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***Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste***

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# WP 1 Review Report - Carbon Dioxide Capture and Sequestration

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**Integrated Waste Management Approach WP 1 Review Report –**
**Carbon dioxide capture and sequestration**

**Executive summary**

There has been an extensive, international scientific and engineering effort on the development of $CO_2$ sequestration technologies over the past few years. Significant progress on the development and, in some cases, demonstration of the technologies for the capture, processing and storage of the $CO_2$ emitted from large fossil fuel power plants, has been made. The key pre- and post-combustion $CO_2$ scrubbing technologies and the oxy-fuel combustion technologies, and the techniques for the purification of the $CO_2$ to the desired quality for further on-site processing, are reasonably well understood and are largely proven at small pilot plant and component testing scale. There are projects, both planned and under way, aimed at the construction and testing of demonstration scale plants. All of the currently available $CO_2$ capture technologies have significant cost and energy efficiency penalties, however, and in parallel with the technology demonstration activities, significant development projects aimed at incremental improvement of the existing state of the art, and at the development of alternative technical approaches, are also in progress.

There are a number of ongoing projects in the North Sea, in Canada and in Algeria, which involve the large scale handling and geological storage of $CO_2$, and the experience of these CCS projects are in addition to the fairly extensive experience of the large scale use of $CO_2$ for enhanced oil recovery in the Texas oilfields, which has been practiced since the 1970s. Further developments of these technologies, and of the ocean storage and other relevant options, are under way.

It is clear that the destructive thermal processing of irradiated graphite will be carried out at much smaller scale, perhaps at a combustion rate of the order of one tonne per hour or so. It is likely that the most appropriate approach to the destructive thermal processing of the graphite will involve combustion at high temperatures in a fluidised bed or grate-fired combustor, with natural gas or oil for light-up and possibly for combustion support purposes.

The relatively modest scale of operation of graphite combustion will also mean that the large scale transport and storage technologies being developed for CCS will not be relevant and some of the smaller scale mineral carbonation or industrial utilisation options for the $CO_2$ may be more relevant.

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# Chapter contents

# 1 Background

The material in this document is concerned with the current status of carbon dioxide capture and sequestration technologies and the potential for their application to the destructive thermal processing of irradiated graphite.

There are two key technical aspects to the destructive thermal processing of irradiated graphite, viz:

- The techniques available for the thermal destruction of the graphite, and
- The radioactive waste management processes and procedures that will be applied to the graphite feed material, and to the off-gases, and the solid and liquid residues from the thermal processing plant.

It should be noted that the key carbon dioxide capture and sequestration are in the development phase, and are being developed principally for processes involving the large-scale utilisation of fossil fuels for power and heat generation. In this context, it should be noted that the total mass of irradiated graphite from all of the Magnox reactors in Britain is only of the order of 50,000 tonnes, and this would generate a total of just under 200,000 tonnes of $CO_2$. This is relatively modest compared to the scale of operation of the large fossil fuel combustion plants. It is unlikely that the owners and operators of large fossil fuel plants would seriously contemplate the co-combustion of the irradiated graphite. The potential technical, regulatory and potential public relations risks would be excessive.

One of the key issues is that irradiated graphite will contain C-14. It is currently considered that the C-14 in graphite has been largely derived from the irradiation of the N-14 in air in the graphite pores. The concentration of C-14 in the graphite is considered to be of the order of 1-100 ppm and the radioactivity associated with 1 g of C-14 is of the order of 17 x1010 Bq. The

$^{14}CO_2$ generated by combustion of the graphite will have, therefore, little impact on the total volume of CO2, but may have a significant environmental impact. The acceptable level of release of C-14 into the atmosphere associated with the emission of CO2 from the destructive thermal processing of the irradiated graphite from the decommissioning of the nuclear reactors in Britain, Europe and the rest of the world will have to be very carefully considered.

It should also be recognised in this context that the irradiated graphite is not a pure substance, and may contain significant levels of impurities arising from manufacture and through its operating life in the reactor when modification and activation of these or of newly introduced impurities may have occurred. It is a normal characteristic of reactor operations that impurities may be carried around the reactor circuit and can accumulate in the graphite.

Pre-treatment of the graphite, and in particular size reduction, prior to thermal processing will be required. It may also be beneficial to pre-treat the graphite to reduce the levels of radioactive impurities prior to destructive thermal processing.

It is most likely that the pre-treated graphite would be processed in a small dedicated and purpose-designed combustion/incineration plant, with natural gas or oil for start-up and possibly combustion support, and fitted with the appropriate gas clean-up and radiation management systems. These may include C-14/C-12 separation or $CO_2$ capture and sequestration facilities, if the levels of emission of C-14 are unacceptable. The appropriate management of any radioactive sold and liquid residues from the process would be key plant design and operational issues, and this would have a major, and at present unknown, impact on the capital and operating costs of the plant.

As stated above, the destructive thermal processing of irradiated graphite will inevitably result in the production of exhaust gases, which may be radioactive, and which will require further treatment. The principal constituents of the exhaust gases are:

- Carbon, principally in the form of $CO_2$,
- Hydrogen , principally in the form of $H_2O$, and potentially

- Chlorine, principally in the form of HCl.

The exhaust gases will also contain a level of entrained particulate material, principally unburned fuel anda sh particles.

It will, in most circumstances, be necessary to fit the thermal processing plant with flue gas treatment equipment, to permit compliance with the relevant environmental and other regulations. The particulate material, and the hydrogen- and chlorine-containing gases are generally reasonably easy to remove from the exhaust gases prior to emission to the atmosphere. The $CO_2$ is commonly present in higher concentrations, and is significantly more difficult to capture.

$CO_2$ is also a greenhouse gas, and there has been significant interest in recent years in the means available for the reduction of the emissions of $CO_2$ to the atmosphere from the utilisation of fossil fuels. For a recent and authoritative discussion of this subject, reference should be made to the IPCC Synthesis Report on Climate Change, 2007 [(1)]. One approach to the reduction of $CO_2$ releases involves the capture of the $CO_2$ produced by the combustion of fossil fuels, principally coal, mineral fuel oils and natural gas, in the large thermal power stations, and the long-term storage of the captured gas. This approach has the attraction that it permits the continuation of the industrial utilisation of fossil fuels, at least in the short-medium term future, with the sequestration of the resultant $CO_2$.

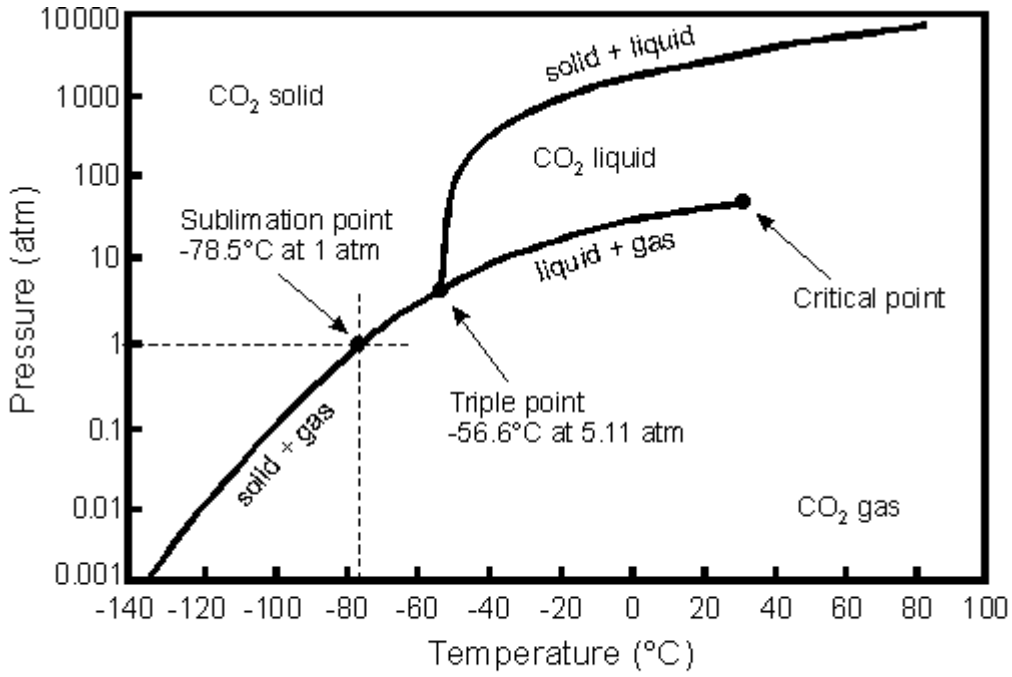
It is considered that the advances made in the technologies available for the capture and storage of CO2 from large fossil fuel combustion plants may be of relevance to the thermal processing of the irradiated graphite, despite the very large differences in the likely scales of operation.

## 1.1 The physical and chemical properties of $CO_2$

CO2 is present in the atmosphere in relatively small quantities, currently of the order of 370 ppmv, but it plays a vital role in the life cycle of both plants and animals. At normal temperatures and pressures, carbon dioxide is a gas, which is significantly denser than air.

The $CO_2$ phase diagram is reproduced in **Figure 1** [(2)]. This is a relatively simple diagram, with three key points, viz:

- A sublimation point,
- A triple point at -56.5°C and 5.1 bar, and
- A critical point at 31.1°C and 73.9 bar.




Pressure-Temperature phase diagram for $CO_2$.

**Figure 1** : The $CO_2$ phase diagram [(2)].

At temperatures and pressures above the critical point, CO2 is in a supercritical state where it behaves as a gas. At high pressures, the density of the gas can approach that of liquid water.

The values of a number of selected physical properties of carbon dioxide are given in Table 1, and some relevant thermodynamic data for $CO_2$ and a number of related compounds are presented in Table 2.

$CO_2$ dissolves in pure water to form an aqueous solution of carbonic acid [3]. The solubility of $CO_2$ is relatively low at less than 0.35 g/100 ml, decreases with increasing temperature and

**Table 1** : Physical properties of $CO_2$ [2]

| Property | Value |
|---|---|
| Molecular weight | 44.01 |
| Critical temperature | 31.1°C |
| Critical pressure | 73.9 bar |
| Critical density | 467 kg/m$^3$ |
| Triple point temperature | -56.5°C |
| Triple point pressure | 5.18 bar |
| Boiling (sublimation) point (1.013 bar) | -78.5°C |
| | |
| ***Gas phase*** | |
| Gas density (1.013 bar at boiling point) | 2.814 kg/m$^3$ |
| Gas density (@ STP†) | 1.976 kg/m$^3$ |
| Specific volume (@ STP) | 0.506 m$^3$/kg |
| Cp (@ STP) | 0.0364 kJ/(mol.K) |
| Cv (@ STP) | 0.0278 kJ/(mol.K) |
| Cp/Cv (@ STP) | 1.308 |
| Thermal conductivity (@ STP) | 13.72 μN.s/m$^2$ |
| Solubility in water (@ STP) | 14.65 mW/(mK) |
| Enthalpy (@ STP) | 1.716 vol/vol |
| Entropy (@ STP) | 21.34 kJ/mol |
| Entropy of formation | 117.2 J.mol/K |
| | 213.8 J.mol/K |
| ***Liquid phase*** | |
| Vapour pressure (at 20°C) | 58.5 bar |
| Liquid density (at -20°C and 19.7 bar) | 1032 kg/m$^3$ |
| Viscosity (@ STP) | 99 μN.s/m$^2$ |
| | |
| ***Solid phase*** | |
| Density of carbon dioxide snow at freezing point | 1562 kg/m$^3$ |
| Latent heat of vaporisation (1.013 bar at sublimation) | 571.1 kJ/kg |

increases with increasing pressure. Carbonic acid is a weak acid, which dissociates in water in two steps, viz:

† STP stands for Standard Temperature and Pressure, which is 0°C and 1.013 bar

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad K_{a1} = 4.2 \times 10^{-7}$$
$$HCO_3 \leftrightarrow H^+ + CO_3^{2-} \qquad K_{a2} = 4.8 \times 10^{-11}$$

The carbonate anion interacts with the cations that may be present in aqueous solution and, since all of the common carbonates are insoluble in water, except for those of ammonium and of the Group IA elements, this interaction results in the precipitation, most commonly of calcium and magnesium carbonates.

