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Separation of CO_2 from Flue Gas: A Review

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Abstract: As a result of human activity, approximately 7 Gt of carbon are emitted to the earth's atmosphere each year. A large portion of this carbon is in the form of gaseous CO_2, and approximately 30% of this CO_2 comes from fossil fuel power plants. In addition to rising levels of atmospheric CO_2, the earth's temperature is increasing. Since CO_2 can act as a trap for heat (similar to the glass in a greenhouse), reduction of CO_2 emissions is an important area of research. Separation and sequestration of CO_2 are near-term goals for emissions reduction. Better fuel efficiency (in power production, transportation, and other areas) can be considered a mid-term goal. An acceptable long-term goal for reducing emissions is using alternate power sources such as nuclear, solar, and wind power. Because separation and sequestration are short-term goals, they are critical and challenging steps for researchers. Methods that are reviewed in this paper include absorption using solvents or solid sorbents, pressure- and temperature-swing adsorption using various solid sorbents, cryogenic distillation, membranes, and several novel and emerging technologies. Upon completion of this review, it was concluded that the most promising current method for CO_2 separation is liquid absorption using monoethanolamine (MEA). While this method is currently most promising, the development of ceramic and metallic membranes for membrane diffusion should produce membranes significantly more efficient at separation than liquid absorption. The other methods investigated in this report are either too new for comparison or appear unlikely to experience significant changes to make them desirable for implementation.

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INTRODUCTION

All of the methods for CO_2 separation outlined in this report can separate CO_2 to a satisfactory degree, depending on the conditions present in the flue gas stream. The challenge, then, is to use a process that is cost-effective at typical pressure, temperature, and composition of flue gas. Some methods deliver high-purity streams of CO_2 but experience significant degradation and damage due to the other components in flue gas. Others are very durable but take too long to achieve acceptable selectivity when separating CO_2. Still others require equipment and operating conditions that are cost-prohibitive. For each process, a description of operating conditions and an explanation of the various steps are presented. Advantages and disadvantages regarding each process are considered, as well. When appropriate, specific materials and their features are addressed for each separation method. Following these process-specific outlines, a summary of development status is presented, which includes all processes considered in this report. A ranking of separation technologies follows the development summary. This ranking takes into account process operating and maintenance costs, cost and ease of retrofitting a power plant, and promise for future efficiency. The final section is selection of a separation technology for current implementation. Tables and figures are presented at the end of this report.

Absorption

The process of CO_2 absorption by a liquid solvent or solid matrix is currently being investigated for scrubbing CO_2 from flue gas streams. Absorption is a process that relies on a solvent's chemical affinity with a solute to preferably dissolve one species over another. In CO_2 absorption processes, a solvent is used that dissolves CO_2, but not oxygen, nitrogen gas, or any other components of a flue gas stream. The CO_2-rich solution is typically pumped to a regeneration column, where the CO_2 is stripped from the solution and the solvent recycled for a new batch of flue gas. The absorption equipment should be placed after the flue gas desulfurization (FGD) step and before the stack. Optimal conditions for absorption are low temperature and high pressure, making this the best location for absorption to occur. In addition, most solvents are easily degraded by compounds such as fly ash, other particulates, SO_x (SO_2, SO_3, and SO_4) and NO_x (NO_2 and NO_3), so the absorption step must take place after electrostatic precipitation (ESP) and FGD. In a typical absorption process, the CO_2-lean flue gas is either emitted to the atmosphere or possibly used in other applications (e.g., chemical production).

Monoethanolamine (MEA) Process

An effective, economical, and traditional solvent that can be used for CO_2 absorption is monoethanolamine (MEA). The flue gas from a fossil fuel power plant is passed through a column in which MEA selectively absorbs CO_2 (Fig. 1). This CO_2-rich solution is then pumped to a tower in which thermodynamic conditions are manipulated to release the CO_2. High pressure and low temperature favor absorption, while low pressure and high temperature result in regeneration of the solvent. The pressure in absorption systems can be atmospheric or can be manipulated (as explained previously) to enhance absorption/desorption. Temperature manipulation (specifically, to release the CO_2 and regenerate the MEA) makes up 70–80% of operating cost. The main area of improvement for this process is finding a new solvent or refining the existing method to minimize regeneration conditions (1).

In Fig. 1, the flue gas is cooled prior to entering the absorption chamber. The temperature should not go below the condensation point of the gas; therefore, the minimum temperature should be above the condensation point of the gas and the solvent's freezing point. After absorption, the CO_2-rich solution is passed through a heat exchanger to recover some of the heat from a hot stream coming from the regenerator. It then goes into the regenerator and is heated to release the CO_2 in solution (if pressure is involved, the pressure is lowered). The CO_2-lean solution is then pumped back into the

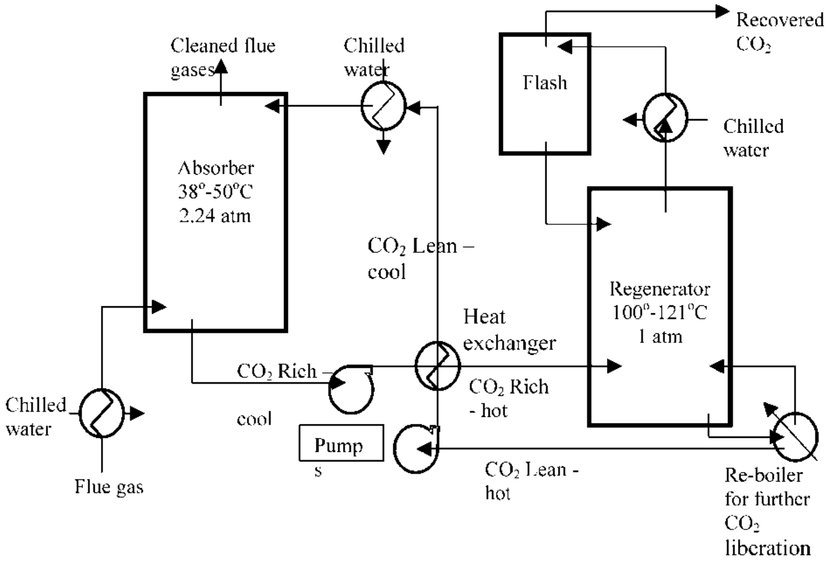

Figure 1. Typical chemical absorption system (2).

absorber for reuse (reusing solvent allows cost reduction; it has no bearing on performance of the solvent unless the solvent degrades with heating or is partially regenerated). The CO_2 liberated in the regenerator goes through a flash chamber where any water or other contaminants are removed, and the clean CO_2 gas stream is collected for storage or sequestration. There are many points where a chilled water stream exchanges heat with a solvent stream; this heat exchanging is a cost-effective method to conserve heat (2). Some small amount of refrigeration is necessary to reduce the temperature of the cold water streams.

The absorption process has many design issues that it must overcome. The most important is regenerability of the solvent (regardless of the solvent, the process is the same). Since it is desirable to carry out the process with as little energy penalty as possible, the solvent activity must have an optimum balance between absorption and desorption rates. Absorption of CO_2 at low temperatures (35–50°C) and relatively low CO_2 partial pressure (proportional to concentration) can occur if the solvent is highly attracted to the solute, but this high attraction between the solvent and CO_2 causes regeneration energy to be high. If the solvent isn't very attracted to CO_2, regeneration is simple, but little loading is possible.

Another concern is oxygen content of the flue gas. High oxygen concentration can corrode carbon steel facilities and cause excessive amine loss. Hindered amines (organic amine compounds with large attached groups that can hinder some interactions) offer some resistance against degradation of the solvent. Acidic gases, such as SO_x, are also a major concern. It is preferable to keep levels of these gases below 0.001% because they form stable salts with the amines used for absorption. A SO_x scrubber is generally more cost-effective than purchasing more solvent to account for the losses. However, since typical SO_x scrubbers only remove 90% of the SO_x in the flue gas, degradation of solvent will be a major issue if MEA is used. Fly ash and NO_x compounds create the same problems as SO_x compounds (any amount of any of these components will cause at least some degradation). Finally, the high temperature (at least 100°C, higher than the maximum ideal temperature for MEA at 45°C) associated with flue gases can degrade solvents and lower the solubility of CO_2. The temperature needs to be decreased to approximately 45°C in the SO_x scrubber upstream from the separation column (3).

