IEA
CLEAN
COAL
CENTRE

POST COMBUSTION CARBON CAPTURE FROM COAL FIRED PLANTS – SOLVENT SCRUBBING

Technical Study

Report Number: 2007/15

Date: July 2007

INTERNATIONAL ENERGY AGENCY

The International Energy Agency (IEA) was established in 1974 within the framework of the Organisation for Economic Co-operation and Development (OECD) to implement an international energy programme. The IEA fosters co-operation amongst its 26 member countries and the European Commission, and with the other countries, in order to increase energy security by improved efficiency of energy use, development of alternative energy sources and research, development and demonstration on matters of energy supply and use. This is achieved through a series of collaborative activities, organised under more than 40 Implementing Agreements. These agreements cover more than 200 individual items of research, development and demonstration. The IEA Greenhouse Gas R&D Programme is one of these Implementing Agreements.

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 its technical study reports on solvent scrubbing capture processes and the reports of its Capture Network. This report complements the reports on solvent scrubbing CO_2 capture already published by IEA GHG and it also provides information on the state of the art of solvent scrubbing processes which has become available since the publication of the IPCC Special Report on CCS. It is therefore being provided to IEA GHG's members, with the permission of IEA CCC. IEA CCC, in cooperation with IEA GHG, is producing a companion review of non-solvent CO_2 capture processes.

ACKNOWLEDGEMENTS AND CITATIONS

This report was prepared by:

IEA Clean Coal Centre
Gemini House
10-18 Putney Hill
London
SW16 6AA
UK

The principal researcher was Robert Davidson.

To ensure the quality and technical integrity of the report it was reviewed by independent technical experts before its release.

The report should be cited in literature as follows:

IEA Greenhouse Gas R&D Programme (IEA GHG), "Post Combustion Carbon Capture from Coal Fired Plants – Solvent Scrubbing", 2007/15, July 2007.

Further information or copies of the report can be obtained by contacting the IEA GHG Programme at:

IEA Greenhouse R&D Programme, Orchard Business Centre, Stoke Orchard, Cheltenham, Glos., GL52 7RZ, UK
Tel: +44 1242 680753 Fax: +44 1242 680758
E-mail: mail@ieaghg.org
www.ieagreen.org.uk

DISCLAIMER

This report was prepared as an account of work carried out by the IEA Clean Coal Centre, making extensive use of information from the IEA Greenhouse Gas R&D Programme. The views and opinions of the author expressed herein do not necessarily reflect those of the IEA Greenhouse Gas R&D Programme, the IEA Clean Coal Centre, their members, the International Energy Agency, nor any employee or persons acting on behalf of any of them. In addition, none of these make any warranty, express or implied, assumes any liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights, including any party's intellectual property rights. Reference herein to any commercial product, process, service or trade name, trade mark or manufacturer does not necessarily constitute or imply an endorsement, recommendation or any favouring of such products.

COPYRIGHT

Post-combustion carbon capture from coal fired plants – solvent scrubbing

Robert M Davidson

CCC/125

July 2007

ISBN 92-9029-444-2

Abstract

The potential use of solvents for carbon dioxide capture from the flue gas from coal fired power plants is reviewed. After an introduction to solvent absorption of CO_2, the use of alkanolamine solvents, particularly monoethanaloamine (MEA) is considered. The degradation of solvents in the flue gas environment and the consequent corrosion problems associated with the degradation products is then examined. The energy consumption for regeneration of the solvents is a key feature in determining the overall costs of solvent scrubbing. There is considerable research on alternative solvents to MEA which have higher capacity for CO_2 capture and lower energy consumption among other attributes. The design of the absorption contactors which facilitate the contact and interaction of the gas and liquid phases can also contribute to lowering the energy consumption of the overall process. Techno-economic studies, process modelling and simulation are also reviewed. Some details of existing demonstration and pilot plants and current national and international R&D programmes are given. Finally, the potential environmental aspects of the solvent scrubbing processes are briefly examined.

This report has been prepared and published in cooperation with the IEA Greenhouse Gas R&D Programme (www.ieagreen.org.uk)

Acronyms and abbreviations

AEEA	aminoethylethanolamine
AEPD	aminoethylpropanediol
ALA	alanine
AMP	aminomethylpropanol
ASCBT	advanced supercritical boiler/turbine
CASTOR	EU carbon dioxide capture and storage project
CCS	CO_2 capture and storage
CO2CRC	(Australian) Cooperative Research Centre for Greenhouse Gas Technologies
COCS	(Japanese) Cost Saving CO_2 Capture System
CORAL	CO_2 removal absorption liquid
DEA	diethanolamine
DEEA	diethylethanolamine
DETA	diethylenetriamine
DGA	diglycolamine
DIPA	diisopropanoloamine
DMMEA	dimethylmonoethanolamine
EDTA	ethylenediaminetetraacetic acid
EPRI	Electric Power Research Institute
FGD	flue gas desulphurisation
FTir	Fourier transform infrared
GAM	gas absorption membranes
GC/AED	gas chromatography-atomic emission detection
GC/MS	gas chromatography/mass spectroscopy
HMDA	hexamethylenediamine
HPLC-RID	high-performance liquid column chromatography-refractive index detection
IEA GHG	IEA Greenhouse Gas R&D Programme
IGCC	integrated gasification combined cycle
ITC	International Test Centre for CO_2 capture
KEPCO	Kansai Electric Power Company
KM-CDR	Kansai-Mitsubishi proprietary Carbon Dioxide Recovery process
KP-1	proprietary packing from KEPCO/MHI
KS-1	proprietary hindered amine solvent from KEPCO/MHI
LHV	lower heating value
MEA	monoethanolamine
MDEA	methyldiethanolamine
MHI	Mitsubishi Heavy Industries
MMEA	methylmonoethanolamine
NGCC	natural gas combined cycle
NMR	nuclear magnetic resonance
NOx	nitric oxide + nitrogen dioxide
PCC	post-combustion capture
pf	pulverised fuel
PP	polypropylene
ppmv	parts per million by volume
PTFE	polytetrafluoroethylene
PZ	piperazine
SMR	Super Mini Ring packing
TBD	triazabicyclodecene
TMG	tetramethylguanidine
UR	University of Regina
USCPF	ultra supercritical pulverised fuel
VLE	vapour-liquid equilibrium

Contents

1 Introduction

I like the idea of capturing carbon. 'Sheriff, there's a bunch of carbon out there, and it's terrorising decent folks hereabouts. Round it up!' (Hoggart, 2006)

In 2000, the IEA Greenhouse Gas R&D Programme (IEA GHG) organised sa workshop to stimulate world-wide collaboration and encourage practical development of CO_2 capture technology. This resulted in the inauguration of the *International Test Network for CO_2 Capture*, the original focus of which was on the capture of CO_2 using regenerable solvent-based scrubbing systems. Topper (2003) provided a brief summary of the first three meetings of the network and further summaries and copies of the presentations at the workshops can be found at its website: http://www.co2captureandstorage.info/networks/capture.htm. This report aims to draw together much of the work carried out in that area by drawing on the presentations and papers by the network members. Relevant material from other sources will also be incorporated where appropriate. The status of CO_2 capture technologies in 2000 was reviewed by Plasynski and Chen (2000) so this report will concentrate on developments since the founding of the International Test Network in that year until the 10th meeting in Lyon, France, in 2007. Recently, a short overview on capturing CO_2 has been produced by IEA GHG (2007a) and Epp and others (2007) have also reviewed post-combustion CO_2 capture.

The importance of CO_2 capture is that it represents 75–80% of the cost of CO_2 capture and storage (CCS), the balance being the cost of transport and storage. Compression, transport, and storage of CO_2 are not addressed in this report.

Audus (2001) assessed the leading options for the capture of CO_2 at power stations. Five CO_2 capture processes were discussed:

- a pulverised coal (pf) power plant working on a super-critical steam cycle with CO_2 capture by scrubbing the flue gas with monoethanolamine (MEA);
- coal feed to an integrated gasification combined cycle (IGCC) with shift conversion of the synthesis gas and CO_2 capture by a physical solvent;
- a natural gas combined cycle (NGCC) with CO_2 capture by MEA scrubbing;
- a NGCC with MEA scrubbing and partial recirculation of the flue gas; and
- partial oxidation of natural gas, followed by shift conversion, CO_2 capture in a physico-chemical solvent, and combustion of hydrogen in a combined cycle.

Although it was then 'accepted wisdom' that MEA was the preferred solvent for CO_2 capture from flue gases, there were problems that needed to be addressed. These included:

- its rate of degradation in the oxidising environment of a flue gas;
- the energy needed for solvent regeneration; and
- corrosion inhibition.

The problems also arise from the characteristics of post-combustion CO_2 capture systems treating flue gas from 'conventional' power plants:

- CO_2 partial pressures are relatively low which is one reason for the resulting significant energy requirements for solvent regeneration; and
- as low pressure 'back end' processes, the flue gas volumes to be treated, and hence equipment sizes, are relatively large (Gibbins and others, 2005).

Plasynski and Chen (2000) have pointed out that the energy required using MEA as a sorbent can cause a 20% reduction of power generation for a pulverised fuel (pf) power plant. A reference example comes from the Ratcliffe power station in the UK (Panesar and others, 2006). At present the thermal efficiency of this station is 38.9% (LHV). If the plant is retrofitted with Advanced Supercritical Boiler/Turbine (ASC BT) technology the efficiency would rise to 44.9%. Further addition of an amine scrubbing CO_2 capture plant would then reduce the efficiency by 20.9 to 35.5%. That is a reduction of 9.4 percentage points for a bituminous coal station. Interestingly, adding post-combustion to a brown coal fired plant has been calculated to produce the same net electrical efficiency of 35.5% (IEA GHG, 2006a).

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 MEA but that the development of ceramic and metallic membranes should produce membranes significantly more efficient at separation than liquid absorption. Ducroux and Jean-Baptiste (2005) agree and have noted that, although chemical solvent absorption is the main commercial process on the market, only limited evolution is expected in this field. They suggested that adsorbents and membranes may be subject to significant developments. However, given the large volume of work that has been reported in recent years, this review will concentrate solely on CO_2 capture by solvent absorption from flue gas. Other post-combustion capture processes will be examined in a future IEA Clean Coal Centre report.

A recent report on CO_2 capture as a factor in power station investment decisions (IEA GHG, 2006c) concluded that, specifically for coal fired plant options, post-combustion capture is viewed as the best available technology, despite the fact that it has not been fully demonstrated.

1.1 Solvent absorption

The IPCC's special report on carbon dioxide capture and storage provides a short description of solvent absorption processes in post-combustion capture (IPCC, 2005). The flow diagram of a commercial operation system is shown in Figure 1.

The cooled flue gas is brought into contact with the solvent in the absorber at temperatures typically between 40 and 60°C,

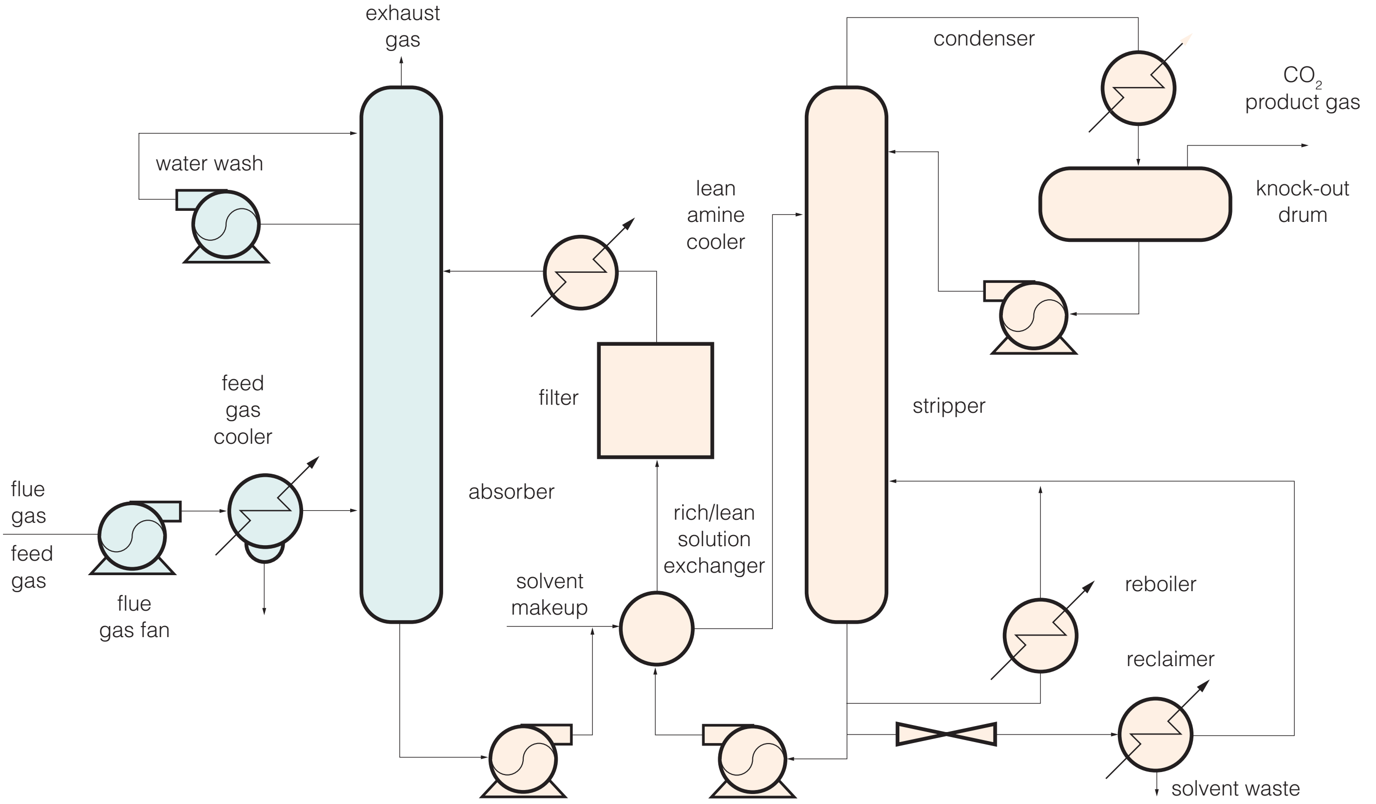


Figure 1 Process flow diagram for CO_2 recovery from flue gas by amine absorption (IPCC, 2005)

CO_2 is bound by the chemical solvent in the absorber. The flue gas is then water washed to balance water in the system and to remove any solvent droplets or solvent vapour carried over, and then it leaves the absorber. It is possible to reduce CO_2 concentration in the exit gas down to very low values, as a result of the chemical reaction in the solvent, but lower exit concentrations tend to increase the height of the absorption vessel. The 'rich' solvent, which contains the chemically bound CO_2 is then pumped to the top of a stripper (or regeneration vessel), via a heat exchanger. The regeneration of the chemical solvent is carried out in the stripper at elevated temperatures (100–140°C) and pressures not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to the stripper, whereas the CO_2 product gas leaves the stripper. The 'lean' solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level (IPCC, 2005).

The IPCC (2005) report also identified the key parameters determining the technical and economic operation of a CO_2 absorption system:

- *Flue gas flow rate* – the flue gas flow rate will determine the size of the absorber and the absorber represents a sizeable contribution to the overall cost.
- *CO_2 content in flue gas* – since flue gas is usually at atmospheric pressure, the partial pressure of CO_2 will be as low as 3–15 kPa. Under these low CO_2 partial pressure conditions, aqueous amines (chemical solvents) are the most suitable absorption solvents.
- *CO_2 removal* – in practice, typical CO_2 recoveries are between 80 and 95%. The exact recovery choice is an economic trade-off, a higher recovery will lead to a taller absorption column, higher energy penalties and hence increased costs.
- *Solvent flow rate* – the solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters and also the chosen CO_2 concentrations within the lean and the rich solutions.
- *Energy requirement* – the energy consumption of the process is the sum of the thermal energy needed to regenerate the solvents and the electrical energy required to operate liquid pumps and the flue gas blower or fan. Energy is also required to compress the CO_2 recovered to the final pressure required for transport and storage.
- *Cooling requirement* – cooling is needed to bring the flue gas and solvent temperatures down to temperature levels required for efficient absorption of CO_2.

The *energy requirement* is a key feature since a large amount of heat is required to regenerate the amine. This heat is typically drawn from the steam cycle and significantly reduces the net efficiency of the power plant (Rao and Rubin, 2002).

For flue gas from coal firing, it is worth adding the sensitivity of the solvent to sulphur dioxide, nitrogen oxides (NOx), and particulates. It is generally recognised that the flue gas must contain very low levels of SO_2 and NOx. The preferred SO_2

concentration is usually set at between 1 ppmv and 10 ppmv. This means that post-combustion CO_2 capture on coal fired power plants requires upstream deNOx and flue gas desulphurisation (FGD) (IEA GHG, 2007b).

The remainder of this report will concentrate on the science and technology of post-combustion capture using solvent absorption processes.

2 Amine solvents

The solvent most frequently encountered for CO_2 capture is monoethanolamine (MEA), an amine solvent, strictly an alkanolamine solvent but the simpler term is most often encountered. Rochelle (2000) briefly outlined the types of amine solvents used for CO_2 capture. These include:

- simple alkanolamines;
- primary – monoethanolamine (MEA) - $(C_2H_4OH)NH_2$;
- secondary – methylmonoethanolamine (MMEA), diethanolamine (DEA) – $(C_2H_4OH)_2NH$;
- tertiary – dimethylmonoethanolamine (DMMEA), methyldiethanolamine (MDEA);
- hindered amines;
- mildly hindered primary – alanine (ALA);
- moderately hindered – aminomethylpropanol (AMP);
- cyclic diamines – piperazine.

A thorough and detailed review of CO_2 capture from flue gas by aqueous absorption/stripping was prepared by Rochelle and others (2001). They covered the thermodynamics, mass transfer kinetics, alkanolamine degradation, and corrosion.

CO_2 solvent extraction is based on the reaction of a weak alkanolamine base with CO_2 which is a weak acid to produce a water-soluble salt. This reaction is reversible and the direction of equilibrium is temperature dependent. It can be represented in simplified form by:

$$CO_2 + 2RNH_2 \overset{\text{cold}}{\underset{\text{hot}}{\leftrightarrow}} RNHCOO^- + RNH_3 +$$

It should be noted that the precise nature of the reaction mechanism has been the subject of debate. However, quantum mechanical calculations by da Silva and Svendsen (2004, 2005, 2006b, 2007), provide support for most accepted mechanisms. Their *ab initio* results suggest that carbamate is formed in a termolecular single-step mechanism. The results also suggest that it would seem unlikely that carbamate species undergo direct conversion to bicarbonate species (da Silva and Svendsen, 2006b, 2007).

