POST COMBUSTION CARBON CAPTURE FROM COAL FIRED PLANTS – SOLID SORBENTS AND MEMBRANES

Technical Study

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BACKGROUND TO THE REPORT

The IEA Greenhouse Gas R&D Programme (IEA GHG) produces technical reports on various aspects of CO_2 capture and storage. IEA GHG also operates a network of researchers on CO_2 capture, which focuses on solvent scrubbing technologies. The IEA Clean Coal Centre (IEA CCC) produces reviews of publicly available information on various aspects of clean coal technologies. This report was produced by IEA CCC in cooperation with IEA GHG. As part of this cooperation IEA GHG provided access to relevant technical study reports and the reports of its CO_2 Capture Network. This report is a companion review to an earlier report on post combustion capture with aqueous solvents (Report no, 2007/15 July 2007). The report has been provided to IEA GHG's members, with the kind permission of IEA CCC. IEA CCC, in cooperation with IEA GHG, is producing a further review on oxy fuel capture processes.

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Post-combustion carbon capture – solid sorbents and membranes

Robert M Davidson

Abstract

This report follows on from that on solvent scrubbing for post-combustion carbon capture from coal-fired power plants by considering the use of solid sorbents and membranes instead of solvents. First, mesoporous and microporous adsorbents are discussed: carbon-based adsorbents, zeolites, hydrotalcites and porous crystals. Attempts have been made to improve the performance of the porous adsorbent by functionalising them with nitrogen groups and specifically, amine groups to react with CO_2 and thus enhance the physical adsorption properties. Dry, regenerable solid sorbents have attracted a good deal of research. Most of the work has been on the carbonation/calcination cycle of natural limestone but there have also been studies of other calcium-based sorbents and alkali metal-based sorbents. Membranes have also been studied as potential post-combustion capture devices. Finally, techno-economic studies predicting the economic performance of solid sorbents and membranes are discussed.

Acronyms and abbreviations

AC — activated carbon
AMP — aminomethylpropanol
AMPD — 2-amino-2-methyl-1,3-propanediol
AP — aminopropylsilyl
γ-APTES — gamma-aminopropyltriethyloxysilane
APTS — aminopropyltrimethoxysilane
BED — N,N′-bis(2-hydroxyethyl)ethylenediamine
BFLM — bulk flow liquid membrane
CFBC — circulating fluidised bed calciner
CLM — contained liquid membrane
COE — coat of electricity
COF — covalent organic framework
DBU — 1,8-diazobicyclo-[5,4,0]-undec-7-ene
DEA — diethanolamine
DIPA — diisopropanolamine
DSC — differential scanning calorimetry
DETA — diethylenetriamine
DT — diethylenetriamine[propyl(silyl)]
ECH — epichlorohydrin
ED — ethylenediamine[propyl(silyl)]
EDA — ethylenediamine
ESA — electrical swing adsorption
FBC — fluidised bed combustion/combustor
FSP — flame spray pyrolysis
FTM — facilitated transport membranes
HMS — hexagonal mesoporous silica
HTC — high temperature calcination
HTlc — hydrotalcite
IGCC — integrated gasification combined-cycle
ILM — immobilised liquid membrane
IRMOF — isoreticular metal organic framework
JPY — Japanese Yen
LDH — layered double hydroxide
MCF — mesocellular siliceous foam
MDEA — methyldiethanolamine
MEA — monoethanolamine
MF — melamine-formaldehyde
MOF — metal organic framework
NETL — (US) National Energy Technology Laboratory
PAMAM — poly(amidoamine) dendrimer
PCC — precipitated calcium carbonate
PEHA — pentaethylenehexamine
PEI — polyethyleneimine
PF — pulverised fuel
PFBC — pressurised fluidised bed combustor
PMMA — poly(methyl methacrylate)
PMP — pyrene methyl picolinimide
PSA — pressure swing adsorption
PTFE — polytetrafluoroethylene
PVA-PAA — poly(vinylalcoholacrylate)
PVDF — polyvinylidenefluoride
SEM — scanning electron microscopy
SLIP — Solvent-Less vapour deposition combined with In-situ Polymerisation
TEA — triethanolamine
TEOS — tetraethoxylane
TEPA — tetraethylenepentamine
TEPAN — tetyraethylenepentaamineacrylonitrile

TGA — thermal gravimetric analysis
TPABR — tetra-n-propylammonium bromide
TPD — temperature-programmed desorption
TSA — temperature (or thermal) swing adsorption
UF — urea-formaldehyde
VSA — vacuum swing adsorption
ZIF — zeolitic imidozalate framework
XPS — X-ray photoelectron spectroscopy
XRD — X-ray diffraction

Contents

1   Introduction

The use of solvents (mainly alkanolamines) has been reviewed in a report on post-combustion carbon capture from coal-fired power plants (Davidson, 2007). Despite the advantages of solvent scrubbing, it was clear that there are several disadvantages, especially the thermal efficiency losses due to the energy needed to regenerate the solvent by driving off the captured CO_2. Other problems include the formation of degradation products formed by both thermal degradation and solvent reaction with flue gas from coal. There are also associated corrosion problems. Satyapal and others (2000) have listed other problems such as the difficulty in handling liquids and the energy penalties associated with the loss of solvents due to evaporation.

In a recent review of methods of separating CO_2 from flue gas, Aaron and Tsouris (2005) concluded that the most promising current method is liquid separation using methanoloamine (MEA) but that the development of ceramic and metallic membranes should produce membranes significantly more efficient at separation than liquid absorption. Current technologies and modelling activities were also briefly reviewed by Ducroux and Jean-Baptiste (2005) who looked at the use of membranes and solid adsorbents in addition to solvent absorbents and cryogenics. They concluded that only limited evolution is expected in the development of chemical absorption based on amines but that the main fields which are subject to significant developments are adsorbents and membranes. Those two fields are the topics covered in this report.

Recently, Yang and others (2008) have reviewed progress in carbon dioxide separation and capture.

The (US) National Energy Technology Laboratory (NETL) has published a review of advances in CO_2 capture technology which are part of the US Department of Energy's Carbon Sequestration Program (Figueroa and others, 2008). This review covers many of the processed that will be discussed in this report as well as some that are not, such as ionic liquids.

This report will begin with mesoporous and microporous adsorbents in which CO_2 adsorption is simply a physical process controlled by the pore characteristics of the sorbent. The addition of chemical functionality such as amine groups has been studied as a means of improving the performance of porous adsorbents so this will be discussed in the following chapter. The next chapter will examine regenerable solid sorbents, mostly involving a chemical cycle of calcination/carbonation reactions to capture the CO_2 and then release it as a pure gas while regenerating the sorbent. A chapter on membranes will follow. The final chapters will provide a brief discussion on techno-economic studies followed by some comments and conclusions.

2 Mesoporous and microporous adsorbents

Pressure swing adsorption (PSA) is a technology used to separate some gas species from a mixture of gases under pressure according to the species' molecular characteristics and affinity for an adsorbent material. It operates at near-ambient temperatures. Special adsorptive materials (for example, zeolites) are used as a molecular sieve, preferentially adsorbing the target gas species at high pressure. The process then 'swings' to low pressure to desorb the adsorbent material. The adsorbent material owes its adsorptive properties to the internal surface area and pore size distribution. The internal surface area of a porous solid is composed of several classes of pores. The volume is accessible to gases and vapours with which reactions may occur and it is not the porosity itself, which interacts directly with the adsorbate but the internal surface of the adsorbent. Mesoporosity and microporosity refer simply to the size of the pores in the adsorbent; micropores have a pore width less than 2 nm whereas mesopores have a pore width between 2 and 50 nm.

Siriwardane and others (2001a) studied three sorbents, an activated carbon and two zeolite molecular sieves, 4A and 13X, that could be utilised in a PSA process for the recovery of CO_2. Volumetric adsorption studies of CO_2, N_2, and H_2 were conducted at 25ºC at pressures up to ~2 MPa. The adsorption isotherms indicated that the uptake of CO_2 was higher than that of the other two gases. However, the focus of this review is on the sorbents studied for CO_2 capture so, at this stage, this chapter will be structured by considering the sorbents rather than the adsorption/desorption method used. Comparisons among the sorbents will be made where appropriate.

A review of sorbents that could be used with PSA processes was published by Yong and others (2002) covering the literature produced prior the time period (from 2000 onwards) covered in this report. They identified:
- carbon based adsorbents;
- metal oxides;
- zeolites;
- hydrotalcite-like compounds.

Yong and others (2002) also listed the properties that the adsorbent must have:
- high selectivity and adsorption capacity for carbon dioxide at high temperature;
- adequate adsorption/desorption kinetics for carbon dioxide at operating conditions;
- stable adsorption capacity of carbon dioxide after repeated adsorption/desorption cycles;
- adequate mechanical strength of adsorbent particles after cyclic exposure to high pressure streams.

2.1 Carbon based adsorbents

The adsorption isotherms of the activated carbon studied by Siriwardane and others (2001a) were found to be extremely reproducible, indicating excellent reversibility of adsorption.

The equilibrium adsorption capacity of the activated carbon at 25ºC and ~2 MPa was about 8.5 mol CO_2/kg of sorbent (equivalent to 374 g CO_2/kg sorbent or 37.4 wt%). From the adsorption isotherms it was determined that the activated carbon has about 9.5×10^{-6} moles of CO_2 per square metre at saturation coverage (1.72–2.07 MPa) and this is very close to the value corresponding to a close packed monolayer coverage of CO_2. So the activated carbon utilises its complete surface area to form the monolayer at higher pressures. It was possible to obtain an excellent separation of CO_2 from a gas mixture containing 14.8% CO_2 and 85.2% N_2 at a flow rate of 5 cm²/min.

Tang and others (2004) pointed out that anthracites have inherent chemical properties, fine structure and relatively low price that make them excellent raw materials for the production of activated carbons. A laboratory-scale fluidised bed was used for the activation of an anthracite. The activated carbons produced had highly developed microporosity and a small amount of mesopores. The surface area could rise to 1071 m²/g with two hours activation time at 890ºC (MarotoValer-and others, 2005). The highest CO_2 capture capacity at 30ºC was 65.7 mg CO_2/g sorbent (6.57 wt%) for the carbon activated for two hours at 800ºC. Contrary to expectations, the CO_2 capacity did not show any clear relationship with the surface area since this carbon had a surface area of 540 m²/g. The anthracite with the highest surface area had a CO_2 capacity of only 4 wt%, probably due to only certain pore sizes being effective for CO_2 adsorption.

Composite carbon sorbents based on activated carbon particles and rubbery polydimethylsiloxane as binder, and several series of organic-inorganic materials were synthesised and characterised as potential new adsorbents for CO_2 capture processes by Bertelle and others (2006a). A series of graphite-polymer composite matrix was also prepared as a reference. It was shown that these composite materials could readily lead to the incorporation of a high content (up to 70 wt%) of carbon fillers. The measured CO_2 sorption capacities indicated that the intrinsic capacity of the activated carbon decreased strongly at low levels of filler content (20 wt%); the sorption capacity of the activated carbon incorporated in the composite sorbent was much lower (down to ⅓) compared with the capacity of the pure adsorbent. Secondly, at medium filler content (30 to 50 wt%), about half the value of the native activated carbon sorption was reached. On the other hand more than 70% of the intrinsic CO_2 capacity could be recovered at high filler loading (70 wt%). The capacity losses were attributed to a high polymer-carbon adhesion which limits the effective available surface area.

Four carbon sorbents, two activated carbons, charcoal, and bituminous coal, were studied by Radosz and others (2008). The sorption capacity data suggested a sorption step near ambient temperature and a desorption step at around 100–130ºC. The selectivity data suggested a low pressure sorption step. The preliminary rate data suggested short sorption cycles. The goal of the work was to explore a low

pressure Carbon Filter Process technology (patent pending), that is, an inline flue gas filter that captures CO_2 on a low cost carbonaceous sorbent, such as activated carbon. It was claimed that the proposed Carbon Filter Process could recover at least 90% of the flue gas CO_2 of 90% purity at a fraction of the cost normally associated with the conventional amine absorption process. The Carbon Filter Process can produce low cost CO_2 because it requires neither expensive materials nor expensive flue gas compression, and it is easy to heat integrate with an existing power plant or a new plant without affecting the cost of the produced electricity too much.

2.2   Zeolites

Zeolites are the aluminosilicate members of the family of microporous solids known as 'molecular sieves'. The term molecular sieve refers to the ability to sort molecules selectively based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. Zeolites occur naturally but can be synthesised. Synthetic zeolites can be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature.

Zeolite molecular sieves 4A and 13X were studied by Siriwardane and others (2001a). At 25ºC the adsorption capacity of CO_2 for molecular sieve 13X was higher than that for molecular sieve 4A at all pressures up to ~2 MPa. At ~2 MPa, the capacity of 13X was 5.2 mol CO_2/kg sorbent (22.9 wt%) compared with 4.8 for the 4A (21.1 wt%). The adsorption isotherms indicated that the adsorption was fully reversible and complete regeneration could be obtained by evacuation of the material after adsorption. At low pressures (<0.172 MPa) the adsorption capacity of 13X was higher than that of the activated carbon also tested but the activated carbon showed significantly higher adsorption than molecular sieves at pressures above 0.345 MPa. Like the activated carbon, the 13X formed a close packed monolayer of CO_2 at saturation at higher pressures. The 13X adsorbent displayed an excellent separation of CO_2 from a gas mixture containing 14.8% CO_2 and 85.2% N_2 at a flow rate of 15 cm²/min (faster than the 5 cm²/min needed for the activated carbon). Siriwardane and others (2001b) compared three sorbents, 13X, activated carbon, and natural zeolite. All showed preferential adsorption of CO_2 over nitrogen, oxygen and water vapour at all pressures up to ~1.72 MPa. 13X showed better CO_2 uptake than the natural zeolite. Water vapour and oxygen did not affect the adsorption of CO_2 on 13X during competitive gas adsorption studies at both low and high pressures but activated carbon showed lower CO_2 uptake in the presence of water vapour and oxygen. A very high CO_2 uptake was observed with 13X during high pressure competitive gas adsorption studies.

Adsorption and desorption studies of CO_2 on both synthetic and natural zeolites were briefly reported by Siriwardane and others (2002). The studies of the three natural zeolites, with different major cations, were followed up by Siriwardane and others (2003). These are inexpensive materials. Studies of

volumetric gas adsorption of CO_2, N_2, and O_2 were conducted at 25ºC up to a pressure of ~2 MPa. Preferential adsorption of CO_2 was observed with all three zeolites. The differences in the observed adsorption were likely to be related to the differences in the chemical nature at the surface, specifically the major cations present, since the average pore diameters were fairly similar. The natural zeolite with the highest sodium content and highest surface area showed the highest CO_2 adsorption capacity of 2.5 to 3 mol/kg of the sorbent at ~1.7 to ~2 MPa (11 to 13.2 wt%). Competitive gas adsorption studies also showed that the zeolite with the highest sodium content gave the best separation of CO_2 from the gas mixtures. Contact time did not affect the extent of adsorption of the zeolites. Temperature-programmed desorption studies indicated that the majority of the physically adsorbed CO_2 was desorbed at room temperature, while some strongly bound CO_2 was desorbed at 115ºC. The CO_2 desorbed at 115ºC was thought to have formed bicarbonate or bidentate carbonate type species. The existence of such species was confirmed by Stevens and others (2008) using in situ infrared spectroscopy. They identified in addition to physisorbed CO_2, bidentate carbonate, bridged bidentate carbonate, monodentate carbonate, and carboxylate. Overall, the most abundant surface species observed throughout appeared to be physisorbed CO_2, which is likely to be largely responsible for the CO_2 capture capacity of the zeolite sorbent.

Five manufactured zeolites were tested by Siriwardane and others (2005) but they pointed out that the CO_2 capture systems would be even more energy efficient if the sorbents were operational at moderate or high temperatures, especially for the removal of CO_2 from high-pressure gas streams, such as those from integrated gasification combined-cycle (IGCC) systems. However, CO_2 adsorption capacities on the zeolites were less at 120ºC than at ambient temperature. The two zeolites with the highest adsorption capacities (13X and WE-G 592) had the largest pore diameters and the highest Na/Si ratios.

Thirteen zeolite based adsorbents were tested by Harlick and Tezel (2004) for use in a PSA application. Their results showed that the most promising zeolite adsorbent characteristics were a near linear CO_2 isotherm and a low SiO_2/Al_2O_3 ratio with cations (sodium) in the zeolite structure which exhibit strong electrostatic interactions with carbon dioxide. If a low pressure CO_2 feed and very low regeneration pressure is used then the NaY and 13X adsorbents are the most suitable for these conditions. At 132 Pa regeneration pressure, the 13X adsorbent performed best. However, when the regeneration pressure was increased to 2630 Pa, the NaY adsorbent performed better than 13X for CO_2 feed pressures greater than 37.5 kPa.

Kim and others (2003) have pointed out that a single stage PSA process using zeolite X is suitable when the concentration of CO_2 is higher than 25%, such as in steel mill. The single stage PSA process generally consists of four steps: pressurisation with feed gas, adsorption, high pressure rinse with product CO_2, and evacuation. However, a two-stage PSA process is more efficient than single stage PSA when the concentration of CO_2 is low, such as in a coal-fired power plant. In the first stage of the two-stage PSA, CO_2 is concentrated to 40–60% from the feed of less than 15% CO_2

and then concentrated to 99% at the second stage. With the two-stage PSA process composed of two adsorber beds for each stage, 99% CO_2 can be recovered.

The effects of operating parameters on vacuum swing adsorption (VSA) performance were studied with a validated numerical simulator by Xiao and others (2008). The adsorbent used was zeolite13X and a feed stream of 12% CO_2 and dry air was used to mimic flue gas. They found that the most important variables governing CO_2 purity, recovery and power consumption (all three of which impact on CO_2 capture cost) were vacuum pressure at the end of pump down, starting vacuum pressure level, amount of product gas used for purge, feed temperature, and rates of adsorption and desorption. A CO_2 product purity of greater than 95% is achievable with a recovery greater than 70% provided a vacuum pressure of at least 3 kPa is used together with a sufficient amount of purge gas. Use of high vacuum pressure levels such as 10 kPa lead to a dramatic drop in CO_2 recovery and purity. For zeolite 13X, an optimum feed temperature as regards product purity appeared to be around 80ºC.

Chabazite, a zeolite mineral, has been studied by Zhang and others (2008b). They prepared chabazite zeolites and exchanged them with alkali and alkaline earth cations to assess their potential for CO_2 capture from flue gas by VSA for temperatures below 120ºC. On the basis of isotherm measurements, they found that sodium- and calcium-loaded chabazite performed better for high temperature CO_2 capture (>100ºC) compared with a commercial NaX zeolite sample. The NaX zeolite performed better at lower temperatures (<100ºC).

A single-bed temperature swing adsorption (TSA) process was employed to determine the ability of zeolite 13X to capture CO_2 preferentially from a mixed CO_2/N_2 gas stream containing 1.5% CO_2 and undergo regeneration in a TSA cyclic process by Konduru and others (2007). The CO_2 capacity of 13X was taken at 90% saturation during the adsorption step and regeneration of the adsorbent was shortened at an effluent concentration of 130 ppm during the desorption step. The capacity at 20ºC and a CO_2 partial pressure of 1.52 kPa decreased, which was expected. In addition, CO_2 was desorbed efficiently with a relative recovery that was high (over 68%), and almost unchanged after several adsorption-desorption cycles. It was concluded that Zeolite 13X showed promise as an adsorbent with substantial capacity for CO_2 uptake, based on the average CO_2 recovery of 84% after five cycles in a TSA cyclic process. It was noted that experiments at higher CO_2 concentrations may confirm the suitability of this technology as an economically sustainable CO_2 capture system.

A potential problem with zeolites is that, if used in fluidised beds, attrition could cause the sorbent to be carried over (Lee and others, 2004). Zeolites 5A and 13X were found to have attrition rates 2.1–4.0-fold higher than activated carbon or activated alumina. This could result in high maintenance costs for the sorbent and problems in the operation of the fluidised bed. On the other hand, the adsorption capacities of 5A and 13X were 2.35 mmol/g (10.34 wt%) and 2.23 mmol/g (9.81 wt%), 1.5–2.7-fold higher than the other sorbents.

2.3   Hydrotalcites

Hydrotalcite is a layered double hydroxide of general formula $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4H_2O$. Recently they have been considered as adsorbent materials for CO_2, for example, Ding and Alpay (2000) studied a PSA process at temperatures up to 480ºC and in the presence of water vapour. The conditions were chosen to depict those of steam reformer processes but it was suggested that they were also appropriate to some flue gas CO_2 recovery processes. Adsorption saturation capacities of 0.65 and 0.58 mol/kg (2.86 and 2.55 wt%) were measured at 400ºC and 480ºC, respectively, under wet feed conditions. Under dry feed conditions, about a 10% reduction of the saturation capacity was observed and also relatively rapid adsorbent degradation. higher temperatures. Adsorbent regeneration was possible by means of a steam purge, but some irreversible loss in capacity was indicated for very long times on-stream (for example, 90 days at 400ºC). Under wet conditions, the fresh adsorbent capacity was measured as 0.51 mol/kg (2.24 wt%), this decreased to 0.45 mol/kg (1.98 wt%) after 90 days on-stream at 400ºC. The rate of deactivation was accelerated at higher temperatures. Kinetic studies suggested mass transfer control for the adsorption, depressurisation and purge steps of operation. This was particularly so for low partial pressures of feed CO_2. Kinetic studies by Soares and others (2005) indicated that the controlling mechanism for mass transfer inside the adsorbents was micropore diffusion. They had studied the removal of CO_2 from gas mixtures at temperatures in the range 150–350ºC using three commercial hydrotalcites.

Mg-Al-CO_3 layered double hydroxides (LDHs) have been prepared and characterised by Ram Reddy and others (2006). All the LDH samples used in the study for CO_2 adsorption were calcined at 400ºC under vacuum (5 kPa) which led to a phase transformation from a highly crystalline LDH form to an amorphous mixed oxide solution form. The samples were degassed at 200ºC for four hours and subsequently reweighed before measuring CO2 adsorption at 200ºC.CO_2 adsorption measurements revealed that ~86% of the total adsorption was reversible. CO_2 adsorption of 0.49 mmol/g (2.16 wt%) at 200ºC was achieved with slightly reduced uptake after each cycle of adsorption. 98% of the initial adsorption capacity was regained on regeneration of the sample at 400ºC. Stability and regenerability of the sample were demonstrated with consistent adsorption uptakes after repeated adsorption/desorption cycles.

Reynolds and others (2006) performed 640 simulations obtained from a cyclic adsorption process simulator, two heavy reflux pressure swing adsorption (PSA) cycles were analysed at the periodic state for the capture and concentration of CO_2 from flue gas at high temperature (302ºC), using a potassium-promoted (K-promoted) hydrotalcite like compound (HTlc). Overall, their results showed that a high temperature PSA process might be feasible for the capture and concentration of CO_2 from flue gases using a K-promoted HT1c. For the simulations carried out with the faster, but reasonable, uptake and release rates of CO_2 in the K-promoted HT1c, CO_2 purities of greater than 90%, even up to 98%, were achieved with this high

temperature PSA process. Very high feed throughputs were also achieved. It was suggested that, from a CO_2 sequestration or sale perspective, at these high CO_2 purities and feed throughputs, it might be economical to employ such a PSA process to recover at least some of the CO_2 from a stack gas, even though the CO_2 recovery might be low since the performance was desorption limited.

MgAl hydrotalcite with carbonate as interlayer anion was synthesised by Fu and others (2008). Brief details of CO_2 adsorption were given. It was suggested that surface hydroxyl pairs and acid-base pairs could react with CO_2 to form bicarbonate and bidentate carbonate species. The CO_2 adsorption capacity was around 9 mg/g (0.9 wt%).

Following an observation that Ca-containing HTlcs took up CO_2 preferentially over NOx, X P Wang and others (2008) investigated the CO_2 adsorption of Ca- and Co-containing oxides at 350ºC. At such a temperature activated carbons and zeolites have low CO_2 capacities. The sorbents were pretreated under nitrogen at 500ºC, then cooled to 350ºC for CO_2 sorption from a CO_2/N_2 gas mixture. CO_2 adsorption reached a steady state after 20 minutes. The best performing compound studied was CaCoAlO with an atomic ratio of 1.5:1.5:1; this compound had a CO_2 adsorption capacity of 1.39 mmol/g (6.12 wt%). The adsorbed species were identified by in situ infrared spectra which indicated the presence of monodentate carbonate, bicarbonate, bidentate carbonate, and bridged carbonate, mainly associated with the Ca.

2.4   Porous crystals

Metal organic frameworks (MOFs) are crystalline compounds consisting of metal ions or clusters coordinated to organic molecules to form one-, two-, or three-dimensional structures that can be porous. In some cases, the pores can be used for the storage of gases such as carbon dioxide.
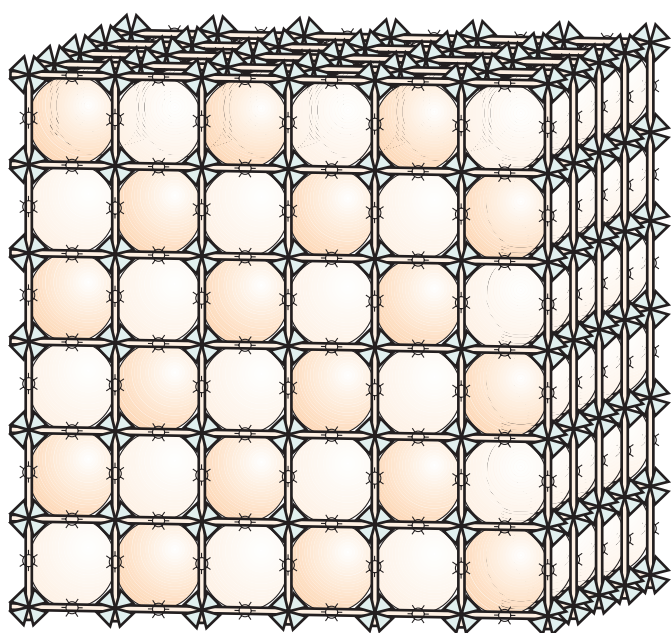
Figure 1   Crystal structure of IRMOF-1 (Low and others, 2005)

Low and others (2005) presented some brief details concerning the synthesis and structure of IRMOF-1, where IRMOF means 'isoreticular metal organic framework'. The IRMOF-1 crystal structure is shown in Figure 1 and consists of a cubic array of Zn_4O units bridged by benzenedicarboxylate. This forms large cages separated by large apertures which can adsorb large quantities of gases with easy diffusion.

Benzenedicarboxylate is not the only linking molecule that can be used and by changing the organic linking molecule a large series of materials can be designed and synthesised. The pores in IRMOFs are larger than those in zeolites and IRMOFs have a large void fraction. Low and others (2005) suggested that modelling results should allow the design of IRMOFs with good selectivity for CO_2 versus other gases in flue gases and gasification streams. IRMOF-1 is reported to be greater than ten times more selective for CO_2 over less polar gases such as N_2, CH_4, and H_2.

Millward and Yaghi (2005) investigated the viability of nine MOFs for CO_2 storage at room temperature including IRMOF-1. MOF-177, composed of 1,3,5-benzenetribenzoate units and zinc clusters, was found to have a CO_2 capacity of 33.5 mmol/g (147.4 wt%) at 3.5 MPa, far greater than that of any other porous material reported. At 3.5 MPa and at ambient temperature, a container filled with MOF-177 can capture nine times the amount of CO_2 in a container without adsorbent, and about two times the amount when filled with benchmark materials like activated carbon and zeolite 13X. Typical surface areas of MOFs are compared with other adsorbents in Figure 2.

