Introduction

The emission of carbon dioxide (CO\textsubscript{2}) from the burning of fossil fuels has been identified as the major contributor to global warming and climate change (International Panel on Climate Change, http://www.ipcc.ch/). However, for the immediate term over the next 20 – 30 years at least, the world will continue to rely on fossil fuels as the source of primary energy. The challenge for the fossil fuel industry is to find cost-effective solutions that will reduce the release of CO\textsubscript{2} into the atmosphere.

Reduction of anthropogenic CO\textsubscript{2} emissions into the atmosphere can be achieved by a variety of means, which has been summarized by Professor Yoichi Kaya of the University of Tokyo and can be expressed as:

\[
\text{CO}_2^\Delta = \text{POP} \times \frac{\text{GDP}}{\text{POP}} \times \frac{\text{BTU}}{\text{GDP}} \times \frac{\text{CO}_2^\ita}{\text{BTU}} - \text{CO}_2^\ita \quad \text{--- Eq. (1)}
\]

where CO\textsubscript{2}^\Delta is the total CO\textsubscript{2} released to the atmosphere, POP is population, GDP/POP is per capita gross domestic product and is a measure of the standard of living, BTU/GDP is energy consumption per unit of GDP and is a measure of energy intensity, CO\textsubscript{2}^\ita/\text{BTU} is the amount of CO\textsubscript{2} released per unit of energy consumed and is a measure of carbon intensity, and CO\textsubscript{2}^\ita is the amount of CO\textsubscript{2} stored/sequestered in biosphere and geosphere sinks. Of the first two measures, reducing the population or the standard of living is not likely to be considered. Consequently, only the three remaining methods can be employed (i.e. reducing energy intensity, reducing carbon intensity and carbon storage).

The focus of this report is on the ability to store the CO\textsubscript{2} in “sinks”, which will eliminate its release to the atmosphere. CO\textsubscript{2} sinks can be grouped in three broad classes based on the nature, location and ultimate fate of CO\textsubscript{2}. These groupings are:

- **Biosphere sinks**, which are active, environmentally sensitive, natural reservoirs for CO\textsubscript{2}. The oceans, forests, and soils (agricultural) ecosystems are members of this class.
- **Geosphere sinks**, which are natural reservoirs for CO\textsubscript{2}, but require anthropogenic intervention in order to make use of the sink. Members of this class include oil reservoirs suitable for enhanced oil recovery (EOR), coal beds, depleted oil and gas reservoirs, and deep aquifers.
- **Material sinks**, which are anthropogenically created/generated pools of carbon. This class includes durable wood products, chemicals and plastics as members.

Further description of these sinks and their storage capacities can be found in Gunter et al. (1998). Geosphere sinks have the capacities to store large quantities of CO\textsubscript{2} in geologic time scale of thousands of years. Currently, the most significant issue that limits the use of geologic sinks as mitigation options is cost (Wong et al., 1999). The cost of disposing of CO\textsubscript{2} is made up of four factors: separation (i.e. capture/separation of CO\textsubscript{2} from other combustion gases), compression, pipelining and injection (pumping and disposal wells).

- **Separation** – The range for the cost of capturing CO\textsubscript{2} from flue gas using amine absorption is Can. $30 -50 per tonne (t) of CO\textsubscript{2}. 

Compression - After purification, the CO₂ is compressed, typically to 13.8 MPa (2,000 psi) for pipeline delivery. It will require multistage compression with cooling between stages. This compression technology is quite mature and does not need further development for CO₂ compression. Typically, compression cost ranges from Can. $8 – 10 /t of CO₂.

Pipelining - Pipelining CO₂ is a well-established commercial technology. The CO₂ pipeline can be laid using normal gas construction method. Pipelining cost ranges from Can. $0.7 to $4 /t CO₂/100 km, depending on construction terrain. Potential problems are pipeline corrosion and gas-liquid two-phase flow.

Injection - Injection of compressed CO₂ into geological reservoirs on land can be carried out with conventional drilling and well technologies. Pumping of CO₂ liquid is relatively inexpensive. Cost for the CO₂ injection will vary with well cost and reservoir injectivity. Typical cost ranges from Can. $2 to $8 /t CO₂.

In summary, capture/separation costs represent the largest financial impediment. Hence, efficient, cost-effective transportation and capture/separation technologies will need to be developed to allow large-scale use of geologic sinks. This is the new driving force for developing CO₂ separation technologies. The CO₂ separation markets are envisioned to be very large indeed.

At the moment, there are three pathways for CO₂ separation: pre-combustion decarbonization, O₂/CO₂ recycle combustion and post combustion CO₂ separation.

In pre-combustion decarbonization fuel is reacted with O₂ and/or steam to produce mainly carbon monoxide (CO) and hydrogen (H₂). The CO is reacted with steam in a catalytic reactor to give CO₂ and more H₂. The CO₂ is separated and the hydrogen can be used as fuel or in a hydrogen fuel cell. This process, in principle, is the same for coal, oil or natural gas. When coal is used, there are more stages of gas purification, to remove particles of ash, sulfur compounds and other compounds. Air or oxygen from a cryogenic air separation plant can be used to react with the fuel. In this way, the CO₂ concentration in the flue gas is increased, improves the separation economics.