The $RNHCOO^-$ species is a carbamate ion and these can be formed by reaction with primary and secondary amines. Two moles of primary or secondary amine are needed to absorb one mole of CO_2. Tertiary amines (R_3N) cannot form carbamates because they lack a hydrogen attached to the nitrogen, instead, they form bicarbonate ions in a reaction in which water acts as a homogeneous catalyst:

$$CO_2 + R_3N \overset{H_2O}{\leftrightarrow} HCO_3- + R_3NH^+$$

The absorption capacity of tertiary amines is greater than for primary and secondary amines; one mole of tertiary amine will absorb one mole of CO_2. This advantage is offset by a lower rate of absorption though. Similarly, mildly hindered amines mainly absorb CO_2 as bicarbonate, not carbamate (Rochelle and others, 2001) so their absorption capacity approaches 1 mole for each mole of CO_2. Singh and others (2006, 2007) point out that steric hindrance by α-substituents on the amine would be expected to slow the rate of the initial reaction with CO_2 to some extent but as 1 mol of amine is released upon hydrolysis of the carbamate, the level of amine available for reaction with CO_2 increases. However, da Silva and Svendsen (2006a, 2007) caution that the name 'sterically hindered' conveys an overly simple physical interpretation of carbamate stability and that too much attention has perhaps been given to sterical effects in explaining variations in reactivity. They add that the effect of a substituent group on the stability of a species can take many forms. Substituent groups can affect donating or withdrawal of electrons through bonds. There can be energetically favourable or unfavourable interactions with groups to which the substituent is not directly bonded (this is steric hindrance). Substituent groups may also affect the accessibility of the solvent to various parts of the molecular surface, thereby changing the solvation energy.

On the basis of their quantum mechanical and solvation modelling studies, da Silva and Svendsen (2006a) found that one group of amines that stand out, in terms of the rate of carbamate formation, is the cyclic amines. They identified two factors accounting for this:

- the carbamate group on the cyclic molecules is completely accessible to solvent, leading to high solvation energies for the carbamate form; and
- the solvation energies of the neutral amines themselves are also relatively low.

Together, these two factors contribute to carbamate formation being favoured. However, the effects will vary with the structure of the cyclic amine which means that this should not be considered as some general rule.

There are also proprietary solvents such as the KS-1 solvent developed by Kansai Electric Power Company (KEPCO) and Mitsubishi Heavy Industries (MHI) (Mimura and others, 2001; Imai, 2002). The KS-1 solvent is a hindered amine which 'has lower amine consumption than the MEA process, but it is still high.' In the case of MEA, amine consumption is usually 2 kg/t of CO_2 recovered (Mimura and others, 2003).

MEA has several advantages over other commercial alkanolamines, such as high reactivity, low solvent cost, low molecular weight and thus high absorbing capacity on a mass basis, reasonable thermal stability and thermal degradation rate. Studies have been directed at finding new amines that are able to capture greater amounts of CO_2 than MEA and also to avoid its disadvantages. These include high enthalpy of reaction with CO_2 leading to higher desorber energy consumption, the formation of stable carbamate, and also the formation of degradation products with COS or oxygen-bearing gases, inability to remove mercaptans, vaporisation losses due to high vapour pressure, and more corrosive effects than many other alkanolamines, thus needing corrosion inhibitors when used in higher concentration (Ma'mun and others, 2005).

2.1 Solvent concentration

Normally, MEA solutions for acid gas absorption contain about 30 wt% MEA. However, Aboudheir and others (2001) reported pilot plant studies on MEA systems at ultra-high concentration, up to 54 wt%. The reasoning behind the studies was that by increasing the amine concentration, its capacity would be increased thus reducing the required solution circulation and, therefore, the plant operating cost. They found that the absorption capacity of the amine was increased as its concentration increases but not a much as might be expected. Increasing the MEA concentration from 18 wt% to 30 wt% increased the CO_2 removal efficiency from about 91% to 96%. Further increasing the concentration of MEA to 54% resulted in a removal efficiency increase to 98%. This was attributed to the high acid-gas vapour pressure over the solution which increases with the MEA concentration, and the heat of reaction which causes the temperature of the solution to increase.

Parametric studies of CO_2 absorption into highly concentrated monoethanolamine solutions was investigated by deMontigny and others (2001). They examined the effects on the overall mass transfer coefficient ($K_G a_v$). The range of concentrations studied was from 3 kmol/m^3 (18 wt%) to 9 kmol/m^3 (55 wt%). It was found that the $K_G a_v$ declined slightly as the concentration increased but then began to rise again at higher concentrations, as shown in Figure 2. This effect was explained by the hindrance of viscosity being overcome by the overwhelming presence of free amine molecules.

In the pilot plant at the natural gas fired Seoul power plant, Eum and others (2005) studied the effects of MEA concentration at 10, 15, and 25 wt%. The 15 wt% and 25 wt% MEA concentration achieved more than 90% CO_2 recovery when the MEA flow rate was above 2.5 m^3/h. The CO_2 recovery with the 10 wt% MEA was much lower but could be raised to over 95% if the MEA flow rate was increased to approaching 3.5 m^3/h. It was suggested that the optimal conditions were 15 wt% MEA at a flow rate of 3.0 m^3/h.

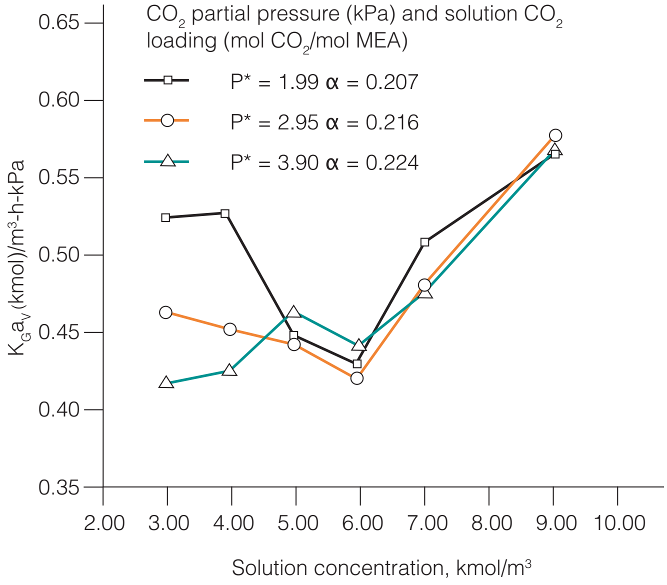


Figure 2 Effect of solution concentration on $K_G a_v$
(DeMontigny and others, 2002)
L = 7.4 m^3/m^2-h G′ = 8.83 mol/m^2-s
CO_2 feed = 15% Packing: IMTP#15

Simulation studies by Abu-Zahra and others (2006, 2007a,b) showed that the thermal energy requirement decreased substantially with MEA concentration. Upon an increase of the MEA concentration from 30 wt% to 40 wt%, the thermal energy requirement decreased by 5–8%. The cost per tonne of CO_2 avoided could be reduced to 33 €/t using a 40% MEA concentration. At 20% MEA concentration this rose to at least 56 €/t.

3 Solvent degradation and corrosion

Solvent degradation and corrosion are related topics in that the degradation products of solvent degradation are commonly associated with the corrosiveness of the solvent solution.

3.1 Degradation

The degradation of alkanolamine solvents has been reviewed by Rochelle and others (2001). There are three main degradation routes:

- carbamate polymerisation;
- oxidative degradation;
- thermal degradation.

Carbamate polymerisation is insignificant at temperatures below 100°C and thermal degradation takes place at temperatures above 205°C. Most degradation is a result of the presence of oxygen in the flue gas.

Supap and others (2001a,b) note that severe operational difficulties are always encountered using amines. One of which is that the amines undergo degradation with oxygen which often contaminates the gas stream; it is usually present in flue gas. They attempted to get a better understanding of the degradation kinetics, essential for a better understanding of the degradation mechanism which could lead to the development of a degradation control technique. To determine the degradation rate of MEA, test solutions were analysed by gas chromatography/mass spectroscopy (GC/MS). It was found that the degradation of MEA depended on temperature, initial MEA concentration, and oxygen concentration. However, the degradation did not follow a simple rate equation; the reaction order changed from a low to a high value as the concentration of MEA increased. An empirical rate equation was produced and calculated rates of degradation were in good agreement with the observed rates within a temperature range of 120 to 170°C. The values obtained for the reaction orders for MEA and O_2 imply that oxidative degradation of MEA is more sensitive to increases in the O_2 concentration than in the MEA concentration. Even though the experimental conditions allowed the reaction to be modelled as a homogeneous liquid-phase reaction, it was concluded that MEA oxidative degradation itself is not an elementary reaction.

Chi and Rochelle (2002) studied the oxidative degradation of MEA at 55°C by measuring the rate of evolution of NH_3 from the amine solution using Fourier transform infrared (FTir) analysis. They found that oxidation rates with 0.4 mol CO_2/mol MEA were 2 times faster than rates in CO_2 unloaded solutions with no additional iron. Iron is an important catalyst in oxidation of MEA to NH_3. The steady state rate of NH_3 production depends linearly on the concentration of the ferrous (Fe^{2+}) ion. However, the ferric (Fe^{3+}) ion did not appear to catalyse oxidation in unloaded MEA. Neither Fe^{2+} nor Fe^{3+} caused degradation to NH_3 without O_2 in loaded or unloaded MEA. It was concluded that the hydroxide radical was responsible for the degradation of MEA to NH_3 based on the evidence that hydrogen peroxide reacts with MEA in the absence of O_2 to produce 1 mol NH_3/mol H_2O_2.

Goff and Rochelle (2003a,b) noted that earlier studies had shown that the degradation products are oxidised fragments of the amine including NH_3, formate, acetate, and peroxides and that the degradation could be catalysed by the presence of various multivalent cations such as iron, copper, nickel, and chromium. Dissolved iron will always be present in the absorber as a corrosion product and copper (II) salts are often added as corrosion inhibitors. Experiments were performed with CO_2 loadings of 0.4 and 0.15, corresponding to the conditions at the top and bottom of the absorber. The oxidative degradation rate of the MEA was again determined by measuring the evolution of NH_3 from the amine solution. It was found that the degradation rate of solutions with high CO_2 loadings increases with increase in the concentration of dissolved iron. The addition of copper further catalyses the degradation rates. At the lower CO_2 loading, it was found that the degradation was faster.

Goff and Rochelle (2004a) also pointed out that MEA, by itself, is a known corrosion inhibitor in aqueous solutions in the absence of CO_2. They suggested that the higher than expected dissolved iron found in plant tests is most likely due to complexing of MEA carbamate with iron. Amine carbamates are known complexing agents. Goff and Rochelle (2004a,b, 2005) reported that, under laboratory conditions, the degradation rates can be mass transfer controlled by the rate of physical absorption of O_2. They concluded that degradation in industrial conditions is probably O_2 mass transfer limited.

Sexton and Rochelle (2006; *see also* Dugas and others, 2007) studied the oxidative degradation of aqueous MEA and piperazine and analysed the products using ion chromatography. The four carboxylic acids (formate, glycolate, oxalate, and acetate) were identified as reaction products of amine degradation. In addition, nitrite, nitrate, and ethylenediamine were found to be significant amine degradation products. Based on the most recent ion chromatography analysis, formate and nitrite were the most abundant products of the oxidative degradation of monoethanolamine in the absence of an inhibitor. Calculated concentrations of products from a high gas flow degradation apparatus confirmed that formate is more abundant than acetate and glycolate. However, nitrate and nitrite concentrations were very low in the high gas flow degradation apparatus. This lends to the hypothesis that nitrate and nitrite are formed through an initial NOx degradation product, which is stripped out in the high gas flow apparatus.

Chi and Rochelle (2002) had reported that ethylenediaminetetraacetic acid (EDTA) and N,N-dihydroxyethyl glycine (bicine) were found to decrease the rate of oxidation in the presence of iron by 40–50%. Goff and Rochelle (2003a, 2004b) tested several inhibitors and chelating agents including EDTA, N,N-dihydroxyethyl glycine (bicine), methyldiethanolamine, and phosphate, as possible degradation inhibitors. Only EDTA was found to be effective. EDTA added at a ratio as low as 1:1 with the dissolved metals resulted in decreasing the degradation rate by half. It was also more effective at inhibiting the degradation catalysed by copper than by iron. Goff and Rochelle (2006) studied several categories of additives that might minimise oxidative degradation of MEA:

- O_2 scavengers and reaction inhibitors – hydroquinone, manganese salts, ascorbic acid, a proprietary 'Inhibitor A', Na_2SO_3, and formaldehyde;
- chelating agents – EDTA, sodium phosphate, and Na_2S_4;
- stable potassium salts – KCl, KBr, and the formate.

They found that only the O_2 scavengers and reaction inhibitors showed a significant enough reduction in the rate of NH_3 evolution to make these viable additives in an industrial application. The proprietary reaction inhibitor was the most attractive of the tested additives. It was found to be effective at inhibiting oxidative degradation catalysed by either or both Fe and Cu although higher concentrations were needed if both were present. Na_2SO_3 and formaldehyde were also found to be effective oxidation inhibitors and are independent of the concentration of CO_2. However, hydroquinone, ascorbic acid, $MnSO_4$, and $KMnO_4$ all increased the rate of NH_3 evolution. The chelating agents proved not to be viable additives since EDTA loses inhibiting capacity with time while phosphate was fairly ineffective as an inhibitor. The stable potassium salts were also ineffective.

Strazisar and others (2002, 2003) studied the collected MEA degradation products in the reclaimer bottoms from the IMC Chemicals Facility in Trona, CA, USA. The reclaimer bottoms represent the residue after the MEA is distilled to remove the degradation products. Combined gas chromatography-mass spectroscopy (GC-MS), combined gas chromatography-Fourier transform infrared absorption spectroscopy (GC-FTIR), and combined gas chromatography-atomic emission detection (GC-AED) were used to identify compounds in the reclaimer bottoms. Several of the compounds observed had been seen in earlier studies but there were some major products that had not been previously observed. Strazisar and others (2003) concluded that their results clearly indicated that there were chemical degradation reactions that occur under plant conditions that do not occur in laboratory experiments with pure gases. They found that carbamate dimerisation, a result of reaction between CO_2 and MEA at high temperatures, was a relatively minor degradation pathway. Acetylated MEA components were the most abundant degradation components and were believed to be the result of reactions between acetic acid and MEA. It was noted that some of the degradation products identified could have been formed in the reclaimer itself rather than in the stripper.

Wilson and others (2003a, 2004) found three major heat stable salts in the MEA solvent used in their pilot unit. These were sulphates, oxalates, and thiocyanates and were formed by the oxidation of MEA. the concentration of the salts increased gradually and reached a maximum of approximately 0.5 wt% within 10 days of operation.

There were also differences in the degradation product slates when the data from the Boundary Dam demonstration plant were compared with those from the University of Regina (UR) natural gas fired technology development plant (Wilson and others, 2005a; Idem and others, 2006a). A wider variety of degradation products were observed in the coal fired Boundary Dam demonstration plant samples, including sulphur compounds, than in samples from the UR pilot plant (*see* Section 3.3). This illustrates the effect of the harsher environment brought about by a coal fired power plant flue gas. Another factor involved could have been the corrosion inhibitor used in the Boundary Dam plant but not in the UR plant. The inhibitor appeared to be a factor in the drastic reduction of the heat duty for regeneration as well as the boosting of the CO_2 loading in the rich MEA. It is possible that the inhibitor may be acting as a catalyst to facilitate degradation reactions. Bello and Idem (2006; *also* Uyanga and Idem, 2007) have reported that the use of sodium metavanadate ($NaVO_3$) as an inhibitor was detrimental to MEA and acted as a catalyst to accelerate MEA degradation.

A comparative study of techniques for analysis of MEA and its degradation products was performed by Supap and others (2006). Gas chromatography-mass spectroscopy (GC-MS) using an intermediate polarity column was found to be the best choice for analysing the degradation products but a high polarity column performed better for analysis of MEA itself. If simultaneous analysis of MEA and its degradation products was required then high-performance liquid column chromatography-refractive index detection (HPLC-RID) was the best and only technique that could accomplish this. The study also revealed that the presence of CO_2 induced more stable products. Therefore, further degradation by reaction with MEA was reduced. Thus, the rate of MEA degradation was seen to be lower than that in the system including O_2 alone.

The pathways for the formation of oxidative products from CO_2 loaded concentrated aqueous MEA solutions during CO_2 absorption from flue gas were studied by Bello and Idem (2005). The effects of temperature, O_2 pressure, MEA concentration, and CO_2 loading on MEA degradation under typical absorber and stripper conditions were examined. The results showed that an increase in temperature or O_2 pressure for both MEA-H_2O-O_2 and MEA-H_2O-O_2-CO_2 resulted in an increase in degradation. An increase in the MEA concentration resulted in the opposite effect for all systems. Reaction pathways were proposed that showed that, in the MEA-H_2O-CO_2 system, O_2 is produced as a degradation product, implying that, even if O_2 was not initially present in the feed gas stream, an oxidative degradation environment could still be created. The number of products and the extent of degradation decreased in the order MEA-H_2O-O_2 > MEA-H_2O-O_2-CO_2 > MEA-H_2O-CO_2. A general mechanistic rate model produced by Bello and Idem (2006) also showed that, in a CO_2 loaded system, the loaded CO_2 acts as a degradation inhibitor. They carried out a comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous MEA with and without sodium metavanadate during CO_2 absorption from flue gases. The sodium metavanadate ($NaVO_3$) is a corrosion inhibitor. The results showed that the presence of $NaVO_3$ and increases in MEA concentration, temperature, or O_2 pressure resulted in an increase in the MEA degradation rate. In contrast, an increase in CO_2 loading led to a decrease in the degradation rate.

The products and pathways for the oxidative degradation of CO_2-loaded and concentrated aqueous solutions MEA and MEA/MDEA mixtures have been studied by Lawal and others (2005). The results showed fewer degradation products were obtained for MEA for both the CO_2-loaded and CO_2-free cases than for the MEA/MDEA mixture. Also, fewer degradation products were obtained with the CO_2-loaded case than for the CO_2-free case for both systems. The results indicate that MDEA is more prone to oxidative degradation and, when used in a mixture with MEA, is preferentially degraded thus protecting the MEA. Even in an oxygen free system, O_2 is produced as a by-product of CO_2-induced degradation. Lawal and Idem (2006) reported that the rates of degradation of MEA and MDEA in the MEA-MDEA-H_2O-CO_2 system were practically zero but both the MEA-MDEA-H_2O-O_2 and the MEA-MDEA-H_2O-CO_2-O_2 systems had rates greater than zero. A higher CO_2 loading in the MEA-MDEA-H_2O-CO_2-O_2 system resulted in a reduction in the rate of MEA and MDEA degradation because of the ability of CO_2 to reduce the solubility of O_2 in the amine.

3.2 Corrosion

The knowledge of corrosion and corrosion control in CO_2 capture units using reactive amine solvents has been reviewed by Rochelle and others (2001) and also by Veawab (2003; *see also* Veawab and others, 1999). Veawab (2003) noted that carbon dioxide capture units using reactive amine solvents are constantly subject to excessive corrosion problems. Based on plant experiences, corrosion takes place in almost every section of the plants. She also noted that corrosion in amine treating plants is influenced by a number of factors including CO_2 loading, amine type and concentration, temperature, solution velocity, and degradation products. CO_2 loading or content in the amine solution is considered to be the primary contributor. Of the ways of suppressing corrosion, the use of corrosion inhibitors is considered to be the most economical method.

