

Appendix E

Post Combustion Advanced CO₂ Capture Processes Review A Final Phase IV Report Prepared by Electric Power Research Institute, July 2014

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Post Combustion Advanced CO₂ Capture Processes Review

1. Background

Since 2006, the Generation Sector of the Electric Power Research Institute (EPRI) has been conducting an on-going, comprehensive effort to investigate the field of emerging technologies for capturing carbon dioxide (CO₂) from post-combustion flue gas. The Canadian Clean Power Coalition (CCPC) has entered into a contract with EPRI to provide them updated information on 21 processes. This report is a summary of that effort. The assessment of the individual technologies listed below remains confidential.

The processes summarized in this report were selected in cooperation with the CCPC, and the summaries included in this report reflect that selection. The processes are presented in the same format as the database entries in the EPRI CO₂ Capture Database. They consist of 21 developing processes generally at early stages of development: Advanced Solvents (7), Adsorbents (7), Membranes (4), Cryogenic (2) and Calcium Looping (1).

The specific processes are listed below:

- **Advanced Solvents**
 - 3H Company, LLC: Self-concentrating solvent
 - Dupont: Advanced amine-based solvent
 - Cefco Global: Potassium carbonate, shockwaves
 - CO₂ Solutions: Enzyme-enhanced solvent
 - Codexis: Enzyme development
 - Ion Engineering: RTIL solvent
 - University of Notre Dame: Ionic liquids
- **Adsorbents**
 - ADA-ES: Adsorbents and process concept
 - Cachys: Metal carbonate salt
 - Innosepra: Proprietary adsorbent
 - InvenTyS: Veloxotherm (activated carbon adsorbent)
 - SRI International: Carbon-based sorbent
 - TDA Research: Alkalized Alumina
 - University of California at Berkeley: MOFs
- **Membranes**
 - GTI: Hybrid membranes
 - MTR: Polaris membrane
 - RTI International: Hollow fiber polymeric membranes
 - University of Colorado: Gelled ionic liquid membrane
- **Cryogenic**
 - ATK: Inertial CO₂ Extraction System (ICES)
 - Sustainable Energy Solutions: Cryogenic CO₂ Capture
- **Calcium Looping**
 - Several researchers

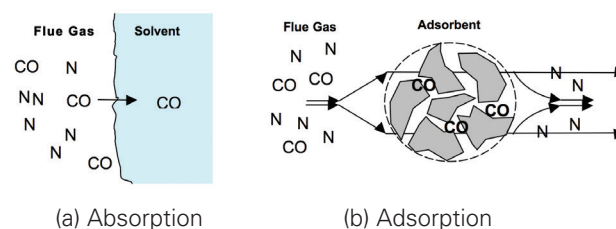
2. CO₂ Capture Technology Basics

CO₂ capture refers to separation of carbon dioxide from the remaining constituents of flue gas. Many separation technologies are mature and widely applied in the chemical, petroleum and other industries. In some cases, these technologies form the core of the entire industry itself. For CO₂, the vast majority of capture approaches rely on traditional separations technologies: absorption, adsorption and membranes. These and other approaches are discussed broadly in this Appendix.

2.1. Absorption

Absorption refers to the uptake of CO₂ into the bulk phase of another material—for example, dissolving CO₂ molecules into a liquid solution. This contrasts to adsorption, where CO₂ molecules adhere to the interior and exterior surface of a solid particle (see Figure 1). Although absorption and adsorption both rely on chemical and physical interactions between CO₂ and a separating material (solution or solid) to selectively separate CO₂ from the other constituents in flue gas, the interaction, mathematical treatment and process configurations differ. Both processes are used widely in the chemical, petrochemical and other industries, with absorption being more common than adsorption.