**Table 2:** Thermodynamic data for selected carbon-containing compounds [2].

| Compound | Heat of formation $\Delta H_f^o$ (kJ/mol) | Gibbs free energy of formation $\Delta G_f^o$ (kJ/mol) | Standard molar entropy $S_f^o$ (J/(mol.K) |
|---|---|---|---|
| CO (g) | -110.53 | -137.2 | 197.66 |
| $CO_2$ (g) | -393.51 | -394.4 | 213.78 |
| $CO_2$ (l) | | -386 | |
| $CO_2$ (aq) | -413.26 | | 119.36 |
| $CO_3^{2-}$ (aq) | -634.92 | | -50.0 |
| $HCO_3^-$ (aq) | -689.93 | -603.3 | 98.4 |
| $CaCO_3$ (s) | -1207.6 (calcite) | -1129.1 | 91.7 |
| $MgCO_3$ (s) | -1113.28 (magnesite) | -1029.48 | 65.09 |

# 2 The current status of $CO_2$ capture technologies

## 2.1 The control of $CO_2$ production from fossil fuel and related sources

The global atmospheric concentration of carbon dioxide is much higher than those of the other greenhouse gases, and the increase in the CO2 concentration in recent years is considered to be predominantly due to the increased utilisation of fossil fuels. The annual global CO2 emissions have increased from 21 gigatonnes to values in excess of 38 gigatonnes, since the 1970s, and there is now an imperative worldwide, recognised at the highest political levels, to arrest and eventually reverse this trend. The current situation is described in some detail and with some authority in the recent Synthesis Report published by the IPCC in 2007.

The principal policy instrument which is currently in place for the reduction of industrial $CO_2$ emissions in Europe is the EU Emissions Trading Scheme (ETS). The objectives and the operational aspects of the scheme are described in some detail in the official EC website [4]

This is a cap and trade scheme, which covers more than 10,000 large industrial installations, which are responsible collectively for close to 50% of the total CO2 emissions within the EU. The operators of each of these installations must monitor and report their CO2 emissions on an annual basis. At the beginning of each trading period, each operator receives or must purchase an initial allocated emissions allowance, which is determined by the EU and, on an annual basis, the plant operator is obliged to return allowances sufficient to cover his total CO2 emissions during the year. If an operator has allowances in excess of his needs he may sell them to others. In principle, provided the traded value of the allowances is high enough, this scheme provides an incentive for power plant operators to invest in operating practices and technologies which will allow them to continue to operate, but at a reduced level of CO2 emissions. This applies both to the retrofit of new technologies to existing plant and to the installation of new plant.

Because the power generation sector is responsible for a large fraction of $CO_2$ emissions in most industrial countries, and because power plants represent a relatively small number of stationary sources of $CO_2$ emissions, the potential for the capture and sequestration of the long-term storage of $CO_2$ from these plants has been the subject of significant study.

There are two topics of interest in this context, viz

- The development of technologies that permit the capture and purification of the $CO_2$ emitted from fossil fuel plants, and
- The bulk transportation and long-term storage of the $CO_2$.

One of the most important sources of information on the $CO_2$ capture and sequestration options is the IEA Greenhouse Gas R&D Programme [(5)], who have published a comprehensive set of technical and other reports on relevant subject areas.

The key carbon dioxide capture and sequestration options are discussed briefly in this section, and it should be noted that the technologies under review are, in the main, those that are applicable to the large coal-fired power plants.

## 2.2 $CO_2$ capture methods applicable to coal-fired power plants

The technologies that are currently available, or may become available in the short-medium term future, for the capture of the carbon dioxide from coal-fired power plants can be listed under three headings [6], viz:

- pre-combustion,
- oxy-combustion and
- post-combustion $CO_2$ capture technologies.

The general characteristics of each of these options are illustrated in **Figure 2**

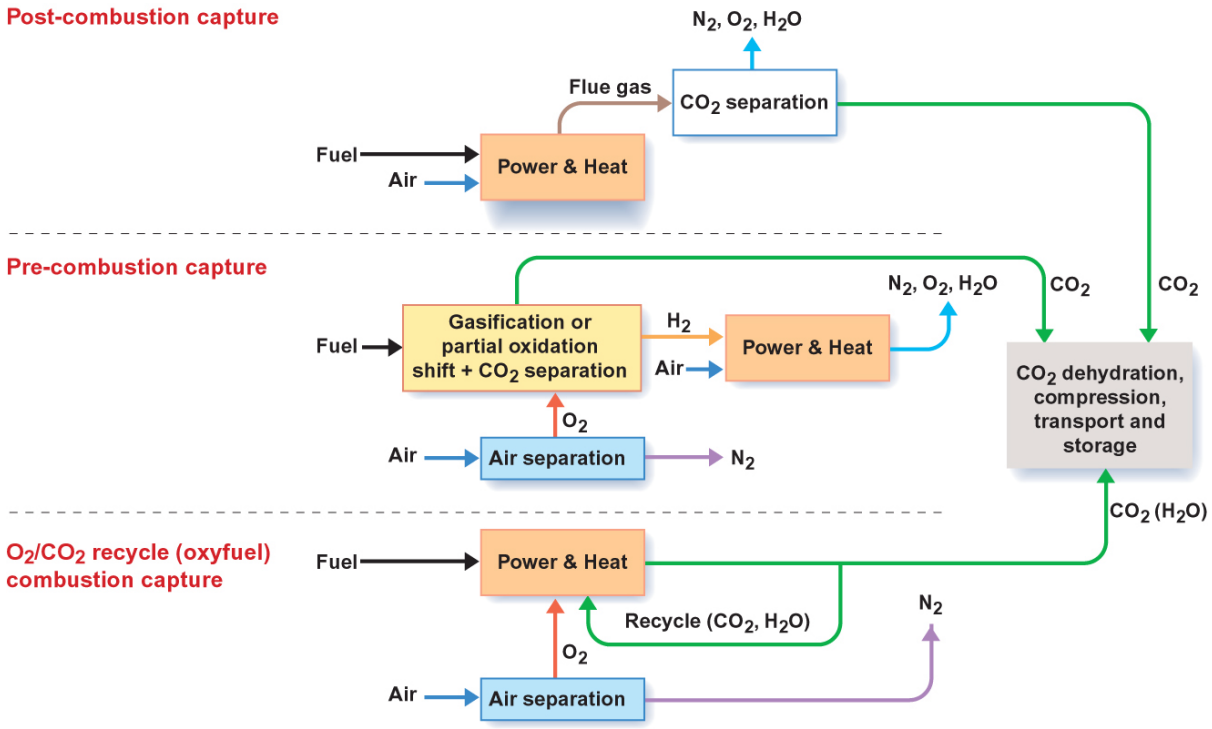



**Figure 2**: Carbon dioxide capture strategies for coal-fired power plants [6]

## 2.3 Pre-combustion $CO_2$ capture technologies

Pre-combustion $CO_2$ capture[5][7] is the term used to describe technologies which involve the pyrolysis or gasification of the solid fuel to produce a gaseous fuel, and the removal of the carbon compounds in this fuel gas, normally as $CO_2$, prior to burning the hydrogen in a gas turbine. The general features of this option are illustrated in **Error! Reference source not found.** 3 [7].

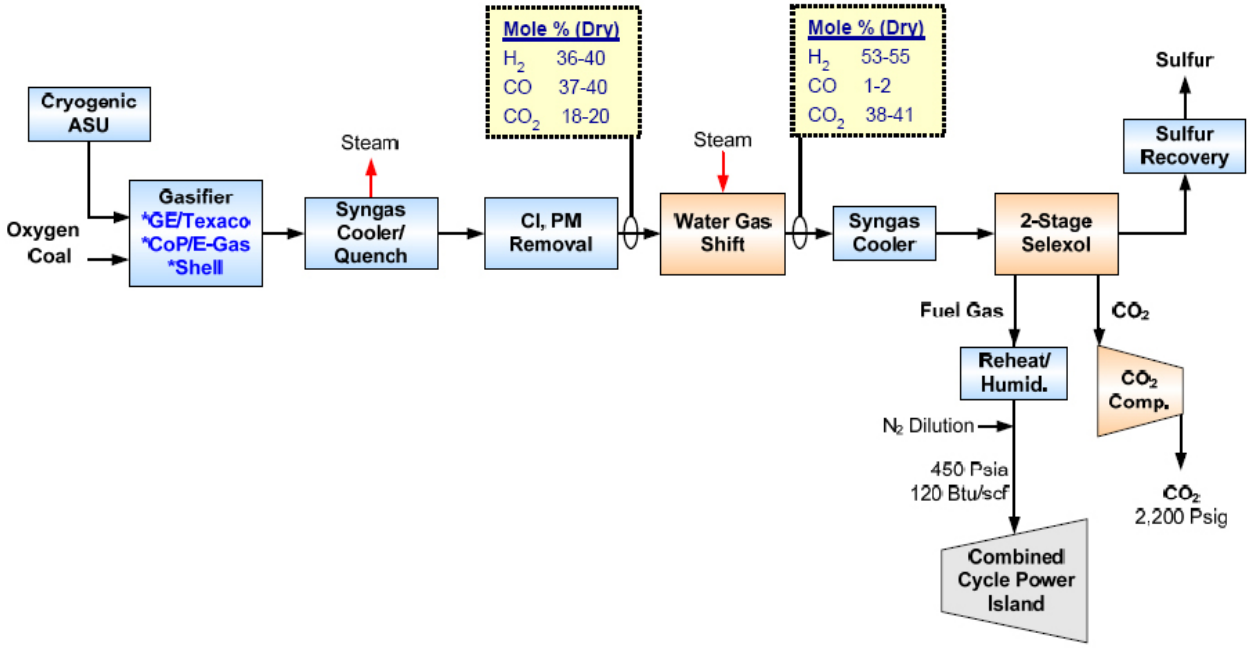



**Figure 3:** Pre-combustion $CO_2$ capture in an IGCC system[7]

Gasification is the partial oxidation of the coal, or any fossil fuel, to produce a gas, often known as a syngas, which has $H_2$ and CO as its main combustible constituents. In conventional Integrated Coal Gasification Combined Cycle (IGCC) plants, the syngas is fired in a gas turbine, after suitable gas cleaning.

In systems involving $CO_2$ capture, the syngas would be reacted with steam to produce a mixture of $CO_2$ and $H_2$. This is the water gas shift reaction, viz:

$$CO + H_2O \rightarrow CO_2 + H_2$$

The $CO_2$ would then be separated, and the residual gas, containing $H_2$ as the principal combustible constituent, would be used as the fuel in a gas turbine, combined cycle plant.

The water gas shift reaction is commonly carried out in a catalyst-packed tubular reactor [8]. The current commercial high-temperature catalysts are usually iron oxide containing 8-14 wt% of $Cr_2O_3$. The iron oxide catalysts are effective in the temperature range 340-590°C. Below 340°C a copper oxide catalyst is required, at much higher unit cost. Since $Cr^{+6}$ is toxic, Fe-Al based catalysts, which can provide higher hydrogen yields compared to Fe-Cr catalysts, have been developed recently, to improve the environmental performance of the process.

