

# **Advanced Post-Combustion CO<sub>2</sub> Capture**

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## 1. Background and Motivation

The total US CO<sub>2</sub> emissions for 2006 were 5934 million metric tons (Mt). Of this, the electricity sector was responsible for 2344 Mt (39.5%). Coal-fired power plants produced 83% of the electricity sector's CO<sub>2</sub> emissions, with most of the remaining emissions from natural gas-fired power plants (EIA, 2007). These emissions were the result of supplying electricity to US homes, businesses, and industry – over 6,000 kWh per person from coal power alone (roughly half the average total US electricity consumption).

In China and India, rapid economic growth and industrialization have resulted in dramatic emissions increases recently and now China, with a population about four times that of the US, is the world's largest CO<sub>2</sub> emitter. More than one coal power plant per week has been built there in recent years. Despite this build, however, Chinese per capita electricity consumption is still much lower than in the US (around 1,500 kWh per year), and India's consumption barely registers on the world scale.

The build of new coal power plants in China and India, and the existing installed base in the U.S. and elsewhere, present a tremendous challenge for reducing global CO<sub>2</sub> emissions over the next several decades. Fortunately, there are opportunities as well as challenges in this situation. Access to the U.S. installed coal base represents an opportunity for data collection, analysis of retrofit potential, and global leadership in CO<sub>2</sub> reductions.

There are essentially three approaches to reducing emissions associated with coal combustion:

- ***Burn less coal.*** In theory, this can be accomplished by both reducing demand for electricity and by substituting other fuels for coal (e.g., nuclear, renewables). In practice, this is very difficult because coal is abundant and relatively inexpensive. Despite concerns about climate change, reliance on coal has been increasing worldwide because there has not been a viable alternative to fill the role coal plays in the world's energy systems. In fact, the recent high oil prices have increased the pressure to expand the use of coal to produce chemicals and transport fuels.
- ***Improve efficiency of coal-fired power plants.*** There is real opportunity for efficiency improvements. However, if these options were aggressively pursued, at best, this effort would only reduce emissions from coal by 10-20% (Beer, 2007). While being a positive step, it is insufficient for developing near-zero emission coal-fired power plant, which may be required by future carbon policy.
- ***Capture and store the CO<sub>2</sub>.*** Carbon dioxide capture and storage (CCS) is the only pathway that can allow the world to continue to enjoy the benefits of using coal while drastically reducing the emissions associated with coal combustion. At

a minimum, CCS can be a bridging strategy to provide time for alternatives to coal to be developed.

This White Paper will focus on the topic of CCS. In particular, it looks at a set of technologies termed “post-combustion CO<sub>2</sub> capture”. We will focus on applications to coal-fired power plants because they constitute, by far, the largest source of CO<sub>2</sub> emissions appropriate for CCS (IPCC, 2005). However, it should be noted that certain industrial processes (natural gas processing, ammonia production, cement manufacture, and more), as well as natural gas-fired power plants are also amenable to CCS.

At a coal-fired power plant, CO<sub>2</sub> is a component of the flue gas. The total pressure of the flue gas is 1 atm and the CO<sub>2</sub> concentration is typically 10-15%. The process of transforming this low pressure, low concentration CO<sub>2</sub> into a relatively pure CO<sub>2</sub> stream is referred to as post-combustion CO<sub>2</sub> capture. This capture step is typically followed by a compression step, where, for ease of transport (usually by pipeline) and storage, the CO<sub>2</sub> is compressed to 100 atm or more.

The idea of separating and capturing CO<sub>2</sub> from the flue gas of power plants did not originate out of concern about climate change. Rather, it gained attention as a possible inexpensive source of CO<sub>2</sub>, especially for use in enhanced oil recovery (EOR) operations where CO<sub>2</sub> is injected into oil reservoirs to increase the mobility of the oil and, thereby, the productivity of the reservoir. Several commercial plants that capture CO<sub>2</sub> from a power plant flue gas were constructed in the late 1970s and early 1980s in the US. When the price of oil dropped in the mid-1980s, the recovered CO<sub>2</sub> was too expensive for EOR operations, forcing the closure of these capture facilities. However, the Searles Valley Minerals Plant in Trona, CA, which uses this process to produce CO<sub>2</sub> for carbonation of brine, started operation in 1978 and is still operating today. Several more CO<sub>2</sub> capture plants were subsequently built to produce CO<sub>2</sub> for commercial applications and markets.

All the above plants used post-combustion capture technology. They ranged in size from a few hundred tons of CO<sub>2</sub> a day to just over a thousand tons a day (Herzog, 1999). Deployment of post-combustion capture technologies for climate change purposes will entail very substantial increases in scale, since a 500 MW coal-fired plant produces about 10,000 tons/day of CO<sub>2</sub>.

There are two major alternate approaches to post-combustion capture:

- ***Oxy-combustion capture.*** Because nitrogen is the major component of flue gas in power plants that burn coal in air (which nearly all existing plants do) post-combustion capture is essentially a nitrogen-carbon dioxide separation. If there were no nitrogen, CO<sub>2</sub> capture from flue gas would be greatly simplified. This is the thinking behind oxy-combustion capture: instead of air, the power plant uses a high purity (≥95%) oxygen stream for combustion of the coal. The oxygen is produced on-site in an air separation plant, which represents the largest cost component in the capture process.

- ***Pre-combustion capture.*** As the name implies, this refers to the capture of CO<sub>2</sub> prior to combustion. This is *not* an option at the pulverized coal (PC) power plants that comprise most of the existing capacity. However, it *is* an option for integrated coal gasification combined cycle (IGCC) plants. In these plants, coal is first gasified to form synthesis gas (syngas, a mixture whose key components are carbon monoxide and hydrogen). The syngas then undergoes the water-gas shift, in which the CO reacts with steam to form CO<sub>2</sub> and additional H<sub>2</sub>. The CO<sub>2</sub> is then removed, and the hydrogen is diluted with nitrogen and fed into a gas turbine combined cycle. The advantage of this approach is that it is much less expensive than the post-combustion capture process. The disadvantages are that there are only a few IGCC plants in the existing coal fleet and IGCC plants are more expensive than PC plants when costs of CO<sub>2</sub> capture are not included.

Post-combustion capture is important because:

- It is compatible with – and can be retrofitted to – the existing coal-fired power plant infrastructure without requiring substantial change in basic combustion technology.
- It is the leading candidate for gas-fired power plants. Neither the oxy-combustion nor the pre-combustion approaches are well suited for gas plants.
- It offers flexibility. If the capture plant shuts down, the power plant can still operate. The other two capture options are highly integrated with the power plant: so if capture fails, the entire plant must shut down. Furthermore, it offers utilities (and regulatory commissions) the option to allow for increased capacity by temporarily curtailing the capture process during periods of peak power demand.
- There has been very slow progress in the commercialization of IGCC for power generation applications. In the US, only two IGCC plants are in operation in the power industry and both were built as demonstration plants. Several utilities are currently considering building IGCC plants; all have considerable obstacles to overcome. The ultimate commercial success of IGCC to provide coal-fired electricity remains uncertain.

Until very recently, it had been widely expected that IGCC power plants with pre-combustion capture would offer the most cost-effective path forward for CCS. In early 2007, for example, there were more than a dozen IGCC project proposals in the US alone. Due in part to dramatic capital cost increases for all technologies, few IGCC proposals survive today. In addition, much of the coal build in the developing world continues to be based on coal combustion – not IGCC – technology. This has stimulated a re-examination of the role of post-combustion capture.

