



## **FACTSHEET – DEVELOPMENTS IN CO<sub>2</sub> CAPTURE TECHNOLOGIES**

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Mining and utilization of coal for energy production is responsible for more than one-third of Australia's greenhouse gas emissions. Methane released during coal mining accounts for approximately 6.5% of Australia's greenhouse gas emissions, while carbon dioxide released during coal-fired electricity generation is responsible for around 30% of national greenhouse gas emissions.

Methane is some 21 times more 'greenhouse active' in comparison to CO<sub>2</sub>. This provides an option to reduce methane's greenhouse contribution by combustion of methane from mine ventilation air stream and drainage gas. An added attraction is the potential to capture and utilize the heat released. However, to minimize the greenhouse gas contribution associated with all of the coal chain, it is likely that the capture and sequestration of the CO<sub>2</sub> released when the coal is utilized will be a future requirement.

Coal-fired power stations represent large point sources of CO<sub>2</sub> emissions and will undoubtedly be the major focus of efforts to capture CO<sub>2</sub>. There is considerable work being done overseas on the development of capture technologies that might be applicable to power stations. The US DOE, through its Vision 21 and Carbon Sequestration R&D programs, and the IEA Greenhouse Gas R&D Program are leading the way in these developments. The efforts are being directed at both pre- and post-combustion capture of CO<sub>2</sub>, with emphasis on reducing energy penalties and operating costs.

### **Pre- Versus Post-combustion Capture**

One option is to remove CO<sub>2</sub> from the flue gas stream after the coal has been combusted. The problem with this option is that the CO<sub>2</sub> is present at low partial pressures (typically less than 0.14 atmospheres) from a conventional pf-fired system. However, if the coal is fired in a pressurised gasifier there is the potential to remove the CO<sub>2</sub> prior to combustion of the fuel gas. The CO/H<sub>2</sub> stream from the gasifier can be passed through a shift converter to produce essentially a CO<sub>2</sub>/H<sub>2</sub> stream, with CO<sub>2</sub> partial pressures of 4 atmospheres or more. This considerably facilitates CO<sub>2</sub> capture.



## CO<sub>2</sub> Capture Technologies

The technologies that are available for capturing CO<sub>2</sub> from such combustion/gasification systems can be characterised as:

- Liquid solvent based technologies
- Solid adsorbent based technologies
- Membrane separators
- Low temperature systems

Novel developments and limitations of the technologies in each of these areas are discussed below.

### Liquid solvent based technologies

These technologies use either a chemical or a physical solvent for capture and separation of CO<sub>2</sub> from gas streams. With chemical solvents, the CO<sub>2</sub> reacts with the solvent and is chemically bound, requiring considerable energy to reverse the process and release the CO<sub>2</sub>. With physical solvents, there is no reaction between the solvent and the CO<sub>2</sub>. The solubility of the CO<sub>2</sub> in the solvent is purely a function of pressure, temperature and the solvent used. The advantage is the avoidance of energy penalties associated with solvent regeneration as the CO<sub>2</sub> is released on flashing the solvent from the high pressure, at which the CO<sub>2</sub> is dissolved, to a lower pressure at which it is collected.

Physical solvents are well suited to applications where the CO<sub>2</sub> is present at a high partial pressure, eg. the syngas stream from a gasifier. One of the most attractive options in this regard is the **Morphisorb Process** that uses 95% by weight aqueous solution of N-acetyl morpholine (NAM) and N-formyl morpholine (NFM). This process offers about 60% less hydrogen loss and 20% lower utility cost compared with the conventional Selexol process used on IGCC plants. In that application it is primarily used to recover H<sub>2</sub>S, although it could also remove CO<sub>2</sub> at the same time. It is claimed that the morpholine solvent has a high affinity for water, hydrogen sulphide and aromatic sulphur compounds and does not undergo hydrolysis reactions at higher temperatures. In addition to these advantages, it is claimed that oxidative degradation of NAM and NFM produces other morpholine derivatives, which do not affect the solubility properties of acid gases.