Veawab and others (1999) found that the corrosivity of CO_2 saturated amines was affected primarily by the CO_2 loading but also by amine type. The corrosivity decreases in the order MEA > AMP > DEA > MDEA. At first, increasing the amine concentration accelerates the system corrosion rate which then decreases gradually as the amine concentration increases further. The effect of amine type probably reflects the differences in the amounts of CO_2 absorbed into the solutions; the greater the CO_2 loading, the higher the corrosion rate. When the differences in CO_2 loading were eliminated the corrosion rates in MEA and DEA were comparable whereas the corrosion rate in AMP was higher.

Although the corrosion mechanism in an aqueous CO_2 solution is not well understood, simulation studies by Veawab and Aroonwilas (2002) have indicated that the bicarbonate ion (HCO_3^-) contributes significantly to corrosion due to its high rate of reduction while water (H_2O) plays a dominant role due to its high concentration in aqueous amine solvents. The hydrogen ion (H^+) or the hydronium ion (H_3O^+) play an insignificant role in the reduction reaction due to the extremely low concentration in amine solutions. A schematic representation of the corrosion process is shown in Figure 3.

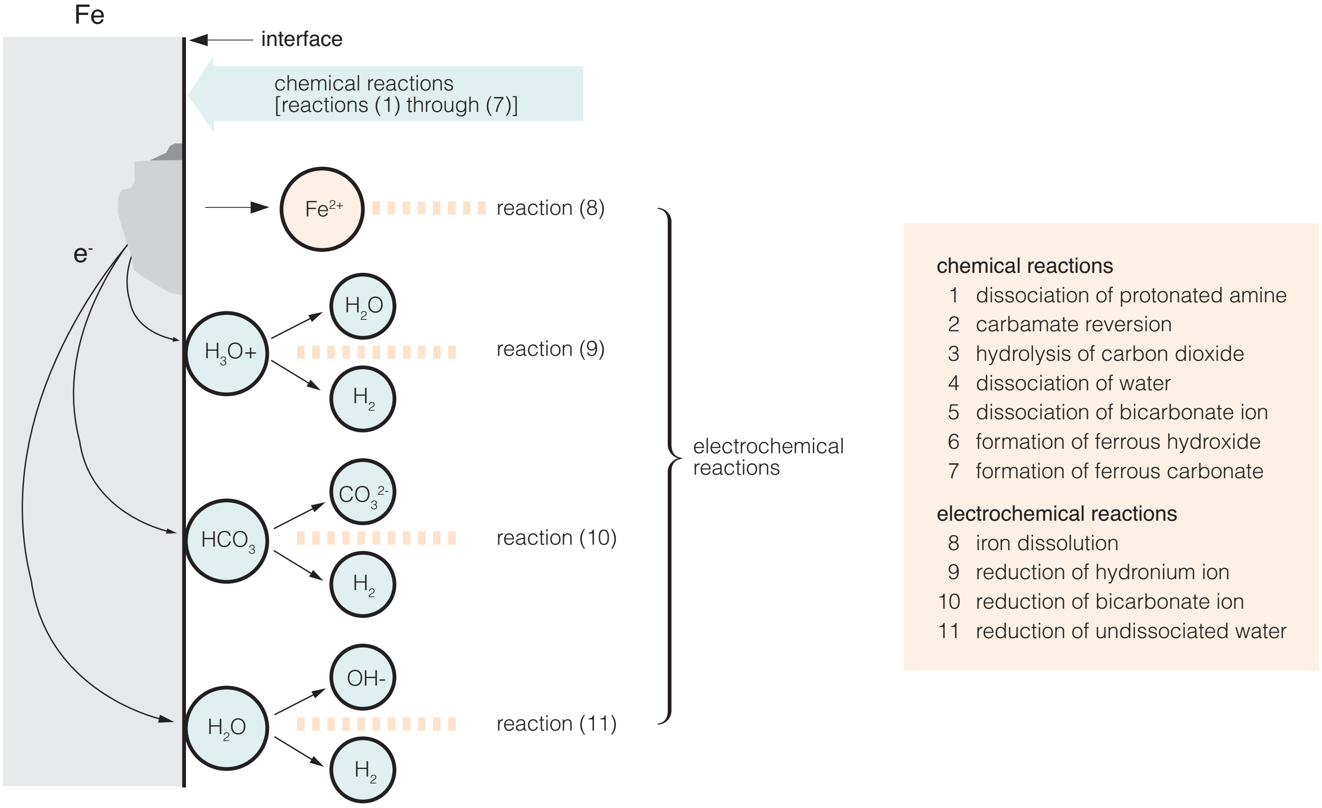


Figure 3 Schematic representation of corrosion process in an aqueous amine-CO_2 environment (Veawab and Aroonwilas, 2002)

The heat stable salts caused by solvent degradation may cause increases in the corrosiveness of the solvent. Tanthapanichakoon and Veawab (2003; *also* Tanthapanichakoon and others, 2006) noted that the knowledge of the corrosiveness of these salts was limited. They examined the corrosion behaviour of carbon steel specimens in aqueous solutions of MEA containing various heat stable salts using electrochemical techniques. It was found that all the test heat stable salts, including acetate, chloride, formate, glycolate, oxalate, succinate, and sulphate, aggravated corrosion of carbon steel. Oxalate was the major contributor to an increased corrosion rate. The effect of heat stable salts on the corrosion of stainless steel 304 was examined using oxalate as a representative salt since it was the most corrosive (Tanthapanichakoon and others, 2006). The experimental results suggested that the presence of oxalate did not deteriorate the corrosion resistance of stainless steel, or have any apparent impact on the corrosion behaviour. None of the salts tested showed a pitting tendency on either carbon steel or stainless steel.

The corrosion effects that may exist in amine treating plants containing a mixture of heat-stable salts was investigated by Srinivasan and Veawab (2006). A series of six salt combinations of formate, oxalate, bicine, acetate, thiosulphate and chloride were tested for the study of salt interaction effects. The results show that the presence of more than one heat-stable salt in the solution did not necessarily increase the corrosion rate although salt concentration was increased. The salt mixture could in fact cause the corrosion rate to either increase or decrease, depending upon type of salts. The increase in corrosion rate was pronounced for the solution containing six salts. The corrosion rate of six salts was approximately 15 times greater than that of solution containing no salt. Thus, the salt mixtures can result in synergistic effects on corrosion rate and pitting tendency. Such effects can be neutral, positive and negative depending upon the salt combination and their interactions. The neutral and positive synergy is undesirable due to the increased corrosion rate, whereas the negative synergy is desirable due to the decreased corrosion rate. Three salt mixtures exhibited positive interaction effect on corrosion rate: formate-oxalate-thiosulphate, and formate-bicine-oxalate-thiosulphate, and formate-acetate-bicine-oxalate-HCl-thiosulphate. It was suggested that the solution should be regularly analysed for acetate, hydrogen chloride, thiosulphate and oxalate since these salts tend to induce the positive synergy.

Veawab and others (2001; *see also* Veawab, 2003) pointed out that inorganic corrosion inhibitors are more favoured in practice than organic compounds because they have superior inhibition performance. However, there are environmental and health concerns about the impact of the use of toxic heavy metal corrosion inhibitors. They investigated low-toxicity organic compounds as an alternative to the extensively used sodium metavanadate (NaVO$_3$). Of these, carboxylic acids have the best inhibition performance (as high as 92%), followed by sulphoxides and long-chain aliphatic amines. The performance of the organic inhibitors improved as their concentration increased. Solution temperature was also found to have a significant effect. An increase in the solution temperature from 40 to 80°C led to a greater inhibition performance. The performance of NaVO$_3$, in contrast, remains high regardless of temperature.

As part of the EU CASTOR project (see Chapter 9), Kittel and others (2006; see also Broutin and others, 2005) have developed an experimental procedure for rapid assessment of corrosion in amine solutions using a pressure vessel under controlled loading conditions. Corrosion tests were performed by weight loss measurements of specimens exposed in the pressure vessel. After preliminary tests with 30% MEA, the testing protocol was applied to measure the corrosion rates of carbon steel and stainless steels in diethylenetriamine (DETA), diethylethanolamine (DEEA) and in a specific solvent formulated within the CASTOR project (referred to as CASTOR 1 solvent). Finally, real solvent (MEA) sampled in the CASTOR pilot plant was also tested. The corrosion rates are summarised in Table 1. The following ranking could be proposed for the corrosivity of different solvents : MEA 30% ≈ DETA 5M $ MEA 30% + inhibitor >> DEEA 2.5M $ CASTOR 1. For all tested solvents, stainless steel AISI 316 was fully resistant. It was noted that the corrosion inhibitor added to MEA 30% offered an efficiency of only 50%, far less than the values usually expected when using inhibitors (>90% efficiency).

Corrosion rates in the CASTOR gas treatment pilot plant were easily monitored by weight loss coupons inserted in the pilot plant. A period of 15 days immersion was sufficient to detect

Table 1 Comparative corrosion rates in μm/y of laboratory tests of different solvent compositions (Kittel and others, 2006)

	AISI 1028 carbon steel	AISI 304 stainless steel	AISI 316 stainless steel
MEA 5 M (30%)	420	55	14
MEA 5 M + inhibitor*	215	< 1	< 1
DETA 5 M (60%)†	615	9	7
DEEA 2.5 M	23	< 1	< 1
CASTOR 1 solvent	< 5	< 1	<1

* real solvent that was sampled in the CASTOR pilot plant

† the DETA concentration of the test was erroneously 5 M (60 wt%) when a concentration of 2.5 M (30 wt%) should have been tested

with a good accuracy the sections with high risks of corrosion. In the pilot plant, and with the reference solvent (30% MEA + inhibitor), the corrosion rate of carbon steel was considerable in the 'lean amine areas', at the outlet of the stripper and at the inlet of the absorber, greater than several mm/y. The areas with the 'rich solvent' exhibited far less corrosion of carbon steel: less than 10 µm/y. In the gas phases, the highest risk seemed to be for the CO_2 outlet: in the case of condensation, CO_2 saturation of the liquid phase could lead to extremely acid and corrosive situation. Some traces of condensation were observed when removing the coupons. Although the corrosion rates measured in this test remained reasonable, it is not impossible that a more severe condensation could occur at a specific area (a specific height) in the gas pipe, creating risks of local corrosion. For all monitoring points, AISI 316 stainless steel always exhibited corrosion rates lower than 50 µm/y, with no evidence of pitting or localised attack.

Solvent samples were taken at regular intervals during the first campaign using MEA as the solvent (Feron and others, 2007). It was found that the heat stable salts showed a steady increase in concentration from the start of the campaign. This coincided with a sharp increase in the iron content of the solvent, most likely as a result of increased corrosion. The standard corrosion inhibitor added to the solutions was apparently not capable of limiting the corrosive action of the solvent.

3.3 Effects of sulphur dioxide

Despite the general view that sulphur dioxide (SO_2) is highly detrimental to MEA absorption processes, there have been few recent studies to quantify its effects. Wilson and others (2005a; *also* Idem and others, 2006a) analysed the solvents used in the Boundary Dam demonstration plant and found that there was a wider variety of degradation products observed in the samples, including sulphur compounds, than in the samples from a natural gas fired test facility. The sulphur compounds may have resulted from contact of aqueous MEA with trace amount of SO_2 that survived the scrubbing process in the SO_2 unit. The presence of the sulphur compounds indicated that it was not possible to regenerate MEA from these compounds in the regeneration unit. However, in pilot tests carried out at MHI's 1 t CO_2/d pilot plant using the KS-1 solvent, an Australian coal was used and two tests were run, one with <1 ppm (dry) of SO_2 at the inlet of the CO_2 absorber and the other with 30 ppm of SO_2, other conditions remained the same. The higher level of SO_2 had no apparent effect on the CO_2 recovery performance. On the other hand, although the concentration of heat stable salts, particularly sulphates, in the form of deteriorated products in the solvent increased with the higher concentration of SO_2, it was as low as 1 wt% of the KS-1 or less.

Recently, a comprehensive study has been conducted to evaluate the contributions of SO_2 and oxygen (O_2) to the degradation of MEA during CO_2 capture from power plant flue gas (Uyanga and Idem, 2007). They also noted that the information on the effects of SO_2, NOx, and fly ash on MEA degradation is scant. The aqueous MEA was contacted with gas mixtures that had SO_2 concentrations in the range 6–196 ppm. It was found that an increase in the concentrations of SO_2 and O_2 in the gas phase and MEA in the liquid phase resulted in an increase in MEA degradation, whereas an increase in CO_2 loading in the liquid phase produced an inhibition effect to MEA degradation. It was pointed out that, if CO_2 capture is operated in the 'rich mode', whereby the lean MEA is still considerably loaded with CO_2 (for example, 0.25 mol CO_2/mol MEA) rather than the 'lean mode' but maintaining the cyclic capacity, CO_2 could actually act as a degradation inhibitor, because this reduces the amount of SO_2 and O_2 that could enter into the aqueous MEA solution to induce degradation. However, the detrimental corrosive effect of excess CO_2 in the system must be taken into account.

Studies of the effects of SO_2 have been carried out at the CASTOR pilot plant (Feron and others, 2007). The Esbjerg plant flue gas is low in SO_2 (~10 ppm) so SO_2 was added to the feed gas to bring the concentrations up to levels that are more representative of current coal fired power stations (~70 ppm). This level could not be maintained throughout the campaign so even higher levels were later added to achieve the originally intended load. At the original low SO_2 levels, its concentration in the flue was not changed by passage through the absorber. No explanation was offered but it is possible, at these low concentrations, that CO_2 is simply preferentially absorbed. At the higher concentrations, SO_2 was reduced by ~95% in the CO_2 absorber. In addition to this the SO_2 concentration was further reduced by the wash section resulting in an overall removal of nearly 99%. The SO_2 accumulates in the solvent as sulphates and other sulphur compounds, although the precise chemical interaction between SO_2 and the solvent was not determined.

The Cansolv process was originally designed for SO_2 scrubbing using a proprietary amine scrubber. Although it has not been used on coal fired plant flue gas, it has been proposed that the process is capable of integrating SO_2 regeneration with CO_2 regeneration since the same solvent can be used for both gases (Hakka, 2007). The solvent is stable to SO_2 and the process eliminates the need for caustic polishing prior to CO_2 capture.

4 Solvent regeneration

It has already been noted that the energy consumption for regeneration is a key feature in determining the overall costs of solvent scrubbing. the energy consumption is commonly referred to as *reboiler heat duty* because the total energy for solvent regeneration is provided by steam passing through the reboiler at the bottom of a regeneration column. The reboiler heat duty is essentially the sum of the energy used for:

- raising the temperature of the CO_2-loaded solution to the boiling point;
- breaking the chemical bonds between the CO_2 and the solvent; and
- generating water vapour to establish an operating CO_2 partial pressure needed for CO_2 stripping.

The level of reboiler heat duty relates directly to the quantity of CO_2 stripped from the regeneration column and the quality of the lean solution fed back to the absorption column; a higher heat duty results in a larger amount of CO_2 product and a leaner solution leaving the regeneration column (Sakwattanapong and others, 2005).

CO_2 capture by the aqueous MEA process was modelled by Freguia and Rochelle (2002, 2003). Disappointingly, an overall optimization showed that there are no economical ways to reduce the steam requirements by more than 10%. The reboiler duty can be reduced from that of a base case representing current industrial operating conditions, by 5% if acids are added to the solvent, by 10% if the absorber height is increased by 20%, and by 4% if the absorber is intercooled with a duty of one-third of the reboiler duty.

Rochelle (2003) reported simulation studies of several flowsheet alternatives for stripper configurations. Jassim and Rochelle (2006) noted that minimisation of the reboiler duty should be a primary objective as a mean of optimising the energy consumption in the stripper. They used Aspen Plus® to simulate stripper configurations and found that multipressure stripping with vapour recompression was the most attractive option. This is shown in Figure 4. Multipressure stripping integrates the stripper with the first two stages of a nine-stage compressor. The first two stages are used to increase the pressure in the stripper. The vapour from the lower-pressure zone is withdrawn to a compressor stage and then reinjected at the next-higher-pressure zone up the column. the stripper overhead vapour is not cooled but instead is routed directly to nine compressor stages. The vapour is cooled to 40°C before it is further compressed to the supercritical state. Multipressure stripping makes use of the latent heat of the overhead water vapour to reduce reboiler duty load and recovers the work of compression to strip more CO_2 within the column. It requires 3–11% less equivalent work than simple stripping.

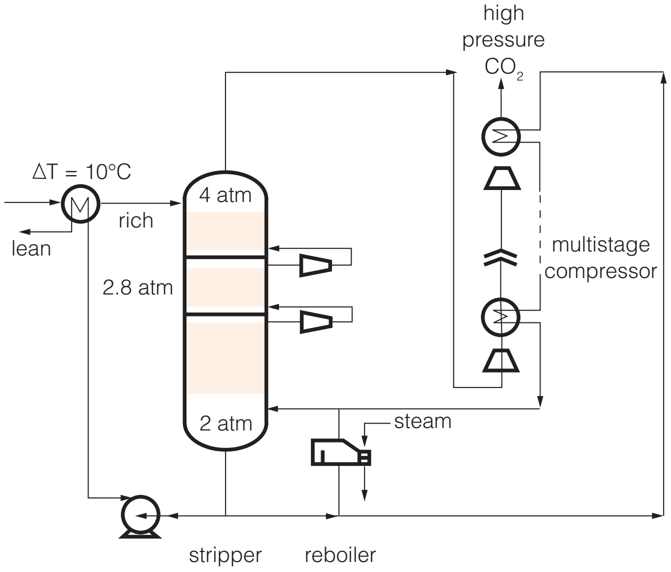


Figure 4 Multipressure stripping with vapour recompression (Jassim and Rochelle, 2006)

However, the stripper configuration may depend upon the solvent properties. Again, using Aspen Plus® modelling, Oyenekan and Rochelle (2006a; *see also* Oyenekan and Rochelle, 2005b) calculated that the solvent heat of desorption (ΔH_{des}) had an effect on the reboiler duty and the equivalent work for stripping. A vacuum stripper was found to be preferred for solvents with $\Delta H_{des} \leq 21$ kcal/(gmol of CO_2) while the multipressure configuration is attractive for solvents, such as MEA, with $\Delta H_{des} \geq 21$ kcal/(gmol of CO_2) with a rich solution of CO_2 at 40°C. Oyenekan and Rochelle (2006b) also considered alternative stripper configurations to minimise energy for CO_2 capture:

- *matrix stripper* – a novel, complex system with a number of strippers;
- *split product stripper* – in which a semi-lean solution is removed from the middle of the absorber and introduced after cross-exchange to the middle of the stripper;
- *internal exchange stripper* – internal heat exchange in the stripper alleviates the effects of temperature change across the stripper by exchanging the hot lean solution with the solution in the stripper; and
- *flashing feed stripper* – in this configuration the rich stream is split into two, one stream is cross-exchanged with the lean stream leaving the bottom of a stripper while the other is sent to a single stage flash vessel.

