

# Technology Review: Post-Combustion Partial Carbon Dioxide Capture for Fossil Fuel Power Plants

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Technical Update, December 2018

EPRI Project Manager

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#### PRODUCT DESCRIPTION

#### **Background**

Carbon capture and storage (CCS) has been studied as a means of reducing CO<sub>2</sub> emissions, but most analysis has focused on technologies that remove 90+% of CO<sub>2</sub> from post-combustion flue gas streams. Recent developments in CO<sub>2</sub> regulation that could be complied with through partial capture from coal plants and opportunities for capture that rely on the lowest cost per ton of CO<sub>2</sub> captured have raised the profile of partial CO<sub>2</sub> capture opportunities and opened the door to funding from governmental sources.

#### **Objectives**

This report aims to identify the status of current CCS technologies and pathways toward cost reduction per ton of CO<sub>2</sub> captured at partial capture rates. Further, it aims to identify the pathways to cost reduction for solvent, sorbent, membrane, and cryogenic systems capturing less than 90% of the CO<sub>2</sub> from post-combustion flue gas streams.

#### **Approach**

EPRI has collaborated with R&D funders and process developers to identify opportunities for cost reductions in CO<sub>2</sub> capture systems for coal and natural gas units, relative to 90% capture designs. Fundamental gas separation process analyses, value engineering studies, and ongoing discussions with CO<sub>2</sub> capture technology developers are key to this effort.

#### Results

This report contains the results of fundamental thermodynamic analyses to identify routes to cost reduction for CCS deployed at <90% capture rates. It also includes results and insights from interviews with 14 process and technology developers on whether their technologies would be able to realize cost savings at lower capture rates. For each technology, the modifications that would be required to optimize performance at lower capture rates are discussed.

#### Applications, Value, and Use

Stakeholders who are evaluating, developing, and deploying carbon capture systems can use this report to understand the potential for process improvement due to decreasing the CO<sub>2</sub> capture rate below 90%. Also identified are research gaps and pathways toward cost reduction that have not yet been studied due to previous lack of funding and interest in partial CO<sub>2</sub> capture technologies.

#### **Keywords**

Carbon Capture and Storage CO<sub>2</sub>, Emissions Controls Partial Capture Coal-fired Power Plants

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A TECHNOLOGY DEVELOPER SURVEY.	A′

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# **1** INTRODUCTION

Coal and natural gas are the predominant fuels for generating electricity worldwide. Not surprisingly, fossil fuel power plants are among the largest point source emitters of CO<sub>2</sub> and collectively represent one of the largest greenhouse gas emitting sectors of the global economy. Coal power plants in particular have been a focus of regulations to curb CO<sub>2</sub> emissions and of research to develop technologies to capture and sequester CO<sub>2</sub>.

Because the impact of CO<sub>2</sub> emissions is global and long-term in nature (i.e., there are no local or regional "hot spots" of health or environmental impacts), regulations on CO<sub>2</sub> emissions can be flexible and aim to minimize aggregate compliance costs. Stakeholders supportive of CO<sub>2</sub> regulations and other measures to reduce greenhouse gas emissions seek to minimize economic disruptions from sharply increasing electricity prices by working to ensure emission reduction requirements and development of lower-cost compliance technologies proceed in tandem.

Greenhouse gas regulations to date tend to employ phased compliance periods and/or emission performance standards allowing initial application of CO<sub>2</sub> capture on coal power plants at removal rates that bring net emissions to levels comparable to uncontrolled natural gas combustion turbine plants, or in some cases slightly higher (e.g., U.S. Clean Air Act, Section 111(b)). Compliance can be achieved by treating part of the flue gas stream with a capture technology that removes CO<sub>2</sub> at a high rate or by treating the full flue gas stream with a capture technology that removes CO<sub>2</sub> at a modest, or partial, capture rate.

Historically, government energy and environmental agencies, such as the U.S. Department of Energy (DOE), have funded research to develop technologies to capture CO<sub>2</sub>, and sponsored related techno-economic studies that compare capture technologies on the basis of 90% removal for coal and natural gas combined cycle (NGCC) plants, despite their difference in uncontrolled CO<sub>2</sub> emission rates. Less attention has been paid to opportunities to economically remove CO<sub>2</sub> from flue gas streams at partial capture rates. However, DOE in 2018 stated that future R&D funding opportunities for coal power plants (which may also extend to NGCC power plants) will allow technology developers to propose designs with the lowest levelized cost, regardless of the percent-removal capture rate.

EPRI is seeking to work collaboratively with R&D funders and process developers to identify opportunities for cost reductions in CO<sub>2</sub> capture systems for coal and NGCC units, relative to 90% capture designs. Foundational to this effort are fundamental gas separation process analyses, value engineering studies, and ongoing discussions with CO<sub>2</sub> capture technology developers.

#### **Coal and Natural Gas Market Trends**

In the United States and elsewhere, coal power plants remain the backbone of the electricity supply system, although the role of natural gas power plants has grown in recent years to become co-equal with coal. In response to reduced demand by electric utilities, coal production in the United States is down. Coal exports have grown, but not to a commensurate degree as demand reduction, and as a result, the coal mining industry is economically depressed. In contrast, natural

gas demand by utilities and other industrial users has risen, along with U.S. production, driven by advances in horizontal drilling and hydraulic fracturing that have boosted extraction from unconventional resources. In 2017, U.S. natural gas production averaged 73.6 billion cubic feet per day, or about 2.1 billion cubic meters per day. Relatively low and stable prices have accompanied increased natural gas supplies.

In terms of U.S. generating capacity additions and retirements, coal power plants accounted for 6.3 GW of the 11.2 GW of the generating capacity retired in 2017. For the first year in at least a decade, no new coal-fired units began commercial operation in 2017. About 4.0 GW of natural-gas-fired power plants were retired in 2017, primarily steam boiler units. About 9.3 GW of new gas-fired generating units were added, of which 8.2 GW were combined cycle units. The U.S. Energy Information Administration (EIA) expects about 21 GW of new natural gas units to come online in 2018. About half of this new capacity consists of combined-cycle units being added to the PJM Regional Transmission Organization, which spans several Mid-Atlantic and Midwestern states.<sup>2</sup>

#### CO<sub>2</sub> Capture for Fossil Fuel Power Plants

Separation of CO<sub>2</sub> from other gases via chemical and physical processes is an established technology, with decades of commercial application in various process industries. The basic approaches to post-combustion CO<sub>2</sub> capture from coal and natural gas flue gases are essentially the same, and include:

- Chemical absorption (solvents)
- Physical and chemical adsorption (sorbents)
- Selective membranes
- Cryogenic processes (anti-sublimation or frosting)

#### Chemical Absorption

Aqueous solutions of monoethanolamine (MEA) and similar solvents to remove CO<sub>2</sub> from raw natural gas, under pressure, have been used commercially for decades by natural gas processors. For over 30 years, adaptations of such amine processes have also been used to remove CO<sub>2</sub> from atmospheric-pressure flue gas from fossil-fuel boilers and petrochemical process heaters, albeit at relatively small scale, until recently. There are now two commercial, amine solvent-based, CO<sub>2</sub> capture processes at >100 MW scale at coal-fired power plants: Boundary Dam in Saskatchewan and Petra Nova in Texas. Both received government support and both earn revenue from CO<sub>2</sub>-enhanced oil recovery (EOR) in nearby oilfields.

As illustrated in the generic regenerable solvent process flow diagram shown in Figure 1-1, flue gas enters the bottom of an absorption column while the solvent, which enters the top and flows countercurrent to the rising flue gas, removes the majority of the CO<sub>2</sub> by chemical absorption. The CO<sub>2</sub>-rich solvent is pumped to a stripping column where it is heated both en route and in the stripping column to release the CO<sub>2</sub> absorbed from the flue gas, yielding a relatively high-purity

<sup>1</sup> http://www.powermag.com/future-looks-bright-for-gas-fired-generation/

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<sup>&</sup>lt;sup>2</sup> EIA. "Natural Gas and renewables make up most of the 2018 electric capacity additions." *Today in Energy,* May 7, 2018.

CO<sub>2</sub> stream for dehydration, compression, and transport. The CO<sub>2</sub>-stripped, or lean, solvent is then cooled en route back to the absorber to capture more CO<sub>2</sub>. Not shown in Figure 1-1, but commonly used, is a water spray cooler to treat the flue gas before it enters the absorber column. Such a "direct contact cooler" ensures that the heat-releasing CO<sub>2</sub> absorption reaction with the solvent doesn't raise the flue gas (and solvent) temperatures in the absorber to levels beyond the effective reaction temperature range. A direct contact cooler also removes fine particulates from the flue gas before it enters the absorption column.

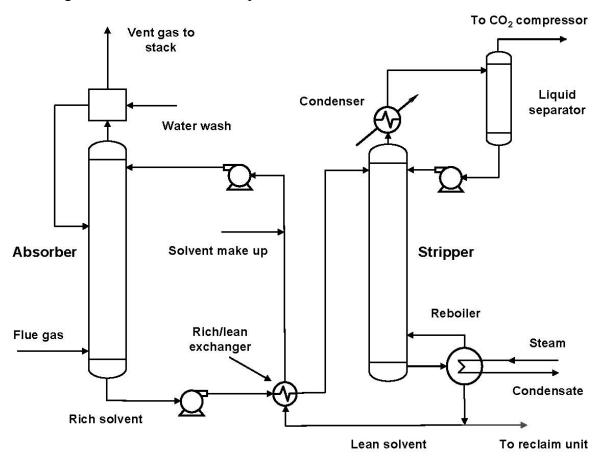


Figure 1-1
Process Flow Diagram for a CO₂ Capture Process Using a Regenerable Liquid Solvent

To provide a high degree of contact between the flue gas and the solvent, in order to promote reaction rates while not inordinately increasing flue gas pressure drop, the absorber column is filled with beds of three-dimensional packing, either randomly oriented or structured. The absorption column size, packing type, and bed sizes are engineered for each specific application, but in general are more costly for NGCC units than for PC units on the basis of \$/ton of CO2 removed due to the lower CO2 concentration. Lean solvent entering the top of the absorber column is distributed evenly over the packing by nozzles or a distributor tray. It then drips downwards, wetting the surfaces of the packing, before collecting in a pool at the bottom. The flue gas entering the bottom of the column flows upward through and around the packing. The solvent flow rate, packing shape, and packing bed size(s) are selected to achieve a desired film thickness of solvent on the packing surfaces and an overall gas-liquid contact area and residence time to promote reaction speed and removal of nearly all the CO2. Flue gas exiting the top of the

absorber column passes through a water wash and mist eliminator system to knock out solvent carry-over before venting to the atmosphere via a stack at the top of the column. The added water also serves to help maintain the solvent dilution at the required level. A very high level of recovery is required from the water wash and mist eliminator equipment to minimize solvent makeup and to minimize solvent emissions ("slip") to the atmosphere.

In a reference design using MEA, CO<sub>2</sub>-lean solvent enters the top of the absorber column at about 110°F (45°C). With the addition of heat from the exothermic CO<sub>2</sub> absorption reaction, the CO<sub>2</sub>-rich solvent leaves the bottom of the absorber at about 140°F (60°C). In some designs, mid-column extraction and return points allow for solvent cooling to maintain effective absorption. The inlet flue gas temperature is normally kept below 150°F (65°C), also to maintain effective CO<sub>2</sub> absorption. The target temperatures for other amine solvents and mixtures of amines and other solvents are generally similar.

From the bottom of the absorber column, the CO<sub>2</sub>-rich solvent is pumped through a rich-lean solvent heat exchanger on its way to the stripping column. In this exchanger, the rich solvent is heated to reduce the thermal duty of the reboiler and the lean solvent is cooled to reduce the need for supplemental cooling to bring the solvent temperature down to the target for the absorber inlet. The heated rich solvent enters the top of the stripper column (which like the absorption column operates at atmospheric pressure) where it is distributed to fall through the column as additional heat is added by solvent circulated through a steam-heated reboiler adjacent the bottom of the column. Overall, the temperature of the solvent in the stripping column is raised to about 250°F (120°C), releasing CO<sub>2</sub>. The required temperature of the reboiler steam could be met by extraction from within a PC or NGCC plant's low-pressure steam turbine, but because such extraction points are usually unavailable, it is more common to take steam from the intermediate-pressure to low-pressure turbine crossover. The stripper column size and reboiler heat duty (steam demand) are engineered for each specific application, but in general are more costly for PC units than for NGCC units on the basis of \$/kW because of the higher CO<sub>2</sub> concentration in coal flue gas.