O₂/CO₂ recycle combustion uses a pure O₂/CO₂-enriched stream for combustion. This option effectively moves the separation (i.e. N₂ from air) upstream in front of the burner. By increasing the oxygen in the feed gas and eventually, by circulating part of the flue gas, a CO₂ concentration of up to 98% by volume can be achieved. Coal combustion at a higher oxygen concentration is particularly attractive not only because it allows reducing the cost of CO₂ separation in the flue gas, but also because it reduces the volume of inert gas (i.e. N₂) in the furnace and thus increase the boiler thermal efficiency (Croiset et al., 1999).

For post combustion CO₂ separation from flue gas, which is the main focus of this report, there are four different approaches, namely

- Chemical and physical absorption
- Solid physical adsorption – pressure swing and temperature swing adsorption
- Low temperature distillation (cryogenic separation)
- Membrane separation

Chemical and Physical Absorption

Chemical Absorption

The chemical absorption process for separating CO₂ from flue gas is borrowed from the gas processing industry. Amine based processes have been used commercially for the removal of acid gas impurities (CO₂ and H₂S) from process gas streams.
Alkanolamines remove CO\(_2\) from the gas stream by the exothermic reaction of CO\(_2\) with the amine functionality of the alkanolamine. Different amines have different reaction rates with respect to the various acid gases. In addition, different amines vary in their equilibrium absorption characteristics for the various acid gases and have different sensitivities with respect to solvent stability and corrosion factors. Alkanolamines can be divided into three groups: (1) primary amines whose members include monoethanol amine (MEA), diglycolamine (DGA); (2) secondary amines whose members include diethanolamine (DEA), di-isopropylamine (DIPA); and (3) tertiary amines whose members include triethanolamine (TEA) and methyl-diethanolamine (MDEA).

In the amine gas processing operation, the gas stream and liquid amine solution are contacted by countercurrent flow in an absorption tower. Conventionally, the gas to be scrubbed enters the absorber at the bottom, flows up, and leaves at the top, whereas the solvent enters the top of the absorber, flows down (contacting the gas), and emerges at the bottom. Dilution of the circulating amine with water is done to reduce viscosity of the circulating fluid. The liquid amine solution containing the absorbed gas is then flowed to a regeneration unit where it is heated and the acid gases liberated. The solvent regeneration can be carried out at low pressures to enhance desorption of CO\(_2\) from the liquid. Some amine solution is typically carried over in the acid gas stream from the regeneration step and the amine solution is recovered using a condenser. The hot lean amine solution then flows through a heat exchanger where it is contacted with the rich amine solution from the contact tower and from there the lean amine solution is returned to the gas contact tower. A typical amine absorption unit is shown in Figure 1.

![Figure 1: Typical Amine Absorption Unit for CO\(_2\) Recovery from Flue Gas](image)

Among the primary amines, MEA has been the traditional solvent of choice for carbon dioxide absorption and acid gas removal in general. MEA is the least expensive of the alkanolamines and has the lowest molecular weight, so it possesses the highest theoretical absorption capacity for carbon dioxide. This theoretical upper absorption capacity of MEA is not realized in practice due to corrosion problems. In addition, MEA has the highest vapor pressure of any of the alkanolamines and high solvent carryover can occur during carbon dioxide removal from the gas stream and in the regeneration step. To reduce solvent losses, a water wash of the purified gas stream is usually required. In addition, MEA reacts
irreversibly with minor impurities such as COS and CS$_2$ resulting in solvent degradation. Foaming of the absorbing liquid MEA due to the build-up of impurities can also be a concern.

There is considerable industrial experience with MEA and most systems at present use an aqueous solution with only 15-25-wt% MEA, mainly due to corrosion issues (GPSA, 1998). Corrosion inhibitors may be added to MEA solution, and this results in an increase in solution strength. In a commercial process, concentration of MEA up to 30-wt% have been employed successfully to remove 80% - 90% of the carbon dioxide from the feed gas (Mariz, 1998). The process has been used to treat flue gas, however, some cooling and compression of the gas is required to operate the system. The solvent composition is proprietary, so royalty costs may be significant. Another commercial process, which uses 20% MEA with inhibitors, is also offered for flue gas treatment (Barchas, 1992).

For the current MEA absorber systems, the adsorption and desorption rates are reasonably high. However, the column packing represents a significant cost, and its energy consumption is also significant for flue gas treatment. In addition, the stripping temperature should not be too high. Otherwise, dimerization of carbamate may take place, deteriorating the sorption capability of MEA.