The greatest advantage of absorption is that there are solvents that can be easily regenerated. MEA has been used for over 60 years in the chemical industry, whereas new solvents operating on the same principles are currently being investigated (4). This is a well-established method of separating CO_2, and the mechanisms and involved thermodynamics are well known. The fact that CO_2 absorbers can be regenerated is possibly the most attractive feature that motivates renewed research efforts focused upon improvement of the absorption process.

Advantages and Disadvantages to Absorption

When the CO_2-rich solution is sent into the regenerator, the solvent can be recycled, thus reducing the cost of material (as opposed to replacing the solvent for each absorption step). However, different conditions demand different solvents. For low-partial pressures of CO_2 (<15 vol. %), liquid solvents like MEA are preferable. For high-partial pressures of CO_2 (>15 vol. %), solid solvents, such as lithium hydroxide and lithium zirconate, are better because they can absorb more CO_2 and are more easily regenerated (5). Also, the separated CO_2 stream from the regeneration column is of high purity. An exact percentage is not reported, but most absorption processes deliver a stream with purity higher than 95%. This is pure enough for sequestration. Another advantage offered by absorption is the nondependence on human operators. Continuous monitoring and automation minimize human duties to addition of amine solvent and inhibitors. Thus, proper instrumentation and surveillance (3) minimize labor cost. Yet another advantage to chemical absorption is that it is so well known, and promising new solvents are already being pilot-tested by two separate companies.

While absorption does have strong advantages, the total cost [including addition of new solvent and other operating and maintenance (O&M) costs] is relatively high, about \$40–\$70/ton CO_2 separated, as reported by Chakma (6). The exact life of a batch of solvent was not reported for MEA or any other solvent, but solvent generally degrades before it is replaced. The energy penalty of the entire absorption process (no O&M costs included) is approximately 0.155 kWh/lb_m CO_2 (\$13.95/ton CO_2), as reported by Gottlicher (7). These two costs are not the same, however. The cost reported by Gottlicher is only the energy penalty necessary to operate the process. The cost reported by Chakma includes the cost of purchasing new solvent and other operational costs. Neither estimate includes capital and installation costs.

In addition to high-regeneration costs, sulfur compounds (SO_x gases) present in flue gases during absorption degrade the solvents currently considered for absorption; approximately 3.5 lb_m of solvent are lost for each ton of CO_2 separated (3). Lost solvent is in the form of salts that do not dissociate in solution; they precipitate out. This phenomenon motivated the development of hybrid systems in which absorption is one of two or more processes used in synergy for CO_2 separation. When absorption is part of a hybrid system, the cost needed for replacing the degraded solvent is lower. The trace gases that are separated (NO_x, SO_x, O_2, and others) are either stored or reacted with other compounds to neutralize their harmful effects.

Improvement is necessary for absorption to be a possibility for CO_2 separation in the future, such as the new PSR^{TM} solvents. They are a family of solvents being developed by a private company that require less heating for regeneration and are able to absorb more CO_2 than MEA. These solvents absorb 20–80% more CO_2 than MEA per unit volume of solvent, which allows them to be circulated more slowly through the system. Since MEA is not as efficient as a PSR solvent, it must be circulated more rapidly through the absorption system to remove the same volume of CO_2; this uses more energy. PSR solvents are also more resistant to degradation from flue gases and cause less corrosion of equipment. The developer did not indicate whether the PSR solvents are being pilot-tested or if they are still at the bench-scale testing stage.

Possibly the most promising absorption process is based on the KS-1, KS-2, and KS-3 solvents being developed by Mitsubishi Heavy Industries (MHI). This family of solvents shows higher CO_2 loading per unit solvent, lower regeneration conditions, and almost no corrosion, degradation, or amine loss. A novel packing material, KP-1, has also been developed that will further improve this process. Development has reached the pilot plant test stage (8) at MHI.

In addition to the Mitsubishi process, the Econamine FG^{TM} process (FG is the title given by the authors) also shows lower overall costs (including O&M). This process improves upon regular MEA absorption by using hindered amines. Hindered amines are similar to regular amine solvents, but specific functional groups are bonded to these solvents that help defend against degradation. This lowers steam costs for regeneration, thereby lowering overall cost. Currently, the Econamine FG process costs \$18.70/ton CO_2 in O&M costs when CO_2 is 13% of the flue gas by volume. It is being modified to further decrease the cost.

Flue Gas Desulfurization

One recent method that has been studied uses the separated SO_x compounds to form a solvent that absorbs CO_2. Laboratory experiments show that up to 2 ft^3 CO_2/lb of flue gas desulfurization (FGD) product can be absorbed. Limestone-based compounds are being used to separate SO_x from flue gas streams prior to absorption. These compounds are then slurried, becoming the solvent for absorption (9). An attractive feature to this design is that many coal power plants already have FGD units equipped; some small amount of additional transport equipment for the slurry to be moved to the absorber would be necessary, minimizing capital cost for retrofitting an existing plant.

Other Possible Solutions

Another approach is to find better methods for ensuring that maximum interaction takes place between the solvent and the flue gases. In a recent experiment (2), a column with gases and conditions typical of flue gases entering an absorption chamber was packed with different materials such as BX gauze, Flexipac, and intalox saddle (made by Norton Chemical Process Products). The packing in the saddle was either random or structured. Absorption took place at approximately 50°C for the MEA, regardless of which packing was used. Regeneration took place at 120°C, similar to the conditions shown in the Fig. 1. This process is often used in current applications at most plants with MEA scrubbers. The structured packing showed the greatest solvent utilization at $43.9 \pm 0.5\%$ (fraction of solvent that absorbed CO_2), while the random packing had only 28.6% utilization. Structured packing involves a certain structure (not specified) to packing the material in the column; random packing involved a random structure to the packing material. Both cases relied on the principle that packing increased the surface area of the solvent, allowing for more interactions with entering gases, decreasing residence time (2).

Another improvement can be made by diluting the MEA solution with organic solvents, such as alcohols, instead of water. The concept is that if the organic solutions have lower heat capacities, the heat of regeneration should be decreased, thus reducing the energy penalty for regeneration. However, while adding methanol to MEA (instead of water) did not significantly decrease the absorption rate, a large amount of methanol evaporated while heating the solution. Thus, methanol is not suitable for regeneration at atmospheric pressure but could be used in high-pressure systems such as the Integrated Gasification Combined Cycle (IGCC). Finding other organic solvents for MEA would be useful for regeneration at atmospheric pressure (2).

Solid Sorbents

Solid absorbents, such as calcium and lithium hydroxides, are also being investigated for use in CO_2 absorption. The temperatures associated with solid sorbents are usually much higher (~800°C for absorption and 1000°C for desorption), but the absorption rates are relatively fast; 50% absorption can be achieved within 1 h, and the absorbent can be totally regenerated in 15 min. In tests (10), the absorption rate dropped off after 1 h, probably due to an impermeable build up of $CaCO_3$ on the surface of the packed beds. Since $CaCO_3$ is a stable mineral, masking of the sorbent could occur, inducing costs for cleaning the sorbent surfaces. These sorbents function by the same mechanisms as wet solvents.

Solid absorbers have similar advantages and disadvantages as wet absorbers. Improving on existing systems is most possible by finding a new material that is more readily regenerated and less prone to degradation. The treatment of the sorbents (to remove $CaCO_3$ deposits, possibly by acid washing) must be investigated to determine whether physic-sorption is a viable process.