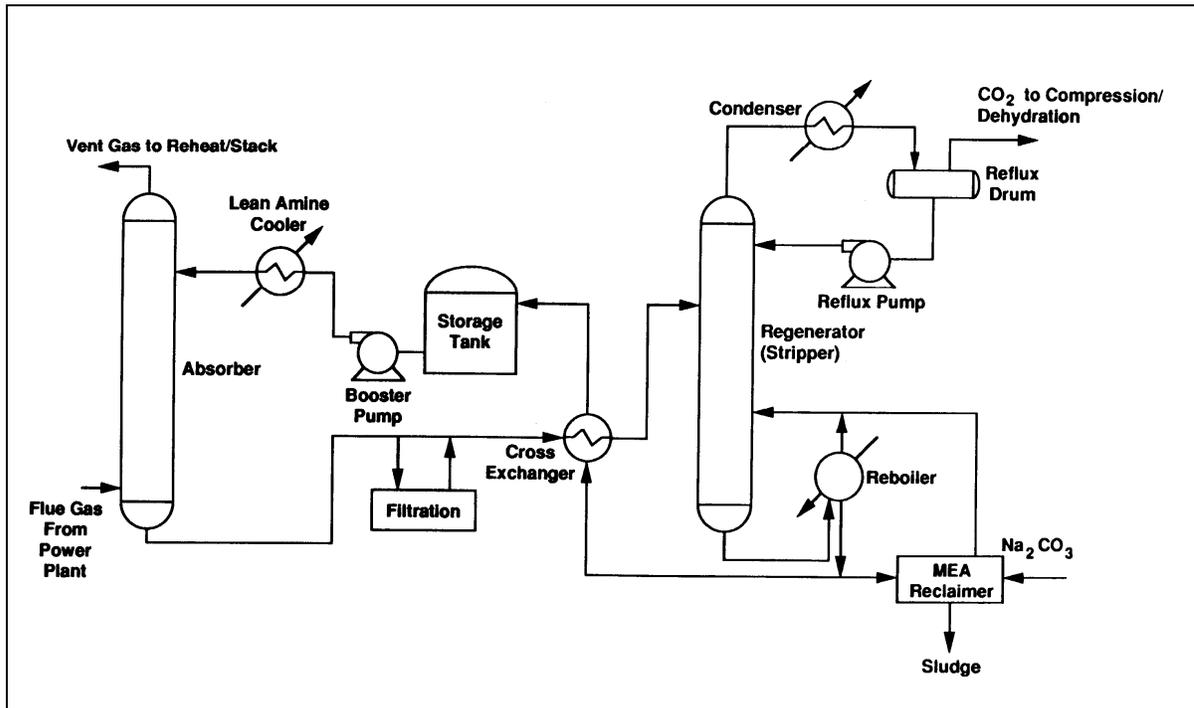
For the reasons discussed above, this paper focuses on near-term as well as advanced post-combustion capture technology that could be applicable to new coal power plants and also to retrofit of existing coal power plants. Specific engineering considerations for retrofits, however, such as steam cycle and steam turbine changes, while generally considered manageable, are outside the scope of this paper. In addition, although this paper focuses on applications to coal power, generally speaking the technologies covered

here would also be applicable to natural gas power plants. Section 2 of the paper reviews the current state of post-combustion capture. Current R&D thrusts are presented in section 3, and section 4 focuses on advanced R&D pathways. Finally, section 5 presents RD&D recommendations.

## 2. Current Status of Post-Combustion Capture

To date, all commercial post-combustion CO<sub>2</sub> capture plants use chemical absorption processes with monoethanolamine (MEA)-based solvents. MEA was developed over 70 years ago as a general, non-selective solvent to remove acid gases, such as CO<sub>2</sub> and hydrogen sulfide, from natural gas streams. The process was modified to incorporate inhibitors that reduce solvent degradation and equipment corrosion when applied to CO<sub>2</sub> capture from flue gas. Concerns about degradation and corrosion also kept the solvent strength relatively low (typically 20-30% amines by weight in water), resulting in relatively large equipment sizes and solvent regeneration costs.

As shown in Figure 1, which depicts a typical process flowsheet, flue gas contacts MEA solution in an absorber. The MEA selectively absorbs the CO<sub>2</sub> and is then sent to a stripper. In the stripper, the CO<sub>2</sub>-rich MEA solution is heated to release almost pure CO<sub>2</sub>. The CO<sub>2</sub>-lean MEA solution is then recycled to the absorber.



**Figure 1.** Process flow diagram for the amine separation process.

### 2.1 Cost of Capture

Table 1 shows representative costs for a supercritical (SC) PC power plant<sup>1</sup> with and without capture based on a modern amine system. Note that the costs include both capture and compression, but exclude transport and storage. These numbers vary over

<sup>1</sup> Current state-of-the-art supercritical plants operate at 24.3 MPa (3530 psi) and 565 C (1050 F) (MIT, 2007).

time and location and do not represent any particular power plant project. Their primary use is to illustrate the relative costs of power with and without CO<sub>2</sub> capture.

The first thing to note is that when a capture and compression system is added, the plant's overall thermal efficiency (the fraction of the energy released by combustion of the fuel that is transformed into electricity) drops from 38.5% to 29.3% (a *relative* decrease of 24%). This is caused by the additional parasitic energy load from the CO<sub>2</sub> capture system. The parasitic load can be broken down into three components:

- Extraction of steam from the plant's electricity-generating turbine to the stripper reboiler accounts for over 60%. The steam provides energy to break the chemical bonds between the CO<sub>2</sub> and the amine; provides heat required to raise the temperature of the amine solution to the operating temperature of the stripper, and sweeps away the released CO<sub>2</sub>.
- Electricity to drive the CO<sub>2</sub> compressors accounts for about a third.
- Electricity to drive the blowers to push the flue gas through the absorber accounts for about 5%.

The drop in thermal efficiency with capture has multiple effects on plant cost. First, 30% more coal must be burned to produce the same amount of electricity<sup>2</sup>. More importantly, as indicated in Table 1, the capital cost of the plant in \$/kW increases by 61%. This is because capital investment increases by 22% or a factor of 1.22 (to pay for the amine absorption process, compressors, etc.) while electrical output decreases by 24% or a factor of 0.76; thus, the investment cost expressed in \$/kW increases by a factor of 1.22/0.76 or 1.61. In other words, parasitic energy drain translates into the consumption of more coal per kWh *and* an increase in plant capital beyond the purchase price of additional equipment. Because of the magnitude of this effect, a *key goal of research in post-combustion capture is to reduce the parasitic energy load*.

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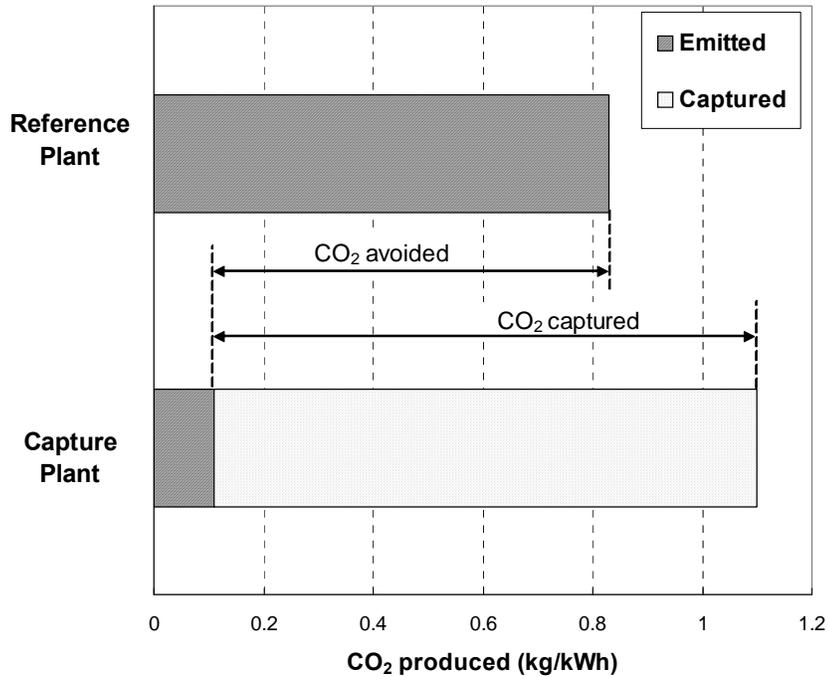
<sup>2</sup> This would also increase the variable operating cost of the plant which could reduce the dispatch factor for the plant. This potentially important impact is ignored in this analysis.

**Table 1.** Updated Capture (including Compression) Costs for Nth Plant SCPC Generation<sup>3</sup>  
(Hamilton *et al.*, 2008)

<b>Reference Plant</b>		<b>Units</b>	<b>SCPC</b>
Total Plant Cost		\$/kWe	1910
CO <sub>2</sub> emitted		kg/kWh	0.830
Heat Rate (HHV)		Btu/kWh	8868
Thermal Efficiency (HHV)			38.5%
LCOE	Capital	\$/MWh	38.8
	Fuel	\$/MWh	15.9
	O&M	\$/MWh	8.0
	Total	\$/MWh	62.6
<b>CO<sub>2</sub> Capture Plant</b>			
Total Plant Cost		\$/kWe	3080
CO <sub>2</sub> emitted @ 90% Capture		kg/kWh	0.109
Heat Rate (HHV)		Btu/kWh	11652
Thermal Efficiency (HHV)			29.3%
LCOE	Capital	\$/MWh	62.4
	Fuel	\$/MWh	20.9
	O&M	\$/MWh	17.0
	Total	\$/MWh	100.3
<b>\$/tonne CO<sub>2</sub> avoided</b>			
vs. SCPC		\$/tonne	52.2

Table 1 reports the mitigation or avoided cost in \$/tonne CO<sub>2</sub> avoided. Because of the parasitic energy requirement, the number of tonnes avoided is always less than the number captured. As a result, the \$/tonne avoided is always greater than the \$/tonne captured. This is shown graphically in Figure 2. The top bar shows the amount of CO<sub>2</sub> emitted per kWh from a reference plant without capture. The lower bar shows the amounts of CO<sub>2</sub> emitted and captured per kWh from the same power plant with 90% CO<sub>2</sub> capture (includes compression). Because of the parasitic energy requirement, more CO<sub>2</sub> is produced *per kWh* in the capture plant. The amount of CO<sub>2</sub> avoided is simply the difference in emissions between the reference plant and the plant with capture.