Any solvent carried over from the stripper by the exiting CO<sub>2</sub> is recovered in a condenser and returned to the top of the stripping column (to reduce solvent makeup demand and improve CO<sub>2</sub> product purity). In PC plants, a small portion of the lean solvent may be extracted from the reboiler and fed to a reclaim unit where any degradation products, such as heat stable salts formed from the reaction of the solvent with the flue gas impurities (SO<sub>2</sub>, NO<sub>2</sub>, etc.), are precipitated out following reaction with caustic soda.<sup>3</sup> In NGCC plants, solvent reclaim is less of a concern because sulfur levels in natural gas are typically low and standard NO<sub>x</sub> controls—dry low-NO<sub>x</sub> combustors and selective catalytic reduction—should avoid high levels of NO<sub>2</sub>.

#### Physical and Chemical Adsorption

As shown in Figure 1-2a, adsorption-based CO<sub>2</sub> capture relies on weak Van der Waals forces for physical adsorption ("physisorption") processes or stronger covalent bonding for chemical adsorption ("chemisorption") processes. In most adsorption processes, flue gas contacts the sorbent material in a column or other structure containing a regenerable sorbent in packed beds or fluidized beds. Regardless of the reactor configuration, the sorbent typically alternates

<sup>&</sup>lt;sup>3</sup> Design Considerations for CO<sub>2</sub> Capture: Version 1. EPRI, Palo Alto, CA: 2007. 1014919.

between being placed in contact with flue gas, where it selectively adsorbs CO<sub>2</sub>, and being isolated from flue gas for regeneration by lowering its pressure and/or increasing its temperature to release adsorbed CO<sub>2</sub>.

In a process employing a packed bed configuration (see Figure 1-2b), the sorbent is stationary, and two or more reaction vessels are used. During the active reaction phase, flue gas flows through the void spaces between the sorbent particles in the packed bed(s), and the CO<sub>2</sub> adsorbs onto the particle surfaces. During regeneration phase, flue gas is diverted to a second vessel with packed sorbent, which continues the active reaction of adsorbing CO<sub>2</sub> from flue gas, while regeneration of the sorbent bed(s) in the first vessel occurs. By using valves or dampers to alternate the flue gas flow between two reaction vessels, which undergo adsorption and regeneration in a cycle, CO<sub>2</sub> can be continually removed from the flue gas.

In a process employing fluidized beds (see Figure 1-2c), flue gas flows upward through a reaction column at velocities such that the sorbent particles are suspended in the gas flow. The sorbent is circulated between a reaction column, where it contacts flue gas, and a regeneration column where the sorbent is heated and CO<sub>2</sub> is released.

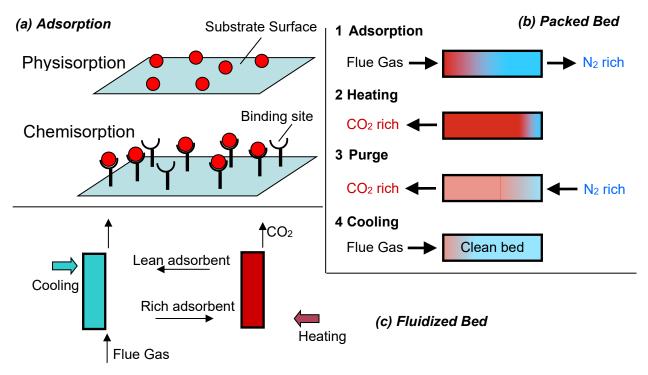


Figure 1-2
Physical and Chemical Adsorption Processes for Flue Gas CO<sub>2</sub> Capture

A potential advantage of adsorption processes is that their regeneration energy requirements are generally lower than those for solvent processes because the heat capacity of the solid sorbent is lower. Potential disadvantages for adsorbents include sorbent particle attrition (and hence the need for makeup, which adds to operating cost), handling of large volumes of solids, maintaining free and evenly distributed flue gas flow pathways, and thermal management of large reaction and regeneration vessels.

Adsorption-based CO<sub>2</sub> capture processes are not commercial at utility scale, but some processes have, or are, being tested at the National Carbon Capture Center (0.1 to 1 MWe scale). A wide variety of sorbent materials are being investigated, ranging from relatively low-cost bulk chemicals to metal organic frameworks and other custom-engineered materials, in some cases impregnated with amines.

#### Membrane Separation

Membranes separate CO<sub>2</sub> from flue gas by a process of selective permeation, as shown in Figure 1-3. Membrane separation processes are used commercially in numerous industrial applications; perhaps most commonly in reverse osmosis purification of water, but also in the separation of CO<sub>2</sub> and other trace gases from natural gas. The membranes typically used in gas separation processes are thin, semi-permeable barriers that selectively allow passage of some molecules (in response to a partial pressure differential driving force) but not others. Commercial membranes generally operate at elevated pressures on the feed (retentate) side; significant challenges lie in developing membranes and processes that are energy efficient and cost-effective for separating CO<sub>2</sub> at low partial pressure from atmospheric-pressure flue gases.

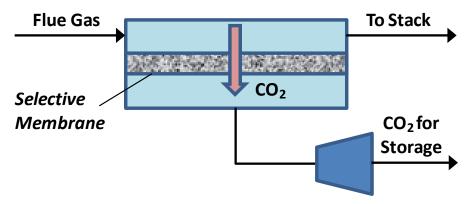


Figure 1-3
Membrane-Based Post-Combustion CO<sub>2</sub> Capture

The development of membranes to separate CO<sub>2</sub> from flue gas is being pursued for two basic types of membranes:

- Molecular sieve membranes feature nano-sized porous holes to allow a target molecule (in this case, CO<sub>2</sub>) to pass through (permeate), given a partial pressure drop between the retentate side of the membrane and the permeate side, while preventing passage of other molecules (primarily N<sub>2</sub>). Many membranes are constructed of two layers, an active layer and a supporting layer, with the active layer performing the actual separation. The supporting layer acts as the foundation and substrate for the active layer. They can be made of inorganic ceramics or organic polymers.
- Solution-diffusion membranes simply solubilize CO<sub>2</sub> in the bulk membrane and CO<sub>2</sub> then diffuses across the membrane. Solution-diffusion membranes can also be made of two or more layers, with a thin CO<sub>2</sub>-selective membrane layer on top of a non-selective thick substrate.

The two factors that define the performance of any membrane are the *selectivity* and the *permeability*. They determine how much material can be filtered, at what speed, at what purity,

and at what pressure differential. Research is focused on increasing the permeability and selectivity, especially for CO<sub>2</sub> versus N<sub>2</sub>. Depending on the selectivity of the membrane, multiple membrane stages may be needed to obtain sufficiently high CO<sub>2</sub> purity. Research has also focused on developing membranes that will perform robustly and have long-term durability against the impurities in coal flue gas.

Like sorbents, membranes also potentially offer CO<sub>2</sub> capture with lower energy requirements than chemical solvent processes. Further, membranes do not require any thermal energy from the base power generating unit (i.e., no extraction from the steam cycle), so gross power production is not reduced and there is no risk of limiting unit turndown or imposing operational impacts on the low-pressure steam turbine, as with thermally driven absorption or adsorption processes. Membranes may also be attractive for partial capture or in a hybrid configuration with another post-combustion CO<sub>2</sub> capture technology.

Challenges for membranes include potential fouling of surfaces from particulate matter and the ability to integrate large-volume processes with compressors/blowers and vacuum pumps into a power plant. Membrane CO<sub>2</sub> capture processes are not commercial at utility scale, but some processes have been or are scheduled to be tested at the National Carbon Capture Center and Technology Centre Mongstad (1+ MWe scale). One is an early phases of project development for testing at the Wyoming Integrated Test Center (10+ MWe scale). Techno-economic studies of membrane CO<sub>2</sub> capture processes have been conducted at utility scale.

#### Cryogenic Processes

CO<sub>2</sub> can be separated from other gases by cooling and condensation. Cryogenic separation is currently used commercially for purification of CO<sub>2</sub> streams that already have a high CO<sub>2</sub> concentration (typically >90%). Much of the R&D to date on cryogenic CO<sub>2</sub> separation has been for oxy-combustion power systems, or CO<sub>2</sub> purification processes which involve higher CO<sub>2</sub> concentrations and pressures at the separation process inlet. CO<sub>2</sub> phase change below the triple point of 75 psia (5.1 bara) results in a solid CO<sub>2</sub> product that causes blockages and difficulties in traditional heat exchange equipment. Above the triple point, cryogenic CO<sub>2</sub> separation has the advantage that it enables direct production of liquid CO<sub>2</sub>, which can then be pumped to transport pressures.

Cryogenic CO<sub>2</sub> separations from flue gas have been proposed and developed, including ambient pressure anti-sublimation ("frosting") of CO<sub>2</sub> with carefully controlled thermal management. One disadvantage is that some flue gas constituents, such as water, must be removed before the gas stream is cooled, to avoid blockages due to solid ice formation. Advantages inherent to cryogenic designs include the capture in a dense phase which minimizes the compression energy requirement and the fact that the process does not depend on a chemical reaction with associated issues of chemical handling, corrosion, and managing reaction kinetics.

#### **Exhaust Gas Recirculation**

Exhaust gas recirculation (EGR) or selective exhaust gas recirculation (S-EGR) has been explored as an approach to facilitate faster or more complete CO<sub>2</sub> removal by increasing the concentration of CO<sub>2</sub> in flue gas entering an absorption or adsorption column or a membrane. EGR and S-EGR also decrease the overall volume of flue gas to be treated. It has been determined by some process developers as essential for attaining economical CO<sub>2</sub> capture from

NGCC units because of the lower CO<sub>2</sub> concentration in NGCC flue gas. Membrane process developers have also proposed its use in CO<sub>2</sub> capture systems for PC units. Elimination of EGR is one possible process simplification for partial CO<sub>2</sub> capture designs, but it is unclear how the cost savings versus performance reduction tradeoffs would compare with other approaches that retain EGR and simplify the CO<sub>2</sub> capture process in other ways.

# **2**COST REDUCTION OPPORTUNITIES: FUNDAMENTAL ENGINEERING ANALYSES

This chapter describes EPRI analyses of the impact of partial capture on CCS system performance and cost.

Costs for implementing carbon capture and storage can be expressed in terms of capital cost (CAPEX) and operating cost (OPEX). Capital costs include the costs of construction and commissioning and are generally governed by the size and complexity of the system. Operating costs include the costs associated with running the capture system and are generally governed by the energy and chemical consumption of a process.

Comparing the costs of 90% capture to partial capture is highly dependent on the technology and process used to perform the separation. Generating meaningful absolute cost numbers for any CCS technology entails analysis of the capture technology, host site, and capital-versus-operating cost tradeoff for that particular technology. However, it is possible to describe relative costs by examining the changes in required equipment, process configuration, and process conditions based on thermodynamic and engineering principles.

The overriding benefit of partial capture of less than 90% of the CO<sub>2</sub> from the entire flue gas stream is that the system does not have expend energy to remove the CO<sub>2</sub> from lower concentrations. This means that the average CO<sub>2</sub> partial pressure that drives the CO<sub>2</sub> from the flue gas is higher, which can enable either a lower energy demand for capture and regeneration or a system with higher mass transfer resistance. It also may enable certain technologies or processes that struggle to remove low concentrations of CO<sub>2</sub> but that may have low capture costs. Dropping the requirement to achieve 90% capture may also eliminate the need for a system component such as a recycle loop that is only necessary to increase the capture rate.