Secondary amines have advantage over primary amines - their heat of reaction with carbon dioxide is lower, 360 calorie/gm (650 BTU/lb) versus 455 calorie/gm (820 BTU/lb). This means that the secondary amines require less heat in the regeneration step than primary amines. From an energy consumption point of view, this is an important consideration when the primary objective is the isolation of carbon dioxide from flue gas.

Tertiary amines react slower with carbon dioxide than primary and secondary amines thus require higher circulation rate of liquid to remove carbon dioxide compared to primary and secondary amines. A major advantage of tertiary amine is their lower heat requirements for carbon dioxide liberation from the carbon dioxide containing solvent. The table below displays data for the heat of reaction between the three amine and carbon dioxide (Skinner et al., 1995).

**Table 1. Heat of Reaction Between Amines and CO$_2$**

<table>
<thead>
<tr>
<th>Amine</th>
<th>MEA</th>
<th>DEA</th>
<th>MDEA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH$_f$ for carbon dioxide in Calorie/gm</td>
<td>455</td>
<td>360</td>
<td>320</td>
</tr>
<tr>
<td>(BTU/lb)</td>
<td>820</td>
<td>650</td>
<td>577</td>
</tr>
</tbody>
</table>

Tertiary amines show a lower tendency to form degradation products in use than primary and secondary amines, and are more easily regenerated. In addition, tertiary amines have lower corrosion rates compared to primary and secondary amines.

It may be pointed out that corrosion has been a serious issue in amine processes. In general, alkanolamines themselves are not corrosive to carbon steel; the dissolved CO$_2$ is the primary corroding agent. As such, the alkanolamines indirectly influence corrosion rate due to their absorption of CO$_2$. The observed corrosivity of alkanolamines to carbon steel is generally in the order.

\[
\text{Primary Amines} > \text{Secondary Amines} > \text{Tertiary Amines} \quad \text{--- Eq. (2)}
\]

Specialty amines are also being formulated for specific purpose, for example, hindered amines. Hindered amine concept is based on the reaction rates of the acid gases with different amine molecules. In the case of CO$_2$ removal, the capacity of the solvent can be greatly enhanced if one of the intermediate reactions, i.e. the carbamate formation reaction can be slowed down by providing steric hindrance to the reacting CO$_2$. This hindrance effect can be achieved by attaching a bulky substitute to the nitrogen atom of the amine molecule. In addition to slowing down the overall reaction, bulkier substitutes give rise to less stable carbamates. By making the amine carbamate unstable, one can theoretically double the capacity of the solvent (Chakma, 1994).
Since 1990, an industrial company and an electric power company in Japan have been working together to develop the KS-1 solvent absorption process (Iijima, 1998). It uses a proprietary sterically hindered amine KS-1 for recovering CO$_2$ from flue gas. The first commercial plant using the newly developed solvent KS-1 has been in operation in Malaysia since October 1999.

To date, all commercial CO$_2$ capture plants use processes based on chemical absorption. Typically the size of the commercial plant is relatively small (maximum 800 t/d), compared to that required for processing power plant flue gas (> 5,000 t/d).

**Limitations of Amine-based Processes and Plausible Technological Advances**

Scrubbing with amine has been practiced in large scale for processing natural gas. The major undesirable impurity in natural gas streams is hydrogen sulfide. Hydrogen sulfide must be removed to very low levels due to its toxic and corrosive nature. Much of the amine scrubbing technology in the past has focused on the removal of hydrogen sulfide; however, for the recovery of carbon dioxide from power plant flue gas the requirements are different. Hydrogen sulfide is not present in flue gas and many of the other troublesome impurities such as hydrocarbons, pipeline gas additives and other sulfur compounds will not be expected to be present in flue gas. Other impurities such as oxygen, sulfur oxides, nitrogen oxides, and particulate matter however are present in flue gas and these substances will present their own special challenges.

The greatest limitation for CO$_2$ recovery from flue gas is the low pressure of the flue gas. CO$_2$ is absorbed much more easily into solvents at high pressure. The only commercially available solvents that can absorb a reasonable amount of CO$_2$ from dilute atmospheric pressure gas are primary and sterically hindered amines, such as MEA, DGA and KS-1, KS-2 and KS-3 series of solvents (Chapel et al., 1999). These solvents can absorb CO$_2$ at low pressures because they have high reaction energies. This results in high-energy requirements to regenerate the rich solvent. However, energy costs may be reduced if the process can be fully integrated with a power plant where significant amount of low-grade heat may be available.

The oxygen content of the flue gas is an issue that must be addressed. Most solvents applicable for flue gas systems degrade to varying degrees in oxidizing atmospheres, which lead to either high solvent losses or expensive reclaiming processes. Oxygen also causes corrosion problems in the process equipment, which can lead to failures or more expensive materials of construction. The use of inhibitors in the solvent to reduce degradation and corrosion appears to work well and produces very good results. Oxygen scavenging has not been commercially demonstrated with flue gases (Chapel et al., 1999).