In summary, different packing materials and organic solvents have various effects on the absorption rate and regeneration energy for the system. The right combination of solvent, packing, and conditions could yield a process that cleans flue gases for a fraction of the current costs. A list of materials and conditions reported thus far for the separation of CO_2 by absorption is given in Table 1.

Adsorption

Adsorption is another method that can be used to separate CO_2 from flue gases generated by fossil fuel power plants. While absorption involves dissolution of CO_2 into the solvent, adsorption is a heterogeneous process. Due to interactivity between sorbent and guest molecules, CO_2 molecules are attracted and trapped by surface groups of the sorbent or physi-sorbed. Conditions can be manipulated that facilitate adsorption or desorption. Flue gases typically contain N_2, CO_2, H_2O, NO_x, SO_x, CO, O_2, and particulate matter when entering the stack, with concentrations varying, depending on the location of the sampling point (11). Many solids have the capability to selectively adsorb CO_2 into small cracks, pores, or just their external surfaces under specific temperature and pressure conditions. Adsorption can be performed on naturally occurring substances such as coal (a method of sequestering CO_2 in coal seams that cannot be mined) or more complex human-made sorbents such as activated carbon, molecular sieves, and zeolites.

The two main methods for adsorption are pressure swing adsorption (PSA) and temperature swing adsorption (TSA). In either case, adsorption rates depend on temperature, partial pressures of CO_2, surface forces (interaction energy between sorbent and CO_2), and pore size or available surface area of the sorbent (12). It has been established that PSA is superior to TSA due to its lower energy demand and higher regeneration rate (13).

Table 1. Materials and conditions used in CO_2 absorption process

Absorbent	Absorption temp (°C)	Absorption pressure (atm)	Desorption temp (°C)	Desorption pressure (atm)	Cost ($/ton CO_2)[a]
MEA	50	2.24	120	1	13.9
MEA (with Fe)	55	1	120	1	None reported
PSR	50	2.24	110	1	None reported
K_2CO_3	45	1	55	0.15	None reported

[a] Cost ($/ton CO_2) based on $0.045/kWh.

There are other methods for adsorption as well, one of the most promising being electrical swing adsorption. In this method, CO_2 is adsorbed onto a molecular sieve and then an electric current is passed through the sieve to efficiently release the CO_2 (14). Although the mechanism of electrical desorption is not well understood, it is believed that it is due to local temperature increase caused by the electrical current (this method is treated further, next).

Figure 2 shows an example of a typical single chamber adsorption system. Flue gases enter the adsorption chamber after being cooled (Stage 1). This brings the temperature of the gases down from the flue gas temperature to the desirable 30°C. The chamber is pressurized by flue gas with compressors to maximize adsorption of CO_2, while the rest of the components of the flue gas are allowed to exit the chamber. A vacuum can then be applied to liberate the CO_2 from the sorbent (Stage 2). This gaseous CO_2 can then be sent via a separate outlet for sequestration (12).

Figure 3 shows a pressure swing adsorber, where two chambers pass the pressure back and forth in a continuous cycle. Flue gases are sent into one of the two chambers and pressure is applied, causing adsorption of the CO_2. The pressure is then transferred to the other chamber, where a new volume of waste gas has been introduced. As that chamber is pressurized, the first chamber is depressurized and the CO_2 is collected. The cycle then continues in a switching mode as waste gases are sequentially injected into the two chambers. The connecting lines and valves shown beneath the tanks in Fig. 3 control the flow of the CO_2 to one collection site and the flow of the rest of the flue gases to the other (15). The conditions shown next in both flow diagrams apply only for one sorbent, carbon fiber composite molecular sieve (CFCMS).

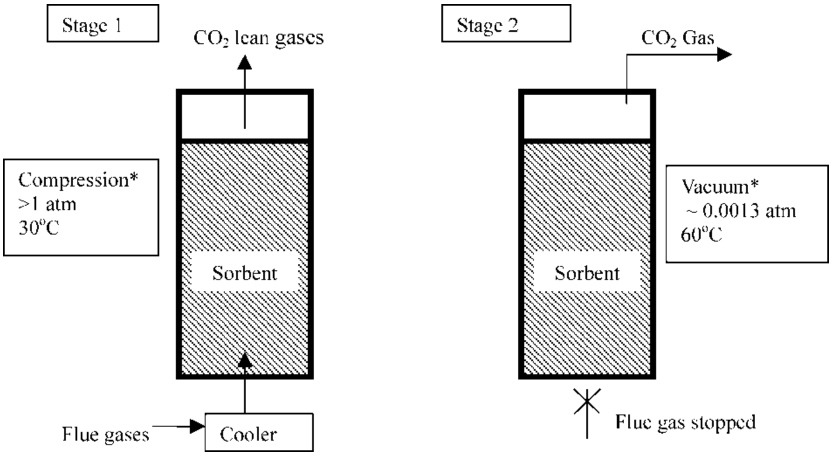

Figure 2. Single chamber adsorption system (11).

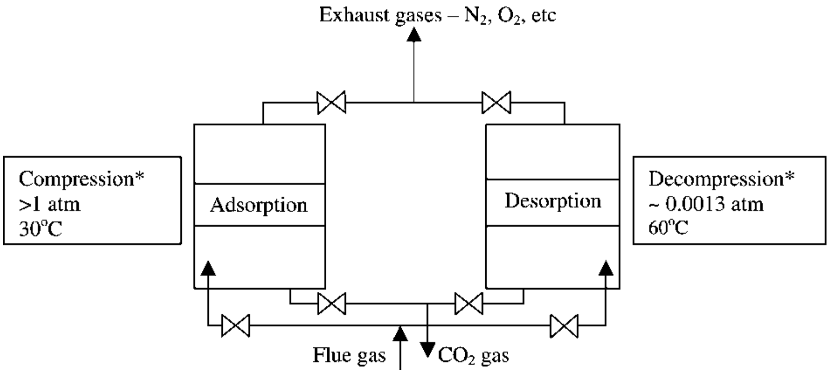

Figure 3. Two-chamber pressure adsorption system (PSA) (15).

Sorbent HSC^+

The conditions for a sorbent called HSC^+ are adsorption at.0059 atm (partial pressure of CO_2) and 25°C and desorption at 0.0013 atm (partial pressure of CO_2) and 40°C. HSC^+ is used to remove CO_2 in space shuttles. Different sorbents are optimized under different conditions, but they can often be used close to atmospheric pressure and room temperature for adsorption, and vacuum combined with higher temperature for desorption (16).

Adsorption has the advantage of easily attainable conditions for proper function and regenerability; HSC^+ operates on a pCO_2 range of 0.0046 atm and 15°C, while CFCMS operates at or below room temperature and atmospheric pressure conditions for both stages of the process. A relatively small amount of energy is therefore required for operation, keeping operating costs down. In addition to lower operating costs, the small range of pressure conditions requires less-complicated equipment. High temperature still presents an obstacle yet to be addressed (16).

Advantages and Disadvantages for Adsorption

Unlike cryogenic separation equipment that must withstand significant temperature changes, or liquid absorption where the solvent can form corrosive solutions with flue gases, physical adsorption only requires vessels capable of withstanding small pressure changes. PSA, like chemical absorption, is based on regenerability of the sorbent. As shown in Figs. 2 and 3, the sorbent can be reused many times for CO_2 separation (12–14, 16). The energy cost for adsorption is \$6.94/ton CO_2 removed at CO_2 concentrations of 28–34 mole %. Mole percent is the same as volume percent, provided that the conditions are not too extreme, such as 0°C and

10 atm (conditions should be reasonably close to ambient conditions). The cost is approximately four times greater when the mole % is from 10–11.5 (this being the most common range of CO_2 partial pressure) (7).