The results showed that the flashing feed stripper operating under near vacuum (30 kPa) was competitive with the multipressure configuration in terms of total energy requirement. Since the flashing feed operating under vacuum operates at a lower temperature, there are opportunities for the use of different materials of construction such as fibre-reinforced plastic (FRP) instead of carbon or stainless steel. The matrix stripper is also quite competitive even though more complex than the flashing feed configuration. The flashing feed configuration gives the least equivalent work at 30 kPa. The flashing feed stripper configuration is shown in Figure 5.

Aroonwilas (2005) has also pointed out that modifying the

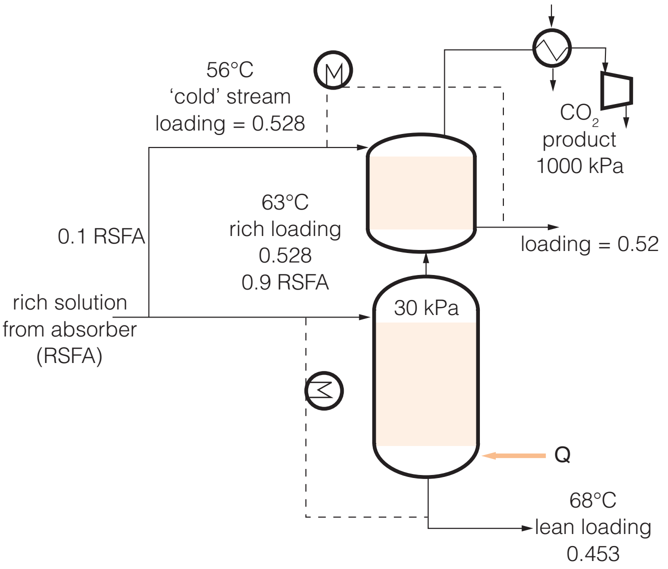


Figure 5 **Flashing feed stripper** (Oyenekan and Rochelle, 2006b)

conventional process configuration is one way of improving the efficiency of energy use. He evaluated the overall performance of a CO_2 absorption process using a split flow configuration and compared it with the performance of a conventional system. The key feature of the split flow system is the division of the CO_2 rich solution from the absorber into two streams. The first stream enters the regenerator at the top, flows downwards, leaves the regenerator at the midpoint and enters the absorber at its midpoint. The second stream enters the regenerator at the midpoint, flows downwards, leaves the regenerator at the bottom and eventually enters the absorber at the top. This split flow system should lead to a lower amount of vapour needed to strip CO_2 from the solution. The system was evaluated using a mechanistic mass transfer and hydrodynamic model which revealed that the split flow configuration presents a great opportunity to reduce the reboiler heat duty for solvent regeneration. It requires less reboiler heat duty for solvent regeneration than the conventional amine plants, while still achieving high CO_2 capture efficiency. The reboiler heat duty can be reduced to as low as 2900 kJ/kg CO_2 with a 95% CO_2 capture efficiency and a large CO_2 cyclic capacity of solution. However, the regenerator height must be increased to accommodate the CO_2 stripping. This indicates a trade-off between a reduction in utility cost and an increase in capital cost. A process optimisation accounting for such a trade-off is required to achieve the lowest cost of CO_2 capture (Aroonwilas and Veawab, 2006c).

The reboiler heat duty for regeneration of aqueous single and blended alkanolamines was evaluated experimentally by Sakwattanapong and others (2005) in a bench-scale system under atmospheric pressure. The experimental results of heat duty were compared with industrial data available in the literature and subsequently correlated with process parameters. The results indicate that the reboiler heat duty relates inversely to CO_2 loading of lean and rich solutions and alkanolamine concentration. The type and composition of blended alkanolamines also affects heat duty; MEA requires the highest reboiler heat duty, followed by DEA and MDEA. The reboiler heat duties of blended alkanolamines are between the heat duties of their parent alkanolamines.

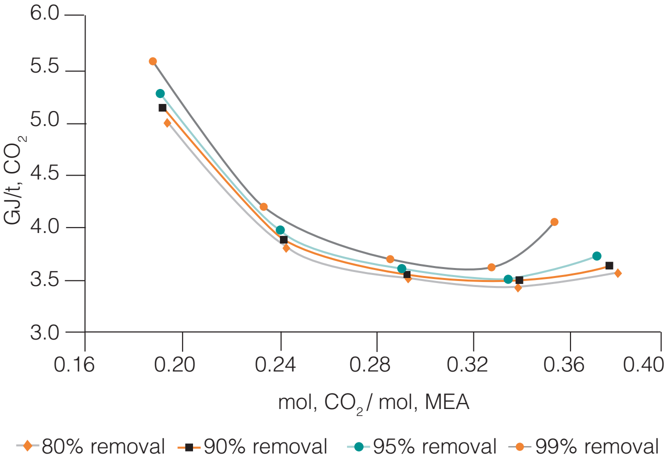


Figure 6 **Thermal energy requirement at various CO_2/amine lean loading for different CO_2 removal** (Abu-Zahra and others, 2006)

Abu-Zahra and others (2006, 2007a), using Aspen Plus® with the Radfrac subroutine, performed a parametric study of MEA processes. A significant finding was that the MEA regeneration thermal energy requirement decreased with the increasing lean loading until a minimum was reached. Next, the thermal energy requirement starts to increase again as shown in Figure 6. For the coal case study with 90% CO_2 removal and a 30 wt% MEA solution, the optimum loading was found to be around 0.32–0.33 mol CO_2/mol MEA, with a thermal energy requirement of 3.45 GJ/t CO_2. It was noted, however, that the solvent circulation rate required increases substantially with increased lean loading.

Simulation studies by Alie and others (2006a) using Aspen Plus® and an integrated process model indicated that the power output of the plant was maximised when the stripper reboiler heat duty was minimised. Therefore, the reboiler heat duty can be used as a suitable surrogate variable for the overall plant thermal efficiency for use in process optimisation studies.

5 Alternatives to MEA

Much research has been devoted to finding or developing solvents that are superior to MEA. A better solvent would not degrade, it would work under normal flue gas outlet conditions, and it would require less energy for regeneration. Some of the ways in which alternative solvents might perform better than MEA include:

- higher capacity for CO_2 capture;
- lower energy for regeneration;
- higher absorption/desorption rates and regeneration at lower temperatures;
- lower volatility and better stability;
- less degradation and lower corrosivity.

The development of better sorbents with lower regeneration energy requirement was identified as the highest priority R&D objective according to an expert elicitation carried out by Rao and others (2003, 2006).

Rochelle and others (2002) point out that steam requirements for stripping can be reduced by using a solvent of greater capacity. However, using solvents with a reduced heat of desorption can have mixed effects because, dependent on the process configuration, it may result in an increase in stripping steam required. Hoff and others (2006) have found that the heat of reaction is a key property for optimisation of the CO_2 capture process with new solvents. For the absorber packing height, a fast reaction approaching irreversibility is beneficial. This is facilitated by a high heat of reaction. In the desorber section, while a low heat of reaction is beneficial for the heat of desorption it reduces the effect of the temperature swing and the driving force for desorption. Then more heat is required to generate stripping steam.

5.1 Alternative alkanolamines

Most of the recent research into alternative solvents has examined alternative alkanolamines in an attempt to reduce the overall energy requirements of the absorber/stripper.

Veawab and others (2002) pointed out that the absorption efficiency of various solvents is often evaluated in 'classical laboratory reactors'. They suggested that it was necessary to use a column (packed or tray) as a gas-liquid contacting device to examine absorption efficiencies. They compared a range of aqueous solutions of alkanolamines using a packed column fitted with a structured packing. the test alkanolamines were the primary amine, MEA; the secondary amines, DEA and diisopropanoloamine (DIPA); the tertiary MDEA. MEA and DEA were found to have superior CO_2 performance over DIPA and MDEA as shown in Figure 7. DIPA and MDEA did not completely remove the CO_2. The CO_2 absorption into the MEA solution took place within only 0.8 m from the column bottom while the DEA required as high as 1.8 m to complete the same task. Hence, the absorption performance of the tested solutions was: MEA > DEA > DIPA > MDEA. The CO_2 loading and liquid load were found to have no impact on the order of the absorption efficiency. However, as the CO_2 loading increased the absorption efficiency decreases due to the reduction of the available reactive alkanolamine concentration. It was found that a blend of MEA with MDEA could circumvent this; at low CO_2 loadings the CO_2 was absorbed by the MEA but, as the CO_2 loading increased, the MDEA, with a slower CO_2 absorption rate, played a dominant role. The energy requirement for solvent regeneration of different amines was reported to be in the order MEA > DEA > MDEA (Veawab and others, 2003). MEA is more difficult to regenerate, thus resulting in higher residual CO_2 loading of lean solution.

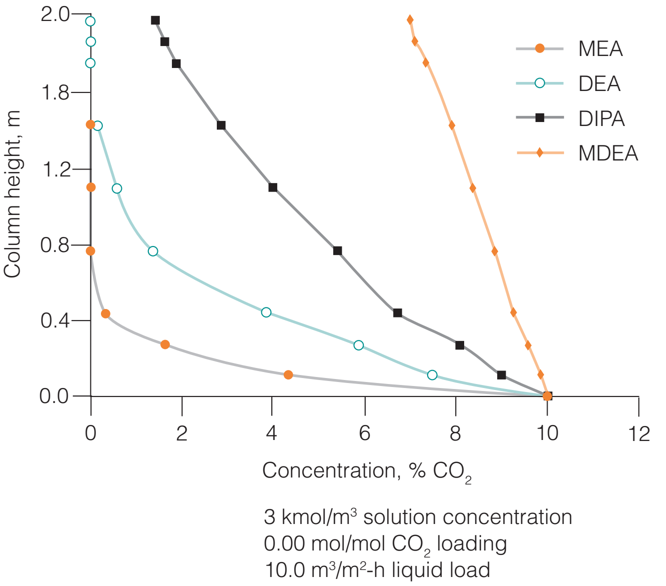


Figure 7 Gas-phase CO_2 concentration profile along the column for single alkanolamine solutions (Veawab and others, 2002)

Yeh and others (2000) compared MEA with a sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP). At the same bed geometry, the conventional MEA performed much better during absorption studies than the sterically hindered AMP. However, CO_2-saturated MEA and AMP solutions were prepared and sprayed over a packed absorber heated to 93°C and the CO_2 release rate recorded. The CO_2 release rate from the AMP solution was about 80% faster than from the MEA solution.

Aroonwilas and Veawab (2004) reported additional work in which 2-amino-2-methyl-1-propanol (AMP) was also studied; its CO_2 removal efficiency of 99% was slightly lower than those of MEA and DEA at 100% for fresh (no CO_2 loading) solvents. When the CO_2 loading was raised to 0.25 mol/mol the relative efficiencies remained the same but at 0.40 mol/mol CO_2 loading, AMP was more efficient than DEA, second only to MEA. Thus the order of the removal efficiency became MEA > AMP > DEA > DIPA > MDEA. The heights of the absorption columns relative to the height of a column using MEA are higher for the alternative solvents; absorption columns using AMP or DEA would be approximately 2.5 times higher. Mixtures of solvents were also tested; these were MEA-MDEA, DEA-MDEA, MEA-AMP, and DEA-AMP. The blends containing MDEA behaved as described by Veawab and others (2002) but the blends containing AMP behaved differently. The AMP blends behaved similarly to MEA alone regardless of CO_2 loading indicating that MEA enhanced the CO_2 absorption rate in the MEA-AMP solution more effectively than in the MEA-MDEA solution. DEA, on the other hand, did not significantly improve the performance of AMP.

A similar sterically hindered amine, 2-amino-2-ethyl-1,3-propanediol (AEPD) was studied by Jang and others (2005). The solubilities of CO_2 in aqueous 10 wt% AEPD solutions were compared with those in other aqueous amine solutions including MEA. It was found that the CO_2 loading capacity of aqueous AEPD solutions was much higher than that in aqueous MEA at higher CO_2 partial pressures although it was less at lower partial pressures.

Dibenedetto and others (2002) reported that two (un-named) diamines were ‘by far’ more efficient than monoamines for CO_2 capturing. They also noted that the carbamates of diamines easily release CO_2 at moderate temperatures. In contrast, the carbamates of monoamines do not release CO_2 easily upon heating.

Dibenedetto and others (2003; *also* Aresta and Dibenedetto, 2003) looked at silyl-alkylamines – two monoamines and two diamines. They found that the diamines were able to absorb twice the amount of CO_2 per mol than the monoamines and that the absorption was reversible with the CO_2 being completely released at 60°C from the neat amines. A 1:1 aqueous solution of one of the diamines was also studied. When heated to 60°C only half the absorbed CO_2 was released.

The absorption of CO_2 into aqueous piperazine (PZ) was studied by Bishnoi and Rochelle (2000) who investigated the reaction kinetics. mass transfer, and solubility. They concluded that the $CO_2/PZ/H_2O$ system has two reaction zones. At low solution loading, the dominant reaction products are piperazine carbamate and protonated piperazine. At high loading, the dominant reaction product is protonated piperazine carbamate. The rate constant is an order of magnitude higher than primary amine such as MEA. Derks and others (2005) obtained experimental data on CO_2 solubility in aqueous PZ solutions. Their data, together with other experimental data, was compared with an electrolyte equation of state model. The model was able to predict CO_2 pressures with an average deviation of 16% from experimental data. Information on the kinetics of absorption of CO_2 in aqueous PZ solutions was reported by Derks and others (2006).

The rate of CO_2 absorption is commonly used as a performance measure of potential solvents but Ma’mun and others (2005, 2007) have suggested combining it with vapour-liquid equilibrium (VLE) measurements to obtain the net cyclic capacity (Q). Using this measure they found that, although most of the other absorbents tested had a poorer performance than MEA, 2-(2-aminoethyl-amino)ethanol (aminoethylethanolamine, AEEA, $H_2N(CH_2)_2NH(CH_2)_2OH$) had a somewhat higher net cyclic capacity than MEA. AEEA had a high absorption rate combined with a high absorption capacity compared with the other absorbents studied. In addition, its vapour pressure was much lower than that of MEA. The regeneration energy requirement for AEEA was found to be lower than that for MEA at lower partial pressure of CO_2 in the feed stream (Ma’mun and others, 2006b). Further experimental and modelling studies of the solubility of CO_2 in 30 wt% AEEA solution have been reported by Ma’mun and others (2006a). Nuclear magnetic resonance (NMR) spectra revealed that the dominant reaction products were protonated carbamates. Kim and others (2006) determined the enthalpies of absorption of aqueous solutions of MEA, MDEA, and AEEA over a range of temperatures from 40 to 120°C. They found that the enthalpy of absorption of CO_2 increased with temperature for all three amines and was also strongly dependent on the CO_2 loading in the solution.

The reactions between the bicyclic guanidine, triazabicyclodecene (TBD), and 1,1,3,3-tetramethylguanidine (TMG) with CO_2 have been studied by da Silva and others (2006). Experimental NMR work and computational chemistry calculations were carried out to determine reaction products and likely mechanisms. The initial results suggested that the reactions differ significantly from those of aliphatic amines and that both compounds have a significant reactivity towards CO_2.

Singh and others (2006, 2007) have investigated the structural effects of alkanolamine amine based CO_2 absorbents on initial absorption rate and capacities. The effect of structure on CO_2 capacity is given in Table 2. Increase in the chain length between a different functional group and the amine group, mostly decreases the initial absorption rate, whereas capacity is increased. Steric hindrance effect is clearly seen in the experimental results since the same effect was also seen when the number of functional groups was increased around the amine group in the alkanolamine absorbent structure. An exceptional increase in initial absorption rate and capacity of alkanolamine absorbents with a six carbon chain length such as hexadimethylenediamine and hexylamine was noticed. Alkyl and amine groups were found to be the most suitable substituted functional groups in order to enhance the capacity and initial absorption rate. On the other hand, substitution of the hydroxyl group decreases the initial absorption rate and increases the capacity. In cyclic amines basicity is increased by substituting alkyl groups at the 2nd and 5th position in the ring. This also increases the initial absorption rate and capacity in the substituted aromatic amine. Also, when alkyl and amine groups were substituted by a side chain in aromatic amines, the capacity and initial absorption rate were increased compared with hydroxyl group substitution.

The kinetics of absorption of CO_2 in aqueous diglycolamine (DGA) have been investigated by Al-Juaied and Rochelle (2006). DGA is a primary amine that can be used at 50–60 wt% amine, resulting in significantly lower circulation rates and energy requirements. It was found that the reaction of DGA with CO_2 is the dominant effect at low loading. At high loading, instantaneous reactions are approached and the diffusion of reactants and products becomes an important phenomenon.

A 'new solvent' for CO_2 capture with a low energy of regeneration has been announced by IFP (Carrette and others, 2007). Only brief details are given for this amine solvent but it involves phase separation of the solvent into a CO_2 lean phase and a CO_2 rich phase. Only a fraction of the solvent is regenerated and the CO_2 rich phase has an 'abnormal' loading for a CO_2 partial pressure of 10 kPa.

5.2 Amino acid salts

Feron and ten Asbroek (2005a,b) have examined the use of amino acid salts in aqueous solutions as alternatives to amine based solutions. They point out that amino acid salts are particularly suitable for use with polyolefin membrane contactors (*see* Section 6.2 below) which provide an opportunity for the reduction in the size of the absorber. An initial kinetic study has been performed on the reaction of CO_2 with various potassium amino acid salt solutions at 298 K by van Holst and others (2006). They note that the salt function ensures the non-volatility of the substance, which is helpful when working at stripper conditions (lowered pressure and elevated temperature). A third advantage of amino acid salts is that several of them produce precipitates when absorbing CO_2. This allows the driving force to be maintained at increased loading and hence lower energy consumption for solvent regeneration. However, this necessitates integrating the heat exchanger into the solvent regenerator. The DECAB process (Feron, 2004; Brouwer and others, 2006) takes advantage of the production of precipitates. Its flowsheet is shown in Figure 8. It is suggested that the costs per tonne of CO_2 captured by the DECAB process could be half the costs of the MEA process. Brouwer and others (2006) also point out that the DECAB process could make use of the same kind of spray towers that are used for flue gas desulphurisation.

The production of precipitates when absorbing CO_2 was studied by Majchrowicz and others (2006) who investigated the potassium, sodium, and lithium salts of taurine (2-aminoethanesulphonic acid), 6-aminohexanoic acid, α-aminoisobutyric acid, and l-alanine ((S)-2-aminopropanoic acid). The chemical composition of the precipitates formed showed that the solid can be the amino acid or it can contain CO_2 species. The precipitate composition was found to change significantly with the solvent composition or remain the same for the different alkaline salts of the same amino acid. The former one was, for example, observed for the potassium and sodium salts of α-aminoisobutyric acid, l-alanine and 6-aminohexanoic acid, and the latter one for the taurine based systems. The potassium salts of the amino acids were found to precipitate the amino acid more easily, whereas the precipitate formed from the sodium salts more often contains CO_2 species.