Sulfur oxides (SO$_2$, SO$_3$) react with MEA to form heat-stable corrosive salts that cannot be reclaimed. It is generally accepted that installing a flue gas desulfurization unit before the absorber is the best way to alleviate the problem. There is a myriad of technologies available for desulfurization, but that is beyond the scope of this report.

A typical flue gas contains some amount of NO$_x$. NO$_x$ generally consists of NO and NO$_2$ in a ratio of from 95:5 to 90:10. The main component NO performs as inert gas and will not affect the solvent. However, NO$_2$ will partially lead to form heat stable salt. Generally some solvent degradation is acceptable in order to avoid the cost of removing the NO$_2$.

Fly ash in the flue gas can cause foaming and degradation of the solvent and plugging and scaling of the process equipment. A wash operation was recommended to reduce the fly ash content to appropriate level to abate the aforementioned problems.

Flue gas entering the absorber at high temperatures can lead to solvent degradation and decreased absorption efficiency. The flue gas must be cooled to a water dew point of 50°C, which can be accomplished in the desulfurization unit or with a direct contact water cooler.
In summary, the recovery of CO$_2$ from combustion flue gas requires significant amount of pre-treatment processing in order to avoid any foul-up in the solvent absorption step. This will add to the cost of CO$_2$. However, significant improvements can be made in the solvent absorption process in terms of optimizing the compositions of the absorbing amines and the gas-liquid contactors.

Considerable work is ongoing in Japan and in Canada (International CO$_2$ Capture Center in Regina, Saskatchewan) on improved amines and processes for the specific task of carbon dioxide capture.

Mimura et al. (2001) describe their recent work in solvent composition. They have developed a series of amine solvents designated as KS-1, KS-2, and KS-3. The composition of these solvents is propriety. The KS-1 solvent has been commercialized in Malaysia where a flue gas containing 8 vol.% CO$_2$ is being treated with 90% CO$_2$ recovery. Corrosion problems were reported to be negligible using this solvent and also that solvent degradation during prolonged operation was slight. They indicated that amine consumption was about 2.0 kg/ton CO$_2$ recovered using a MEA process while for the Malaysia plant using KS-1, solvent loss was 0.35 kg/ton CO$_2$ recovered. With improved solvents currently in the pilot phase, they indicate that solvent loss may be further reduced to ~0.1 kg/ton CO$_2$ recovered. Steam consumption was 1.5 ton of low-pressure steam per ton CO$_2$ recovered. It is claimed that K-3 is better than K-1 and K-2 in terms of energy consumption for solvent regeneration. A pilot plant test using KS-3 under coal fired boiler flue gas containing 14-vol% CO$_2$ (dry basis) and 50 ppm SO$_x$ showed a CO$_2$ recovery of 90% (Mimura et al., 1999), and sodium hydroxide was believed to be used in the solvent regeneration by converting the heat-stable salt due to reaction of SO$_x$ with the amine to free amine and Na$_2$SO$_3$.

The Canadian group has also developed a series of proprietary designer solvents designated as PSR solvents (Veawab et al., 2001). The PSR solvents have been designed to specifically for the separation of CO$_2$ from flue gas streams. The PSR solvents may be used at higher amine concentration than conventional MEA solvents and at a higher loading of CO$_2$. The key features claimed for the PSR solvents are lower regeneration temperature, lower solvent circulation rate, lower solvent degeneration rate, and lower corrosion rate.

Another area that has been investigated for improved CO$_2$ separation is the gas-liquid contactor. A low-pressure gas stream containing low (5 - 15 %) quantities of CO$_2$ means that the volume of gas to be processed is large for the quantity of recovered CO$_2$. Improvements in the packing materials in the gas-liquid contact towers, have been reported by both the Canadian group (Aboudheir et al., 2001) and the Japanese group. The result is a smaller gas-liquid contactor, for a given CO$_2$ capture capacity.

**Physical Solvent**

For physical absorption, CO$_2$ is physically absorbed in a solvent according to Henry’s Law, which means that they are temperature and pressure dependent with absorption occurring at high partial pressures of CO$_2$ and low temperatures. The solvents are then regenerated by either heating or pressure reduction. The advantage of this method is that it requires relatively little energy; but the CO$_2$ must be at high partial pressure. Hence, it is suitable for recovering CO$_2$ from Integrated Gasification Combined Cycle (IGCC) systems where the exhaust CO$_2$ would leave the gasifier at elevated pressures. Typical solvents are Selexol (dimethylether of polyethylene glycol) and Rectisol (cold methanol).

Selexol has been used since 1969 to sweeten natural gas, both for bulk CO$_2$ removal and H$_2$S removal. Absorption takes place at low temperature (0 - 5°C). Desorption of the rich Selexol solvent can be accomplished either by letting down the pressure (CO$_2$ removal) or by stripping with air, inert gas or steam. Hydrocarbons, COS, CS$_2$ and mercaptans are also removed by the solvent. Additionally, the low absorption temperature used requires that the lean solvent be returned to the absorber via a refrigeration unit. The Exxon plant at La Barge, Wyoming, USA uses two Selexol processes in series, one for removing H$_2$S and other for removing CO$_2$.