Chemical-based solvents are effective at removing CO<sub>2</sub> from a gas stream irrespective of the concentration or partial pressure of the CO<sub>2</sub>, as the CO<sub>2</sub> reacts with, and is chemically bound to, the solvent. They are, therefore, well suited to the post-combustion capture where the partial pressures of CO<sub>2</sub> are relatively low. Their disadvantage is that considerable energy must be expended to reverse the chemical reaction to regenerate the solvent and recover the CO<sub>2</sub> in concentrated form. There are three chemical solvent-based processes that should be considered:



- The *Econamine FG* or a similar technology represents the conventional process that might be used for removing CO<sub>2</sub> from gas streams with high efficiency in a packed column. It uses a 10-30% by wt solution of monoethanolamine (MEA) as a chemical solvent for CO<sub>2</sub>. Its limitation for application to flue gases from coal-fired systems arises from the very low tolerance that MEA has for SO<sub>x</sub> and NO<sub>x</sub> (must be less than 10 ppmV) and its susceptibility to degradation in the presence of oxygen and carbon monoxide. The presence of particulate matter in the flue gas above a concentration of 3 mg/Nm<sup>3</sup> leads to sludge formation in the gas processing equipment that ultimately reduces CO<sub>2</sub> recovery efficiency.
- The *PSR Process* that originated from the University of Regina, Canada, uses a mixture of simple and hindered proprietary amines. It is being tested on a 4 tonne per day CO<sub>2</sub> capture facility at the SaskPower 875 MW Lignite-fired Boundary Dam Power Station under the auspices of International Test Centre for CO<sub>2</sub> capture (ITC), a consortium of 13 industry and government organisations including two Canadian universities. The mixtures of amines are selected to minimise energy penalties, solvent degradation and corrosion potential. Where both the gas stream pressure and CO<sub>2</sub> partial pressure are high (for example natural gas and refinery gas streams) physical solvents such as Sulfolane are also added to the amine mixture. This approach not only combines the benefits of physical and chemical solvents, but it also gives the PSR process a unique ability to handle gas streams where CO<sub>2</sub> content varies with time, for example in enhanced oil recovery operations.
- The *MHI Process*, developed by Mitsubishi Heavy Industry of Japan, uses a solvent called KS-1, probably a hindered amine such as methylaminoethanol. It is claimed to be tolerant to the combined presence of SO<sub>x</sub> and NO<sub>x</sub> up to 50 ppmv, and to have low rates of solvent loss.

The three chemical solvent processes described above are compared in Table 1.

### **Solid adsorbent based technologies**

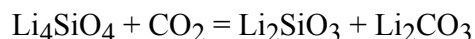
There is considerable effort being applied worldwide to developing solid sorbents, as these offer the possibility of avoiding the sensible and latent heat loads associated with vapourisation of water that occurs with aqueous chemical/physical solvent processes. Spent amine solvent contains nearly 70% water and needs to be preheated from 60°C (absorber outlet) to 120°C (regenerator bottom) during regeneration. As a result, nearly 30 to 40% of energy demand for solvent regeneration during conventional amine scrubbing is due to sensible heat and latent heat of vaporisation of water. By eliminating this extra energy demand, the overall energy efficiency of CO<sub>2</sub> capture and separation can be substantially improved.

Some of the other more significant developments in solid adsorbents are as follows:

- The *EniTechnologie Process* uses non-volatile amines on alumina support to absorb CO<sub>2</sub>. The process is still at early development stage and uses a mixture of diethanolamine and N, N'-bis(2-hydroxyethyl)ethylenediamine as the active agents. The maximum specific CO<sub>2</sub> capture obtained at room temperature so far is reported as 9.6% by wt of the sorbent. Regeneration of the sorbent requires heating of the solids to 100°C under vacuum. According to the proponents of this process, the specific CO<sub>2</sub> capture needs to be higher than 11% by

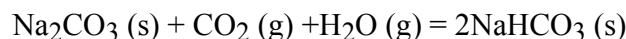
weight of sorbent and the overall system pressure loss less than 3.5 kPa before this process could be considered as being on par with conventional liquid solvent based processes.