Although the aforementioned advantages may exist for certain processes, partial capture has the downside of not capturing the same amount of CO<sub>2</sub>. Less CO<sub>2</sub> captured means that the emissions from the plant will be higher and the cost of the system will not be amortized over as large a quantity of CO<sub>2</sub>. For systems that require flue gas treatment prior to capture, such as for sulfur removal or cooling, there will be no reduction in the cost of these processes to offset the reduction in the CO<sub>2</sub> captured, which makes the cost per ton abated higher than for the 90% capture case. Similarly, any mass transfer capture device flow rate will need to be scaled based on the total flue gas flow and not on the amount of CO<sub>2</sub> captured. On the back end, there will be no change to the CO<sub>2</sub> compression and transportation costs per ton because those systems only see the CO<sub>2</sub> once it has been concentrated. Thus, for most capture processes, partial capture results in a lower total capital cost but may or may not result in a lower specific capture cost (\$/t-CO<sub>2</sub> captured) depending on whether the process can be simplified in the partial capture case and on the capital-versus-operating cost tradeoff for that technology applied to a specific host site.

#### **Energetic Impact of Partial Capture**

The energy required for CCS is provided in the form of thermal energy to regenerate a solvent or sorbent, compression energy to drive gas through a membrane or compress the product, and compression or refrigeration energy to run a cryogenic process. Regardless of the form of energetic input, thermodynamics limit the minimum amount of energy that is required to perform the separation.

To separate a mixture such as flue gas into its pure components, a minimum amount of work must is required.<sup>4</sup> This value can be calculated by noting that the minimum work is equal to the change in Gibbs function (free energy) of a reversible process.

$$E_{\min} = \Delta G \equiv \Delta H - T \Delta S \tag{1}$$

where  $E_{min}$  is the minimum energy (work) required,  $\Delta G$  is the change in Gibbs function,  $\Delta H$  is the change in enthalpy, T is absolute temperature, and  $\Delta S$  is the change in entropy. Eq. (1) implies that the *minimum* energy needed for separation under isothermal conditions is equal to that of the reverse process (i.e., isothermally mixing pure components). Because no reaction takes place,  $\Delta H$  is zero, and the minimum work for separation is only the change in entropy of mixing.

As a reasonable approximation, we may assume the flue gas is an ideal binary mixture of CO<sub>2</sub> and "inerts," which gives:

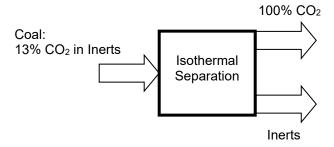
$$E_{\min} = \Delta G_{mix} = -T\Delta S_{mix} = -RT \sum_{i} x_{i} \ln x_{i} = -RT \left[ x_{CO2} \ln x_{CO2} + (1 - x_{CO2}) \ln(1 - x_{CO2}) \right]$$
 (2)

where  $\Delta G_{mix}$  is the change in the Gibbs function due to mixing (per mole of mixture), R is the universal gas constant, T is the absolute temperature,  $\Delta S_{mix}$  is the change in entropy due to mixing,  $x_i$  is the mole fraction of component i, and  $x_{CO2}$  is the mole fraction of CO<sub>2</sub>. Note that Eq. (2) reflects the entropy change per mole mixture when the mixture is separated completely into pure components. Figure 2-1(a) shows a schematic. Also note that  $\Delta G_{mix}/x_{CO2}$  is the change in Gibbs function per mole CO<sub>2</sub>.

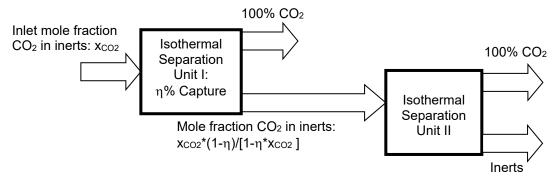
Note that in practical processes, the separated CO<sub>2</sub> stream is never 100% pure. It often contains some amount of other flue gas components—e.g., water, oxygen, nitrogen, etc.—that transport with the CO<sub>2</sub> from the flue gas. These other components must often be further separated by methods such as compression to achieve a stream that is close to 100% pure CO<sub>2</sub> for transportation and storage. Because the final product is close to 100% CO<sub>2</sub>, the energy associated with this additional separation is obviously incorporated into the above calculation. Note that if the separation process does not yield near 100% CO<sub>2</sub>, then this additional work *must* be done in, for example, the compression train if the final product is to be close to 100% pure CO<sub>2</sub>.

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<sup>&</sup>lt;sup>4</sup> "Post-Combustion CO<sub>2</sub> Capture Technology Development." EPRI Report 1016995 (2008).



(a) Isothermal Separation into Pure Components. For separation of a mixture into pure components, the entropy change is given by Eq. (2).



(b) Isothermal Separation into Mixtures. For the partial separation of a mixture in Separation Unit I, the entropy change is equal to that of the overall separation into pure components (Separation Units I+II) less that of Separation Unit II, as shown in Eq. (3).

**Figure 2-1. Isothermal Separation.** The minimum work required to affect an isothermal separation is equal to the change in entropy of mixing.

However, separating flue gas into pure components is not necessarily required for CO<sub>2</sub> capture. For example, we may require only fractional CO<sub>2</sub> capture, as shown in the "Isothermal Separation Unit I" of Figure 2-1(b).

To calculate the entropy of mixing in Unit I, which is the CO<sub>2</sub> capture process of interest, we calculate the entropy of mixing of the overall separation of Units I and II into pure components, and subtract the entropy of mixing in Unit II. If  $x_{CO2}$  is the inlet mole fraction of CO<sub>2</sub> in flue gas, and  $\eta$  is the fraction of CO<sub>2</sub> captured in the first separation, then  $(1-\eta)x_{CO2}$  /[1- $\eta x_{CO2}$ ] is the mole fraction of CO<sub>2</sub> fed into Unit II. Eq (2) therefore implies that the entropy change in Unit I (per mole CO<sub>2</sub> captured) is given by:

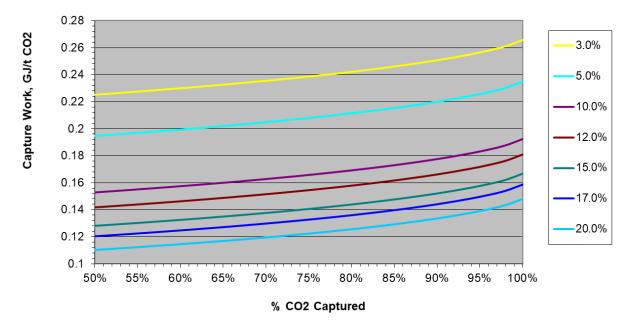
$$E_{\min} = \Delta G_{\min}^{I} = \Delta G_{\min}^{I+II} - \Delta G_{\min}^{II} = -RT \left( \Delta S_{\min}^{I+II} - \Delta S_{\min}^{II} \right)$$

$$= -\frac{RT}{\eta x_{CO2}} \left[ x_{CO2} \ln x_{CO2} - (1 - \eta) x_{CO2} \ln((1 - \eta) x_{CO2}) + (1 - \eta x_{CO2}) \ln(1 - \eta x_{CO2}) \right]$$
(3)

Equation 3 can be used to calculate the minimum work of CO<sub>2</sub> capture, both for coal and NGCC at any capture rate.

Figure 2-2 shows the results of applying Equation 3 over a representative range of inlet flue gas concentrations and capture rates. Note that the minimum energy requirement decreases per ton of CO<sub>2</sub> captured for all cases as the capture rate decreases. The magnitude of this decrease is

dependent on the inlet CO<sub>2</sub> concentration. For systems with low inlet CO<sub>2</sub> concentration, the energy savings per ton of CO<sub>2</sub> is greater than for systems with high inlet CO<sub>2</sub> concentrations. However, the relative energy savings show the reverse trend. The percent decrease in work required peaks at low inlet concentrations of CO<sub>2</sub> and diminishes as the inlet CO<sub>2</sub> concentration rises due to the higher absolute energy penalty of capture at low inlet CO<sub>2</sub> concentrations.



**Figure 2-2 Effect of CO<sub>2</sub> Capture Percentage on Minimum Capture Work**. The legend at right shows the inlet CO<sub>2</sub> concentration. Dropping the CO<sub>2</sub> capture percentage from 90% to 60% yields a decrease in minimum work of between 8% and 13% with lower CO<sub>2</sub> inlet concentrations showing a smaller relative decrease.

#### **Cost Reduction Opportunities for Solvents**

Carbon capture by solvents is the most commercially developed and best studied method of capture. A process diagram of a typical regenerable solvent CO<sub>2</sub> capture system is shown in Figure 1-1.

The capture rate in solvent systems is governed primarily by the absorber conditions, solvent thermodynamics, mass transfer, and degree of stripping. The first three variables pertain to absorber operation, where the flue gas comes into contact with the solvent and the CO<sub>2</sub> is removed. The degree of stripping describes how much CO<sub>2</sub> remains on the solvent after the regeneration step before it is introduced at the top of the absorber column.

When only partial CO<sub>2</sub> capture is required, the height and gas residence time in the absorber can be decreased. The result of this change would be decreased total capital cost due to building a smaller unit and less pressure drop for the gas in the absorber. Although the solvent rich loading is generally determined based on the CO<sub>2</sub> inlet concentration in the flue gas, the solvent temperature, and the vapor-liquid equilibrium, the lean loading is optimized based on rich-lean heat exchanger ("cross exchanger") and regenerator operation. Because of that optimization, the lean loading is normally determined independent of the outlet concentration of CO<sub>2</sub> and the solvent loadings are unlikely to change between 90% capture and partial capture cases using the

same solvent.<sup>5</sup> For any system handling the solvent downstream of the absorber (cross exchangers, stripper, compressor), there would be no change in OPEX per mass of CO<sub>2</sub> captured while the CAPEX would be increased due to scaling effects for processing smaller quantities of CO<sub>2</sub>. All other systems in the flue gas pathway, such as flue gas cooling, additional sulfur scrubbing, water wash, and particulate control would still need to be designed on the basis of the volume of flue gas processed, thus increasing the CAPEX and OPEX per mass of CO<sub>2</sub> captured.

Another way to take advantage of the potential for higher CO<sub>2</sub> driving force is to use solvents that have good thermodynamic properties but slow mass transfer. Systems with slow kinetics have been studied, including how to promote and accelerate reactions through the use of catalysts and enzymes such as carbonic anhydrase. Although these systems are limited by the difficulty in capturing 90+% of the CO<sub>2</sub> in the gas stream, they may be enabled when only partial capture is required. This could also help pave the way for ionic liquids and non-aqueous solvents that have high viscosities that limit the mass transfer into the solvent.

Solvent systems are designed to take advantage of a solvent's strong affinity for CO<sub>2</sub> at low temperatures and weaker affinity at high temperatures. This temperature dependence is described by a variation of the Van't Hoff equation:

$$P_{CO2}^* \propto e^{\Delta H/RT}$$
 at constant solvent loading (4)

Where  $P^*_{CO2}$  is the equilibrium partial pressure of CO<sub>2</sub> based on the solvent conditions,  $\Delta H$  is the heat of absorption, R is the gas constant, and T the temperature of absorption for a system in equilibrium and constant solvent loading. For an exothermic process (i.e., where  $\Delta H$  is negative) the pressure of CO<sub>2</sub> increases rapidly with an increase in temperature at constant loading. Solvent systems are designed such that the loading of the solvent at the exit from the stripper must be low enough to allow absorption from the CO<sub>2</sub>-lean flue gas at the exit of the absorber. In order to accomplish this, the ratio of partial pressure of CO<sub>2</sub> in the stripper bottoms and the partial pressure of CO<sub>2</sub> at the top of the absorber is limited to:

$$\frac{P_{CO2stripper,bottom}}{P_{CO2absorber,top}} < \frac{P_{CO2stripper,bottom}^*}{P_{CO2absorber,top}^*} = e^{\frac{\Delta H}{R} \left(1/T_{absorber,top} - 1/T_{strpper,bottom}\right)}$$
(5)

For partial capture cases, the CO<sub>2</sub> partial pressure at the top of the absorber is significantly higher than for the 90% capture case. This allows either a lower temperature ratio between the absorption and stripping steps or a solvent that has a lower heat of absorption. A lower temperature ratio means less heating and cooling of the solvent, yielding lower CAPEX from smaller required heat exchanger surfaces. It also allows a lower regeneration temperature, which decreases the energetic impact of steam extraction but also decreases the regeneration pressure of CO<sub>2</sub> in the stripper, increasing the compression work required. The lower heat of absorption would equate to a solvent with less affinity for CO<sub>2</sub>, which decreases the thermal energy required to desorb the CO<sub>2</sub> from the solvent, but may not ultimately decrease the energy penalty due to lower stripper pressure or lower cyclic capacity. However, it is unlikely that any partial capture

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<sup>&</sup>lt;sup>5</sup> Neeux, T et al. "A Rigorous Optimization Method of Operating Parameters for Amine based CO<sub>2</sub> Capture Processes". *Energy Procedia*, 2013

case for post-combustion CO<sub>2</sub> capture would allow a low enough heat of absorption to enter the physical solvent regime at ambient conditions and so would likely result in modifications of solvent blends to tune them to specific adsorption and regeneration conditions.