Rectisol has mainly been used to treat synthesis gas, hydrogen and town gas streams and removes most impurities. The coal gasification plant in North Dakota, USA uses a Rectisol process to separate CO$_2$ from
a mixture of H₂, CO and CO₂. In general, the solvent is chilled methanol but other solvents are also available for special applications.

**Alkaline Salt – Based Processes**

Many processes have been developed for carbon dioxide removal utilizing the alkali salts of various weak acids. Many salts have been proposed such as sodium and potassium salts of carbonate, phosphate, borate arsenite and phenolate (Kohl and Reisenfeld 1985). The most popular salts in the industry have been sodium carbonate and potassium carbonate.

Sodium and potassium carbonate aqueous solutions have a number of problems in practice. The solutions tend to react only relatively slowly with carbon dioxide and the heat requirements for regeneration of the solution is large compared to the various alkanolamine based processes. Potassium carbonate promoted by piperazine or other promoters has been considered for CO₂ separation. Vacuum stripping for solvent regeneration has been used, and vapor recompression may be required. Low cost and minimal degradation of the solvent are the primary advantages of this process.

Solution concentrations are limited by the precipitation of bicarbonate salts and solution temperatures are high. Foaming is also reported to be a concern. Corrosion problems may be severe depending on input gas composition, but various corrosion inhibitors have been employed effectively in some circumstances. Sometimes stainless steel has been used for the plant (Benson, 1954).

**Separation Processes other than Chemical and Physical Absorption**

**Solid Physical Adsorption – Pressure Swing and Temperature Swing Adsorption**

An adsorption process consists of two major steps: adsorption and desorption. The technical feasibility of a process is dictated by the adsorption step, whereas the desorption step controls its economic viability. Strong affinity of an adsorbent for removing the undesired component from a gas mixture is essential for an effective adsorption step. The stronger the affinity, however, the more difficult it is to desorb the gas impurity and the higher the energy consumed in regenerating the adsorbent for reuse in the next cycle. The desorption step, therefore, has to be very carefully balanced against the adsorption step for an adsorption step to be successful.

The main advantage of physical adsorption over chemical or physical absorption is its simple and energy efficient operation and regeneration, which can be achieved with a pressure swing or temperature swing cycle. The primary adsorption material under consideration is zeolite. The concerns over this technology are scale up and the need to develop CO₂ specific adsorbent materials.

**Low Temperature Distillation (Cryogenic Separation)**

Low temperature distillation (cryogenic separation) is a commercial process commonly used to liquefy and purify CO₂ from relatively high purity (> 90%) sources. It involves cooling the gases to a very low temperature so that the CO₂ can be liquefied and separated.

Distillation generally has good economies of scale. This method is worth considering where there is a high concentration of CO₂ in the waste gas. The advantage is that it produces a liquid CO₂ ready for transportation by pipeline. The major disadvantages of this process are the amount of energy required to provide the refrigeration and the necessary removal of components that have freezing points above normal operating temperatures to avoid freezing and eventual blockage of process equipment.

For post combustion flue gases, the waste streams contain water and other trace combustion by-products such as NOₓ and SOₓ, several of which must be removed before the stream is introduced to the low temperature section. Moreover, these by-products are usually generated near atmospheric pressure.
These tend to make cryogenic process less economical than others in separating CO$_2$ from flue gas. However, it is a serious contender for high-pressure gases such as in pre-combustion decarbonization processes.

**Membranes**

Separation membranes are thin barriers that allow selective permeation of certain gases. They are predominately based on polymeric materials. Membranes for gas separation are usually formed as hollow fibers arranged in the tube-and-shell configuration, or as flat sheets, which are typically packaged as spiral-wound modules. The membrane process has been widely used on the commercial scale for hydrogen recovery from purge gases in ammonia synthesis, refinery and natural gas dehydration, sour gas removal from natural gas, and nitrogen production from air. Compared to absorption separation, the advantages of the membrane process are:

1) It does not require a separating agent, thus no regeneration is required;
2) The systems are compact and lightweight, and can be positioned either horizontally or vertically, which is especially suitable for retrofitting applications;
3) Modular design allows optimization of process arrangement by using multi-stage operation; and
4) Low maintenance requirements because there are no moving parts in the membrane unit.

A number of solid polymer membranes are commercially available for the separation of CO$_2$ from gas streams, primarily for natural gas sweetening. These membranes selectively transmit CO$_2$ versus CH$_4$. The driving force for the separation is pressure differential across the membrane. As such, compression is required for the feed gas in order to provide the driving force for permeation, and the separated CO$_2$ is at low pressure and requires additional compression to meet pipeline pressure requirements. The energy required for gas compression is significant when a very high pressure is required.