Simulation studies have been performed to investigate the applicability of MOFs to the adsorption separation of CO_2 from flue gas by Yang and others (2007). The MOF they studied was Cu-BTC which is synthesised from copper(II) ions and 1,3,5-benzenetricarboxylate groups. The results of the molecular simulations showed that MOFs are promising materials for separating CO_2 from flue gases. Monte Carlo simulation was used by Babarao and others (2007) to compare the adsorption of pure and mixed CO_2 and CH_4 in three nanosized porous adsorbents, silicalite (an Al-free zeolite),
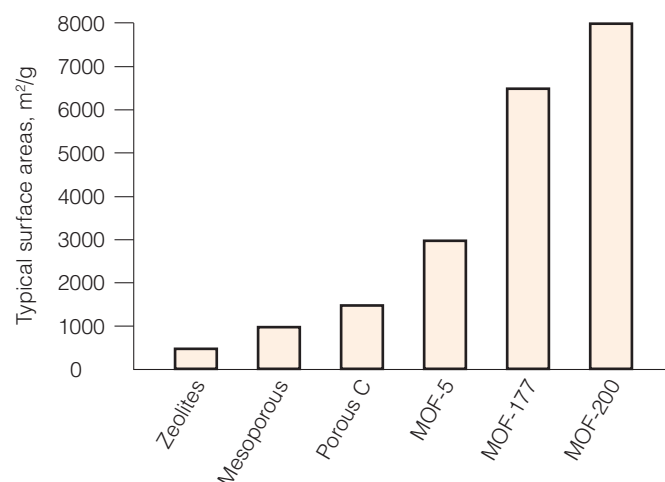
Figure 2   Typical surface areas of MOFs compared with other adsorbents (Yaghi, 2006)

C_{168} schwarzite (a nanoporous carbon membrane), and IRMOF-1. The adsorption capacity for pure CO_2 and CH_4 in IRMOF-1 was substantially higher than for the other two adsorbents. CO_2 was preferentially adsorbed over CH_4 in all three adsorbents and the adsorption selectivity was similar. A molecular simulation study was performed to screen MOFs for CO_2 storage potential by Babarao and Jiang (2008a). The best MOFs for CO_2 adsorption exhibited a counterbalance of high capacity and low density. Due to its compact atomic packing, a covalent organic framework (COF-102) exhibited high capacity at low pressures and also represented a promising material for CO_2 adsorption. Covalent organic frameworks (COFs) are synthesised solely from light elements (H, B, C, N, and O) that are known to form strong covalent bonds. They consist of organic linkers covalently bonded with boron oxide clusters (Babarao and Jiang, 2008b).

Atomistic simulation studies have been performed on CO_2 storage in COFs by Babarao and Jiang (2008b). Three-dimensional (3D) COFs were found to have high free volumes, porosity, and surface area. The 3D COF-105 and COF-108 have the largest capacity for CO_2 adsorption at high pressures compared with other COFs, although the adsorption is lower at low pressures. Since the pores in an adsorbent are almost fully filled at high pressures and adsorption approaches saturation, adsorbent with a larger free volume has more space to accommodate sorbate molecules and hence exhibits a higher capacity. At 3 MPa, the capacities in COF-105 and COF-108 were calculated to be 82 and 96 mmol/g, respectively (361 and 422 wt%). These exceptionally high values are two to three fold greater than in MOF-177 reported by Millward and Yaghi (2005). However, although the gravimetric capacities of COF-105 and COF-108 are greater than other COFs, on a volumetric basis the capacities are close due to the cancelling effect of the framework density.

Liang and others (2008b) have compared a MOF, Cu -BTC [$Cu_3(BTC)_2(H_2O)_3$ in which BTC is benzene-1,3,5-tricarboxylate], with zeolite 13X for potential application in a PSA system. The CO_2 capture performance was evaluated by a series of sorption isotherms for CO_2, CH_4, and N_2 measured at 0 to 1.5 MPa at temperatures of 25ºC and 105ºC. The results show that the working capacity of Cu-BTC in a PSA system at 25ºC is almost four times that of the benchmark material zeolite 13X and it also showed higher CO_2/N_2 and CO_2/CH_4 selectivities at higher pressure range (greater than 0.15 MPa) and lower energy requirement for regeneration than zeolite 13X. Cu-BTC was also stable in O_2 at 25ºC. However, the CO_2 adsorption capacity of Cu-BTC declined significantly after water sorption.

Arstad and others (2006) prepared a selection of MOF adsorbents that maintain open porosity upon desolvation and tested them as low temperature adsorbents for CO_2. The best adsorbents reached carbon dioxide capacity levels of 10 wt% at atmospheric pressures of CO_2 and as high as 60 wt% at ~25 MPa CO_2 pressure and 25ºC. The observed capacities were proportional to the specific surface area and pore volume of the adsorbents. However, the selectivity for water adsorption was significantly higher than for CO_2. The presence of water also reduced the adsorption capacity of CO_2 in gas mixtures. It was suggested that niche applications of

the MOF adsorbents may therefore be found for removal of CO_2 from dry high pressure gas mixtures.

Figueroa and others (2008) note that desirable characteristics for MOFs are low energy requirement for regeneration, good thermal stability, tolerance to contaminants, attrition resistance, and low cost.

Research on MOFs is currently being supported by NETL and a factsheet can be found at http://www.netl.doe.gov/ publications/factsheets/project/Proj315.pdf.

2.5 Effects of flue gas impurities

Tests performed by Stevens and others (2008) involving both CO_2 and H_2O have shown that the two species compete for the same adsorption sites on the zeolite surface. The capture of CO_2 from a 12% synthetic flue gas stream at a relative humidity of 95% at 30ºC was examined by G Li and others (2008a). A zeolite 13X adsorbent was used and the migration of the water and its subsequent impact on capture performance was evaluated. Binary breakthrough of CO_2/water vapour was performed and indicated a significant effect of water on CO_2 adsorption capacity, as expected. Cyclic experiments indicated that the water zone migrates a quarter of the way into the column and stabilises its position so that CO_2 capture is still possible although decreased. The formation of a water zone creates a 'cold spot' which has implications for the system performance. The recovery of CO_2 dropped from 78.5% to 60% when moving from dry to wet flue gas while the productivity dropped by 22%. Although the concentration of water leaving the bed under vacuum was 27 vol%, the low vacuum pressure prevented condensation of water in this stream. However, the vacuum pump acted as a condenser and separator to remove bulk water. An important consequence of the presence of a water zone was to elevate the vacuum level thereby reducing CO_2 working capacity. Thus, although there is a detrimental effect of water on CO_2 capture, long-term recovery of CO_2 is still possible in a single VSA process. Pre-drying of the flue gas steam is not required.

The effect of flue gas impurities on CO_2 capture performance from flue gas at coal-fired power stations by vacuum swing adsorption has been studied by Zhang and others (2008c). They focused on the effect of water vapour on the pressure/vacuum swing adsorption process, especially the influence of water vapour in the product purge gas. The adsorbents studied were CDX (an alumina/zeolite blend), alumina, and NaX zeolite. CDX and 13X zeolite were used by G Li and others (2008b) to study the competition of CO_2 and H_2O in CO_2 capture. CDX is a superior desiccant compared with 13X zeolite and was used a 'guard-bed layer' above a main layer of 13X to remove water (3–4 vol%) and capture CO_2 (10–12%) simultaneously at 30ºC. The water was found to be successfully held in the CDX layer. The double layered single bed CO_2/H_2O VSA obtained 76.9% CO_2 recovery with 67% purity.

In Section 2.4, it was noted that, for the MOFs studied by Arstad and others (2006), the selectivity for water adsorption

was significantly higher than for CO_2. The presence of water also reduced the adsorption capacity of CO_2 in gas mixtures. Liang and others (2008b) also observed that the CO_2 adsorption capacity of MOFs declines after water adsorption.

3 Functionalised solid sorbents

The CO_2 adsorption capacity of activated carbons and other mesoporous sorbents, governed by physical adsorption, can be increased by introducing nitrogen functional groups to their structure.

Przepiórski and others (2004) treated commercially available activated carbon with ammonia at temperatures ranging from 200 to 1000ºC. It was found that absorption of CO_2 was enhanced by ammonia treatment. This was attributed to the presence of C-N and C=N groups introduced to the carbon structure by the ammonia treatment. observed. The sample treated at 400ºC exhibited the highest ability to adsorb CO_2 (0.076 g CO_2/g C, 7.6 wt%) at 36.15ºC and 102.5 kPa. Higher temperatures did not result in additional enhancement in adsorption and samples treated at temperatures above 400ºC showed a gradual decrease to absorb CO_2.

Carbon sorbents were prepared by hydrolysing sugar and mixtures of 50 wt% sugar and nitrogen-containing compounds (acridine, carbazole, proline, and urea) by treatment with sulphuric acid (Arenillas and others, 2005a; *also* Smith and others, 2005a,b). A urea-formaldehyde (UF) resin was also carbonised and activated under the same conditions as the sugar based sorbents. Overall, the results showed that, although the amount of N incorporated to the final adsorbent is important, the N-functionality seems to be more relevant for increasing CO_2 uptake. Thus, the adsorbent obtained from the UF resin with thermal activation had the highest N content but a low CO_2 adsorption capacity (~1 wt% at 25ºC). However, the adsorbent obtained from carbazole co-hydrolysis, despite the lower amount of N incorporated, showed a higher CO_2 uptake, up to 9 wt% at 25ºC, probably because the presence of more basic nitrogen functionalities as determined by X-ray photoelectron spectroscopy (XPS). According to the XPS measurements, the sample with the N-functionality that produced the highest CO_2 adsorption was the only one with oxidised nitrogen which gave to the nitrogen an extra basicity.

A suite of high nitrogen content carbon matrix adsorbents were prepared by Drage and others (2007a) from the activation of urea-formaldehyde (UF) and melamine-formaldehyde (MF) resin, using K_2CO_3 as a chemical activation agent incorporated into the resin on polymerisation. For all the adsorbents, the highest adsorption capacity occurred at room temperature, after which capacity decreased with increasing temperature. The adsorption process was found to be completely reversible, with all the adsorbents returning to their initial mass after switching from the reactive gas, CO_2, to non-reactive N_2 at 100ºC. The CO_2 adsorption capacity displayed a hybrid adsorption between physisorption and chemisorption; it was determined to be dependent upon both textural properties and, more importantly, nitrogen functionality. The mass of CO_2 adsorbed per unit of surface area and nitrogen for the MF-derived adsorbents greatly exceeded that for the UF resin. Different surface chemistry, more specifically nitrogen functional groups, could account for this. Higher adsorbent activation temperatures resulted in a decrease in CO_2 adsorption. On the other hand, higher temperatures seem to generate more favourable textural properties for adsorption. In the activation of UF resin above 600ºC the majority of the nitrogen incorporated into the carbon matrix is a component of six-membered polyaromatic structures. This evolution of the nitrogen functionalities with increasing activation temperature explains the decreasing affinity of the surface of the adsorbents to CO_2 with the functional groups capable of generating the most basic adsorbent surface, for example amine groups, eliminated by increased activation temperature, especially over 600ºC.

A commercial granular activated carbon was modified by treatment with gaseous ammonia at different temperatures (600–900ºC) by Pevida and others (2007) then, later, two activated carbons in the range of 200–800ºC (Pevida and others, 2008b). Ammonia decomposes at high temperatures with the formation of radicals, such as NH_2, NH and H. Those radicals may react with the carbon surface to form functional groups, such as $-NH_2-$, -CN, pyridinic, pyrrolic, and quaternary nitrogen. Characterisation by temperature-programmed desorption (TPD) and XPS revealed that ammonia treatment at temperatures higher than 600ºC incorporated nitrogen mainly into aromatic rings while, at lower temperatures, nitrogen was introduced into more labile functionalities such as amide-like groups. CO_2 capture capacities at 25ºC of the treated carbons increased with respect to the parent carbons. In particular, for one of the activated carbons, CO_2 capture capacities rose from 7 wt% to 8.4 wt% after treatment at 800ºC. Ammonia treatment did not notably change the textural properties of the parent carbons. The CO_2 capture capacity was not directly related to the total nitrogen content of the adsorbents but to specific nitrogen functionalities that are responsible for increasing the CO_2 adsorbent afinity.

Plaza and others (2008b) compared two methods of producing CO_2 capture adsorbents. The first was activation with CO_2 and the second was heat treatment with ammonia gas (amination and ammoxidation). Amination was carried out at 800ºC in ammonia gas and the ammoxidation at 300ºC in an ammonia gas and air mixture. Both amination and ammoxidation introduce nitrogen into the carbon structure, up to 5 wt%, turning the carbon surface more basic, without the need of carrying out a preoxidation treatment. Activation with CO_2 developed microporosity in the samples to a greater extent than amination and ammoxidation, thus enhancing the CO_2 uptake at atmospheric pressure. Ammoxidation introduced 4 wt% of nitrogen into the carbon matrix. However, the ammoxidised sample did not show a higher CO_2 capture capacity than the starting char. However, the aminated samples presented significantly higher capacities than the starting char, and higher in fact than those of the CO_2 activated samples.

3.1 Immobilised amine sorbents

Rather than simply introducing non-specific basic nitrogen

functionality into mesoporous sorbents, a better approach might be to introduce amine functionality. *Immobilised amine sorbents* might be expected to show similar reactions to liquid amines in the typical absorption process, with the added advantages that solids are easier to handle and that they do not give rise to the corrosion problems caused by the circulation of highly basic solutions.

NETL has supported research in this area and a factsheet can be found at http://www.netl.doe.gov/publications/ factsheets/ rd/R&D122.pdf. In one approach, liquid impregnated solid sorbents that capture CO_2 in the presence of water vapour at temperatures from 30–60ºC have been developed. In another approach, amines compounds capable of capturing CO_2 have been attached to various substrates, and the capture capacity for CO_2 has been measured in laboratory experiments. The sorbents showed better CO_2 capture capacities and lower regeneration temperatures than the conventional amine based liquid solvent scrubbing process. A large-scale preparation of one of the sorbents at a commercial company has been conducted successfully, and the sorbent showed promising results during bench-scale flow reactor tests with simulated coal combustion gas streams. The sorbent is reported to have CO_2 removal efficiency of 99% with good removal capacity.

3.1.1 Polymer and resin supported sorbents

It is possible to coat solid polymers with liquid amines in order to combine the high surface area of the polymeric support with the CO_2 removal efficiency of a liquid amine. Polyethyleneimine (PEI) and diethanolamine (DEA) are two amines that can be applied to support surfaces. Such sorbents were originally developed for space life support systems. Satyapal and others (1999, 2000) developed a CO_2 sorbent in the form of 300–600 micron acrylic based polymer beads coated with a liquid amine. It was found to be capable of removing a maximum capacity of ~8 wt% CO_2 from an air stream and, when tested over hundreds of adsorption-desorption cycles, showed no loss in performance. The heat of adsorption was ~94±8 kJ/mol CO_2 (Satyapal and others, 2000). The sorbent could be regenerated using vacuum desorption at ~1 Torr (~133 Pa). However, such sorbents were developed for space life support systems and are too expensive for use in post-combustion capture in power plants or other large-scale applications (Gray and others, 2003a).

Amine sorbents in an adsorbed state, immobilised on a nonionic polymeric support were studied by Filburn and others (2005). The main objective was to discern the amine type most effective in removing carbon dioxide from a gas stream containing low levels of CO_2. The effect on CO_2 capture of modification of primary amines to secondary amines by reaction with acrylonitrile was also evaluated. The acrylonitrile/amine reaction formed a Michael adduct. The modified amines provided nearly a factor of 2 increase in CO_2 removal capacity compared with the original primary amines. Michael addition reaction products of ethylenediamine (EDA) and tetraethylenepentamine (TEPA) were immobilised within the pores of high surface area poly(methyl methylacrylate) PMMA solid beads by Gray and others (2005a). The primary

amine sites present in the EDA and TEPA were converted to secondary amine sites by reacting them with acrylonitrile. The performance of the new immobilised modified solid amine sorbents were evaluated to determine their carbon dioxide capture capacities in a temperature swing system using a 10% CO_2/2% H_2O/He gas stream. Over the studied temperature range of 20–65ºC, it was determined that the CO_2 capture capacities significantly improved at temperatures of 45–65ºC. The average CO_2 capture capacities for the sorbents over four adsorption/desorption cycles ranged from 3.4 to 6.6 moles of CO_2/kg sorbent (15–29 wt%). The thermal stability of the sorbents was also investigated over a ten cycle study in which it was apparent that the there was room for improvement. The results suggested that there could be potential applications of these sorbents in the capture of CO_2 from flue gas streams.

The two-ring sterically hindered amidine base 1,8-diazobicyclo-[5,4,0]-undec-7-ene (DBU) was immobilised on polystyrene and polymethylmethylacrylate beads by Gray and others (2006a,b). DBU based sorbents can capture CO_2 at a 1:1 molar ratio by forming the DBU bicarbonate. DBU acts as a tertiary amine and has the stoichiometric capability of capturing CO_2 at a 1:1 R-NH_2/CO_2 molar ratio unlike primary and secondary amines that have a 2:1 molar ratio. The immobilised DBU solid sorbents were found to have acceptable stability over the adsorption/desorption temperature range of 25–87ºC (the boiling point of pure DBU is 127ºC at atmospheric pressure and it is totally decomposed at 175ºC). The sorbents also exhibited acceptable CO_2 capture capacities of 3.0 mol CO_2/kg sorbent at 25ºC (13.2 wt%); however, at the critical operational temperature of 65ºC, the capacity was reduced to 2.3 mol/kg sorbent (10.1 wt%, Gray and others, 2008). However, it was pointed out that, in order for the solid amine sorbents to be competitive with existing monoethanolamine (MEA) liquid systems, CO_2 capture capacity must be in the range of 3–6 mol CO_2 /kg sorbent (13.2–26.4 wt%).

Diethanolamine (DEA) supported amberlite acrylic ester resin substrate was tested at laboratory scale by Notaro and Pinacci (2007). The sorbent's CO_2 capacity and its correlation with the principal process parameters were studied. The DEA-amberlite sorbent had a CO_2 adsorption capacity of 1.7 wt% measured with a 10% v/v mixture of CO_2 in N_2, at 25ºC and 60 Nl/h total gas flow corresponding to a 0.44 Nlh^{-1}g^{-1} spatial velocity. No CO_2 seemed to remain after the regeneration step carried out at 80ºC, suggesting that the adsorption process is fully reversible. A preliminary energetic analysis of the desorption stage showed a 15% energy saving for the diethanolamine (DEA)-amberlite solid sorbent compared with employing a 30 wt% DEA in aqueous solution. A further 30% energy saving was possible because the sorbent could be regenerated at a lower temperature (75ºC instead of 120ºC for the DEA aqueous solution).

3.1.2 Carbon supported sorbents

Commercial solid sorbents are very expensive so efforts have been made to seek out less expensive substances that can be converted into high surface area materials easily. The unburned carbon in fly ash is one such material.

Solid sorbents were generated by the chemical treatment of carbon-enriched fly ash concentrates with various amine compounds by Gray and others (2002). However, the performance of the best sorbent produced was only able to reach 0.77 wt% CO_2 capture capacity at 30ºC compared with 8–9 wt% for existing commercially-available sorbents. Gray and others (2004a) treated carbon-enriched fly ash concentrates with 3-chloropropylamine hydrochloride solution at 25°C. The amine treatment process was successful in improving the CO_2 capture capacities of the fly ash carbon concentrates. The best sample had a CO_2 capture capacity of 174.5 µmol/g (0.77 wt%), and was regenerable for an additional test (140.6 µmol/g or 0.62 wt%). In comparison with commercially available sorbents with surface areas of 1000–1700 m²/g and CO_2 capture capacities of 1800–2000 µmol/g (7.92–8.80 wt%), the amine-enriched fly ash carbon was only able to achieve 9% of the CO_2 capture capacity. However, the surface area of the amine-enriched sorbent was only 27 m²/g, which may account for its low CO_2 capture capacity.

One-step activation by steam can successfully increase the surface area and pore volume of high carbon fly ash. The activated samples produced by Maroto-Valer and others (2004, 2008) presented very different surface areas and pore volumes due to the difference in the physical and chemical properties of their precursors. One sample had a surface area of 538 m²/g after 60 minutes activation and 1075 m²/g after 120 minutes. It had a CO_2 adsorption capacity of 40.3 mg/g at 30ºC but only 7.7 mg/g at 120ºC. This was chosen for testing with impregnation with various amines. The impregnation of the amines significantly reduced the surface area and pore volume of the activated fly ash. The CO_2 adsorption capacities are listed in Table 1 in which the numbers in the sample names refer to the adsorption temperatures. The adsorption capacity of the methyldiethanolamine (MDEA) loaded sample increased significantly at higher temperatures.

Another fly ash sample (FAS10) was deashed to remove the non-porous inorganic material thus increasing the surface area from 284 m²/g to 731 m²/g. The raw and deashed samples were impregnated with PEI. The CO_2 adsorption capacities are shown in Table 2. The PEI impregnated deashed sample could adsorb as much as 93.6 mg CO_2/g at 75ºC.

Further studies on the effects of deashing and subsequent oxidation by nitric acid have been reported by Zhang and others (2004). The nitric acid treatment increased the micropore surface area and pore volume but had little effect on the mesopore surface area and pore volume. After steam activation, the nitric acid treated samples had the highest CO_2 adsorption capacities. However, in spite of doubling the capacity after PEI impregnation, this was less impressive than the increases for the samples that had only been deashed.

Carbon adsorbents from fly ash have also been studied by Arenillas and others (2005b; *also* Smith and others, 2005a,b). The carbon obtained had high ash and nitrogen contents, with a low sulphur content. It was then impregnated with organic bases such as polyethyleneimine aided by polyethylene glycol using the method described by Xu and others (2003b). The CO_2 sorbents produced were more effective at high

Table 1 CO_2 capture using activated fly ash carbon (AC) and its chemical loaded counterparts at different temperatures
(Maroto-Valer and others, 2004)

Sample	CO_2 uptake, mg CO_2/g adsorbent	CO_2 uptake, wt%	CO_2 uptake, mol CO_2/mol chemical
AC-30	40.3	4.03	
AC-70	18.5	1.85	
AC-120	7.70	0.77	
AC-MDEA-30	17.1	1.71	0.046
AC-MDEA-70	30.4	3.04	0.82
AC-MDEA-100	40.6	4.06	0.109
AC-MDEA-120	16.1	1.61	0.044
AC-DEA-30	21.1	2.11	0.050
AC-DEA-70	37.1	3.71	0.089
AC-DEA-100	16.3	1.63	0.039
AC-DEA-120	4.20	0.42	0.010
AC-MEA-30	68.6	6.86	0.095
AC-MEA-70	49.8	4.98	0.069
AC-MEA-100	25.3	2.53	0.035
AC-MEA-120	5.50	0.55	0.008
AC-AMP-30	22.3	2.23	0.045
AC-AMP-70	14.0	1.40	0.028
AC-AMP-100	5.20	0.52	0.011
AC-AMP-120	2.80	0.28	0.006

Table 2 CO_2 adsorption/desorption capacity of FAS10 and its deashed counterpart before and after PEI loading
(Maroto-Valer and others, 2004)

Sample	CO_2 uptake, mg CO_2/g adsorbent	CO_2 uptake, %
FAS10-30	17.5	1.75
FAS10-75	10.3	1.03
DEM-FAS10-30	43.5	4.35
DEM-FAS10-75	22.0	2.20
FAS10-PEI-75	62.1	6.21
DEM-FAS10-PEI-75	93.6	9.36

temperatures (that is, up to 5 wt% at 75ºC). The textural properties of the raw material, and in particular the mesopore content seemed to be the dominant factor for obtaining a good dispersion of the polymer into the pore channels. By

impregnating the same substrate with amines of different molecular masses, diethanolamine (DEA) and tetraethylenepentaamineacrylonitrile (TEPAN), different CO_2 adsorption capacities from 4 to 6 wt% at 75ºC could be achieved.

High surface area powdered anthracites which had been surface treated were studied by Maroto-Valer and others, 2005; *also* Tang and others, 2004b) to assess their suitability as low-cost CO_2 sorbents. The treatments included NH_3 heat treatment and PEI impregnation. The NH_3 heat treatment increased the surface area of the activated samples, especially at lower temperatures (650ºC) but the PEI impregnation resulted in a dramatic decrease in surface area. This decrease was attributed to pore blockage and surface coverage by the PEI. At higher activation temperatures both treatments increased the CO_2 capture capacity of the activated anthracites due to the introduction of basic nitrogen groups onto the surface. At 75ºC the absorption capacity of anthracite activated for three hours at 850ºC was 2.15 wt% but that of the PEI-treated sample was still quite low at 2.63 wt%.

Low-cost carbon materials such as olive stones were evaluated as potential adsorbents for CO_2 capture by Plaza and others (2006). In order to improve the performance of these adsorbents, basic amine functionalities were incorporated through two different approaches: impregnation with PEI, and chemical functionalisation in a two-step process. The influence of temperature upon the CO_2 capture capacity of the adsorbents was evaluated in a thermogravimetric analyser. The adsorbents obtained in this work showed high CO_2 capture capacities at room temperature (up to 98 mg/g adsorbent, 9.8 wt%), but lower performance at higher temperatures, presenting capacities at 100ºC up to 18 mg/g adsorbent (1.8 wt%). The adsorption process was totally reversible in all cases, as the CO_2 was completely desorbed by simply applying vacuum.

Three alkylamines were evaluated as a potential source of basic sites for CO_2 capture by Plaza and others (2007) using a commercial activated carbon as a support. The amine coating increased the basicity and nitrogen content of the carbon but drastically reduced its mesoporous volume, the factor mainly responsible for CO_2 physisorption. Thus the capacity of the raw carbon was reduced at room temperature. However, at medium temperatures (70–90ºC), the contribution of chemisorption associated with the incorporated amino groups may improve the performance of the carbon.

The use of multi-wall carbon nanotubes as supports for amine sorbents has been suggested by Fifield and others (2004) because they have high surface areas. The amine sorbent studied was pyrene methyl picolinimide (PMP) in which the pyrene anchors the molecule to the carbon surface and the amine group captures the CO_2. More recently, C Lu and others (2008) have reported that carbon nanotubes modified with 3-aminopropyltriethoxysilane showed improved CO_2 capacity of 9.63 wt% compared with 6.92 wt% for the untreated adsorbent. The improvement for a granular activated carbon was much less marked; 7.95 wt% compared with 7.29 wt%.

3.1.3 Silica supported sorbents

Solid phase hexagonal mesoporous silica (HMS) modified using aminopropyltrimethoxysilane (APTS) and related compounds have been studied by Delaney and others (2002). The modified silica produced very high surface area material with varied concentrations of surface bound (tethered) amine and hydroxyl functional groups can which react with CO_2 as shown in Figure 3. CO_2 adsorption experiments were carried out at 20ºC for 75 minutes. After 75 minutes, the gas flow was changed to argon so as to monitor the CO_2 desorption. Approximately 90% of the adsorbed CO_2 was desorbed immediately and the remaining CO_2 was removed by heating the adsorbent to 65ºC.

The extent of the surface modification by aminopropyl-functionalised substrates was characterised as the number of tethered amino groups per nm^2 of the substrate surface area ('tether-loading'). It was found that the product prepared from amorphous silica gave a substantially higher tether-loading than for the HMS derived products at low silane concentration (Knowles and others, 2004). It was suggested that the morphology of amorphous silica, its greater accessibility of the mesopores and the larger average pore diameter, permitted better entry and faster diffusion of the reagent molecules. However, it was an HMS substrate that had the highest CO_2 absorption capacity of 6.31% on a mass basis. All the products exhibited capacities that corresponded to a CO_2/N molar ratio of ~0.5 consistent with the formation of carbamates. In general, the higher surface area substrates led to APTS modified products with the best CO_2 adsorption capacities.

Molecular modelling studies by Chaffee (2004, 2005) indicated that, when APTS was introduced into the mesopores of the silica, it spread out over the surface forming many hydrogen bonds. It was speculated that the formation of this 'surface film' may limit the number of silane molecules that can coordinate to and, hence, react with the surface OH groups. This could explain why the tether loadings reported by Knowles and others (2004) were not as high as expected if
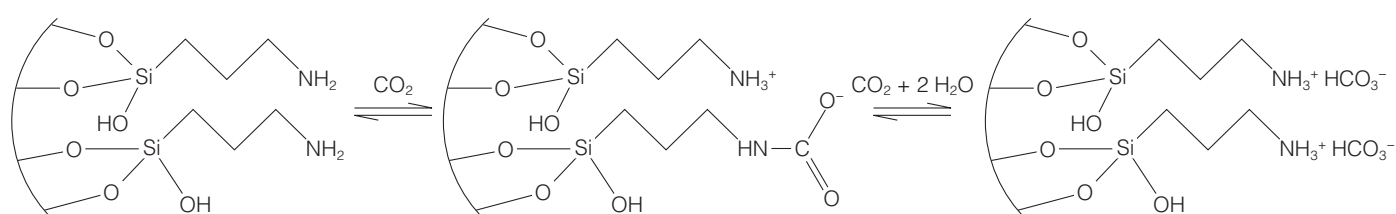
Figure 3   Surface reaction of tethered amine groups with CO_2 (Knowles and others, 2005a)

all surface silanols were accessible. The modelling also illustrated some of the interactions that may occur between the hybrid surface and gas-phase CO_2 when they are brought into proximity of each other. As shown in Figure 4, there is a clear tendency for CO_2 to form H-bonds, both with the tethered amine groups and with residual surface OH groups. CO_2 molecules can also be confined in structural pockets on the surface. In the figure, the green CO_2 molecule appears to be confined by strong H-bonding.