#### **Cost Reduction Opportunities for Sorbents**

Capture via solid sorbents is analogous to solvent technologies in that a combination of thermal and compression energy is required for the cyclic loading and regeneration of a carbon capturing medium. However, there are several unique aspects to solid sorbent systems that differ from the solvent analysis and will be discussed in this section.

Solid sorbents can be used for CO<sub>2</sub> capture in multiple configurations but are generally divided into fixed bed and moving bed configurations. In fixed bed configurations the flue gas flows through a bed of solid particles until the bed is nearly saturated with CO<sub>2</sub>, at which point that bed is regenerated through thermal, vacuum, or steam regeneration and the flue gas is diverted to a second newly-regenerated bed. In moving bed systems, the sorbent is transported between adsorption and regeneration conditions and behaves more like a counter-current solvent configuration.

Solid sorbent systems, like all separation processes, generally suffer from a tradeoff between purity and recovery at a given energy consumption. If the sorbent is allowed to become completely saturated, there is likely to be some CO<sub>2</sub> that escapes the system and is not captured. Conversely, if the sorbent is not completely saturated, the amount of CO<sub>2</sub> captured will decrease per cycle and more co-constituents will be captured along with the CO<sub>2</sub>, which increases the energy penalty and decreases the product purity. This can be mitigated by arranging beds in different configurations with flue gas flow paths routed through multiple beds in series (simulated moving bed) or with multi-step processes with complex flow patterns, as is common in vacuum swing adsorption systems. These complex processes tend to introduce additional cost in the form of piping, blowers, and other equipment; larger dead volumes; longer cycle times; and higher gas pressure drop through the system. By decreasing the required amount of CO<sub>2</sub> captured, some of these system complexities can be eliminated, especially for fixed bed systems by allowing full saturation of the bed prior to regeneration.

Moving bed solid sorbent systems often struggle to capture 90% of the CO<sub>2</sub> due to a range of issues. Smaller particles may increase the mass transfer and hence rate, but require slower gas velocities (and thus larger equipment), are more difficult to handle, and experience higher carryover rates. Counter-current contacting is required for high removal rates, but often moving bed solid sorbent systems rely on staged cross-current fluidized beds to approximate a counter-current contactor. Additional stages would increase the capture rate but also add complexity, cost, and pressure drop, while decreasing operational flexibility. Partial capture systems could enable simpler fluidized bed systems that can have lower energy penalty and improved flexibility compared to traditional solid sorbent systems.

Another benefit of partial capture operation is the use of sorbents that do not capture CO<sub>2</sub> effectively at low CO<sub>2</sub> concentrations. Solid sorbent isotherms can either be steeper at low CO<sub>2</sub> concentrations and are concave down – such as the Langmuir isotherm – or steeper at higher CO<sub>2</sub> concentrations and are concave up at relevant CO<sub>2</sub> concentrations. For sorbents that have higher CO<sub>2</sub> uptake rates at low concentrations of CO<sub>2</sub>, the CO<sub>2</sub> concentration profile in sorbent beds is self-sharpening as the low-concentration front moves more slowly than the high-concentration

front. The opposite is true in sorbents with isotherms that experience steeper uptake at higher CO<sub>2</sub> concentrations, where the CO<sub>2</sub> concentration profile spreads out as the low concentration front moves more quickly than the higher concentration front. These materials are generally not good choices for 90% CO<sub>2</sub> capture; however, they may represent some of the best materials in terms of low energy penalty of capture. An example of sorbents that are concave up at low concentrations but have impressive energetic performance are the amine-appended metal organic frameworks (MOFs) developed by the University of California at Berkeley<sup>6</sup> and commercialized by Mosaic Materials.

#### **Cost Reduction Opportunities for Membranes**

Membrane separation for CO<sub>2</sub> capture occurs by CO<sub>2</sub> partial pressures in the flue gas driving transport through a selective membrane to a lower pressure region. The membrane configuration that is the best studied for this application includes a cross-current capture module that is able to capture a portion of the CO<sub>2</sub> at low pressure and a sweep module that captures the remaining CO<sub>2</sub> through counter-current sweep by the incoming secondary combustion air as shown in Figure 3-2. All of the CO<sub>2</sub> removal is not performed by the capture module because the lowest partial pressure of CO<sub>2</sub> achievable by a cross-current membrane is the CO<sub>2</sub> partial pressure on the permeate side of the membrane. Increasing the capture rate means lowering the permeate pressure and increasing the compression energy required to compress the CO<sub>2</sub> to pipeline pressure. High capture rates also would necessitate lower driving forces across the membrane, which results in larger membrane area and higher CAPEX.

As a result, membrane systems would likely show the greatest benefit from lessening CO<sub>2</sub> removal rates below 90% capture. This would be in the form of eliminating the CO<sub>2</sub> sweep module and its associated pressure drop and boiler derate, as well as reducing the overall membrane area or increasing the capture pressure.

#### **Cost Reduction Opportunities for Cryogenic Systems**

Traditional refrigeration cryogenic systems cool the entire flue gas stream until CO<sub>2</sub> condensation or solidification separates the dense phase from the gas phase. Careful thermal integration is then used to reheat the entire flue gas stream while cooling the incoming flue gas stream. Refrigeration supplies the cooling energy necessary for overcoming the heat of phase change and any thermal losses. The coldest temperature the flue gas experiences dictates the level of CO<sub>2</sub> removal. For refrigeration-based cryogenic systems, the majority of the cost is associated with the thermal management and refrigeration loops. The slight extra cooling required to cool to 90% capture rate or even higher does not significantly increase the total cost of the system and generally decreases the cost on a per ton of CO<sub>2</sub> captured basis.

One proposed system for solid CO<sub>2</sub> capture through cooling by supersonic expansion, however, would see a very significant performance improvement under partial capture conditions. While the Orbital ATK/ACENT labs Inertial CO<sub>2</sub> Extraction System (ICES) system is no longer under

<sup>&</sup>lt;sup>6</sup> McDonald, T. et al. "Capture of Carbon Dioxide from Air and Flue Gas in the Alkylamine-Appended Metal-Organic Framework mmen-Mg<sub>2</sub>(dobpdc)" JACS, 2012.

active development due to difficulties in achieving 90% capture from coal-derived flue gas, it has the potential for improved results at partial capture conditions.

EPRI analysis of this process through NETL award DE-FE0013122 showed several problematic aspects of the original embodiment of this process. The entails expanding flue gas in a supersonic converging-diverging nozzle to hypersonic speeds. At these conditions, the temperature and pressure drop sufficiently to cause CO<sub>2</sub> to form a solid, which is separated inertially. The remaining gas is then slowed down in a diffuser to recover pressure to allow atmospheric discharge.

The main issues with this system were found to be the heat addition at low temperature due to phase change, which inhibits the gas cooling and solids formation and necessitates even faster flow, and the momentum extraction in the form of solids removal from the gas stream. This momentum extraction yields lower pressure recovery in the diffuser for the remaining gas and excess heat from kinetic energy dissipation in the recovered solids. The low pressure recovery means a higher inlet pressure must be supplied and the kinetic heating causes CO<sub>2</sub> vaporization reducing the amount of CO<sub>2</sub> captured. In order to achieve 90% capture, a recycle of the vaporized CO<sub>2</sub> in its carrier gas must be added, which further increases the required capture rate thus increasing the capture velocity and exacerbating the heating and momentum issues. These issues also make the ICES system the rare capture technology that works better at lower inlet CO<sub>2</sub> concentrations.

Lowering the capture rate to about 75% would allow both lower capture velocities, and hence less pressure recovery losses due to momentum removal and heat addition, and the elimination of the CO<sub>2</sub> recycle loop. Together, these improvements would greatly reduce the inlet pressure requirement, which is by far the largest energy consumption of the process. Although the process still has technical issues that need to be addressed, such as particle nucleation, growth, and migration, the thermodynamic energy of capture, and hence OPEX, could be improved and the CAPEX lowered, potentially more so than for traditional capture technologies such as solvents.

<sup>7</sup> A.H. Berger and A.S. Bhown. Thermodynamic Analysis of Post-Combustion Inertial CO<sub>2</sub> Extraction System, Energy Procedia 114 7-16, 2017

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## 3

## COST REDUCTION OPPORTUNITIES: TECHNOLOGY DEVELOPER INTERVIEWS

To understand technology developer insights and activities to optimize post-combustion CO<sub>2</sub> capture processes economically, irrespective of capture rate, telephone interviews were conducted with a selection of technology developers using the questionnaire in Appendix A as a guide. Many, but not all, of the developers have received DOE funding using a 90% CO<sub>2</sub> capture design criterion.

Technology developers interviewed included:

#### **Solvent Processes**

- Shell Cansolv
- HTC Purenergy
- Ion Engineering
- Carbon Clean Solutions
- Gas Technology Institute
- University of Kentucky / Center for Applied Energy Research
- University of Texas—Austin

#### **Sorbent Processes**

- TDA Research
- Inventys

#### **Membrane Processes**

- Membrane Technology Research
- Gas Technology Institute
- Air Liquide

#### **Cryogenic Processes**

- Sustainable Energy Solutions
- Orbital ATK / Aerospace and Clean Energy Technologies

Several developers are pursuing multiple CO<sub>2</sub> capture approaches; early-stage developments are generally not summarized below. Abbreviated correspondence was also conducted with other

developers, including SRI International, who has yet to evaluate the performance of its mixed salt absorption process at CO<sub>2</sub> capture rates other than 90%.

#### **Chemical Absorption Systems**

Developers of CO<sub>2</sub> capture processes using regenerable solvents generally believe their processes are most economical at high CO<sub>2</sub> capture rates—the range for survey respondents was 65% to 97% (for coal flue gas). The rationale was that because these processes tend to be capital intensive and have significant economies of scale (i.e., the equipment cost scale factor exponent is low), they needed high tonnages of CO<sub>2</sub> removal over which to amortize capital costs. In other words, the capital savings for smaller, partial capture systems would be modest and, in terms of \$/ton-CO<sub>2</sub> removed, would be more than offset by the drop in tonnage of CO<sub>2</sub> removed at partial capture rates. Developers generally believed that the economic optimum capture rate for NGCC plants would be lower than for PC plants, say 80–85% on natural gas flue gas for a process that had a 90% optimum capture rate on coal flue gas.

The types of process modifications that might be cost-effective for regenerable solvent processes designed for least levelized cost, as opposed to needing to meet a 90% capture criterion, include shorter absorption columns and smaller packing beds, design changes to pumps and heat exchangers, and a smaller process unit footprint. There was a consensus among developers that their fundamental process chemistry would not change for partial CO<sub>2</sub> capture.

#### Shell Cansolv

Shell Cansolv commercially offers at least two amine solvents for removal of CO<sub>2</sub> from power plant flue gases in a process configuration similar to Figure 1-1. Its DC-103 solvent (50% amine, 50% water, by weight) is currently used at SaskPower's coal-fired 110 MW (net) Boundary Dam Unit 3, along with a solvent-based SO<sub>2</sub> removal system heat-integrated with its CO<sub>2</sub> removal process. The heating requirement to regenerate the DC-103 solvent is reported by Shell Cansolv as averaging 1000 Btu/lb-CO<sub>2</sub> (2.33 GJ/tonne-CO<sub>2</sub>). Shell Cansolv's DC-201 solvent was proposed for CO<sub>2</sub> capture at a Scottish & Southern Energy Generation Limited (SSE) NGCC unit (340 MW, full flue gas flow) at its Peterhead plant in Aberdeenshire, Scotland. Shell Cansolv is also the "CO<sub>2</sub> partner" for the proposed KEA Fortum waste-to-energy project in Norway.