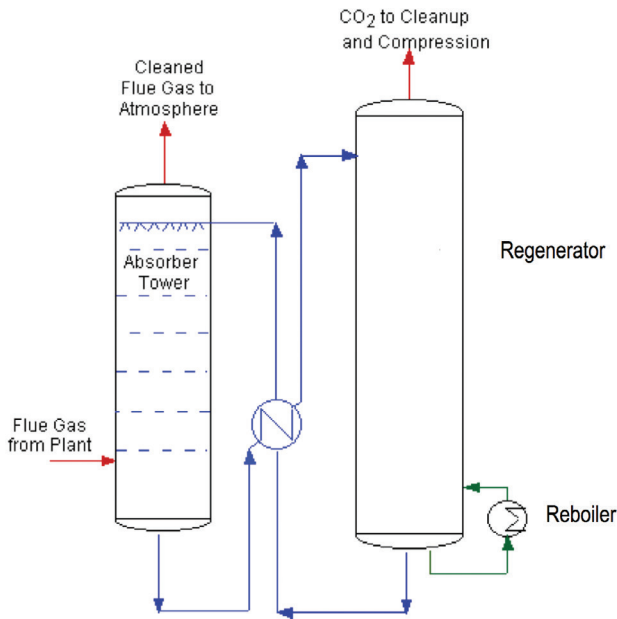
Figure 1: Absorption and Adsorption of CO₂



(a) Absorption refers to CO₂ dissolving in a liquid solution. (b) Adsorption refers to CO₂ adhering onto exterior and interior surfaces of a solid particle.

Figure 2 shows a typical process configuration employing an absorber. Flue gas and the liquid absorption solution contact each other in a column that provides interfacial area between the gas and liquid phases. The separation of CO₂ from flue gas occurs primarily through the high solubility of CO₂ in the solution relative to that of other flue gas constituents. The CO₂-loaded solution is then sent to a regenerator, where it is typically heated to liberate CO₂ from the solution. The warm, CO₂-lean solution is sent to a heat exchanger and then back to the absorber for reuse.

Figure 2: Absorption Process



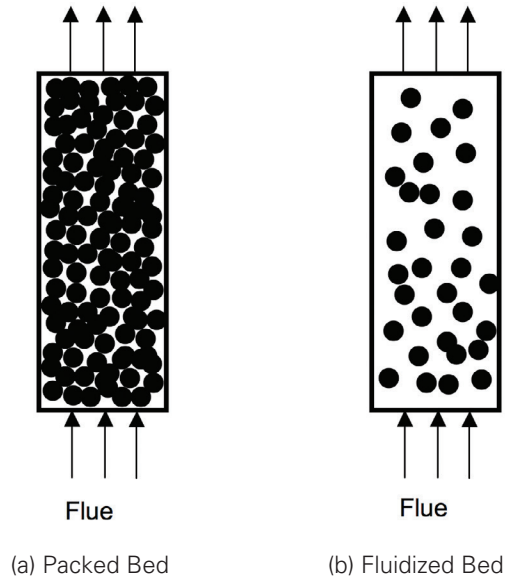
Flue gas is contacted with a solution that selectively absorbs CO_2 in a tower. The CO_2 -containing solution is then sent to a regenerator column where it is heated to desorb the CO_2 from the solution.

2.2. Adsorption

Adsorption refers to uptake of CO_2 molecules onto the surface of another material, to which they adhere via weaker Van der Waals forces (physisorption) or stronger covalent bonding (chemisorption). This contrasts to absorption, where CO_2 molecules dissolve into the bulk of the material itself, also using Van der Waals or covalent bonding.

Adsorption processes can be implemented several different ways. The most common are packed beds and fluidized beds, as shown in Figure 3. In a packed bed, adsorbent is loaded into a column and flue gas flows through the void spaces between the adsorbent particles. In fluidized beds, flue gas flows at higher velocities such that the adsorbent particles are suspended in the gas flow. In both approaches, the adsorbent selectively adsorbs more CO_2 relative to the other constituents passing through the column.

Figure 3: Adsorption Processes



(a) In a packed bed, flue gas flows through the interstitial spaces between adsorbent particles packed tightly in a column. (b) In a fluidized bed, flue gas flows at sufficiently high velocities to suspend the adsorbent particles within the column.