- The **Toshiba Process** has been further improved with respect to the choice of adsorbent. Lithium orthosilicate has now been proposed as the preferred adsorbent due to its five times higher reaction rate compared to the lithium zirconate that was initially selected. The reversible adsorption/desorption reaction still proceeds within the same temperature range (450 to 650°C) used with lithium zirconate:



This process is not suitable for capture and separation of CO<sub>2</sub> from coal fired power plant flue gas due to uncertainties associated with interactions of flue gas impurities (SO<sub>x</sub>, NO<sub>x</sub>, HCl, HF, particulate matter, etc) with the adsorbent material and the very high temperature (around 650 °C) required for sorbent regeneration.

- The **RTI Process** is a recent development that uses sodium carbonate as solid sorbent for CO<sub>2</sub> capture and separation. The reaction of CO<sub>2</sub> with sodium carbonate is reversible at 200 °C according to the following equilibrium:



The carbonation reaction occurs in the presence of water vapour at temperatures as low as 41°C. The maximum sorbent capacity utilisation so far has been found to be 65% after 6.5 hours of exposure in the laboratory conditions. The process may not be suitable for coal-fired power plant flue gas treatment due to the presence of SO<sub>x</sub>, NO<sub>x</sub>, HCl and HF and particulate impurities that would certainly consume the sorbent.

Other relevant work in this field, funded by DOE, includes work at (i) NETL on the use of zeolites-13X, (ii) Oak Ridge National Laboratory on the use of carbon fibre composite molecule sieves with electric swing desorption, and (iii) Ohio State University where calcium carbonate is precipitated from a calcium hydroxide solution under controlled pH conditions. With respect to application to coal-fired systems, the zeolite systems have some attraction because of the low temperature at which they would operate, while the ORNL process may have an application for CO<sub>2</sub> removal from an IGCC fuel gas. However, all systems are still in their early stages of development.

### **Membrane Separators**

These technologies are being developed in an effort to do away with the large and costly conventional gas-liquid contacting towers. Conventional packed or plate columns have operating limits in terms of gas and liquid flow rates due to flooding, weeping and flow channeling problems. Foaming and solid precipitation or deposition within these columns can also have detrimental effects on the contacting efficiency of such devices. Since a conventional power plant flue gas has usually less than 15% by vol CO<sub>2</sub> content and large volume flow rates, use of conventional towers for liquid solvent based CO<sub>2</sub> removal results in large diameter columns (as

large as 18 metres). As a result, the cost of equipment construction, installation and maintenance, as well as the cost of land required to accommodate CO<sub>2</sub> removal plant remains very high.

Membranes tend to have as much as 1000 times more surface area per unit volume in comparison with the conventional packed columns and avoid direct contact between gas and liquid streams. The CO<sub>2</sub> containing gas passes on one side of the membrane and the absorbing liquid on the other in a crossflow type of arrangement. This results in a more compact device with wider operating range compared to a conventional tower, so that equipment and land related plant investment costs are lower. This is the basis for the development of liquid solvent and membrane based CO<sub>2</sub> removal technologies such as the TNO and Kvaerner processes. Figure 1 shows a schematic of gas separation using membrane technologies.

### ***TNO Process***

The TNO Institute of Environmental and Energy Technology<sup>1</sup> in the Netherlands has developed a macro-porous polypropylene membrane that uses an aqueous solution of an alkali amino acid salt as the solvent. The use of a conventional amine solvent (30 weight% MEA) with polypropylene membranes has been found to lead to solvent leakage occurs and consequent total loss of CO<sub>2</sub> separation efficiency.

A non-sterically hindered amino acid, such as taurine, has a stoichiometric CO<sub>2</sub> carrying capacity half of that of a sterically hindered amino acid such as glycine or alanine. However, it forms carbamate compounds as intermediates upon reaction with CO<sub>2</sub>, which are easy to decompose. On the other hand sterically hindered amino acids form bi-carbonates, which are much more stable intermediates. Thus, the TNO system uses both types of amino acids to help optimise CO<sub>2</sub> carrying capacity and thermal energy demand for solvent regeneration.