A polyolefin membrane gas absorption system for acid gas removal has been developed based on the use of dedicated absorption liquids (CO_2 Removal Absorption Liquid – CORAL) which are mixtures of salts and amino acids (Feron, 2002, 2003a, 2004; Feron and ten Asbroek, 2005a,b). It was found that there was no deterioration in the CORAL liquid in the presence of air, unlike MEA which degrades in the presence of oxygen. The CORAL solvent is also less corrosive than MEA and shows no loss of active components.

5.3 Sodium carbonate solutions

Knuutila and others (2006) point out that, at the beginning of the 20th century, sodium carbonate solutions ($Na_2CO_{3)}$ were used in dry ice plants to separate CO_2 from flue gas. After alkanolamines were introduced the use of sodium carbonate solutions rapidly decreased. This was mainly because CO_2 absorption was faster with alkanolamine solutions and very high CO_2 removal efficiencies could be achieved. However, there are advantages that may make sodium carbonate based systems feasible for CO_2 capture. Sodium carbonate solutions are non-hazardous, non-volatile and the corrosion rate is low. They are also non-fouling and do not degrade. Finally, the heat of reaction between sodium carbonate and CO_2 is much lower than the heat of reaction between an MEA solution and CO_2. Sodium based chemicals are already used in power plants for flue gas desulphurisation (FGD). The possibility to combine CO_2 and SO_2 removal makes sodium chemicals very attractive. Pilot testing is being carried out to determine the feasibility of the sodium carbonate process for combined CO_2 and SO_2 capture. A research programme is planned at the universities of Dortmund and Duisberg to study CO_2 capture by alkali carbonates (Epp and others, 2007).

Cullinane and Rochelle (2003, 2004, 2005b) have examined aqueous blends of piperazine and potassium carbonate (K_2CO_3), this will be discussed in section 5.5.

5.4 Ammonia

Yeh and others (2004, 2005) have compared the carbon dioxide transfer capacities of aqueous ammonia (NH_3) solutions and MEA and found that the CO_2 carrying capacity of an 8 wt% NH_3 solution was 0.07 g CO_2 per g of solution compared with 0.036 for a 20 wt% MEA solution. The energy requirement for liquid mass circulation of ammonia solution is approximately 50% of MEA solution for equal weight of CO_2 carried. The thermal energy required to regenerate CO_2 from the rich solution is substantially less for the NH_3 solution than for the MEA solution. The ammonia solution is the basis of the *Aqua Ammonia Process* which could capture SO_2, NOx, and CO_2 from flue gas (also HF and HCl) without absorbent degradation or corrosion problems. The by-products of the process include ammonium bicarbonate, nitrate, and sulphate which could be used as fertilisers. As much as 60% of the carbon can be released from an ammonium bicarbonate solution but an ammonium carbonate solution resulted in only 38% carbon regeneration under the same temperature conditions. Test results demonstrated that a 62% reduction in regeneration energy is possible due to the higher loading capacity of the aqueous ammonia solution, its lower heat of reaction, and its lower heat of vaporisation compared with standard MEA solutions.

Park and others (2006) have also investigated aqueous ammonia solutions but noted that its drawbacks were the loss

Table 2 Total capacity of various aqueous amine based absorbents (Singh and others, 2006)

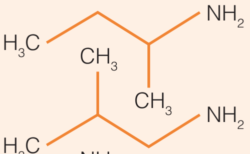
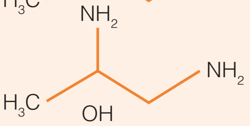
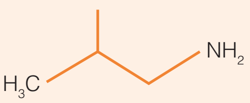
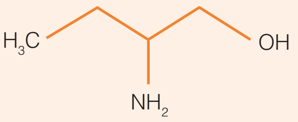
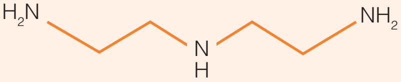
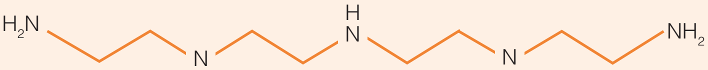
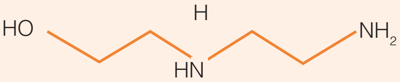
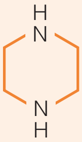
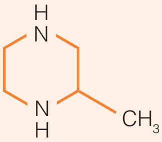
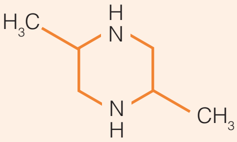
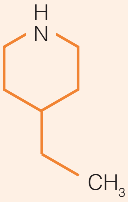
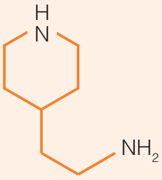
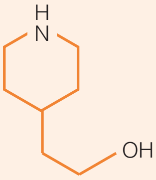
Aqueous absorbent Effect of chain length		Structure	CO_2 loading (moles CO_2/moles amine)
CH_3 group	ethylamine		0.91
	propylamine		0.77
	butylamine		0.86
	n-pentylamine		0.72
	hexylamine		1.52
NH_3 group	ethylenediamine		1.08
	1.3-diamino propane		1.30
	1.4-diamino butane		1.26
	hexadimethylenediamine		1.48
	1.7-diaminoheptane		1.34
OH group	monoethanolamine		0.72
	3-amino-1-propanol		0.88
	4-amino-1-butanol		0.84
	5-amino-1-pentanol		0.83
Effect of side chain			
CH_3 group	sec butylamine		0.84
	isobutylamine		0.78
NH_3 group	1.2-diamino propane		1.27
OH group	1-amino-2-propanol		0.89
	2-amino-1-butanol		0.88

Table 2 continued

Aqueous absorbent Effect of number of functional group		Structure	CO_2 loading (moles CO_2/moles amine)
CH_3 group	n-propylethylenediamine		1.66
NH_3 group	diethylenetriamine		1.83
	triethylenetetramine		2.51
	tetraethylenepentamine		3.03
OH group	n-(2-hydroxyethyl) ethylenediamine		1.15
	n,n-bis (2-hydroxyethyl) ethylenediamine		1.20
Cyclic amine			
Position of substituted alkyl group			
	piperazine		1.22
	2-methyl piperazine		1.22
	trans piperazine - 2.5 dimethyl		1.28
Effect of functional group			
	n-ethylpiperazine		1.15
	2-(1-piperazinyl) ethylamine		1.81
	2-(1-piperazinyl) ethanol		0.84

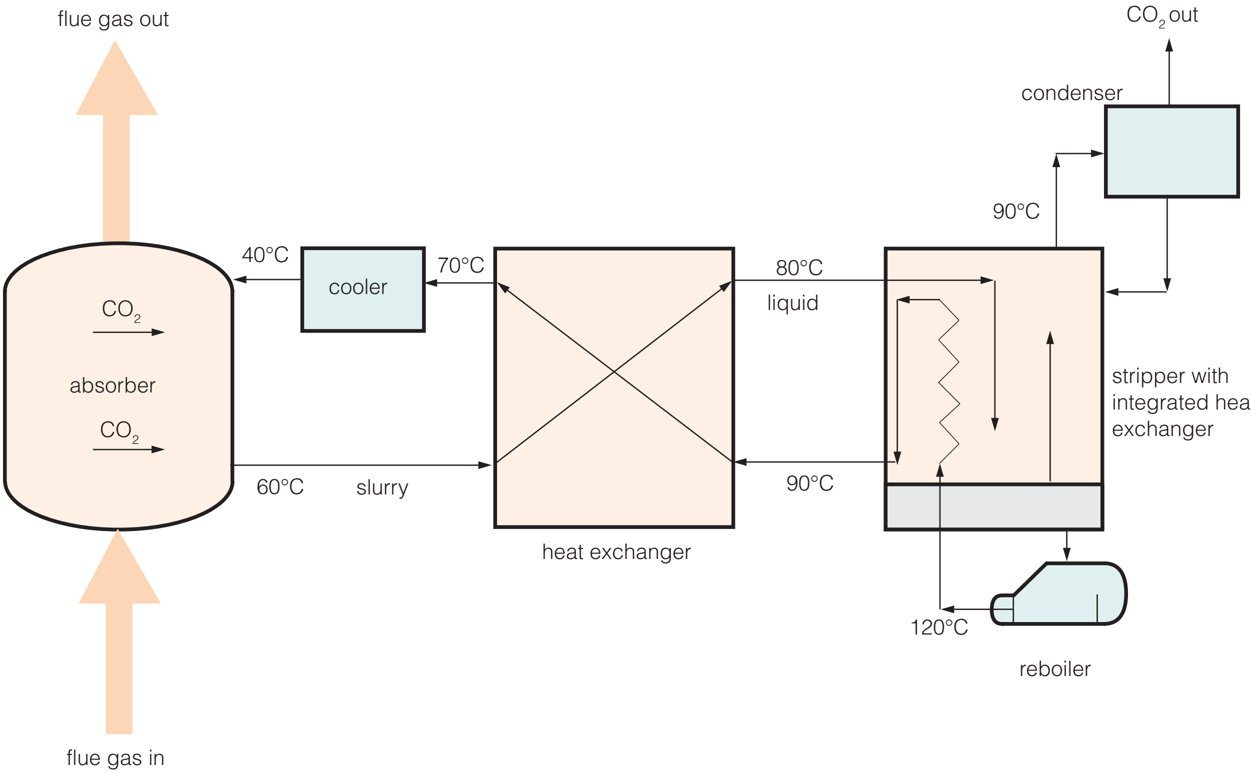


Figure 8 Simplified flowsheet of DECAB process (Feron and ten Asbroeck, 2005a)

of ammonia due to its volatility and the formation of precipitates. Ammonia scrubbing technology is also being studied as a means of combined removal of CO_2 and SO_2 at Tsinghua University in China (Wang, 2007).

Alstom (2006), in collaboration with EPRI, has announced that a 5 MW pilot plant is planned in the USA which will use chilled ammonia (Modern Power Systems, 2006b; Rhudy, 2006, 2007). The US$10 million pilot plant will capture CO_2 from a portion (~1%) of the flue gas at the We Energies' Pleasant Prairie coal fired power plant in Kinosha, WI. The chilled ammonia process uses only 50% of the energy used in the MEA process. The absorber operates at an optimum temperature of 2–16°C and the cooling of the flue gas to these low temperatures minimises ammonia losses. It is estimated that the CO_2 avoided cost for a supercritical pf plant would be 19.7 US$/ton of CO_2 compared with $51.1 for the equivalent MEA process. The power reduction for a plant equipped with chilled ammonia scrubbing would only be about 10%.

AEP announced plans on 15 March 2007 to begin capture of up to 100,000 t CO_2/y at its coal fired Mountaineer plant in West Virginia and to store it on site in a deep saline reservoir (AEP, 2007; *see also* http://www.aep.com/citizenship/crreport/climatechange/theroleoftechnology.asp). The capture technology to be used at Mountaineer is a chilled ammonia application. A successful validation project there is expected to result in a scaling up of the technology for capture of 1.5 Mt CO_2/y. The larger version will be used on the 450 MW Northeastern plant in Oklahoma. The technology is claimed to have the potential to capture up to 90% of a plant's CO_2.

5.5 Blended solvents

Idem and others (2006a) noted that a mixture of amines can have the reactivity of primary or secondary amines at similar or reduced recirculation rates but also low regeneration costs similar to those of tertiary amines. They compared the performance of aqueous 5 kmol/m^3 MEA with that of an aqueous 4:1 molar ratio MEA/MDEA blend of 5 kmol/m^3 total amine concentration as a function of the operating time. The tests were conducted using two pilot CO_2 capture plants of the International Test Centre for CO_2 Capture (ITC; discussed below in Chapter 9). Two different sources (natural gas and coal) and compositions of flue gas as well as two different modes of solvent regeneration were studied.

The studies of the solvent regeneration showed that, for the natural gas flue gas, the reboiler heat duty could be reduced significantly by employing a mixed amine instead of a single amine. However for coal flue gas, from the Boundary Dam plant, the opposite was the case. This differing behaviour was investigated further. CO_2 loading is a test of the capacity of the solvent to absorb CO_2 in the absorption column; it is commonly expressed in terms of mol CO_2/mol of total amine. At lean CO_2 loadings the behaviour in both plants was similar; more CO_2 stripping was achieved from the mixed amine system. Therefore the difference between the natural gas and the coal plants could not be attributed to the stripping performance of the solvent. For the natural gas flue gas, the rich amine CO_2 loadings for the mixed amines were the same as or just slightly lower than for the MEA alone. In the case of the coal flue gas, the rich amine loading for the mixed solvent was clearly below that for the single amine. This lower rich amine loading for the mixed amine means that the capacity of this solvent to absorb CO_2 was significantly reduced in the case of the coal flue gas. It was suggested that this loss in capacity could be attributed to the chemical stability of the solvent. Chemical analysis of the solvents showed that there was a wider variety of degradation products observed in the Boundary Dam demonstration plant samples, including sulphur compounds. This illustrates the effect of the harsher environment brought about by a coal fired power plant flue gas. This obviously affected the mixed amine solvent chemical stability more than the single amine.

Veawab and Aroonwilas (2006) have found that MEA and MDEA have a synergistic effect on the reboiler heat duty. For a blend of MEA and MDEA, the reboiler heat duty is lower than would be expected from the simple average obtained from the relative concentrations of the two solvents. Huttenhuis and others (2007) have reported that MEA seems to be a very good accelerator for MDEA. A small amount of MEA added to an aqueous MDEA blend results in a significantly shorter absorption column. They conclude that aqueous blends of MDEA/MEA may be competitive with aqueous MEA due lower reboiler heat duty, less corrosion, and better stoichiometry.

Combinations of an aqueous MDEA solution with several primary and secondary alkanolamines have been studied by van Loo and others (2007) using a rate based model simulating the absorption process in a tray column. The performance of the alkanolamines as accelerators or activators of MDEA absorption was examined. Of the accelerators studied, MEA was found to be the most successful. Only a small amount of MEA is required. Adding only 1 mol% of MEA to an aqueous MDEA solution was able to reduce the number of trays from 40 to 29; 2.5 mol% MEA reduced the number of trays to 25. Other existing and non-existing (fictitious) amines were also modelled but it was concluded that a significantly better performing accelerator than MEA does not seem to exist.

Bishnoi and Rochelle (2002a,b) investigated a blend of piperazine and MDEA. Bishnoi and Rochelle (2002b) reported that 5 wt% PZ/45 wt% MDEA provides almost two orders of magnitude and more enhancement than 50 wt% MDEA at low loading and one order of magnitude enhancement at moderate loading. PZ/MDEA solvents outperform MEA/MDEA and DEA/MDEA blends at the same concentration.

The solubility and absorption rate of CO_2 into MEA/PZ/water were measured by Dang and Rochelle (2003). They found that the absorption rate of CO_2 at 40 and 60°C in aqueous MEA with 0.6 to 1.2 M PZ is 1–5–2.5 times greater than in MEA alone. At loadings of less than 0.4 mol CO_2/mol amine, the PZ species contributes more than 60% of the total absorption rate. At more than 0.6 mol CO_2/mol amine, the species $PZCOO^-$ accounts for more than 40% of the total absorption rate. For most cases studied, MEA had a 20–30% contribution to the total absorption rate over the whole range of loading. Piperazine at 24 mol% of the total amine decreased the CO_2 equilibrium pressure by 50% and enhanced the absorption rate by 50 to 100%. The CO_2 enhancement factor decreased by a factor of 0.6 to 2 as loading decreased from 0 to 0.5 mol CO_2/mol amine. Dugas and others (2007) have reported that a 7 m MEA/2m PZ blend has a 45% greater CO_2 capacity than MEA alone at 40°C. The blend also shows faster CO_2 absorption rates.

Cullinane and Rochelle (2003, 2004, 2005b) have examined aqueous blends of piperazine and potassium carbonate (K_2CO_3). In this case the potassium carbonate is the absorber species since an increase in K_2CO_3 produces an increase in capacity whereas the capacity is nearly independent of piperazine concentration. Piperazine is an effective promoter of CO_2 absorption in aqueous K_2CO_3; its addition increases the rate of CO_2 absorption by a factor of 10 from the value in unpromoted solutions at 60°C. It also raises the heat of CO_2 absorption. However, the heat of absorption is less than that in MEA solvents (Cullinane and others, 2005). A lower heat of absorption would allow the design of more energy efficient processes. The thermodynamics of CO_2 absorption into aqueous K_2CO_3 and piperazine has been modelled by Cullinane and Rochelle (2005a), Hilliard and Rochelle (2005) and Hilliard and others (2006) who reported that the heat of CO_2 absorption did not appear to be a strong function of temperature. The kinetics have been modelled by Cullinane and Rochelle (2006). Using the stripper model developed by Cullinane and others (2005), Oyenekan and Rochelle (2005a) showed that energy savings of 29–33% could be achieved by using 5m K^+/2.5 m PZ compared with MEA at a stripper pressure of 160 kPa with a 5°C temperature approach.

Park and others (2005) measured the absorption rates of CO_2 into aqueous mixtures of MDEA and hexamethylenediamine (HMDA). They found that, as the concentration of HMDA increased, the calculated apparent absorption rate constants were enhanced by 25% (0.7 wt% HMDA) to 292% (14.4 wt% HMDA) compared with 20.5 wt% MDEA. It was concluded that the mixture of MDEA with HMDA could improve the economics of continuous absorption by increasing the absorption rate and reducing the size of the absorber. Aqueous solutions of MEA (20 wt%), AMP (20 wt%), and a blend of

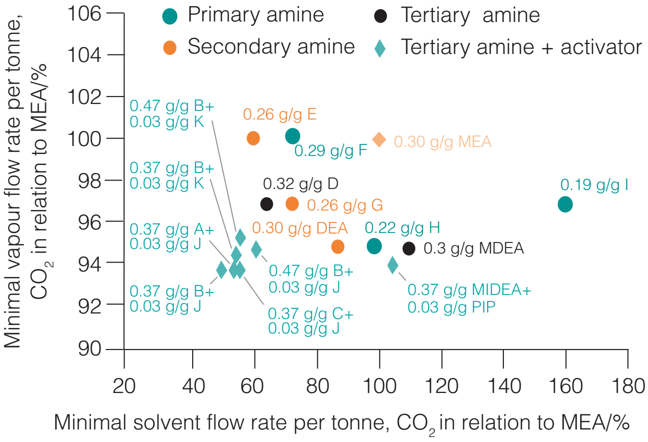


Figure 9 **Results of thermodynamic method for solvent comparison: ranking of solvent flow rate and desorber vapour flow rate in relation to MEA** (Notz and others, 2006)

AMP (20 wt%) with HMDA (5.10, 15, and 20 wt%) were studied by Han and others (2006). All absorbents showed similar absorption rates but the mixture of AMP and HMDA showed a higher capacity for CO_2 absorption. It was concluded that the mixture of HMDA in AMP aqueous solution enhances the reaction rate and absorption capacity of AMP more than those of MEA and also that steric hindrance and the amino group in the amine affect the absorption capacity but not absorption rate.