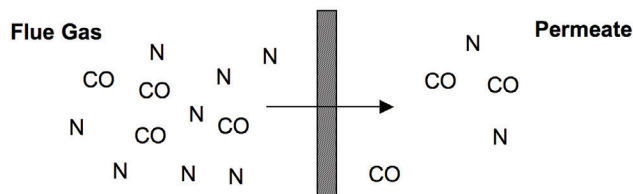
During operation, particles in a packed bed gradually become saturated with CO_2 and are unable to adsorb more, after which CO_2 “breaks through” the bed. In practice, feed gas flow is switched to a second packed bed before the first becomes fully saturated. While this second bed is being loaded, the first bed is regenerated by heating the adsorbent or lowering the pressure to release the adsorbed CO_2 , which then exits the column. The cycle is then repeated. This cyclic process can be operated so that CO_2 is continually removed from flue gas and is commonly referred to as Pressure Swing Adsorption (PSA), Vacuum Swing Adsorption (VSA), or Temperature Swing Adsorption (TSA), depending on which approach is used to regenerate the bed. The adsorbent properties and mass transfer coefficients dictate the process design and how effectively CO_2 is separated from flue gas.

The CO_2 -loaded adsorbent can also be regenerated in a fluidized bed. In general, a portion or all of the saturated solids in the bed are removed, regenerated by temperature or pressure, and fed back into the reactor. Note that in either process, the energy for separation in adsorption comes from changes in temperature or pressure imposed on the adsorbent when operating in a cyclic process.

2.3. Membranes

Membranes can separate CO₂ from flue gas because the transport speed of a gas constituent through the membrane is related to its solubility in the membrane material (analogous to solubility in a liquid solvent) and its diffusivity through the membrane material. If CO₂ has a higher solubility in the membrane or has a higher diffusion coefficient than other constituents of flue gas, then CO₂ preferentially permeates it. Figure 4 shows a schematic. In some cases, chemical agents that selectively react with CO₂ are added to the membrane to facilitate CO₂ transport.

Figure 4: Membrane



Flue gas is contacted with a membrane that selectively transports CO₂.

CO₂ will transport across a membrane only if the partial pressure of CO₂ is higher on the side of the membrane that contacts the flue gas than on the other. A partial pressure gradient of CO₂ can be obtained by pressurizing the flue gas on one side of the membrane, applying a vacuum on the other side of the membrane, or both. In effect, this pressure differential supplies the energy for separation.

2.4. Cryogenic Processes

Cryogenic CO₂ capture is the separation of CO₂ from a gas stream via chilling of the gas stream to the point that solid CO₂ forms and can be collected. Because the CO₂ is captured as a solid, the majority of the compression can then be accomplished by heating the CO₂ back up to the gaseous state within a fixed volume and does not require significant compression equipment or energy. Cryogenic carbon capture does not require a chemical separation or separation material that has to interact with the CO₂. Instead, the main consideration is the efficient and effective heat transfer to chill the gas stream to the point that CO₂ undergoes deposition and forms a solid that can be collected as well as the collection of that solid.

Unlike traditional cryogenic processes, such as cryogenic distillation of air in which the chilled products are liquid, CO₂ forms a solid when chilled below its triple-point pressure of 5.1 bar. This means that traditional heat-transfer exchangers cannot be used because of the formation of solid buildup on the cold surfaces. Instead, the CO₂-containing stream must be cooled using alternate cooling methods. The development of alternate cooling and chilling methods are the primary research activities in the area of cryogenic CO₂ capture. Some of the methods that have been proposed include using a chilled liquid as the heat transfer medium, chilling the CO₂ stream through expansion in a turbine, and chilling the CO₂ stream through expansion and acceleration to supersonic speeds.

There are several advantages to cryogenic CO₂ capture. Because the CO₂ is captured as a solid, the need for significant compression is eliminated. Further, cryogenic capture requires only electrical input, not steam, which means that there does not have to be any modification of the steam cycle or power plant operation with the addition of cryogenic capture. Another benefit is that there is no separation medium that comes into contact with the flue gas that can be poisoned or that needs to be replaced, potentially making operation simpler. With additional testing, the claims that the energy penalty can be significantly lowered through heat integration in cryogenic CCS can also be evaluated.