There are two significant drawbacks that make adsorption currently unfavorable as a stand-alone process. The first is that the system cannot easily handle large concentrations of CO_2, usually between 0.04% and 1.5% (5). Most power plants have much higher concentrations of CO_2 in flue gases, approximately 15% (11). The second is that available sorbents are not selective enough for CO_2 separation from flue gases. The sorbents' ability is usually based on pore size. When CO_2 is the target to be selectively adsorbed, gases smaller than CO_2 can also penetrate the pores. N_2 is the gas that most commonly fills up pore space in sorbents. This makes the process less efficient as a lower degree of CO_2 separation can be achieved in each cycle. The purity of the CO_2 stream is affected by the sorbent used, since various sorbents will adsorb varying amounts of N_2 (the most common impurity). Research to develop sorbents capable of very selectively binding CO_2 is underway. Another drawback is that adsorption is slow. For example, the HSC^+ system cleans enough air to support a full crew of astronauts in the space shuttle [only 7 kg/day (16)]. While this is an acceptable rate for such a small-scale application, the cost of making this system large enough to accommodate a typical power plant would be prohibitively high. For typical materials, the residence time for maximum adsorption depends on the sorbent, but 20 min is a reasonable estimate (16). When dealing with large volumes of flue gas, as in a power plant, this is just too slow to be practical. A list of example materials, conditions, and costs is shown in Table 2.

Despite these disadvantages, physical adsorption can play a satisfactory role in a hybrid system. Since it requires a low concentration of CO_2 for optimum performance, it could be placed after another separation process. Research is currently being conducted to find more selective sorbents, sorbents with higher capacities, better operating conditions, and more efficient packing structures. If these goals can be met, adsorption can be made a viable method for separating CO_2 in the future.

Table 2. Materials and conditions used in CO_2 adsorption process

Sorbent	Adsorption temp (°C)	Adsorption pressure (atm)	Desorption temp (°C)	Desorption pressure (atm)	Cost (\$/ton CO_2)[a]
CFCMS	30	1.97	60	0.001	27.8
HSC^+	25	0.04	40	0.008	Not reported

[a] Cost (\$/ton CO_2) based on \$0.045/kWh.

Cryogenic Distillation

Cryogenic separation relies on the assumption that all components of the flue gas are removed except for the N_2 and CO_2 prior to cooling. Once all of the other gases and particulates are completely removed, the remaining gas is sent into a cryogenic chamber where the temperature and pressure are manipulated to cause the CO_2 to liquefy.

Under the right conditions [the triple point for CO_2 is −56.6°C and ~7.4 atm (17)], CO_2 will condense while N_2 remains as a gas. This distillation allows N_2 to escape through an outlet at the top of the chamber while the highly concentrated liquid CO_2 can be collected at the bottom of the chamber (15).

A similar method termed "refrigeration under pressure" also condenses the CO_2 from a mixture with N_2 but uses more intense pressurization and somewhat higher temperature than cryogenic distillation. The refrigeration under pressure system is also slightly more complicated in its various components as well (17). Following are basic flow diagrams of cryogenic distillation chambers and a refrigeration system under pressure.

Figure 4 shows a simple distillation tower. The whole apparatus is kept in a cold room. Flue gases, after having NO_x, SO_x, and H_2O removed, enter the compressor. The flow then proceeds through the heat exchanger, where the N_2 exiting the tower picks up heat from the entering flow. The CO_2 liquefies or solidifies in the tower (15).

An alternative cryogenic distillation process outlined in Fig. 5 incorporates a step that separates the CO_2 from a flow that has not been pretreated (no components of the flue gas have been removed). After leaving the boiler, the flue gas enters a chamber cooled by a refrigerant stream. Water is condensed to avoid chemical corrosion, particulate matter is removed by appropriate traps, and heat is recovered. Maximum recovery of acid rain–causing gases can be effected with minimal energy penalty. CO_2, O_2, and N_2 are then directed through an adjacent chamber counter in flow to the

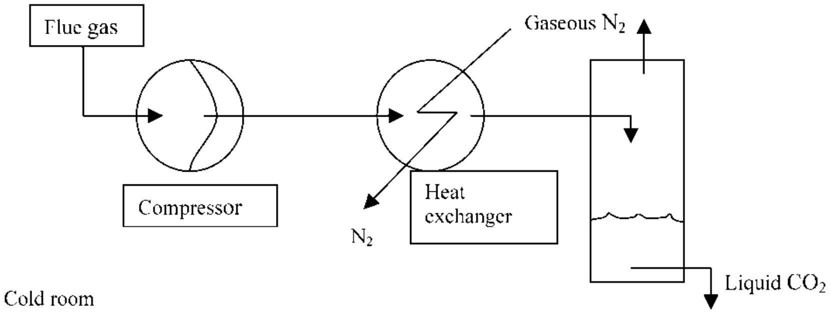

Figure 4. Cryogenic separation (after removal of SO_x, NO_x, H_2O, etc.) (15).

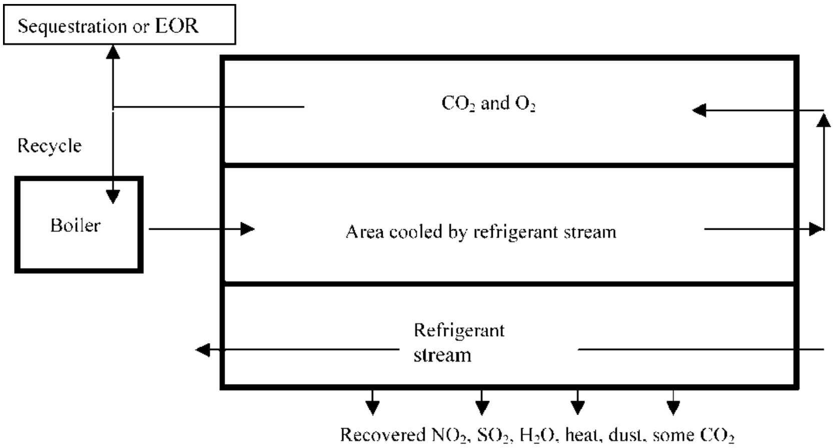

Figure 5. Cryogenic distillation method (18).

entering gases. This helps in cooling the gases for separation. Some of the resulting gases (mostly O_2) are recycled through the boiler while the high-purity liquid CO_2 is stored (18).

The method of refrigeration under pressure is shown in Fig. 6. Raw flue gas enters condensers A and B to have nearly all remaining water removed. After compression in chamber C, gases enter cooling area D and split into two flows; one flow is directed through the bottom coolers (similar to A and B) and the other is passed through the heat exchanger to give heat to the exiting flow. Both entering flows are cooled prior to entering the separation unit E. The gas is then cooled further, and the CO_2 is separated (as a liquid or solid, depending on conditions). The CO_2-lean (primarily N_2, and some

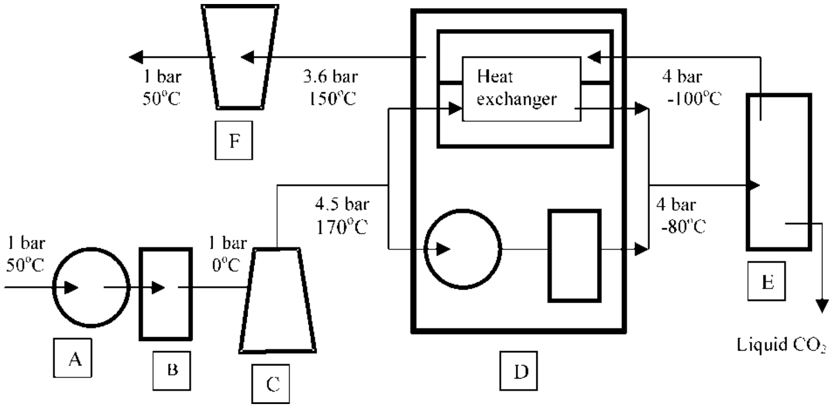

Figure 6. Refrigeration under pressure (17).

O_2, SO_x, NO_x, etc.) gas is then directed to the heat exchanger to cool entering gases before they move to the decompression turbine F. The clean gases are then released.