The commercial membranes for CO$_2$ separation are mainly prepared from cellulose acetate, polysulfone, and polyimide. These membranes are primarily tailor-made for natural gas processing and not specifically developed for flue gas separation. The selectivity of CO$_2$/N$_2$ of these membranes is generally in the range of 20 ~ 40, depending on the operating temperature. Because of the specific characteristics of flue gas composition, and the specific features of the separation (i.e. large volumetric flow rate, low source pressure, high temperature, and the relatively low commodity value of CO$_2$), further development may be required for economically capturing CO$_2$ from flue gas on a large scale.

**Novel Separation Technologies**

**Hybrid Membrane/Amine Processes**

It may be desirable to apply amine and membrane technologies in tandem, thereby forming a hybrid process, to capture CO$_2$ from flue gas. Micro-porous hollow fiber membranes are evolving as a new technology for CO$_2$ separation using amine-based chemical absorption processes. Micro-porous membranes are used in the gas-liquid unit where the amine solution is contacted with the CO$_2$ containing flue gas. The principle advantage of the micro-porous membrane is the reduction in the physical size and weight of the gas-liquid contacting unit. Unlike conventional membrane separation, the micro-porous hollow fiber membrane separation is based on reversible chemical reaction, and mass transfer occurs by diffusion of the gas through the gas/liquid interface just as in the traditional contacting columns.

The hollow fiber membrane itself does not contribute to the separation but instead acts as a contacting medium between the gases the liquid. There are a number of advantages to using the gas-liquid membrane contactors, including:

1) High gas/liquid contact area due to the high packing density of the hollow fibers (500 to 1,500 m$^2$/m$^3$ versus 100~250 m$^2$/m$^3$ for a conventional column).
2) Foaming is eliminated since because the gas flow does not impact the solvent and there is no connective dispersion of gas in the liquid.
3) The membrane acts as a partition between the gas and liquid, and the gas/liquid flow rate ratio may vary in a wide range without causing flooding problems.
4) The available gas/liquid contact area is not disturbed by variations in flow rates. This means the process can tolerate a wider range of process condition variations.
5) Solvent degradation is minimized as oxygen (a degradation agent to amines) is prevented from intimate contact with the solvents.
6) Unlike the absorption column that can only be operated vertically, the hollow fiber membrane contactor may be operated in any orientation to suit the overall plant layout.

Three companies: Kvaerner (Norway), TNO (Netherlands), and the Alberta Research Council (Canada) are the active players pursuing micro-porous membrane contactors for flue gas treatment (Falk-Pedersen et al., 2001, Herzog and Falk-Pedersen, 2001, http://www.cirmac.com/, Rangwala, 1996)

**Emerging Technologies from the USA R&D Programs**

The USA research program on CO₂ capture is more diverse including basic research and technology development. One of the thrusts of this program is directed to capturing CO₂ from synthesis gas, reformer gas, which ties in with the Vision 21 R&D Program. Capture cost is expected to be lower as we can take advantage of the pressure available from the reactor beds. The following are selected projects funded under the various USA R&D programs, which hopefully will give a sense of direction of the emerging technologies that might be expected in the longer term:

**Absorption:**
- Vortex Tube Contactor, which is an extension of the Ranque-Hilsch vortex tube technology. The project studies CO₂-liquid absorption kinetics, solvent regeneration requirements and scale-up parameters for vortex contactors. In a vortex contactor, solvent and gas under high pressure are injected into a tubular reactor where they expand and accelerate to create a cylindrical flow of fine mist down the tube, enhancing capture of the gas in the solvent.

**Adsorption:**
- Dry Regenerable CO₂ Sorbents
  The project is to develop a CO₂ separation technology that uses a regenerable, sodium based sorbent to capture CO₂ from flue gas. Thermodynamic analysis and preliminary laboratory tests indicate that the technology is viable. Process data will be collected to assess the technical and economic feasibility of the various process configurations.

**Membranes:**
- Membrane Reactor
  The project is to develop an inorganic, palladium-based membrane device that can reform hydrocarbon fuels to mixtures of hydrogen and CO₂ and at the same time separates the high value H₂. The CO₂ can be recovered in a compressed form.
  - Thermally Optimized Membrane
    Structurally altered polymeric membranes are being developed and optimized for high temperature operation (100 to 400°C) to enhance integration with power generation and industrial systems.