There are also several drawbacks to cryogenic capture. Currently cryogenic CCS is a fairly new technology, and many of the system integrations and full demonstrations have not been tested at a meaningful scale. In addition, because CO₂ capture from a gas stream through deposition is a new and complex issue, seemingly simple solutions may require additional process or integration steps to become technically feasible. In order to prevent ice and moisture formation, the flue gas stream must be dehydrated prior to cryogenic capture. Also, because the entire energy requirement is supplied via electricity as opposed to low grade steam, the energy impact on the power plant may be higher than other processes. Often cryogenic processes rely on extensive heat integration, which makes start up and shutdown potentially difficult.

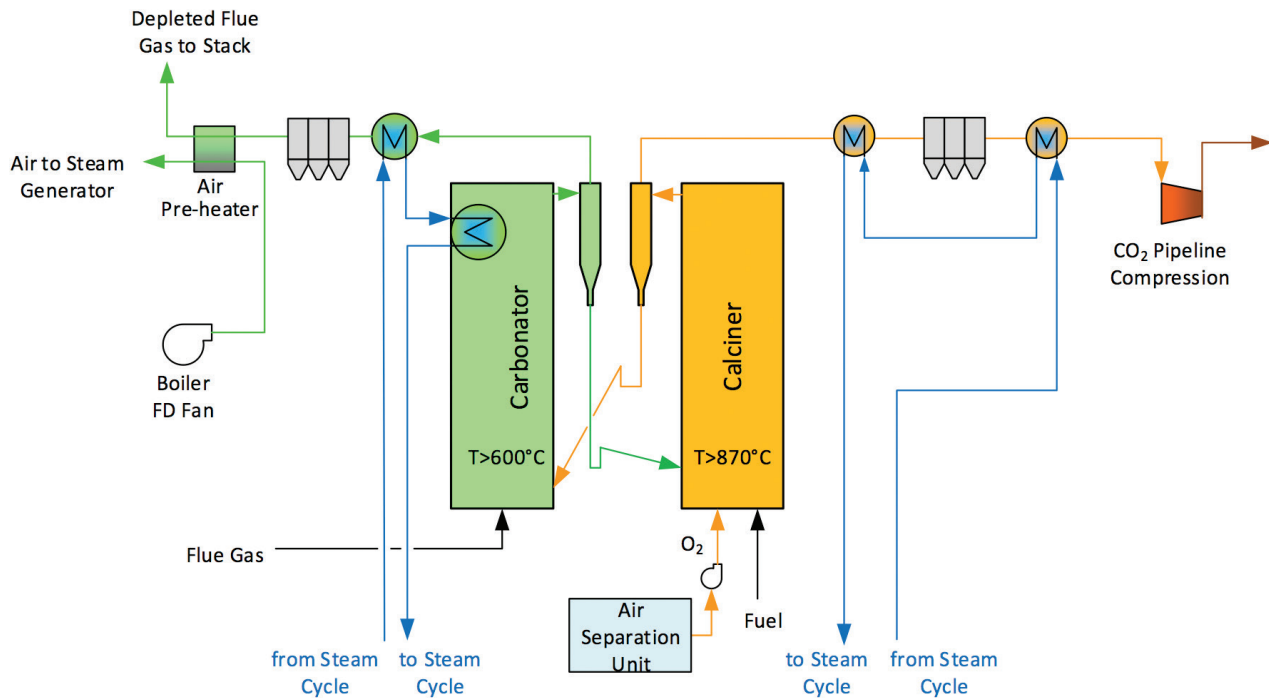
2.5. Calcium Looping

CO₂ is chemically captured by reaction with lime (CaO) at temperatures above about 600°C (1110°F). The calcium carbonate formed is then calcined at a temperature above about 870°C (1600°F). A flow schematic is shown in Figure 5. Particular features of this process:

- The reactors are likely to be circulating fluidized beds similar to CFBC boilers in common use.
- The heat of calcination is supplied by an oxy-fuel flame to avoid diluting the product CO₂ with atmospheric nitrogen.