At present there is a significant research effort on the development of a cost-effective approach to the separation of the $CO_2$ from the water gas shift reactor product stream. Potential systems include:

- Chemical solvents — principally amines
- Physical solvents — glycols, methanol, ionic liquids
- Chemical and physical sorbents — metal-organic frameworks
- Membranes — polymer, ceramic, hollow fibre membrane supports

The key $CO_2$ separation and purification processes are described in a little more detail in Section 3, below.

Although there are plans to build further large IGCC power plants in Europe and elsewhere, the pre-combustion $CO_2$ capture technology described above is still very much in the research and development phase.

## 2.4 Oxy-combustion $CO_2$ capture technologies

Oxy-combustion[5][9] involves the combustion of a fossil fuel in a mixture of oxygen and recycled flue gas, rather than air, to produce a flue gas which comprises mainly $CO_2$ and water, rather than nitrogen and $CO_2$. The $CO_2$ concentration in the flue gas from an oxy-combustion

firing system is, therefore, much higher than in the flue gas from an air firing system, and hence the $CO_2$ can be cleaned, compressed and stored with significantly less downstream processing than would be necessary with air firing.

The key elements of the process are illustrated in Figure 4. The oxygen required for combustion in the oxy-combustion plant, is obtained from a dedicated air separation unit. The oxygen is mixed with the flue gases recycled from the FGD plant exit, to provide the combustion medium for the pulverised coal.

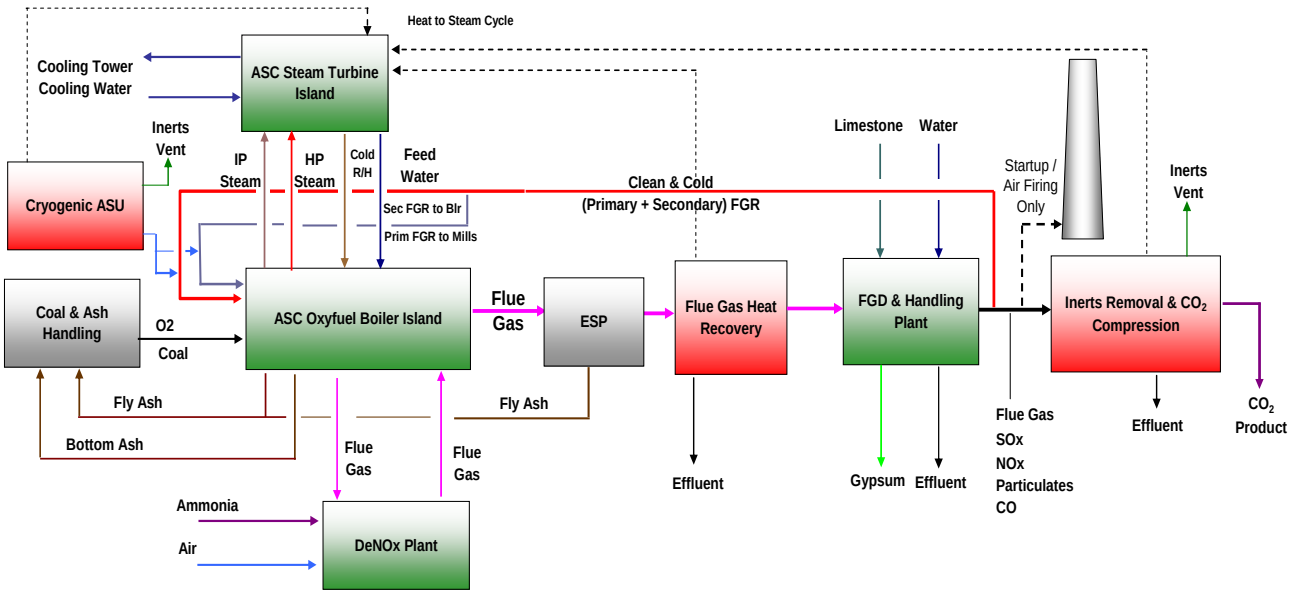



**Figure 4:** Oxy-combustion $CO_2$ capture applied to a large pulverised coal-fired power plant [9]

The flue gas exhaust stream from the oxy-combustion process is chilled and compressed to separate out some of the impurities to provide a $CO_2$ product of the required quality.

The oxy-combustion of fossil fuels with $CO_2$ capture is not, as yet fully commercial, however integrated pilot plants have been or are currently being built, and detailed plans to build

commercial power plants and to convert existing thermal power plants to oxy-combustion are being developed at the present time.

## 2.5 Post-combustion $CO_2$ capture technologies

Post-combustion $CO_2$ capture technology[5] is applicable to any combustion process, including conventional gas, oil and coal-fired boilers, and gas turbines. In post-combustion $CO_2$ capture, the $CO_2$ is removed from the flue gas in a scrubbing system, conventionally using amines as solvents for the $CO_2$. $NO_2$ and $SO_x$ can react with the amine solvent to form stable, non-regenerable salts. Post-combustion $CO_2$ capture on coal fired power plants therefore requires upstream de-$NO_x$ and flue gas desulphurisation, to the required standards, prior to entry to the scrubber. The loaded solvent is heated in a separate solvent regeneration unit to recover the $CO_2$ for further processing, and to regenerate the solvent.

This type of system is illustrated in **Figure 5**. The post combustion $CO_2$ separation systems are described in a little more detail in Section 3 below.

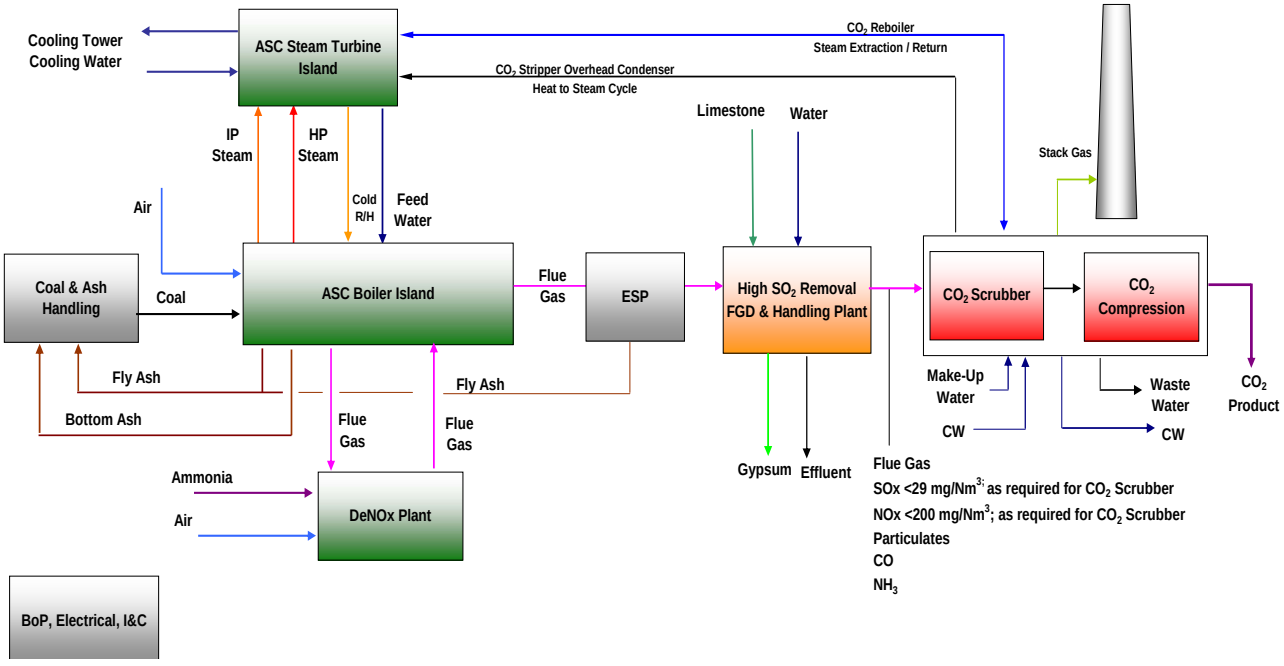



**Figure 5:** Post-combustion $CO_2$ capture [9]

## 2.6 Chemical looping as an alternative approach to $CO_2$ capture

A number of chemical looping methods[10] have been given some consideration recently as potential alternative methods for the combustion process or for capturing the $CO_2$ contained in the flue gas from fossil fuel combustion.

The basic principle of **chemical looping combustion** involves the separation of the oxidation process into two steps, as illustrated in Figure 6[11]. The oxygen is introduced to the gaseous fuel in the fuel reactor in the form of a metal oxide 'oxygen carrier'. The depleted metal oxide is then carried to the 'air reactor' where it is re-oxidised by contact with air. The heat energy is generated in the fuel reactor by the oxidation of the fuel. The waste gas stream from the fuel reactor contains principally carbon dioxide and water, and these can be separated relatively easily for further processing.

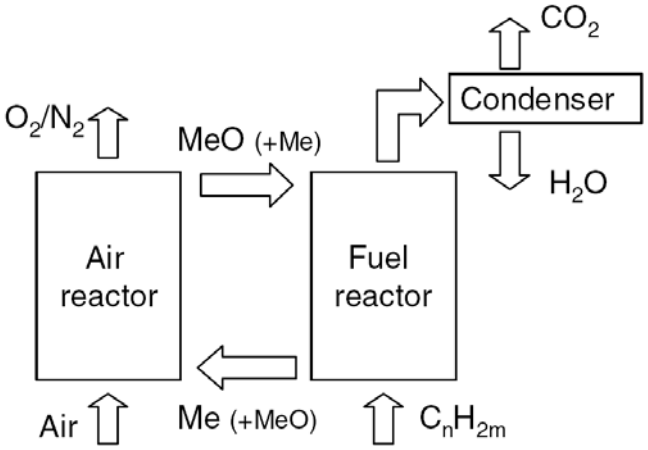
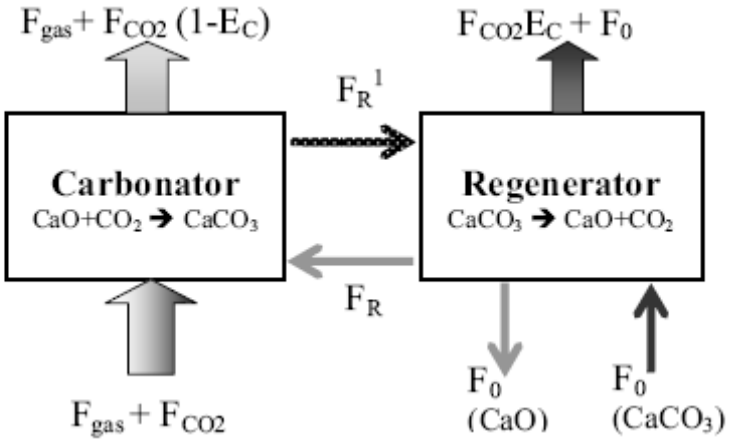



**Figure 6:** Chemical looping combustion: the basics[11].

The major potential advantage of the proposed chemical looping combustion systems is that they can generate a relatively concentrated $CO_2$ stream with no requirement for an oxygen separation unit.

The **post-combustion chemical looping process** consists of a carbonator and a regenerator (calciner), as shown in **Error! Reference source not found.** 7[12]. In the carbonator, which is operated at around 600°C, the $CO_2$ is removed from the flue gas by reaction with lime to form

$CaCO_3$. The lime sorbent is then regenerated in a separate regenerator unit at temperatures in excess of 950°C.