**Electrical Swing Adsorption (ESA):**

The ESA system developed by Oak Ridge National Laboratory uses a novel carbon-bonded activated carbon fiber as the adsorption material (Burchell et al, 1997, Judkins et al., 2001). This material is called carbon fiber composite molecular sieve (CFCMS). Activation conditions for the CFCMS can be varied to increase or decrease pore size, pore volume and surface area to improve the effectiveness of the carbon fiber as a CO₂ adsorbent. The monolithic material is rigid and strong, resistant to attrition and dusting, and because of its continuous carbon skeletal structure, is electrically conductive. An adsorbed gas may be
quickly and efficiently desorbed by the passage of an electric current, thereby allowing a low energy, electrical swing system. The electrical energy required for desorption is approximately equal to the heat of adsorption of the adsorbed gas. It is possible to regenerate the CFCMS in the absence of a temperature increase, potentially reducing swing cycle time and improving separation efficiency. Several separations have been demonstrated such as the separation of \( \text{H}_2 \) from experimental gas mixtures containing \( \text{H}_2 \) and \( \text{H}_2\text{S} \) or \( \text{H}_2 \) and \( \text{CO}_2 \); separation of \( \text{CO}_2 \) from \( \text{CH}_4 \); and the separation of \( \text{CO}_2 \), \( \text{CO} \), \( \text{H}_2\text{S} \) and \( \text{H}_2\text{O} \) from a variety of gas mixtures. The technology is at an early stage of development. There is great need for R&D focused specifically on \( \text{CO}_2 \) separation and capture. For example, development of modified activation procedures to render the CFCMS more or less selective for \( \text{CO}_2 \), systematic study of CFCMS to maximize its adsorptive capacity for \( \text{CO}_2 \) and integration of CFCMS with sequestration technology.

**CO\(_2\) Hydrate Separation Process for Synthesis Gas:**

This process is based on initial experimental studies conducted at the California Institute of Technology (Caltech) from 1993 to 1995. \( \text{CO}_2 \) hydrate will form at temperatures near 0°C and pressures from 10 to 70 atmospheres, depending on the other gases present and the partial pressure of the \( \text{CO}_2 \) in the gas stream. The \( \text{CO}_2 \) hydrate separation process is a two-stage process. First, “nucleated water”, saturated with \( \text{CO}_2 \) is formed in the first reactor, where circulating ammonia provides the cooling. Shifted synthesis gas (\( \text{CO}_2 \), \( \text{H}_2 \) and other gases) enters the second reactor together with the nucleated water, at pressures from 6 to 20 atmospheres; \( \text{CO}_2 \) hydrates form rapidly and fix all \( \text{CO}_2 \) entering the reactor. \( \text{H}_2 \) is collected as the off-gas. The process is a good fit with future coal gasification systems where the shifted synthesis gas streams come out at pressures of 20 atmospheres or above, and \( \text{CO}_2 \) partial pressure of 8 atmospheres or more, ideally meeting \( \text{CO}_2 \) hydrate forming requirements. In addition, \( \text{H}_2\text{S} \) present in the synthesis gas is also absorbed in the “nucleated water”, due to the high solubility of \( \text{H}_2\text{S} \) in water. Therefore, there is no need for a \( \text{H}_2\text{S} \) removal and sulfur recovery system in this process.

Laboratory work by Los Alamos National Laboratory (LANL) validated the Caltech claim that hydrates can be produced in a flow-through system. This demonstration is an essential first step for industrial implementation of the hydrate technology. Equilibrium experiments have established the benefits of gaseous and liquid \( \text{CO}_2 \) hydrate promoters. The promoters lower the initial formation pressure of the hydrate, thereby increasing scrubber efficiency and allow operation far from the freezing temperature. This simplifies operation and reduces the cooling required which is a major cost of operation. Since \( \text{H}_2 \) is inert and does form a hydrate, no \( \text{H}_2 \) will be lost which is not the case with other processes. Performance of greater than 97% \( \text{H}_2 \) recovery and greater than 86% \( \text{CO}_2 \) separation has been achieved. Preliminary process evaluation shows that it has significant advantage over conventional \( \text{H}_2\text{S} \) and \( \text{CO}_2 \) removal, stripping and \( \text{CO}_2 \) compression processes from both energy efficiency and overall cost perspectives. Preliminary economics show that \( \text{CO}_2 \) separation and sequestration can be achieved in the range of $10 to 11/tonne of \( \text{CO}_2 \) (Spencer et al., 1999).

Potential barriers to this technology are: the ability to release \( \text{CO}_2 \) from the hydrate in an energy efficient manner; efficient capture of \( \text{CO}_2 \); stable pre-hydrate; and trace contaminants interfere with hydrate formation.

**Sorbent Energy Transfer System (SETS):**

SETS transfers the energy of the fuel to the air without bringing the carbon along. The SETS works by using the fossil fuel (gasified coal, petroleum fuels or natural gas) in a pressurized fluidized bed to reduce a metal oxide, thereby producing a metal (or lower valence metal oxide), \( \text{CO}_2 \) and water. The water is condensed and its energy used to raise steam leaving a stream of pure \( \text{CO}_2 \) at 3 - 6 atmospheres that can be sequestered. The metal oxide is burned or re-oxidized in air to produce heat and the metal oxide required for the reduction step.