As the world's longest running commercial, utility-scale CO<sub>2</sub> capture project on an electrical generating unit, Boundary Dam has provided Shell Cansolv, SaskPower, members of the International CCS Knowledge Centre, and the broader CCS community with numerous detailed learnings. Most have been related to process equipment and operations, including a combination of amine degradation and solvent foaming in the columns that required greater reclaimer operation, which was resolved by adding an activated carbon filtration system for amine cleaning. The stripper column packing was also replaced. Amine makeup costs were subsequently reduced. The system has also experienced some heat exchanger fouling, an amine tank leak, and a leak in the compressor train. CO<sub>2</sub> purity has been consistently high (>99%) with residual O<sub>2</sub> low enough to meet pipeline specifications without additional treatment. 9 Shell

<sup>&</sup>lt;sup>8</sup> "Shell Cansolv CO<sub>2</sub> Capture Technology: Achievement from First Commercial Plant," A. Singh and K. Stéphenne, Energy Procedia 63, 2014.

<sup>&</sup>lt;sup>9</sup> Combustion Technology Status: 2017 Update. EPRI, Palo Alto, CA: 2015. 3002011209.

Cansolv reports few issues with the DC-103 solvent formulation itself. In 2018, the CO<sub>2</sub> capture system was operating at a high availability rate until a June storm damaged transmission lines and Unit 3 generating equipment at the Boundary Dam power plant.

With respect to partial CO<sub>2</sub> capture opportunities, Shell Cansolv believes that the least levelized cost CO<sub>2</sub> capture rate for its aqueous amine solvents on coal flue gas is about 85% (or higher) because the system's capital cost dominates the levelized cost calculation. Higher CO<sub>2</sub> capture rates allow for a relative reduction in the size of some equipment per ton of CO<sub>2</sub> captured. Nonetheless, process modifications that Shell Cansolv conjectures may be economical at partial capture rates include a shorter absorption column, less packing, and a lower solvent circulation rate.

#### **HTC Purenergy**

HTC Purenergy has developed and tested an absorption-based process for removing CO<sub>2</sub> from power plant flue gases, in a configuration similar to that shown in Figure 1-1, using proprietary RS<sup>TM</sup> (amine) solvents licensed from the International Test Center in Regina, Saskatchewan. HTC Purenergy has not disclosed the composition of the RS<sup>TM</sup> solvents, but in describing the performance of RS-2 at SaskPower's Boundary Dam pilot plant (which preceded the Unit 3 retrofit), HTC Purenergy claims a regeneration energy of 1.1 kg of steam per kg of CO<sub>2</sub>. In work with utilities, HTC Purenergy demonstrated its process on coal flue gas at 5 MWe scale at SSE's Ferrybridge Power Station in Scotland. HTC Purenergy was selected competitively to supply a 120 MWe demonstration system for Basin Electric's Antelope Valley Power Plant and performed front-end engineering design (FEED) studies (before a decision by the host site not to proceed). HTC Purenergy claims that its RS solvent process had been selected on the basis of: high rate of absorption, solubility and capacity of CO<sub>2</sub>, good mass transfer performance, resistance to corrosion and fouling, resistance to oxidative degradation, low volatility, and low regeneration energy.

HTC Purenergy's current business development focus is on applications where captured CO<sub>2</sub> can be sold as a commodity (e.g., oilfields) as opposed to being treated as a regulated waste. Its emphasis on modular design allows the CO<sub>2</sub> capture process unit to be fabricated more cost-effectively in a factory setting using standard components and materials (e.g., pumps, piping, motors, blowers, etc.) and shipped on skids for field assembly. HTC Purenergy believes this approach will be particularly advantageous for CO<sub>2</sub> capture projects in locations with high labor costs, such as Norway. Its "multi-blend" RS solvents are custom-designed for a given application's specific flue gas composition. Its Delta Reclaimer System<sup>TM</sup> optimizes recovery of multi-blend solvents and glycols. In addition to aiming to reduce capital costs through a simplified design, HTC Purenergy seeks to reduce operating costs by minimizing waste disposal, lowering utilities (steam, power, water) consumption, and requiring less frequent replacement of solvents.

HTC Purenergy completed an LCDesign<sup>TM</sup> (low cost) modular unit for Husky Energy, Inc., in 2015, for an application at a heavy-oil project near Lashburn, Saskatchewan, to capture 33 tons (30 tonnes) of CO<sub>2</sub> per day, for use in EOR, from a natural gas once-through steam generator (used for heavy oil steamflood). [Husky Energy is currently hosting an Inventys VeloxoTherm<sup>TM</sup> CO<sub>2</sub> capture system at this scale at Lashburn.] HTC Purenergy's Delta Purification System<sup>TM</sup> (reclaimer) is installed at the Husky Energy Lashburn CO<sub>2</sub> capture plant.

In terms of market-entry designs, HTC Purenergy sees value in simplification, such as eliminating mid-column absorber column intercooling, even if overall process efficiency is a bit lower. It sees solvent management as key to reliability, and considers its Delta reclaimer a success—it's used not just for CO<sub>2</sub> solvents, but also for glycol to avoid well disposal.

Regarding partial CO<sub>2</sub> capture opportunities, an HTC Purenergy study from 2006–07 optimized its process flue gas capture rate at about 90% on a PC unit and at about 85% on an NGCC unit. HTC Purenergy still believes that 90% capture would be best for flue gas streams with greater than 8% (vol.) CO<sub>2</sub> concentration, and 85% capture would be best for NGCC flue gas.

#### ION Engineering

ION Engineering's "advanced liquid absorption system" uses advanced amines in a regenerable solvent process configuration similar to that shown in Figure 1-1. ION Engineering has built a proof-of-concept, 50-kW facility in Colorado; tested at the National Carbon Capture Center (1100 hours at 0.6-MWe scale); and tested at Technology Centre Mongstad (12 MWe scale) on low CO<sub>2</sub> concentration flue gas from a natural gas-fired cogeneration unit and on relatively high CO<sub>2</sub> concentration flue gas from a refinery residuum fluid catalytic cracker. ION Engineering claims its process has a regeneration energy of 1160–1203 Btu/lb-CO<sub>2</sub> (2.7–2.8 GJ/tonne). 10

Overall, ION Engineering is satisfied with its solvent. It claims fast kinetics and low corrosion, without additives, at low levels of water in the aqueous solvent solution. It notes the need for a certain amount of water to promote heat transfer in the stripping column. Alternatively, some type of in situ heater could be used in the column.

ION Engineering's current business development focus is to build a 25–50 MWe commercial unit and re-examine optimization opportunities in its process. With respect to the latter, it wants to reduce regeneration energy. The company also believes there are opportunities to improve its amine slip emissions controls to reduce capital and operating costs. It is also refining its online liquid analyzer for process control, which it tested at Technology Centre Mongstad, with the aim of better maintaining the water balance as temperatures change. ION Engineering is also conducting an engineering design study and developing a budgetary cost estimate for a 300 MWe CO<sub>2</sub> capture retrofit at Nebraska Public Power District's coal-fired Gerald Gentleman Station (Unit 2) in Sutherland, NE.

Regarding the advantages of partial CO<sub>2</sub> capture, ION Engineering did not see a strong economic case for partial capture per se. It considers its processes' least levelized cost point at 85–95% capture for U.S. and Canadian coals and market conditions (where capital costs are relatively high, and fuel costs are relatively low). However, ION Engineering did see considerable opportunities for savings in eliminating the costly equipment redundancy needed to achieve 90% capture *consistently*. If there were a greater tolerance for unavailability or off-spec operation, overall annual CO<sub>2</sub> capture rates would be reduced, but CO<sub>2</sub> removal in \$/ton would likely improve. An example noted by ION Engineering would be if CO<sub>2</sub> capture process could

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<sup>&</sup>lt;sup>10</sup> "ION Advanced Solvent CO<sub>2</sub> Capture Pilot Project," E. Meuleman, 2016 NETL CO<sub>2</sub> Capture Technology Meeting, 2016.

accommodate SO<sub>X</sub> spikes (e.g., from FGD upsets) in the flue gas pre-treatment and absorption systems.

ION Engineering believes design optimization studies would yield different results for cost structures different from those in North America. For example, in China where equipment and labor costs are low, but fuel costs were relatively high, a capture process unit could be built with taller columns and more heat integration, but steam for regeneration would need to be conserved. The net CO<sub>2</sub> capture rate might not be significantly different than a North American design, but the configuration and process flows would be. In Japan and South Korea, where equipment, labor, and fuel costs are all high, columns might be shorter and there would still be a focus on conserving steam. The overall capture rate might be a bit lower, but not at the levels considered partial capture.

#### Carbon Clean Solutions, Ltd.

Carbon Clean Solutions, Ltd. (CCSL) has developed a regenerable solvent designated "APBS" (and advertised as a direct substitute for MEA) for a conventional absorption process configuration (see Figure 1-1) coupled with a novel approach to heat integration. The process has been tested at small pilot scale at the Maasvlakte coal-fired power plant in Rotterdam (Netherlands), at the National Carbon Capture Center on coal flue gas and simulated natural gas flue gas, at Technology Centre Mongstad (3500 hours at 12 MWe scale) on flue gas from the natural gas-fired cogeneration unit and the refinery's residuum fluid catalytic cracker, and at the University of Kentucky's Center for Applied Energy Research. Results showed that CCSL's solvent has high CO<sub>2</sub> loading capacity, low corrosivity (inhibitors not needed), low regeneration energy, and few emissions (measured slip was at parts-per-billion levels). CCSL also claims that its solvent has resistance to thermal degradation, no foaming tendencies, and little reactivity with SO<sub>2</sub> and NO<sub>2</sub>.

In a commercial industrial application in India (soda ash production), a CCSL CDRMax<sup>TM</sup> process unit rated at 66,000 tons (60,000 tonnes) per year is capturing CO<sub>2</sub> from a 10 MW coal-fired boiler for re-use within the facility. A similarly sized CDRMax is being built at another specialty chemicals plant in India using a coal flue gas source.

In 2017, CCSL completed basic engineering for two larger-scale CO<sub>2</sub> capture projects in Norway vying for government support for follow-on FEED studies: a Yara International fertilizer plant that would capture 1080 tons (980 tonnes) of CO<sub>2</sub> per day from reformer flue gas (subsequently not selected for further funding), and a Fortum Oslo Varme waste-to-energy plant at Klemetsrud that would capture 1800 tons (1630 tonnes) of CO<sub>2</sub> per day, which will receive FEED funding.

CCSL sees an opportunity for partial CO<sub>2</sub> capture more as a developmental step than as a lower-cost design point. Because it believes that early projects will provide so many learnings and insights for cost savings in future designs, CCSL suggests that initial power plant projects should be designed for 65–70% capture, rather than at a more expensive 90% removal rate, so that the requisite learnings come via a lower initial demonstration plant investment. It considers its own pilot units at the National Carbon Capture Center and Technology Centre Mongstad to have been "overdesigned."

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<sup>&</sup>lt;sup>11</sup> Combustion Technology Status: 2017 Update. EPRI, Palo Alto, CA: 2015. 3002011209.

CCSL believes that once initial demonstration learnings are incorporated into subsequent designs, the capture rate can be increased to the least levelized cost value. CCSL expects that this may be less than 90% capture. It conjectures that 65–80% capture may offer the least levelized cost, with coal flue gas being toward the higher end of the range and natural gas flue gas toward the lower end.

CCSL solvents are also being used in joint development efforts, including a project with the Gas Technology Institute (with DOE funding) known as ROTA-CAP, which involves rotating packed bed flue gas-to-solvent countercurrent contactors (in lieu of conventional absorber and stripper columns). Testing will use simulated and natural gas flue gases.