<sup>3</sup> This cost assumes: 2007\$, Nth plant (i.e., ignores first mover costs), 90% capture, 85% capacity factor, bituminous coal (Illinois #6), does not include transport and storage costs, assumes today's technology (i.e., no technological breakthroughs required), assumes regulatory issues resolved without imposing significant new burdens, assumes operations at scale (i.e., 500 MW<sub>e</sub> net output before capture).



**Figure 2.** Graphical representation of avoided CO<sub>2</sub>. The avoided emissions are simply the difference between the actual emissions per kWh of the two plants. Note that due to the parasitic energy requirement (and its associated additional CO<sub>2</sub> production), the amount of emissions avoided is always less than the amount of CO<sub>2</sub> captured.

The mitigation cost in \$/tonne CO<sub>2</sub> avoided is particularly significant because it is the quantity with which the permit price for a cap-and-trade system should be compared. As indicated in Table 1, the mitigation costs for the capture plant come to about \$52/tonne of CO<sub>2</sub> avoided. Typically, transport and storage add about \$10 more, making the total CCS mitigation cost around \$62/tonne of CO<sub>2</sub> avoided. The latter figure suggests the magnitude of the cap-and-trade permit price that is required to make CCS commercially viable, assuming current technology and no other policy incentives.

## 2.2 Potential for Reducing the Parasitic Energy Loss

As noted above, the parasitic loss due to capture and compression is 24%. About one-third (8%) is due to compression, with the rest (16%) attributable to separation. A key question is how much improvement is possible. To answer this question, a rough “minimum work” calculation is frequently conducted along the lines outlined in Appendix A. There it is shown that:

- The minimum work of separation (for 90% capture) = 43 kWh/t CO<sub>2</sub> captured
- The minimum work of compression = 61 kWh/t CO<sub>2</sub> compressed

By comparison, a typical SCPC power plant without carbon capture produces one tonne of CO<sub>2</sub> for every 1200 kWh of net power generated. It follows that the *minimum* energy requirement for separation (as a percentage of net power production) is  $[43 \text{ kWh/t CO}_2 \text{ captured}] \times [9\text{t captured}/10\text{t produced}] / [1200 \text{ kWh/t CO}_2 \text{ produced}] = 3.2\%$ . The estimated *actual* parasitic load (16%) is 5 times that. By comparison, the estimated minimum energy requirement for compression is  $[61 \text{ kWh/t}] \times [9\text{t}/10\text{t}] / [1200 \text{ kWh/t}] = 4.6\%$ . The estimated actual parasitic load (8%) is less than 2 times that. This suggests that there is considerably more room for improving the efficiency of the separation process than for the compression process.

In a typical SCPC power plant without capture, only 38.5% of the energy released by burning the fuel is transformed into electricity – i.e., the “first law efficiency” is 38.5%. The remaining 61.5% can be considered waste heat. Use of some of that waste heat to drive CO<sub>2</sub> capture reduces parasitic power consumption. For example, without the use of waste heat, the separation parasitic load would be about double the 16% stated above. Estimating the maximal extent to which a given plant’s waste heat is applicable to CO<sub>2</sub> recovery will require a more complex analysis than the one outlined in Appendix A – i.e., an “exergy” analysis of an integrated power plant/CO<sub>2</sub> capture system.

### 2.3 Commercial vendors

In the 1970’s, when a commercial market was developing for CO<sub>2</sub> captured from power plants (mainly for use in EOR), two processes were developed. One was by Kerr-McGee and the other was by Dow Chemical. The former was based on a 20% MEA solution and used primarily with coal-fired boilers (Barchas and Davis, 1992). The latter was a 30% MEA solution used primarily on natural gas plants (Sander and Mariz, 1992). Today, the Dow technology (ECONAMINE FG) is licensed by Fluor and the Kerr-McGee technology by ABB/Lummus. Several installations worldwide use these technologies.

Three other vendors also offer commercial amine processes:

- **MHI in Japan** developed a process named KM-CDR based on a proprietary solvent termed KS-1 (probably involving a hindered amine) that they offer commercially for gas-fired plants (with an offering for coal-fired plants under development). They claim that their process is the most energy efficient of the commercial offerings. Four commercial units for gas-fired plants have been built with this technology, with four more under construction. Tests are currently being conducted at the pilot scale on coal-fired flue gas (Kishimoto *et al.*, 2008).
- **HTC Pureenergy** is offering a process package. It is based on research done at the International Test Centre at the University of Regina that developed a mixed amine solvent. One way they are attempting to lower costs is by offering modular units that can be pre-fabricated. They have a unique marketing strategy, whereby they will finance, construct and manage the process. They also have an option in which they will own and operate the process.

- **Aker Clean Carbon in Norway** also offers a commercial package. The Just Catch process was initiated by Aker Clean Carbon AS with support from a larger industrial consortium (Sanden *et al.*, 2006). Just Catch is aimed at developing and verifying an amine based technology in a cost efficient manner. The preliminary results are based on a set of feasible technological improvements where the further engineering design is performed with the principal goal of facilitating cost-effective solutions, minimizing technical and economic risks, and developing confidence in cost estimation.
- **Cansolv** is offering a CO<sub>2</sub> capture process is based on a recently developed amine system using a proprietary solvent named Absorbent DC101™ (Cansolv, 2008). The solvent is based on tertiary amines, and probably includes a promoter to yield sufficient absorption rates to be used for low pressure flue gas streams (Hakka and Ouimet, 2006). With the use of oxidation inhibitors this process can be applied to oxidizing environments and where limited concentrations of oxidized sulfur exist. It is claimed that this process can also simultaneously remove other acidic contaminants and particulate material, such as SO<sub>x</sub>, and NO<sub>x</sub>. Two demonstration plants of the Cansolv CO<sub>2</sub> capture system have been built. One in Montreal, Canada, for capture of CO<sub>2</sub> from flue gas of a natural gas fired boiler, and one in Virginia, for CO<sub>2</sub> capture from flue gas of a coal fired boiler. No commercial plants have yet been built.

### 3. Current R&D Thrusts

Figure 3 outlines the various technology pathways to post-combustion capture. Most of these pathways are discussed in this section; the exploratory technologies are reviewed in section 4.

#### Flue Gas R&D Pathways

<b>ABSORPTION</b>  <b>MEA, other alkanolamines</b> <b>Blended alkanolamines</b> <b>Piperazine</b> <b>MEA/Piperazine</b> <b>K<sub>2</sub>CO<sub>3</sub>/Piperazine</b> <b>Less corrosive amines</b> <b>Less degradable amines</b> <b>Low ΔH<sub>rxn</sub> amines</b> <b>Chilled Ammonia</b> <b>Nonaqueous solvents</b>	<b>Reactive SOLIDS</b>  <b>CaO</b> <b>Na<sub>2</sub>CO<sub>3</sub></b> <b>NaOH/CaO</b> <b>Li<sub>2</sub>O/Li<sub>2</sub>ZrO<sub>3</sub></b> <b>Li<sub>4</sub>SiO<sub>4</sub></b>	<b>ADSORPTION</b>  <b>ZEOLITES</b> <b>5A, 13X, MCM-41</b>  <b>CARBON,</b> <b>SILICA,</b> <b>ALUMINA</b> <b>Amine-doped</b> <b>Potassium salt-doped</b>	<b>MEMBRANES</b> <b>Gas/Liquid Contactors</b> <b>Permselective and high-temperature Polymers</b>  <b>BIOLOGICAL</b> <b>Algae (photosynthesis)</b> <b>Carbonic anhydrase (enzyme-catalyzed CO<sub>2</sub> hydrolysis)</b>  <b>EXPLORATORY ADSORPTION on self-assembling organic nanochannels, &amp; metal/organic frameworks</b> <b>ABSORPTION by polyamines, ionic liquids</b>

### 3.1 Absorption

In absorption (or “scrubbing”) flue gas is contacted with a liquid “absorbent” (or “solvent”) that has been selected because carbon dioxide dissolves in it more readily than nitrogen – i.e., it is *selective* for CO<sub>2</sub>. The process takes place in tall columns (“towers”) known as scrubbers, in which turbulent flow promotes rapid CO<sub>2</sub> transfer from gas to liquid. Differences in density make it easy to separate the emerging gas and liquid.

To recover the captured CO<sub>2</sub> the loaded solvent is pumped to a “stripper” in which it is exposed to hotter CO<sub>2</sub>-free gas, typically steam. Heating of the solvent causes desorption of the CO<sub>2</sub> (and traces of nitrogen). The stripped liquid is pumped back to the scrubber, while the steam/CO<sub>2</sub> mixture is cooled to condense the steam, leaving high-purity CO<sub>2</sub> suitable for compression and, after transportation to an appropriate site, sequestration.

The *capital* costs of scrubbing decrease as the *rates* of CO<sub>2</sub> absorption/stripping (“mass transfer”) increase. This is mainly because smaller absorbers and strippers – with correspondingly shorter gas/liquid exposure times - are required when CO<sub>2</sub> transfer rates are higher. *Operating* costs are also lower when the scrubber and the stripper are smaller because correspondingly less electrical energy is consumed as blower and pump *work* that drives the gas and liquid through them. However, the principal operating expense is for the energy consumed as *heat*, primarily to generate steam, but also to warm the loaded solvent.