[1] denotes presence of CaO and CaCO3 in stream

**Figure 7:** Chemical looping post combustion $CO_2$ capture[12]

One of the key difficulties with this approach is that limestone particles which is repeatedly calcined at temperatures in excess of 950°C rapidly loses its reactivity due to sintering, which tends to reduce the surface area available for reaction.

In **chemical looping gasification,** which is illustrated in **Figure 8**[13], the continuously looping solid oxygen-carrier ($CaSO_4$) is used to partially oxidise the fuel to form water and carbon monoxide (CO). These species are converted to $CO_2$ and $H_2$ in a shift reactor, and a regenerative carbonate cycle, similar to the post-combustion chemical looping, described above, is employed to separate the hydrogen from the $CO_2$. The chemical looping gasification process, therefore, produces a stream of hydrogen that can be used as a fuel or as feedstock for chemical processes, and a $CO_2$ stream for sequestration.

To date, the chemical looping systems described above, have been tested in bench scale apparatus and in small-scale pilot plants. The practical application of these technologies in full-scale commercial plants is likely to be in the medium to long term future.

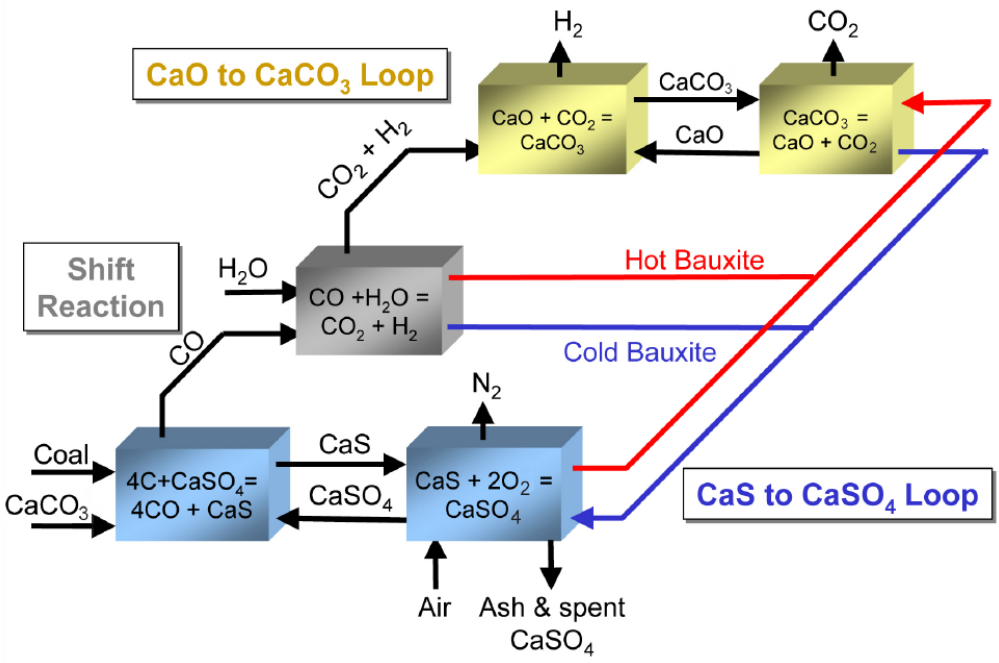



**Figure 8:** Chemical looping gasification with hydrogen production and $CO_2$ capture[13].

# 3 Carbon dioxide utilisation and storage

## 3.1 $CO_2$ purification technologies

It is clear from the material presented in Section 2 above that a number of different technologies are available for the capture of $CO_2$ from coal-fired power plants. It is also clear that a number of different carbon dioxide purification systems may be required depending on the requirements of the $CO_2$ capture process and of the downstream transport and storage arrangements.

The key carbon dioxide purification options for the pre-and post combustion $CO_2$ capture systems and for the oxy-fuel combustion systems will be discussed briefly in this Section.

### 3.1.1 $CO_2$ treatment processes for pre-combustion capture systems

The current state-of-the-art for pre-combustion $CO_2$ capture involves the use of a glycol-based solvent called Selexol[8][14] for the extraction of the $CO_2$ from the product of the shift reactor. Selexol is a liquid physical solvent, which was developed by Allied Signal in the 1950's, and which is currently being used for $CO_2$ removal in industrial chemical process plants. The solvent is a mixture of the dimethyl ethers of polyethylene glycol, with the general formula $CH_3(CH_2CH_2O)_nCH_3$, where n is between 3 and 9. Selexol is a true physical solvent, and does not react chemically with the absorbed gases.

As an example of current industrial practice, the application of the Selexol process at a coke gasification facility in Coffeyville, USA[14], for the separation of $CO_2$ and $H_2S$ from the syngas stream, is illustrated in Figure 9. The syngas from the oxygen-blown gasification unit is

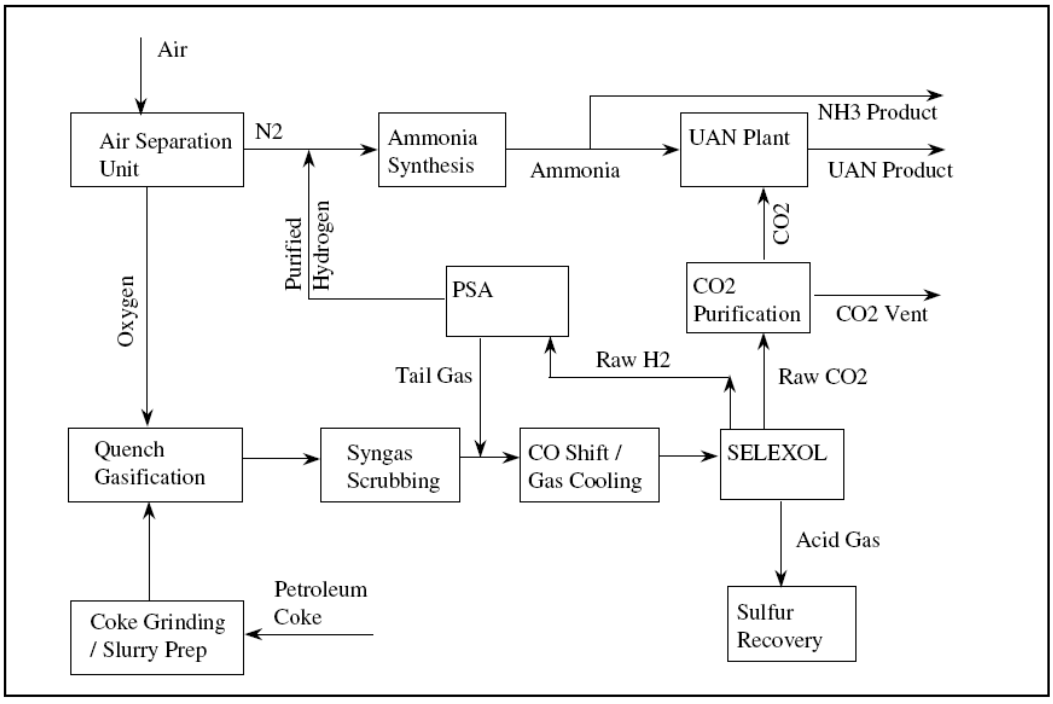



**Figure 9:** Block flow diagram for the coke gasification to ammonia project at Coffeyville, USA[14].

scrubbed and then processed through the shift reactor to produce a stream rich in $CO_2$. The absorbed $CO_2$ is desorbed by flash regeneration of the solvent in a series of stages. The raw hydrogen is sent for further processing. The regenerated $CO_2$ stream is further purified using

an activated zinc oxide bed and a platinum oxidation catalyst to obtain the required $CO_2$ quality. The final purity of the $CO_2$ stream is 99%.

Using a physical solvent is generally considered to be preferable for the removal of the $CO_2$ from the syngas streams in pre-combustion systems, because the syngases from the water gas shift reactor tend to have relatively high $CO_2$ concentrations. The solubility of acid gases in physical solvents increases linearly with the $CO_2$ partial pressure.

The chemical solvents, such as methyldiethanolamine (MDEA) and diethanolamine (DEA), have relatively high absorption capacity at low $CO_2$ partial pressures, but their adsorption capacity tends to level out at higher partial pressures.

### 3.1.2 $CO_2$ treatment for oxy-fuel combustion systems

As an illustration of the current thinking on the $CO_2$ purification systems associated with Oxy-fuel systems, the $CO_2$ treatment plant proposed for a coal based oxy-combustion facility that was described in a report from the IEA Greenhouse Gas R&D Programme[15], is presented in Figure 10 and Figure 11.

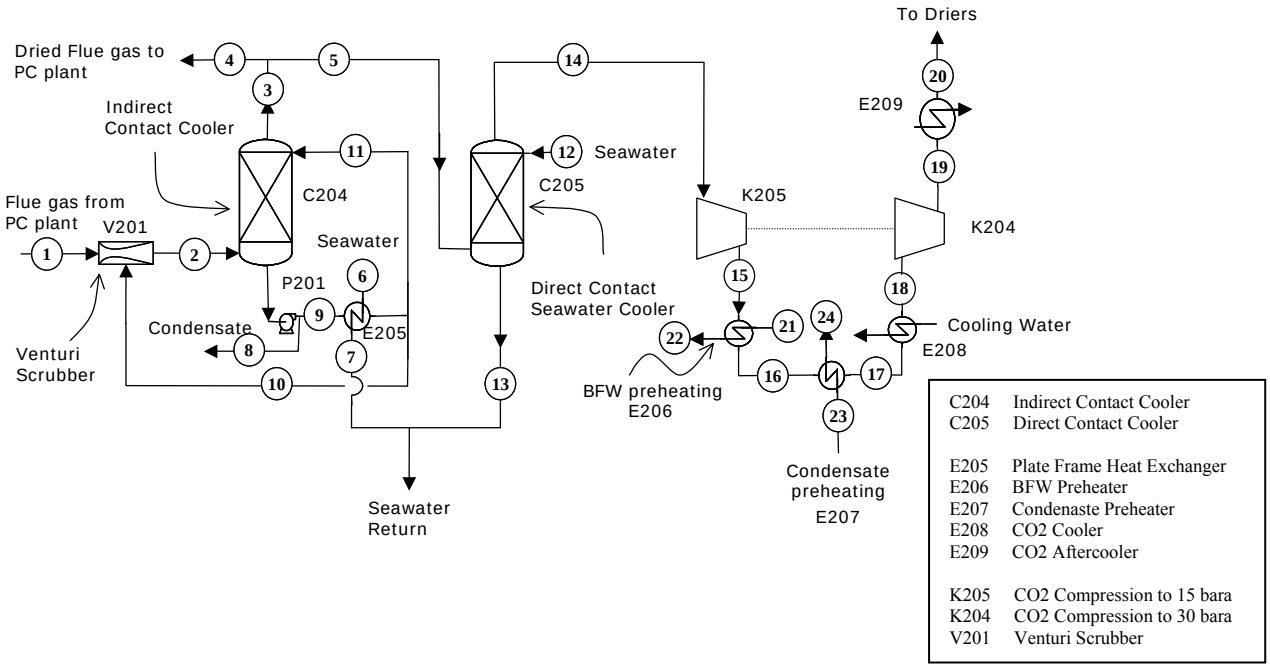



**Figure 10:** Process flow diagram – $CO_2$ cooling and compression to 30 bara[15]

The first part of the $CO_2$ treatment, illustrated in Figure 10, involves the cooling of the $CO_2$-rich flue gas from the oxy-fuel combustion plant, removing the moisture by condensation, and the compression of the dry $CO_2$ stream to 30 bar.