Studies by Knowles and others (2005a) showed that both the mass uptake per unit surface area and the heat evolved per unit surface area increased with the N content of the tether. Hence, their results showed that the higher N content of the tether leads to a higher CO_2 capacity on the adsorbent surface. It was also reported that the materials were able to adsorb CO_2 in the presence of moderate amounts of water. In the presence of water, CO_2 capacity of one hybrid material was found to be enhanced, although the rate of desorption was diminished (Knowles and others, 2005b)

Knowles and others (2005b) reported that the extent of functionalisation of various siliceous substrates was limited to 1.5 tethers per square nanometer of the substrate surface. Hydrogen bonding interactions between the surface silanol species and the silane amine groups could limit the extent of surface functionalisation. Knowles and others (2006a) suggested that a greater extent of surface functionalisation might be achieved if the amine group was rendered to have less affinity for the substrate surface during functionalisation. They found that reacting the amines with HCl, CO_2, and H_2O to form ammonium chloride, carbamate, and hydroxide species could result in higher tether-loading. The higher loadings resulted in higher CO_2 adsorption capacities for the porous products. The adsorption capacities reached 7.3 wt% at 20ºC and 6.9 wt% at 75ºC. Knowles and Chaffee (2007) prepared aminopropyl-functionalised hexagonal mesoporous silica products by sonication of mixtures of APTS and the
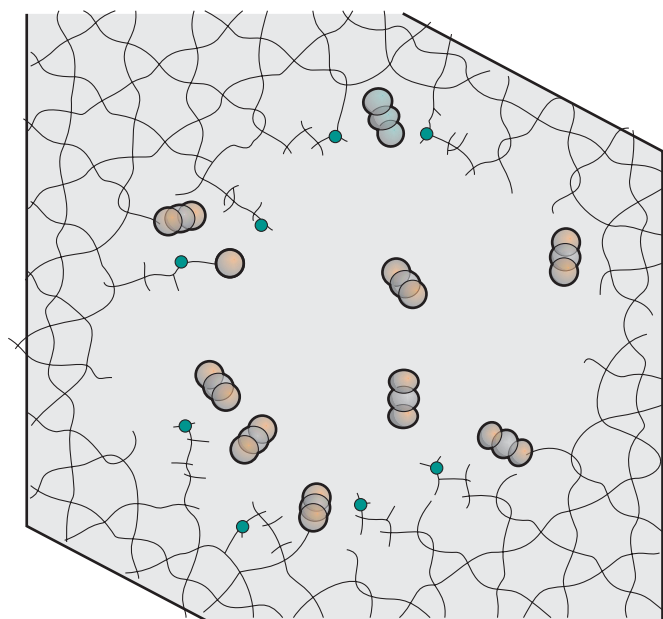
Figure 4   Molecular model illustrating H-bonding interactions between CO_2 molecules and the mesopore surface (Chaffee, 2004)

silica dispersed in toluene at 55ºC. The sonication was expected to improve the dispersion of the silica in the solvent and also the diffusion of the silane throughout the mesoporous substrate. The tether-loadings of the sonication products were found to increase with sonication time (up to 1.8 tethers.nm^{-2}). As expected, the sonication products were also found to have higher CO_2 sorption capacities (up to 5.3 wt%) than the corresponding product prepared by the conventional approach.

Knowles and others (2006b) prepared a series of diethylenetriamine[propyl(silyl)] (DT) functionalised silicas and compared them with aminopropylsilyl (AP) and ethylenediamine[propyl(silyl)] (ED) functionalised silicas reported earlier (Knowles and others, 2005a). The DT-functionalised materials were generally found to have greater CO_2 adsorption capacities for a given surface tether-loading than the analogous AP- or ED-functionalised materials under anhydrous conditions at 20ºC. Nevertheless, the DT-functionalised materials generally achieved lower amine efficiencies than the analogous AP- and ED-functionalised materials. This was thought to be due to reduced accessibility of CO_2 to the surface-bound amine groups brought about by entanglement (reduced mobility) of the longer hydrocarbon chains within the mesoporous domain and the relative proximity of amine pairs. Under moist conditions the CO_2 capacity was reduced possibly due to pre-adsorption of water on physisorption sites in the silica.

SBA-15 is a mesoporous silica material with a uniform pore size of 21 nm and a surface area of 200–230 m²/g. CO_2 adsorption/desorption on SBA-15 grafted with γ-(aminopropyl)triethoxysilane has been studied by Chang and others (2003). The large uniform pore size of SBA-15 facilitates CO_2 diffusion inside of the pore, allowing rapid CO_2 adsorption on the surface amine sites. CO_2 was found to adsorb on the amine sites in the form of carbonate and bicarbonate which desorb as CO_2. Repeated CO_2 adsorption and sorbent regeneration studies showed that amine grafted on SBA-15 exhibited hydrothermal stability and allowed repeated use without loss of CO_2 capture capacity.

Zheng and others (2004, 2005a) synthesised an ethylenediamine (EDA) modified SBA-15 mesoporous silica and characterised its CO_2 adsorption properties. The CO_2 adsorption capacity of the EDA-SBA-15 sorbent was around 20 mg/g (2 wt%) at 25ºC and 1 atm (~0.1 MPa) with 15% CO_2 (by volume) in N_2. Desorption of CO_2 occurred at 110ºC and the adsorbent was stable in air up to 200ºC. The CO_2 adsorption capacity of the EDA-SBA-15 was not influenced by moisture. It was recognised that the adsorption capacity of the sorbent was not adequate for the reduction of CO_2 emission at large scale economically; a further increase in capacity is necessary. One of the reasons for the low CO_2 adsorption capacity was thought to be that not all the EDA groups tethered to the surface were active for CO_2 capture. Zheng and others (2005b) reported a method to release and activate the EDA groups latched to the surface by hydrogen bonding with residual silanol groups. This was accomplished by backfilling with propylsilane groups in supercritical propane. This produced an adsorption capacity 2.6–3.1 times greater than the untreated EDA-SBA-15.

An amine-enriched SBA-15 sorbent was compared with a proprietary immobilised amine sorbent by Gray and others (2003a,b). The SBA-15 slightly outperformed the commercial sorbent. With the surface nitrogen value of 7.13% for the SBA-15, the total amount of CO_2 captured was 1.89 moles/kg (8.3 wt%) compared with 1.82 moles/kg (8.0 wt%) for the commercial sorbent with a surface nitrogen value of 17.7%. The better performance was attributed to the more accessible amine sites on the SBA-15 sorbent. A later study involved a reformulated immobilised amine sorbent, the exact formulation of which was not disclosed although it was based on a secondary ethyleneamine (Gray and others, 2004b, 2005b). In this case the reformulated sorbent had a higher average CO_2 capture capacity over the SBA-15 sorbent. Tarka and others (2006a,b) reported that the amine-enriched SBA-15 sorbent had a CO_2 transfer capacity of 6.4 moles per kg of sorbent at 54ºC (28.2 wt%) and could be completely regenerated by heating to 99ºC for one hour,

Aminosilane-modified SBA-15 adsorbents have been developed by Yamamoto and others (2005) and the adsorption capacities in the presence and absence of water were studied. It was found that the adsorption capacities were comparable in dry and wet conditions. In particular, the adsorption capacity of the SBA-15 grafted with (3-riemethoxylsilylpropyl)diethylenetriamine (TA) reached 1.28 mol/kg (5.63 wt%) in the presence of water vapour at 60ºC.

A simple strategy of impregnating a porous sorbent with a liquid adsorbent was studied by Madariaga and others (2006). The solid support consisted of precipitated silica Tixosil 38X (SiO_2) with a high porosity value and an average diameter of 160 µm. The impregnation liquids were Jeffamine T-403, which is a polymeric primary amine, and monoethanolamine (MEA). During the impregnation process the particles were wetted with a solution of the amine and then the solvent was evaporated. Since it is desirable to have the maximum loading of the active compound to react with CO_2, evaporation was carried out under vacuum to avoid air trapping inside the pores and thus increasing the loading of the amine within the particles. When the impregnated particles were compared with an adsorbent for a dry gas, it was found that the particles had a higher CO_2 sorption capacity than the same volume of activated carbon. This difference was larger in the presence of water vapour, probably due to the formation of bicarbonate.

Liang and others (2006, 2008a) have reported the preparation and characterisation of a stepwise growth of a mesoporous silica (SBA-15) bound melamine dendrimers together with their CO_2 absorption capacities. The melamine based dendrimers contain a mixture of primary, secondary, and tertiary amine groups providing a range of active sites with varied basic strength. The experimentally determined CO_2 adsorption capacities were found to be similar to, but less than the capacities predicted on the basis of interaction with the primary amine groups only. The adsorption capacities were described as not particularly impressive. Chaffee and others (2006b) investigated melamine based dendrimers bound within the channels of mesocellular siliceous foam (MCF). MCF has larger pores than SBA-15; it consists of uniform spherical cells in the diameter range of 16–42 nm that are interconnected by uniform windows to create a continuous three-dimensional (3D) pore system. CO_2 adsorption experiments indicate that primary amines were likely the only type of functional group in the dendritic structures to interact with CO_2. The maximum CO_2 adsorption capacity obtained at 20ºC was 4.0 wt%. However, the heats of adsorption, in the range of 30–35 kJ/mol, were found to be considerably less than those for amine solvents, suggesting that the energy requirement for sorbent regeneration could be lower.

The aziridine (ethylene imine) monomer was polymerised on the surface of SBA-15 by Hicks and others (2008a,b) to prepare a hyperbranched aminosilica (SBA-HA). The organic loading of the grafted hybrid aminosilica was determined to be 7.0 mmol N/g material. The sorbent was found to be capable of adsorbing CO_2 reversibly with very high capacities of 3.1 mmol CO_2/g material at 25ºC (13.6 wt%). The advantage of this adsorbent over previously reported adsorbents rests in its large CO_2 capacity and multicycle stability. The material was recycled by thermally desorbing the CO_2 from the surface with essentially no changes in capacity. The organic groups on the surface were stable in the temperature range between 25 and 130ºC due to the covalent attachment between the support and the organic groups.

A modified mesoporous silica based molecular sieve (MCM-41) was investigated by Xu and others (2002a,b, 2003b; Song and others, 2004). They called the large pore volume MCM-41 substrate a 'basket' and this was turned into a 'molecular basket' for CO_2 adsorption by immobilising the sterically branched polymer PEI into the channels of the MCM-41. The details of the adsorbent preparation have been described by Xu and others (2003b). A CO_2 adsorption capacity of the produced MCM-41-PEI as high as 215 mg CO_2/g PEI (21.5 wt%) was obtained at 75ºC, which was 24 times higher than that of the MCM-41 alone and twice that of the pure PEI. With an increase in the CO_2 concentration in the CO_2/N_2 gas mixture, the CO_2 adsorption capacity increased. The cyclic adsorption/desorption operation indicated that the performance of the adsorbent was stable; although it was later reported by Xu and others (2004a) that it was not stable when the operation temperature was higher than 100ºC. When the PEI loading was higher than 30 wt%, the mesoporous molecular sieve of MCM-41 showed a synergistic effect on the adsorption of CO_2 by PEI. The highest synergistic effect was obtained when the PEI loading was 50 wt%. When the PEI loading was 75 wt%, the synergistic effect decreased. It was also reported that a the addition of polyethylene glycol can increase, not only the CO_2 adsorption and desorption rate, but also the CO_2 adsorption capacity (Xu and others, 2002b, 2003b).

An interesting observation by Xu and others (2002a) was that the adsorption of CO_2 into PEI or MCM-41 is an exothermic process. Accordingly, the adsorption capacity should decrease with the increase of temperature. However, the adsorption capacity increased with increasing temperature in this study. Figure 5 shows the proposed hypothetical explanation for this. At low temperature, the PEI exists in the channels of MCM-41 like nanosized particles. In this case, only the CO_2 affinity sites on the surface of the particles can readily react with the CO_2. The affinity sites inside the nanosized particles

a) low temperature
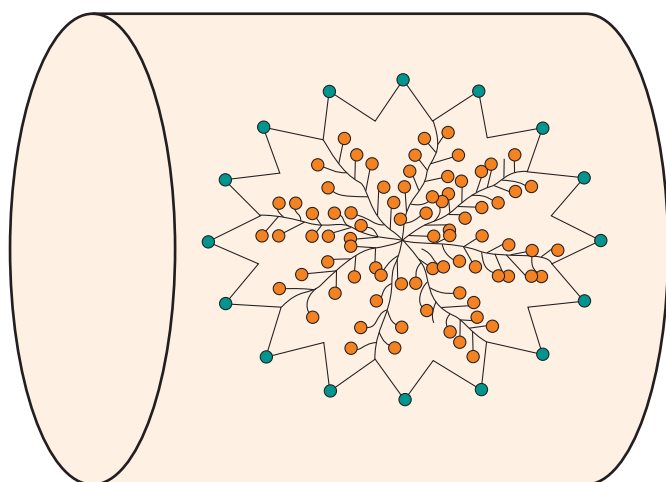
b) high temperature
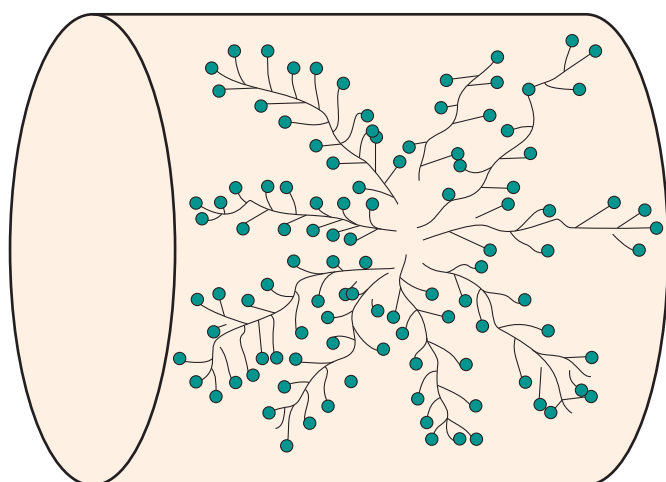
● active CO_2 adsorption sites   ● hidden CO_2 adsorption sites

Figure 5   Schematic diagram of PEI status in MCM-41 (Xu and others, 2002)

can only react with the CO_2 when the CO_2 is diffused into the particles. This is a kinetically (diffusion)-controlled process, since the access of CO_2 to the affinity sites inside the PEI particles will be subject to the diffusion limitation, and CO_2 may reach more affinity sites if the diffusion time is sufficiently long. In this case, more affinity sites will be exposed to the CO_2 and thus the adsorption capacity will increase when using a short adsorption time.

The model was further developed to explain the synergistic effects on the CO_2 adsorption which are only observed at high PEI loading (Xu and others, 2003b). When the PEI loading was low, the pore size of the adsorbent slightly decreased. In this case, the PEI was mostly adsorbed on the inner pore wall of the MCM-41 support. Both physical adsorption and chemical adsorption contribute to CO_2 uptake in this case. The adsorption capacity was even smaller than that of the linear adsorption capacity. With increasing PEI loadings, the pore size further decreased. At the same time, because more PEI was loaded into the channels, the chemical adsorption of CO_2 became much more dominant than that of the sorbent

with low PEI loadings. The physical adsorption on the unmodified pore wall of MCM-41 (and the capillary condensation in the mesopore) became negligible when compared with the chemical adsorption force. In addition, the mesoporous molecular sieve MCM-41 had a synergistic effect on the adsorption of CO_2 by PEI in the confined mesoporous pores. Therefore, the CO_2 adsorption capacity increased. The highest synergistic adsorption gain was obtained when the mesoporous channels were completely filled with PEI at about 50 wt% PEI loading. When the PEI loading further increased to 75 wt%, the synergistic adsorption gain was smaller than that with PEI loading of 50 wt%. The largest amount of PEI that can be theoretically loaded into MCM-41 is 50 wt%. For the adsorbent with PEI loading of 75 wt%, the excess PEI would be coated on the external surface of the molecular sieve particles.

The adsorbent was tested with simulated flue gas containing 14.9% CO_2, 80.85% N_2, and 4.25% O_2 by Xu and others (2002c, 2004a). At 75ºC the adsorbent showed separation selectivity of over 1000 for CO_2/N_2 and 180 for CO_2/O_2.

PEI can exist in linear and branched forms leading Xu and others (2004b) to investigate whether this made a difference to the sorbent performance. They found that the adsorbent prepared with linear PEI showed both a higher CO_2 capacity and a faster CO_2 adsorption/desorption rate than that prepared using branched PEI.

A series of PEI impregnated mesoporous silica support materials was prepared by Son and others (2008) and tested in terms of CO_2 adsorption-desorption behaviour under various conditions. Examination of their textural properties indicated that the fundamental pore structure remained intact after about 50 wt% PEI loading; beyond this apparent threshold, PEI begins to be coated on the external surface of the mesoporous silica support materials, consistent with the model of Xu and others (2003b). All the PEI loaded mesoporous silica samples exhibited reversible CO_2 adsorption-desorption behavior with >99% recovery, and the CO_2 adsorption capacities of the materials were substantially higher than that of pure PEI and varied following the sequence of KIT-6 > SBA-16 ≈SBA-15 > MCM-48> MCM-41, as generally dictated by the average pore diameter of the support. Pore diameter of the support material was again the most important variable with respect to controlling the adsorption kinetics, provided that all of the 50 wt% of PEI could be accommodated inside the pores. Son and others (2008) believed that 3D pore arrangement in mesoporous silica materials facilitates enhanced CO_2 adsorption kinetics. Overall, KIT-6, having the largest pores in a 3D arrangement, achieved the highest CO_2 adsorption capacity (135 mg CO_2/g adsorbent, 13.5 wt%) in the fastest response time. KIT-6 with 50 wt% PEI loading exhibited the best performance, superior to zeolite 13X, as a CO_2 adsorbent at 75ºC, and maintained stability during a 900 minute adsorption-desorption cycle without deterioration.

The effect of pore size has been examined by Zeleňák and others (2008). They studied three amine-modified silica molecular sieves. The sorption capacity was found to depend on the surface density of amine groups and on the pore size of

the mesoporous silica. The molecular sieves with larger pores and higher surface density of amines possessed higher sorption capacity. The largest pore size silica (SBA-15) showed the highest CO_2 sorption capacity of 1.5 mmol/g (6.6 wt%) at 25ºC. The lower limit for pore size of mesoporous silicas to be used in preparation of efficient amine-based sorbents was found to be approximately 3.5 nm. Below this size of pores the amine adsorption sites inside the pores are inaccessible for CO_2 molecules due to their limited diffusion into the pores.

Grafting amines on to silica does not necessarily improve its CO_2 sorption capacity; Knöfel and others (2007) functionalised SBA-16 silica with the diamine $(CH_3O)_3Si-(CH_2)_3-NH-(CH_2)_2-NH_2$ and found that the amounts of CO_2 adsorbed at 3 MPa were ~6.5 mmol/g (~28.6 wt%) for the non-grafted silica samples and 4.6 mmol/g (20.2 wt%) for the functionalised silica. It was suggested that there was probably a too much amine initially incorporated into the porous system of the silica.

A liquid impregnated solid sorbent has been developed by US National Energy Technology Laboratory and patented (US Patent 6,908,497 B1, 21 June 2005). The solid material mentioned in the patent is bentonite, a clay consisting mostly of montmorillonite. It consists of continuous layers of silica sheets. This clay based sorbent reported by Siriwardane and others (2006, 2007a, 2007b; *also* Siriwardane and Robinson, 2008) consists of amines, glycols, and ethers incorporated in the clay matrix. This sorbent showed stable sorption performance at 40ºC and at atmospheric pressure during a 25-cycle test, and regenerability at 80–100ºC. The presence of steam and 20 ppm of SO_2 did not appear to affect the performance of the sorbent. The sorbent was prepared for both fixed and fluidised bed applications. The CO_2 removal efficiency of the sorbent was 99%, and it has a CO_2 capture capacity of 3.6 moles/litre (2.1 mol/kg, 9.2 wt%) obtained at 40ºC. This CO_2 capture capacity value corresponded to a delta loading (amount of CO_2 that could be recovered when the sorbent is regenerated at 100ºC in the presence of CO_2) value of 2.8 moles/litre (~7.2 wt%) which is close to the minimum acceptable value based on the specific heat capacity of the clay support.

A clay based sorbent was reported by Siriwardane and others (2007b) which consisted of amines, glycols, and ethers incorporated in a clay matrix. This sorbent showed stable CO_2 sorption performance at ambient temperature and atmospheric pressure during a multicycle test, and regenerability at 80–100ºC. The sorbent was prepared for both fixed bed and fluidised bed applications. The sorbent's performance was not affected by the presence of steam. The CO_2 removal efficiency of the sorbent was 99%, and it had an 'acceptable' CO_2 capture capacity of 4.2 mol/litre (2.1 mol/kg, 9.24 wt%) obtained at 40ºC.

Based on adsorption isotherms and kinetic data, Pirngruber and others (2008) have performed a preliminary analysis of the performance in VSA or TSA process for a series of different amines (including PEI) immobilised on a silica support by grafting or impregnation. The adsorbents were tested for CO_2 adsorption in simulated flue gases. The

absolute sorption capacity of silica samples grafted with mono-, di- or triamines was found to be rather low. Polyamines impregnated on silica can adsorb a lot more CO_2, but their regeneration is more difficult. Primary amines seem to be strongest adsorption sites for CO_2. When part of the primary amines is reacted with acrylonitrile, the basicity of the samples is moderated, which is favourable for regeneration. However, irrespective of the choice of the solid sorbent, the design of a pressure swing adsorption process faces difficulties, which are related to the huge volume flows that have to be dealt with. The number of adsorption columns is imposed by hydrodynamic considerations (pressure drop limitations) rather than by the properties of the adsorbent itself. Moreover, a clever mode of regeneration has yet to be found. It was concluded that neither conventional TSA nor conventional VSA operation seem to be viable options.

3.1.4 Alumina supported sorbents

A large number of solid sorbents were produced by impregnation of high surface area, high pore volume solid supports with suitable amines by Contarini and others (2003). Silica, silica-zirconia, alumina and clay supports were tested with some alkanolamines and polyamines. The best performances were exhibited by the alumina based sorbents impregnated with alkanolamines, which reversibly trapped CO_2 by 6.5–9.6 wt% of the sorbent. A preliminary technical economic evaluation indicated that there was a need for a 50% increase in the specific CO_2 capture activity of the sorbent and an increase in gas permeability in order to be competitive with amine solvent technology.

A series of solid sorbents was synthesised by Plaza and others (2008a) by immobilising liquid alkylamines and alkanolamines on the surface of a mesoporous alumina. The CO_2 capture performance of the sorbents and their thermal stability was studied by thermal gravimetric analysis. The basic nature of the sorbents was expected to be favourable for their application in the adsorption of CO_2. However, impregnation had a negative effect on the texture of the resultant sorbents, as revealed by the significant decrease in the BET surface areas. This decrease is a consequence of pore blockage by the amine film. CO_2 adsorption on amine-impregnated alumina cannot be explained by a single process, as it can be controlled by physical/chemical sorption or by mass transfer. Therefore, the type and load of amine used to impregnate the support and the temperature of the process need to be optimised. In the absence of water, tertiary amines cannot capture CO_2 since they cannot form carbamates. Hence, CO_2 adsorption can occur only by physisorption and this is less than with the raw alumina since the presence of the tertiary amine reduces the surface area. Sterically hindered amines also perform poorly. The better performing amines were those with more than one amino group in their structure and their capture capacity increased with increasing temperature as shown in Figure 6. The explanation offered was that the CO_2 diffusivity through the amine film improved with increasing temperature allowing more amine groups to react as previously suggested by Xu and others (2002a). The sample impregnated with diethylenetriamine (DETA) had the highest CO_2 capture
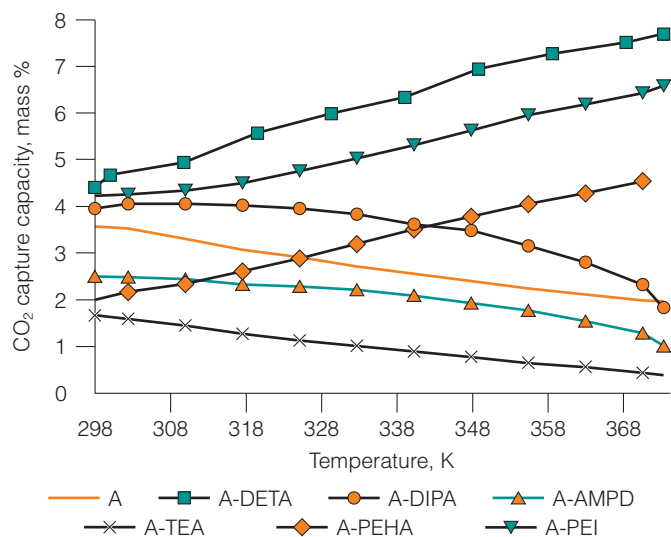
Figure 6 **Effect of temperature on the CO_2 capture capacity of the commercial alumina (A) and the immobilised amines** (Plaza and others, 2008)

capacity throughout the studied temperature range (25–100ºC). A-DETA doubled the CO_2 capture capacity of the raw alumina at 25ºC (6 versus 3 wt%). Moreover, A-DETA presented about 8 wt% CO_2 uptake at 100ºC, whilst the raw alumina only achieved 1 wt% of CO_2 capture at the same temperature. A temperature of 100ºC would reduce the need to cool the flue gases in post-combustion capture systems.

3.1.5   Zeolite supported sorbents

Zeolite 13X was impregnated with monoethanolamine (MEA) with loadings of 0.5–25 wt% by Jadhav and others (2007). The adsorbent with a 10 wt% loading showed an improvement in CO_2 adsorption capacity over the unmodified zeolite by a factor of around 1.6 at 30ºC, whereas at 120ºC, the efficiency improved by a factor of 3.5. A small MEA loading (0.5 wt %) had very little effect on the CO_2 adsorption capacity. With the highest loading (25 wt %), the CO_2 capacity decreased. This was attributed to reduced surface area and pore volume and restricted access to adsorption sites for CO_2 at higher loadings. The 10 wt% MEA-modified adsorbent also emerged as a potential adsorbent for CO_2 in the presence of moisture. The performance of the adsorbent was also satisfactory after three cycles of adsorption. It successfully retained adsorption capacity although there was a slight loss of capacity after the first cycle attributed to some irreversible adsorption in the first cycle that could not have been desorbed at the selected pretreatment temperature.

NETL is supporting research on metal monolithic amine-grafted zeolites for CO_2 capture and a factsheet can be found at http://www.netl.doe.gov/publications/factsheets/project/Proj467.pdf.

3.1.6   Glass fibre supported sorbents

A sorbent for CO_2 capture was developed by P Li and others

(2008) based on coating PEI on a glass fibre matrix using epichlorohydrin (ECH) as a cross-linking agent. The formation of a network structure between ECH and PEI was to enhance the thermal stability of the adsorbent. The maximum CO_2 adsorption capacity achieved was 4.12 mmol CO_2/g total adsorbent (18.1 wt%) and 13.56 mmol CO_2/g PEI (59.66 wt%) on the adsorbent at 1 atm (~101 kPa), 30ºC, and about 80% relative humidity, with 57% utilisation of the amine compound. The sorbent had high thermal stability at about 250ºC, a low regeneration temperature of 120ºC, and was stable in the presence of moisture.

3.1.7   Xerogel supported sorbents

Derivatised aliphatic diamines bearing a silyl group have been studied by Dibenedetto and others (2003; also Aresta and Dibenedetto, 2003). The diamines were more efficient for the reversible uptake of CO_2 than monoamines but they could also be converted into silica *xerogels* with high porosity and surface area. The xerogels were found to absorb and desorb CO_2 from a gas mixture in a very short time and for several cycles in a batch system.

3.1.8   Porous crystals

Metal organic frameworks (MOFs), discussed in Section 2.4, can also contain amine groups in the organic linking group. One such is the amino-functionalised IRMOF-3 with one amino group present. Millward and Yaghi (2005) suggested that CO_2 was attracted to the nitrogen either through hydrogen bonding or via interaction with the lone electron pair. Babarao and Jiang (2008a) used molecular simulation to screen metal-organic frameworks for CO_2 adsorption. They found that adsorption in IRMOF-1-$(NH_2)_4$ was higher than that in IRMOF-1 at low pressures. At higher pressures the reverse was true because the four introduced -NH_2 groups reduced the free volume and accessible surface area which are the primary controlling factors at high pressures.