Water itself is much more soluble to CO<sub>2</sub> than to N<sub>2</sub>. However, its *capacity* for CO<sub>2</sub> is still so low that capturing industrial-scale amounts of CO<sub>2</sub> would require the circulation of prohibitively large water flows. *Organic* solvents offer greater CO<sub>2</sub> solubilities and are, therefore, widely deployed to recover it, especially from high-pressure mixtures such as natural gas. However, the near-atmospheric pressures in coal-fired power plants favor use of aqueous solutions of chemicals that *react reversibly* with dissolved CO<sub>2</sub> – i.e., that combine with CO<sub>2</sub> in the scrubber and release it at the higher temperatures in the stripper.

Early systems for recovering CO<sub>2</sub> from industrial gas streams employed hot potassium carbonate solutions that react with dissolved CO<sub>2</sub> to form potassium bicarbonate. However, for many decades now the additives of choice have been *amines* (Kohl and Nielsen, 1997).

#### 3.1.1 Amines

Amines are water-soluble organic chemicals that contain reactive nitrogen atoms. As noted earlier, in CO<sub>2</sub> separation operations the workhorse amine is *monoethanolamine* (MEA). Many other amines and, especially in recent years, amine *blends* such as MEA plus methyldiethanolamine (MDEA), have also been utilized.

Amines react rapidly, selectively and reversibly with CO<sub>2</sub> and are relatively nonvolatile and inexpensive. However, they are corrosive and so require more expensive materials of construction. In addition, they do gradually volatilize (which can be especially problematic in the case of MEA) and they degrade, especially in the presence of oxygen

and/or sulfur dioxide, both of which phenomena necessitate the timely injection of fresh solution.

The considerable amounts of thermal energy required to strip CO<sub>2</sub> from loaded MEA solutions are an acceptable expense when the CO<sub>2</sub>-purged gas is valuable. However, as emphasized earlier, when MEA is applied to flue gas purification in conventional absorber/stripper systems, the parasitic energy consumption is considerable. As indicated in Table 1, the combined costs of CO<sub>2</sub> capture and compression raise the price of generating electrical power by over 60%. Reducing that percentage is a primary goal of R&D activity, much of which has been exploring the performance of alternative reactants including amines other than MEA (Bonenfant *et al.*, 2003). The results have been encouraging.

*Sterically hindered* amines have been developed that bind more CO<sub>2</sub> per molecule than MEA (Sartori and Savage, 1983). However, the energy savings relative to MEA are partially offset by capital cost increases for the larger scrubbing equipment that is necessitated by lower absorption *rates*. Alternatively, MEA has been blended either with amines that are less corrosive and require less steam to regenerate (Aroonwilas and Veawab, 2004), or with the additive piperazine (PZ) that is of limited solubility in water and more volatile than MEA but markedly accelerates CO<sub>2</sub> absorption and allows use of lower MEA concentrations (Dang and Rochelle, 2003).

Recent computer simulations indicate that alternative *design configurations*, including operation at multiple pressure levels, can reduce energy requirements for CO<sub>2</sub> capture with PZ+MEA and PZ+MDEA, followed by compression, to 20% of power plant output (Jassim and Rochelle, 2006; Oyenekan and Rochelle, 2007).

### **3.1.2 Ammonia**

Ammonia-based solutions offer possibilities for developing absorption processes based on less corrosive and more stable solvents. At the same time, since ammonia is a toxic gas, prevention of ammonia “slip” to the atmosphere is a necessity. Despite this disadvantage, considerable attention has been drawn to aqueous ammonia (AA) solutions by a decade-old report of superior CO<sub>2</sub> capture performance (Bai and Yeh, 1997). The CO<sub>2</sub> uptake per kg of ammonia is estimated to be 3 times that per kg of MEA (Yeh and Bai, 1999).

Furthermore, a recent economic study (Ciferno *et al.*, 2005) notes that the amount of steam required to regenerate AA (per kg of captured CO<sub>2</sub>) is 1/3 that required with MEA (see also Resnik *et al.*, 2004), and estimates that operating and capital costs with AA are, respectively, 15% and 20% less than with MEA. The projected costs of CO<sub>2</sub> capture and compression are only 18-21% of the total cost of electrical power production, which are comparable to the aforementioned calculated cost reductions obtainable via optimization of piperazine-based absorption process configuration.

Ammonia-based systems operate efficiently at lower temperatures than those required for conventional MEA-based scrubbing. The lower temperatures also minimize ammonia volatility and the potential for its slippage. The chemistry is for the most part analogous to that in potassium carbonate solutions, with ammonium ion replacing potassium ion: dissolved ammonium carbonate reacts with CO<sub>2</sub> to form ammonium bicarbonate. However, at the very low absorber temperatures of 0-10°C in the Chilled Ammonia process (CAP), ammonium bicarbonate precipitates as a solid, which requires different handling.

Because the reaction is reversible at lower temperatures than with amine-based solvents, low-quality waste heat available at power plants may be more thoroughly exploited to release captured CO<sub>2</sub> in the strippers of ammonia-based systems.

A further, potentially exploitable advantage is that, unlike MEA, which is degraded by SO<sub>2</sub>, ammonium carbonate reacts with SO<sub>2</sub> to form ammonium sulfate and with NO<sub>x</sub> to form ammonium nitrate, both of which are marketable as fertilizers. Thus, ammonia-based CO<sub>2</sub> capture may be carried out either separately from or simultaneously with the scrubbing of sulfur and nitrogen oxides.

In a demonstration facility with a startup scheduled for 2011, Powerspan is planning to capture CO<sub>2</sub> from a 120 MW power plant flue gas using an AA system that will be constructed downstream from AA-based SO<sub>x</sub>/NO<sub>x</sub> control equipment (McLarnon, 2007). Powerspan is currently operating a 20 tons CO<sub>2</sub> per day of pilot facility at FirstEnergy's R. E. Burger plant. Similarly, Alstom Power is testing a 35 tons CO<sub>2</sub> per day CAP-based facility at the We Energies Pleasant Prairie Power Plant.

There will be great interest in the extents to which laboratory and pilot scale successes – including capture and recycle of the toxic ammonia vapor generated in the stripper - are replicated at industrial scale. In the meantime, researchers are actively investigating techniques for further improving AA performance, including the use of additives that reduce evaporative ammonia losses without sacrificing CO<sub>2</sub> capture performance (You *et al.*, 2008).

## 3.2 Adsorption

### 3.2.1 Physical sorbents

Carbon dioxide may be recovered from flue gas with a variety of nonreactive sorbents including carbonaceous materials and crystalline materials known as zeolites. High porosities endow activated carbon and charcoal with CO<sub>2</sub> capture capacities of 10-15% by weight. However, their CO<sub>2</sub>/N<sub>2</sub> selectivities (*ca.* 10) are relatively low. Because of this disadvantage, the projected capture costs including that of compression are such that carbon-based systems become practical only when the required CO<sub>2</sub> purity is at most 90% (Radosz *et al.*, 2008). Zeolitic materials, on the other hand, offer CO<sub>2</sub>/N<sub>2</sub> selectivities 5-10 times greater than those of carbonaceous materials. However, their CO<sub>2</sub> capacities are 2-3 times lower (Konduru *et al.*, 2007; Merel *et al.*, 2008). Moreover, zeolite performance is impaired when water vapor is present.

To be competitive with liquid solvents, solid sorbents must be less sensitive to steam and offer substantially greater capacities and selectivities for CO<sub>2</sub> than currently available physical sorbents (Ho *et al.*, in press).

### 3.2.2 Chemical sorbents

When heated to 850°C, calcium carbonate (CaCO<sub>3</sub>, limestone) releases CO<sub>2</sub> (calcines) and thereby transforms to calcium oxide (CaO), which recombines with CO<sub>2</sub> at 650°C. These reactions have a long history of service in industrial processes. Limestone is also widely employed to capture flue gas SO<sub>2</sub>. However, it loses capacity over time and, especially if deployed to capture *both* CO<sub>2</sub> and SO<sub>2</sub>, requires frequent replacement (Rodriguez *et al.*, 2008).

The CaO/CaCO<sub>3</sub> system nonetheless remains attractive because of its high CO<sub>2</sub> capture capacity and long track record. Furthermore, it offers possibilities for power plant configurations that: (a) maximize the benefits of feeding otherwise prohibitively expensive oxygen rather than air (thereby obviating the need for post-combustion CO<sub>2</sub>/N<sub>2</sub> separation), (b) exploit the availability of high level heat, and (c) improve energy efficiency by generating steam from heat released in the carbonation reaction (Manovic and Anthony, 2008; Romeo *et al.*, 2008). Consequently, CaO/CaCO<sub>3</sub>-based CO<sub>2</sub> capture is the focus of continuing intensive research activity.