- The high temperatures dictate careful integration with the steam generation process to ensure that thermal energy is recovered to the steam side at usefully high temperatures.
- In an optimal thermal design, the energy cost for CO₂ capture will largely come from two sources: auxiliary power used in the air separation unit serving the calciner, and exergy losses from the temperature difference between calcination and carbonation. The former reduces net power directly. The latter produces a subtle effect in how heat is transferred from the gas side to the steam side and may be a minimal effect as both calciner and carbonator operate at or above steam temperatures in common use.

Figure 5: Calcium Looping CO₂ Capture Process Schematic



3. Status of Post-Combustion CO₂ Capture Technologies

Post-combustion CO₂ capture refers to the separation of CO₂ from flue gases. Common technologies for separating CO₂ are absorbents (solvents), adsorbents (solids) and membranes. A review of these technologies is provided in Appendix D.

3.1. Absorption (Solvents)

Of all major separation processes, absorption is essentially mature from a process perspective. Absorption processes are common in the chemical process industries, and there is significant commercial experience with their operation. This stems from the fact that absorption processes are generally less expensive for large-scale separations, easier to operate and more robust than other processes. Additionally, compared to solids, solvents offer more opportunities to exploit chemical differences in components of a mixture in order to separate them. As a result, all of the more-developed CO₂ capture processes are solvent based. Example processes and products include aqueous monoethanolamine (MEA), Fluor's Econamine Plus, Mitsubishi's KM-CDR, Cansolv's CO₂ capture process and Alstom's chilled ammonia process.

During the period of this study, we observed no breakthrough developments in solvent-based CO₂ capture processes. In aqueous solvents, no new classes of chemistries were introduced. The existing approach of reacting the acidic CO₂ with a basic nitrogen atom in aqueous solutions of amines, ammonia and amino acids has largely continued. Process developers rarely disclose their specific chemistry, but most will identify the class of chemistry, e.g., primary amines, secondary amines, blends, etc. Though these chemistries have been widely studied already and keep advancing, they offer only incremental gains over each other. Additional incremental gains are offered by improvements in process design. Like the chemistry counterparts, these process improvements also tend to be proprietary. Still, because of widespread use of absorption processes, even such incremental advances are commercially significant.

Other solvents include non-aqueous ones such as ionic liquids or phase separation materials. They offer potential advantages of reduced regeneration energy consumption and are being developed at largely academic institutions or very small companies. The major challenges include little operational data of such systems at large scales even in other industries, their potential cost and a longer time needed to achieve commercial scale. There are vast numbers of such chemistries possible, as in the case of ionic liquids, and the challenge is often which subset to focus on. Water in flue gas can also sometimes reduce the performance of such non-aqueous solvents. Other challenges could include high viscosity, slower kinetics and a potential high cost. Overcoming these challenges is a part of the ongoing research activity at various institutions.

Remaining approaches to absorption, which have a longer path to commercialization, involve changing the absorption chemistry itself or using promoters (catalysts) to enhance the rate of absorption, a common one being the use of carbonic anhydrase as a catalyst to increase the kinetics of aqueous CO₂ reactions. Most of these are at early-lab scale testing. All of these remaining approaches also aim to reduce the energy of regeneration, while some offer the additional advantage of potentially reducing the gas-liquid contactor volume.

3.2. Adsorption (Solids)

Adsorption is less commonly practiced in the chemical process industry. Because adsorption can be used in different process configurations, both adsorbent properties and process design can strongly influence the effectiveness of a separation. Consequently, developing adsorption processes for very large-scale CO₂ capture requires development of both adsorbent materials and corresponding processes.