Zeolitic imidazolate frameworks (ZIFs) are porous crystalline materials with tetrafhedral networks that resemble those of zeolites (B Wang and others, 2008). Imidazole is a five-membered aromatic heterocyclic ring containing two nitrogen atoms. Hayashi and others (2007) suggest that ZIFs potentially have the advantages of both inorganic zeolites (for example, high stability) and of MOFs (for example, high porosity and organic functionality). They reported the synthesis of three porous ZIFs that are expanded analogues of zeolite A. The ZIFs had functionalised purinate cage walls and displayed a strong interaction with CO_2. ZIFs have been synthesised by Banerjee and others (2008) from either zinc(II)/cobalt(II) and imidazolate/imidazolate-type linkers. Three of the ZIFs synthesised had high thermal stability (up to 390ºC), chemical stability, and high porosity with surface areas up to 1970 m2/g. They also exhibited unusual selectivity for CO_2 capture from CO_2/CO mixtures. Their capacity for CO_2 was described as 'extraordinary'; one litre of ZIF-69 can hold 82.6 litres (162 g) of CO_2 at 0ºC under ambient pressure. The synthesis and characterization of two porous ZIFs (ZIF-95 and ZIF-100) have been reported by B Wang and
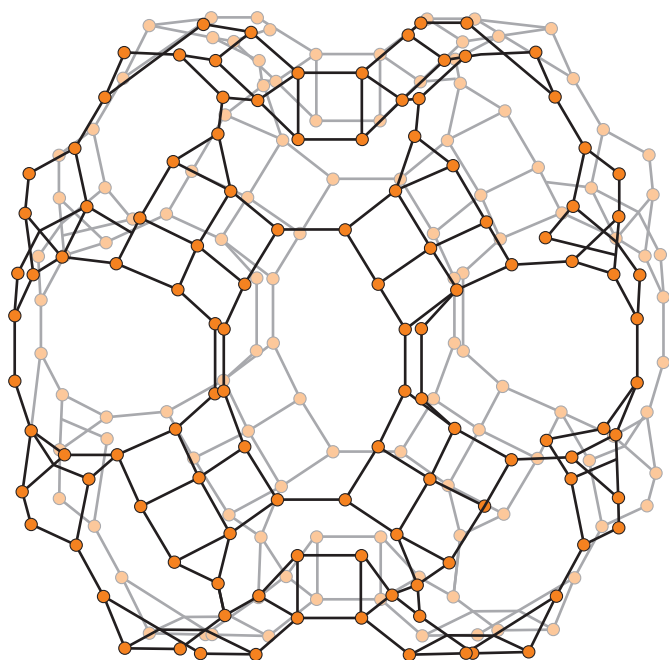
Figure 7   Ball and stick diagram of cages in ZIF-100 (B Wang, 2008)

others (2008). The two ZIFs have structures of a scale and complexity previously unknown in zeolites. A ball and stick diagram of the cages in the 'beautifully complex structure' of ZIF-100 is shown in Figure 7.

Carbon dioxide, methane, carbon monoxide and nitrogen adsorption isotherms were measured for both ZIFs, which clearly showed a disproportionately high affinity and capacity for CO_2. ZIF-100 outperformed ZIF-95 and the prototypical adsorbent BPL carbon, which is widely used in industry owing to its ease of desorption and regeneration. Both ZIFs showed complete reversibility of adsorption, indicating that they might serve as selective carbon dioxide reservoirs. One litre of ZIF-100 can hold up to 28.2 l (55.4 g, or 1.7 mmol/g of ZIF-100, 7.5 wt%) of CO_2, at 0ºC and 15.9 l (31.2 g, 4.2 wt%) at 25ºC. The high selectivity of the ZIFs for CO_2 was attributed to the combined effects of the slit width of the pore apertures being similar in size to CO_2 and the strong quadrupolar interactions of carbon with nitrogen atoms present in the imidazolate links.

3.1.9   Self supported sorbents

Drage and others (2007c,e) pointed out that the activation of the melamine-formaldehyde (MF) resin (Drage and others, 2007a, discussed at the beginning of this chapter) by heating to high temperatures can destroy the original functionality, with the most potent groups for the adsorption of CO_2, such as amine groups, being lost or converted. They explored *nanocasting* or *templating* by which means high surface area adsorbents can be generated without the need for heat treatment or activation. In nanocasting an inorganic diluent such as silica is used as a template to shape the growing polymer. This template is removed by dissolution but the polymer remains as an 'image', inheriting the porosity of the template. Porous MF resins were synthesised in the presence

of 7 nm and 14 nm fumed silica as a templating agent. The solid MF/silica product was treated with sodium hydroxide solution and then dried at 120ºC. The adsorption capacity was highest at 25ºC and decreased gradually with increasing temperature. The capacity and decrease in adsorption of CO_2 at elevated temperature was superior to the performance of a standard commercial activated carbon. However, it was suggested that, although the nanocasting technique is effective in producing high surface area materials, exploration of different polymer types is required to generate adsorbents containing sufficiently basic nitrogen. Amines would be preferable to the amide and triazine ring nitrogen groups of the MF resin.

Further carbonisation to generate the adsorbents was carried out by heating the samples at 10ºC/min up to 400, 500, 600, and 700ºC for 1 hour (Pevida and others, 2008a,c). The carbonised adsorbents presented CO_2 capture capacities up to 2.25 mmol/g at 25ºC (9.9 wt%), outperforming many commercial activated carbons. Both texture and surface chemistry influenced the CO_2 capture performance of the prepared adsorbents: while for adsorbent carbonised at 700ºC, physisorption seemed to be the controlling mechanism while for the samples carbonised at 500ºC a favourable chemistry appeared to determine CO_2 capture. If an adequate and well developed porosity is joined to a favourable chemistry, the CO_2 adsorption capacity is considerably enhanced. Examination of the composition of surface nitrogen revealed a change in nitrogen composition from carbons containing triazine ring nitrogen to more stable pyridinic and tertiary nitrogen with increasing carbonisation temperature. These functionalities present less affinity for CO_2.

3.2   Effects of moisture, NOx, and SO$_2$

Xu and others (2002c, 2003c, 2004c, 2005; Song and others, 2007) tested their 'molecular basket' adsorbent (*see Section 3.1.3 above*) with simulated flue gas containing 14.9% CO_2, 80.85% N_2, and 4.25% O_2. In the presence of 10% moisture the CO_2 adsorption capacity was ~40% higher than that in the dry gas mixture. This was described as a major advantage since there would be no need to remove moisture from the flue gas prior to CO_2 capture. The maximum promoting effect of the moisture was at concentrations approaching that of CO_2 in the flue gas (Xu and others, 2004c, 2005). They also used coal-fired flue gas containing 420 ppm NOx and 420 ppm SO_2 (Xu and others, 2003a,c). The selectivity of CO_2/NOx was 10.7 and that for CO_2/SO_2 was 2.86 but very little NOx or SO_2 desorbed after adsorption indicating the need to remove them from flue gas prior to CO_2 capture.

Fauth and others (2006) have reported a study on the effect of trace flue gas contaminants on tetraethyleneamineacrylonitrile (TEPAN) and N,N′-bis(2-hydroxyethyl)ethylenediamine (BED) impregnated within a high surface area poly(methyl methacrylate) support by a solvent evaporation method. The effects of moisture, NO/NOx, and SO_2 on the performance of the sorbent were examined. The presence of water vapour did not influence CO_2 uptake by the sorbents. Adsorption of NO was found to be negligible during testing at 750 ppmv NO.

Both CO_2 and NO (>5 ppmv maximum) were simultaneously desorbed upon thermal regeneration at 90ºC. A CO_2 absorption capacity of 2.1 mol CO_2/kg sorbent (9.24 wt%) was achieved over three consecutive adsorption/desorption/ regeneration cycles. In experiments with 750 ppmv SO_2 present in the flue gas mixture, the sorbents were found to lose activity in incremental amounts with each consecutive cyclic adsorption/desorption/ regeneration operation. In the adsorption stage an instantaneous drop in SO_2 was observed but SO_2 was not desorbed by thermal regeneration at 90ºC. The adsorption of SO_2 indicates that there would be a need for upstream removal of SO_2 prior to CO_2 capture by immobilised amine sorbents.

Pirngruber and others (2008) studied the effects of water on adsorption and desorption of a series of adsorbents with immobilised amines on a silica support (*see* Section 3.1.3) and found that moisture had a small negative effect on the adsorption of CO_2. For desorption, water did not have a beneficial effect on the desorption of CO_2 by displacement of CO_2 from the sorption sites. This result is in line with the observation that water does not affect the adsorption capacity of CO_2 very much. The sorption sites of the two molecules seem to be different and do not interfere with each other. The quantity of adsorbed water is, however, non-negligible; at 8% H_2O in the feed (a typical concentration found in flue gases) the quantity of adsorbed water was measured gravimetrically to be 1.5 mol/kg (2.7 wt%), the same order of magnitude as the CO_2 adsorbed.
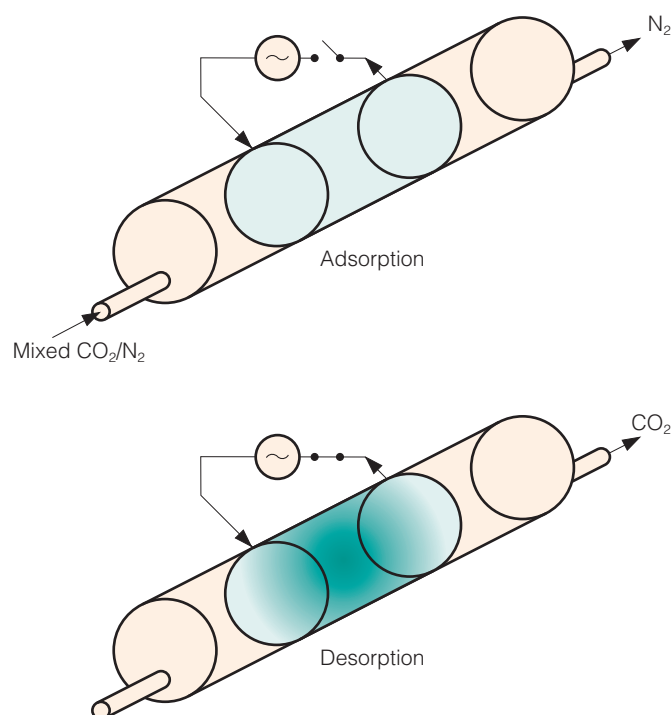
3.3 CO_2 desorption and adsorbent regeneration

Methods of obtaining a pure gas stream of CO_2 from solid sorbents can include pressure swing adsorption (PSA), vacuum swing adsorption (VSA), or temperature swing adsorption (TSA). Chaffee and others (2006a) point out that the need to pressurise the feed gas in PSA largely rules it out for flue gas containing only 10–15% CO_2. On the other hand, they suggest that the flexibility of the VSA process to changes in feed conditions is one of its strengths. They have constructed a pilot-scale VSA plant for the study of the capture of CO_2 from CO_2/N_2 streams. Table 3 summarises the performance achieved in the pilot plant for 6- and 9-step cycles for a feed gas containing 12% CO_2. A purity of over 90% can be achieved with a recovery of 60–70% for a 9-step cycle.

VSA applied to the impregnated carbons prepared by Plaza and others (2007) did not achieve complete regeneration due to the chemisorption character of these adsorbents. However, when physisorption type adsorbents (such as zeolites) are used, VSA seems to be an adequate operation mode for CO_2 capture.

Drage and others (2006a,b, 2008a,b) have investigated the regeneration of adsorbent produced by the impregnation of a proprietary mesoporous inorganic support with 40 wt% polyethyleneimine (PEI). They studied thermal swing absorption (TSA) and thermally assisted PSA. In the TSA cycle, adsorption of CO_2 was performed at 75ºC for 40 minutes followed by desorption for a range of times (1, 2, and 3 minutes) at temperatures ranging from 110 to 180ºC. Above 145ºC, whilst approximately 90% of the original adsorption capacity was recovered, the adsorption capacity on the second regeneration cycle decreases. At 180ºC there was a greater than 10% loss in recovered adsorption capacity. The decline in adsorbent performance was attributed to irreversible carbamate formation above 130ºC although the exact chemical species was not determined. Infrared spectral analysis indicated that, possibly, amide type bonding could be present (Drage and others, 2007b,d). Later, the loss of adsorption capacity was attributed to the bonding of CO_2 into the PEI polymer by the formation of a urea type linkage above 135ºC (Drage and others, 2008a,b). It was concluded that TSA in a CO_2 atmosphere is not a feasible method for the cycling of PEI based adsorbents. The use of nitrogen stripping gas at elevated temperatures (140ºC) was used to demonstrate the regeneration of the adsorbent using small quantities of stripping gas. Although nitrogen was used as a stripping gas in this example, and would not be used in real application of the technology, the results demonstrated that there is potential for the use of steam stripping as a means of regeneration.

Figure 8   Conceptual design of electrical swing adsorption (Delaney and others, 2006b)

Table 3	Performance data for 6-step and 9-step VSA cycles (Chaffee and others, 2006a)	
Performance	6-step cycle without purge	9-step cycle without purge
Purity, %	82–83	90–95
Recovery, %	60–80	60–70
Power, kW per t/d carbon captured	4–8	6–10
Energy penalty, %	8–15	12–20

In the thermally assisted PSA cycle, adsorption was performed at 75ºC using a simulated flue gas with 15% CO_2 and 85% N_2. Desorption was carried out in a stream of pure nitrogen to simulate pressure swing by lowering the partial pressure of CO_2. Regeneration was performed at a range of N_2 flow rates (50–100 ml.min^{-1}) and over a temperature range of 75–140ºC. Increasing the temperature from 120ºC to 140ºC resulted in an increased amount of CO_2 being desorbed.

Delaney and others (2006a,b) have investigated mesoporous carbon based adsorbents functionalised with amines. Prepared in monolithic form, their electrically regenerable properties may make them suitable for CO_2 capture by electrical swing adsorption (ESA). Rapid and uniform desorption of CO_2 can be achieved by passing an electrical current through the carbon adsorbent. The conceptual design is shown in Figure 8.

3.4   Comments

Knowles and others (2005b) admit that the CO_2 adsorption capacities of aminopropyl-functionalised materials to date are not outstanding. However, they argue that there are insufficient data in the literature to distinguish whether higher CO_2 adsorption capacities can be achieved. The development of functionalised amine sorbents will depend on improving characteristics such as high thermal stability, excellent CO_2 stability, high CO_2 adsorption capacity, easy CO_2 desorption, and reversible regeneration.

4 Regenerable solid sorbents

The role of solids in CO_2 capture has been the subject of a 'mini review' by Harrison (2005) who pointed out that solid based processes possess many potential advantages including:

- a wide range of operating temperatures;
- reduced energy penalties;
- avoidance of liquid wastes;
- the relatively inert nature of solid wastes.

In solid based processes, sorbent is consumed and CO_2 captured during reaction and the CO_2 is liberated as the sorbent is regenerated. Recently, the term 'chemical looping' has been applied to this cycle. The term is probably better known in the context of chemical looping combustion in which metal oxides are used to supply oxygen to a fuel gas and are subsequently regenerated by reaction with air. CO_2 looping cycles have been reviewed by Anthony (2008) and use a sorbent capable of carbonation to remove CO_2 from a combustion or gasification environment:

$$M_xO + CO_2 = M_xCO_3$$

The resulting carbonate is then regenerated:

$$M_xCO_3 = M_xO + CO_2$$
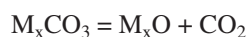
4.1 Natural minerals

From a cost point-of-view, natural minerals such as limestone (calcium carbonate, $CaCO_3$) should have a fairly obvious advantage. However, the use of natural calcium carbonates as regenerable CO_2 sorbents is limited by the rapid decay of the carbonation conversion with the number of cycles of carbonation/calcination, where calcination is the regeneration reaction (Abanades, 2002). The basic concept is shown in Figure 9.

Studies have shown that the recarbonation reaction is far from
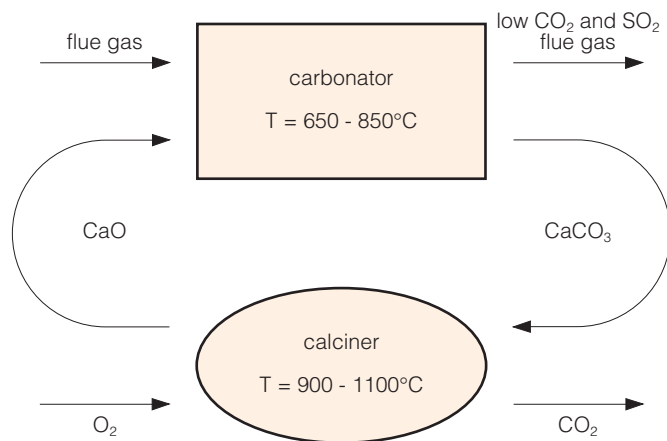
reversible in practice. After an initial, rapid reaction period, a much slower second stage follows, controlled by diffusion in the $CaCO_3$ layers. The limestone deactivation mechanism is discussed below in Section 4.1.1. Thus, there is a need for a fresh feed of sorbent to compensate for the decay in activity during sorbent recycling. Nevertheless, Abanades and others (2003) proposed that 'a modest supply of fresh limestone, comparable to the use for sulphur control purposes, is enough to compensate for the intrinsic decay in sorbent activity'.

A system was studied by Abanades and others (2003) in which the flue gas is fed into the carbonator containing a sorbent containing CaO (lime) at temperatures typically between 600 and 750ºC. The carbonation reaction produces $CaCO_3$. The calcination/regeneration reaction produces CO_2. Fresh sorbent is fed continuously into the system to compensate for the decay in sorbent capacity. The key innovation in the systems being developed is that the heat to sustain the calcination reaction is transferred from the combustor generating the CO_2 . Therefore, the process comprises a combustion chamber where any type of fuel is burned with air, preferably at temperatures above 1000ºC, generating a high temperature gas flow of combustion gases with a CO_2 content between 3% and 17% in volume depending on the fuel and the air excess used during combustion.

Abanades and others (2003) calculated that it would be possible to operate a CO_2 capture system with efficiencies of over 80% with fresh sorbent addition comparable to those used for sulphur control in some power stations burning high sulphur fuels. This still involves large quantities of fresh sorbent in the order of 50–100 t fresh limestone/h for a 1000 MWt power plant based on coal (Grasa and others, 2007a). Volumes such as that are only acceptable because limestone has a very low unit cost, is widely available, and the sorbent and its products are not hazardous materials. If lower CO_2 capture efficiencies of 50–70% were acceptable, then the system could run with much lower quantities of fresh sorbent. For comparison, according to figures from Couch (1994), the coal requirements of such a plant would be about 400 t/h. Based on experiments in fluidised bed carbonator-combustor systems, Rodrigo-Naharro and Clemente Jul (2008) have found that, in order to maintain the activity, a flow of 0.813 kg of fresh limestone would be needed per 1 kg of coal. Ströhle and others (2008) have calculated that, for a 1052 MWe coal-fired reference plant there would be a solids mass flow of around 7000 t/h with a fresh make-up feed of 55 t/h. Despite the need for fresh sorbent, CO_2 capture based on carbonation/calcination cycles have some inherent advantages compared with other approaches:

- the efficiency penalties are intrinsically low because both the capture and sorbent regeneration processes are carried out at high temperatures;
- the sorbent is cheap and widely available;
- most of the individual process units are commercially proven and/or there exist similar large-scale commercial processes;
- no hazardous materials are involved.

Figure 9   Schematic of lime carbonation/ calcination cycle (Bosoaga and Oakey, 2007a)

The low carbonation levels of the sorbent in the carbonator have an impact on the calcination/regeneration part of the cycle; the heat demand in the calciner is dominated by the heating of inert solids (Rodriguez and others, 2008) in the calciner for different fuels and boundary conditions. For flue gases with no ash and no sulphur, aiming at 70% CO_2 capture, the heat requirement is about 37% when no make-up flow of fresh sorbent is required because the carbonation relies on the residual activity (7–8%) of the CaO towards carbonation at very high cycle numbers. High make-up flows of fresh limestone reduce this effect by increasing the average reactivity of the sorbent, but they also increase the heat demand in the calciner to calcine the fresh feed of limestone. The effect of high ash content in the fuel produces an increase of the amount of solids circulating in the loop, and this tends to increase the heat requirement.

Abanades and others (2004b) have suggested that, because recarbonation requires high reaction rates and has a high reaction enthalpy, fluidised beds are a natural choice as reactors. In a critical review of post-combustion CO_2 separation technologies, Chen and others (2006) agree, concluding that fluidised bed is the only practical configuration.

Shimizu and others (1999) had earlier performed a conceptual study of using a twin fluidised bed reactor for removing CO_2 from combustion gases. Abanades and others (2004b) conducted carbonation-calcination tests in batch mode in a pilot scale circulating fluidised bed carbonator. The experiments demonstrated that CO_2 capture from combustion flue gases can be effective at temperatures around 650ºC. Despite the decay in reactivity of the CaO, it was found that the fluidised bed was an effective CO_2 absorber even after 11 cycles.

Fluidised beds can, not only be used as reactors, but also the capture of CO_2 by CaO could be incorporated into fluidised bed combustors (FBCs). A series of reference case examples was studied by Abanades and others (2005). They concluded that natural limestones are suitable for FBC systems because of their low price and availability despite their limited performance as regenerable sorbents. However, it was admitted that several uncertainties exist and need to be addressed before carrying out an economic comparison with existing CO_2 capture processes or other novel concepts currently under development.

CO_2 capture using lime as a sorbent in an entrained mode has been proposed by Arias and others (2006). They found that it is strongly affected by temperature with the best results being obtained at 550ºC. It was concluded that reasonable levels of CO_2 capture can take place in real combustion environments. However, later work was to be performed using a twin fluidised bed carbonator/calciner (Bosoaga and Oakey, 2007a,b).

A 75 kWth pilot-scale atmospheric dual fluidised bed combustion system for in situ CO_2 capture has been constructed by CANMET in Canada (Hughes and others, 2004a, 2005; Salvador and others, 2005). The system consists of two fluidised bed reactors: a sorbent calciner/regenerator, which is a circulating fluidised bed combustor upgraded for operation with oxyfuel firing using flue gas recycle, and a combustor/carbonator, which is divided into two stages and designed for the separation of combustion/sulphation and carbonation. D Y Lu and others (2007, 2008) have reported preliminary results. A high CO_2 capture efficiency (>90%) was achieved for the first several cycles, which decreased to a still acceptable level (~75%) even after more than 25 cycles.

Experimental results from a 30 kWth test facility operated in continuous mode using two interconnected circulating fluidised bed reactors as carbonator and calciner have been reported by Abanades and others (2008). Attrition of the limestone was very intense in the first calcinations but the remaining solids showed little tendency thereafter. Capture efficiencies between 70% and 97% were obtained under realistic flue gas conditions in the carbonator reactor as long as there was a sufficient bed inventory and solids recirculation rate, even with highly deactivated CaO.

Another in situ method has been suggested by Grasa and others (2005): direct injection of fine lime particles into the exhaust duct of a boiler. This was studied at laboratory and pilot scale and CO_2 reductions in the order of 30–40% were achieved within a few seconds of nominal particle residence time.

Natural minerals other than limestone have been proposed as sorbents for CO_2 capture. Bandi and others (2005) screened some and found that natural carbonates from the dolomite group were promising. The cyclic stability is dependent on their chemical composition. An increased concentration of inert matter in an absorbent had a positive influence on the cyclic stability. Huntite ($CaMg_3(CO_3)_4$) was a good illustration of this; it contains three MgO and only one CaO. Its cyclic stability is considerable higher than that of conventional dolomite (CaO/MgO $\approx$1) Natural silicates, usually complex compounds containing different silicates and carbonates, show a poor ability for CO_2 absorption, but the cycle and mechanical stability of some, such as spurrite ($Ca_5(CO_3)(SiO_4)_2$), was very good. The presence of steam in the gas atmosphere and loading degree of the sorbent was found to influence the CO_2 absorption behaviour. Steam improved the reaction rate, but had a damaging effect on the sorbent pore structure by accelerating the sintering and clogging the pores. The coating of sorbent particles with SiO_2 or Al_2O_3 improved their attrition resistance; however, the absorption capacity decreased gradually with increasing amounts of coating substance. Sun and others (2005a) tested several sorbents and found that dolomite gave the best reversibility. They attributed the good performance of dolomite to the calcined MgO acting as an inert under their carbonation conditions, enhancing diffusivity for diffusing species crossing the carbonated product layer on the sorbent.

Not only can other natural minerals be considered but other natural calcareous materials could act as sorbents for CO_2 from combustion gases. Ives and others (2008) have compared chicken eggshells and mussel shells with limestone. Interestingly, it was found for all three sorbents that the carrying capacity of CaO for CO_2 degraded at a similar rate. The carrying capacity was roughly proportional to the volume

of pores narrower than ~100 nm. It was suggested that these narrow pores contain both the surface area for CO_2 to absorb and the empty volume to accommodate the product, $CaCO_3$. The resistance of eggshells to attrition was broadly comparable to that of Purbeck (UK) limestone.

4.1.1 Limestone deactivation mechanism

Typically, a limestone's carrying capacity falls from an initial value of ~79% to only about 20–30% after ~30 cycles (Fennell and others, 2007a).

The mechanism by which the limestone deactivates was studied by Abanades and Alvarez (2003) who interpreted the observed conversion limits in the reaction of CO_2 with lime in terms of a certain loss in the porosity associated with small pores and a certain increase in the porosity associated with large pores. In the carbonation part of every cycle, the $CaCO_3$ fills up all the available porosity made up of small pores plus a small fraction of the large voids, limited by the thickness of the product layer that marks the onset of the slow carbonation rate.

A long series of carbonation/calcination cycles (up to 500) was studied by Grasa and Abanades (2006a,b) of CaO derived from natural limestones by thermal gravimetric analysis. Figure 10 shows the result of a typical experiment, showing that the sorbent capture capacity decreases with the number of cycles and the three characteristic features in the cycles.

They found that calcination temperatures above 950°C and very long calcination times accelerate the decay in sorbent capacity. Other variables have a 'comparatively modest' effect on the overall sorbent performance. Most limestones behave in a similar way. Capture capacity decreases dramatically in the first 20 cycles but it appears that there is a residual conversion of about 7–8% that remains constant after many hundreds of cycles and it seems insensitive to process conditions. It was suggested that the existence of a residual

conversion could be important in the design of CO_2 capture systems based on limestone as a regenerable sorbent.

Wang and Anthony (2005) suggested that, by analogy with the deactivation of catalysts by sintering, the sintering of sorbents is the cause of the CO_2 capacity decay. However, Lu and others (2006) doped some synthetic calcium sorbents with silica and found that this did not noticeably enhance their durabilities. They suggested that the main factor in the decaying carbonation performance in multiple carbonation/decarbonation cycles was the blockage and collapse of the pore structure rather than sorbent sintering effects. The pore volume may not be the only factor involved though; Fennell and others (2007a) calculated that the theoretical carrying capacity of an hydrated CaO sample should have increased to only ~32% after recalcination. In fact it increased to ~52%. It was suggested that part of the drop in carrying capacity was caused by a loss in the reactive surface area, for example, rather than simply a loss of pore volume.

Fennell and others (2007b) studied the effects of repeated cycles of calcination and carbonation on five different limestones using a hot fluidised bed of sand. This, unlike thermal gravimetric analysis, exposed the limestone to attrition in the bed. They found that, for most limestones, losses due to attrition amounted to less than 10% of their mass over the course of a typical experiment, lasting about eight hours. The carrying capacity of the CaO for CO_2 was found to be roughly proportional to the voidage inside pores narrower than ~150 nm in the calcined CaO before carbonation began. Morphological changes, including reduction in the pores narrower than 150 nm within a calcined limestone, were found to be responsible for much of the fall in carrying capacity with increasing number of cycles.