Alkali metal-based sorbents also capture CO<sub>2</sub>, primarily via reactions that transform metal carbonates into bicarbonates, with steam as a co-reactant as when CO<sub>2</sub> reacts with aqueous carbonate solutions. Highly porous sodium-based sorbents operate efficiently in the same temperature range as aqueous amines (25-120°C), but have considerably lower CO<sub>2</sub> capture capacity (Lee *et al.*, 2008). Lithium-based sorbents that function best at 400-500°C offer higher CO<sub>2</sub> capacities (Venegas *et al.*, 2007; Ochoa-Fernandez *et al.*, 2008). The long-term stability and performance of alkali metal-based sorbents under actual flue gas conditions remains to be established.

CO<sub>2</sub> capture by *amines immobilized within porous sorbents* has been an increasingly active area of research; a practical system has been deployed for CO<sub>2</sub> capture in a space mission life support system (Satyapal *et al.*, 2001). A variety of amines, sorbent supports and immobilizing techniques have been tested (Gray *et al.*, 2005; Knowles *et al.*, 2006; Hicks *et al.*, 2008; Yue *et al.*, 2008) and the results have been quite promising. Several amine-derived sorbents exhibit high CO<sub>2</sub> uptake/release capacity and stability in the 50-120°C range. Furthermore, the absence of large quantities of circulating water should make thermal energy requirements for CO<sub>2</sub> release appreciably lower than those of amine based absorption/stripping. As noted above regarding alkali metal-based sorbents, to be commercially viable, these sorbents must be shown to operate stably for extended periods under actual flue gas conditions

### 3.3 Membrane-based Separations

A third mature technology under consideration for CO<sub>2</sub> capture is membrane-based separation. Membranes, which generally consist of thin polymeric films, owe their selectivities to the relative rates at which chemical species permeate. Differences in permeation rates are generally due (in the case of *porous* membranes) to the relative sizes of the permeating molecules or (in the case of *dense* membranes) their solubilities and/or diffusion coefficients (i.e., mobilities) in the membrane material. Because permeation rates vary inversely with membrane thickness, membranes are made to be as thin as possible without compromising mechanical strength (which is frequently provided by non-selective, porous support layers).

As is true of membrane-based filtration and desalting of water, membrane-based gas separation is a well-established, mature technology. Many large plants are operating worldwide to recover oxygen and/or nitrogen from air, carbon dioxide from natural gas, and hydrogen from a variety of process streams. As is the case with true of absorption and adsorption, economic considerations dictate that membrane systems recover CO<sub>2</sub> from flue gas *selectively*.

Membrane permeation is generally *pressure*-driven – i.e., the feed gas is compressed and/or the permeate channel operates under vacuum and/or a sweep gas is employed. Due to the low partial pressure of CO<sub>2</sub> in the flue gas, this constitutes a major challenge for the membrane-based compared to liquid absorbents or solid adsorbents that are *thermally* regenerated (i.e., heated to strip the captured CO<sub>2</sub>).

#### 3.3.1 Polymeric Membranes

Recently, Favre and coworkers (Bounaer *et al.*, 2006; Favre, 2007) and Wiley and coworkers (Ho *et al.*, 2006, 2008) published the results of extensive calculations that explore the dependence of CO<sub>2</sub> capture costs on membrane selectivity, permeability and unit price. Most significantly, for membranes to be competitive with amine-based absorption for capturing CO<sub>2</sub> from flue gases, their CO<sub>2</sub>/N<sub>2</sub> selectivities (i.e., permeability ratios) must be in the 200 range.

With rare exception, the selectivities of available polymers fall well below that. While many have selectivities of 50-60, they tend to be less permeable, i.e. their fluxes are low (Powell and Qiao, 2006). Once again, cost effectiveness may be achievable only when separation is promoted by a CO<sub>2</sub>-selective chemical reaction.

Ho and coworkers (Zou and Ho, 2006; Huang *et al.*, 2008) have demonstrated that by virtue of their reversible reactions with CO<sub>2</sub>, amines can raise the CO<sub>2</sub>/N<sub>2</sub> selectivity of polymeric membranes to 170 while also boosting CO<sub>2</sub> fluxes. If these encouraging results are sustainable for extended periods of operation, such systems will merit serious consideration as candidates for CO<sub>2</sub> capture at coal-fired power plants.

### 3.4 Membrane Absorption

An alternative approach to CO<sub>2</sub> capture is to use porous membranes as *platforms for absorption and stripping*. In this embodiment, which has attracted considerable interest, membranes serve primarily to separate gas and liquid. Carbon dioxide and nitrogen each transfer easily through nonselective, gas-filled membrane pores. Selectivity is provided by the liquid, which, as usual, is typically an aqueous amine solution (deMontigny *et al.*, 2006; Shimada *et al.*, 2006). One advantage of this approach is that, unlike the case with conventional absorbers, with membrane absorbers there are no inherent restrictions to gas and liquid flowrates.

The performance, when measured in terms of mass transfer rates per unit module volume, can exceed those of absorption and stripping in conventional columns. Furthermore, modularity makes membrane systems easy to replace or expand. However, economies of scale do not apply to modular systems, whereas they do favor traditional, large absorption and stripping columns.

### 3.5 Biomimetic Approaches

In addition to absorption, adsorption and membrane-based systems, a wide variety of exploratory approaches are under development. Some that have shown promise take their cues from living systems that have evolved highly efficient systems for capturing and/or converting CO<sub>2</sub>.

There have been several exploratory studies of the use of the enzyme carbonic anhydrase, which is the most efficient catalyst of CO<sub>2</sub> reaction with water, to promote CO<sub>2</sub> scrubbing from flue gases (Bond *et al.*, 2001). By immobilizing carbonic anhydrase in a bioreactor, Bhattacharya *et al.* (2004) quadrupled the rate of CO<sub>2</sub> absorption in water.

Microalgae systems, which have long been under investigation for CO<sub>2</sub> capture from air (Cheng *et al.*, 2006), are especially attractive because *they consume* CO<sub>2</sub> in photosynthesis. This obviates the need for CO<sub>2</sub> compression and sequestration. Furthermore, the algae biomass can serve as animal feed or an effectively carbon-neutral fuel (Skjanes *et al.*, 2007).

### 3.6 Other Approaches

Another approach that has been proposed is to cool the flue gas to low temperatures so that the CO<sub>2</sub> is separated as dry ice (Younes *et al.*, 2006). After the initial paper, no further information has been forthcoming.

## 4. Advanced R&D Pathways

Current technologies for the recovery and separation of CO<sub>2</sub> and other compounds from gas streams (broadly classified into the three categories: absorption, adsorption, and membrane processes, as discussed above) are relatively mature. In almost all absorption and adsorption processes, the separation step entails the formation of molecular complexes, through physical and/or chemical interactions, that must then be reversed through significant increases in temperature. The concomitant need to heat large volumes of sorbents and subsequently to cool these materials to prepare them for the next sorption cycle is wasteful both thermodynamically (unnecessary heating and cooling of inert materials) and dynamically (large thermal mass of inert materials limits heat transfer rates leading to larger required equipment sizes).

While continued improvements in performance of the above technologies can be expected with further research and development, new concepts and materials could provide significant breakthroughs in the performance and costs of capture technologies. Advanced R&D pathways seek to eliminate or at least minimize these large thermal swings, through a greater reliance on structured materials, possibly stimuli-responsive, entropic (e.g., shape selective) rather than enthalpic interactions between the sorbate and the separations media, and through the application of stimuli, e.g., an electric field, to modify the separation environment in order to release the captured solute. Some of these promising new approaches are reviewed in this section.

### 4.1 Solid Adsorbents

The traditional use of carbonaceous materials for CO<sub>2</sub> adsorption is limited by low CO<sub>2</sub>/N<sub>2</sub> selectivities, and while the more structured zeolites have significantly higher selectivities, they have significantly lower capacities, and their performance is impaired when water vapor is present. Advanced research in the development of new adsorbent materials indicates some promising approaches that may overcome many of the limitations of the currently available adsorbents. Some of these approaches are discussed here.

#### 4.1.1 Metal-Organic Frameworks

Metal organic frameworks (MOFs) are porous crystalline solid materials with well-defined cavities that resemble those of zeolites (Millward and Yaghi, 2005; Bourelly *et al.*, 2005; Mueller *et al.*, 2006). They can be tuned to vary the cavity size, accessibility and interactions with molecules contained within the cavity. They are open structures with high capacities for gaseous species and have good diffusional properties. They may not always be sufficiently stable for the conditions under which they would need to be applied in flue gas treatment, however. More recently, nano-systems researchers at UCLA (Banerjee *et al.*, 2008; Wang *et al.*, 2008) have synthesized and screened a large number of zeolitic-type materials known as zeolitic imidazolate frameworks (ZIFs). A few of the ZIFs have been shown to have good chemical and thermal stability in water and in a number of different organic solvents, an advantage over traditional Si-based

zeolites, whose performance can be degraded in the presence of steam, for instance. CO<sub>2</sub> capacities of the ZIFs are high, and selectivity against CO and N<sub>2</sub> is good. As there is a great deal of flexibility in the kinds of ZIF structures that can be synthesized, it is likely the new materials with even better adsorption selectivity and capacity can be developed in this way.