Advantages and Disadvantages to Cryogenic Distillation

Cryogenic distillation has one advantage over most other separation processes: its product is liquid CO_2, which is ready for transport via pipeline or tanker for sequestration. In addition to being ready for transport, the CO_2 recovery is very high (CO_2 purity after distillation can exceed 99.95%) (18). The cryogenic process, however, is extremely energy intensive. The energy required to keep the system cool (often using liquid nitrogen) makes the current process cost ineffective. The other "drawback" to the cryogenic process is that it cannot be used alone. NO_x, SO_x, H_2O, and O_2 must all be removed from the flue gas prior to the process shown above in Fig. 4. If H_2O is in the stream when the gases enter the chamber, it will freeze and could clog the pipes (the water could also corrode the equipment). The cost for cryogenic distillation is predicted by lab-scale experiments to be approximately \$32.7/ton CO_2 separated (7). This can be compared to the absorption cost of \$13.9/ton CO_2 removed and adsorption's \$27.8/ton CO_2 (as stated previously).

Refrigeration under pressure offers similar benefits to cryogenic separation, with similar drawbacks. While the cost for cooling under pressure is lower than that for cryogenic separation, more energy is required to pressurize the gases. To reduce the cost, a heat exchanger may be introduced to assist in cooling entering gases and heating exiting gases. The exiting gases also power a turbine that generates energy, offering some repayment for the energy required for the rest of the process. The energy penalty for this process depends on the degree of separation. If 90% of the CO_2 is captured, the overall efficiency of the plant is decreased from 38% (before any CO_2 removal) to 26%; the efficiency is 31% when 50% of the CO_2 is removed. The efficiency of 38% was an arbitrary decision by the investigators of the referenced work.

Both of these methods of separating CO_2 are fairly new and have room for improvement and optimization before their applications. They operate with similar principles, and due to their nature, are readily used in hybrid systems. Lowering the energy required and eliminating the limitations of both methods are the focus of current research.

Membrane Diffusion

The use of membranes has been established as a means of separating CO_2 from light hydrocarbons in the fuel and chemical industries. Membranes are also traditionally used to separate hydrogen gas from various other gases. Inorganic, metallic, polymeric, and solid – liquid are all forms of membranes used today (19).

The selectivity of polymeric membranes is based on their ability to interact with the target molecule. Whatever molecule is to be separated interacts with the membrane and is allowed to diffuse across, either by solution-diffusion or absorption-diffusion mechanisms.

The principle of ceramic and metallic membranes, which are porous, is that only gases of a certain size are able to pass through the pores of the membrane. So these membranes act as a sieve to separate CO_2 from larger gas molecules. The flue gases from a fossil fuel power plant are sent at atmospheric pressure into a chamber that is divided by a membrane; the CO_2 passes through the membrane into another part of the chamber where it is collected at a lower pressure (typically 10% of the feed pressure).

In addition to the above stated membranes, gas absorption membranes are also being researched. These consist of microporous solid membranes impregnated with a liquid absorbent. In this arrangement, CO_2 selectively diffuses across the membrane and is captured and removed by the liquid absorbent. This allows for individual control of gas and liquid flows and minimizes complications such as flooding, channeling, and foaming (12). Research shows that the thickness of the membrane plays an integral role in the permeance of the system. A membrane that is 10-μm thick would be 20 times more permeable than a membrane that is 200-μm thick (20). The gas absorption membrane system is a hybrid of solid membranes and liquid absorption.

In Fig. 7, the flue gases simply enter the separation tank, and the CO_2 diffuses across the membrane. The pressure on the permeate side is approximately 10% of the feed side; this pressure difference, once initiated by a vacuum, will continually pull CO_2 across the membrane. The separated CO_2 is blown to a collection tank, and the flue gases exit for further treatment, such as oxidation of NO_x and SO_x, recycling of O_2 for combustion, and condensation of water vapor. Sometimes these gases are separated prior to

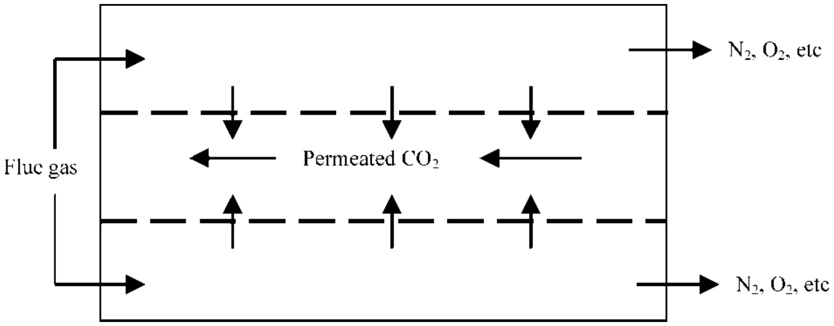

Figure 7. Simple membrane separation tube (15).

entering the separation tank because they can harm the membrane. If this is the case, the membrane just has to separate CO_2 from N_2 (15).

With a two-stage separator (see Fig. 8), the same process applies, except the gases that permeated the membrane in the first chamber are again separated in a second separation tank. This approach provides greater separation and a gas stream that is more suitable for carbon sequestration. The unpermeated gases from both tanks are sent to the same receiver for further treatment. While double separation yields a much higher purity stream of CO_2 (89.1% instead of 46.4% at 25°C with a single stage) (21), it generally costs twice as much as traditional amine separation processes (22).

Advantages and Disadvantages for Membrane Diffusion

The greatest asset to membrane separation is simplicity. While pressure swing adsorption (PSA) requires the equipment for swinging pressure and cryogenic distillation must endure extreme temperatures, the only equipment necessary for membrane separation is the membrane and fans. There are almost no moving parts, and the construction is fairly simple. The flue gases must be compressed somewhat before separation (ideal pressure is approximately 1.01 atm), but this compression is much smaller than that necessary for PSA. Membrane separators do suffer, however, because they are either not selective enough or they are not very permeable to CO_2. Currently, it is a trade-off; membranes that are very selective are not very permeable, while permeable membranes allow other gases besides CO_2 to permeate, requiring a secondary separation. This results in a low-purity stream of CO_2 (the exact percent was not reported in the available literature). The presence of impurities, however, should not appreciably affect the sequestration capacity of an underground formation; this is addressed in the Geosequestration section. Also, many organic membranes do not perform well at high temperatures, typical of flue gases exiting the stack. The difference between the pressure of the flue gases and the permeated gases (a factor of 10) also causes problems for membranes that are not structurally stable.

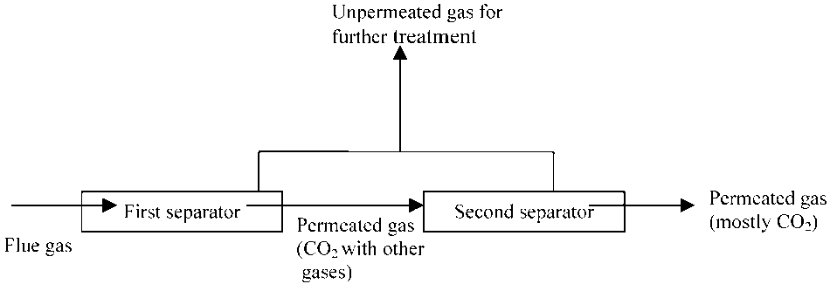

Figure 8. Example of two-stage separator (20).

Gas absorption membranes suffer the same drawbacks that absorption does: the incoming gases can contain chemicals that foul or otherwise poison the solvents (12). Gas absorption membranes are also less structurally stable than metal or ceramic membranes are predicted to be. A list of membranes and their conditions is shown in Table 3.

Research is being done to find new metallic, ceramic, and alumina membranes. These membranes would better withstand the high temperature of the entering gases [350°C ideally (23)] and the pressure changes associated with the gas flow through the chamber. Since gas absorption has higher permeability and selectivity for CO_2, methods of making the solvent stage of the membrane more chemically stable are being intensely researched (11, 18, 19). The presence of water vapor in the pores of membranes has also been studied. It was found that when water vapor clogs micropores, permeability decreases for both N_2 and CO_2; however, the decrease to N_2 permeability was so great that it was immeasurable while CO_2 permeability decreased by only a factor of 10 (small compared to the decrease in N_2) (24). Additionally, the membranes in development must be able to withstand the presence of SO_x and other compounds that typically pose problems for CO_2 separation units since they are located before the FGD unit.