#### Gas Technology Institute

The Gas Technology Institute (GTI) teamed with PoroGen to develop the CarboLock<sup>TM</sup> CO<sub>2</sub> capture process, a membrane-like contactor-assisted absorption system that improves mass transfer per unit volume relative to conventional absorber and stripper columns. A CarboLock "compact column" module is only 5 feet (1.5 m) tall, and contains membrane-like nano-porous hollow fibers made of polyether ether ketone (PEEK) through which flue gas flows and contacts a liquid solvent. Although at micron scale, it can be visualized as like a shell and tube heat exchanger with solvent on shell side and flue gas in the tubes. The hollow fibers serve to increase reaction surface area, like a "super-packing." A fluorinated compound coating makes the PEEK fibers hydrophobic, keeping pores open and absorption rates high. The PEEK fibers are compatible with a broad range of solvents, including conventional CO<sub>2</sub> absorption amines. Solvent regeneration is accomplished by a combination of heating (with low-pressure steam, akin to a conventional stripping column reboiler) and flashing.

Because the PEEK fiber contactors enable a significantly higher gas-liquid mass transfer rate relative to column with either trays or packing, the CarboLock system features smaller, modular vessels, which are claimed to be less expensive collectively than an absorption column. The modular nature of CarboLock also enables it to accommodate changing unit (flue gas) loads by valving off banks of contactors at low load levels. Ongoing testing will continue through mid-2019 at the National Carbon Capture Center for a 28-module skid of PEEK contactors using an activated methyl diethanolamine solvent.

Operation requires the liquid (solvent) side of the hollow fiber to be at a pressure about 0.5 psi (0.035 bar) higher than the flue gas side. An optimization study of flue gas boost pressure is under way, with testing ranging from 1–5 psi (0.07–0.35 bar). It is important to control humidity of the inlet flue gas to maintain water balance in the modules. Because of the hollow fiber and nano-pore configuration, there is less transfer of oxygen into the solvents and less solvent degradation with reduced formation of heat-stable salts. Solvent carryover and emissions are reduced as well. With an amine solvent, testing to date has shown no frothing, perhaps because there is less agitation and no hydrocarbons in the solvent.

The 5 feet (1.5 m) height of the modules limits the maximum CO<sub>2</sub> capture rate to about 90–92%, but in practice it may be less (although above the rates normally considered as partial capture). The CarboLock design of short, modular contactors makes it aesthetically easier to site than a tall absorption column, especially for plants in more urban/suburban locations.

#### University of Kentucky / Center for Applied Energy Research

The University of Kentucky's CAER facilities serve as a locus for development of CO<sub>2</sub> capture processes by research teams including CAER staff and also for testing and refinement of CO<sub>2</sub> capture processes developed by others. Work cosponsored by EPRI at CAER examines novel CO<sub>2</sub> capture solvents, novel capture processes, degradation inhibitors, and corrosion inhibitors. Work funded chiefly by DOE has led to the development of a two-stage solvent stripping process in which lean solvent existing a conventional reboiler-heated stripper and lean/rich solvent heat exchanger is routed to a second stripping column where it is contacted with warm humid air to further remove CO<sub>2</sub>. The additionally released CO<sub>2</sub> (modest in amount) is recycled with moist air back to the power plant's combustion system or flue gas train, resulting in flue gas higher in CO<sub>2</sub> entering the absorber (improving its efficiency). Thus, the solvent is returned to the absorber "leaner" with a greater capacity to absorb more CO<sub>2</sub>. A liquid desiccant process developed by CAER for production of the warm moist air also provides cold water for process cooling.

Regarding design considerations for CO<sub>2</sub> capture from natural gas flue gas, CAER researchers have observed that because of lower CO<sub>2</sub> loading in the flue gas from NGCC units, the solvent circulation rate can be reduced relative to the volume of flue gas flowing through the absorber (as compared with coal flue gas). For a given absorber packing bed, the reduction in liquid solvent flow may create an issue with insufficient wettability of the packing. CAER researchers see the desired solvent film thickness on the packing surface as 50–100 microns. Thus, it believes process developers may need to change the packing in absorber columns treating NGCC flue gas to a shape with less surface area (or a smaller bed) relative to the packing used with coal flue gas.

With respect to the levelized-cost economics of partial CO<sub>2</sub> capture, a CAER researcher conjectured that for coal flue gas, capture rates below 80% would be uneconomic for an absorption process because its high capital cost would not be amortized over enough tons of CO<sub>2</sub> removed. Regarding solvent regeneration energies being compared with the regeneration energy requirement for MEA, an adjustment should be made for solvents requiring higher steam temperatures that do not account for the greater power cycle loss for steam extracted at a higher temperature (assuming use of energy recovery if the steam extraction is at higher conditions than that required by the stripping column reboiler).

#### University of Texas

University of Texas at Austin (UT Austin) researchers have conducted wide ranging R&D on concentrated piperazine as a solvent in absorption processes and in hybrid processes with absorption and other CO<sub>2</sub> capture technologies. Because piperazine requires regeneration to "very lean" levels to get good process performance, UT Austin researchers have also developed a two-stage and an "advanced" flash stripper as an alternative to a conventional reboiler-stripping column. Piperazine's thermal stability lends itself to a flashing-based approach to regeneration. Testing has taken place at the National Carbon Capture Center.

UT Austin researchers believe that the economically optimum capture rate for the concentrated piperazine process is 97–98% on coal flue gas. CO<sub>2</sub> capture at this high rate has been achieved on coal flue gas at the National Carbon Capture Center and on natural gas flue gas at the UT Austin. Relative to a 90% CO<sub>2</sub> capture design and the "sunk cost" of the absorption column, incremental capture can be achieved economically by adding more packing. Because of the

flashing-based approach to regeneration, the incremental capture does not entail sharp increases in steam consumption as is observed in amine solvent processes with reboiler-stripper column regeneration.

UT Austin researchers have also identified potential cost saving measures, including the integration of a flue gas pre-treatment direct contact cooler into the bottom section of the absorption column.

#### **Physical and Chemical Solid Adsorption Systems**

Adsorption-based CO<sub>2</sub> capture processes appear as though they may be most economical at CO<sub>2</sub> capture rates lower than 90%.

#### TDA Research

TDA Research (TDA) and partners are developing a near-isothermal CO<sub>2</sub> capture process using an alkalized alumina sorbent in a series of fixed packed beds with manifolding and dampers to direct flue gas and regeneration steam among the beds in a simulated moving bed configuration. In a design for PC plants, CO<sub>2</sub> is adsorbed from flue gas at atmospheric pressure and a temperature of 230–390°F (110–200°C). Desorption is accomplished by direct contact with low-pressure steam, also at atmospheric pressure, which both heats the sorbent by about 15–18°C (8–10°C) and functions as a sweep gas. During desorption, nitrogen is released first and diverted, followed by the release of CO<sub>2</sub>, which is collected. Regeneration energy is a significant factor in the levelized cost equation, and TDA is focused on reducing steam consumption per ton of CO<sub>2</sub> captured. The alkalized alumina sorbent is a low-cost, commercially available material. Although the CO<sub>2</sub> adsorption reactions are fast, large volumes of sorbent will be needed for a commercial utility-scale application. TDA has investigated alternative configurations for application at scale (e.g., circulating bed, rotating wheel), but believes a stacked, stationary bed approach with ducting and dampers will be best. Flue gas pre-treatment to remove SO<sub>X</sub>, especially SO<sub>3</sub>, is needed. Emissions of sorbent are not expected.

Building upon laboratory and small field pilot tests, a 10-bed system at 0.5 MWe scale was installed at the National Carbon Capture Center in 2017. Commissioning was completed in early 2018. A batch of pelletized sorbent was found not to be fully calcined and it was reprocessed by the manufacturer. Following a planned outage at NCCC, testing is scheduled to commence in late 2018.

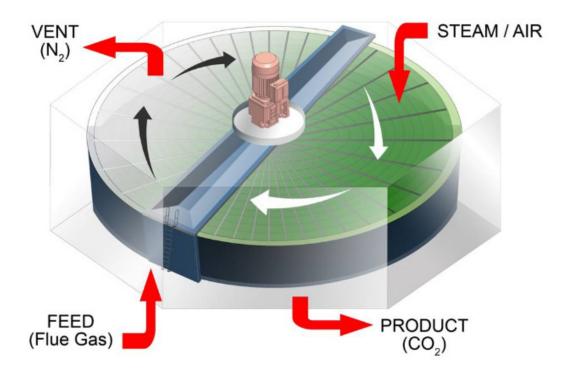
With respect to the economics of CO<sub>2</sub> capture rate, TDA has not conducted an optimization analysis but believes that the capture rate with the least levelized cost will be lower than 90%, perhaps around 80%. Steam usage for regeneration is not a linear function of the tons of CO<sub>2</sub> regenerated. Steam usage increases sharply as the CO<sub>2</sub> capture rate is increased to very high levels (i.e., 99%).

#### Inventys

Inventys has developed the VeloxoTherm<sup>TM</sup> temperature-swing adsorption process configured as spaced sheets of sorbent within a continuously rotating "air heater like" wheel that sequentially contacts flue gas in an adsorption section, a heat-adding regenerator (steam or warm air to liberate the adsorbed CO<sub>2</sub> for processing), and an air cooling section (see Figure 3-1). Gas flows may be facilitated by fans/blowers and vacuum pumps. Rotational speed is on the order of 1

revolution per minute. The temperature swing is nominally from 100–230°F (40–110°C). Inventys is exploring opportunities to use the heat of CO<sub>2</sub> compression to assist with regeneration. Initial development and testing used a commercial activated carbon sorbent; Inventys has subsequently tested amine-doped and metal organic framework sorbent systems. Inventys claims low capital costs and a pathway to a levelized cost of \$30/ton (\$33/tonne) of CO<sub>2</sub> captured. Development has been guided by levelized cost reduction rather than a target CO<sub>2</sub> removal rate criterion.

The recent business development focus of Inventys has been on industrial applications, with customers including a Canadian cement plant and an oil producer. A project under construction for Husky Energy near Lloydminster, Saskatchewan, will capture 33 tons (30 tonnes) of CO<sub>2</sub> per day from a natural gas-fired steam generator for use in Husky Energy's heavy-oil EOR program. Commissioning is scheduled to commence in early 2019. Inventys claims to also have a design for a 330 ton (300 tonne) of CO<sub>2</sub> per day system.



Used with permission from Inventys Thermal Technologies, Inc.

Figure 3-1 Schematic of Inventys' VeloxoTherm Technology

## **Membrane Systems**

DOE and membrane developers believe that their CO<sub>2</sub> capture system designs with the least levelized cost are likely to be at capture rates much less than 90%. For example, Membrane Technology and Research, Inc. (MTR) said its most economical design point is likely at 50–65% capture. Savings come from process simplification, including the potential omission of staged

removal configurations, turboexpanders, and CO<sub>2</sub> concentration measures (for coal flue gas), as well as use of smaller blowers and/or vacuum pumps.

Membranes that are selective for CO<sub>2</sub> over N<sub>2</sub> also tend to readily permeate H<sub>2</sub>O. For high moisture coals and natural gas, membrane-based CO<sub>2</sub> capture systems will result in substantial amounts of flue gas water permeating the membrane and eventually being recovered in the CO<sub>2</sub> compression train.

A recent decision by DOE to relax its design criterion for R&D funding of 90% capture on coal flue gas should help project developers find more economical configurations for both PC plants and NGCC plants.

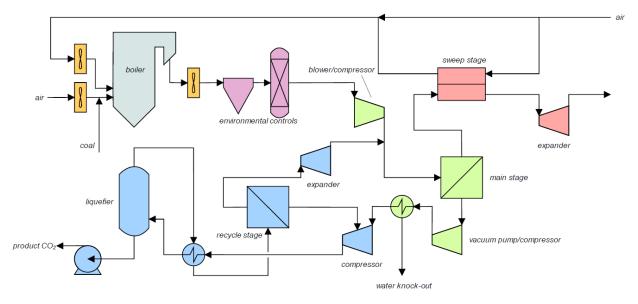
## Membrane Technology and Research, Inc.