#### **4.1.2 Functionalized Fibrous Matrices**

The need for both high capacity and fast diffusional response in adsorbents can be addressed by using chemically modified fibrous materials to show adsorptive selectivity and capacity for CO<sub>2</sub>. Li *et al.* (2008*a,b*) attached polyethylenimine to glass fiber matrices through appropriate coupling chemistry to develop an adsorbent with high CO<sub>2</sub> capacity that worked more effectively in a humid environment, and that could be completely regenerated at high temperature, without loss of performance.

#### **4.1.3 Poly (Ionic Liquids)**

A new class of solid adsorbents based on the polymerization of ionic liquids (these are discussed below) has been reported by Tang *et al.* (2005*a,b*). These polymers exhibited enhanced sorption capacity and rates relative to those observed for the room temperature ionic liquids. It was inferred from the results that the mechanism for the CO<sub>2</sub> capture was bulk absorption rather than surface adsorption. Bara *et al.* (2008) showed similar enhanced selectivity in polymerized ionic liquid gas separation membranes.

### **4.2 Structured Fluid Absorbents**

#### **4.2.1 CO<sub>2</sub> Hydrates**

Spencer (1999) and others have suggested that CO<sub>2</sub> hydrates be exploited for CCS, in which CO<sub>2</sub> is incorporated in the cages, or clathrates, formed by water molecules under high pressure (7 - 20 bar) and low temperatures (0 - 4°C), as dictated by thermodynamic constraints on the formation of these hydrates. Their concept was not to use the water hydrates as a recyclable absorption medium, although it is conceivable to do so, but rather to sequester directly the hydrate slurry. It has been reported more recently that tetrahydrofuran (THF) reduces the incipient equilibrium hydrate formation conditions, and a process has been described that involves three hydrate stages coupled with a membrane-based gas separation process at an operating pressure that is substantially less than the pressure required in the absence of THF (Linga *et al.*, 2007, 2008).

Compression costs were estimated to be reduced from 75 to 53% of the power produced for a typical 500 MW power plant. The importance of this work lies in the use of additives to enhance and expand the range of application of water clathrates, and points to possible new approaches for the design of suitable absorbents under more general conditions.

### 4.2.2 *Liquid Crystals*

While the concept of relying on the physical hosting of the solute in a structured cavity such as provided by CO<sub>2</sub> hydrates is appealing, the reliance on water as the clathrating agent restricts the accessible range of operating conditions for such processes, although this range can be expanded with the use of additives such as THF. Other structured materials such as liquid crystals, on the other hand, provide potentially more flexible stimuli-responsive sorbents for gas sorption purposes, as their operational temperature ranges can be tuned to be compatible with a given process. Liquid crystals constitute an unusual state of matter in that they can exhibit ordered crystalline-like structures with liquid-like properties over certain temperature ranges, but above a well-defined transition temperature convert to more traditional liquid phases. The restructuring of this phase can be achieved by a slight drop in temperature, or by the application of a suitable electric or magnetic field. As an example, Chen *et al.* (1993, 2000) and Hsueh *et al.* (1994) measured the physical absorption of CO<sub>2</sub> in films of a liquid crystal exposed to pure CO<sub>2</sub> over the temperature range spanning the solid to liquid phase transition. Their experimental results showed that the amount of CO<sub>2</sub> absorbed by the liquid crystalline phase is significantly less than that absorbed in the isotropic liquid. The liquid crystals can be ordered dramatically by very small changes in temperature (1°C) or, in principle, by the application of a strong electric field across the liquid crystal film. Furthermore, their reversibility on physical sorption and desorption of CO<sub>2</sub> with very small external perturbations showed a stimulus-responsive CO<sub>2</sub> separation. The gas solubility in conventional liquid crystals, however, is unacceptably low for CO<sub>2</sub> separation from flue gases, although it is comparable to the capacities exhibited by water clathrates. Note, however, that none of the work done to date on liquid crystals has been focused on using these systems for separations purposes, and thus there is ample scope for enhancing CO<sub>2</sub> capacities through appropriate design of the molecules. Means for the enhancement of CO<sub>2</sub> sorption capacities in liquid crystal systems are required, and advanced materials R&D in this area will require a strongly interdisciplinary approach, drawing on synthetic chemistry, physical characterization, and molecular modeling.

### 4.2.3 *Ionic Liquids*

Another area that has demonstrated great potential and in which there is currently a great deal of interest is the field of ionic liquids. Ionic liquids are organic salts with melting points usually near room temperature, below 100°C. An unexpectedly large solubility of CO<sub>2</sub> gas in ionic liquids was first reported by Blanchard *et al.* (1999) (see also Anthony *et al.*, 2002). Since then, a growing interest has developed in exploring and understanding the solubility of various gases in ionic liquids (Wu *et al.*, 2004; Anderson *et al.*, 2007). Recently, it has been reported that the CO<sub>2</sub> absorption and desorption rates in poly (ionic liquid)s are much faster than those in ionic liquids and the absorption/desorption is completely reversible (Anderson *et al.*, 2007; Tang *et al.*, 2005a,b). The gas absorption capacity of ionic liquids, both in monomeric and polymeric materials, depends on the chemical and molecular structure of the ionic liquids, especially the anions (Tang *et al.*, 2005a). In general, ionic liquids are characterized by extremely low vapor pressures, wide liquid ranges, non-flammability, thermal stability, tunable polarity, good electrolytic properties and easy recycling (Cadena *et al.*, 2004). These

attributes make them attractive candidate sorbents for CO<sub>2</sub> capture and separation from post-combustion flue gases from coal-fired power plants; however, desorption of CO<sub>2</sub> in ionic liquid media and regeneration of the sorbent require significant thermal energy (Trilla *et al.*, 2008). In addition, the viscosity of ionic liquids is relatively high, about 5-fold higher than that of a traditional aqueous solution of MEA (Meidersma *et al.*, 2007) and increases with CO<sub>2</sub> loading, leading to an additional energy penalty in pumping the sorbent.

### **4.3 Non-Thermal Regeneration Methods**

#### **4.3.1 Electrical Swing Adsorption**

Adsorption processes such as with activated carbon, zeolites and other mesoporous adsorbents are generally carried out in thermal swing operations where the adsorption occurs at a given temperature and the desorption and sorbent regeneration is achieved at a significantly higher temperature. Again, the thermal load adds to decreased efficiency of these capture processes. To overcome these issues, an isothermal Electrical Swing Adsorption process has been proposed (Judkins and Burchell, 1999*a,b*; Burchell *et al.*, 2002). Specifically, the adsorption media are selected to be electrically conductive such that when a power supply is applied across the matrix, a current passes through the matrix, with a resulting desorption of the adsorbed component. It has been claimed that the desorption is not through resistive heating of the matrix, but rather through a direct electrical effect on the sorbate-sorbent interactions, but no specific mechanisms have been advanced for such interactions. A similar process has been proposed for an electro-desorption compressor (Pfister *et al.*, 2003), in which the sorbate is adsorbed at a low pressure, and desorbed at a significantly greater pressure; again, it is claimed that the desorption reaction is essentially non-thermal. While much progress has been made in identifying sorbents with the appropriate electrical properties, it is still not clear what the mechanisms for the enhanced desorption processes are. Advanced research should focus on understanding these mechanisms and, once they are understood, on exploiting this understanding in the design of more effective adsorbents, with possibly more controlled stimuli-responsive properties. Molecular modeling could play a large role in such endeavors.

#### **4.3.2 Electrochemical Methods**

The electrochemical separation and concentration of CO<sub>2</sub> from a dilute gas mixture has been demonstrated using a benzoquinone as the carrier within a suitable solvent phase (either an organic solvent or an ionic liquid) (Scovazzo *et al.*, 2003). Specifically, CO<sub>2</sub> is able to bind efficiently to the benzoquinone in its reduced or charged state, but is released readily when the carrier is oxidized. This appears to be a promising approach for the post-combustion capture of CO<sub>2</sub> since it does not require significant heating and subsequent cooling of the sorbent phase for regeneration and preparation for the next sorption cycle, and there is ample opportunity for the development of new materials and processes based on such redox approaches. The redox-active carriers must be able to undergo reduction and oxidation in both the presence and absence of the sorbate, must exhibit the desired selectivity and capacity for CO<sub>2</sub> in the reduced state, with a significant

reduction in the capacity when the carrier is oxidized. The reaction kinetics should be sufficiently rapid that the reaction does not limit the overall sorption/desorption processes.

