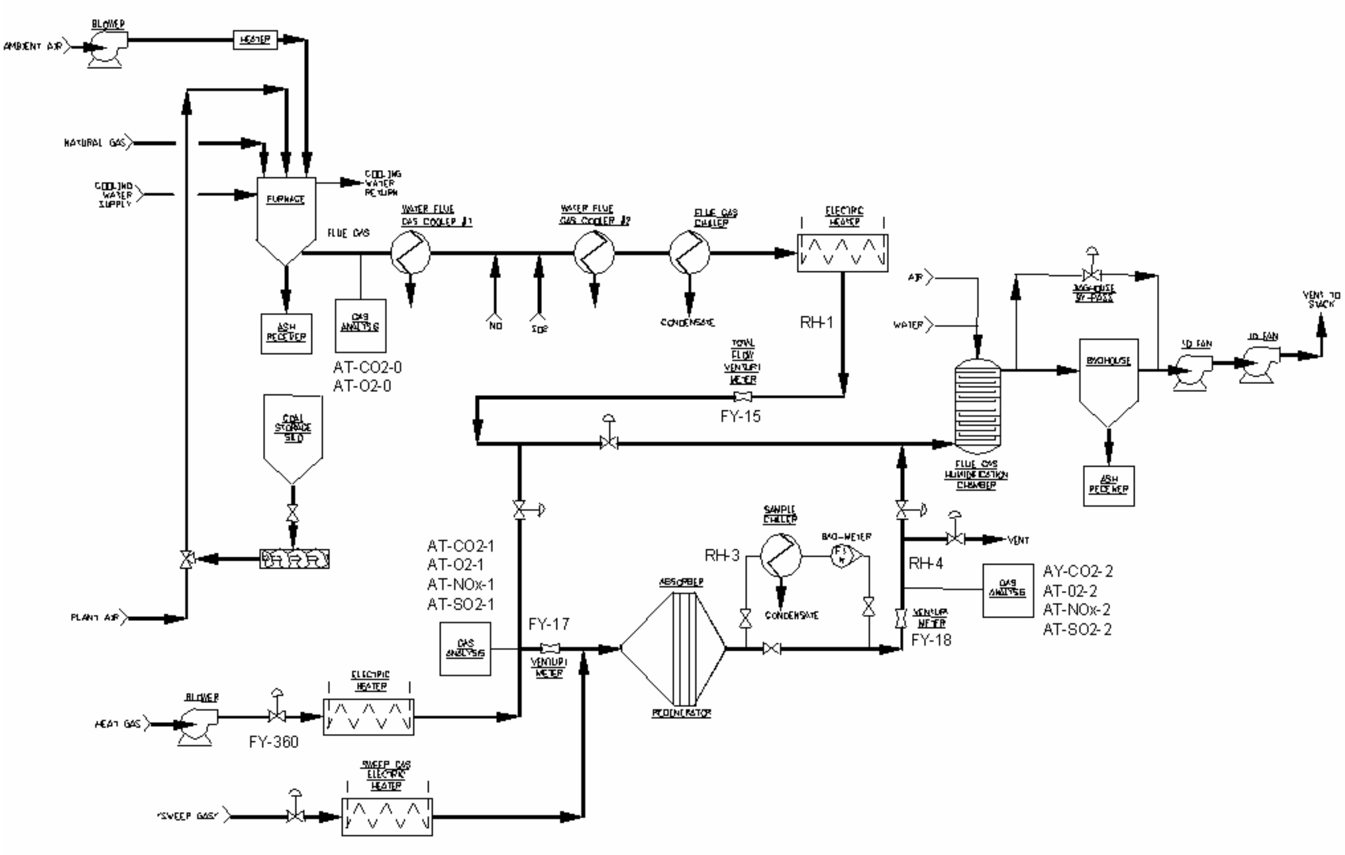

Figure 5: Modular $CO_2$ Capture Facility – Zeolite Study

Numerous process changes were added to the flue gas line upstream and downstream of the adsorber. Continuous emission monitors (CEMs) for carbon dioxide were added at both locations, and humidity probes were installed to monitor moisture levels. These instruments in conjunction with existing CEMs for $SO_2$, $NO_x$, and $O_2$ were used to characterize removal levels across the vessel. Gas venturi meters were added at both locations to monitor changes in flow rates across the adsorber. Since the same single vessel was intended for both adsorption and regeneration steps, gas isolation valves were implemented to switch the process stream between flue gas and inert sweep gas passing through the adsorber/regenerator. Two input streams for regeneration were incorporated, including a low flow sweep gas of 50 lb/hr and a high flow heat gas of 200 lb/hr. The sweep gas was used to desorb $CO_2$ from the sorbent, whereas the heat gas was used to effect significant changes in sorbent bed temperature. Both streams were electrically preheated prior to their admission into the vessel.

As mentioned before, the MCCF was used in the study of a physical adsorbent to remove $CO_2$ from flue gas. This material (zeolite 13X) was chosen based partially on its commercial use and availability as a physical adsorbent for $CO_2$. The objective was to establish baseline performance of the MCCF using a commercially available material. Results indicated favorable $CO_2$ removal and the adsorption reaction was highly exothermic. Moisture was found to negatively impact the performance of the zeolite; the material is used commercially as a desiccant. Other flue gas contaminants, including $SO_2$ and $NO_x$, were adsorbed onto the zeolite. The $CO_2$ adsorption reaction was most favored at temperatures near 38°C. Thermal regeneration can be conducted at 120°C for dry flue gas application, but much higher temperature (350°C) is required after moisture-laden flue gas is processed.

Future modifications to the MCCF will occur in the near term to extend the capabilities of the system. Elevated process temperatures can be reached and the ability to attain vacuum during regeneration will be incorporated into the system to allow pressure swing type operation. The increased versatility of the unit presents an excellent opportunity to develop a solid experimental data base with a particular $CO_2$ capture/separation technology.

## SUMMARY

Various techniques for the capture/separation of $CO_2$ from power generation point sources are being investigated within the in-house research effort at NETL. The novel technologies include a wet scrubbing technique that use an ammonia-based solvent to absorb carbon dioxide from the flue gas of a pulverized coal-fired power plant; a physical solvent process to remove $CO_2$ from fuel gas of an IGCC system at elevated temperature and pressure; hybrid membranes separating $CO_2$ from fuel gas produced by coal gasification; and solid, regenerable sorbents that can be employed in either flue gas or fuel gas applications. All these techniques have the potential for significant cost savings and plant thermal efficiency improvements as compared to conventional $CO_2$ capture techniques. Future system analyses will attempt to integrate these methods into various power generation schemes with the intent of further optimizing the process with respect to plant efficiency. The most promising technologies can be further demonstrated in NETL's Modular $CO_2$ Capture Facility.

## DISCLAIMER

Reference in this report to any specific commercial process, product, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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