An experimental parametric study of the CaO based sorbent capacity under carbonation/calcination cycles has been carried out by Manovic and Anthony (2008a). The influence of various parameters was examined. These included particle size, impurities, limestone type, temperature, and influence of
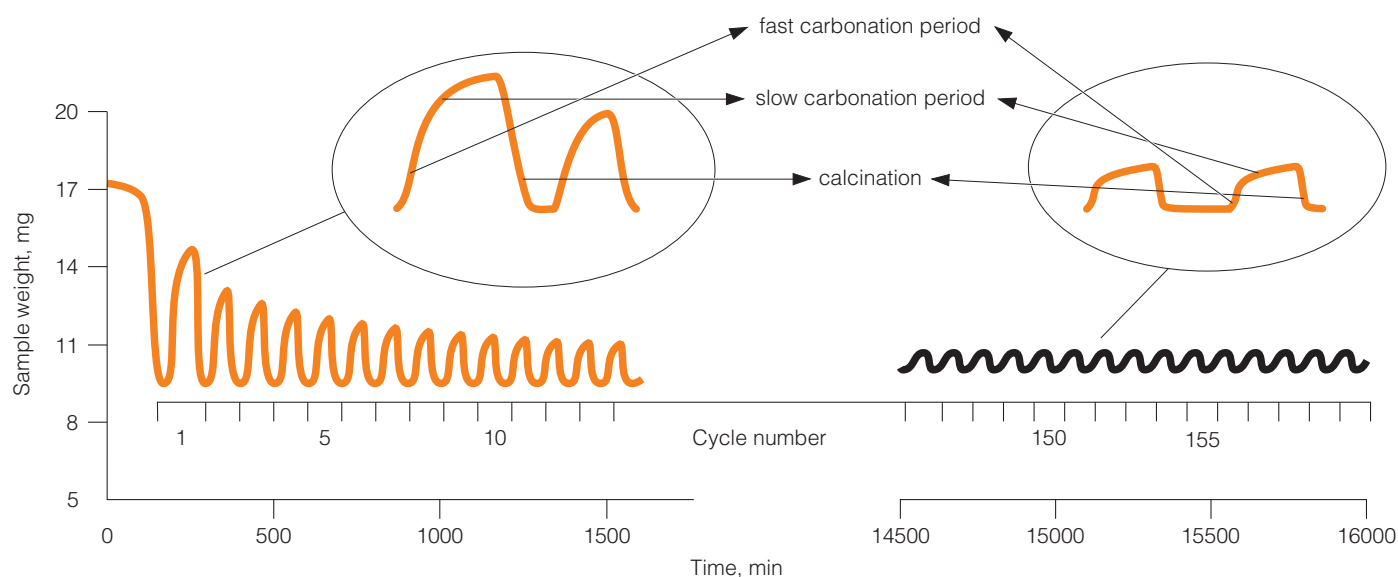
Figure 10 The flow diagram of the lime carbonation/calcination cycle (Grasa and Abandes, 2006a)

the effective CO_2 concentration surrounding reacting particles, as well as carbonation/calcination duration and temperature stresses in different reactor types. It was found that increasing temperature in the range of 650–850ºC has a negative effect on the sorbent activity. Particle size is unimportant in terms of the sorbent CO_2 carrying capacity, and any differences are likely to be a function of impurity content in samples of different particle size. Prolonged carbonation accelerates the sorbent activity decay, while an opposite effect is produced for the prolonged sorbent exposure to calcination conditions in an inert atmosphere. It was concluded that the formation and decomposition of $CaCO_3$ is a critical step for sorbent sintering and its subsequent decay in activity. A comparison of scanning electron microscopy (SEM) images of spent sorbent samples obtained in different reactor types showed that thermal stresses are mainly responsible for sorbent particle fracture.

Sun and others (2007b) studied the pore size distributions for limestone samples from test under various calcination/carbonation cycling conditions. They proposed a pore evolution model based on the premise that, in practice, the calcination stage always involves sintering. The sintering directs ions to fill intergranular space or vacancies to transfer from smaller to larger pore space. The resulting pores have a bimodal size distribution: pores <220 nm related to the original calcination and pores >220 nm resulting from pore growth due to fast CO_2-catalysed vacancy flow. During subsequent carbonation, reaction occurs in the smaller pores and the CaO surface of the larger pores contributes little to the carbonation because of their low surface area. The smaller pores are filled preferentially rather than the larger ones. During the next calcination stage, there is a reduction in the amount of smaller pores due to sintering. As the number of smaller pores decreases so does the CaO utilisation.

Sun and others (2008) have suggested that the pore size distribution evolution provides an explanation for the sharp turn of some limestone carbonations. Bimodal pore size distribution, probably arising from sintering during calcination, accounts for this pattern. When pores smaller than 300 nm are filled, the reaction turns into a slow reaction because of loss of most surface area and increasingly important product-layer diffusion.

A tentative mechanism of textural transformations that may take place in the cycling environment was presented by Lysikov and others (2007). Freshly calcined sorbent recarbonates incompletely because of the shrinking of the particles during the first decomposition. In the following cycles, newly formed CaO grains grow and agglomerate. The necks between adjacent CaO grains thicken and reinforce until they are thick enough to not be broken during the recarbonation stage. Finally, the newly formed network of the interconnected CaO particles 'skeleton' ceases the sorbent sintering. Only the outer layer of the skeleton recarbonates, while its internal CaO core is protected by the product $CaCO_3$ layer and may be considered as a refractory support for outer reactive CaO shell. Thus, after formation of the skeleton, the sorbent capacity stabilises.

A model explaining the loss of sorbent activity has been
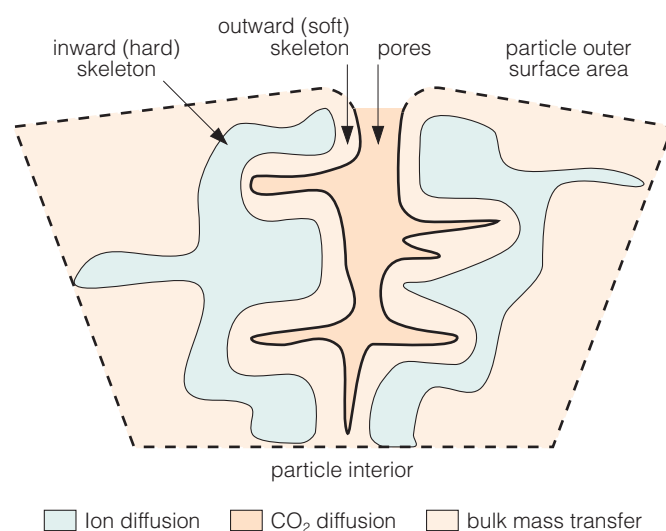
Figure 11 Schematic of proposed pore-skeleton model (Manovic and Anthony, 2008)

proposed by Manovic and Anthony (2008). This is shown schematically in Figure 11. During cycling, two different types of mass transfer in the sorbent particles must occur in parallel: bulk diffusion connected to the formation/decomposition of $CaCO_3$ and ion diffusion in the crystal structure of CaO. Ion diffusion in CaO stabilises its crystal structure but with no significant effect on particle morphology and corresponding carbonation conversions. Bulk mass transfer occurred during formation and decomposition of $CaCO_3$, and this led to major changes of morphology (that is, to sintering and loss of small pores and sorbent activity). During CO_2 cycles, competition occurred between ion diffusion and bulk mass transfer, and two types of structure or skeleton were formed: an internal unreacted structure and an external structure in which carbonation/calcination proceeded. The internal skeleton can be considered as a hard skeleton that stabilises and protects the particle pore structure. The external structure or skeleton can be considered to be a soft skeleton that easily changes during $CaCO_3$ formation and decomposition, resulting in changes of particle morphology. Manovic and Anthony (2008b) point out that it should be noted that the terms internal and external skeleton are not related to the particle but to the pores: outer or external means that this part of the skeleton is exposed to pores and surrounded by the gas that fills pores. The model predicts that, as a result of CO_2 cycles, pore size distribution changes and that smaller pores transform into larger ones, leading to a loss of pore surface area and loss of activity.

4.1.2 Effects of SO_2

The effects of sulphur dioxide on calcium oxide sorbents were studied by Iyer and others (2003) who found that the formation of calcium sulphate reduced the regenerative capacity of the sorbent. The ratio of carbonation to sulphation was found to decrease monotonically from about 35 at 400–500ºC to about 3 at 700ºC.

Calcium based sorbents are of course widely used to capture SO_2 from flue gas and it might be expected that, if used to

capture CO_2, then simultaneous capture of the two gases might be possible.

Simultaneous carbonation and sulphation were investigated under simulated fluidised bed combustor temperatures (750–850ºC) by Sun and others (2005b) in an atmospheric pressure thermogravimetric reactor and, later, a pressurised reactor (Sun and others, 2007a). SO_2 was found to impede cyclic CO_2 capture, with calcination rates diminished by the sulphate outer shells enveloping the sorbent particles with an impermeable shell. Pore blockage by the sulphate products resulted primarily from direct sulphation during the later stage of each cycle. Loss in sorbent reversibility could not be prevented but was improved by higher CO_2 partial pressures. Simultaneous CO_2/SO_2 capture characteristics of three limestones in a fluidised bed reactor were also studied by Ryu and others (2006a,b). Unsurprisingly, the measured CO_2 capture capacity decreased as the number of cycles increased but also as the SO_2 concentration increased. On the other hand, the SO_2 capture increased with the number of cycles and the SO_2 concentration. The total (CO_2 and SO_2) calcium utilisation decreased as the number of cycles increased, but the effects of SO_2 concentration on the total calcium utilisation were different for individual limestones and depended on the limestone sulphation patterns. The limestone sulphation patterns reflected the difficulty of SO_2 penetration into the limestone particles. For one limestone (hard to penetrate), the total calcium utilisation decreased with increasing SO_2 concentration. However, for two other limestones (easy to penetrate), the total calcium utilisation was almost independent of SO_2 concentration for the range investigated. The results showed that SO_2 reduces the CO_2 capture capacity of limestone and that the limestone sulphation patterns affect the CO_2 capture capacity.

Y Li and others (2005) conducted experiments in a dual-environment thermogravimetric reactor to investigate the interaction between calcination, sulphation, and carbonation for a limestone that had previously been shown to sulphate primarily in an unreacted core manner. Their results indicated that CO_2 can reactivate partially sulphated sorbent particles, contributing to an increase in overall calcium utilisation efficiency. It was concluded that SO_2 and CO_2 do not interact independently with limestone. Instead, each affects the ability of sorbents to capture the other: CO_2 enhances the ability of the sorbent to capture SO_2, whereas SO_2 reduces its ability to capture CO_2.

Grasa and others (2008) found that SO_2 reacts with the deactivated CaO resulting from repetitive carbonation/calcination reactions CaO resulting from repetitive calcination/carbonation reactions. Therefore, the deactivation of CaO as a result of the presence of SO_2 is lower than one would expect if one assumes that SO_2 reacts only with active CaO. Changes in the texture of the sorbent due to repetitive carbonation/calcination cycles tend to increase the sulphation capacity of the sorbents tested. This suggests that the purge of deactivated CaO obtained from a CO_2 capture system could be a more effective sorbent of SO_2 than fresh CaO. Nevertheless, it remains the case that the presence of SO_2 always accelerates deactivation of the sorbent with respect to CO_2 capture.

Studies by Mašek and others (2008) using a pressurised fluidised bed system have shown that presence of SO_2 results in considerable sulphation of Ca-based sorbents causing the blockage of pores and therefore decreasing the CO_2 capture capacity of the sorbent. When exposed to relatively low concentrations of SO_2, the extent of sulphation of sorbent particles was limited to the outer layers and its effects were thus less marked. On the other hand, when exposed to high concentrations of SO_2, the presence of sulphur was identified even in the centre of the sorbent particles. In addition, it was found that besides the detrimental effects of SO_2 concentration, increasing total pressure in the reactor further reduces the sorbent capture capacity. Increased calcination temperature at higher pressures did not lead to improved sorbent performance. Overall, the results from experiments at 0.4 MPa showed considerably lower capture capacity even for sorbents prepared by calcination in presence of relatively low concentrations of SO_2 compared with sorbents prepared at atmospheric pressure.

4.1.3 Improving calcium sorbent performance

Manovic and Anthony (2008a), in their parametric study on the CO_2 capture capacity of CaO based sorbents, found that the grinding of the sorbent results in better reaction cycle properties for the powder obtained. They suggested that this was unlikely simply due to the particle size decrease and suggests that it may be possible to achieve sorbent activation by grinding. However, other methods have been studied in order to improve sorbent performance.

Thermal activation

Manovic and Anthony (2008b) have reported that thermal pretreatment can improve limestone sorbent performance. In comparison with untreated sorbents, preheated sorbent showed better conversions over a longer series of CO_2 cycles. In some cases sorbent activity actually increased with cycle number; the effect was particularly pronounced for powdered samples preheated at 1000ºC. This increase of conversion with cycle number was designated as self-reactivation. It was suggested that, in addition to changes in the porous structure of the sorbent, changes in the pore skeleton produced during preheating strongly influence subsequent carbonation/calcination cycles. This is shown schematically in Figure 11 in Section 4.1.1 above. During the thermal pretreatment, bulk diffusion occurs only during calcination but, when the decomposition of $CaCO_3$ is completed, ion diffusion continues leading to skeletal structure stabilisation and the formation of a hard skeleton.

Hydration

Limestone sorbents are used for SO_2 capture in fluidised bed combustors. However, the efficiency of the process is limited and limestone utilisation in the range of 30–45% is not uncommon. One method of reactivating the limestone is hydration by water or steam with steam reactivation being the most promising technology (Anthony and others, 2007). Steam hydration has also been studied as a means of improving the long-term conversion of limestone-derived sorbents for in situ capture of CO_2 in a fluidised bed

combustor (Hughes and others, 2004b). Steam hydration increases both the pore area and pore volume of CaO. At 150ºC it improved the long-term performance of the sorbent, resulting in directly measured conversions as high as 52% and estimated conversions as high as 59% after up to 20 cycles. It was estimated that the increase in conversion had improved the economics of the capture process to the point where commercialisation was attractive. When carbonating in the temperature range from 700ºC to 740ºC, calcination temperatures from 700ºC to 900ºC can be used without seriously reducing the conversion of CaO for CO_2 capture over multiple cycles. It was concluded that processes based on this approach are expected to be able to reduce CO_2 emissions from coal-fired fluidised bed combustors by up to 85%, while avoiding excessive sorbent replacement. The work also provided evidence that the presence of impurities in the limestone is beneficial in maintaining the treated sorbent's pore size and volume over multiple cycles.

Manovic and Anthony (2007a) studied the steam reactivation of spent CaO based sorbents to improve the reversibility of multiple CaO-CO_2 capture cycles. After reactivation of calcined samples under atmospheric conditions the sorbents had even better properties for CO_2 capture in comparison with the original sorbents. The average carbonation degree over ten cycles for the reactivated sorbent approached 70%, significantly higher than for the original sorbent (35–40%). The reactivated sorbents also had better sulphation characteristics than the original sorbent (Manovic and Anthony, 2007b). The steam hydration reactivation characteristics of three limestone samples were studied by Manovic and Anthony (2008c). Reactivation after multiple CO_2 capture cycles was done with a saturated steam pressure at 200ºC and also at atmospheric pressure at 100ºC. It was found that the presence of a carbonate layer strongly hinders sorbent hydration and adversely affects the properties of the reactivated sorbent with regard to its behaviour in both sulphation and multiple carbonation cycles.

Hydration of calcined samples under pressure was found to be the most effective method to produce superior sulphur sorbents. It was concluded that separate CO_2 capture and SO_2 retention in fluidised bed systems enhanced by steam reactivation is promising even for atmospheric conditions if the material for hydration is taken from the calciner. The main limitation for sequential SO_2/CO_2 capture enhanced by steam reactivation in FBC systems may be sorbent attrition. In real FBC systems attrition phenomena may be expected, leading to higher sorbent loss. The sulphation and carbonation properties of the hydrated sorbents were reported in greater detail by Manovic and others (2008a). SEM results showed that the steam reactivated samples, even after very high levels of sulphation, retained considerable porosity, suggesting that near-quantitative sulphation might be possible after sulphation periods of hours (that might be experienced in a real fluidised bed combustor). Cyclic carbonation tests showed that spent samples also have better capacity for CO_2 capture. Runs of ten cycles were performed and the reactivated samples typically showed 50% conversion by the last cycle, which was 10% higher than conversions seen with the original samples. The results suggested that residues from FBC CO_2 capture cycles need not be regarded as a waste product; on the

contrary, after steam hydration after at most 15 minutes, they revert to high-quality sorbents with a very high capacity for SO_2 retention or additional CO_2 capture.

An investigation of samples obtained in conditions very close to those expected in a real FBC was carried out by Manovic and others (2008c). These samples were quite different from those examined earlier which had been obtained in idealised conditions. Hydration of spent sorbents by steam under atmospheric pressure and at 100ºC for as little as 15 minutes was found to produce samples with a very small amount (10%) of unreacted CaO. More importantly, the samples had improved morphology (pore surface area and distribution) and it was suggested that further work on enhancing the properties of such sorbents by hydration may yield even better results. Particles having undergone CO_2 looping cycles have large cracks that grow during hydration and contribute to sample swelling and particle fragility. It was found that the hydrated sorbents could very easily crush; a significant proportion of the reactivated sorbent is transformed into powder. This predisposition to fracture could result in difficulties in terms of their handling in FBC systems due to intensified attrition and consequent elutriation from the reactor.

The reactivity of CaO in the product after limestone decomposition in a CO_2 atmosphere fluidised bed was tested by Y Wang and others (2007). They found that the complete hydration conversion times at 650ºC under 2.0 MPa steam partial pressure were 8, 9, and 11 min for limestone decomposed at 950, 1000, and 1020ºC. Decomposition of limestone particles (0.25–0.5 mm) in a steam dilution atmosphere (20–100% steam in CO_2) was investigated by Y Wang and others (2008) using a continuously operated fluidised bed reactor. Upon hydration, the time required for complete conversion of the CaO produced with steam dilution to Ca(OH)$_2$ was six minutes, nearly half that for CaO produced without dilution (100% CO_2). In the carbonation of CaO to $CaCO_3$, the carbonation conversion of the CaO produced was nearly 70% for the CaO produced with steam dilution, whereas the conversion was about 40% for the CaO produced in 100% CO_2 which indicates that the reactivity of the CaO was greatly improved by limestone decomposition in steam dilution.

The effect of steam hydration on the performance of CaO
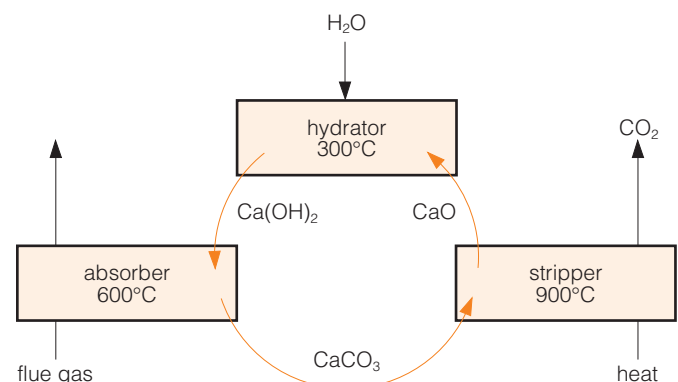
Figure 12 Schematic of hydrated lime cycle
(Zeman, 2008)

sorbents for CO_2 capture has been investigated by Zeman (2008) who hydrated lime for five minutes at 300ºC at atmospheric pressure in a mixture of steam and CO_2. The hydrated lime cycle is shown schematically in Figure 12. After ten capture cycles, 60% of the lime remained active at the end.

It has been reported by Fennell and others (2007a) that it is possible to regenerate spent CaO by reaction with saturated humid air. By reacting spent CaO overnight with moist, ambient air, in a vessel containing water at the bottom, the sorbent can be regenerated to ~55% carrying capacity (moles of CO_2 per mole of CaO).

4.2   Synthetic calcium sorbents

Synthetic calcium sorbents have been studied as a means of increasing surface area and reactivity compared with sorbents derived from naturally occurring limestone.

A wet precipitation process was tailored to synthesise high surface area precipitated calcium carbonate (PCC) by Gupta and Fan (2002; *also* Gupta and others, 2002). The pores of PCC predominantly lie in the mesoporous range (5–20 nm). The CaO sorbent obtained from PCC (PCC-CaO) was less susceptible to pore pluggage than CaO from naturally occurring limestone and attained over 90% conversion. PCC-CaO was also capable of maintaining its high reactivity (>90%) over two carbonation/calcination cycles at 700ºC. Sakadjian and others (2003) reported that, although the PCC-derived sorbent had high initial surface areas, it experienced a large drop in surface area due to the high temperatures involved in the carbonation and regeneration steps. It was found that vacuum calcination aided the preservation of the desired surface area. A surface area of 19.84 m²/g was achieved when a vacuum was used to regenerate the sorbent whereas the surface area of the sorbent was consistently lower than 13 m²/g when the regeneration was carried out under nitrogen flow. Sakadjian and others (2008) have reported the findings of demonstration tests performed in a 9 kg/h coal-fired facility. Over 90% CO_2 capture and near 100% SO_2 capture were achieved on a once-through basis.

CaO sorbents have been synthesised by Lu and others (2006; *see also* Smirniotis, 2005b, 2007) by the calcination of the following precursors:
- calcium nitrate tetrahydrate;
- calcium oxide;
- calcium hydroxide;
- calcium acetate monohydrate.

The sorbent prepared from the acetate resulted in the best uptake characteristics for CO_2. SEM revealed that this sorbent had a 'fluffy' structure that probably contributes to its high surface area and pore volume. In a wide operating window of 550–800ºC, this sorbent achieved high carbonation of more than 94 mol%. When the carbonation temperature was 700ºC, about 90% of the sorbent carbonated with CO_2 within the first ten minutes. It also showed a capability of maintaining its reversibility over multiple carbonation/decarbonation cycles,

even in the presence of 10 vol% water vapour. In a 27-cycle carbonation/decarbonation experiment, it maintained a fairly high conversion of 62%. Sun and others (2005a) have reported that calcium acetate can achieve more than 90% conversion for the initial carbonation but it has no obvious superiority over other sorbents in reversibility.

Calcium based carbon dioxide sorbents were developed in the gas phase by flame spray pyrolysis (FSP) technique by Smirniotis (2007) and compared to the ones made by standard high temperature calcination (HTC) of selected calcium precursors. The FSP-made sorbents were solid nanostructured particles having twice as large specific surface area (40–60 m²/g) as the HTC-made sorbents (that is from calcium acetate monohydrate). All FSP-made sorbents showed high capacity for CO_2 uptake at high temperatures (500–800ºC) while the HTC-made ones from calcium acetate monohydrate demonstrated the best performance for CO_2 uptake among all HTC-made sorbents. However, after about 120 cycles, the performance of the HTC-made sorbents decreased almost linearly with increasing cycles. In multiple carbonation/decarbonation cycles, FSP-made sorbents demonstrated stable, reversible and high CO_2 uptake capacity sustaining maximum molar conversion at about 50% even after 60 such cycles.

Y Li and others (2007) investigated the modification of limestone by acetic acid. Their results showed that the carbonation conversion of calcium acetate was much greater than that of limestone at the carbonation temperature range of 600–700ºC. When the calcination temperature was 920ºC with 80 vol% CO_2 atmosphere and the carbonation temperature was 650ºC with 15 vol% CO_2 in the reaction gas, the carbonation conversion of calcium acetate reaches as high as 0.54 after 15 calcination/carbonation cycles. At a calcination temperature of 1050ºC, calcium acetate still maintains a high conversion. Sintering has a much smaller effect on the CO_2 capture capability of calcium acetate than that of limestone. The acetification of limestone enhances the surface area and pore volume of calcined limestone and these are retained even over multiple cycles.

Grasa and others (2007a,b) have reviewed some of the recent literature on synthetic sorbents that aim to overcome the decay in capture capacity of natural limestone sorbents. Using thermal gravimetric analysis, they also tested three different CaO precursors to repetitive carbonation/calcination cycles. The CaO precursors were:
- calcium acetate;
- calcium oxalate;
- calcium hydroxide.

The object of using synthetic precursors is to obtain calcium oxides with a high surface area and a more stable pore structure.

It was found that the synthetic sorbents degraded rapidly when tested under realistic conditions using calcination temperature over 900ºC and high partial pressures of CO_2; Grasa and others (2007a) considered 700ºC to be 'mild'. Calcium acetate performed best of the sorbent precursors tested showing a conversion of over 20% after

100 carbonation/calcination cycles. However, the conclusion was reached that none of the reviewed synthetic sorbents have a chance to compete with the 'modest' performance of natural limestones that show two competitive advantages: the maintenance of a suitable CO_2 capture capacity under demanding process conditions and their intrinsic low cost.

4.3   Doped calcium sorbents

Salvador and others (2003) studied the reactivation of CaO using Na_2CO_3 and NaCl additives and also carbonating the lime in pure CO_2. Na_2CO_3 and NaCl additives failed to reactivate the CaO having the reverse effect of severely reducing the CO_2 capture capacity in FBC tests. Thermal gravimetric analysis (TGA) experiments on two limestones showed no effect due to the addition of Na_2CO_3, but a marked improvement upon the addition of up to 3 wt% NaCl, raising the overall capacity to an almost constant value of 40% through 13 cycles. Sun and others (2005a) reported that 2% Na_2CO_3 solution on limestone enhanced the slower stage carbonation but its performance decayed rapidly. Experiments have been performed where particles of limestone that were doped with small amounts of a salt (for example, Na_2CO_3) showed a small improvement in long-term carrying capacity, but larger dopings produced a marked reduction in capacity (Fennell and others, 2007b). A high purity limestone studied by Manovic and others (2008b) failed to show any favourable effect after thermal activation. Doping experiments showed that both high Na content and lack of Al in the limestone cause poor self-reactivation performance after thermal pretreatment.

A number of basic sorbents based on alkali metals doped on CaO supports were synthesised, characterised, and tested for the sorption of CO_2 and selected gas mixtures simulating flue gas by Smirniotis (2003). He reported that, of all the alkali metals, caesium was the most promising. Within the first 100 minutes the sorption over Cs/CaO reached 40 wt% CO_2/sorbent. Reddy and Smirniotis (2004; *see also* Smirniotis, 2007) reported that the performance of the alkali metals as dopants on CaO followed the order Li < Na < K < Rb < Cs, which reveals a strong relationship between the sorption characteristics and the increase of the electropositivity or equivalently atomic radii of the alkali metals. The sorption capacity at 600ºC over 20% Cs/CaO was about 50 wt% CO_2/wt sorbent; the rate of sorption was also very high. The CO_2 desorption was reversible by increasing the temperature about 100ºC above the adsorption temperature. X-ray photoelectron spectroscopy (XPS) revealed that the adsorption of CO_2 was taking place on Cs_2O rather than CaO on supports prepared with ~20% loading of Cs. At higher loadings there was no further improvement in performance. The Cs/CaO sorbent showed zero affinity for N_2 and O_2 and low affinity for water. In fact, in the presence of water vapour, the adsorption of CO_2 increased to the highest capacity of 77 wt% CO_2/g of sorbent (Smirniotis, 2005a, 2007; Roesch and others, 2005). At high temperatures, water and NO promote shrinking effects by decreasing particle size and simultaneously forming uniform pore sizes. In the presence of nitric oxide, a rapid CO_2 uptake was observed within the first two minutes.

'Refractory' silica, titania, and zirconia were doped on flame spray pyrolysis sorbents by a flame technique; sorbents with zirconia exhibit better stability than the other sorbents (Smirniotis, 2007). All Si/Ca, Ti/Ca, and most Zr/Ca sorbents showed performance deterioration during long term running except for the Zr/Ca (3:10). The one having Zr to Ca of 3:10 molar ratio exhibited stable performance. The calcium conversion kept stable around 64% during 102-cycle operations at 973 K. This stable performance was ascribed to the refractory zirconia preventing possible particle sintering and structure collapse during reaction.

Smirniotis (2007) also reported that CaO sorbents doped with cerium oxides may survive under atmospheres containing SO_2 by repelling SO_2 from the sorbent's surface. Sorbents with high surface area and porosity are capable of reaching high conversion (70%) within two minutes and can maintain high conversion at severe operating conditions.

4.4   Supported calcium sorbents

Experimental studies were carried out by Hoffman and others (2002) to identify and evaluate novel sorbents that could be used in dry, regenerable scrubbing processes for the capture of CO_2. The sorbents tested included include calcium oxide on a lanthanum-alumina substrate, and two zirconia substrates. Further work on these sorbents was reported by Fauth and others (2003, 2004). The lanthanum additive was introduced to impart high temperature stability to the alumina support. However, the overall performance of the Ca/La-alumina sorbent was concluded to be unsatisfactory with respect to CO_2 capture. Pore pluggage due to a calcium carbonate product layer formation appeared to be a plausible cause. The Ca/zirconia sorbents performed better. Regeneration of the Ca/zirconia sorbents was quickly achieved by elevating the temperature from 500 to 750ºC under nitrogen. The experiments were carried out at temperatures potentially representative of an integrated gasification-combined cycle so the applicability of these supported sorbents to post-combustion capture is not clear.