In the second phase, illustrated in Figure 11, the raw $CO_2$ at 30 bar is dried further, and the inert gases (principally $N_2$ and Ar) and oxygen are separated, to produce a stream with >95 mol% $CO_2$. The $CO_2$ is then compressed to 110 bar for pipeline transmission.

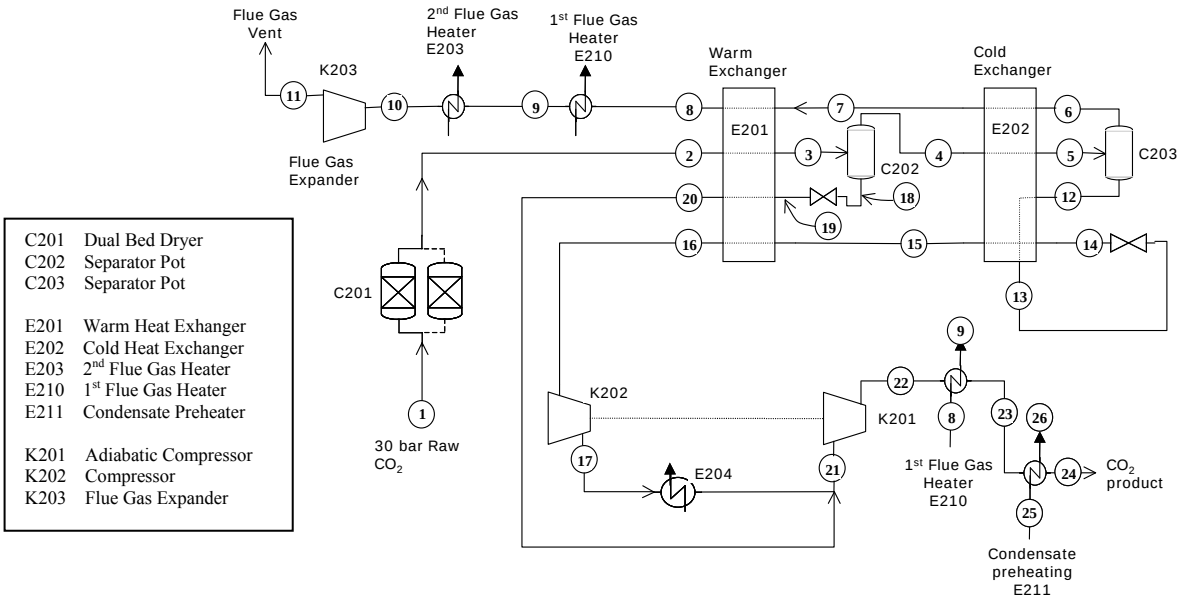



**Figure 11:** Process flow diagram – $CO_2$ and inerts removal and compression to 110 bar[15]

The results of the study work indicated that the effects on cost of installing a two or three stage flash process, or one with a distillation stage, were modest, but that the higher purity systems carry a small parasitic power penalty. The principal effect of producing higher purity $CO_2$ is a reduction in the $CO_2$ capture efficiency since more $CO_2$ has to be vented with the condensable impurities. If the $CO_2$ purity is increased from 95% to 98%, for instance, there is a reduction of 2.3% in the quantity of $CO_2$ captured, but there is little effect on the cost of electricity.

### 3.1.3 $CO_2$ treatment plant for post-combustion capture

#### *3.1.3.1 Amine solvents for post-combustion $CO_2$ capture*[2][16]

The schematic flow diagram for a commercial system for solvent absorption process in post combustion capture is illustrated in **Figure 12**. The combustion flue gas is cooled and brought into contact with the amine solvent in the absorber tower, at temperatures typically in the range 40-60°C. The $CO_2$ is absorbed by the chemical solvent as it passes up through the tower, and the cleaned gas is then washed with water to remove any solvent droplets or vapour carried over. The cleaned flue gas then leaves the absorber and is sent for further processing or is exhausted to the atmosphere.

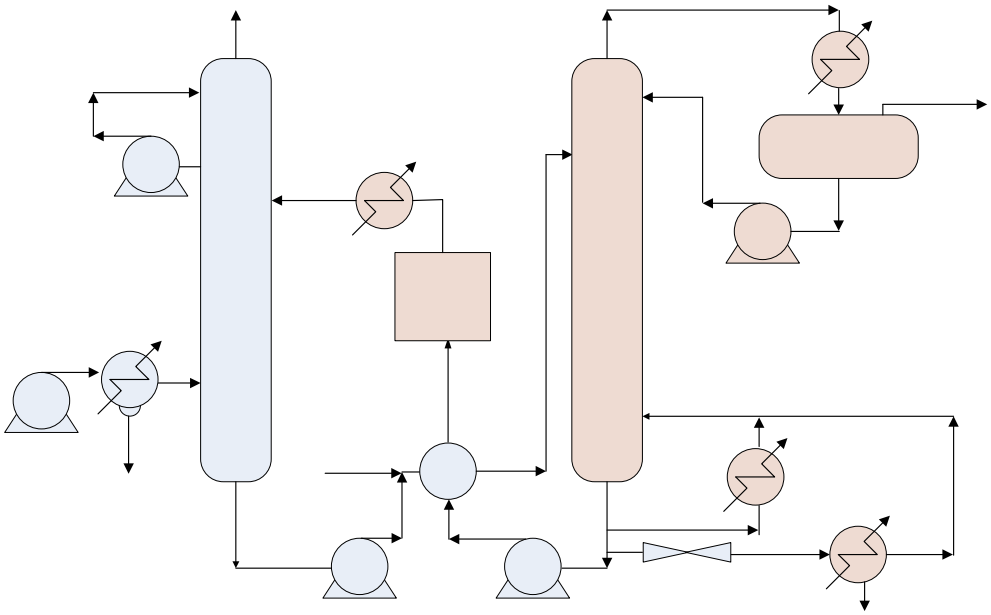


**Figure 12:** Chemical absorption process for post combustion $CO_2$ capture[24]

The 'rich' solvent, containing the chemically-bound $CO_2$, is then pumped to the top of the stripper or regeneration vessel, via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100-140°C) and at close to atmospheric pressure. The $CO_2$ product gas leaves the stripper via the condenser.

The 'lean' solvent is pumped back to the absorber tower via the lean/rich amine heat exchanger and a further lean amine cooler to bring it to the absorber temperature level.

One of the key parameters that can determine the economic operation of the solvent scrubbing processes is the energy requirement, which is principally associated with the heat required to regenerate the amine. This is typically drawn from the power plant steam cycle, and this significantly reduces the net cycle efficiency of the power plant.

Amine scrubbing systems have been used for more than 60 years for the removal of hydrogen sulphide and $CO_2$ from hydrocarbon streams. The solvent most frequently used for $CO_2$ capture is monoethanolamine (MEA), an alkanolamine compound. MEA has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and thus high absorbing capacity on a mass basis, reasonable thermal stability and thermal degradation rate.

The degradation of alkanolamine solvents occurs by three major routes[16], viz:

- carbamate polymerisation,
- oxidative degradation and
- thermal degradation.

The rate of carbamate polymerisation is insignificant at temperatures below 100°C and thermal degradation only takes place at temperatures above 205°C. For the scrubbing of combustion flue gases at low temperatures, the amine degradation is largely due to the presence of significant oxygen concentrations in the flue gas. This is a major problem with raw flue gases from coal fired systems.

The acid gases present in coal combustion flue gases, e.g. $SO_2$ and $NO_2$, react with MEA to form heat-stable salts, and this process reduces the $CO_2$ absorption capacity of the solvent[17]. These acid gas species have to be removed with reasonably high efficiency if amine scrubbing systems are to be used for $CO_2$ capture.

A number of demonstration and pilot plants have been, or are currently being, built to study amine-based and other solvents for the capture of $CO_2$ from coal and natural gas flue gases[16], including:

- On the pilot plant at the University of Texas in Austin, USA, an MEA campaign was conducted as a baseline to compare $CO_2$ absorption and stripping performance using an experimental potassium carbonate/piperazine solvent.

- At Seoul thermal power plant, in Korea, a pilot plant treating 2 tonnes per day of $CO_2$ has been operated using MEA as the absorbent in a real flue gas side stream from Boiler Unit 5, a natural gas-fired boiler.

- The CASTOR pilot plant, at Esbjerg power station in Denmark is a 1 tonne per hour unit using 30% aqueous MEA solution. The plant was operated at 93% $CO_2$ removal efficiency, producing approximately 850 kg/hour of $CO_2$.

- The ELEL slipstream pilot plant at Brindisi Sud power station, at 2.25 tonne $CO_2$ per hour, which will use 20 wt% MEA solution, is currently being built

- The Australian Low Emissions Technology Demonstration Fund (LETDF), is currently building two post-combustion capture projects. One is a natural gas combined cycle plant powered by coal bed methane, the other is a 25 tonnes per day capture plant on International Power's 1600 MW Hazelwood brown coal pf plant in Victoria's Latrobe Valley.

- At the $CO_2$ extraction plant at the Boundary lignite fired power plant in Southern Saskatchewan, Canada, the pilot plant was used to evaluate the performance and reliability of proprietary $CO_2$ solvent extraction technologies, and to obtain engineering data that can be used for the design of commercial scale $CO_2$ absorption units.

#### *3.1.3.2 The Fluor Econamine FG Plus$^{SM}$ Technology*

Most alkanolamine systems do not operate particularly well in coal combustion flue gas environments, because the amine will rapidly degrade in the presence of oxygen. This is avoided in the Econamine FG$^{SM}$ solvent by the addition of a proprietary inhibitor[18]. This inhibitor also helps to protects the internal surfaces of the equipment against corrosion, permitting the utilisation of lower cost materials of construction.

The flowsheet for the Fluor Econamine FG$^{SM}$ $CO_2$ scrubbing system is fairly conventional, and is very similar to that presented in Figure 12. There are 23 commercial plants worldwide that are now using the Econamine FG$^{SM}$ technology.

The $CO_2$ recovery plant in the Florida Power and Light power plant in Bellingham, treats 327 tonnes per day of $CO_2$, and has been in operation since 1991. This facility is the only commercial-scale $CO_2$ recovery unit in the world operating on gas turbine flue gas. The $CO_2$ concentration in the flue gas is very low, around 3 vol%, and the oxygen concentration in the flue gas is high, around 13 vol%. The quality of the $CO_2$ product is suitable for use in the food and beverage industry, i.e. is of higher purity than is needed for Enhanced Oil Recovery.

Fluor has developed a further improved process called Econamine FG Plus$^{SM}$ which is now being offered commercially. The predominant amine for the solvent still remains MEA, but the new formulation has increased reaction rates and higher capacity for $CO_2$. Another feature for Econamine FG Plus$^{SM}$ is a modified slit flow configuration which utilises two parallel regeneration schemes, i.e. flash regeneration and steam stripping. The new configuration uses less steam than the standard Econamine FG$^{SM}$ arrangement, and has absorber inter-cooling to reduce the temperature in the middle of the absorber packed beds. This has two major effects, viz:

- the overall absorption rate of $CO_2$ is increased thus reducing the absorber size and capital cost, and
- the rich solvent loading is increased, thereby reducing the solvent circulation rate and energy requirement in the stripper/reboiler.

As with all the amine solvent systems, the Econamine FG Plus$^{SM}$ sorbent is affected by the formation of heat stable salts in the solution due to the presence of $SO_x$, and $NO_x$, and by the presence of gas-borne particulates. Suitable flue gas treatment is therefore needed upstream of the Econamine FG Plus$^{SM}$ absorber.