The University of Stuttgart has screened new solvents for further testing in the pilot plant built as part of the CASTOR integrated EU project (Notz and others, 2006, 2007). The identities of the new solvents have not been revealed but blends of tertiary amines with an activator have shown a high potential for reduction of solvent flow rate and regeneration energy. The minimal solvent flow rate per tonne of CO_2 is shown in Figure 9.

5.6 Comments

At the beginning of this chapter, it was noted that Rochelle and others (2002) had warned that using solvents with a reduced heat of desorption can have mixed effects because, dependent on the process configuration, it may result in an increase in stripping steam required. In Chapter 4 it was noted that Oyenekan and Rochelle (2006a) had calculated that the solvent heat of desorption (ΔH_{des}) had an effect on the reboiler duty and the equivalent work for stripping. The effects of heats of desorption were not the same in different stripper configurations. Despite the search for better reagents for CO_2 absorption, Draxler and others (2005) suggest that this may not be worthwhile. They examined the relative contributions to the overall energy consumption for an amine-based separation for a variety of actual and hypothetical amines. Their calculations suggested that different amine structures will not result in a better overall energy demand. The calculations were limited to single amines however, and not to blends.

6 Absorption contactors

An important part of an absorption system is the means by which the gas and liquid phases come into contact with each other; sufficient contacting area is needed for the gas and liquid phases to interact. This can be achieved by using *packed columns* or *gas absorption membranes*.

6.1 Packed columns

Packings are used to facilitate mass transfer of the CO_2 into the solvent. High efficiency packings can be classified as random or structured. Random packings are discrete pieces of packing of a specific geometrical shape which a 'dumped' or randomly packed into the column shell. Structured packings are composed of ordered crimped layers of corrugated sheets or wire mesh that are stacked in the column. The unique design of these types of packing promote liquid spreading and gas/liquid contact area while minimising wasteful pressure drop (Seibert and others, 2005).

Park and others (2004) studied the performance of three random packing materials, Raschig rings, Intalox saddle, and Pro-Pak and found that the specific surface area and the void fraction were important physical properties. The specific surface area affects operating hold-up (the difference between the total hold-up, which is the volume of liquid present in the void spaces of the packing per volume of packing, and the static hold-up which is the liquid volume per unit volume that does not drain from the packing when the liquid supply to the column is stopped). The void fraction affects flue gas pressure drop. Pro-Pak had the highest operating hold-up and the lowest flue gas pressure drop and, consequently, the highest CO_2 removal efficiency. A simple rate equation for CO_2 absorption in a randomly packed column using MEA has been developed by Gabrielsen and others (2006).

A novel random packing called a Super Mini Ring (SMR) was compared with stainless steel pall rings by Habaki and others (2006). They found that the SMR offers higher absorption performance due to its larger effective surface area and that the required height of the packed column could be reduced by 20% relative to a pall ring column.

Yeh and others (2000) studied CO_2 absorption in packed columns, comparing structured packing with traditional random (or dumped) packing (ceramic Intalox saddle). The structured packings were Flexipac and BX gauze. Flexipac showed only a minimal improvement over the 40.1% absorber efficiency of the random packing but at an absorber to CO_2 mole ratio of 1.4, BX gauze improved the packed column efficiency by about 50% over that of the random packing.

Aboudheir and others (2001) reported that a better removal efficiency of CO_2 can be achieved by using high-capacity packing. The results of a study by deMontigny and others (2001) showed, 'quite convincingly' that structured packing (4A Gempak) significantly increased the overall mass transfer coefficient ($K_G a_v$). This was over twice the value obtained with two random packings. Four stainless steel structured packings were studied by Aroonwilas and others (2001). The results of the study indicated that the mass transfer coefficient varies significantly, not only with operating parameters such as liquid load, liquid CO_2 loading, and liquid temperature, but also with design parameters, that is the pattern of packing arrangement and initial liquid distribution. The ways of arranging the successive packing elements is shown in Figure 10 and it was found that both the (conventional) 90° and the 45° packing arrangements provided great and comparable efficiency. However, parallel 0° rotation causes the packing efficiency to decline significantly (by over 70%).

A packing, KP-1, was developed by the Kansai Power Company and Mitsubishi Heavy Industries (Mimura and others, 2003). It is composed of an uneven surface lattice plate structure, similar to an earlier packing developed by the two companies. The newer packing is lighter and has a lower number of parts than the earlier one in order to bring down the cost so that it would be competitive with random packing and structure packing.

Seibert and others (2005) developed a technique for direct measurement of the contact area for gas/liquid contacting. The results obtained were 'as expected'; the packings with the larger specific surface area provided the larger gas/liquid contact areas and structured packings provided greater contact areas.

Studies in an MEA pilot plant at The University of Texas at Austin showed that the structured Flexipac 1Y packing

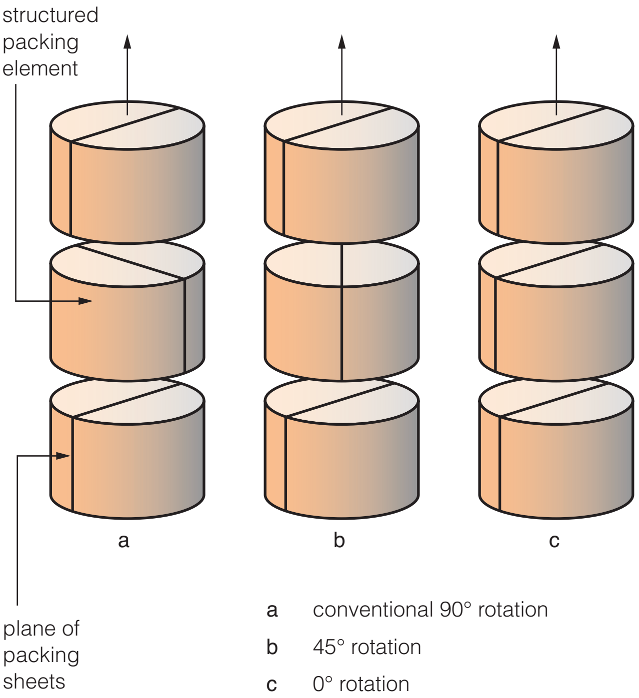


Figure 10 Arrangement of successive packing elements (Aroonwilas and others, 2001)

achieved 1.5 times more mass transfer than the high performance unstructured packing (Koch-Glitsch IMTP #40) due to an increased wetted area (Dugas and others, 2006). Mass transfer coefficients for the two packings were very similar.

As part of the EU CASTOR Project, new high capacity structured packings are being tested. Alix and Raynal (2006) report studies on MellapakPlus 252 Y, developed by Sulzer Chemtech Ltd. It was found that the liquid flow in the packed bed is homogeneous, and there is no local liquid accumulation at the junction of two packing elements.

6.2 Gas absorption membranes

Feron and ten Asbroek (2005a,b; *see also* Feron, 2003a) describe the principles of membrane gas absorption. These absorbers are porous, water repellant, polymeric membranes. The gas phase remains separated from the liquid absorbent as a result of the hydrophobicity of the membrane. The flue gas stream is fed along one side of the membrane and the CO_2 will diffuse through the gas filled pores of the membrane, on the other side of which they will be absorbed into the absorbent solution. The principles of membrane gas absorption are shown in Figure 11.

Membrane gas/liquid contactors have been studied by Kværner Oil & Gas (Falk-Pedersen and others, 2001). Gas absorption membranes have several advantages over conventional contacting columns:

- high packing density;
- high flexibility with respect to flow rates and solvent selection;
- no foaming, channelling, entrainment, or flooding;
- high turndown ratio;
- insensitivity to motion;
- flexibility with respect to the orientation of the unit(s);
- significant savings in weight.

The study was to verify the three most critical parameters:

- possible wetting of the membrane;
- the total mass transfer coefficient;
- the project economy.

It was found that conventional membrane modules could not be used due to poor mechanical stability, low active membrane surface, and high production cost. GORE-TEX® ePTFE membranes were found to be the best suited membranes with a very high mass transfer coefficient. Pilot tests compared membrane contactors with conventional columns packed with Sulzer Mellapak 250 Y structured packing and found that a 60–75% reduction in size and weight could be achieved. Kværner's objectives included reducing size and weight for offshore applications (Herzog and Falk-Pedersen, 2001). Size and weight may not be such a problem for coal fired power plants though.

The effectiveness of gas absorption membrane (GAM) modules was compared with more traditional packed columns by deMontigny and others (2003). The performance was evaluated using the overall mass transfer coefficient ($K_G a_v$) as a basis. The membrane contactor contained microporous polypropylene (PP) hollow fibre membranes and the packed absorption column contained Sulzer DX structured packing. It was found that the $K_G a_v$ values for the GAM module were two times higher than those obtained for the packed column. Thus, GAM modules can be built smaller than packed columns but still offer the same operating performance. A polytetrafluoroethylene (PTFE) membrane was tested later

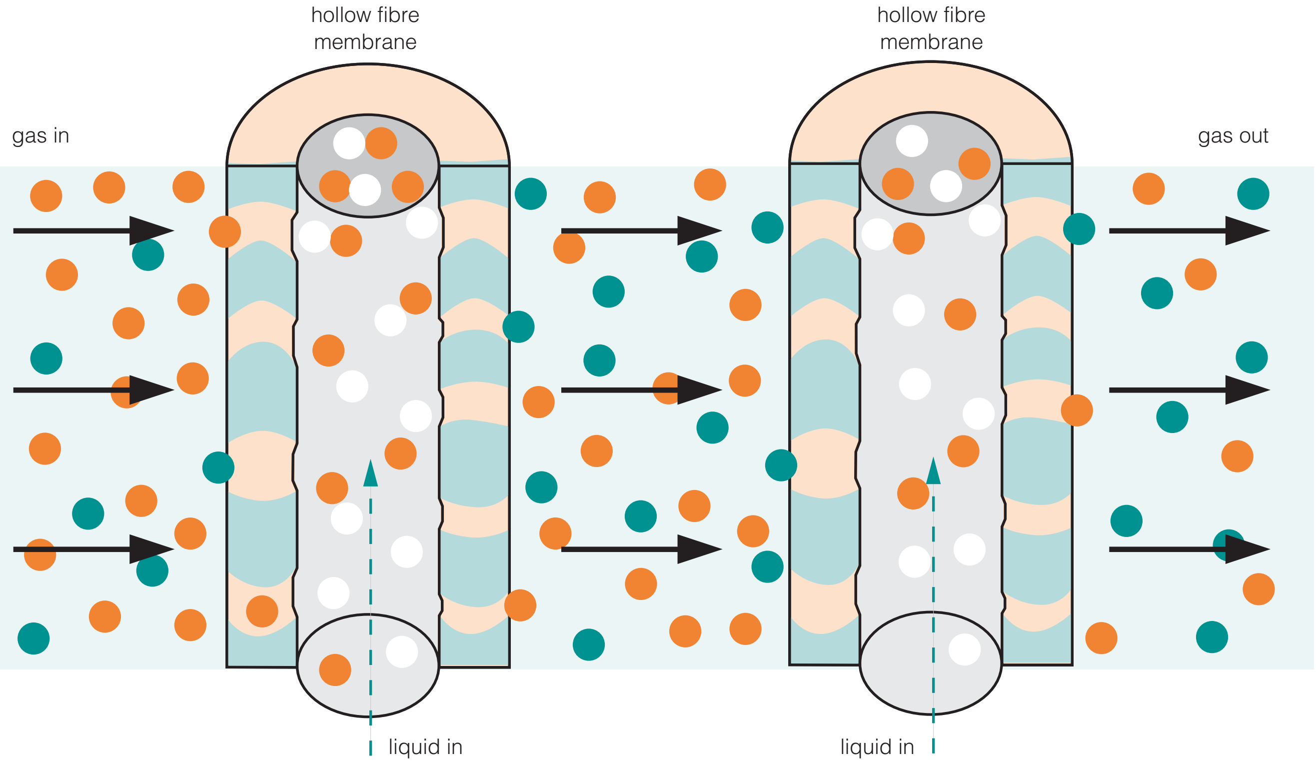


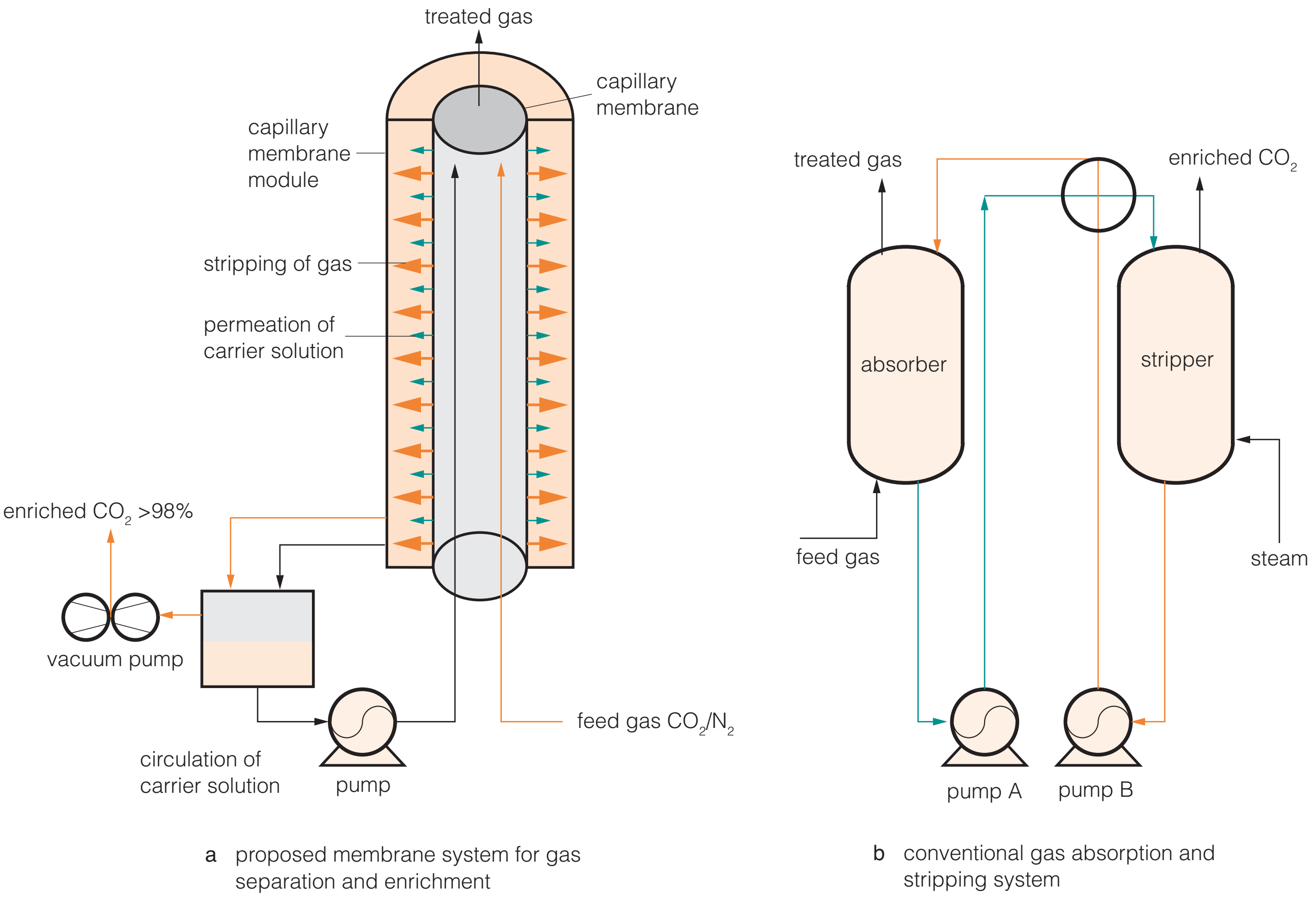
Figure 11 Principle of membrane gas absorption (Feron and ten Asbroek, 2005a)

(de Montigny, 2004; deMontigny and others, 2005). Again the experiments showed that membrane contactors are superior to packed columns with structured packings. The degree of improvement ranged from 20 to 430% depending on operating conditions. The PTFE membranes produced a better performance than the PP membranes which were susceptible to wetting.

Feron and ten Asbroek (2005a,b) point out that commercially available porous polyolefin membranes are not suitable for use with aqueous solutions of ethanolamines such as MEA. This is a result of their low surface tension and chemical interactions resulting in the liquid seeping through the membrane. This is one of the drivers for their study of amino acid salt solutions as CO_2 absorbers, as noted in Section 6.2 above. These could be used with inexpensive polyolefin membranes (often developed for other applications such as in medicine).

Twelve different flat sheet membranes have been tested by van der Vaart and others (2006). They determined the breakthrough pressure, the pressure at which the membrane starts leaking liquid to the gas side, and found that the membranes could be divided into two groups. One group performed poorly while the other performed well. However, it was apparent that the membrane material, polypropylene, polyethylene, or polytetrafluoroethylene, was not the determining factor. With respect to mass transfer, it was found that all membranes were sufficiently permeable to ensure a very low contribution to the overall mass transfer resistance. The choice of a membrane could then be based on considerations like chemical stability, environmental impact and costs. The fact that among the highest permeable membranes there were also some membranes with a favourably high critical entry pressure was considered to be quite promising. Realistic CO_2 membrane fluxes are in the order of hundreds of grams per square metre per hour.

Capillary membrane modules made with polyethersulphone capillary ultrafiltration membranes have been made by Teramoto and others (2003). In their hybrid process, both a feed gas and an absorbent solution are supplied to the inside of the hollow fibres. It is not the gas but a CO_2 carrier solution that permeates the membrane. While the gas and the liquid flow upward inside the hollow fibres, the absorbent solution absorbs CO_2 selectively. Most of the absorbent solution, which contains dissolved CO_2, permeates the membrane to the permeate side of the module maintained at reduced pressure, where the dissolved CO_2 is stripped and recovered as enriched CO_2. In this way, the carrier solution is circulated throughout the module allowing the simultaneous separation and enrichment of CO_2 from simulated flue gases as shown in Figure 12. Therefore, only one unit is necessary for absorption and stripping of CO_2. This type of membrane was called a ‘bulk flow liquid membrane’ (BFLM). The modules were tested by supplying a feed gas and a CO_2 carrier solution to the lumen side (the high pressure feed side). Most of the carrier solution passed through the membrane to the permeate side (the low pressure side) where it liberated the CO_2 to form a lean solution. The lean solution was then recirculated to the



a proposed membrane system for gas separation and enrichment

b conventional gas absorption and stripping system

Figure 12 Comparison of proposed membrane gas separation system with conventional gas absorption and stripping system (Terramoto and others, 2004) lumen side. MEA, DEA, and AMP were used as the CO_2 carrier solvents. In the tests, it was found that AMP and DEA ere more effective than MEA. CO_2 in the model gas was successfully concentrated from 5 to 15% to more than 98%. The maximum CO_2 removal was 31% but this was considered to be rather high given that the mean residence time was very short, 0.14 s. The membrane proved to be very stable over a discontinuous one month study, extending to 2–4 months in a later study in which eight amines were tested (Teramoto and others, 2004). Among the eight amines tested as the CO_2 carrier, 2-(butylamino)ethanol (BAE) was found to be the most effective.