Membrane Technology and Research, Inc. is developing composite membranes with high CO<sub>2</sub> permeance and selectivity for CO<sub>2</sub> (and H<sub>2</sub>O) over non-polar molecules such as N<sub>2</sub> and O<sub>2</sub> for power plant flue gas applications. Its current commercial membrane, Polaris<sup>™</sup> is made of hydrophilic polymers sheets formed into spiral-wound membrane modules 8 or 12 inches (20 or 30 cm) in diameter and 40 inches (1 m) in length. The modules are packaged into a shipping container with a CO<sub>2</sub> removal capacity of about 20,000–30,000 tons annually.

The membrane configuration includes membrane modules for both main-stage capture and air-sweep to increase capture rate. The sweep membrane modules use a countercurrent gas flow arrangement that employs incoming combustion air as a sweep gas to enhance the separation driving force created by CO<sub>2</sub> partial pressure differences. In 11,000 hours of testing at 1 MWe scale at the National Carbon Capture Center, Polaris membrane performance trended as expected, with a modest and generally linear decline over time. A larger test of Polaris membranes (~10 MWe) is planned for the Wyoming Integrated Test Center.

MTR has tested designs for the membrane contactor to minimize pressure drop. As an alternative to traditional "reverse osmosis style" membrane construction, MTR built a planar "frame and plate style" membrane unit, which was tested at NCCC. MTR has assumed a 3-year membrane life in economic analyses but believes the membranes will last longer.

A generic design for an MTR all-membrane CO<sub>2</sub> capture system is shown in Figure 3-2. Recent MTR process refinements have reduced the flue gas blower exit pressure to about 17–20 psia (1.2–1.4 bara) as well as removed the expander. For least-cost capture on PC units, MTR would forgo exhaust gas recirculation to reduce boiler integration/modifications and shorten the retrofit construction timeline. MTR estimates that the economically optimal capture rate on coal flue gas is about 50% if CO<sub>2</sub> sales is the primary economic driver and at about 60–65% if compliance with greenhouse gas regulations is primary economic driver. MTR is seeking to test some of its modified design concepts at Technology Centre Mongstad by building an approximately 1 MWe system between the pipe rack and the Aker chemical absorption plant.



Courtesy of Membrane Technology and Research, Inc.

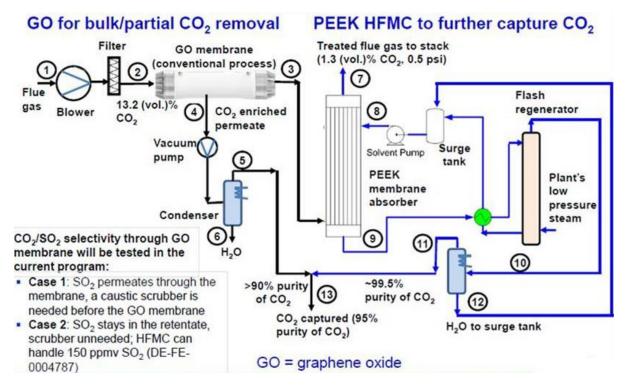
Figure 3-2 MTR Conceptual Membrane-Based CO₂ Capture Process for PC Units

## Gas Technology Institute

The Gas Technology Institute has teamed with the University of South Carolina and others to develop graphene oxide membranes for CO<sub>2</sub> capture from power plant flue gases. Two configurations are currently being developed, laboratory tested, and evaluated in technoeconomic studies: (1) membranes only, and (2) a hybrid of membranes and a PEEK contactor-based absorption process.

In the membrane-only configuration, GTI is examining a two-stage approach, designated GO<sup>2</sup>, in which one membrane is highly permeable and one membrane is highly selective. A blower adds pressure to the feed (retentate) side of the membrane system and a vacuum pump reduces pressure on the permeate side to facilitate CO<sub>2</sub> (and H<sub>2</sub>O) separation. GTI expects that a three-year DOE project scheduled to start in late 2018 will provide considerable insight into the potential of graphene oxide membranes.

In the hybrid configuration, designated GO-PEEK, a very thin graphene oxide membrane precedes the PEEK contactor modules for a "first cut" CO<sub>2</sub> (and H<sub>2</sub>O) separation that reduces the CO<sub>2</sub> loading to the PEEK modules and solvent flash regeneration unit, which in turns enables design modifications to reduce capital and operating costs (see Figure 3-3). The design goal for the hybrid configuration was established as 90% CO<sub>2</sub> capture on coal flue gas at 95% purity after separating the water by condensation and blending the CO<sub>2</sub> captured by the membrane (at a target purity of 90%) and the PEEK contactor-absorption system (at a target purity of 99.5%). An economic optimization has not yet been conducted, but it could show improved levelized costs with equipment sizes that yield capture rates less than 90%.



Courtesy of Gas Technology Institute

Figure 3-3
Schematic of the GTI Staged Graphene Oxide Membrane and Polyether Ether Ketone High Surface Area Solvent Contactor for Flue Gas CO<sub>2</sub> Removal

GTI anticipates that GO<sup>2</sup> membranes may ultimately have levelized costs of less than \$30/ton (\$33/tonne) of CO<sub>2</sub> removed, which is lower than its projected ultimate cost of \$35/ton (\$39/tonne) of CO<sub>2</sub> removed for the hybrid graphene oxide membrane and PEEK contactor chemical absorption systems.

### Air Liquide

Air Liquide has developed a CO<sub>2</sub> capture process using an industrial gas processing membrane (for CO<sub>2</sub> removal from natural gas) that operates effectively at cold temperatures. A schematic of the process is shown in Figure 3-4. Flue gas is compressed to about 230 psia (16 bar), dehydrated, and cooled to about -20°F (-30°C). The cooled flue gas mixes with recycled gases from the liquid-vapor separator before entering the hollow-fiber polyimide separation membrane. The CO<sub>2</sub>-rich gas that permeates the membrane is compressed and cooled to condense CO<sub>2</sub>. The liquid CO<sub>2</sub> separates from the liquid-vapor separator and is pumped to the pipeline pressure before potentially being used to cool other streams. Gas leaving the membrane is heated and expanded through a compander to generate a very low temperature stream that provides cooling for the process.

The membrane fibers are covered with thin layer of dense, slightly permeable polymer, which provides extensive surface area. Air Liquide's commercial membrane modules are cylindrical, 12 inches (0.3 m) in diameter and 30 inches (0.8 m) long, and arranged in parallel.

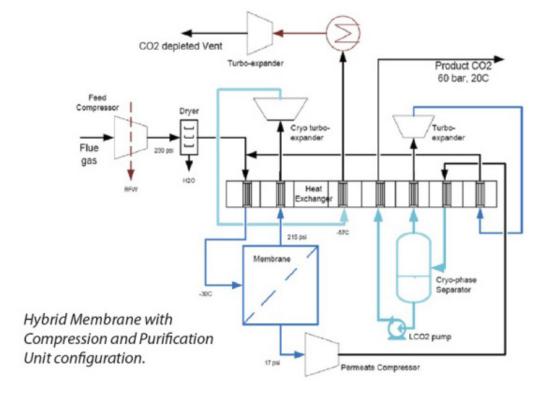
For PC flue gas, the single-stage polyimide membrane concentrates the gas stream CO<sub>2</sub> content to about 60%. A subsequent liquefaction step raises CO<sub>2</sub> purity to >99%. At low temperatures,

Air Liquide's polyimide membrane exhibits two to four times the selectivity for CO<sub>2</sub> over N<sub>2</sub> as it does at ambient temperatures, with comparable CO<sub>2</sub> permeance. Compressing the flue gas prior to the separation membrane reduces the size of equipment and allows the CO<sub>2</sub> to be subsequently liquefied at relatively higher temperatures. The low operating temperature of the membrane also avoids condensate issues because the dewpoint is low.

Air Liquide's cold membrane technology was tested for 3600 hours at 0.3 MWe scale on coal flue gas at the National Carbon Capture Center.

Air Liquide's current business development focus is on reducing capital costs; it is less concerned with process energy consumption. Its new polyimide membrane (designated "PI-2") has better CO<sub>2</sub> permeability, and Air Liquide is working to reduce its manufacturing cost. Air Liquide has not examined partial CO<sub>2</sub> capture configurations per se, and expects that the economically optimum capture for its process on coal flue gas is 80–90%.

Air Liquide is also examining a hybrid process that expands residue gas through a turbine for power generation.



Source: U.S. Department of Energy

Figure 3-4
Process Flow Diagram for Air Liquide Cold Membrane/Cryogenic Liquefaction CO₂ Capture System

#### **Cryogenic Systems**

## Sustainable Energy Solutions

Sustainable Energy Solutions is developing two cryogenic CO<sub>2</sub> capture processes to separate CO<sub>2</sub> from power plant flue gases:

- Compressed flue gas (CFG) process
- External cooling loop (ECL) process

Both processes include flue gas conditioning, de-sublimating ("frosting") heat exchange, recuperative heat exchange, solid separation, and CO<sub>2</sub> pressurization steps. In the CFG process, the flue gas is modestly compressed and cooled to slightly above the frost point of CO<sub>2</sub>. The gas is then expanded, further cooling the stream. In the ECL process, a refrigeration loop is used in lieu of the expansion step for the final cooling. For both approaches, liquid CO<sub>2</sub> and gaseous nitrogen are produced.

In the ECL process, the flue gas is cooled to condense out moisture. It then undergoes an additional dehydration step and enters a heat recovery/chilling loop. In the loop, the flue gas is cooled by a refrigerant to roughly -180°F (-120°C), which precipitates 90% of the CO<sub>2</sub> from the flue gas.

The solid CO<sub>2</sub> is collected in a solid separator and compressed; after heating to a liquid state, it is then pumped to pipeline pressures. As the CO<sub>2</sub>-depleted flue gas and solid CO<sub>2</sub> are each heated to ambient temperature in a heat recovery unit, the refrigerant is cooled to near -180°F (-120°C). In this arrangement, the refrigerant is heated and cooled primarily in the heat recovery units, and only a small portion of the total chilling is provided by expansion and mechanical work.

Conventional heat exchangers can plug and lose thermal conductivity if solid particles form on the surfaces. To avoid this issue, Sustainable Energy Solutions has proposed a direct contact column to cool the flue gas by direct mixing with a cold contacting liquid. Such direct cooling should cause the CO<sub>2</sub> to form solid particles on, or in, the liquid. The resulting solid/liquid slurry can be collected, separated, and pressurized in an extruder. The solid CO<sub>2</sub> can then be further purified and pressurized to pipeline pressures.

The process is presently at 1 tonne of CO<sub>2</sub> per day scale. The company plans to build a pilot of about 5 MWe for testing with a variety of flue gases (including simulated or actual natural gas flue gas). The most recent pilot plant work by Sustainable Energy Solutions has been on cement plants.

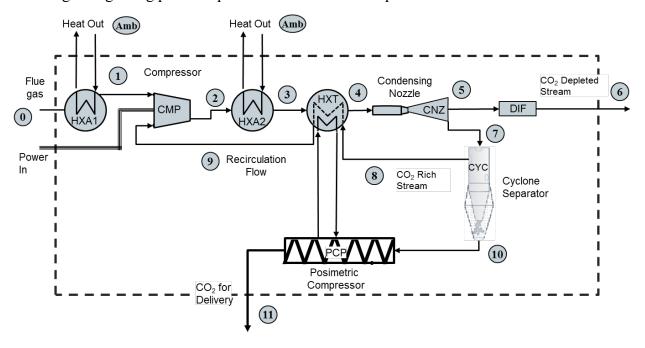
To employ partial CO<sub>2</sub> capture with either the ECL or CFG "frosting" process, Sustainable Energy Solutions would operate the cooling cycle at less cold temperatures. However, it has not evaluated the economics of partial capture, and conjectures that its economically optimum CO<sub>2</sub> capture may be above 90%.

## Orbital ATK / Aerospace and Clean Energy Technologies

The inertial CO<sub>2</sub> extraction system investigated by Orbital ATK and Aerospace and Clean Energy Technologies compresses, cools, and flows flue gas through a converging-diverging nozzle at supersonic speeds to cool the gas stream to the point that CO<sub>2</sub> frosts to solid particles (see Figure 3-5). The main energetic consumption in the process is the compressors to overcome

the pressure drop in the ICES system due to heat generation during solids formation and high temperature momentum extraction in the supersonic flow. For 90% capture, the inlet pressure has to be above 175 psi (12 bar) to overcome these losses and allow atmospheric discharge.