Creation of more stable solid and liquid membranes will determine whether membrane separation can stand alone as a CO_2 capture process or whether it may have to be part of a hybrid separation system.

Hydrate Formation and Dissociation

One method for separating CO_2 from flue gases is to use hydrate formation separation. Hydrates are ice-like structures in which water forms a cage with cavities where small gases such as CO_2 can be trapped. While other gases can get trapped in these cavities, CO_2 is often the most likely occupant (a better hydrate former than other gases, under induced conditions). A maximum of 8 CO_2 molecules can be trapped in a cage of 46 water molecules. This gives a mole fraction of 0.148 but a weight fraction of 0.31 g CO_2/g H_2O (25). The SIMTECHE process for hydrate separation is shown in Fig. 9.

Table 3. Materials and conditions for membrane diffusion CO_2 separation

Material	Temperature (°C)	Pressure (atm)
Organic	25	1.01
DAMA[a]	25	1.00
Ideal metallic or ceramic	350	1.00

[a] DAMA is 2-(N, N-dimethyl)aminoethyl methacrylate (DAMA) grafted onto microporous polyethylene (PE). All materials are shown in Table 4.

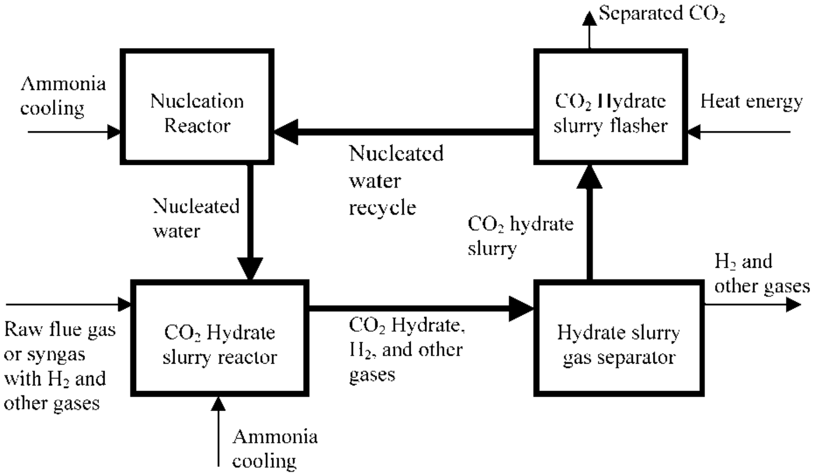

Figure 9. CO_2 hydrate separation method (21).

Since water readily forms hydrates with CO_2 ($T = 0°C$, $P = 12.3$ atm), the separator can capture CO_2 and allow the waste gases to escape. The flue gases enter the hydrate slurry reactor so that the CO_2 can be hydrated. Hydrates do not form above 10°C or much below 4 atm. Conditions on the ocean floor where CO_2 hydrates are being researched for sequestration are approximately 4°C and 8.88 MPa (26). In the case of syngas separation (Fig. 9), the CO_2 hydrate slurry goes to the slurry separator where the H_2 is removed. This is a highly pure stream and can be used for future hydrogen cells or chemical reactions. The process described above would most likely be used in an integrated gasification combined cycle (IGCC) application, but a similar process could be adapted for a hydrate separator at a pulverized coal plant. Using heat from the ammonia cooling exchangers, the hydrates are melted and the CO_2 rich stream is collected for sequestration or utilization. The nucleated water is then recycled (27).

The advantage to using hydrate formation for separating CO_2 from flue gas or syngas in an IGCC reactor is that it may not be more energy-intensive than traditional means (chemical absorption, PSA, etc.) and the product can be easier for transport than CO_2 gas. Conventional amine scrubbers, pressure swing adsorption (PSA), and other methods impose energy penalties up to 35% for coal-fired plants. Hydrate formation, while not actually performed in a plant, is believed to impose an energy penalty of only 4.4% in an IGCC system (25). In addition, the presence of H_2S actually makes CO_2 hydrate formation easier to achieve; when H_2S is 10% of the gas stream, CO_2 forms hydrates at 88.8 atm. This makes the possibility of incorporating hydrate formation separation in the near future more feasible (28).

Hydrate formation is limited for current separation applications because it requires high pressures (~88.8 atm). While PSA requires high pressure, it is not of the same order as that for hydrate formation. In addition, the temperature for formation is quite low, ~0°C, especially compared to the temperature of flue gases from coal plants. A significant amount of energy would be required to cool the flue gases to a suitable temperature, and then more energy would be required for pressurization.

Another concern for hydrate formation research regards the initial reason for hydrate research: when transporting natural gas through cold areas under pressure, hydrates formed and plugged the lines. In bench-scale tests, hydrates plugged the apparatus. Mechanisms to prevent hydrate plugging must be set in place for this method to function properly in a plant application. While some conversion rates were as high as 35% (that is, 35% of the CO_2 that entered the reactor was captured in the hydrate form), better phase contacting could increase the efficiency of hydrate separation. Other major areas of improvement are how to remove the heat of formation and how to keep a steady flow despite multiple phases (liquid CO_2, hydrate, liquid water, and ice) (27).

Addition of Tetrahydrofuran (THF) for Hydrate Formation

Investigations were also performed for CO_2 hydrates that sought to maximize the formation amount. One barrier to the use of hydrate formation is the high pressure involved. It was found that the addition of THF lowered the pressure necessary for hydrate formation from 82.4 atm to 4.69 atm. In addition, it was found that lowering the temperature in the presence of THF by only 6 K increased the mol % of CO_2 in hydrate form from 39% to 61%. THF is used only in small quantities, and conditions are not such that THF loss or degradation should be a problem. The THF can also easily be recycled with the nucleated water after CO_2 has been liberated (see Fig. 9). The optimum conditions determined in this experiment were approximately 2°C and 3.95 atm, 70 mol % $CO_2 + 30$ mol % N_2 gas mixture, and 3 mol% THF (3% when THF is added to the CO_2/N_2 mixture). Further research is being conducted to determine the effect of varying concentrations of THF and other hydrate promoters (29).

Electrical Desorption

Various methods using electricity for separating CO_2 have been proposed. One method uses an electric current to liberate CO_2 from a physical sorbent. The only sorbent mentioned in the literature found was a quinone carrier. Similar to PSA or TSA, electricity is the means to liberate the CO_2 trapped in the sorbent. The sorbent used is electrically conductive, and only a small amount [actual amount not specified (14)] of energy is required, making this a promising technology. The material proposed for this process was included in this report (14). Very little research has been done regarding this method to date.

Redox Technology

Another method proposed by the National Renewable Energy Laboratory is to use a redox active carrier to bind the CO_2 to itself at high pressure and then release it at low pressure. The carrier's ability to bind with the CO_2 is determined by whether the carrier is reduced or oxidized; reduction allows the carrier to pick up CO_2 while oxidation causes it to release the CO_2. This cycle is shown in Fig. 10. CO_2 from the atmosphere can also be separated using this process.

Gas is sent into a chamber where the electrically activated sorbent is located. At low pressure, the sorbent is reduced so that it can bond with the CO_2 (reduction takes place via an electrical circuit). The other waste gases are then evacuated. Once the other gases have exited, the sorbent is oxidized and the pressure is raised, allowing the sorbent to release the CO_2.