The use of polyethersulphone, polysulphone, and polyethylene hollow fibre membrane modules with DEA has been studied by Okabe and others (2006). The energy consumption calculated for each membrane were 0.132 kWh/kg CO_2 to 0.156 kWh/kg CO_2, which were about 35% to 41% of the conventional method. An example process which substituted the membrane/absorption hybrid method for the stripper of the conventional absorption method was studied and the calculated 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 a very energy efficient process and the cost of the equipment was also expected to be reduced.

7 Techno-economic studies

While the efficiency penalties of carbon capture are generally easy to understand; how these translate into the cost of CO_2 capture is less clear. One of the first studies comparing the thermal and economic performance of fossil fuel power plants with and without CO_2 capture was performed by the Electric Power Research Institute (EPRI, 2000). The general conclusion was that for power plants with CO_2 capture and using bituminous coal, the technology with the lowest cost of electricity was IGCC with pre-combustion capture from the syngas using physical absorption by Selexol. An implied conclusion was that pulverised coal firing with post-combustion capture from flue gas using chemical absorption by MEA was not an economic or efficient way to proceed. Since publication of that study, several improvements have been identified that enhance the thermal and economic performance of post-combustion CO_2 capture technology. Gibbins and others (2002) compared the EPRI findings with data from the IEA GHG and concluded that amine scrubbers are much better than previous studies show. Further, that the costs for CO_2 capture were lower than IGCC for new pulverised coal plant as well as the cost of electricity. They also concluded that costs were likely to be even lower for *suitable* retrofit plant. A more recent study by Wheeldon and others (2006) shows that with these CO_2 capture improvements, new, highly efficient pf plants are competitive with IGCC.

Dave and others (2001) pointed out that there are many engineering and site-specific factors which need to be addressed before the results of generic studies can be translated to local conditions, in their case Australian. A detailed technical and economic analysis of amine-based CO_2 capture was conducted for two black coal fired Australian power plants located at coastal and inland sites. A feature of Australian power plants is that their environmental regulations for SO_2 and NOx are less stringent that in Europe or the UK, hence the amount of SO_2 in typical flue gas (~250 ppmv, wet basis) is well above the 10 ppmv limit beyond which solvent losses in amine-based processes begin to have a significant effect on operating costs. Thus, in addition to carbon capture, commercially available SO_2 and NOx control technologies would have to be retrofitted. It was found that removing the SO_2 and NOx prior to CO_2 capture had a relatively small negative impact on overall plant efficiency. However, the plant operating efficiency goes through a minimum at around 60% SO_2/NOx removal. Below 60%, the cost of consumables (mainly MEA) outweighs the additional capital investment needed for SO_2/NOx removal. Above 60%, the savings made in MEA loss are overshadowed by the additional capital investment required. The results suggested that there would be little incentive for Australian black coal fired power plants to invest in NOx reduction technologies beyond low NOx burners and that sorbent injection into the furnace would be sufficient for SO_2 removal.

The different situation in Europe concerning NOx and SO_2 removal has been studied by Féraud and others (2006) for three boiler/fuel cases being considered by the CASTOR project. They reported that additional NOx abatement beyond that required to meet environmental legislation is not likely to be required for amine scrubbing. Limestone gypsum flue gas desulphurisation (FGD) plants can be designed to reduce SO_2 emissions down to 10 mg/Nm^3. However in some cases of lignite firing, the SO_3 levels entering the amine scrubber could slightly exceed the suppliers' suggested targets B unless additional economically acceptable measures can be taken to reduce them. Raising the performance of FGD plants to these levels would increase capital costs by up about 7% and operating costs by up to 27%. Through life costs would be increased by up to 17%. However, these cost increases represent only a few euro cents per tonne of CO_2 captured, over a 25 year plant life.

Ho and others (2006) also analysed CO_2 recovery from a new build Australian supercritical pulverised black coal power plant flue gas. Using a computer program incorporating CO_2 capture economics and technical calculations, several parameters were optimised to obtain the specific CO_2 capture cost. The cost of capture using commercially available MEA solvent was estimated to be 47 US$/t CO_2 avoided in the baseline (current commercial scale) case. The cost of chemical solvent absorption system is highly dependent on the energy required to regenerate the CO_2 in the stripper. The energy penalty for this system was calculated to be 36% of the total energy output from a 500 MW power plant. The energy consumption for the solvent regeneration step accounts for 55% of the total energy loss, with the remaining power required for compression and pumping.

The analyses of the relative costs for various options for reducing and capturing CO_2 from existing pulverised coal power plants has been described by Simbeck and McDonald (2001). The analyses, which started as site-specific engineering studies, were standardised and summarised into single-page spreadsheets that include mass and energy balances plus capital cost buildups and economics. The results of the analyses revealed that there appear to be potential improvements in technology integration. For example, small amounts of natural gas can be effective in consuming all the residual oxygen in the flue gas, thus reducing the cost of amine CO_2 scrubbing.

The Canadian Clean Power Coalition studied three technologies for CO_2 removal: amine scrubbing, O_2/CO_2 combustion, and gasification (IEA GHG, 2004a; Stobbs and Clark, 2005). Three typical Canadian coal types were used: bituminous, subbituminous, and lignite. The main results of the studies are listed in Table 3. It was found that the cost of electricity with CO_2 capture was 50% higher than the then current rates, but lower than prior studies. Gasification ranked first and amine scrubbing next, even with non-optimised processes. However, it was concluded that amine scrubbing appeared to be relatively mature, one of the lowest cost options, and ready to apply to power plant applications for capturing CO_2.

Table 3 Technical and economic comparison of CO_2 capture technologies (Stobbs and Clark, 2005)

Fuel		Bituminous	Subbituminous		Lignite	
Technology		gasification			amine	oxyfuel
COE (90%CF)	CDN$/MWh	107	97	131	116	152
Cost	million CDN$	1,330	1,490	1,590	1,370	2,310
CO_2 emitted	t/MWh	0.116	0.111	0.182	0.060	0.145
CO_2 captured	%	86	89	86	95	90
CO_2 avoided	t/MWh	0.65	0.74	0.71	0.82	0.74
Cost CO_2 avoided*	CDN$/t	47	52	88	57	112
Capacity	MW gross	594	629	555	454	629
Economic capacity	MW net	445	437	361	311	373
Net heat rate (HHV)	kJ/kWh	11,410	13,810	13,240	12,530	14,880
Efficiency (HHV)	%	31.6	26.1	27.2	28.7	24.2
Unit cost	CDN$/kW net	3,000	3,400	4,400	4,400	6,200

* cost of CO_2 avoided is defined as the increase in cost of electricity in $/MWh (evaluated case minus selected base case) divided by the decrease in tonnes of CO_2 emitted per MWhnet (selected base case minus evaluated case)

Table 4 Deterministic results for a new 500 MW plant (Rao and Rubin, 2002)

	Reference plant	With CO_2 control
Net plant capacity, MW (net)	462	326
CO_2 emission rate, g CO_2/kWh (net)	941	133
SO_2 emission rate, g SO_2/kWh (net)	2.45	0.0003
NOx emission rate, g NOx/kWh (net)	0.45	0.58
CO2 sequestered, 106 tonne CO_2/year		2.58
Cost of electricity, US$/MWh (net)	49.2	97.0
CO_2 mitigation cost, US$ tonne CO_2 avoided		59.1

In an effort to better understand the technological options for CO_2 capture and storage, Rao and Rubin (2002) carried out a technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plants. Their model was applied to study the feasibility and cost of carbon capture at both new and existing coal fired power plants. The reference plant was assumed to be a new 500 MW (gross) unit burning low-sulphur US coal meeting current US standards for SO_2, NOx, and particulates. Table 4 shows the deterministic results for the reference plant.

Addition of the CO_2 capture system raises the capital cost of the reference plant from US$571 million to US$705 million. However, different assumptions about power plant design, coal properties, plant operation, and CO_2 control system design can have significant effects on the CO_2 mitigation costs and are responsible for many of the cost differences found in the literature. These 'uncertainties' were included in the model and resulted in the overall cost of CO_2 avoided showing a range of 32–73 $/t (95% probability interval) with a mean cost of 51 $/t CO_2 avoided.

An analysis of retrofit options for existing plants showed that the large energy requirements of CO_2 capture lead to a more substantial loss of plant capacity compared with a new plant affording better heat integration. The overall cost of CO_2 capture is likely to be greater than that of a new plant despite the lower cost of electricity for plants that are fully or partially amortised. There may also be site-specific difficulties encountered in retrofit applications.

Rao and Rubin (2006) point out that the typical capture efficiency assumed in the literature for amine-based CO_2 capture systems applied to pulverised coal fired plants is 90%. They considered:

- the basis for choosing values of capture efficiency;
- whether the values currently assumed are the most cost effective for the applications chosen; and
- the factors that determine or affect the most cost effective level of CO_2 control.

The effects of systematically varying the CO_2 capture efficiency of an amine-based system over a broad range for a new pulverised coal plant were examined. The reference gross plant sizes were 650 and 1000 MW supercritical plants

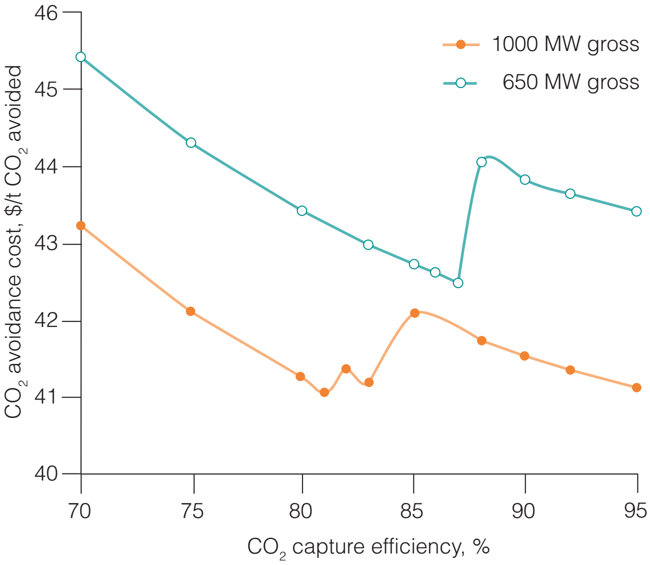


Figure 13 CO_2 mitigation cost as a function of the desired capture efficiency of the CO_2 capture system (Rao and Rubin, 2006)

burning medium sulphur bituminous (Pittsburgh) coal. The cost effectiveness of the CO_2 capture system was evaluated for a range of capture efficiencies and the results are shown in Figure 13. For the two reference plants, the most cost effective removal efficiencies were ~81% for the 1000 MW plant and ~87% for the 650 MW plant. At these removal efficiencies the net capacity of the plants is 714 MW and 455 MW respectively. It was also pointed out that, at 95% capture efficiency the cost effectiveness for the 1000 MW plant is almost as low as the minimum at 81% capture efficiency. This is due to the way that capture train size and number affect capture cost. Thus, there is not always a single value of cost effective capture efficiency. Simulation studies carried out by Abu-Zahra and others (2006, 2007b) confirm that the cost of CO_2 avoided does not vary between 80 and 95% but increases at higher CO_2 removal values.

Rao and Rubin (2006) also considered a scenario where the desired CO_2 reduction was lower than the cost effective levels identified for the two reference plants. A potential cost saving strategy would be to bypass a portion of the flue gas while operating the CO_2 capture system at higher efficiency to achieve the desired overall CO_2 reduction. They found that, for all cases involving flue gas bypass for the 650 MW plant, the minimum CO_2 avoidance cost was achieved by operating the amine scrubber at the highest capture efficiency (95%).The increased energy costs of higher CO_2 removal are more than offset by the reduced coat of processing and compressing a smaller flue gas stream.

The cost of CO_2 avoided as used by Rao and Rubin (2006) is calculated as:

$$\text{cost of CO}_2\text{ avoided (\$/t)} = \frac{(\$/\text{kWh})_{\text{ccs}} - (\$/\text{kWh})_{\text{ref}}}{(\text{tCO}_2/\text{kWh})_{\text{ref}} - (\text{tCO}_2/\text{kWh})_{\text{ccs}}}$$

where the subscripts 'ref' and 'ccs' refer to the reference plant and capture plant, respectively. However, Alie and others (2006b; *see also* Alie, 2005) take issue with the way that the cost of CO_2 avoided and the cost of electricity are calculated in many economic studies. They point out that the calculations used assume that coal units operate at their maximum continuous rating and are nearly fully committed. Analysis of operating data for Ontario revealed that this was not the case. They also point out that the CO_2 recovery factor is strongly dependent on market forces and cannot be known in advance. A model in which the reference case is the entire electricity system is proposed to avoid the bias introduced by selecting a reference plant. Initial results have revealed that there appears to be significant economic benefit to be realised by having CO_2 capture processes with variable rates of CO_2 capture.

A life cycle assessment for CO_2 capture was carried out by Muramatsu and Iijima (2003). They compared a 'base case' of power generation with a conventional CO_2 capture technology (the 'NEDO case') and the improved technology developed by MHI/KEPCO ('MHI case'). The net power generating efficiency of the base case was 40.6%. The study showed that, with CO_2 capture technology, the net efficiency fell to 33–30% and the total life cycle electricity generation efficiency including off-site energy consumption was 32–29%. For the carbon balance, when a CO_2 capture ratio of 90% was applied, the CO_2 emission reductions were 86–85% over the entire fuel cycle including off-site emission. The MHI capture technology was shown to be more efficient than the 'conventional technology'. Imai and Ishida (2005) also calculated that CO_2 capture without excessive electric power cost is possible by using the 'Advanced KS-1' CO_2 capture technology with an appropriate CO_2 recovery ratio.

A study on the performance and costs of plants based on current technology was carried out for IEA GHG (2004b; *see also* Davison, 2007). The study looked at two 'commercial' processes, Fluor's MEA Econamine FG^{+SM} process and MHI's hindered amine KS-1 process. At that time, Fluor and MHI's existing capture units were at gas fired plants. It was calculated that the thermal efficiency capture penalty of the Fluor process was 9.2 percentage points and 8.4 for the KS-1 process. The electricity cost penalty was respectively 1.85 and 2.02 ¢/kWh and the corresponding costs of CO_2 avoidance were 29.5 and 30.9 US\$/t CO_2. The capital cost of the Fluor plant was 533 US\$/kW net power, lower than the 687 \$ for the MHI plant. The two reference case plants without capture were slightly different in that the the MHI plant used an MHI FGD unit. A major conclusion of the study was that the energy consumption of these latest generation processes was significantly lower than in conventional MEA scrubbing processes. An interesting finding was that, when postulated data for 2020 plants were considered, the production cost resulting from the power plant developments were of the same order as the cost of capture in the current market.

There is therefore a chance that the developments in power plants will offset the current estimates of carbon dioxide capture cost (Roberts and others, 2005).

Gibbins and others (2005) produced a set of six rules that should be followed to achieve optimal post-combustion CO_2 capture system performance in power plant applications. They suggested that the rules should be taken into consideration when assessing the likely performance of power plants with post-combustion capture. The rules are:

1 Add heat to the steam cycle at as high a temperature as possible (that is, be prepared to use best available steam conditions if commercially justified).
2 Reject heat from the steam cycle, in the steam extracted for solvent regeneration, should be at as low a temperature as possible.
3 Produce as much electricity as possible from any additional fuel used, consistent with rejecting heat at the required temperature for solvent regeneration.
4 Make use of waste heat from CO_2 capture and compression in the steam cycle.
5 Use the latest solvent developments.
6 Exploit the inherent flexibility of post-combustion capture.

Chalmers and others (2006; Chalmers and Gibbins, 2007) have followed up on point 6 by using a plant model to investigate plant flexibility. The base case for the coal plant was a supercritical plant operating at 44% efficiency at 100% load (based on LHV and no capture); with capture of 85% of CO_2, the efficiency is 35%. The baseline assumptions were:

Base Case (no capture)	750 MW plant, maximum net output
Base Case (capture)	750 MW plant, maximum net output with 85% of CO_2 produced captured and rich solvent regenerated immediately.
Vent all CO_2	As capture base case, but with capture plant not operating. Thus net MW out increased for all percentage loads since no capture energy penalty, but also higher CO_2 emission.
Store 85% CO_2 as produced	As capture base case, but with capture plant storing rich solvent to be regenerated later (*see* next case for an example). Thus net MW out increased for all percentage loads subject to any balance of plant restrictions. There is still a small capture energy penalty, but also low CO_2 emissions.
Double regeneration	As capture base case, but with an additional volume of solvent regeneration (that is, all CO_2 from current production captured with rich solvent regenerated immediately, but rich solvent flow rate increased by adding solvent from storage tank).

Although there was an additional marginal cost of electricity associated with additional regeneration, this was counteracted by additional net output to generate more profit at other times. It was also noted that there were additional potential benefits by switching some fuel supply at pulverised coal plants to biomass, including plants with carbon capture.

Gibbins (2006) compared the electricity costs for power plants built with capture and found that, although industry standard ultra supercritical pulverised fuel (USCPF) plants had higher capital and operating costs than IGCC with capture, the IGCC plants would operate at a lower thermal efficiency than the USCPF. Wheeldon (2006) showed that this is especially the case for subbituminous coal, where pf with post-combustion capture may be the most economic choice. The study shows that increasing pf efficiency to decrease CO_2 emissions reduces significantly the thermal and economic penalties associated with CO_2 capture. A recent study by Rubin and others (2007b) took into account recent increase in capital costs but affirmed earlier findings that IGCC plants with CCS generally have a lower total cost of electricity than a similarly sized pf plant with CCS for bituminous coals. However, it was also found that for low-rank coals IGCC was either comparable in cost (for subbituminous coal) or higher in cost (for lignite coal) than a pf plant with capture. Failure to include CO_2 transport and storage costs in addition to CO_2 capture costs also was shown to affect comparisons of alternative systems.

Gibbins and others (2004, 2006a, 2006b) have considered the implications for building ‘capture ready’ power plants. The ideal ‘capture ready’ approach would allow a plant to be built which had the both the same costs and performance as a normal plant without capture when it was built, and then also the same performance and equivalent capital cost as a plant that was built with capture from the outset after capture is added at some time in the future. Examples of how a pulverised coal plant could be made ‘capture ready’ include investing in high efficiency (or upgradeable) FGD and turbine modifications to facilitate steam extraction for the amine-based capture systems. There are economic benefits for ‘capture ready’ plant if CO_2 capture becomes mandatory. The total additional electricity cost for ‘capture ready’ pulverised coal plant was estimated to be 42.6%, but for ‘capture unready’ plant this could amount to 69.5%. In the UK, RWE npower (2007a) have announced that they propose to build a new supercritical 1600 MW coal fired plant in Tilbury, Essex. The plant will be ‘capture ready’ in that it will be designed to accommodate carbon capture and storage technology, although the capture technology to be used was not made clear. It is planned to be operational in 2013. Proposals for another 2400 MW ‘capture ready’ plant at Blyth were announced two months later (RWE npower, 2007b).