A Ca based sorbent was synthesised by Z Li and others (2005) consisting of 75 wt% CaO and 25 wt% $Ca_{12}Al_{14}O_{33}$ (mayenite), starting from pure calcined CaO and a solution of $Al(NO_3)_3 \cdot 9H_2O$ (aluminium nitrate ennehydrate) in water with the addition of 2-propanol, which acted as a dispersant. Mayenite is a mixed oxide, produced by the solid state reaction between CaO and Al_2O_3 at temperatures between 800 and 1000ºC. The sorbent showed a good uptake of CO_2, attaining 45 wt% (corresponding to ~73% of the maximum theoretical uptake of the free CaO); furthermore, this value was maintained over 13 cycles under mild calcination and carbonation conditions (850ºC in 100% N_2 and 700ºC in 20% CO_2 in N_2, respectively), when tested in a TGA using particles, 45 µm in diameter. Z Li and others (2006) reported that, under the mild calcination conditions, the $CaO/Ca_{12}Al_{14}O_{33}$ attained 41 wt% CO_2 capture after 50 carbonation/calcination cycles. When more severe calcination conditions (980ºC, 100% CO_2) were used, the capture of $CaO/Ca_{12}Al_{14}O_{33}$ decreased from about 52 wt% in the first cycle to about 22 wt% in the 56th cycle; even so, this

was still higher than that of dolomite and limestone under the same severe calcination reaction conditions. When the calcination temperature in the sorbent preparation stage was higher than 1100°C, the cyclic carbonation reactivity declined. The lower CO_2 capture was attributed to the formation of $Ca_3Al_2O_6$, which decreases the ratio of CaO to binder in the sorbent.
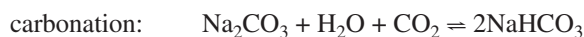
Pacciani and others (2008) have used coprecipitation and hydrolysis of CaO to produce Ca based synthetic sorbents suitable for capturing CO_2 in a fluidised bed. The hydrolysis technique was somewhat similar to the method used by Z Li and others (2005). The sorbents consisted of CaO dispersed on an inert support, either mayenite ($Ca_{12}Al_{14}O_{33}$) or MgO. Their composition, CO_2 uptake, volume in small pores (2–200 nm) and resistance to attrition were measured and compared with those of limestone and dolomite. The sorbents produced by coprecipitation proved to be too soft to withstand the mechanical stresses in the fluidised bed. Those produced by hydrolysis were harder and more densely packed and showed the highest uptake and resistance to attrition. Those on a mayenite support suffered a lower degree of attrition than those on MgO. Initially, the synthetic sorbents achieved a lower uptake of CO_2 than natural limestone or dolomite but, after 20 cycles of carbonation and calcination, two mayenite-supported sorbents exceeded the uptake of both limestone and dolomite, when subjected to the same regimes of reaction. A direct relationship was found between the uptake of CO_2 by a synthetic sorbent and the volume available inside small pores (<200 nm).

4.5　Alkali metal sorbents

An experimental study was reported by Hoffman and Pennline (2000, 2001) which evaluated the potential of alkali metals for use as dry, regenerable sorbents for the capture of CO_2 from a gas stream. Potassium carbonate (K_2CO_3) was found to be applicable for CO_2 capture at low absorption temperatures of less than 145°C. TGA experiments were carried out on sorbents made from potassium carbonate supported on a high surface area activated alumina at loadings of 12.2 and 17.1 wt% K. The results indicated that CO_2

captured was favoured at 50–60°C, with sorbent utilisation strongly decreasing at 80–100°C. The higher K loading did not provide additional benefit for CO_2 capture. The sorbent was regenerated at 150°C.

Research on sodium carbonate as a dry regenerable sorbent has been supported by NETL and a factsheet can be found at http://www.netl.doe.gov/publications/factsheets/project/Proj1 98.pdf. Studies have been reported by Green and others (2003) and in more detail by Liang and others (2004). The reactions are:

carbonation:　　$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2NaHCO_3$

decarbonation:　$2NaHCO_3 \rightleftharpoons Na_2CO_3 + H_2O + CO_2$

It was found that CO_2 capture was effective in the temperature range of 60–70°C while regeneration occurred in the range of 120–200°C. Capture of as much as 90% of the CO_2 was possible and, after regeneration, pure CO_2 could be obtained after condensation of the water produced. Little or no reduction in either carbonation rate or sorbent capacity was observed in limited multicycle tests. However, it was recommended the active Na_2CO_3 should be dispersed on a support such as alumina to provide attrition resistance.

The following compounds were tested by Nelson and others (2005, 2006):
- calcined sodium bicarbonate (SBC) – $NaHCO_3$;
- calcined trona (hydrated sodium carbonate bicarbonate) – $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$;
- calcined potassium bicarbonate – $KHCO_3$;
- supported carbonate sorbents.

It was considered that fixed bed operation was not feasible but that entrained bed might be a better option. It was suggested that commercial carbonate materials may not work in entrained beds because the harsh flow conditions result in severe attrition of commercial materials and the reactivity may not be adequate for short residence time of entrained bed reactors. However, supported sorbents should combine attrition resistance inherent to support material and reactivity of carbonate material. A supported sorbent was developed

Table 4	Multicycle tests of RTI sorbent (Nelson and others, 2005)						
Cycle	1	2	3	4	5	6	7
Absorption							
CO_2 removed, litres	16.72	18.30	17.67	14.11	13.24	15.89	14.97
% CO_2 removal, maximum	95	93	94	93	92	92	92
Start temperature, °C	61	60	56	60	64	61	65
Temperature rise, °C	4	13	11	10	12	13	11
Regeneration							
CO_2 released, litres	16.88	15.24	18.07	10.06	13.39	12.29	n/a
Start temperature, °C	187	166	189	186	141	150	n/a
Average temperature, °C	163	154	160	158	151	156	n/a

which consisted of 15% Na_2CO_3 and 85% ceramic support which was tested in a pilot-scale entrained bed test rig. The results of the absorption/regeneration multicycle tests are shown in Table 4. 90% CO_2 removal was demonstrated in the test reactor and sorbent reactivity was maintained over seven cycles (>90%). There was also negligible attrition over seven cycles. The amount of CO_2 removal increased and percentage CO_2 removal decreased with higher starting CO_2 concentration. The supported sorbent removed more CO_2 and a higher percentage of CO_2 than commercial SBC and trona. The energy needed for regeneration was calculated to be 72% of the competing monoethanolamine (MEA) solvent process. Further, by using carbonate materials for CO_2 capture, 11% additional power could be produced in a coal-fired power plant compared with CO_2 scrubbing by an MEA type amine process.

Later, a bench-scale co-current, down-flow contactor was built (Nelson and others, 2006). Using this, 90% CO_2 removal was achieved in flue gas with 10% and 15% CO_2 using the supported sorbent. However, it was also found that 90% CO_2 removal is possible using pure sodium bicarbonate. Most tests showed 60–70% removal in flue gas with 10% and 15% CO_2. Preliminary economic analyses have indicated that the process has potential to be significantly less expensive than existing MEA systems.

Field tests of the Dry Carbonate Process were conducted by Nelson and others (2008) using simulated, natural gas-derived, and coal-derived flue gases and the supported sorbent. Concentrated CO_2 was removed by a TSA process. The system was operated for a total of 235 hours. The system has been demonstrated to run continuously for extended periods of time and has achieved greater than 90% capture of CO_2 under various process conditions. The sorbent has demonstrated stable performance that was not found to diminish over the course of hundreds of cycles. It is planned to test the process at pilot scale in a unit capable of capturing 1 ton of CO_2 per day.

Using spray drying techniques, Ryu and others (2003, 2004) have prepared sorbents containing 50, 30, and 20 wt% Na_2CO_3 and investigated their properties using TGA. The TGA capture capacities of the sorbents were found to decrease markedly from 58% to 9% of the theoretical capture capacity of each sorbent. Later, Ryu and others (2005, 2006) prepared formulations containing 20–35 wt% of either Na_2CO_3 or K_2CO_3. Laboratory-scale tests indicated that two of the sorbents, designated Sorb NX30 and Sorb KX35, had almost all the requirements for a commercial fluidised bed reactor process. They showed near complete regeneration below 120ºC with a possible regeneration window of 80–160ºC. They had superior attrition resistance and high CO_2 sorption capacity along with high bulk density. A fluidised bed process cannot be used if there is too much particle loss due to low attrition resistance and bulk density (J B Lee and others, 2008). Tests reported by Yi and others (2005, 2006a; *also* Ryu and others, 2006) showed that Sorb NX30 was capable of capturing all of the 10% CO_2 in flue gas within three seconds of residence time in a bench-scale fast fluidised bed reactor. Ryu and others (2006) have reported that, after 20 hours in the fluidised bed reactor, the CO_2

removal of Sorb NX30 sorbent was maintained at 100% for about 12 minutes and then it exponentially dropped to about 40%. It was suggested that the sudden degradation of CO_2 removal performance in the fluidised bed reactor may not be related to the sorbent performance itself but rather, partly due to water vapour affects on the carbonation reaction in a simulated flue gas and to regeneration conditions in the fluidised bed. Tests carried out on Sorb KX35 showed that its CO_2 removal ranged from 26–73% but was also rather sensitive to the water vapour content among other parameters (Yi and others, 2006b, 2007a). The 20-hour continuous operation conducted in the fluidised bed reactor indicated that Sorb KX35 had a CO_2 removal capacity of 50–73% at steady state and could be regenerated and reused. Tests of a potassium sorbent, Sorb KX40, in the fluidised bed reactor, showed that, as the solid circulation rate increased from 7 to 36 kg/m²/s, the mean voidage in the riser reactor decreased from 0.99 to 0.94. The CO_2 removal efficiency rose from 23% to 55% because the contact frequency between the sorbent and the CO_2 in the feed gas increased. Thus, Sorb KX40, showed 55% CO_2 removal performance even at a dilute phase of voidage of 0.94 and at a residence time of three seconds (Yi and others, 2008).

Yi and others (2007b) noted that increasing the water vapour content in the feed gas gave rise to an increase in the overall CO_2 removal by potassium based solid sorbents. Seo and others (2006, 2007) studied a sodium carbonate based sorbent, Sorb NX35, which they pretreated with water vapour before carbonation to increase reactivity and CO_2 removal in the initial stage. In a bubbling fluidised bed reactor, the sorbent showed near complete CO_2 removal capacity under a simulated flue gas stream at 50ºC carbonation followed by 300ºC regeneration in a nitrogen stream. Tests showed that the Sorb NX35 sorbent was capable of 80% sorbent utilisation and greater than 90% regeneration capacity without structural deterioration even at 300ºC.

A dry potassium carbonate based sorbent (SorbA) prepared by a spray drying method was tested by Park and others (2008) in a dry sorbent CO_2 capture system consisting of two fluidised bed reactors for carbonation and regeneration. Real flue gas from a 2 MW coal-fired circulating fluidised bed combustor was used. The CO_2 capture processes were operated in a very stable manner with continuous solids circulation btween the two reactors. The average CO_2 removal was above 70% during 2 hours operation, but the reactor temperature of the lower mixing zone in the carbonation reactor was maintained around 100ºC. In fact, the lower the carbonation temperature, the higher the reactivity of the SorbA. It was found that more than 90% CO_2 removal was achievable using SorbA. Thus, an additional in-bed type heat transfer unit has been installed in the carbonation reactor to reduce reactor temperature under 80°C.

Potassium carbonate sorbents have been prepared by Lee and others (2006a; *also* Lee and Kim, 2007) on a variety of supports such as activated carbon, TiO_2, Al_2O_3, MgO, SiO_2, and various zeolites. The CO_2 capture capacities and regeneration properties were measured in the presence of H_2O in a fixed bed reactor during multiple cycles of CO_2 capture at 60ºC and regeneration at 130–400ºC. The K_2CO_3 sorbents

supported on activated carbon (AC), TiO_2, MgO, and Al_2O_3 showed excellent CO_2 capture capacity of 86, 83, 119, and 85 mg CO_2/g sorbent and could be completely regenerated at 150, 150, 350, and 400ºC respectively. The reason for the higher regeneration temperatures of the MgO and Al_2O_3 supported sorbents was the formation of compounds from reactions of the K_2CO_3 with the supports that could not be completely converted back to the carbonate at lower temperatures. The CO_2 capture capacity and CO_2 absorption rate were found to depend on the concentration of water vapour in the reactor. This is due to the generation and maintenance of the active species, $K_2CO_3 \cdot 1.5H_2O$. Some of the sorbents, such as K_2CO_3/AC need to have moisture present in the activation stage in order to produce the active species (Lee and others, 2006b). In general, the sorbent with the best potential was found to be K_2CO_3/TiO_2 which, unlike K_2CO_3/AC, did not need pretreatment with water vapour (Lee and Kim, 2007).

In the tests carried out by Lee and others (2006a), the MgO supported sorbent had, initially, the highest CO_2 capture capacity but this deteriorated rapidly when regeneration was carried out at 200ºC. Later studies by S C Lee and others (2008) have concentrated on MgO based sorbents impregnated with K_2CO_3. These sorbents exhibit high CO_2 capture capacities because MgO, as well as K_2CO_3, can absorb CO_2 in the presence of water vapour even at low temperatures. The CO_2 capture capacity of MgO increases markedly with relative humidity. As before, it was found that the MgO supported sorbent exhibited excellent regeneration properties above 350ºC.

Lithium sorbents have also been tested; Hoffman and others (2002) identified lithium zirconate as a promising sorbent. The mechanism of CO_2 sorption/desorption on lithium zirconate was studied by Ida and Lin (2003) using TGA, differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Pure Li_2ZrO_3 powders were prepared from lithium carbonate and zirconium oxide. The reaction between lithium zirconate and CO_2 can be represented as:

$$Li_2ZrO_3 \text{ (s)} + CO_2 \text{ (g)} \rightleftharpoons Li_2CO_3 \text{ (s)} + ZrO_2 \text{ (s)}$$
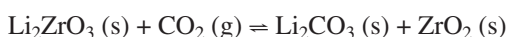
The reaction proceeds to the right to form lithium carbonate at temperatures near 500ºC, while the reverse reaction proceeds at temperatures above 700°C. It was found that pure Li_2ZrO_3 can absorb up to ~20 wt% of CO_2. However, despite its high CO_2 sorption capacity, the sorption rate is slow. Experiments were also carried out using Li_2ZrO_3 modified by additions of lithium carbonate and potassium carbonate. The modified Li_2ZrO_3 showed a dramatically improved rate of sorption, about 40 times faster than pure Li_2ZrO_3 at 500ºC, although it was still low. It was suggested that the melting of the lithium/potassium carbonates plays an important part in the enhanced CO_2 sorption rate. This indicates that diffusion of the CO_2 in the solid Li_2CO_3 that is produced is the rate limiting step in the pure Li_2ZrO_3 case. There was little difference in the CO_2 desorption rates between pure and modified Li_2ZrO_3.

TGA experiments performed by Fauth and others (2004) showed that the rate of CO_2 absorption by lithium zirconate

was continuous with time on stream. Under nitrogen, rapid regeneration of the lithium carbonate product occurred at temperatures greater than 700ºC. Fauth and Pennline (2004; Fauth and others, 2005) studied a number of binary and ternary eutectic salt modified Li_2ZrO_3 sorbents and found that the combination of binary alkali carbonate, binary alkali/alkaline earth carbonate, ternary alkali carbonate, and ternary alkali carbonate/halide eutectics with Li_2ZrO_3 noticeably improved the CO_2 uptake and absorption capacity. TGA experiments were carried out under isothermal conditions at temperatures between 450 and 700ºC. It was suggested that the formation of a eutectic molten carbonate layer on the outer surface of reactant Li_2ZrO_3 particles aids in facilitating the transfer of gaseous CO_2 during the sorption process. The ternary K_2CO_3/NaF/Na_2CO_3 eutectic and Li_2ZrO_3 combination at 600 and 700ºC produced the fastest CO_2 uptake rate and highest CO_2 capacity.

Sorbents based on lithium orthosilicate (Li_4SiO_4) have been studied by Kato and others (2002, 2003, 2005; *also* Essaki and others, 2004) using TGA. The absorption is ascribed to the mechanism whereby lithium oxide (Li_2O) in the Li_4SiO_4 crystal structure reacts reversibly with CO_2 at around 500ºC:

$$Li_4SiO_4 + CO_2 \rightleftharpoons Li_2SiO_3 + Li_2CO_3$$

This is shown schematically in Figure 13. Li_4SiO_4 was found to exhibit:
- a large CO_2 capacity;
- rapid absorption;
- suitability for a wide range of temperature and CO_2 concentration;
- reusability.

In comparison with Li_2ZrO_3, Kato and others (2002) found that:
- lithium orthosilicate absorbs CO_2 about 30 times faster than lithium zirconate at 500ºC in 20% CO_2 gases;
- lithium orthosilicate absorbs CO_2 at 500ºC in 2% CO_2 in which lithium zirconate shows little absorption and;
- lithium orthosilicate absorbs CO_2 even from the ambient air at room temperature.

Regarding the practical use of these materials as CO_2 absorbents for power plants, a pellet-type absorbent was thought to be realistic. Therefore, the removal efficiency of a packed bed reactor using pellets of Li_4SiO_4 was investigated. The reactor achieved almost 100% CO_2 removal at 500ºC
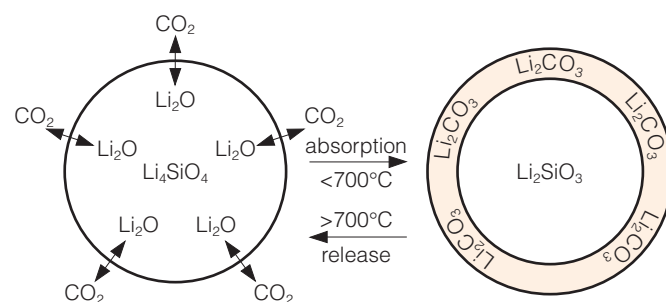
Figure 13 Reaction model of CO_2 absorption and emission by lithium silicate (Kato and others, 2005)

(Essaki and others, 2003). The reproducibility of CO_2 absorption and regeneration for cylindrical pellet type lithium orthosilicate was studied by Kato and others (2004). The pellets were heated at 600°C for absorption and 800°C for regeneration in gas flowing conditions of 20% CO_2 for up to 50 cycles. The reproducibility was evaluated by the retention ratio of the absorption rate to the initial one. The following conclusions were reached:

- the absorption rate of cylindrical pellet was dramatically decreased by the cyclic test;
- 5 wt% Li_2ZrO_3 addition was very effective for improving the reproducibility of the pellet by maintaining 90% of the surface area even after 50 cycles;
- the evaporation of Li_2CO_3 generated as a result of CO_2 absorption was slight;
- no phase transitions were observed;
- degradation of absorption rate was mainly caused by the decrease of contact area with CO_2 due to grain growth.

Kato and others (2006) also studied lithium orthosilicate doped with potassium carbonate and titanium nitride. Pure Li_4SiO_4 needs to be heated to more than 800°C to desorb CO_2, otherwise degradation of the absorption properties tends to occur. With the doped samples the desorption temperature could be decreased to 700°C and the absorption rate was found to be maintained at about 90% of the initial value.

The sorption/desorption reactions of the lithium compounds have mostly been studied at high temperatures. However, it is worth noting that Kato and others (2002; *also* Essaki and others, 2004) have pointed out that both lithium zirconate and lithium orthosilicate can react with CO_2 at room temperatures as well as high temperatures. Their experimental results indicated that a lithium silicate absorbent can absorb atmospheric CO_2, with 100% removal efficiency at room temperature.

4.6   Comments

As Harrison (2005) has pointed out, the key factors in the further development of solid processes are the cost and durability of the reactive solids, along with the development of technology to manage the large solid circulation rates. However, a more obvious problem is the high volume of fresh sorbent needed to counteract the decay in sorbent capacity especially when using natural limestone. This would limit the suitability of carbonation/calcination cycles for retrofitting existing plants.

5   Membranes

A comprehensive review of carbon dioxide selective membranes was produced by Shekhawat and others (2003). They identified the following classes of materials as having prospects for CO_2 selective membranes in flue gas or fuel gas applications:

● hybrid material;
● mixed matrix-type material;
● hydrotalcite-type materials;
● perovskite-type material.

However, since most of the literature on membranes for CO_2 capture is dominated by their applications for pre-combustion capture. In this report, only membranes considered to be suitable for post-combustion coal-fired flue gas applications will be considered, so the categories discussed will not match the list produced by Shekhawat and others (2003).

If it were possible to use the selective permeation of gases through a membrane in post-combustion CO_2 capture, it would be possible to capture the CO_2 in a single step. Gas permeation takes advantage of the differences in permeation rates through a polymeric or mineral membranes. However, Bounaceur and others (2006a,b) have pointed out that investigations of membranes for post-combustion are scarce. They attempted to clarify the potential role and place of membrane permeation processes in post-combustion capture and found that the membranes that are currently available are not sufficiently selective. Most available membranes have CO_2/N_2 selectivities (separation factors) less than 50, whereas a selectivity of above 100 is needed. If the flue gas contains 20% or more CO_2, then currently available materials can attain reasonable recoveries. There is a need for materials development so that power plant flue gas can be treated with membranes.

Note that membrane contactors for CO_2 absorption will not be discussed in this report although they have features in common with facilitated transport membranes discussed in Section 5.4. The difference is that membrane contactors are used only in the absorber stage and a separate stripper is still required. Membrane contactors were discussed in the earlier companion report on solvent scrubbing (Davidson, 2007).

Recently a European integrated project called NanoGLOWA has been set up to develop nanostructured membranes and installations for application in CO_2 post-combustion capture from power plants (Raats and others, 2008). To date, little information has been published but the progress can be followed on the project website http://www.nanoglowa.com/.

5.1   Polymeric membranes

The use of polymeric CO_2/N_2 gas separation membranes for the capture of CO_2 from power plant flue gases has been recently extensively reviewed by Powell and Qiao (2006). They reviewed the topic by examining the gas permeation properties of membranes in the light of their chemical

structure and focused on dense film membranes. The use of membranes for the capture of carbon dioxide from flue gas is limited by the following factors:

● the low concentration of CO_2 in flue gas;
● the high temperatures of flue gas can rapidly destroy a membrane unless the gas is cooled below 100ºC;
● the membranes need to be resistant to the harsh chemical environment of the flue gas;
● creating a pressure difference across the membrane will require significant amounts of power which will lower the thermal efficiency of the power plant.

Thus, for a membrane to be useful for the capture of carbon dioxide, Powell and Qiao (2006) suggested that it should possess a number of properties, namely:

● high carbon dioxide permeability;
● high carbon dioxide/nitrogen selectivity;
● thermally and chemically robust;
● resistant to plasticisation;
● resistant to ageing;
● cost effective;
● able to be cheaply manufactured into different membrane modules.

Earlier mathematical modelling of membrane systems by Carapellucci and Milazzo (2003) had suggested that polymeric membranes were 'ill-suited' for post-combustion CO_2 capture. The high excess air levels yield significant O_2 and low CO_2 concentrations in the flue gas resulting in a sharp deterioration in membrane performance compared with simple CO_2/N_2 separation. However, Favre (2007) has suggested that the potential of dense polymeric membranes for flue gas treatment may have been underestimated. Even so, he repeated the conclusion of Bounaceur and others (2006a,b) that, for membranes to compete with solvent absorption in terms of energy requirement, the CO_2 content of the feed gas must exceed 20%. There remains a need for improvement in membrane permeability of the most selective polymers, together with the production of thin active layers.

Powell and Qiao (2006) noted that the class of polymer with the largest volume of research is polyimides. This is due to their gas transport properties, good physical properties, potential structural variations, and ease of membrane formation. Much of the research seems to address their H_2/CO_2 separation properties suggesting that the context is pre-combustion rather than post-combustion.

However, there have been studies directed at the use of such polymers in power stations. Duthie and others (2005) noted that the commercial use of dense, polymeric gas separation membranes is limited to ambient temperature. They investigated the permeability of cast and annealed polyimide membranes in carbon dioxide at temperatures up to 100ºC and pressures up to 2.5 MPa. Plasticisation of the membranes was found to be suppressed in the membranes thermally annealed at 290ºC in the temperature and pressure range tested. However, the annealing process caused a small degree of

cross-linking, leading to a reduction of CO_2 permeabilities by a factor of 2–3.

Callahan and others (2006) proposed that SLIP polyimide membranes could be used for post-combustion CO_2 capture from power plants. SLIP (Solvent-Less vapour deposition combined with In-situ Polymerisation) membranes have been developed by the Lawrence Livermore National Laboratory where it was discovered that they show much greater CO_2 separation selectivity than conventional membranes (O'Brien and others, 2006a,b). SLIP membranes could conceivably achieve 90% capture of CO_2 from coal-fired power plants. They not only could require significantly lower power for the plant's separation process, they could reduce costs to between ⅓ to ⅙ of today's conventional MEA (monoethanolamine) process (https://eed.llnl.gov/co2/8.php). Callahan and others (2006) have proposed a demonstration of the technology at the coal-fired Navajo Generating Station or the Coronado Plant near the Navajo Nation. The target cost of the membrane system is expected to be 65% lower than conventional amine based technologies

'Cardo-type' polymers have been studied as materials for polymeric CO_2/N_2 separation membranes by Karashima and others (1999). Cardo-type polymers have a loop structure in which a cyclic group is directly bonded to the polymer main chain. The cardo-type polymers studied included bulky bis-phenylfluorene moieties as the loop structure. It was found that cardo-type polyimide asymmetric hollow fibre membranes showed higher CO_2/N_2 permeation selectivity than commercially available hollow fibre membranes. Tests showed that the permeation selectivity remained unchanged for 8000 hours. The CO_2 permeability decreased slowly with the elapsed time. The decrease was linear with time on a log scale. The half-life period was extrapolated to be 100,000 hours. The influence of minor species in the flue gas was studied. The presence of water vapour reduced the permeabilities of the other components but the effect on N_2 permeability was so much larger than that on CO_2 that the CO_2/N_2 permeation selectivity increased.

A cardo-type polyimide showed the highest CO_2/N_2 selectivity and CO_2 permeability during the screening of many newly synthesised cardo-type polymers by Mano and others (2003). They conducted a structure function relationship analysis looking at CO_2/N_2 selectivity and CO_2 permeability. They identified new cardo-type polyimide structures for CO_2 separation. They then developed wet spinning technology to produce an asymmetric hollow fibre membrane, and incorporated the membrane in the module. They carried out a preliminary test with the cardo-type polyimide PI-PMBP64 membrane module using real exhaust gases. Durability testing was conducted using the flue gas after desulphurisation from a pulverised coal-fired power station and the exhaust gas from a converter of a steel mill. In another series of tests, they found that the CO_2/N_2 separation coefficient of the PI-PMBP64 hollow fibre module over a period of 3500 hours was the same for both cylinder gas (simulation gas) and for real gas from a steel mill. The CO_2 concentration found in a steel mill is above the 20% limit above which the energy penalty decreases significantly (below the amine absorption threshold) and

already existing dense polymer materials could be possible candidates (Bounaceur and others, 2006a). An economic analysis was carried out for CO_2 separation using cardo polyimide hollow fibre membranes followed by a liquefaction process was carried out by Kazama and others (2005a). This will be discussed in Section 6.4 but, briefly, it showed that the membrane module was cheaper than amine absorption when the CO_2 content of the gas to be treated was 25% or more.

5.1.1 Effects of moisture

The effects of condensable minor components on the gas separation performance of polymeric membranes for CO_2 capture has been studied by Scholes and others (2008). They noted that condensable components in flue gas, in particular water, undergo competitive adsorption with carbon dioxide within the membranes, resulting in a reduction in CO_2 permeability. Furthermore, on a longer timescale plasticisation of the membrane can occur, turning the glassy polymer to a more rubbery state, which alters both gas permeability and selectivity. The impact of water on three glassy polymeric membrane materials was studied, Matrimid, polysulphone, and 6FDA-TMPDA (a polyimide). It was found that Matrimid 5218 experiences competitive sorption only, where permeability decreases proportional to the relative humidity of the feed gas, and therefore the amount of water accumulated within the microvoids. For polysulphone and 6FDA-TMPDA, both competitive sorption and plasticisation occurs, resulting in an initial reduction in CO_2 permeability due to water competition followed by an increase in permeability as the gas diffusivity increases due to increased free volume.

5.2 Ceramic membranes

The use of ceramic membranes has been studied as a way of capturing CO_2 from emission gases at high temperature. Osada and others (1999) developed a membrane composed of microporous silica formed on the outer side of a microporous substrate of alumina. The thin silica membrane was deposited by a sol-gel method. Three membranes were prepared. For the SiO_2 (TPABr) membrane the coating sol was prepared from a mixture of tetraethoxylane (TEOS), C_2H_5OH, H_2O, HCl, and tetra-n-propylammonium bromide (TPAbr). The other membranes were SiO_2 (γ-APTES) in which γ-APTES is gamma-aminopropyltriethoxysilane, and SiO_2-ZrO_2. For all the membranes, humidity had an effect on the permeation selectivity (the preferential permeation of CO_2 compared with N_2); water enables the permeation of CO_2 but prevents the permeation of N_2. The permeation selectivities fell as the temperature rose although the SiO_2-ZrO_2 had a permeation selectivity of 12.9 (CO_2/N_2) at 150ºC.

NETL has supported research into a novel dual functional membrane and a factsheet can be found at http://www.netl.doe.gov/publications/factsheets/project/Proj333.pdf. The membrane consists of a microporous inorganic siliceous matrix with amine functional groups physically immobilised or covalently bonded on the membrane pore walls. It is anticipated that strong interactions

between the permeating CO_2 molecules and the amine functional membrane pores will enhance surface diffusion of CO_2 on the pore wall of the membrane with subsequent blocking of the transport of other gases, such as O_2, N_2, and SO_2. In this way, the new membrane is expected to exhibit higher CO_2 selectivity compared with prior, purely siliceous membranes that perform separations based on difference in molecular size only.