#### *3.1.3.3 Kansai Mitsubishi Carbon Dioxide Recovery process*

Mitsubishi Heavy Industries (MHI) offer a proprietary post-combustion flue gas $CO_2$ recovery system called Kansai Mitsubishi-Carbon Dioxide Recovery (KM-CDR) which has been

developed from the generic amine gas treatment processes[19]. The system is based on a proprietary solvent KS-1™, which has low corrosiveness and does not require a specific corrosion inhibitor. The KS-1™ system also offers superior $CO_2$ absorption and regeneration, lower solvent degradation rates, a lower solvent circulation rate and, with other patented equipment, has less solvent loss when compared to other amine based systems.

MHI has constructed four commercial $CO_2$ capture plants for recovering $CO_2$ from the combustion of natural gas and oil, and another four plants are currently in the pipeline. To develop the system for coal fired gas streams, a 10 t $CO_2$/day demonstration facility was recently built in Matsushima, southern Japan. It is proposed that flue gas containing 14 vol% $CO_2$ will be taken at a rate of 1750 $Nm^3$/hr in a slip stream from a coal fired boiler at Matsushima power plant.

#### *3.1.3.4 HTC Purenergy $CO_2$ Capture Technology*

HTC in Regina, Canada has developed a $CO_2$ capture technology based on a relatively conventional scrubber unit, with the use of HTC Designer Solvents, which incorporate propriety capacity enhancers, reaction rate promoters, solvent stabilisers and corrosion inhibitors that can be tailored to specific applications.

#### *3.1.3.5 Chilled ammonia process for $CO_2$ capture*

Alstom has developed, and tested at laboratory scale, a process that uses chilled ammonia to capture $CO_2$ from combustion flue gases[20]. The basic process flow diagram is presented in **Figure 13**. There are as three separate process blocks, viz:

- The first step involves the cooling of the flue gas, by direct injection of refrigerated water. As the gas is cooled, much of the water condenses, carrying some of the residual contaminants. The cooled flue gas leaves the cooling unit at 2°C and with less than 1% moisture.
- The second process step is $CO_2$ absorption, using an aqueous slurry containing a mixture of ammonium carbonate (AC) and ammonium bicarbonate (ABC). Any residual ammonia is captured by a cold-water wash and returned to the absorber.
- The third step takes the $CO_2$-rich ABC slurry and pumps it to the high pressure (1,200 to 1,500 psi) regenerator unit, through a heat exchanger, which increases the

temperature to around 80°C. The $CO_2$ released from the slurry at the elevated temperature in the regenerator is washed and sent for further processing. The lean AC is returned to the absorber tower, via the heat exchanger.

The only by-product of the entire process is a small amount of water; it can either be treated for disposal by the plant's waste water system, or is recycled and reused.

Alstom, together with the Electric Power Research Institute (EPRI) and We Energies, has launched a pilot project to demonstrate $CO_2$ capture from coal-fired power plants using the chilled ammonia process. It is proposed that the pilot plant, rated at the equivalent of 1.7 MW, will capture $CO_2$ from a flue gas side stream at Pleasant Prairie Power Plant, a 1,224 MW coal-fired generating station.

Alstom and Statoil are also planning to test chilled ammonia technology for $CO_2$ capture from flue gases from natural gas combined cycle power plants. A 40 MW facility will be built at

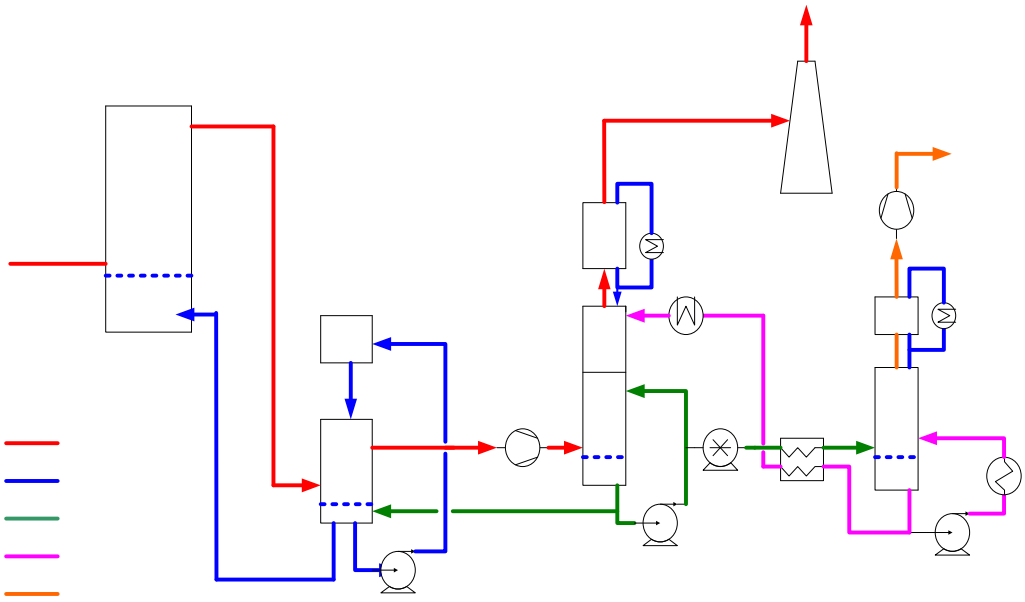


**Figure 13:** Schematic of the Alstom chilled ammonia process[27]

the Mongstad refinery in Norway for testing and product validation. It will be designed to capture at least 80,000 tons per year of $CO_2$ from flue gases from the cracker unit at the refinery or from a new combined heat and power plant being built by Statoil and is scheduled to be in operation by 2010. The test and product validation facility is expected to enter operation by 2009-2010 with the first operation and testing phase to last 12-18 months.

### 3.1.4 Novel $CO_2$ purification methods currently being tested in bench scale rigs

The incorporation of the currently available $CO_2$ separation technologies to a power plant does result in substantial cost and efficiency penalties, and there is significant scope for technical improvement.

**Membrane separation techniques** tend to be significantly less energy intensive, since they require no phase change in the process, and they have been used successfully in a number of industrial applications. The commercially available polymeric materials[21] are, however, not stable in the demanding environments in power plant flue gas streams. In general, as the glass transition temperature of the polymer is approached, the membrane selectivity is significantly reduced. The current membrane materials are subject to chemical degradation by the process stream, a problem that is exacerbated by the relatively high operating temperatures. Polybenzimidazole (PBI)-based composite polymeric-metallic membranes are currently being developed with the aim of achieving a combination of high selectivity, high permeability, chemical stability, and mechanical stability at elevated temperatures (>150 °C).

A dual-functional silica-based membrane is currently being developed[22]. This consists of a micro-porous inorganic siliceous matrix with amine functional groups, physically immobilized or covalently bonded on the membrane pore walls. It is anticipated that the relatively strong interactions between the $CO_2$ molecules and the amine functional groups on the membrane pores will enhance the $CO_2$ selectivity compared to the siliceous membranes that perform the gas separation solely on the differences in molecular size.

**Ionic liquids**[23] are currently being investigated as an alternative to commercial amine for use in capturing $CO_2$ from the flue gas in coal and natural gas–fired power plants. Tests on 1-n-hexyl-3-methylimidazolium tris (pentafluoroethyl) trifluorophosphate indicated that $CO_2$ is significantly more soluble in this liquid than is $O_2$.

## 3.2 The transportation of $CO_2$[24]

Pipelines are most commonly employed for the bulk transportation of $CO_2$. The gaseous $CO_2$ is typically compressed to a pressure above 8 MPa in order to avoid two-phase flow regimes and to increase the fluid density. The first long-distance $CO_2$ pipeline came into operation in the early 1970s and, in the USA alone, more than 2,500 km of pipelines for $CO_2$ are in use, principally for enhanced oil recovery. These pipelines operate in the 'dense phase' mode, at ambient temperature and high pressure.

In certain circumstances, the use of ships could be economically more attractive. Liquefied petroleum gases (LPG, principally propane and butane) are transported on a larger commercial scale by marine tankers. $CO_2$ can be transported by ship in much the same way (typically at 0.7 MPa pressure), but this currently takes place on a relatively small scale because of limited demand. The properties of liquefied $CO_2$ are similar to those of LPG, and the technology could readily be scaled up to large $CO_2$ carriers if a demand for such systems were to materialize. Similarly, road and rail tankers also are technically feasible options for smaller quantities of gas. These systems transport $CO_2$ at a temperature of -20°C and at 2 MPa pressure.

## 3.3 The bulk storage of $CO_2$[24][25]

As illustrated in **Figure 14**, there are three principal options that are potentially available for the long-term bulk storage of $CO_2$, viz:

- storage in suitable geological formations,
- ocean storage, i.e. the direct release of $CO_2$ into the ocean water column or on the deep sea floor, and
- industrial fixation of $CO_2$ into inorganic carbonates.

### 3.3.1 Underground geological storage

Of the three options listed above, geological storage is generally considered to be the most viable technically, economically and environmentally. There are three main storage options, viz:

- depleted or near-depleted oil and gas fields
- deep saline aquifers (porous rock layers containing salty water deep underground), and
- unmineable coal seams.

Porous rocks that hold or, as in the case of depleted oil and gas reservoirs, have previously held fluids, such as natural gas, oil or brines, are potential candidates for $CO_2$ storage. Suitable formations can occur in both onshore and offshore sedimentary systems. Coal beds may also be used for storage of $CO_2$ where it is unlikely that the coal mining will later be mined, and provided that bed permeability levels are sufficient.

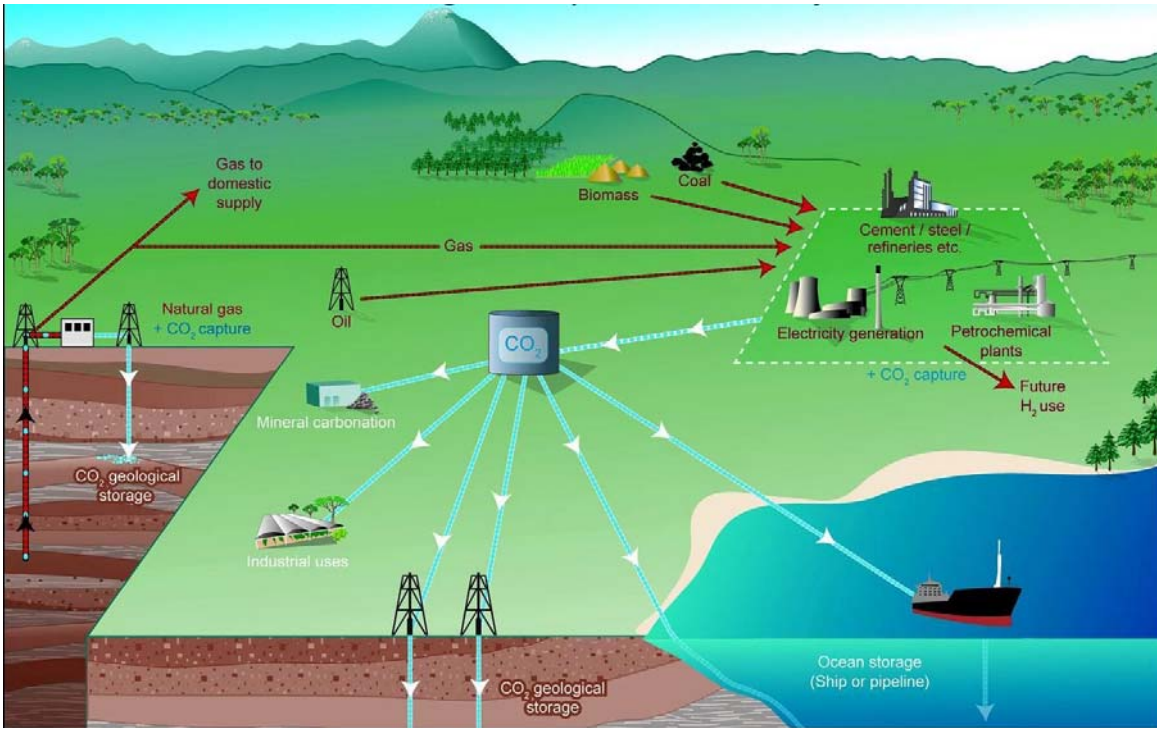



**Figure 14:** Schematic diagram of possible CCS systems showing the sources of the CCS might be relevant, transport of $CO_2$ and storage options[24]

While there are significant uncertainties associated with the current estimates, it is considered that the global capacity to store $CO_2$ deep underground is substantial. Depleted oil and gas reservoirs are estimated to have a storage capacity of 675–900 gigatonnes of $CO_2$. Deep saline formations may have a storage capacity of at least a further 1,000 gigatonnes, and some studies suggest it may be an order of magnitude greater than that. The quantification of the upper end of the range is difficult and further studies are required. The capacity of unmineable coal formations is uncertain, with estimates ranging from 3 to 200gigatonnes.