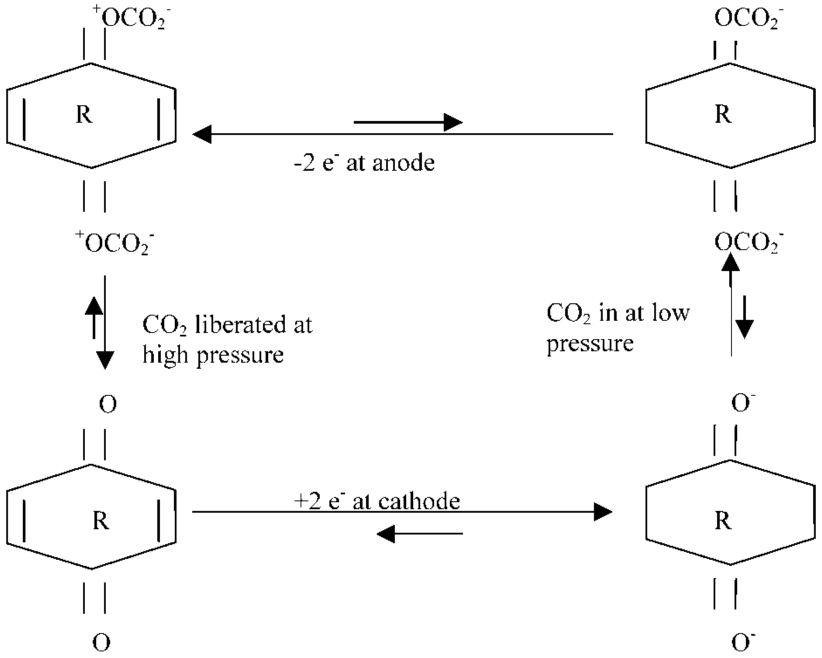

Figure 10. Redox cycle for quinone carrier (30).

Once the CO_2 is released, the sorbent is again reduced via the circuit so that it can pick up more CO_2 in a new cycle (30).

Electrochemical separation is a relatively new process, but it has promise, especially when used to liberate CO_2 adsorbed onto certain materials. No cost data were included in the results from preliminary testing (probably because it hasn't reached benchscale testing yet). If coupled with a clean energy source, high separation rates for very low energy input can be achieved.

Ammonium Carbonation

Separation of CO_2 from flue gas streams can be achieved by reacting the CO_2 with ammonia gas and water vapor in a gas-phase reaction. The reaction proceeds according to the following equation:

$$CO_2 + NH_3 + H_2O \longrightarrow NH_4HCO_3\ (s) \tag{1}$$

This reaction can be achieved by bubbling raw flue gas through an aqueous ammonia solution. The NH_4HCO_3 forms a stable solid while the N_2 and other gases that were in the flue gas stream continue through for release or treatment. In testing (11), the flue gas was bubbled through a water bath kept at 40°C and then sent to the reactor to be bubbled through the ammonia solution. In benchscale testing (12), the reaction proceeded at room temperature and ambient pressure, indicating that the energy penalty for this method would be lower than most current methods (such as amine scrubbing, adsorption, etc.). It should be noted here that the solid product is to be used as a soil fertilizer, instead of being regenerated to recover the CO_2. Maximum CO_2 removal percentages were reached after approximately 400 min of residence time. The flow rate ratio (NH_3: flue gas) that yielded the highest CO_2 conversion percentage of 48% was 0.12; lower flow rate ratios yielded lower conversion rates. While a higher NH_3 to flue gas ratio yields a higher conversion rate, computer modeling suggests that 20–60% conversion would be the best return. Another promising result of this study (12) is that the residence time in the reactor can be cut from 188 s to 47 s if the flow rate of the gas mixture is quadrupled (these times correspond to the 20–60% conversion, which takes less time than the 100% conversion). Decreasing residence time had no measurable effect on the conversion rate. This shows that if a large-scale version of this apparatus is used, large volumes of flue gas can be efficiently cleaned. This process also removes SO_2. The efficiency of SO_2 removal reaches its maximum after 0.4 s, so it too is a very fast reaction (9).

Another aspect taken into consideration was surface area of the reactor. When the reaction was taking place, it was observed that the ammonium bicarbonate formed on the walls. A vacant reactor and one packed with glass wool were tested for CO_2 removal efficiency. The reaction rate was the same for both cases, indicating that the reaction proceeds in the gas phase independent of reactor surface area (10). This process is shown in Fig. 11.

In addition to being fast (see above) and efficient, this process yields a valuable product—fertilizer. China has used a similar process for 40 ys to currently produce 28.7 million tons of ammonium bicarbonate per year (31). Selling the fertilizer would help offset the cost of the process and would aid in soil and subsoil sequestration of the CO_2. The fertilizer would be used by plants in photosynthesis, fixing the CO_2. The fertilizer would also facilitate plant growth, a means of separating CO_2 from the atmosphere and sequestering it. Further studies to ascertain the reaction kinetics and optimal reactor conditions could show this to be a viable process for CO_2 separation (10).

All costs reported in Table 4 are operating costs only; replenishing solvent for absorption, cleaning sorbent for adsorption, and other maintenance costs are not included. Capital cost for purchase and installation of separation units is not included either. The cost for membrane separation is ~0 because the process proceeds by diffusion. Some small energy penalty will be entailed from fans used to move the flue gases, but this was not reported in the literature.

Summary of Development Status

Absorption using chemical solvents is already in commercial application. The solvents currently used are not as efficient as the next generation being developed. These new solvents are in the pilot plant testing stage. Physical adsorption is used in some chemical commercial applications, but not for CO_2 separation. Development of a sorbent that can function despite high CO_2 concentration and is selective enough to be economically viable is still in lab testing. Cryogenic distillation is also used in industry to produce pure

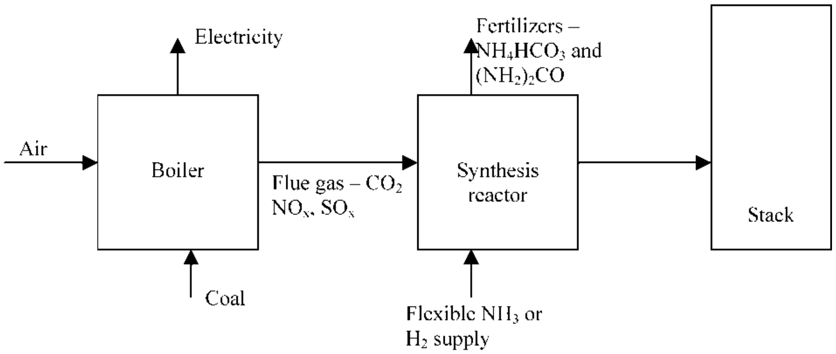

Figure 11. Ammonium carbonation fertilizer production.

Table 4. Summary of materials and conditions for separation of CO_2 by various processes

Process	Material	Temperature (°C)	Pressure (atm)	Operating cost ($/ton CO_2)
Absorption	*Liquid*			
	MEA	50 (A) & 120 (R)	2.24 (A) & 1 (R)	13.9
	MEA (with Fe)	55 (A) & 120 (R)	1 (A) & 1 (R)	NR
	PSR	50 (A) & 100 (R)	2.24 (A) & 1 (R)	NR
	K_2CO_3	45 (A) & 55 (R)	1 (A) & 0.15 (R)	NR
	Solid	800 (A) & 1000 (R)	Atmospheric	NR
	LiOH			NR
Adsorption	CFCMS	30 (A) & 60 (D)	19.7 (A) & 1 (D)	27.8
	HSC^+	25 (A) & 40 (D)	0.039 (A) & 0.008 (D)	NR
				NR
Cryogenic		−56.6	7.4	32.7
	Refrigeration under pressure	−100	3000	NR
Membranes	Organic	25	1.01	NR
	DAMA	25	1.00	NR
	Ceramic, metallic (ideal)	350	1.00	NR
Hydrate		0	12.3	NR

A represents absorption or adsorption.

R represents regeneration.

D represents desorption.

NR = not reported in the literature.

Moisture content and particulate amounts (such as mass) were not found in the literature for any of the above processes.

Costs ($/ton CO_2) based on $0.045/kWh.