#### **4.4 Summary and Conclusions**

Advanced R&D on selective CO<sub>2</sub> capture is required to develop new separations aids that have high capacity and selectivity for CO<sub>2</sub> under the typical operating conditions found in flue gas emissions. One avenue of research will be the continued development of specialized adsorbents with finely controlled structure, such as uniform, well-defined cavities and pores, as found with MOFs and ZIFs, that can provide high selectivities and capacities for CO<sub>2</sub> in flue gases, while still being sufficiently robust to the presence of the other components, such as water vapor. The functionalization of adsorbent surfaces (e.g., fibrous matrices, etc.) to provide the desired separations capability and rates is also a target of opportunity for advanced R&D, while liquid phase absorbents such as ionic liquids will continue to be an active area of research, with the continuing goal of optimizing their physical as well as chemical properties. Another research area that deserves attention is the development of non-thermal methods (e.g., electric swing adsorption, electrochemical methods) for regeneration of the sorbents, liquid or solid, which will call for the development of new separation media that are more finely-tuned in their responses to externally-applied stimuli. These requirements pose stimulating challenges for the synthesis of new materials, aided most likely by detailed molecular modeling of sorbate/sorbent interactions, and for new integrative module designs that enable their effective implementation in a process environment.

## 5. RD&D Recommendations

From the above review of post-combustion capture technologies, one can make a few observations:

- In theory, there are many approaches to post-combustion capture.
- The state of development of these various approaches varies widely.
- If one had to deploy the technology today, the only real option is a chemical absorption process (e.g., scrubbing with amines or ammonia).

In giving RD&D recommendations, it is important to articulate the program goals. For CCS in general (and post-combustion capture in particular) program goals should include both near-term solutions (which can help with development of a commercial technology market in which CCS responds to legislative mandates or carbon costs) and longer-term, improved solutions (which can enable deeper reductions at less pronounced costs). In some discussions, the near-term and longer-term solutions are considered at opposite ends of the RD&D spectra, and both have strong proponents today. However, the reality going forward is that a robust CCS RD&D program will both respond to the shorter-term needs and anticipate the longer-term by creating and maintaining an RD&D pipeline that begins with basic research and ends with commercial demonstrations for worthy technologies.

Since strong rational arguments can be made for each emphasis on either the shorter-term or longer-term scenarios, we recommend that the viewpoints implied by each of them be considered in putting together a research portfolio. This includes activities aimed at “technology readiness” (so the technology can provide a significant amount of emissions reduction) as well as activities aimed at significant cost reductions (through high risk, high reward projects). In other words, *it is essential to develop a portfolio approach for post-combustion capture RD&D.*

In order to provide a solid basis for this portfolio R&D approach we recommend development of a national statistical database describing features of the existing U.S. coal fleet that are most relevant to assessment of post-combustion capture technology. This database might draw on data currently provided to US EPA, US DOE, FERC, and other organizations, but should include, at a minimum, a statistical representation of the current coal fleet in terms of flue gas temperature, moisture, CO<sub>2</sub>, oxygen and sulfur dioxide concentrations, steam cycle and steam turbine parameters, as well as metrics for physical space available at the plant site for retrofit equipment and metrics for local electrical system reserve margin or excess capacity. This information would feed into the portfolio approach, which we envision as a research pipeline.

For convenience, we divide the pipeline into 4 sections:

- *Exploratory research* will feed the pipeline. Much of the technologies described in section 4 fall into this category. Since many of these technologies are high risk, high reward, the number of projects in this part of the pipeline should be the

- ***Proof of concept research*** is the next stage of the pipeline. Projects where the exploratory research looks promising will be expected to proceed to this stage. The goal of this phase of the research is to understand whether the technology under consideration is appropriate for the task of post-combustion capture. Activities may include laboratory work to synthesize materials, measurements of basic properties, and analysis of behavior in realistic environments (such as those found at power plants). This is a key stage in the pipeline, in that it becomes much more expensive to move a project to the next stage (pilot plants). The more work done at the proof of concept stage raises the odds that the next stage will be successful if one decides to move forward.
- ***Pilot scale testing*** is the next part of the pipeline. The size of these pilot projects will typically be on the MW or tens of MW scale, so individual project costs can rise significantly. For example, Vattenfall’s 30 MW<sub>th</sub> pilot plant for oxy-combustion capture cost about \$100 million.
- ***Demonstration projects*** are the final stage of the pipeline. The scale of a demonstration project is typically 100s of MW and costs could easily exceed a billion dollars per project. At least a few demonstration projects are needed before the technology can claim “commercial readiness”. These demonstration projects will need to absorb (and hopefully eliminate) first mover costs and will set a baseline for cost and performance of future commercial plants.

***In parallel with the RD&D pipeline, there is a need for competent, objective, and independent analysis of the various technologies in the pipeline.*** Money for RD&D is always limited, and good analysis tools can help inform what areas look the most promising. This is especially important in the early stages of the pipeline, where one will be limited in the number of technologies to promote to the relatively expensive pilot plant stage.

While having good, independent analytic tools sound like an obvious component, it is usually hard to implement. In many cases, we are asking the analysis to compare apples to oranges to grapefruits. Secondly, most of the data going into these models are from the technology developers, who want to show their technology in the best light. Therefore, we recommend doing this analysis at a very fundamental level – having it be a gatekeeper (rather than ranking the processes). Here are some key components that should be required:

- Energy and mass balances. These are the bases for all processes. Yet, in reading the literature, we are amazed at the claims made about new processes in which no energy and mass balances are provided.

- How does the process match the design criteria? For post-combustion capture, processes need to work well at atmospheric pressures and relatively low CO<sub>2</sub> concentrations (i.e., 5-15% by vol.). We need to understand how the processes deal with the impurities in flue gas, including SO<sub>x</sub>, NO<sub>x</sub>, oxygen, and water, as well as trace amounts of metals, chlorides, and particulate matter. Estimates need to be made of the recoveries of and selectivities for CO<sub>2</sub> that can be expected.
- In the power industry, processes with high availability are critical. Therefore, it is important to understand the robustness and the operability of a process.
- In this early stage, costs should not be considered major decision criteria. Any cost estimates for a process at an early stage of development are highly uncertain. However, some basis should be provided for assuming that it will be feasible for the process to be cost-effective.
- Preliminary lifecycle impacts analysis. A preliminary ‘fatal-flaw’ analysis should be performed to assess whether each process has potential for more than niche deployment given critical raw materials or manufacturing constraints, or potential environmental or social impacts.

We can now combine the above framework with the technology assessments supplied earlier to see what the post-combustion capture RD&D pipeline looks like today. We’ll start at the demonstration project end and work backwards.

- **Demonstration projects.** The G8 has stated a goal of 20 CCS demonstration projects worldwide completed by 2020 (includes post-, pre-, and oxy-combustion, as well as capture from non-power sources). However, in terms of CCS from a power plant, we are still waiting for demonstration project #1. One of the proposed demonstration projects furthest along in its planning, a project in the UK, calls for post-combustion capture. From the project web site<sup>4</sup>: *The Government selected post-combustion capture on coal for the demonstration project as it is most likely to have the biggest impact on global CO<sub>2</sub> emissions and because it can be retrofitted once the technology has been successfully demonstrated at a commercial-scale.* The current timeline shows a start date of the demonstration plant as 2014. In the near-term, it seems almost a certainty that any demonstration project involving post-combustion capture will need to be based on chemical absorption technology. In the US, the recently passed stimulus package contains money for CCS demonstration projects, while in Europe, revenues from 300 million permits from the European Trading System have been reserved to fund CCS demonstrations.
- **Pilot plants.** At present, pilot activity is focused on testing alternative solvents. At GHGT-9, several groups presented papers reporting pilot activities involving various forms of amines, including CSIRO from Australia (Cottrell *et al.*, 2008), MHI in Japan (Kishimoto *et al.*, 2008), the University of Regina in Canada (Idem *et al.*, 2008), and the EU CASTOR project in Denmark (Knudsen *et al.*, 2008). Alstom and EPRI reported that a 35 tonnes/day of CO<sub>2</sub> chilled ammonia process

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<sup>4</sup> <http://www.berr.gov.uk/whatwedo/energy/sources/sustainable/ccs/ccs-demo/page40961.html>

pilot plant was in operation at the We Energies Pleasant Prairie Power Plant in Wisconsin (Kozak *et al.*, 2008). In addition, Powerspan reported that a 20 tonnes/day of CO<sub>2</sub> pilot plant based on their ammonia process (the ECO<sub>2</sub> process) was nearing completion at FirstEnergy's R.E. Burger Plant in Shadyside, OH (McLarnon and Duncan, 2008). Beyond these chemical absorption technologies, there do not seem to be obvious candidates for new pilot tests in the pipeline at this time.

- ***Proof of Concept.*** There are a large number of technologies being examined at this stage. As described earlier, they include the categories of adsorption, membrane-based separations, biomimetic approaches, as well as advanced approaches looking at new materials (e.g., liquid crystals, ionic liquids or metal organic frameworks) incorporating new designs (e.g., electric swing). However, while a broad range of technologies are being researched, it seems that increased effort (e.g., more funds, more relevant expertise) is needed in this area. This statement is based on the observation that while many technologies are being investigated, at present there are very few candidates ready to advance to the pilot stage.
- ***Exploratory Research.*** This is the research that feeds the pipeline. It is encouraging that a number of new concepts and technologies have recently been considered for post-combustion capture. However, this is just a start and more interest needs to be generated in the basic science community to consider new technologies and approaches for post-combustion capture. Not only is it important to attract new ideas, but it is also important to attract the leading researchers in their field. Having the best researchers lead the effort greatly improves the chance of success. Therefore, it is important to create programs that will attract these world-class researchers.