5.3 Carbon membranes

Hollow fibres of deacetylated cellulose acetate have been carbonised under CO_2 flow up to 550ºC. The permeability for different gases (CO_2, N_2, O_2) were tested and used as the input for process simulation by He and others (2008). The simulation results indicated that the hollow fibre carbon membranes show a potential application for CO_2 capture from flue gas in post-combustion power plant. A CO_2 recovery of 67% needs a total hollow fibre carbon membrane area of 1.62×10^7 m². The captured CO_2 would have a purity of 88%. The total energy demand and capital costs were calculated to be 2.5 GJe and US$197 per tonne of CO_2 avoided. The research was carried out under the EU NanoGLOWA project (Raats and others, 2008).

5.4 Composite and functionalised membranes

The preparation of composite membranes from glassy polymers (cellulose derivatives) and carbon fillers was investigated by Bertelle and others (2006b) to obtain mixed matrix materials for CO_2 separation from flue gas. Mixed matrix membranes having filler contents varying from 10 to 60 wt% were successfully obtained but only brief details were provided in the paper.

Membranes can also be functionalised analogous to the functionalised solid sorbents discussed in Chapter 3. For example, DeSisto (2003) investigated the ability of amine functionalisation to enhance the CO_2 transport in silica

membranes. Specifically, he examined three synthesis techniques for functionalising silica membranes with amino groups that resulted in different surface chemistries of the silica membranes. These differences were correlated with changes in the CO_2 facilitation characteristics. It was found that high loadings of amino groups where interaction with the silica surface was minimised promoted the highest CO_2 transport. S Kim and others (2003) briefly described mesoporous silica membranes (MCM-41 and MCM-48) containing surface-attached 3-aminopropyl groups.

Kumar and others (2005) investigated an effective method of surfactant removal for the preparation of defect-free cubic pore structure MCM-48 silica membranes. They also studied the effect of attachment of basic polymeric polyethylenimine (PEI) groups to the MCM-48 pore surface on the gas separation properties of the MCM-48 membranes. During CO_2/N_2 permeation, CO_2 is selectively adsorbed on the PEI groups and forms the surface carbamate species. To permeate, CO_2 has to undergo adsorption, diffusion and desorption steps as it has great affinity for the PEI groups. Meanwhile, N_2 is not adsorbed to a significant extent and permeates through pore spaces which are not occupied by the PEI groups by diffusion only. Therefore, N_2 permeates faster than CO_2 resulting in 97.7% N_2 in the permeate gas at 25ºC reducing to 89.4% at 90ºC.

A composite membrane with high CO_2/N_2 selectivity and CO_2 permeance has been developed by Kazama and others (2005b, 2006a,b; *also* Duan and others, 2006). The basis of the membrane is porous, commercially available polysulphone ultrafiltration hollow fibre membrane substrates. A thin layer of chitosan was deposited directly beneath the inner surface of the substrate because it has a potential affinity for the hydrophobic substrate and the hydrophilic poly(amidoamine) dendrimer which was impregnated on to the chitosan layer. The poly(amidoamine) dendrimer PAMAM acts as a hybrid active layer for CO_2 separation. The composite membrane was described as a 'molecular gate' and a conceptual diagram is shown in Figure 14.
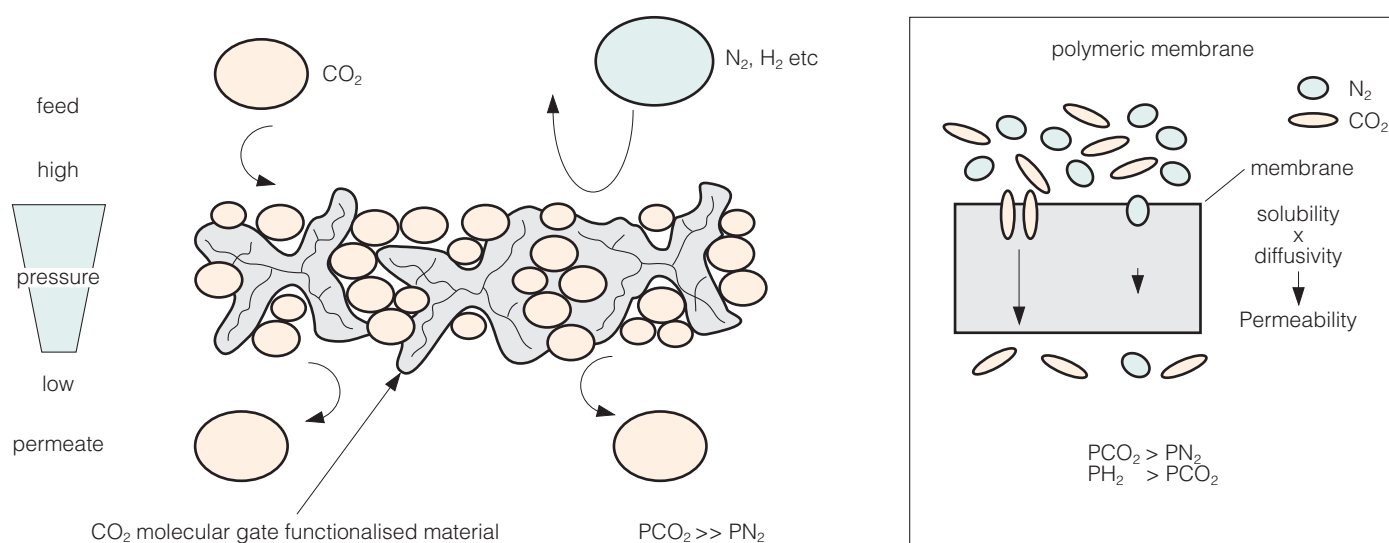

Figure 14 Conceptual diagram of CO₂ molecular gate function (Kazama and others, 2006)

One metre long commercial-sized modules of the membrane were produced and tested by the US National Energy Technology Laboratory (NETL) for removal of CO_2 from a simulated flue gas mixture. They initially showed an excellent CO_2/N_2 selectivity ranging from 110 to 169, much higher than that of about 30 for a polymeric membrane; Duan and others (2006) reported a value of 230 at a pressure difference of 97 kPa at 40ºC. This higher selectivity was believed to derive from possible interactions between the CO_2 molecules and the PAMAM dendrimer. However, the results obtained at NETL indicated some degradation in system performance of the modules.

5.5 Facilitated transport membranes

Facilitated transport membranes (FTM) rely on the formation of complexes or reversible chemical reactions of components present in the gas stream with compounds present in the membrane called carriers. These complexes or reaction products with the carriers are then transported through the membrane (IPCC, 2005). A schematic of how FTMs work is shown in Figure 15. Kovvali and others (2000) state that major advantages of FTM over conventional polymeric membranes include higher permeabilities for reacting species such as CO_2 and the resultant high selectivities for non-reacting species such as N_2. However, FTM is especially advantageous for removal of CO_2 when it is present in low concentrations so may be less favoured if used in CO_2 capture from flue gas.

Matsufuji and others (1999) reported the development of membranes composed of an aqueous amino acid solution. The specific amino acid was not revealed. It was reported that the CO_2/N_2 separation factor remained above 100 for five weeks if the concentration of SO_2 supplied to the membrane was less than 10 ppm.

FTMs include immobilised liquid membranes (ILMs) where the carrier in a solvent, usually water, is immobilised in the pores of the membrane; the solvent is physically trapped but not chemically bonded to the membrane. However, their stability is limited by the lack of chemical bonding, evaporation of solvent during operation. Chen and others (1999, 2000, 2001; *also* Kovvali and others, 2000) studied selective CO_2 separation from CO_2-N_2 mixtures by immobilised liquid membranes. Sodium carbonate-glycerol and glycine-Na-glycerol membranes were used. The flat membrane substrates were hydrophilised polyvinylidenefluoride (PVDF) and hydrophilised
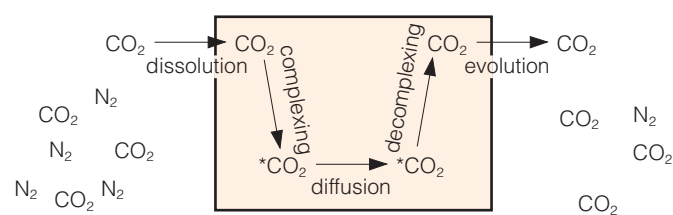
polypropylene Celgard 2500. Hydrophilised polysulphone was later used as a hollow fibre substrate. The ILMs were prepared by immersion of the substrate in the carrier solution. The glycine-Na-glycerol ILMs were found to be superior to the sodium carbonate-glycerol membranes due to the higher concentration of glycine-Na in glycerol. They produced mechanically stable performance and were operated for more than 600 hours continuously for the flat membrane substrates (300 hours for the hollow fibres) without any deterioration in performance. However, an increase in the partial pressure of CO_2 reduced the CO_2 permeability and its selectivity.

The glycerol in the ILMs developed by Chen and others (1999, 2000, 2001) acts as the solvent for the CO_2 carriers but, in itself, has an inherently low selectivity for CO_2. Its major advantage is that it is essentially a non-volatile liquid which accounts for the stability of the ILMs containing it. The 'molecular gate' dendrimer, PAMAM, was used as the ILM carrier immobilised in the pores of hydrophilised polyvinylidene fluoride (PVDF) flat membrane films by Kovvali and others (2000) and reported in more detail by Kovvali and Sirkar (2001). The PAMAM acts as both the liquid membrane medium as well as the carrier for facilitated CO_2 transport over N_2. However, a small amount of glycerol was found to increase the operating range of relative humidity of the feed gas stream. A 75% dendrimer-25% glycerol mixture was found to have a substantially increased relative humidity operating range while maintaining the CO_2 permeance and selectivity close to the levels observed in a pure dendrimer ILM.

Although glycerol itself has an inherently low selectivity for CO_2, Kovvali and Sirkar (2001) investigated glycerine carbonate as a solvent/carrier for use in ILMs on the grounds that it is likely to have a high solubility for CO_2. It was found that pure glycerol carbonate ILMs retained their CO_2/N_2 selectivity around 80–130 over a large range of CO_2 partial pressures. Their CO_2 selectivity was not affected by the absence of humidity in feed and sweep streams. The CO_2 permeability through pure glycerol carbonate ILMs improved in the presence of humidified feed streams. Addition of small amounts of facilitating carriers such as poly(amidoamine) dendrimer (PAMAM) and sodium glycinate appeared to help CO_2 facilitation significantly at low CO_2 partial pressures. However, at high CO_2 feed partial pressures, there was a loss of selectivity with the addition of the carriers.

An FTM with potassium carbonate aqueous solution immobilised in a polymer gel was studied by Okabe and others (2003). The facilitated transport membrane had a two-layered structure; one a polymer gel containing a carrier solution that reacts with CO_2, and the other a porous membrane which supported the gel layer. The support membrane for the gel layer was a hydrophobic polytetrafluoroethylene (PTFE) porous membrane and the polymer gel was a vinylalcoholacrylate salt (PVA-PAA). This composite membrane was dipped into the potassium carbonate (K_2CO_3) aqueous solution of 2 mol/kg, which was already known as a CO_2 absorbent. The cross-linked PVA-PAA layer absorbed the carrier solution to form the gel layer. The polymer gel membrane preserved a high selectivity for about six months under a high humid gas mixture,

Figure 15 Schematic of facilitated transport membrane (Luebke and others, 2007)

simulating combustion flue gas. The K_2CO_2 aqueous solution played an important part in keeping the membrane wet, and polymer gel played an important role in maintaining the membrane's stability. It was suggested that the polymer gel membrane has potential for practical use for recovering CO_2 from combustion gas. Later studies by Okabe and others (2007) showed that a gel-supported membrane immobilising an aqueous 2 mol/kg solution of K_2CO_3 worked well for 6 months. However, it was also observed that SO_2 in the flue gas obstructed CO_2 transportation because the SO_2 restrained the CO_2 from dissolving into the carrier solution and decreased the concentration of the carrier at the gas-liquid interface. This undesirable effect of SO_2 was weakened by the addition of potassium sulphite (K_2SO_3) and disappeared at the low concentration of 0.1 mol/kg K_2SO_3. NO and NO_2 had no influence on CO_2 transportation through the membrane.

A facilitated transport membrane using a capillary membrane module with permeation of the amine carrier solution was developed by Teramoto and others (2003a,b). CO_2 in the feed gas could be concentrated from 5–15% to more than 98% and the selectivity of CO_2 over N_2 was in the range 430 to 1790. The membrane was very stable with no deterioration observed over a discontinuous one month testing period. Teramoto and others (2004) called it a 'bulk flow liquid membrane' (BFLM) and tested it with model flue gases. The membrane support medium was polyethersulphone and amines were used as CO_2 carriers. The carrier solutions were continuously supplied to the feed side (high-pressure side) of the microporous membrane where they reacted selectively with CO_2. The carrier solution was then allowed to permeate to the receiving side (low-pressure side) where the solution released CO_2. The liquid is returned to the feed side by a pump. The membrane system is shown in Figure 16.

Teramoto and others (2004) noted that the BFLM has some disadvantages. For example, it requires a liquid circulation pump and needs much larger amounts of carrier than FTMs. However, preliminary estimations were that the energy consumption was 0.28 kWh/kg of CO_2, only 55% of the energy consumption compared with the gas absorption/stripping process using the KS-1 solvent. The membrane modules tested were very stable over a discontinuous 2–4 month testing period with no decrease in
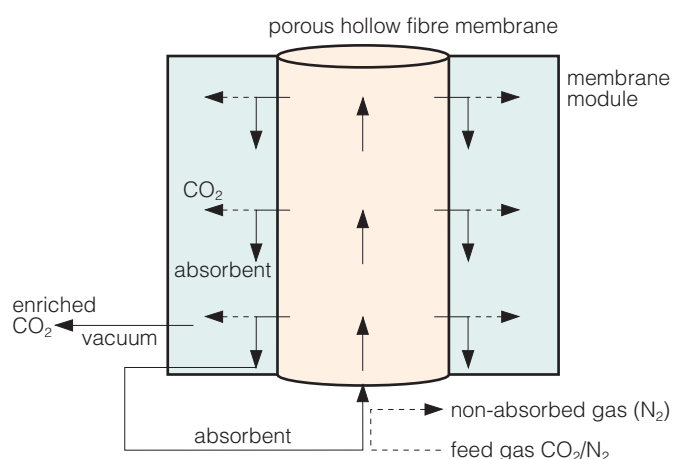
Figure 16 Schematic of membrane absorption method (Okabe and others, 2006)

permeability and selectivity. Among the eight amines tested as the CO_2 carrier, 2-(butylamino)ethanol (BAE) was found to be the most effective.

Hollow fibre membrane modules using several materials such as polyethersulphone, polysulphone, and polyethylene were fabricated by Okabe and others (2006). They found that the energy consumption calculated for each membrane ranged from 0.132 to 0.156 kWh/kg of CO_2, which was about 35% to 41% of the chemical absorption method. The total volume of the membrane module was significantly smaller than the volume of a conventional stripper. It was concluded that the membrane/absorption hybrid method was very energy efficient process and the cost of the equipment was also expected to be reduced. Okabe and others (2008) have been studying the modification and improvement of the process developed by Teramoto and others (2003b, 2004), which they have called a membrane flash process, to apply it for practical use in the field of CO_2 separation and recovery. They found that aluminum oxide was the most suitable material for the membrane flash process using commercial membranes.

A modified facilitated transport membrane permeation process was developed by Qin (2005). The details given for the process are sketchy other than it uses an 'accelerated carrier' but it was claimed that the membrane process provides both higher CO_2 mass transfer coefficient and CO_2/N_2 selectivity. The process can produce a >99 vol% CO_2 stream from a flue gas stream containing 10 to 15 vol% CO_2 with a recovery of >90%. Further, that the membrane system is stable when the flue gas contains SOx, NOx, HCl and HF, when they are bulk-removed by conventional deNOx and deSOx technologies. It was claimed that the increase in cost of electricity with CO_2 capture was 34.3% compared with 64–87% of conventional absorption/stripping.

A novel CO_2 selective polymeric membrane that contained both mobile and fixed amine carriers was prepared by Huang and others (2008) and the permeation properties were measured at ≥ 100ºC. CO_2 capture from gas mixtures was studied with a simulated feed gas while using steam as the sweep gas. The membrane incorporated both fixed and mobile amine carriers into cross-linked poly(vinylalcohol) (PVA). Based on the measured CO_2 permeability and CO_2/N_2 selectivity, a mathematical model was developed to evaluate the separation performance of a hollow fibre module that was composed of the membrane. The modelling results showed that a CO_2 recovery of >95% and a permeate CO_2 dry concentration of >98% were achievable from a 21.06 mol/s flue gas stream with a 0.61 m hollow fibre module containing 980,000 fibres.

Several different membrane based, facilitated transport carbonate/bicarbonate reactors were designed by Trachtenberg and others (2005) with facilitation by the enzyme carbonic anhydrase described as 'the most efficient CO_2 conversion catalyst'. This enzyme is found in nearly all living species as a means of converting CO_2 to bicarbonate and the reverse. Tests by Bao and Trachtenberg (2006) showed that liquid membranes containing carbonic anhydrase and alkaline carbonate solutions as facilitators have higher permeance and selectivity than those made of DEA or
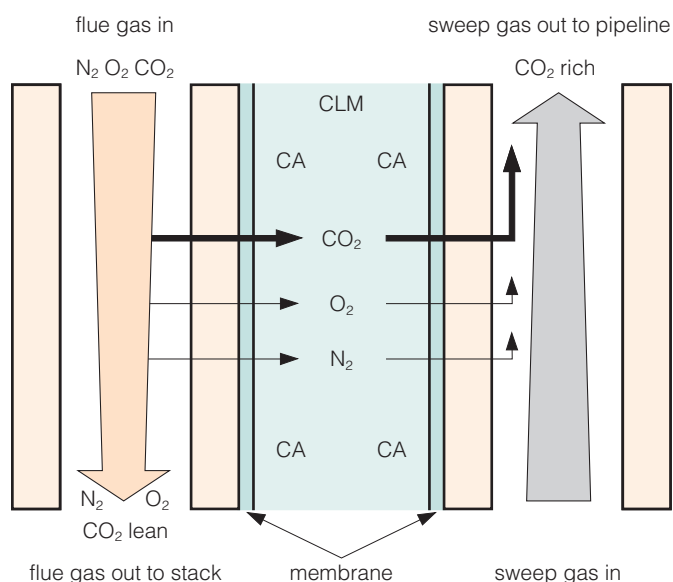
Figure 17 Schematic of the operation of the CLM permeator (Trachtenberg and others, 2006)

alkaline carbonate alone. A dual hollow fibre permeator was constructed by Trachtenberg and others (2006) using microporous polypropylene woven fibres. The feed and sweep fibres were arranged orthogonally. Gases were delivered to the bore side of the fibres. The shell side, between the fibre mats (mean thickness 250 μm), was filled with the contained liquid membrane (CLM), which could flow perpendicularly. The CLM was readily accessible and thus could be supplemented or replaced as needed. The CLM consisted of 3 mg/ml carbonic anhydrase and 1.0 M sodium bicarbonate. The gas phase remains separated from the CLM as a result of the hydrophobicity of the membrane. As shown schematically in Figure 17, the flue gas stream and the sweep gas are fed into the hollow fibre lumen. The flue gas stream diffuses through the gas filled pores of the membrane. At the gas/liquid interface, on the other outer side of the membrane, the gas components are absorbed into the CLM. Carbonic anhydrase at the interface greatly increases the rate of conversion of CO_2 to bicarbonate facilitating absorption of CO_2 into the CLM. A pressure swing drove desorption of CO_2 into the sweep fibres. The difference in chemical absorption for CO_2 and physical absorption for O_2 and N_2 resulted in high selectivity for CO_2. The device is stable, exhibiting high permeance, and high selectivity. The modular system design can be scaled to any required size thus reducing the investment costs. It was claimed that the system captures CO_2 at a low energy and low cost promising to be a cost effective technology for CO_2 capture.

Trachtenberg (2007) addressed several issues concerning the use of the permeator in a pulverised coal burning boiler. He found that:

- clean-up of particulate and SOx would be needed to minimise the probability that sticky particles, derived from sulphate nucleation on particles, might attach to the membrane surface;
- the greater the particulate and SOx load at the permeator mouth, the more maintenance will be required;
- the maintenance required with higher loadings of particulates and SOx may include cleaning the

membrane with low strength caustic solutions followed by drying of the membrane but, if this process were required at high frequency, it would be costly and time consuming;
- high particulate and SOx loading may lead to decreased membrane life, due to frequent cleaning.

The flue gas contaminant of dominant concern for removal during pre-treatment is SOx. The acceptance concentration for SOx was calculated to be 7.08 ppm. Higher concentrations could be accepted at the cost of requiring additional efforts are made to maintain acceptable CLM chemistry. However, it was noted that the permeator acceptance limit for SOx is in line with that for other CO_2 capture technologies. A preliminary test of a 0.5 m² permeator was reported by Trachtenberg and others (2008). The permeator achieved 85% removal of CO_2 from a 15.4% CO_2 feed stream.

5.6   Hybrid membrane processes

Min and others (2001) have suggested a hybrid system combining pressure swing adsorption (PSA) with membrane units. At the front end hollow fibre modules of asymmetric polysulphone concentrate the feed stream from 15% to 40% and, at the next stage the PSA unit produces a purified gas rich in CO_2. The PSA unit uses zeolite molecular sieve 13X. A purity of 99% CO_2 can be obtained in this way. It was suggested that, with the simple configuration, low operating cost and maintenance expenses, membrane processes could be an economic alternative to conventional gas separation processes.

Another hybrid membrane process, although not strictly post-combustion, has been suggested by Feron (2006). By enriching, the oxygen in the combustion gas, to an O_2/N_2 selectivity of 10, it would be possible to produce a CO_2-enriched flue gas that would be more amenable to membrane separation. This is a hybrid oxyfuel/post-combustion capture system.

5.7   Comments

In their review of progress in carbon dioxide separation and capture, Yang and others (2008) came to the conclusion that membrane separation processes provide several advantages over other conventional separation techniques; a membrane combining high flux, high selectivity and high stability is not realistic at this stage but mixed-matrix membranes provide hopes. Further, membrane processes as energy saving, space saving, easy to scale-up, could be the future technology for CO_2 separation.

Certainly, there may be hopes for the future but there would seem to be considerable challenges as well.

6 Techno-economic studies

It is not the intention of this chapter to provide an authoritative techno-economic assessment of solid sorbent and membranes as means of CO_2 capture in coal-fired power plants but, rather, simply to report on the limited number of assessments that have been made in this area where there are very few data available on which to base, especially economic, assessments. Most of the system reported so far are still very much confined to the laboratory or fairly small test facilities.

If sorbents were used to capture CO_2 from flue gas, then the mass flows of the sorbent would be very large. Therefore the ratio of fresh sorbent make-up to the sorbent flowing in the capture/regeneration cycle would have to be kept as low as possible to keep the costs within reasonable limits. Abanades and others (2004) used a common mass balance for all sorbent processes in order to define a parameter that highlights the minimum sorbent performance required to keep sorbent make-up costs at an acceptable level. Absorption with monoethanolamine (MEA) was used as a techno-economic baseline. The values of the manufacturing cost of a unit of sorbent needed to react with 1 mole of CO_2 (C_s^*) was estimated for several sorbents and compared with the calculated value for MEA of 0.544 US$/mol CO_2 at year 2000 prices. These were compared with $N_{1/2}$, a value that indicates that 50% of the sorbent units (molecules or particles) have completed the sorption/desorption cycle more than $N_{1/2}$ times. For MEA, it was assumed that, on average it cycles approximately 4500 times before it is lost from the system or encounters a poison that irreversibly deactivates it. The required performance index of a sorbent against the manufacturing cost of a unit of sorbent is shown in Figure 18.

It was argued that synthetic adsorbents based on substrates
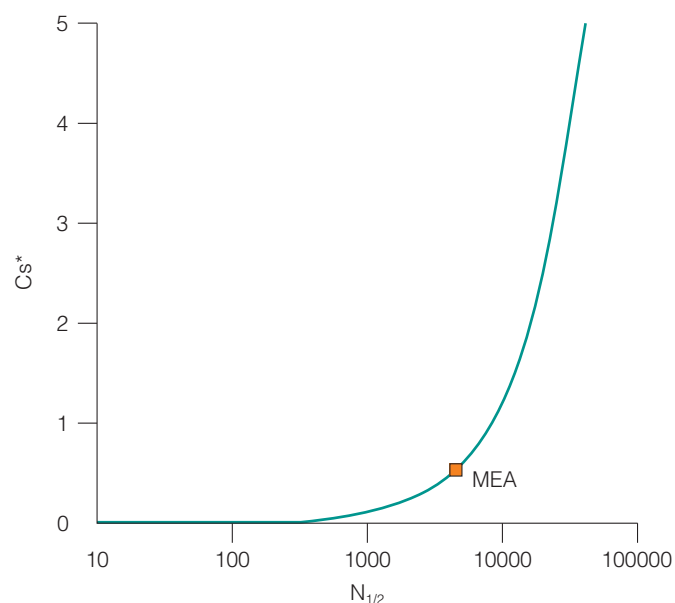
Figure 18 Required performance of a sorbent vs. the manufacturing cost of a unit of sorbent needed to react with 1 mol of CO_2 (Abanades and others, 2004a)

like active carbon or zeolites are common in many industrial separations. When their target is to remove a minor contaminant in a large gas flow, or to produce a high value-added product, the cost of the sorbent referring to 1 tonne of the impurity removed, or to the product produced, is allowed to be high. However, this cannot be the case in CO_2 capture systems, where the flow of the impurity is very large and the price of the product has to be very low. If CO_2 sorbents are to be developed using these substrates, their performance needs to be demonstrated after hundreds to thousands of sorption/desorption cycles.

Sorbents based on natural limestones cannot maintain a high capture capacity beyond 20 cycles, and large quantities of limestone make-up are required for CO_2 control. This can only be acceptable because of the extremely low price of crushed limestone and because the exhausted calcines might have some downstream value as a feedstock for the cement industry.

6.1 Mesoporous and microporous adsorbents

Ho and others (2008b) note that, historically, the recovery of CO_2 using pressure swing adsorption (PSA) systems has been in industries such as natural gas processing and hydrogen production. In these industries, the feed gas is available at a high pressure and low temperature, and thus, CO_2 can be recovered by using a readily available driving force such as the pressure difference between the high feed pressure for adsorption and a lower pressure for desorption. However, there has been limited technical experience in recovery of CO_2 from industrial streams such as post-combustion flue gas. Ho and others (2008b) examined the economic feasibility of PSA for recovering CO_2 from post-combustion power plant flue gas. Their analysis considered both high-pressure feed and vacuum desorption using the commercial zeolite adsorbent 13X, which has a working capacity of 2.2 mol/kg (9.68 wt%) and CO_2/N_2 selectivity of 54. The results showed that using vacuum desorption reduces the capture cost from US$57 to US$51 per ton of CO_2 avoided and is comparable in cost to CO_2 capture using conventional MEA absorption of US$49 per ton of CO_2 avoided. A sensitivity analysis was also presented showing the effect on the capture cost with changes in process cycle; feed pressure and evacuation pressure; improvements in the adsorbent characteristics; and selectivity and working capacity. The results showed that a hypothetical adsorbent with a working capacity of 4.3 mol/kg (18.92 wt%) and a CO_2/N_2 selectivity of 150 could reduce the capture cost to US$30 per ton of CO_2 avoided. It was made clear, however, that the results of the study were not correct on an absolute basis but were only indicative.

Zhang and others (2008a) have examined the effect of process parameters on the power requirements of VSA for CO_2 capture from flue gas and conducted experimental work on a purpose-built three-bed CO_2 VSA pilot plant using commercial 13X zeolite. Both 6-step and 9-step cycles were

used to determine the influences of temperature, evacuation pressure and feed concentration on process performance (recovery, purity, power and corresponding capture cost). A simple economic model for CO_2 capture was developed. It was found that the feed gas temperature, evacuation pressure and feed concentration have significant effects on power consumption and CO_2 capture cost. Their data demonstrated that the CO_2 VSA process has good recovery (>70%), purity (>90%) and low power cost (4–10 kW/tonne CO_2 captured per day) when operating with 40°C feed gas provided relatively deep vacuum is used. The operating capture cost was found to vary considerably as the process configuration is altered and was calculated to be in the range of US$12–32 per tonne of CO_2 avoided.