CO_2, but not in the quantities involved in flue gas separations. Air separation units also operate by cryogenic distillation. The energy requirements and other costs associated with this method inhibit progress. Cryogenic distillation for CO_2 separation is still at the benchtesting phase. Membrane diffusion is also used in some chemical applications, but not for CO_2 separation yet. Development of membranes capable of surviving and functioning well at pre-FGD conditions is necessary before testing can get out of the lab test phase. In all of the above processes, trace constituents of the flue gas are emitted to the atmosphere or treated further in some other process. The literature reviewed for this summary only addressed CO_2 separation, not further treatment of the flue gas. Hydrate formation, electrical desorption, and ammonium carbonation separations are all novel concepts still in laboratory testing.

Ranking of Most Promising Technologies

If all of the methods above are considered and ranked, it appears to us that the most promising individual method for CO_2 separation is membrane diffusion. The conditions are the most easily attainable since ideal operating pressure is atmospheric and temperature can reach up to 350°C. This higher temperature allows the system to operate without a cooler since the high-temperature flue gases do not damage the membrane. While polymeric membranes capable of operating under these conditions have not yet been discovered, metallic and ceramic membranes show great promise. In addition, due to the nature of the membranes, the energy required for operation is relatively small. The gas diffuses across the membrane, so the only energy penalty is that necessary to move the gas through the system. Also, membrane separation units are predicted to be easy to retrofit to existing power plants, allowing current plants to remain in operation (retrofitting is easy enough that proposals have been made to research placing small filters on car tailpipes to separate CO_2 from exhaust). The only drawback to membranes such as those described above is that they are still at the research and development stage; no material yet has been found to operate at a high enough temperature. Thus, the cost of these membranes is largely unknown. The future for membranes is very promising, however, making membranes appear to be the most promising CO_2 separation option.

The second most promising process is absorption. The conditions are relatively easy to meet for absorption and regeneration, causing the energy penalty to be fairly low. Since absorption is a well-established process, much is known about it, guiding further research and improvement. Developing new solvents that are resistant to degradation and not corrosive to the equipment is necessary. Also, easier regeneration and faster loading are issues to be resolved prior to use of absorption. Retrofitting existing plants with chemical absorbers is predicted to be relatively easy, however, especially since some coal-fired plants already have chemical absorbers incorporated in their designs.

Though absorption is second in our ranking, the Mitsubishi and Econamine FG processes could make absorption the preferable method for separating CO_2 if they are as efficient in application as they have been in pilot testing. The low energy requirements could make these processes as efficient as a membrane separation system for a traditional coal-fired system.

Adsorption is third as it has the next lowest energy penalty for operation. The conditions for PSA are not as difficult to manipulate or achieve as for cryogenic distillation, but are still more difficult than absorption or membrane diffusion. Finding new sorbents with better selectivity and determining the best conditions for adsorption will determine whether this process is viable for the future; current materials do not show a high enough CO_2 selectivity to make adsorption cost effective. Retrofitting existing plants with adsorbers would be more costly than absorbers and membranes because its equipment is more elaborate than the first two and large-scale separation by adsorption has not been initiated as of yet; better separation is required before this technology moves to the next stage in development.

The least promising process to us is cryogenic distillation. While it does deliver a highly pure stream of liquid CO_2 that is ready for transport and sequestration, the conditions are hard to achieve and maintain, causing the highest energy penalty. In addition, the equipment is much more elaborate than the other methods to withstand the extreme conditions necessary for proper function. Retrofitting with cryogenic distillation equipment would suffer the same drawbacks as adsorption: it is not already in use (so it would not be a mere upgrade, like absorption) and its equipment is expensive. Further research to find methods of making the conditions for distillation more easily attained will determine whether cryogenic distillation will advance to pilot-plant testing.

Hydrate formation, electrocatalysis, and ammonium bicarbonate formation are all very new concepts for CO_2 that are still in lab testing. These methods, upon further investigation, may prove efficient enough to progress to benchscale testing in the near future.

Hybrid systems are a new concept that has reached the pilot-test stage in development. The PIEMSA plant in Spain uses cryogenic distillation to separate air components and absorption to separate H_2 from the raw syngas. These two processes do not specifically target CO_2; however, after separation, CO_2 is the only gas left, making it easy to sequester.

The most promising design concept for a hybrid system is IGCC (PIEMSA and the commercial plant in Sweden are examples). Other hybrid systems are possible where multiple methods are combined to offer higher degrees of CO_2 separation. These systems are not as efficient as IGCC, however, because the conditions for each separate process are very different from the rest. For example, combining chemical absorption with hydrate formation to separate CO_2 in two steps and have liquid CO_2 as the product would require a large amount of energy; there is a difference of almost 200°C between the regeneration temperature and the distillation temperature and a pressure difference of almost 6.58 atm. With further research, hybrid systems utilizing hydrate formation, ammonium bicarbonate formation, and electrocatalysis (with the four traditional methods compared previously) may be the choice for power plant design due to their streamlined integration of processes, high CO_2 separation, and capability to utilize the other components of the separated gas streams.

All of the costs included above are for operation only, unless otherwise specified. Capital costs for membranes cannot be determined since satisfactory membranes have not yet been developed. Suitable materials for adsorption have also not been identified, so their cost is unknown. Absorption has relatively known capital costs, but the suppliers of the equipment and solvent determine those prices. Also, MHI and the makers of Econamine FG^{TM} have not released prices for their processes or equipment. Finally, the cost for the equipment necessary for cryogenic separation was not found in the literature, probably because it has not reached pilot testing yet.

Selection of a Separation Technology

Based on the results of this literature review, it is reasonable to select absorption as the currently best method for CO_2 separation. A typical flow diagram showing the basic unit operations of absorption is shown in Figure 1. It is expected, however, that once membrane materials are developed to carry out the separation at relatively high temperatures, membrane separation will be the most economical approach. This is a subject of current research.

Although Fig. 12 places most of the separation systems at the stack, processes such as cryogenic distillation, some absorption and adsorption,

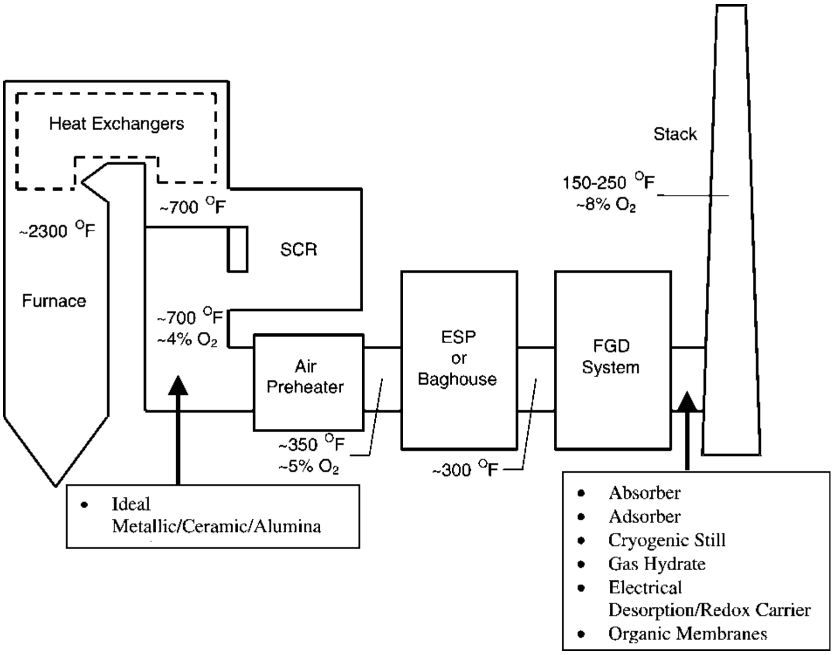

Figure 12. Placement of various separation systems based on operating conditions.

and gas hydrates will require further cooling and compression (despite stack conditions) of gas prior to operation. This will raise the cost, but the units are placed at stages that best satisfy their operating conditions.

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