To reduce program costs, to accelerate technology development, and to ensure that post-combustion capture technology is available globally when and where it is needed, we suggest that some of these RD&D efforts (including demonstrations) might be conducted in cooperation with developing economies such as China and India. In those countries new coal plants are being built at an astonishing rate, and the costs for construction (and RD&D) are significantly lower than in the US. In fact, in some respects, low-carbon energy technology is advancing faster overseas than in the U.S. (witness the GreenGen IGCC under construction with carbon capture in China today, and the large-scale CO<sub>2</sub> geological sequestration effort likely to commence in the near term at a Shenhua coal facility in China). Consideration of a US RD&D program for post-combustion capture as part of a global cooperative endeavor therefore is recommended.

Our conclusions and recommendations on the current status of post-combustion capture technology are:

- A portfolio approach to RD&D, developed in an international context, is required.

- Only chemical absorption technologies are well enough developed to be considered for demonstration.
- Reducing the parasitic energy load is a critical research goal.
- There is a big gap in the RD&D pipeline in the moving of technologies from proof of concept stage to pilot plant stage. Efforts should be focused to close this gap. One strategy to address this gap is to engage experts who have relevant expertise, but that are currently outside the CCS research community.
- Demonstrations are important beyond their immediate goals (i.e., to demonstrate a technology). They give visibility and credibility to the field and can be used to inspire new ideas and new researchers.
- Most technologies currently in the RD&D pipeline will fail. Therefore it is critical to keep feeding the pipeline with new ideas and new researchers to increase the overall chances of success.
- To help make informed decisions along the way, there is a need to develop competent, objective, and independent analysis methodologies for evaluating the various technologies in the pipeline.

The final question is what the cost of this program will be. We estimate the cost of an 8-10 year research program in Table 2 below. Note that this is total cost of program, including research funds from both the private and public sector. Also note that it for only post-combustion capture technology – a complete CCS budget would also need to address other capture approaches (i.e., pre-combustion, oxy-combustion), as well as transport and storage.

**Table 2.** Estimated cost of an 8-10 year US post-combustion research effort.

<b>Component</b>	<b># of projects</b>	<b>Cost per project (millions of \$)</b>	<b>Total Cost (millions of \$)</b>
Demonstration	5	750 (500-1000)	3750
Pilot Plants	15	50 (25-100)	750
Proof of Concept	30	10	300
Exploratory Research	50	1	50
Simulation/analysis			100
Contingency			1000
<b>TOTAL</b>			<b>5950</b>

The basis for these estimates is as follows:

- ***Demonstration project.*** This cost per project number is an order of magnitude estimate for a demonstration plant based on estimates from the *The Future of Coal* (MIT, 2007) the experience of FutureGen, and other estimates. Of course, the exact details of what a demonstration looks like can vary widely, as would costs. We envision both retrofit and, potentially, new power plants in the 200-300 MW range that capture about 60% of the exhaust CO<sub>2</sub> (to give the plant parity with emissions from a natural gas power plant, see Hildebrand and Herzog, 2008).

- ***Pilot plants.*** Pilot plant activity today includes plants sized to process flue gas associated with 1-5 MW of electricity production, as well as plants sized to process flue gas associated with 10's of MW of electricity production. Many technologies have pilot plants built at both scales. Therefore, we anticipate the need for about 15 pilot plant tests. The cost range is attributed to the different size of pilot plants to be built. Many of these would be constructed as slip stream retrofits to existing installations.
- ***Proof of Concept.*** The cost of these projects will be variable – some may be only a few million, while others could be \$20 million or more. Our estimate is based on what a reasonable average cost might be.
- ***Exploratory Research.*** We feel it is important to cast a wide net, so we encourage funding many of these projects. After spending about \$1 million, enough information should be generated to decide whether it is worthwhile to move to the proof of concept stage.
- ***Simulation/analysis.*** The *Future of Coal Study* suggested \$50 million dollars per year on this task to cover all parts of CCS technology. Based on this estimate, we scaled it down to a level for post-combustion capture technologies only.
- ***Contingency.*** Because of the uncertainty in the estimates (and in future prices), we have included a 20% contingency.

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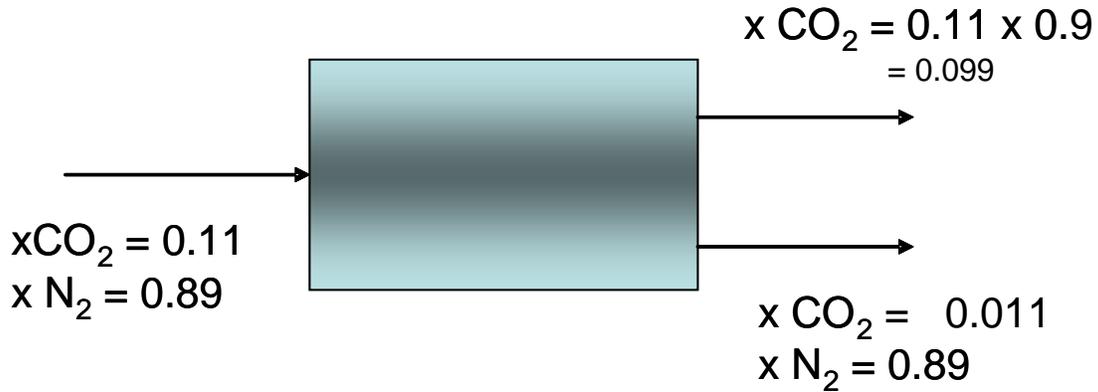
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## Appendix A. Minimum Work Calculation



### *Ideal work of separation:*

Consider 1 mole of gas containing 11% CO<sub>2</sub> and 89% N<sub>2</sub>. We will assume separation at 298 K and assume 90% capture of CO<sub>2</sub>.

For a steady flow system, we have the minimum thermodynamic work as:

$$W_{\min} = W_{\text{flue gas}} - W_{CO_2} - W_{N_2}$$

$$W_{\min,FG} = -RT \left( \frac{x_{CO_2}}{x_{CO_2} + x_{N_2}} \ln \left( \frac{x_{CO_2}}{x_{CO_2} + x_{N_2}} \right) + \frac{x_{N_2}}{x_{CO_2} + x_{N_2}} \ln \left( \frac{x_{N_2}}{x_{CO_2} + x_{N_2}} \right) \right)$$

$$W_{\min,FG} = -8.314 \times 298 \times (0.11 \ln 0.11 + 0.89 \ln 0.89)$$

$$W_{\min,FG} = 0.859 \text{ kJ/gmol flue gas}$$

$$W_{\min,CO_2} = 0 \text{ since it is a pure stream}$$

$$W_{\min,N_2} = -RT \left( \frac{x_{CO_2}}{x_{CO_2} + x_{N_2}} \ln \left( \frac{x_{CO_2}}{x_{CO_2} + x_{N_2}} \right) + \frac{x_{N_2}}{x_{CO_2} + x_{N_2}} \ln \left( \frac{x_{N_2}}{x_{CO_2} + x_{N_2}} \right) \right)$$

$$W_{\min,N_2} = -8.314 \times 298 \left( \frac{0.011}{0.011 + 0.89} \ln \left( \frac{0.011}{0.011 + 0.89} \right) + \frac{0.89}{0.011 + 0.89} \ln \left( \frac{0.89}{0.011 + 0.89} \right) \right)$$

$$W_{\min,N_2} = 0.163 \text{ kJ/0.901 gmol FG}$$

$$= 0.181 \text{ kJ/gmol FG}$$

$$W_{\min} = 0.859 - 0.181$$

$$= 0.678 \text{ kJ/gmol FG}$$

Since 90% CO<sub>2</sub> is captured i.e.  $0.9 \times 0.11 = 0.099$  gmol CO<sub>2</sub>/gmol flue gas  
W min, normalized = 6.85 kJ/ gmol CO<sub>2</sub> = 0.001904 kWh/ gmol CO<sub>2</sub> = 43 kWh/tonne  
CO<sub>2</sub> captured

The above result holds for 90% capture.

***Ideal work of compression:***

Work of compression = Availability at 110 bar – Availability at 1 bar

From NIST webbook

Temperature (K)	Pressure (bar)	H (kJ/mol)	S (J/mol-k)
298	1	22.257	120.54
298	110	11.166	50.979

Availability = H – TS

At 1 bar, availability = -13.664

At 110 bar, availability = -4.0257

Work of compression = 9.638 kJ/mol = 61 kWh/t CO<sub>2</sub> compressed

***Power plant work:***

From the MIT Coal Study:

SCPC plant

500 MW

415t CO<sub>2</sub>/hr

500000kW/415 t/hr = 1200 kWh/t CO<sub>2</sub> produced