Overall, it is generally considered that the potential storage sites are widely distributed across many of the major sedimentary basins worldwide. This is illustrated in **Figure 15**. The available storage sites are considered to be adequate to store a significant proportion of the projected fossil fuel $CO_2$ emissions into the long term future.

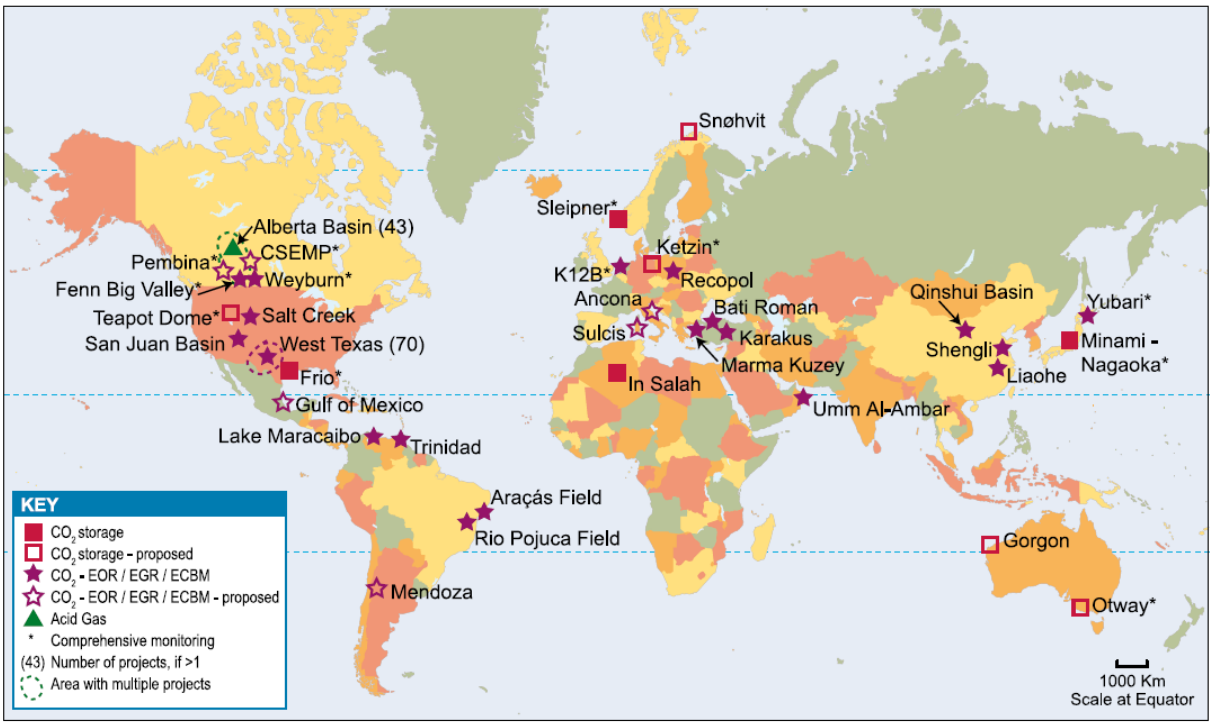



**Figure 15:** Location of sites where activities relevant to $CO_2$ storage are planned or under way[24].

#### 3.3.1.1 Existing $CO_2$ storage projects

The demonstration of the large scale geological storage of $CO_2$ is ongoing in three projects, viz:

- The Sleipner Project in the North Sea is operated by Statoil in Norway, and has been in operation since 1996. It involves the re-injection of $CO_2$, which is co-produced with natural gas, into a deep aquifer overlying the offshore Sleipner field.

- The Weyburn project in Canada in Saskatchewan, Canada has been in operation since 2000. The project involves the injection of $CO_2$ for Enhanced Oil Recovery at an oilfield near Weyburn, Saskatchewan, Canada. The carbon dioxide for the process was produced in the Great Plains synfuels coal gasification plant in Beulah, North Dakota USA, and a 325 km pipeline was constructed to supply the $CO_2$ to the Weyburn field. In 2002 the rate of $CO_2$ injection increased to 6300 tonnes per day, including 1300 tonnes per day of $CO_2$ recycled from oil production.

- The In Salah project in Algeria, involves the re-injection of around 1 million tonnes per annum of $CO_2$ into a lower level of the gas field, where the reservoir is filled with water.

In addition to these projects, significant quantities of $CO_2$ are injected annually for EOR, mostly in Texas, USA, where EOR commenced in the early 1970s. Much of the $CO_2$ injected for EOR is extracted with the oil, from which it is separated and then re-injected.

#### 3.3.1.2 Storage technology and mechanisms

The current approach to the injection of $CO_2$ into deep geological formations makes use of a number of the technologies that have been developed in the oil and gas exploration and production industry, and for other large scale underground injection activities, such as natural gas storage, the deep injection of liquid wastes, and acid gas disposal (commonly mixtures of $CO_2$ and $H_2S$).

$CO_2$ storage in hydrocarbon reservoirs or deep saline formations is generally expected to take place at depths below 800 m, where ambient pressures and temperatures will usually result in $CO_2$ being in a liquid or supercritical state. Under these conditions, the density of $CO_2$ will be close to that of crude oil.

After injection into the storage formation, the retention of the $CO_2$ depends on a combination of physical and geochemical trapping mechanisms. Physical trapping to block upward migration of $CO_2$ is provided by the cap rock, above the storage formation. Additional physical trapping can be provided by capillary forces that retain the $CO_2$ in the pore spaces of the formation. In many cases, however, one or more sides of the formation remain open, allowing for lateral migration of $CO_2$ beneath the cap rock. In these cases, other trapping mechanisms may become important.

Geochemical trapping involves the reaction of the $CO_2$ reacts with the in-situ fluids and host rock. In the first instance, the injected $CO_2$ dissolves pore water. The $CO_2$-laden water becomes significantly denser and sinks through the formation. Chemical reactions between the dissolved $CO_2$ and rock minerals can also occur to form ionic species, so that, over prolonged periods of time, some of the injected $CO_2$ can be converted to solid carbonate minerals.

$CO_2$ can also be preferentially absorbed onto coal or organic-rich shales, replacing gases such as methane. In these cases, the $CO_2$ will remain trapped as long as pressures and temperatures remain stable. These processes would normally take place in shallower formations than for $CO_2$ storage in hydrocarbon and saline reservoirs.

### 3.3.2 Ocean storage

It may prove possible to inject $CO_2$ directly into the deep ocean at depths greater than 1,000 m, where most of it would remain stored for long periods of time. This approach has not yet been deployed or demonstrated at any reasonable scale of operation and is still very much in the research phase.

Carbon dioxide is soluble in water and there is a natural exchange of $CO_2$ between the atmosphere and the ocean surface under equilibrium conditions. If the atmospheric concentration of $CO_2$ increases significantly, the ocean gradually takes up some additional $CO_2$. In this way, the oceans have absorbed about 500 gigatonnes of $CO_2$ of the total 1,300 gigatonnes of anthropogenic emissions over the past 200 years. As a result of the increased

atmospheric $CO_2$ concentrations from human activities, the oceans are currently taking up $CO_2$ at a rate of about 7 gigatonnes per year. Most of this carbon dioxide now resides in the upper ocean and this has resulted in a decrease in the pH of about 0.1 at the ocean surface. To date, there has been no measurable change in the pH in the deep ocean.

The results of ocean observations and modelling work both indicate that $CO_2$ injected into the ocean will be retained for several hundred years, and that the fraction retained increases with increasing depth of injection. It may also be possible to increase the fraction retained by forming solid $CO_2$ hydrates and/or liquid $CO_2$ lakes on the sea floor, and by dissolving limestone to neutralize the acidic $CO_2$, although these options would require significant quantities of material, and energy for materials handling.

The injection of a few gigatonnes of $CO_2$ will produce measurable changes in the ocean chemistry in the region of injection, and the injection of hundreds of gigatonnes will produce larger changes in the region of injection, and will eventually produce measurable changes over the entire ocean volume.

It has also been demonstrated that adding $CO_2$ can harm marine organisms. Observed phenomena include reduced rates of calcification, reproduction, growth, circulatory oxygen supply and mobility, as well as increased mortality over time. Immediate mortality of some organisms is expected close to the injection points or to $CO_2$ lakes. The long term effects of direct $CO_2$ injection into the ocean on ocean organisms or ecosystems over large ocean area and long time scales have not yet been studied, and it is also unclear how individual species and ecosystems respond to sustained chemical changes.

### 3.3.3 Mineral carbonisation and industrial uses[24]

Mineral carbonisation refers to the fixation of $CO_2$ using alkaline-earth oxides, i.e. magnesium oxide (MgO) and calcium oxide (CaO) to produce magnesium carbonate ($MgCO_3$) and calcium carbonate ($CaCO_3$). The quantities of the metal oxides that can be found in earth's crust exceed that required to fix all the $CO_2$ that would be produced by the combustion of all of the available fossil fuel reserves, although much of this is already in the form of carbonates. Under ambient conditions, the carbonates are stable over long time scales. The process of

mineral carbonization occurs naturally but, in nature, the process occurs very slowly. Research in the field of mineral carbonization has therefore focused on finding process routes that can achieve useful reaction rates and make the process more energy-efficient.

Current industrial uses of $CO_2$ include chemical and biological processes where $CO_2$ is a reactant, such as in urea and methanol production, as well as various technological applications that use $CO_2$ directly. The volumes are relatively small and most of the industrial products of process using $CO_2$ have short lifetimes, i.e. do not represent a long-term sink for $CO_2$.

# 4 The costs of $CO_2$ capture and storage

## 4.1 The costs of $CO_2$ capture and purification

A number of cost estimates of $CO_2$ capture and separation technologies, i.e. pre-and post combustion and oxy-fuel systems, applied to large coal-fired power plants, have been carried out over the past few years. The preferred basis on which to compare different systems is to estimate the cost per tonne of avoided $CO_2$ emissions.

The overall results of a number of these studies are summarized in the following table (**Table 3**).

Table 3:Costs of $CO_2$ capture and purification

| **Technology** | **Costs (€ per tonne of avoided $CO_2$ emissions)** |
|---|---|
| **IPCC study**[24] | |
| IGCC + Selexol | 11-31 |
| Pulverised coal + MEA | 24-42 |
| **BERR study**[26] | |
| Pulverised fuel + Oxyfuel | 31.8 |
| Pulverised fuel + MEA | 32.5 |
| **IEA GHG Study**[16] | |
| Pulverised fuel + Fluor | 24.2 |
| Pulverised fuel + MHI | 25.3 |
| **Alstom study**[27] | |
| Pulverised fuel + MEA | 39 |
| Pulverised fuel + Chilled ammonia | 15 |

It should be recognized that all of the studies listed above are based on different scenarios, and on assumptions about process plant capital costs, and plant performance and availability, which have yet to be demonstrated in practice. In some cases, the cost estimates have been prepared by the process developer, and should be regarded with caution.