Published data of Feron<sup>2</sup> suggests that the solvent used in this process has thermal energy requirement for regeneration comparable to MEA. The polypropylene membranes seem to have limited life above 120°C. Hence, it is likely that the regenerator for the spent solvent would still have to be a conventional column with packing. Thus, for large-scale CO<sub>2</sub> removal and recovery, the TNO membrane absorbers do not offer either the ease of operation or the scope to reduce the cost of plants substantially. Also, there is no data currently available on either the solvent loss due to permeation of impurities such as SO<sub>x</sub>, NO<sub>x</sub>, HCl and HF into the solvent through the membrane or, the impact of particulate deposition on the membrane surface. Given that these impurities are present in the flue gas from a coal-fired power plant, application of this process for such cases is questionable. Table 2 compares the TNO process with conventional MEA based technology for CO<sub>2</sub> removal.

### ***Kvaerner Process***

This process uses GoreTex<sup>TM</sup> membranes and it is similar to the TNO process except that it uses PTFE (teflon) as the membrane material with amine solvents such as MEA, MDEA and DIPA in aqueous solution. Kvaerner claims that their membrane based absorption/regeneration system weighs 47% less and occupies 39% less foot print area compared to conventional technology.

Thus far, most of the development has been focussed on offshore gas production facilities where space is at a premium. For CO<sub>2</sub> recovery from a coal-fired power plant flue gas, no performance data for the Kvaerner process with respect to the presence of SO<sub>x</sub>, NO<sub>x</sub>, HF, HCL and particulates in the flue gas is currently available. A private communication from Kvaerner<sup>6</sup> suggests that their membrane absorbers are not recommended for using in a “dirty” service.

Table 2 compares this process with both the Kvaerner process with conventional MEA based technology for CO<sub>2</sub> removal. Both PSR and MHI processes are currently being tested under laboratory conditions in PTFE membrane systems.

### ***RITE Process***

This process, developed by the Japanese Research Institute of Innovative Technology for the Earth (RITE), uses cardo polyimide membranes<sup>3</sup>. Cardo polyimide membranes have very high selectivity for CO<sub>2</sub>/N<sub>2</sub> separation (up to 45) and high permeability for CO<sub>2</sub> in comparison with other polymeric membranes. They are easy to fabricate into hollow fibre modules and have excellent thermal stability up to 120°C.

At present the operating costs associated with such membranes appear to be prohibitively high. Cardo polyimide membranes developed by RITE have been found to have a working life in laboratory tests of around 8000 hours at 40°C, so that the entire membrane based CO<sub>2</sub> recovery unit would be up for either a complete replacement or a major overhaul within a year of operation.

### **Low Temperature Systems**

One means of separating CO<sub>2</sub> from other gases is to reduce the temperature of the stream via cryogenic processes until the CO<sub>2</sub> condenses. It is best suited to high-pressure streams with relatively high concentrations of CO<sub>2</sub>, as might be found in pre-combustion type applications. Problems can occur if there are other condensable gases (such as water) in the stream. These must be removed before carrying out the cryogenic step due to blockage problems as a result of the formation of ice. Studies by the IEA<sup>4</sup> have shown that the use of cryogenics does not appear to be attractive in its own right but might be more so when one includes the need to liquefy the CO<sub>2</sub> prior to transport.

A novel approach is being investigated in the US, using the SIMTECHE process, to separate CO<sub>2</sub> using water at close to freezing point via the formation of CO<sub>2</sub> hydrates. It is claimed that the process shows promise for shifted syngas streams<sup>5</sup>.

### **Other Options for CO<sub>2</sub> Capture**

There are other options for capturing the carbon in coal that are based on variations to the conventional combustion or gasification systems. These include:

#### **A. Oxy-fuel combustion**

With oxy-fuel combustion the coal is fired with oxygen rather than air so that the flue gases contain a concentrated stream of CO<sub>2</sub>. Recycling part of the CO<sub>2</sub> flue gas stream controls flame temperatures in the combustion zone. The system has been the subject of considerable



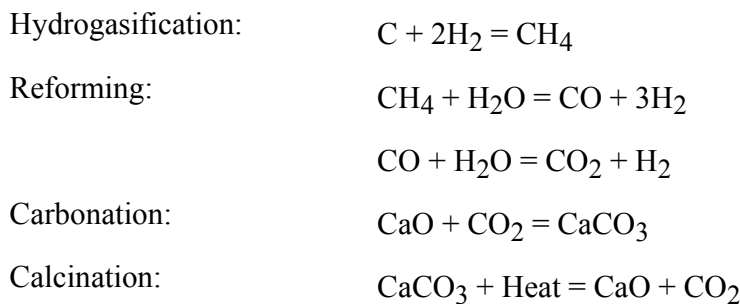
development through CANMET. Oxygen concentrations in the flue gas are reduced to around 0.5% compared to 5% in a PF-fired system. Sensible heat losses are reduced and it is claimed that there is the possibility of recovering the latent heat of the moisture in the gas stream. Essentially the flue gas stream only needs to be dried and compressed for transport to disposal.