6.2 Immobilised amine sorbents

Tarka and others (2006a,b) investigated the amine-enriched SBA-15 sorbent for use in a traditional fixed bed, a fluidised bed, and a novel radial flow fixed bed and also compared them with MEA wet scrubbing technology. Table 5 compares the basic design parameters for the four systems and also the plant performance and economics with CO_2 capture . The fluidised bed has the smallest pressure drop and requires a slightly reduced amount of sorbent over both the fixed bed and the novel radial flow fixed bed. At an expected 10 US$/kg of sorbent cost, the reduced sorbent requirement could result in a $2–4 million reduction in the capital cost of

Table 5a	Design results and economic analysis of CO_2 capture using amine enhanced solid sorbents (Tarka and others, 2006b)				
	Flow rate per unit, m³/s	Absorber units	Total sorbent mass required, tonnes	Pressure drop, Pa	Total footprint, m²
Conventional MEA	118	8–10	n/a	7–41	460–840
Amine-enriched sorbent					
Fixed bed	36	63	1600	41	5295
Fluidised bed	71	8	1100	2	650
Novel fixed bed					
Parallel flow	71	8	3500	15	690
Series flow	142	4	1300	20	900

Table 5b					
	ID fan load, MW	Solvent pump load, MW	Gross plant size, MW	Cost of electricity, ¢/kWh	Cost of electricity increase, %
MEA scrubber	22.4	3	491	7.56	55
Fluidised bed	6.5	n/a	465	6.88	41
Novel fixed bed					
Parallel flow	15.9	n/a	474	693	42
Series flow	19.4	n/a	478	634	30

Table 5c		
	Initial sorbent cost, million US$	Annual sorbent replacement cost, million US$/y
MEA wet scrubbing*	94	8.1
Fixed bed	15	7.5
Fluidised bed	11	22
Novel fixed bed		
Parallel flow	35	18
Series flow	13	6.5
* MEA cost listed is total system cost		

the system, or up to a 25% reduction in cost. It was thought likely, however, that the fluidised bed reactor would significantly increase the attrition rate of the amine enhanced solid sorbent, as compared with the two-year replacement rate predicted for a fixed bed system, and that sorbent replacement costs would outweigh the advantages of the reduced sorbent requirement. The economic and performance details of a PF power plant with CO_2 capture by MEA wet scrubbing or an amine enhance solid sorbent were modelled. It was found that the reduced plant size, combined with reduced capital costs over the MEA system could result in a 15–16% decrease in cost of electricity with CO_2 capture for the traditional fixed bed system and for the series flow novel fixed bed reactor over the wet scrubbing case. These plants are also more efficient with a 9–14% decrease in parasitic load over the MEA case. The fluidised bed and parallel flow novel fixed bed reactor have an 8–9% decrease in cost of electricity (COE) with CO_2 capture over MEA and result in a 29% and 19% decrease in system parasitic load, respectively. The reduction in parasitic load is primarily due to a reduction in system pressure drop.

As reported in Section 3.1.1, a preliminary energetic analysis by Notaro and Pinacci (2007) of the desorption stage showed a 15% energy saving for the DEA-amberlite solid sorbent compared with employing a 30 wt% DEA in aqueous solution. A further 30% energy saving was possible because the sorbent could be regenerated at a lower temperature (75ºC instead of 120ºC).

The immobilised DBU solid sorbents studied by Gray and others (2008) and discussed in Section 3.1.1, exhibited acceptable CO_2 capture capacities of 3.0 mol CO_2/kg sorbent at 25ºC (13.2 wt%); however, at the critical operational temperature of 65ºC, the capacity was reduced to 2.3 mol/kg sorbent (10.1 wt%). However, it was pointed out that, in order for the solid amine sorbents to be competitive with existing monoethanolamine (MEA) liquid systems, CO_2 capture capacity must be in the range of 3–6 mol CO_2 /kg sorbent (13.2–26.4 wt%).

6.3   Regenerable solid sorbents

It was noted above that the use of natural sorbents can only be acceptable because of the extremely low price of crushed limestone and because the exhausted calcines might have some downstream value as a feedstock for the cement industry (Abanades and others, 2004a). Abanades and others (2007; *also* Romeo and others, 2006) further considered the cost structure of this type of system. They presented the basic economics of a complete system including three key cost components:
- a full combustion power plant;
- a second power plant working as an oxyfired circulating fluidised bed calciner (CFBC);
- a fluidised bed carbonator interconnected with the calciner and capturing CO_2 from the combustion power plant.

The key cost data for the two major first components are well established in the open literature. It was shown that there is

scope for a breakthrough in capture cost to around 15 $/t of CO_2 avoided with this system. This is mainly because the capture system is generating additional power (from the additional coal fed to the calciner) and because the avoided CO_2 comes from the capture of the CO_2 generated by the coal fed to the calciner and the CO_2 captured (as $CaCO_3$) from the flue gases of the existing power plant, that is also released in the calciner. Simply put, the oxyfired CFBC is not only avoiding the CO_2 from its own coal combustion feed, but all the CO_2 coming from the flue gases of the neighbouring power plant. The oxyfired plant captures about twice the CO_2 than it generates from the combustion of its own coal feed. Romeo and others (2008) point out that, under these conditions, the capture system is able to generate additional power at 26.7% efficiency (LHV) after accounting for all the penalties in the overall system, without disturbing the steam cycle of the reference plant that retains its 44.9% efficiency. A preliminary cost study of the overall system produced a capture cost around 16 €/t CO_2 avoided and an incremental cost of electricity of just over 1 €/MWh.

The results tests on calcium based sorbents were projected, using an Excel based economic model, to estimate the 30-year levelised cost of CO_2 capture per tonne for a utility-scale power plant by MacKenzie and others (2007). An order of magnitude capital and operating estimate for a 360 MW pressurised fluidised bed combustor (PFBC) is presented, assuming a western Canadian location. Additional costs for calciners, oxygen plant, and related equipment necessary to create a Ca based CO_2 chemical capture cycle were presented separately. These costs were evaluated in a series of spreadsheets, and the impact of process flows, as well as capital, operating/maintenance, and feedstock costs were determined in a sensitivity analysis. The estimated cost per tonne for CO_2 capture was found to be approximately CA$23.70. This figure was compared with the cost for amine scrubbing technologies. A literature search found a wide range of equivalent capture costs from $39 to $96 (2005 Canadian dollars), depending on report specifics. It was concluded that Ca based sorbents have the potential to be cost competitive with other existing capture technologies.

Process analysis of CO_2 capture from flue gas using Ca based carbonation/calcination cycles has been carried out by Z Li and others (2008). A detailed mass balance, heat balance, and cost of electricity (COE) and CO_2 mitigation for the carbonation/calcination cycles with three Ca based sorbents in dual fluidised beds were calculated and analysed to study the effect of the Ca based sorbent activity decay on CO_2 capture from flue gas. The three sorbents considered were: limestone, dolomite and $CaO/Ca_{12}A1_{14}O_{33}$ (75/25 wt %) sorbent. was presented. The design and operating conditions of this process system were found to be highly dependent on the Ca based sorbent used. The difference in conversion of sorbent between absorber and regenerator, ΔX, was an important design variable affecting all other parameters greatly (for example, fresh sorbent make-up, amount of coal and oxygen required in the regenerator). In practical operation, because of the fast calcination reaction, it is very likely that calcination in the regenerator will be nearly complete. This was assumed in most of the analysis and, thus, ΔX was equivalent to the conversion in the absorber. The economic analysis (COE and

CO_2 mitigation cost) indicated that dolomite and $CaO/Ca_{12}A1_{14}O_{33}$ are promising sorbents. Limestone is not attractive because of its fast activity loss, and, thus, because of the very large amount of make-up sorbent required. Although $CaO/Ca_{12}A1_{14}O_{33}$ has higher adsorption capacity and cyclic stability than that of limestone and dolomite, its cost, more than four times that of limestone and dolomite, makes the process more expensive, except at very low ΔX, where the amount of fresh sorbent is the lowest. Using dolomite and $CaO/Ca_{12}A1_{14}O_{33}$ the COE increases by 36–40% compared to the base COE of a supercritical plant while capturing 85% of the CO_2 which is lower than any other competing CO_2 capture technologies, except IGCC with CO_2 capture as shown in Table 6. It was concluded that a synthesised sorbent with high performance and low cost would be highly beneficial for the CO_2 capture process from flue gas using carbonation/calcination cycles. The results were also compared with those produced by MacKenzie and others (2007). The results from Z Li and others (2008) indicated higher COE and CO_2 mitigation cost, even without including tax. This was due to higher capital, operating, and fuel costs.

Romano (2008) compared the thermal efficiency of a coal-fired plant with calcium oxide carbonation for post-combustion CO_2 capture, regenerated in a fluidised bed calciner via oxyfuel combustion of coal with full oxy-combustion and amine based plants. He calculated a net LHV efficiency of 37.4% for the selected reference case, with 97% of the CO_2 captured, compared with 36.3% for full oxy-combustion and 32.6% for the amine based plant. However, it was conceded that plant complexity is higher than the competitive technologies.

Material and energy balances of the carbonation/calcination process for post-combustion CO_2 capture have been performed using ASPEN PLUS software by Ströhle and others (2008a). They evaluated the process efficiency in terms of CO_2 capture yield and energy requirements. The overall plant efficiency and the CO_2 capture efficiency depend on various parameters. An increase in make-up or circulating flow leads to a higher CO_2 capture efficiency, however, on cost of a lower plant efficiency. In general, overall plant efficiencies of 41.5% (without CO_2 compression) with CO_2

capture efficiencies of 85% seemed to be feasible. For a 1052 MWe coal-fired reference plant with an original net efficiency of 45.6%, Ströhle and others (2008b; *also* Epple and Ströhle, 2008) have calculated that the energy penalty for the carbonation/calcination process for post-combustion CO_2 capture is 2.75 percentage points for a total CO_2 capture efficiency of around 87%. The CO_2 avoidance costs for the plant were found to vary strongly with investment costs, interest rate and availability of the plant. On average, they amounted to around 18.4 €/t CO_2 (including CO_2 compression), the same order of magnitude as those for an oxyfuel plant, but significantly lower than for MEA scrubbing. However, it is noted that most assumptions concerning the carbonation/calcination process are based on laboratory tests and that further experiments at sufficient scale are necessary. A 1 MWth test plant is currently being erected at TU Darmstadt for further investigations regarding the technical implementation of the process. Hawthorne and others (2008) have also simulated the carbonation/calcination process for the 1052 MWe coal-fired reference plant with an original net efficiency of 45.6%. The simulation calculated the required coal, oxygen, and fresh limestone inputs to the process and also the heat streams to be utilised in the steam cycle. The carbonation/calcination process requires an additional 1600 MWth of heat, which is approximately 40% of the total heat input to the retrofitted power plant, and results in a total CO_2 capture efficiency of 88%. The retrofitted steam cycle which includes an air separation unit (ASU) and integrated CO_2 conditioning unit with interstage cooling increases the net generated power from 1052 MWe to 1533 MWe, resulting in an overall electric efficiency of 39.2%.

6.4   Membranes

A computer simulation was carried out by Matsumiya and others (2003) to estimate the energy and cost for a CO_2 separation process with a membrane applied to the exhaust flue gas from a 1000 MW coal combustion power plant. In membrane processes a pressure difference across the membrane is needed as a permeation driving force. Three kinds were investigated:

Table 6	Comparison of COE with other CO₂ capture technologies (Li and others, 2008)			
	COE, ¢/kWh	Capital cost, $/kW	%COE increase	Efficiency %, HHV
Amine, subcritical	8.16	2500	70	25.1
Amine, supercritical	7.69	2400	61	29.3
Amine, ultrasupercritical	7.34	2340	57	34.1
Oxyfuel	6.98	2300	46	30.6
IGCC	6.51	2120	27	31.2
Calcination/carbonation	6.31–6.54	2576–2702	36–40	31.0–32.8

The %COE increase represents in the %COE increase from the plant without CO_2 capture. For the carbonation/calcination the base plant is that of a supercritical plant.
The data for the CO_2 capture technologies other than calcination/carbonation is taken from Beér (2007)

- Decompression membrane separation process: the pressure of the supply side is almost at atmospheric pressure and that of the permeation side is decompressed by a vacuum pump.
- Compression membrane separation process: the flue gas is compressed at the supply side by a compressor and the pressure of the permeation side remains at atmospheric pressure. The energy of high pressure residue gas is recovered by an expander.
- Compression/decompression membrane separation process: the flue gas is compressed at the supply side by a compressor and the pressure of the permeation side is decompressed by a vacuum pump. The energy of high pressure residue gas is recovered by an expander.

It was found that the energy for CO_2 separation is considerably greater in the compression membrane separation process. There is little difference between the consumed energies of the decompression membrane separation process and the compression/decompression membrane separation process. The total cost of the system is the least when the compression/decompression membrane separation process is adopted.

Lin and others (2007) agree that feed gas compression uses more power but have also pointed out that vacuum operation (decompression) of a membrane process does not save much power and uses much more membrane. Their data are shown in Table 7. They suggested that multistage separations were needed. It was also suggested that membrane processes could recover 90% CO_2 at the expense of 18% power generated but that higher permeance membranes and lower cost membrane modules are desired.

Teramoto and others (2004) noted that preliminary estimations for their BFLM process (discussed in Section 5.4) were that the energy consumption was 0.28 kWh/kg of CO_2, only 55% of the energy consumption compared with the gas absorption/stripping process using the KS-1 solvent.

Qin (2005) has claimed that the increase in cost of electricity with CO_2 capture was 34.3% for the Chembrane facilitated transport membrane hybrid process compared with 64–87% for conventional absorption/stripping. The process can reduce the capture cost to 10–20 US$/ton of CO_2 avoided. Table 8 shows the data provided.

Callahan and others (2006) have calculated that the total capture and storage compression cost for their SLIP membrane process (discussed in Section 5.1) would be 15.60 US$/ton of CO_2 avoided with the capture cost alone being 11.90 US$/ton of CO_2 avoided for a 500 MW pulverised coal power plant. Preliminary estimates by Trachtenberg and others (2006; *also* Trachtenberg, 2007), based on a process engineering model, have indicated that the enzyme based facilitated transport membrane reactor could have a CO_2 avoided cost of 27.5 US$/tonne compared with $47.1 for the MEA base case. Trachtenberg and others (2008) have compared the energy costs with those of the EU Castor project using MEA as the solvent and claim that the enzyme based permeator will have energy costs about one third of those for the MEA process.

Table 7 One-stage membrane separation – 70% CO_2 recovery (Lin and others, 2008)

Type of operation	Membrane area, 1000 m²	Power consumption		Permeate CO_2 concentration, %
		MW	%	
Vacuum operation	1800	45	7.5	63
Compression operation	250	68	11	59

Table 8 Comparison of CO_2 capture cost by chemical absorption/stripping and Chembrane membrane hybrid process (Qin, 2007)

	Conventional absorption/ stripping	Chembrane membrane process
Energy penalty for PC plant, %	22–29	12.2
Capture cost, $/t CO_2 avoided)	42–55	13.5–20
Capture cost, ¢/kWh	3.7–5.2	1.27–1.80
Increase in cost of electricity with CO_2 capture,%	64–87	34.3

In contrast to the claims of some membrane developers, Chen and others (2006) have noted that, even though the current MEA process is still too expensive and needs to be improved, current commercial membranes are still not competitive. This is shown in Figure 19. They concluded that membrane processes using high pressure operation are impractical and, further, that any separation processes that need compression of the flue gas will not be attractive. Figure 19 has been updated by Svendsen (2008) but, even so, more advanced membranes are still outside the operational area of MEA systems. Yan and others (2008) point out that statements that membrane separation systems are superior to chemical absorption are somewhat arbitrary unless and until the membrane pore wetting and plugging problems can be solved.

Ho and others (2006) examined the effect of membrane characteristics, operating parameters, and system design of membrane based CO_2 removal systems. The total cost per tonne of CO_2 avoided for separation, transport, and storage were compared for the separation of CO_2 from a black coal-fired power plant in Australia. The results showed that the membranes then available had a total cost of 55–61 US$/tonne of CO_2 avoided; a higher cost than can be achieved using an MEA absorption system. The capture cost was dominated by the costs of flue gas and post-capture compression. Later, Ho and others (2008a) investigated how costs for CO_2 capture using membranes can be reduced by operating under vacuum conditions. The flue gas is
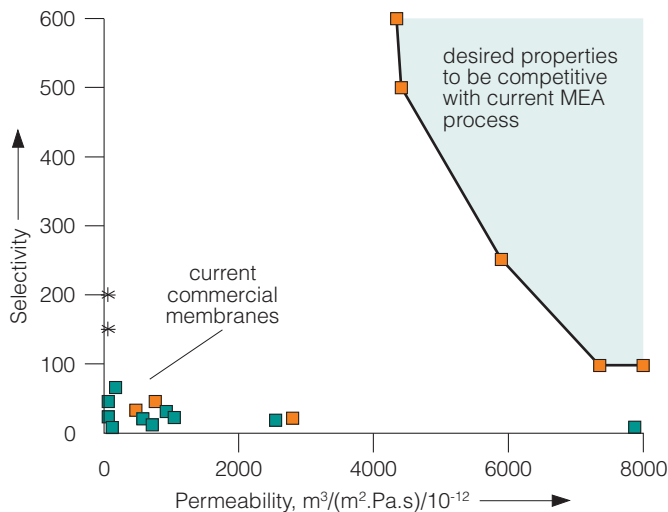
Figure 19 Current economic performance of membrane separation process and its required quality to compete with current MEA process (Chen and others, 2006)

pressurised to 15 kPa, whereas the permeate stream is at 8 kPa. Under these operating conditions, the capture cost is US$54/tonne CO_2 avoided compared with US$82/tonne CO_2 avoided using membrane processes with a pressurised feed. This is a reduction of 35%. The effect on the capture cost of improvements in CO_2 permeability and selectivity. The results show that the capture cost could be reduced to less than US$25/tonne CO_2 avoided when the CO_2 permeability is 300 barrer (2250 x10^{-18} $m^2s^{-1}Pa^{-1}$), CO_2/N_2 selectivity is 250, and the membrane cost is US$10/$m^2$. However, currently, there exist no commercial membranes with these combinations of high permeabilities and selectivities for CO_2/N_2. Additionally, it was pointed out that current commercial membranes suffer from degradation of performance over time due to a variety of factors, and operation is limited to near-ambient temperature. These are the challenges that will be needed to be overcome to make CO_2 capture using membrane technology a competitive option.

It was noted in Section 5.1 that the CO_2 concentration found in a steel mill is above the 20% limit above which the energy penalty decreases significantly (below the amine absorption threshold) and already existing dense polymer materials could

be possible candidates (Bounaceur and others, 2006a,b). An economic analysis was carried out for CO_2 separation using cardo polyimide hollow fibre membranes followed by a liquefaction process was carried out by Kazama and others (2005a). The reason for including the liquefaction stage was that, in Japan, CO_2 sources are not always close to storage sites, and so liquefaction of CO_2 would be important for transporting it.

The cost breakdown for treatment of flue gases from steel works and coal-fired power stations by membrane separation and amine absorption is shown in Figure 20. The total cost of CO_2 separation and liquefaction from an exhausted gas were estimated at 4900 JPY/t of CO_2 for a flue gas from steel works (CO_2 concentration: 26.8%) and 7300 JPY/t of CO_2 for a flue gas from a coal-fired power station (CO_2 concentration: 13.2%). The total cost of CO_2 separation and liquefaction strongly depends on the CO_2 concentration of source gases. The equivalent cost of an amine absorption was 5300 JPY/t of CO_2 for steel works. For a CO_2 concentration around 25% or more, membrane separation has an advantage in the CO_2 separation and liquefaction cost. Energy required in CO_2 separation and liquefaction was 0.28 kWh/kg of CO_2 for steel works. In the cost breakdown of CO_2 separation with a membrane, the electricity consumption of the vacuum pump, which induces a pressure difference between a feed side and a permeate side of a membrane, contributed 50% or more of the total cost. For a coal-fired power station, the total cost for membrane separation is higher, but, if the liquefaction stage is ignored, the costs are about even. The higher liquefaction costs for the membrane process reflect the CO_2/N_2 selectivity value of 81 compared with the 99% capture ability of the amine solvent.

Using Nordrhein-Westfalen as a reference power plant, Zhao and others (2008) simulated a detailed process optimisation of mass and energy balances for multistage membrane systems used for CO_2 capture. A single-stage polymer membrane can only achieve a CO_2 separation degree of 50%. Thus a two-stage cascade membrane system was developed for post-combustion capture based on an ideal feed gas composition of 14 mol% CO_2 and 86 mol% N_2. The simulation indicated an energy penalty of 8.5% points, described as 'quite promising', which approaches the lower limit of the state-of-the-art chemical absorption method with 8–14% points energy loss. The total capture cost of membrane
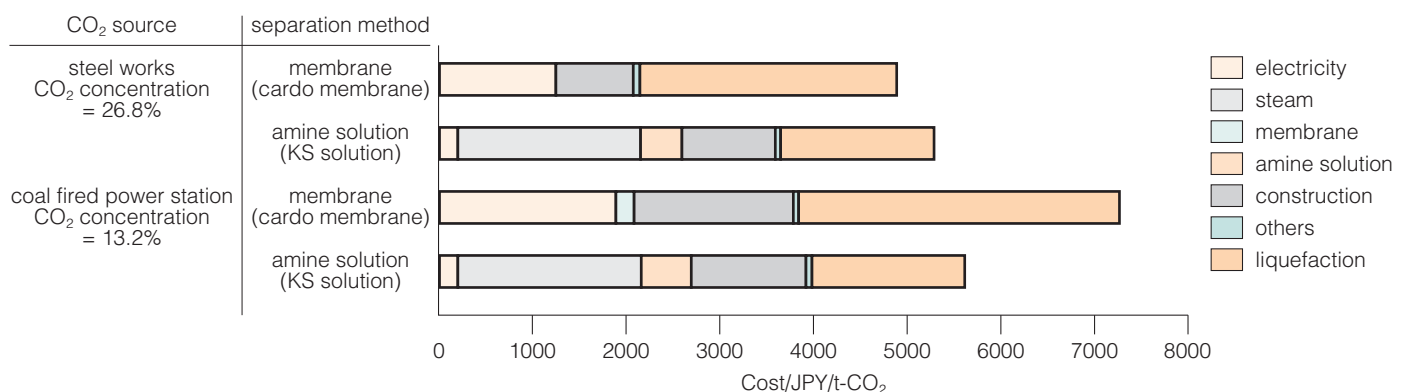
Figure 20 Cost breakdown of CO_2 separation and liquefaction of membrane separation and amine absorption from flue gases of steel works an coal-fired power station (Kazama and others, 2005)

process is dominated by the equipment cost, not energy cost for driving the system. It was suggested that if CO_2/N_2 gas separation membranes could be developed to enhance the permeability keeping the current selectivity level (43); then CO_2 capture cost could be reduced from approximately 57 to 40 €/t separated CO_2 (CO_2 permeance increased from 0.5 to 1.4 m³/m²hbar). This would be quite competitive against MEA absorption of 30–50 €/t separated CO_2. However, it was pointed out that the simulation had been performed for an ideal binary gas mixture not a real flue gas.

7   Conclusions

The preparation of this report has revealed the considerable weight of research activities into solid sorbents and membrane systems for post-combustion CO_2 capture. The aim of much of this research is cost reduction: to find a process that is cheaper than solvent scrubbing processes. NETL has produced a figure which plots the cost reduction benefits against the time to commercialisation, although both the benefits and the time are not specified (Figueroa and others, 2008). The technologies relevant to post-combustion capture are shown in Figure 21.

Simple porous solid sorbents such as activated carbons and zeolites are probably not well-suited to post-combustion CO_2 capture. Their CO_2 capacities and their CO_2/N_2 selectivities are not very high and they would need to use expensive pressure swing adsorption processes or variants of PSA. The much higher CO_2 capacity metal organic frameworks (MOFs) and their derivatives look promising but are at an early stage of development. They would need to be produced quite cheaply on a very large scale to be used for CO_2 capture in power plants and they need to be proven to work with real flue gases.

Functionalised solid sorbents, especially immobilised amine sorbents, would seem to be a logical improvement upon simple mesoporous adsorbents. However, the results of much research has not been that encouraging. It would appear that the increase in CO_2 capacity by the functional groups seems to be offset by the reduction of porosity caused by the functional groups filling the pores.

Dry, regenerable, solid sorbents have the great advantage of being cheap, especially if they are based on natural limestone. Even their loss of capacity with cycling does not seem to be that worrying if it remains at about 20–30% after ~30 cycles (Fennell and others, 2007a). This capacity is still higher than that of the simple and the functionalised porous adsorbents. However, the requirements for fresh limestone feed seem to be of the same order as the coal requirements of a plant. This would certainly limit their use for retrofitting plants unless there is a great deal of stockpile space available and probably a nearby cement plant to take the calcined waste lime produced.

Membrane systems for post-combustion CO_2 capture also appear to be at an early stage of development and possibly better-suited to use in pre-combustion applications. Their placing in the same column as solid sorbents in Figure 21 seems quite optimistic. Again, there is a need for testing with real flue gas under power plant conditions.

The potential success of solid sorbents and membranes will
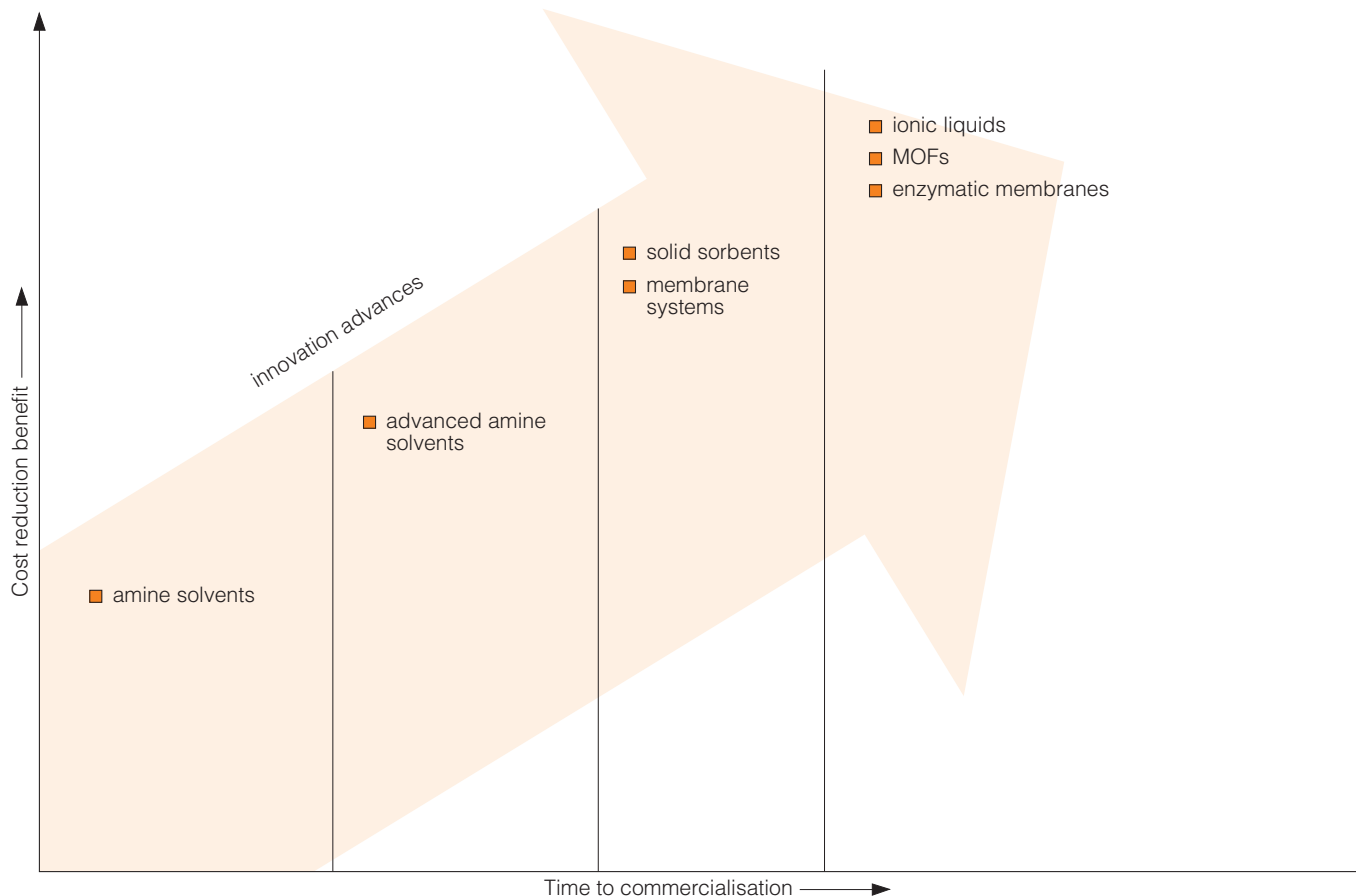
Figure 21 Innovative CO_2 capture technologies – cost reduction benefits versus time to commercialisation (Figueroa and others, 2008)

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depend on whether it is true that only limited evolution is expected in the development of chemical absorption based on amines and that significant developments will be made in the development of adsorbents and membranes. Certainly, there is scope for continued research especially concerning their behaviour in real coal-fired power plant conditions.

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