## 4.2 The costs of $CO_2$ transport and long term storage of bulk $CO_2$[24]

The costs of transport are very dependent on the mode of transport, the scale of operation and the distance travelled. For large-scale, long distance transport, excluding liquefaction, costs of the order of 30-35 US$ per tonne of $CO_2$ have been suggested.

There have been a number of estimates of long-term $CO_2$ storage costs for the United States, Australia and Europe, based on representative geological characteristics for these regions. In some cases, the original cost estimates include compression and pipeline costs and corrections have been made to derive storage costs. These estimates include capital, operating and site characterization costs, but exclude monitoring costs, remediation and any additional costs associated with the potential long-term liabilities.

Onshore storage costs for saline formations in Europe for depths of 1000–3000 m are of the order of 1.9–6.2 US$ per tonne, with a most likely value of 2.8 US $ per tonne. The estimated costs for offshore storage over the same depth range, with reuse of existing oil and gas platforms is between 4.7–12.0 US$ per tonne, i.e. it is clear that the offshore costs are significantly higher than the onshore costs, as would be expected.

As for the monitoring of storage sites, the repeated use of seismic surveys was found to be an effective monitoring technology at Sleipner. Seismic monitoring costs have been reviewed recently for an onshore storage project for a 1000 MW power plant with a 30-year life. Assuming repeat surveys at five-year intervals during the injection period, monitoring costs were estimated as 0.03 US$/t$CO_2$. This result suggests that seismic monitoring may represent only a small fraction of overall storage costs.

Estimates of the life-cycle monitoring costs have been made for two scenarios:

- storage in an oil field with EOR and
- storage in a saline formation,

The results suggested that for the basic case with no explicit $CO_2$ leakage, both scenarios cost around 0.05 US$/t$CO_2$, based on a discount rate of 10%. The basic monitoring package included periodic seismic surveys, micro-seismicity, wellhead pressure and injection-rate monitoring.

If leakage were to occur, and enhanced $CO_2$ monitoring were to be required, the costs increased to 0.069–0.085 US$/t$CO_2$. The enhanced package included all of the elements of the 'basic' package and added periodic well logging, surface $CO_2$ flux monitoring and other advanced technologies.

It was believed that the augmented monitoring programme would be sufficient to detect and locate the leakage and may be able to quantify leakage rates as well. The assumed duration of monitoring includes the 30-year period of injection, as well as further monitoring after site closure of 20 years for EOR sites and 50 years for saline formations. Increasing the duration of monitoring to 1000 years increased the discounted cost by 10%. These calculations are made assuming a discount rate of 10% for the first 30 years and a discount rate of 1% thereafter.

# 5 Conclusions

It is clear from the technical review material presented above that there has been an extensive, international scientific and engineering effort on the development of $CO_2$ sequestration technologies over the past few years. Significant progress on the development and, in some cases, demonstration of the technologies for the capture, processing and storage of the $CO_2$ emitted from large fossil fuel power plants, has been made.

The key pre- and post-combustion $CO_2$ scrubbing technologies and the oxy-fuel combustion technologies, and the techniques for the purification of the $CO_2$ to the desired quality for further on-site processing, are reasonably well understood and are largely proven at small pilot

plant and component testing scale. There are projects, both planned and under way, aimed at the construction and testing of demonstration scale plants. All of the currently available $CO_2$ capture technologies have significant cost and energy efficiency penalties, however, and in parallel with the technology demonstration activities, significant development projects aimed at incremental improvement of the existing state of the art, and at the development of alternative technical approaches, are also in progress.

There are a number of ongoing projects in the North Sea, in Canada and in Algeria, which involve the large scale handling and geological storage of $CO_2$, and the experience of these CCS projects are in addition to the fairly extensive experience of the large scale use of $CO_2$ for enhanced oil recovery in the Texas oilfields, which has been practiced since the 1970s. Further developments of these technologies, and of the ocean storage and other relevant options, are under way. The current thinking is that the principal barriers to the large scale implementation of geological or undersea storage of $CO_2$ are likely to be legal or political, rather than technical.

Clearly, these developments are aimed specifically at the sequestration of the $CO_2$ from large fossil fuel power plants, which emit $CO_2$ at a rate of several hundreds of tonnes per hour, and many of the problems being addressed by the developers of $CO_2$ sequestration technologies are associated with the large scale of operation of the $CO_2$ capture equipment and the very large transport and storage facilities that will be required.

It is clear that the destructive thermal processing of irradiated graphite will be carried out at much smaller scale, perhaps at a combustion rate of the order of one tonne per hour or so. It is likely that the most appropriate approach to the destructive thermal processing of the graphite will involve combustion at high temperatures in a fluidised bed or grate-fired combustor, with natural gas or oil for light-up and possibly for combustion support purposes.

There may also be some interest in the non-destructive thermal and other processing of the irradiated graphite, i.e. processes intended to release volatile contaminants into the vapour phase, for further treatment, with no significant change to the condition of the graphite.

For the thermal destruction of graphite, the efficient recovery of heat and steam/power generation will not be a significant issue, and this will have a significant bearing on the selection of the relevant carbon capture technology. In this scenario, it is most likely that, if very efficient $CO_2$ capture and purification prior to further processing is required, then post-combustion scrubbing, or perhaps a membrane separation technology, is likely to be the most appropriate approach.

The relatively modest scale of operation of graphite combustion will also mean that the large scale transport and storage technologies being developed for CCS will not be relevant and some of the smaller scale mineral carbonation or industrial utilisation options for the $CO_2$ may be more relevant.

# 6 References

[1] Climate Change 2007: Synthesis Report; Intergovernmental Panel on Climate Change; 2007; http://www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf; (Accessed May 2008).

[2] Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. A., IPCC Special Report on Carbon Dioxide Capture and Storage, Intergovernmental Panel on Climate Change, Cambridge University Press, 2005.

[3] Shakhashiri, Chemical of the week, Carbon dioxide, http://scifun.chem.wisc.edu/CHEMWEEK/pdf/CarbonDioxide.pdf (Accessed September 2008)

[4] Details of the EU Emissions Trading Scheme are available at: ec.europa.eu/environment/climat/emission.htm (Accessed September 2008)

[5] Reports on carbon dioxide capture and storage are available at: www.ieagreen.org.uk (Accessed September 2008)

[6] Elwell, L. C., Grant, W. S., Technical overview of carbon dioxide capture technologies for coal-fired power plants, 2005, http://mpr.com/energy/extras/co2_capture.pdf (Accessed June 2008)

[7] Ciferno, J. P., $CO_2$ capture: comparison of cost & performance of gasification and combustion-based plants, Workshop on Gasification Technologies, Denver, Colorado, March, 2007.

[8] Doctor, R. D., Molburg, J. C., Thimmapuram, P., Berry, G. F., Livengood, C. D., Life-cycle $CO_2$ emissions for air-blown gasification combined-cycle using Selexol, National AIChE conference, Washington, August 1993.

[9] Panesar, R., Lord, M., Simpson, S., White, V., Gibbins, J., Reddy, S., Coal-fired advanced supercritical boiler / turbine retrofit with $CO_2$ capture, 8th International Conference on Greenhouse Gas Control Technologies, Trondheim, Norway, June, 2006

[10] Beal, C., Andrus, H., Mohn, N., Putting combustion and gasification in the loop; Modern Power Systems 2005

[11] Gayan, P., de Diego, L. F., Garcia-Labiano, F., Adanez, J., Abad, A., Dueso, C., Effect of support on reactivity and selectivity of Ni-based oxygen carriers for chemical-looping combustion, Fuel **87**, 2641-2650, 2008.

[12] Hawthorne, C., Charitos, A., Perez-Pulido, C. A., Bing, Z., Scheffknecht, G., Design of a dual bed system for the post combustion removal of $CO_2$ using CaO. Part 1: CFB carbonator reactor model., 9th International conference on CFB with 4th VGB workshop, Hamburg, 13-16 May, 2008.

[13] Hybrid combustion-gasification chemical looping coal power technology development, U.S. Department of Energy-Office of Fossil Energy, National Energy Technology Laboratory, http://www.netl.doe.gov/publications/factsheets/project/Proj329.pdf (Accessed May 2008).

[14] Breckenridge, W., Holiday, A., Ong, J. O. Y., Sharp, C., Use of SELEXOL® Process in Coke Gasification to Ammonia Project, Laurence Reid Gas Conditioning Conference, Oklahoma, February 2000.

[15] Oxy combustion process for $CO_2$ capture from power plant Report No. 2005/9; IEA Greenhouse Gas R&D programme , 2005.

[16] Davidson, R. M., Post-combustion carbon capture from coal fired plants-solvent scrubbing, CCC/125, IEA Clean Coal Centre, 2007.

[17] Rubin, E. S., Rao, A. B., A technical, economic and environmental assessment of amine-based CO2 capture technology for power plant greenhouse gas control, Report no. DOE/DE-FC26-00NT40935, Carnegie Mellon University, Center for Energy and Environmental Studies, Pittsburgh, PA, 2002.

[18] Reddy, S., Scherffius, J., Freguia, S., Roberts, C., Fluor's Econamine FG PlusSM technology – An enhanced amine-based $CO_2$ capture process, 2nd National Conference on Carbon Sequestration, Alexandria, VA, May, 2003.

[19] Mitchell, R., Mitsubishi Heavy Industries' carbon capture technology, Carbon Capture Journal, February, 2008.

[20] Carbon capture: Inside Alstom's chilled ammonia $CO_2$ capture system, Power, Feb 2008, http://findarticles.com/p/articles/mi_qa5392/is_200802/ai_n25137627 (Accessed July 2008)

[21] Thermally optimized membranes for separation and capture of carbon dioxide, U.S. Department of Energy – Office of Fossil Energy, National Energy Technology Laboratory, http://www.netl.doe.gov/publications/factsheets/project/Proj194.pdf, (Accessed 12 July 2008).

[22] Novel dual functional membrane for controlling carbon dioxide emissions from fossil-fueled power plants, U.S. Department of Energy-Office of Fossil Energy, National Energy Technology Laboratory, http://www.netl.doe.gov/publications/factsheets/project/Proj333.pdf (Accessed 12 July 2008).

[23] Design and evaluation of ionic liquids as novel absorbents, U.S. Department of Energy – Office of Fossil Energy, National Energy Technology Laboratory, http://www.netl.doe.gov/publications/factsheets/project/Proj332.pdf (Accessed 12 July 2008).

[24] Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L., Carbon dioxide capture and storage – Summary for policymakers and technical summary, Intergovernmental Panel on Climate Change, 2005.

[25] POSTnote 238, Carbon capture and storage (CCS), March 2005, http://www.parliament.uk/documents/upload/POSTpn238.pdf (Accessed June 2008)

[26] Xu, B., Stobbs, R. A., White, V., Wall, R. A., Future $CO_2$ capture technology options for the Canadian market, Report no. Coal R309 BERR/Pub URN 07/1251, UK Department for Business Enterprise & Regulatory Reform, 2007.

[27] Black, S., Bade, O., Padban, N., Gal, E., Morris, E., Rhudy, D., Chilled ammonia process for $CO_2$ capture, Power-Gen Europe, Madrid, Spain, 26 – 28 June 2007