CANMET are now in Phase 6 of their oxy-fuel program with emphasis on burner development and integrated emission control (eg. Hg emissions). With oxy-fuel combustion, low NOx emissions are achieved, as CO concentration is high near the burner although it is low at exit from the furnace. In a retrofit application one does not need to use high purity air, as there will be leakage of air into the boiler system anyway.

Economic feasibility studies of pf-fired systems performed thus far actually show little difference in cost between the oxy-fuel combustion and post-combustion amine scrubbing options.

### **B. The ZECA process**

This is the process currently being pursued by Zero Emission Coal Alliance (ZECA) consortium members. The alliance was formed in year 2000 and at present has 18 members from US and Canadian private industry and government agencies. The process looks at conversion of coal to synthesis gas via hydrogasification. Subsequent separation of CO<sub>2</sub> from the synthesis gas is by way of the carbonation of lime. The individual reaction sequence is as follows:



Calcination of calcium carbonate releases pure CO<sub>2</sub> that is finally converted to magnesite (magnesium carbonate) by reaction with serpentine or olivine mineral matter, providing stable, long-term sequestration of CO<sub>2</sub>:



The sequestration process is currently hampered by reaction kinetics for magnesium carbonate formation from serpentine or olivine. The details of the energy penalties for sequestration by this route have not yet been finalised since the process is still at early stages of development. However, published data from ZECA implies that 3.2 tonnes of serpentine mineral ore will be

required to sequester 1 tonne of CO<sub>2</sub>. There is currently no information available on the environmental impact of mining serpentine at such a large scale.

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**Table 1. Comparison of PSR & MHI Processes with Conventional MEA Process**

| Parameter                                       | PSR               | MHI                                      | MEA                                       |
|---|-------------------|--|---|
| Solvent   | Formulated Amines | Hindered Amines                          | 30% by Weight MEA                         |
| Solvent Loss (kg/ton of CO <sub>2</sub> )       | 0.65              | 0.35                                     | 2 to 3                                    |
| CO <sub>2</sub> Carrying Capacity               | 1.2 to 1.8        | 2  | 1   |
| Regeneration Energy Required                    | 0.6 to 0.8        | 0.7 to 0.8                               | 1   |
| Corrosion Rate (mpy)                            | 2                 | 2  | 9.5                                       |
| SO <sub>x</sub> , NO <sub>x</sub> etc Tolerance | Not known         | 50 ppmV SO <sub>x</sub> /NO <sub>x</sub> | < 5 ppmV SO <sub>x</sub> /NO <sub>x</sub> |
| CO <sub>2</sub> Removal Cost (US \$/Tonne)      | ~21               | ~20                                      | ~28                                       |

**Table 2. Comparison of TNO & Kvaerner Processes with Conventional MEA Process**

| Parameter   | TNO  | Kvaerner   | MEA  |
|---|--|--|--|
| Solvent   | Aminoacids   | 30% by Weight MEA                                    | 30% by Weight MEA                                    |
| Membrane  | Polypropylene  | PTFE   | -  |
| Regeneration Energy Required                      | 1  | 1  | 1  |
| CO <sub>2</sub> Carrying Capacity                 | 1  | 1  | 1  |
| SO <sub>x</sub> , NO <sub>x</sub> etc Tolerance   | Not known  | Not known  | < 5 ppmV SO <sub>x</sub> /NO <sub>x</sub>            |
| Likely CO <sub>2</sub> Removal Cost (US \$/Tonne) | ~25<br>(3.5% by Vol. CO <sub>2</sub> , 50% Recovery) | ~30<br>(3.5% by Vol. CO <sub>2</sub> , 80% Recovery) | ~32<br>(3.5% by Vol. CO <sub>2</sub> , 80% Recovery) |