Adsorbents being developed for CO₂ capture exhibit a variety of origins, characteristics and chemistries. EPRI's own work has characterized a class of adsorbents in collaboration with University of California at Berkeley, Lawrence Livermore National Labs and Rice University.¹ Based on this work, we have identified several hundred potential new zeolites that could lower the energy consumption of CO₂ capture. Additional computational work is currently underway that will further screen the promising materials.

¹ L. C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhowan, M. Deem, M. Haranczyk, and B. Smit. "In Silico Screening of Carbon-Capture Materials." *Nature Materials*, 11, 633-641 (2012). doi:10.1038/nmat3336.

As was the case with ionic liquids in solvents, other types of materials are also being investigated at early stages for adsorbents. Examples include metal organic frameworks (MOFs), but none of these have yet advanced beyond lab-scale testing, with large-scale production and accompanying process development largely unknown. In addition, it is not yet known whether the benefits of using better novel adsorbents will be sufficient to offset their cost.

Additional advances are being made in process improvement, and these could be as impactful as advances in novel materials. Virtually all of these process improvements are considered proprietary. Like absorption, a combination of materials and process improvements combined with close integration with a power plant is going to be needed to significantly advance adsorption technology. Unlike absorption, however, adsorption is not as widely used in chemical process industries at large scales and therefore large-scale operations may present additional challenges.

3.3. Membranes

Industrially, membrane separation processes are much less common than either absorption or adsorption. With few exceptions, such as reverse osmosis for desalination, large-scale membranes are not commonly used in the chemical process industries. For gas separations, only one utility-scale equivalent commercial membrane facility is operational: a UOP (Separex) membrane system that removes CO₂ from natural gas with a gas flow rate equivalent to the flue gas flow rate from a 300-MW power plant. Though this polymer is not suitable for separating CO₂ from flue gas, it does show that the general scale of existing membranes is within the range required for coal-fired power plants, even though membrane applications at utility-scale are exceedingly rare.

Membrane technologies advanced somewhat in 2012 for CO₂ capture. Examples include gelled ionic liquids, facilitated transport and hollow fibers for use as gas-liquid contactors. These are not new technologies, but in general, they do represent the slight uptick in membrane research for CO₂ capture relative to previous years. Additional activity can be seen in process development with membranes. However, like absorbents and adsorbents, much of the membrane materials development and process development are proprietary.

Coal-fired power plants present some unique challenges for membranes. One challenge is particulates that can deposit on the membrane surface, decreasing its permeability or damaging it physically over time. Another

issue is that membranes deployed at utility-scales will be modular using tens of thousands of membrane modules arranged in an array that distributes flue gas through the networked array. These types of challenges have not yet been addressed by membrane developers since they have not yet reached any meaningful scale. The DOE-NETL has funded membrane projects that started to address these issues in 2013 and 2014.

3.4. Cryogenic Processes

Cryogenic gas separation is a mature technology that has been used for air separation since the early 1900s. However, cryogenic capture of CO₂ from power plant flue gas has very different requirements than existing cryogenic capture processes. While air separation systems cool the air to create liquid N₂, O₂, Ar and other trace components, carbon dioxide forms a solid when chilled at atmospheric pressure, or any pressure below the triple-point pressure of 5.1 bar. As such, the main issues with CO₂ capture are the heat transfer with solid CO₂ deposition and subsequently collecting the CO₂.

Currently, the largest pilots for capturing CO₂ from flue gas using cryogenic capture are still on the 15 kW scale and do not have full integration of all heat exchange streams, which is vital for energy recovery and calculating the energy consumption of a full process. While there are only a couple of companies looking at developing cryogenic CO₂ capture technologies from power plant flue gas, there are several different methods of active development that are currently under investigation. These capture routes include cooling the incoming flue gas via contact with a heat exchange liquid, cooling the gas stream through expansion, and cooling via accelerating the flue gas to supersonic speeds. In each case these are early stage concepts, but have the possibility of breakthroughs compared to processes that rely on advances in separation materials.