The nozzles are substantial at a few hundred feet (~100 m) long and are arranged horizontally. If the design basis was only partial capture, the nozzles could be shorter. Some small particulate matter in the coal flue gas is helpful, as it creates nucleation sites for the CO<sub>2</sub>, but this is not critical. Solids are separated from the gas stream before it is decelerated and vented through a stack. The collected CO<sub>2</sub> particles are pressurized as a solid, using much less energy than gas compression, while being heated back to ambient conditions. Testing has only been at laboratory scale with two-dimensional nozzles. Orbital ATK conjectures that the ICES capture process could be economical at 30–50%. EPRI has performed a more complete analysis of this process and insights regarding partial capture are described in Chapter 2.



Source: ACENT Laboratories

Figure 3-5
Process Flow Diagram for Orbital ATK / ACENT Labs ICES Process with CO<sub>2</sub> Recycle

## 4

## **R&D RECOMMENDATIONS**

## Stakeholders for Technology Development and Demonstration

Partial CO<sub>2</sub> capture research will need to proceed on the basis of superior economics, and its R&D will be driven by entities focused on lower-cost compliance, particularly in the nearer term, when emission standards and other regulations can be met with partial capture, especially where CO<sub>2</sub> sales is not a significant element in overall CO<sub>2</sub> capture economics.

CO<sub>2</sub> capture process developers with technologies at or near commercial readiness are likely less concerned with proving the suitability of their processes at partial capture rates than they are with finding immediate, real-world opportunities with favorable economics to get projects on the ground that generate revenue and provide a living laboratory for process improvement and cost reduction. This generally means finding project opportunities near CO<sub>2</sub> off-takers, such as oil producers seeking CO<sub>2</sub> for EOR, and where there is an established regulatory framework that can process permit applications, provide economic certainty about incentives or avoided costs, certify sequestered CO<sub>2</sub>, and offer long-term liability relief. For applications where CO<sub>2</sub> will be geologically sequestered only, existing or publicly supportable transportation and storage infrastructure will be key (e.g., under the North Sea). Public acceptance will also be vital.

## **Large-Scale Demonstration Projects**

Demonstration of any new technology for the electric power industry at scale is normally a prerequisite to commercial sales. For post-combustion CO<sub>2</sub> capture on pulverized coal plants, this step has been attained by SaskPower and Shell Cansolv at Boundary Dam Unit 3 and by the Petra Nova team (using MHI KM-CDR technology) at NRG's W.A. Parish Unit 8. Both of these projects are at nominally 90% capture rates and both received substantial private and government investment. Thus, there isn't a compelling demand to demonstrate CO<sub>2</sub> capture for PC plants at partial capture rates per se, but rather to demonstrate lower cost CO<sub>2</sub> capture for PC plants, regardless of capture rate.

DOE's suspension of funding in 2015 for FutureGen 2.0 and the Hydrogen Energy California project and the U.K. government's cancellation of the £1 billion CCS Competition in 2015 have underscored CCS project developers' concerns about reliance on direct investment or subsidies by government agencies. However, full-scale CO<sub>2</sub> capture projects do not appear to be proceeding without some type of substantial government incentive. With the trend for government support for CCS moving away from large contributions toward a demonstration project's capital cost, incentives are more likely to be "market oriented," such as a regulatory program imposing a cost on CO<sub>2</sub> emissions through a tax or creating a revenue opportunity for emissions avoidance through tradeable market instruments or tax credits. With regard to the latter, project financiers prefer programs with long periods of certainty of revenue or cost avoidance, as may be incorporated in contract for difference programs, cap-and-trade schemes with a floor price, and tax credits such as the U.S. Internal Revenue Service's Section 45Q. Of course, the magnitude of incentives, as well as their duration, needs to be sufficient to overcome the high costs of early market projects.

Changes in the power industry are also challenging the economics of applying CO<sub>2</sub> capture to PC and NGCC units. With the growth of intermittent renewable resources on the electric grid, fossil power plants are being called on for greater load-following and cyclic duty, which tends to reduce their capacity factors. For CO<sub>2</sub> capture processes with substantial capital costs, high capacity factors are needed to achieve reasonable levelized \$/ton-CO<sub>2</sub> removed or \$/MWh costs. Further, the addition of some CO<sub>2</sub> capture processes can extend unit startup time (especially for NGCC units), reduce its ramp rate capability, and increase its minimum load operating point (without turning off the CO<sub>2</sub> capture system). In regional transmission organizations (RTO) with "integrated" or other forms of competitive markets, the growth of renewables and self-generation has led to longer periods of depressed energy prices, short periods of high energy prices, and greater reliance on revenue from provision of grid support services. A PC or NGCC unit with CO<sub>2</sub> capture, especially an early mover project, operating in such an RTO will need some type of market support, such as designation as "must run" or dispatch loading order preference, to assure it gets enough dispatch hours to meet its CO<sub>2</sub> capture goal and to amortize the capture system's capital cost.

Locations with revenue potential for sale of CO<sub>2</sub> to oil producers for EOR include the United States, Canada, and Middle East. Areas with large chemical manufacturing complexes are also potential purchasers of large quantities of CO<sub>2</sub>.

In contrast to an emphasis on large-scale projects for CO<sub>2</sub> capture, one process developer suggested that the industry would be able to glean more "learning by doing" lessons, and subsequently be able to reduce costs more quickly, from many smaller projects (i.e., industrial scale and utility pilot scale) than fewer large-scale projects.

## Partial CO<sub>2</sub> Capture Research Needs and Opportunities

Based on interviews with CO<sub>2</sub> capture process developers, it appears that few companies and research institutions have had the opportunity to evaluate their current processes or modified or alternative processes for least levelized cost. Individual process developers generally know their specific additional R&D needs to validate or modify existing processes for partial capture on PC and NGCC units, but may not have investigated alternative chemistries or process configurations. Partial (and 90%) CO<sub>2</sub> capture R&D needs are also found at the system or balance-of-plant level. Examples follow.

**Development of novel CO<sub>2</sub> capture processes.** Some solid sorbent and cryogenic processes have been ignored due to their difficulty in achieving 90% capture rates. However, some processes show significant potential for economical CO<sub>2</sub> capture despite low capture rates. This can be due to the process residing near a thermodynamic limit, which enables low energy operation but does not allow flexibility to increase capture rate above a specific value that may be less than 90%.

Modifications of existing CO<sub>2</sub> capture processes. Processes that have been created to meet a 90% removal target may not operate most efficiently at that removal rate. Although some systems operate at near-equal efficiency at 99% capture, others may be more efficient at removal rates below 80%. For those processes with economically optimal CO<sub>2</sub> removal at lower capture rates, often the chemistry and process has been modified to enable higher rates of capture, such as through adding recycle loops, modifying flow rates, adding extra steps, or increasing

regeneration temperatures. These process modifications may unnecessarily increase the levelized cost of capture.

Conversion of partial capture processes to higher capture rates. A regulatory environment that promotes the development and deployment of partial-capture of CO<sub>2</sub> from fossil fuel power plants may require more stringent emissions reductions in the future. Understanding the options for transitioning partial-capture applications to 90+% capture installations would provide more certainty for developers and utilities looking to build partial-capture systems. Options for retrofitting partial CO<sub>2</sub> capture to 90+% capture include: selective CO<sub>2</sub> exhaust gas recirculation using an air sweep to increase the CO<sub>2</sub> concentration in the boiler and reduce overall emissions; expansion of the partial capture unit to increase the capture percentage such as through increasing the absorber height; exchanging the separation agent with one that can perform at 90% capture, even if it is less efficient; and exploring opportunities for capture from low CO<sub>2</sub> concentration streams.

Process equipment simplification and value engineering studies. One approach to partial capture is simply to remove equipment redundancy from a nominal 90% capture design and accept more unavailable hours or off-spec operation. However, while such an approach will clearly reduce capital costs (\$/kW), it is unclear if it will reduce levelized costs (i.e., \$/ton-CO<sub>2</sub> removed or \$/MWh). Value engineering studies can help determine whether the capital savings justify an availability loss. Such analyses require data (or estimates) on component failure rates and repair times, and there may be a paucity of such data for CO<sub>2</sub> capture equipment. Nonetheless, cursory analyses can help focus cost reduction efforts and determine the merits of simplified equipment configurations operating at modest annual CO<sub>2</sub> capture rates.

**Process pinch point review.** Most process developers have conducted some degree of design review and testing for application on PC units, and to a lesser extent, NGCC units. However, at partial capture rates, there may be different heat and mass balances and process pinch points. Analysis could potentially identify process or equipment modifications that could address process pinch point limitations.

Optimal use of cooling water in a fossil power plant with CO<sub>2</sub> capture. Today's fossil power plants today are likely to face water use restrictions in many jurisdictions. Because chemical absorption processes for CO<sub>2</sub> capture can have substantial cooling demands, capture system design may be impacted by the need to use dry or hybrid cooling. Further, having sufficient plot space for additional cooling equipment is a basic screening question when evaluating the retrofit potential of a given PC or NGCC plant. If a plant with wet cooling towers is restricted from using additional water, engineers will need to determine what type of cooling system and potential water recovery and recycle systems best allocate the existing water supply between the base generating unit and the CO<sub>2</sub> capture process.

#### **Conclusions and Recommendations**

Partial capture of CO<sub>2</sub> via removal of less than 90% of the CO<sub>2</sub> from the full flue gas stream shows the potential for enabling energetically favorable technologies. The benefit of that energetic improvement from minimum work analysis is likely to be in the range of 9–13% of the work required for capture and show an even smaller energetic benefit compared to the total work required for carbon capture, compression, transportation, and storage. For most partial capture technologies, the total project cost should be lower relative to higher capture rates, but the

specific capture cost (\$/t-CO<sub>2</sub> captured) is likely to be higher unless there is a process simplification that can be implemented. Additionally, partial capture may be beneficial for technologies that show an improvement over existing processes but are unable to achieve 90% capture without adding significant complexity and cost.

# A

## **TECHNOLOGY DEVELOPER SURVEY**

The following survey was used as a means of guiding conversations with developers and was not used as a standalone document to be completed and returned. It was conducted in conjunction with a similar "CCS on natural gas" survey that is the subject of EPRI report 3002013876.

- 1. Are you actively developing one or more CO<sub>2</sub> capture technologies for power plant flue gases? If so, what are the fundamental process type(s) and trade name(s)?
- 2. Where and when do you see markets for the technologies you are working on? What are the primary market drivers? Which plant type(s) do you see applying CO<sub>2</sub> capture first—coal, gas, biomass, oilfield/industrial cogen, or other?
- 3. For coal power plant applications, DOE uses a nominal capture rate design basis of 90%. Are there lower capture rates that may be more cost-effective from a levelized \$/ton-CO<sub>2</sub> or \$/MWh basis? For an application only requiring partial capture, would it be more economical or otherwise preferred to operate at 90+% capture on a slipstream or to treat the full flue gas stream at a lower capture rate?
- 4. Assuming a greenhouse gas emissions regime where a power plant can elect to capture CO<sub>2</sub> at any capture rate, what do you believe would be the most economical capture rate for your process on a levelized \$/ton-CO<sub>2</sub> or \$/MWh basis? Can you quantify or estimate this for coal plants and for natural gas combined cycle plants? What are the main areas of potential savings from use of partial capture (cap ex and op ex)? Are there different process configurations or chemistries that you identified but chose not to pursue because they couldn't meet a 90% capture criterion? From an LCOE perspective, are there sweet spots (capture % range) for partial capture on the full flue gas steam versus a higher capture rate on a slipstream?
- 5. If you haven't had the opportunity to consider optimization for least levelized cost (including partial capture designs) or for natural gas flue gas, but the opportunities arose, what would you investigate for your process (e.g., chemistry, process, sizing, or operating conditions)? Do you have plans to pursue this?
- 6. What other technical or regulatory developments could improve the economics of your CO<sub>2</sub> capture process for coal and natural gas combined cycle power plants?
- 7. [For developers in the pre-commercial stage.] Do you have a timeframe for scale-up and commercialization of your technology? What will be your next-step activities?

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