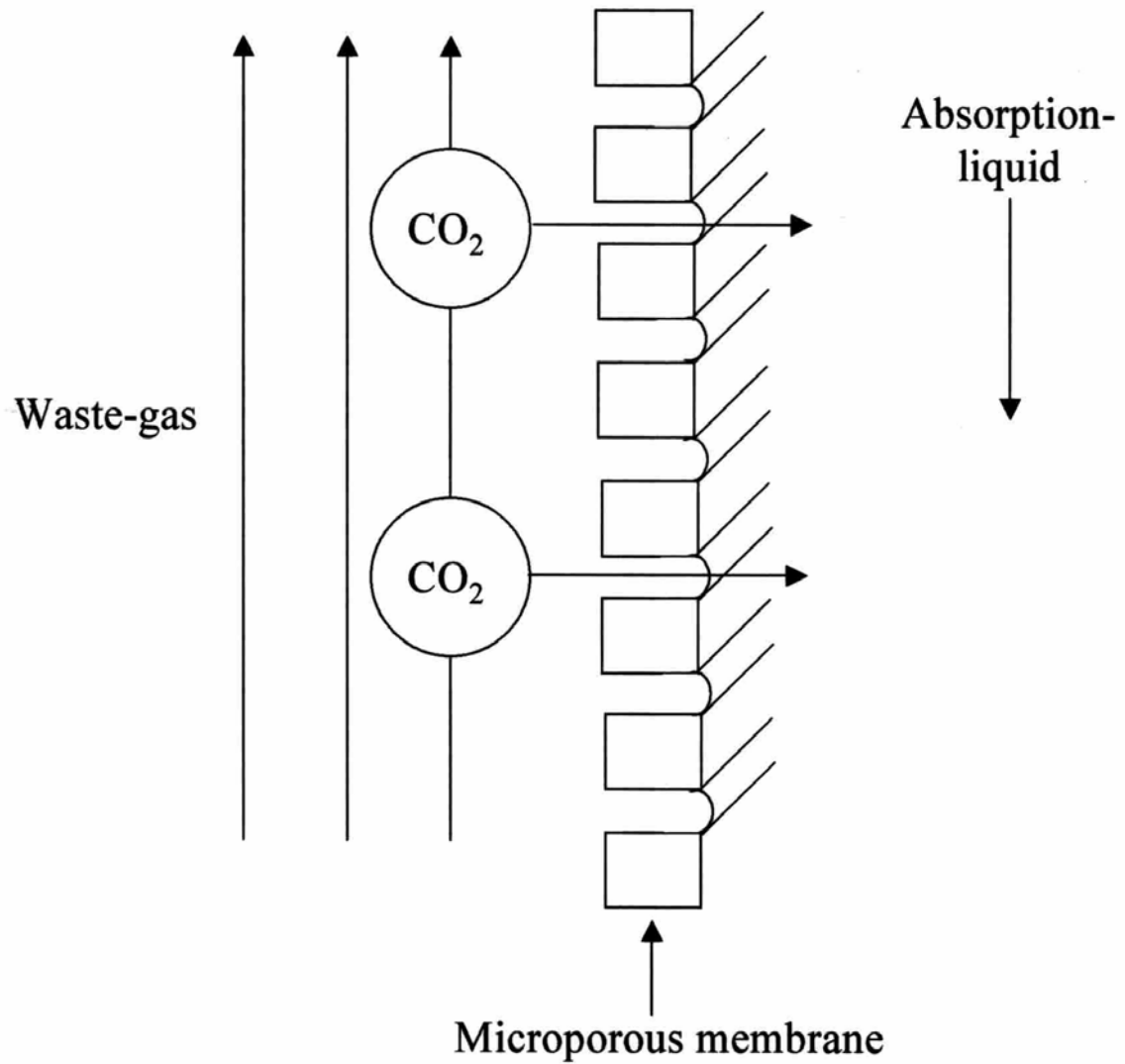


Figure 1. Schematic of CO<sub>2</sub> separation using a solvent/membrane system