SETS utilizes the full chemical potential of combustion of the fuel, even though the net reaction is carried out in two steps. However, as a result of the two-step process, no additional energy is needed to separate \( \text{CO}_2 \) from the combustion products, and the concentrated \( \text{CO}_2 \) steam produced can be further compressed for sequestration with very little additional energy.
Both iron and nickel based oxygen sorbents have been tested. The lower cost iron based sorbents were strong, attrition resistance, and had enough oxygen capacity to fully oxidized fuel to CO₂ and stream. Measurements of the attrition rate showed that the iron-based sorbents would last for more than 1,000,000 cycles. However, testing also demonstrated that the iron-based sorbents could not be used for extended period at temperatures above 800°C because the iron sinters into larger, less reactive crystallites. This temperature limitation would not allow the system to take advantage of modern, high efficiency gas turbines typically operating today. In this aspect, the Ni based sorbent fared better. It had excellent activity, strength, attrition resistance, and the ability to fully oxidize fuel (CH₄) to CO₂ and steam at 1,050°C without sintering.

Because the sorbents have very high surface areas and are small and porous to reduce mass transfer resistance, they can be fully oxidized in 3 seconds and reduced in less than 18 seconds. Thus, the SETS process can be carried out in small, high throughput (transport and fluidized bed) reactors. Because the reactors are small, internally insulated and do not require exotic materials the capital cost of the system is very low.

SETS can capture CO₂ for sequestration. Costs are on the order of US $10 – 20/ton for separation and compression to pipeline pressures (Copeland et al., 2001).

The last three novel concepts being developed which could be the breakthrough technologies of the future. CO₂ hydrate separation is currently aimed at synthesis gas separation. Its application to combustion flue gas has not been assessed. Electrical swing adsorption is a completely new technology of separation. Its potential is tremendous. The Sorbent Energy Transfer System opens a new way of burning fuels.

Conclusions

The threat of global warming and climate change provides a new driving force for CO₂ separation technologies. The separated CO₂ can be used for enhanced oil and gas recovery and for geological storage, thus eliminating its release to the atmosphere. Capture and storage of CO₂ is the only option that allows the world’s huge investment in the fossil fuel infrastructure to be used whilst at the same time bringing about a major reduction in CO₂ emissions.

The greatest limitation for CO₂ recovery from flue gas is the low pressure of the flue gas. CO₂ is absorbed much more easily into solvents at high pressure. The only commercially available solvents that can absorb a reasonable amount of CO₂ from dilute atmospheric pressure gas are primary and sterically hindered amines, such as MEA, DGA and the KS- series of solvents. These solvents can absorb CO₂ at low pressures because they have high reaction energies. This results in high-energy requirements to regenerate the rich solvent. However, other separation processes such as physical adsorption, low temperature distillation and membranes have serious limitations when used for CO₂ separation from flue gas.

CO₂ separation from flue gas is commercial now using chemical absorbents such as MEA and the KS-series of solvents. Chemical absorption is used to supply CO₂ to the food industry but at a scale about 10 times smaller than would be required for mitigation. CO₂ scrubbing with amine has been borrowed from the natural gas processing industry. The major undesirable impurity in natural gas streams is hydrogen sulfide. Hydrogen sulfide must be removed to very low levels due to its toxic and corrosive nature. Much of the amine scrubbing technology in the past has focused on the removal of hydrogen sulfide; however, for the recovery of carbon dioxide from power plant flue gas the requirements are different. Hydrogen sulfide is not present in flue gas and many of the other troublesome impurities such as hydrocarbons, pipeline gas additives and other sulfur compounds will not be expected to be present in flue gas. Other impurities such as oxygen, sulfur oxides, nitrogen oxides, and particulate matter however are present in flue gas and these substances must be removed before the chemical absorption step. These add to the cost of CO₂ separation. In the short term, significant improvements can be made to the chemical
absorption process in optimizing the compositions of the absorbing amines, improving the performance of the gas-liquid contactors and the overall heat utilization by better heat integration with the CO$_2$ source plant.

In the intermediate term, a hybrid membrane/amine process has promise. Micro-porous hollow fiber membranes are evolving as a new technology for CO$_2$ separation using amine-based chemical absorption processes. Micro-porous membranes are used in the gas-liquid unit where the amine solution is contacted with the CO$_2$ containing flue gas. The principle advantage of the micro-porous membrane is the reduction in the physical size and weight of the gas-liquid contacting unit. Unlike conventional membrane separation, the micro-porous hollow fiber membrane separation is based on reversible chemical reaction, and mass transfer occurs by diffusion of the gas through the gas/liquid interface just as in the traditional contacting columns.

The present impediment to CO$_2$ separation using current technologies is high costs. If costs are to be reduced in a meaningful way, CO$_2$ feed streams with a higher concentration/pressure of CO$_2$ will have to be exploited. This implies that in the intermediate term separation of CO$_2$ from waste gas streams such as coal gasification and syntheses gas should be seriously considered.

In the longer term, CO$_2$ capture technologies would not be limited to amine-based technologies. This concept is displayed in Figure 2 along with other projections of future cost reductions (compare to the current chemical absorption technology). Separation technologies such as hydrate formation, various membranes and many others that are currently in the developmental stage, offer the promise of significantly reduced costs.

![Figure 2: Potential Cost Reduction of CO$_2$ Production](image)

(Ovals Represent Amine-Based Processes, Rectangles Represent Other Processes)
References