While cryogenic CCS from flue gas is still a new technology, cryogenic CO₂ capture has been deployed for non-flue gas applications at large scale. Cryogenic CCS has been used for acid gas removal from natural gas since the 1980s. The current largest installation is at the Shute Creek natural gas processing plant near LaBarge, Wyoming at a scale of six million tonnes of CO₂ per year². CO₂ separation from liquefied natural gas can make use of a modified distillation column that uses the cooled liquid to collect solid CO₂ as a slurry and then further purify the CO₂ in a slurry separator. This is not possible with the gas/solid separation of CO₂ from flue gas, and would require an external heat-transfer fluid to accomplish, which introduces many additional complexities.

2 Condon, C. and Kelman (ExxonMobile), S. Shute Creek Facility and Control Freeze Zone Updates. Wyoming EORI 6th Annual CO₂ Conference, July 2012

While cryogenic CO₂ capture from flue gas is still at early technology readiness levels, there are plans for larger pilots to be built in 2014 and 2015 that would be able to test larger, scale and more integrated pilots that are still less than one MW. There are opportunities for significant breakthroughs in cryogenic CCS, especially regarding the size and complexity of capture units, though testing on more meaningful scale with heat and process integration is required to evaluate developers' claims.

3.5. Calcium Looping

Calcium Looping CO₂ capture is a temperature swing absorption process. It is similar to solid sorbent CO₂ capture technology in that CO₂ reacts exothermically with a solid and then is endothermically regenerated at a higher temperature. The major difference between calcium and other sorbents is the temperatures at which the reactions occur. CO₂ capture occurs by carbonation, formation of calcium carbonate, at temperatures greater than about 600°C (1110°F). The sorbent regeneration is essentially the same as calcining limestone to produce lime (calcium oxide) and occurs at temperatures in excess of 870°F (1600°F). Heating the calcium carbonate to this temperature (from 600°C) is likely to be accomplished by oxy-coal firing of the regenerator to keep the product CO₂ from being diluted with atmospheric nitrogen. Circulating fluidized bed reactors, similar to those used for steam generation, are anticipated for both the CO₂ capture and regeneration reactors.

The very high temperatures involved require the CO₂ capture process be intermediate to the combustion/heat transfer that generates steam or for other high temperature heat recovery. The overall combustion/heat transfer scheme will, in many ways, be similar to that employed for fluidized bed power plants employing limestone for SO₂ capture. It is also strongly related to production of lime from limestone for Portland cement manufacture.

Managing the chemistry of calcium-based CO₂ capture and regeneration is informed by the long history of lime production from limestone. Lab-scale studies of the chemistry as it might be applied to CO₂ capture have largely focused on sorbent utilization in the capture process, the fraction of the lime that actually reacts with CO₂ over many carbonation-calcination cycles. These lab studies include pre- and in-service treatments that can achieve acceptable CO₂ utilization. Low calcium utilization results from sintering of the solids as well as consumption of calcium to form calcium sulfate from fuel sulfur. Lower utilization requires larger calcium inventories as well as addition of fresh calcium/removal of unreactive calcium. The spent calcium might be acceptable for Portland cement production. For this reason, initial deployments of this technology are anticipated to be co-located with Portland cement plants.

The largest deployment of a complete calcium looping CO₂ capture plant is the CaOling project³, a 1.7 MWth process development unit in La Perida, Spain. Operations began in 2012.

4. Conclusion

All of the processes summarized here have significant potential advantages but they also all have significant challenges to overcome. In our review, none of these processes appear to have potential to provide major breakthroughs.

Of those presented, the concepts that could benefit from help in moving their development forward would be ionic liquids, enzyme promotion of solvents, solid sorbents in the form of MOFs, the cryogenic processes and those concepts that employ phase-change materials.

Future work in this area that might be considered could include:

- Updating of status of the processes and identification of previously unknown processes
- Investment into one or more of the developing processes
 - Through working with EPRI
 - Through funding independent projects
- Fuel cell project
 - This is a concept that uses flue gas to feed a molten carbonate fuel cell. It separates the CO₂ from the flue gas and produces new power.

³ <http://www.caoling.eu/>