The IEA GHG (2007b) has prepared a definition of a ‘capture ready’ plant. It is one which can can include CO_2 capture when the necessary regulatory or economic drivers are in place. The aim of building plants that are capture ready is to reduce the risk of stranded assets and ‘carbon lock-in’. Developers of capture ready plant should take responsibility for ensuring that all known factors in their control that would prevent installation and operation of CO_2 capture have been identified and eliminated. This might include:

- a study of options for CO_2 capture retrofit and potential pre-investments;

- inclusion of sufficient space and access for additional facilities that would be required; and
- identification of reasonable route(s) to storage of CO_2.

Process economic analysis, determination of capital and operating expenses, and overall process evaluation with reference to technical and economical performance criteria have been carried out by Abu-Zahra and others (2006, 2007a,b). By varying operating parameters – percentage CO_2 removal, MEA solvent concentration, lean solvent loading, and stripper operating pressure – an optimum process was designed. The thermal energy requirement in the capture process was the most important factor, contributing about 40% to the total operating costs of the process. The optimal process for a new 600 MWe bituminous coal fired power plant case was: 90% CO_2 removal, 40 wt% MEA, 240 kPa stripper bottom pressure equiovalent to a temperature of 128°C. Regarding the optimum lean solvent loading, the results showed a shallow minimum at a range of lean solvent loading values (0.25–0.33 mol CO_2/mol MEA). The energy required for the optimum process was found to be 3.0 GJ/t CO_2, which is a large reduction compared with 3.9 GJ/t CO_2 for the base case. The thermal efficiency fell from 45% (LHV) to 33% for the optimised case compared with 31% for the base case. The cost of CO_2 avoided for this optimum process was found to be 33 €/t CO_2 avoided compared with the base case value of 39 €/t CO_2.

An evaluation of the technical and economic impacts of removing CO_2 from and existing US coal fired plant (AEP's Conesville No. 5 unit, OH) has been carried out (Ramezan and others, 2006). Retrofitting an 'advanced' MEA capture system at four CO_2 capture levels (90%, 70%, 50%, and 30%) was investigated. No major technical barriers were found except that it would be difficult if not impossible to accommodate all the new CO_2 capture equipment on the site if all six units were to be retrofitted. Energy requirements and power consumption were found to be high. The CO_2 mitigation costs increased slightly from $51 to $66/ton CO_2 avoided as the capture level decreased from 90 to 30%. A nearly linear decrease in the cost of electricity with reduced CO_2 capture indicated that there is no optimum CO_2 recovery level.

It was noted above that Veawab and others (2002) had investigated blends of MEA with MDEA. A feasibility study carried out by Veawab and Aroonwilas (2005a) suggested that blended MEA-MDEA presented a promising cost saving opportunity for CO_2 capture. A more comprehensive feasibility study followed which consisted of technical evaluations of overall process performance and analysis of process cost for both MEA-MDEA and DEA-MDEA blends (Veawab and Aroonwilas, 2005b, 2006a). It was found that both MEA-MDEA and DEA-MDEA are potential solvents that can alter MEA and present cost saving opportunities for CO_2 capture. Such cost saving is primarily attributed to a trade-off feature of the energy consumption during solvent regeneration and the CO_2 capture performance. These two blends require less energy to strip CO_2 in the regenerator compared with MEA reflecting a lower steam cost, while their CO_2 capture performance is lower reflecting a larger capital investment. The favourable saving can be achieved when MEA-MDEA and DEA-MDEA processes are operated with an appropriate mixing ratio and under appropriate operating condition. A case study using MEA-MDEA as an example exhibits 67% reduction in steam cost and 13% overall cost saving. The cost distribution of single and blended amines is shown in Figure 14.

The optimal integration of CO_2 capture into (particularly supercritical) power plants has been simulated by Aroonwilas and Veawab (2006b, 2007). They found that the energy penalty for CO_2 capture can be minimised by:

- using advanced amine technologies, such as MEA-MDEA solvent and split-flow configuration;
- drawing a suitable steam pressure to the CO_2 capture unit, for example, 200 kPa for MEA-MDEA regeneration;
- operating the CO_2 capture unit at a high removal efficiency to obtain an acceptable value of CO_2 avoided per energy penalty; and
- choosing a flue gas delivery scheme that is suitable for the CO_2 capture efficiency.

An important question remains, 'what can we expect the costs of amine scrubbing to be in the future?' Rubin (2005; *see also* IEA GHG, 2006b; Rubin and others, 2007a) addressed this question by considering historical 'experience curves' of analogous technologies such as flue gas desulphurisation systems. Based on these he concluded that the current cost estimates for all larger scale plants with CCS should be taken with a 'grain of salt' until verified by full-scale projects. Analysis of the various technologies indicated that, in most cases, the capital costs have reduced by 10–15% for each doubling of installed capacity. The corresponding reduction in operation and maintenance was 5–30%. Based on learning rate data for analogous process technologies, the cost of electricity from power plants with CO_2 capture was predicted to reduce by 10–18% after 100 GWe of capacity has been installed. It was recognised that the concept of a constant learning rate could be an oversimplified representation of actual cost data. It was also noted that, if radically new CO_2 capture technologies or plant designs were to be developed and adopted commercially, the resulting cost reductions could be greater than those estimated (Rubin and others, 2007a).

A different approach was pursued by Rao and others (2003, 2006) which involved expert elicitation to understand what experts in the field believe about possible improvements in some of the key underlying parameters that govern the performance and cost of amine-based CO_2 capture technology. The experts' opinions were then used in an integrated power plant modelling framework. This indicated that significant improvements were possible over the next decade, assuming R&D support in the area continues to grow steadily and new large-scale applications are realised. The development of better sorbents with lower regeneration energy requirement was identified as the highest priority R&D objective.

The cost of CO_2 capture by post-combustion amine scrubbing in a near zero emissions power plant has been examined by the IEA GHG (2006d). It was noted that, in principle,

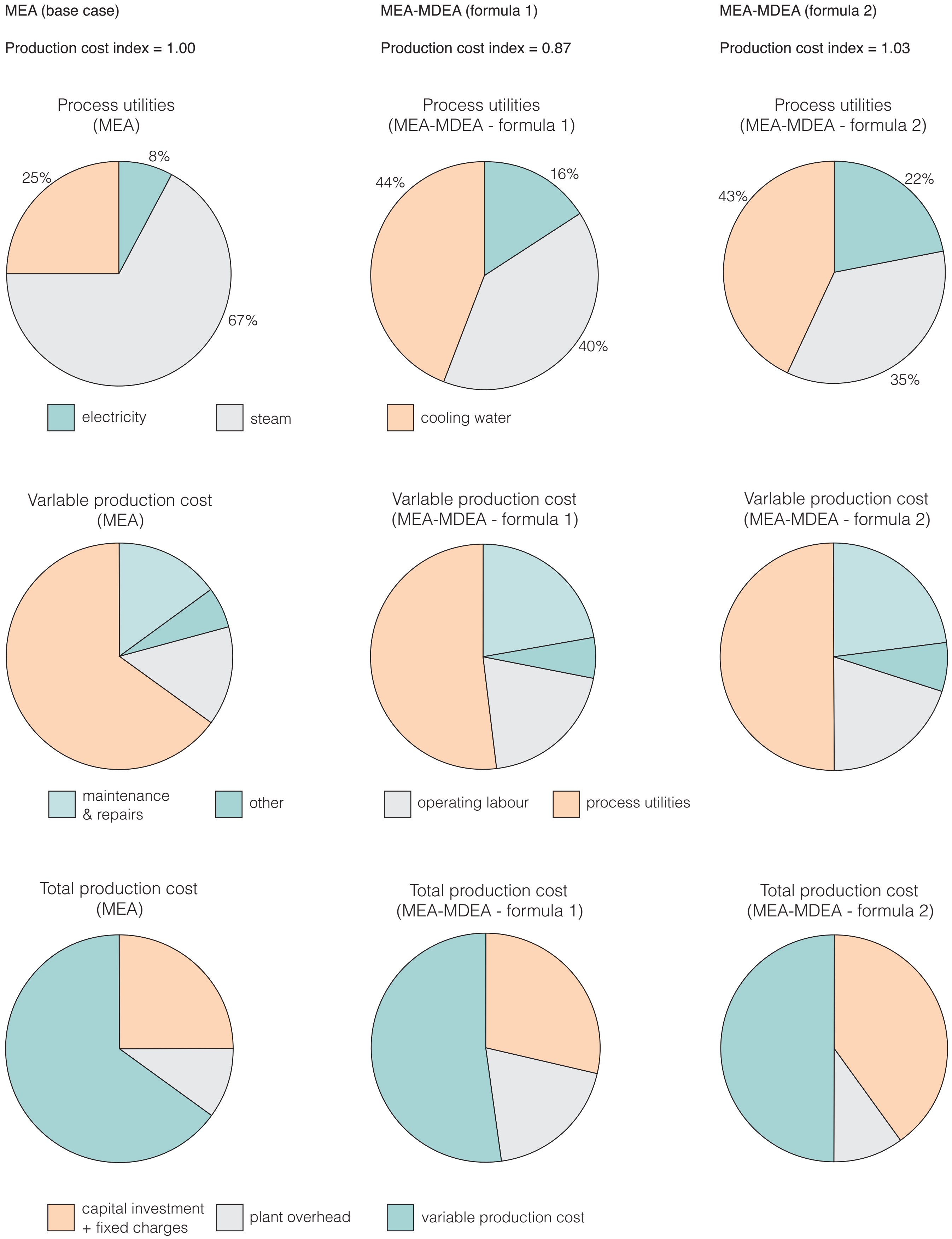


Figure 14 Cost distribution of single and blended amines (Aroonwilas and Veawab, 2006a)

virtually all the CO_2 in flue gas could be captured. However, it was concluded that the marginal costs of achieving near zero emissions with post-combustion capture are excessive.

From a purely economic point of view it would be far better to invest in more power stations with optimum capture than fewer of near zero emission performance.

8 General process modelling and simulation

There have been many examples of process modelling and simulation in recent years, some of which are discussed in other sections of this report. The advantage of modelling and simulation is that potential plant designs and configurations can be tested more quickly and much less expensively than in pilot or demonstration plants. Models can indicate the best directions to pursue or, conversely, those that would probably lead to dead ends. It is not intended to discuss modelling and simulation in detail but simply to illustrate the ways in which they have been used in process development.

Reference has already been made in Chapter 7 to the model used by Rao and Rubin (2002, 2006) to assess amine-based CO_2 capture technology for power plants. The model was introduced to the International Test Network on CO_2 capture at its third workshop (Rubin and Rao, 2002a) and updates have been provided in later workshops (Rubin and Rao, 2002b; Rubin, 2003; Rubin and others, 2004). More details of this *Integrated Environmental Control Model* developed by Carnegie Mellon University's Department of Engineering & Public Policy can be found at http://www.iecm-online.com.

The purpose of the model is to calculate the performance, emissions and cost of employing alternative environmental control methods in a coal-fired power plant. The model consists of a base plant and various control technology modules; these modules may be implemented together in any desired combination. A graphical user interface (GUI) facilitates the configuration of the technologies, entry of data, and retrieval of results.

Alie and others (2002a,b) described a model for simulating CO_2 capture from pulverised coal fired power plants using Aspen Plus® and reported that the 'out-of-the-box' software models the CO_2-MEA-H_2O vapour liquid equilibrium (VLE) adequately. They found that the minimum reboiler heat duty occurred when the CO_2 loading to the absorber was 0.20 mols CO_2/mol MEA.

Aspen Plus® was also used by CO_2 capture by Freguia and Rochelle (2002, 2003) to model the aqueous MEA process. The model was built to analyse the effect on energy requirements of several process variables. The goal was to find operating conditions that allow CO_2 removal with less energy. The absorber and stripper were both modelled with Rate-Frac, a rate-based model framework in Aspen Plus®. In the absorber, the reactions involving CO_2 were described with a kinetic model. In the stripper all the reactions were set to equilibrium, due to the higher operating temperature. This approach required that a rigorous thermodynamic model and a rigorous rate model be implemented in Aspen Plus®. A significant result has already been noted in Chapter 4; an overall optimisation showed that there are no economical ways to reduce the steam requirements by more than 10%.

Aroonwilas and others (2003a,b) have written computer programs that simulate the CO_2 absorption performance of columns packed with structured packings. They performed simulations of CO_2 absorption into aqueous MEA over a wide range of operating conditions (Aroonwilas and others, 2003a). Essential simulation results were the concentration of CO_2 in gas phase, concentration of reactive species in the liquid phase, variation in the column temperature, mass transfer coefficients, and effective interfacial area for mass transfer at different axial positions along the absorption column. The simulation also provided liquid distribution plots representing the quality of liquid distribution (or maldistribution) across the cross section of the column. It was also possible to determine the packing height required for each structured packing for a given CO_2 capture target. A computer program to simulate three different types of structured packing that simulated the mass transfer inside CO_2 absorption systems using sodium hydroxide (NaOH) and MEA solutions was also developed by Tontiwachwuthikul and Aroonwilas (2002; *see also* Aroonwilas and others, 2003b). The packings were Gempak 4A, Mellapak 500Y, and Mellapak 550X. A model of the performance of a CO_2 absorber containing Sulzer DX structured packing was developed by deMontigny and others (2006b).

A rigorous model for predicting the behaviour of CO_2 absorption in packed bed absorption columns has been developed by Aboudheir and others (2006). The validity of the model was confirmed by comparing the predictions with experimental data for the CO_2-MEA system. It was then applied to absorption in aqueous AMP and the results with experimental data from two pilot plant studies. The results were in close agreement with the measured values. For a randomly packed column, the average absolute deviations between the predicted and measured data in terms of CO_2 concentration and temperature profiles were 9.7% and 2.3% respectively. For a structured packed column, the average absolute deviation between the predicted and measured concentration profiles was 13.8%.

In the search for better solvents, Poplsteinova and others (2005) point out that reliable vapour-liquid equilibrium (VLE) models are needed for the testing of the thermodynamic properties of various absorbents and their effect on the absorber performance. They developed a VLE model for CO_2-H_2O-alkanolamine systems based on phase equilibrium conditions for neutral species and chemical equilibria for all elementary reactions in the system.

Tobiesen and Svendsen (2006) developed a computational model for the regeneration unit of an MEA-based absorption plant (earlier results were presented by Tobiesen and Svendsen, 2004 and Tobiesen and others, 2005a). The model was developed to investigate operating the desorber at higher pressures than normal (>0.2 MPa). Operation at a higher pressure could avoid or reduce the recompression of the captured CO_2 to the storage pressures of 10–14 MPa. The model simulated the addition of an inert immiscible component to the desorber in order to provide an independent addition to the pressure, thereby allowing the total pressure to be increased. The modelling revealed that the reboiler duty increases as the inert hydrocarbon is added to the system. Hence, it is probably not feasible to increase pressure in the desorber to the extent that a CO_2 recompression unit can be avoided. On the other hand, an increased desorber pressure could reduce compression costs. Further, if a reduction in reboiler temperature were required in the case of excessive corrosion or solvent degradation, the addition of an organic component could greatly reduce the temperature albeit at the expense of increased reboiler duties. As part of the EU CASTOR Project, Tobiesen and others (2006a; *see also* Tobiesen and others, 2005b) reported experimental validation of the model. Operating data from the first MEA campaign at the CASTOR Esbjerg CO_2 capture pilot plant were compared with simulations performed with the model (Tobiesen and others, 2006b). The experimental data showed that there are limitations in the model when simulating the desorber but that it gives good agreement when simulating the absorber and the overall process. The evaluation of the desorber shows that the equilibrium model may be challenged due to lack of stripping in the lower desorber packing. The simulated total reboiler duty is 3.9 MJ/t CO_2 while the experimentally determined value was 4.0. The simulations indicate that the lean loading for the MEA solvent is around 0.27 with a rich loading of 0.46 giving an approach to equilibrium at the rich exit of 94%. A reasonable steam amount is used for the experimental absorption rate of 89% giving a reboiler duty of 4 MJ/t CO_2. An optimisation with respect to circulation rate and lean loading shows that a lean loading of about 0.24 and a circulation rate of 15.5 m^3/h gives the best performance when 90% CO_2 is removed from the flue gas in the present pilot plant and operational conditions.

A packed column model to simulate the performance of a membrane absorber has been developed by deMontigny and others (2006a). Originally, the model was developed to simulate CO_2 absorption into aqueous MEA in a packed column. The original model was modified for membrane based absorption systems and it was demonstrated to predict the performance of the membrane system with reasonable accuracy. Thus, packed column models can be modified with relative ease to simulate the performance of membrane based absorber systems.

9 Demonstration and pilot plants

Although there are small commercial plants in existence, they were not designed to capture CO_2, rather their function was to produce it for use as food-grade CO_2, or for enhanced oil recovery (EOR). This chapter will describe existing and planned pilot plants where the intention is to demonstrate the capture of CO_2.

The CO_2 extraction plant at Boundary lignite fired power plant in southern Saskatchewan, Canada, was originally used to provide CO_2 for EOR. Several years after it had ceased producing CO_2, a collaborative International Test Centre for CO_2 capture (ITC) was established by the University of Regina (Barrie and Wilson, 2000; Barrie, 2002b; Wilson, 2003, 2004; Wilson and others, 2001, 2003b, 2005a,b; Tontiwachwuthikul, 2002a,b; Booth, 2005; Idem and others, 2006b, http://www.co2-research.ca/) and test results from the recommissioned pilot plant were reported by Barrie (2002a, 2002c, 2003), Wilson (2004), and Wilson and others (2003a, 2004, 2005a). The pilot plant had been idle for 12 years; its recommissioning is described by Skoropad and others (2003). The pilot plant was used to evaluate the performance and reliability of proprietary CO_2 solvent extraction technologies and to obtain engineering data that can be used for the design of commercial scale CO_2 absorption units. The feed to the pilot plant comes from the power station necessitating a baghouse unit to remove fly ash and a two-stage wet scrubbing system to remove SO_2. The flue gas entering the amine extraction unit is virtually free of fly ash and SO_2. The CO_2-rich amine solution from the extraction unit is then passed to a regenerator column where the CO_2 is liberated from the amine by heating. A process flow diagram is shown in Figure 15. Tests showed that the CO_2 removal efficiency of the plant was in the range of 75 to 90% and varied with the reboiler heat duty used for solvent regeneration. CO_2 absorption occurred mostly in the lower portion of the absorber.

Phase I of the project and research has been completed on schedule and within budget (Wilson and others, 2005b). The results indicated that the overall energy penalty to operate a retrofit MEA CO_2 capture facility could be reduced to 50% of the previously reported values. The data from the Boundary Dam plant have been compared with those obtained at the University of Regina technology development pilot plant (Wilson and others, 2005a). The differences in the degradation product slates have been discussed in Section 3.1 above.

At The University of Texas at Austin an existing pilot plant was converted into an integrated absorber/stripper system. It consists of two carbon steel columns (~9.1 m high and ~42.7 cm id) with multiple penetrations and a number of observation windows. A schematic of the plant is shown in Figure 16. The first campaign carried out established the base case scenario for the piperazine/potassium carbonate solvent although a major portion of it was devoted to the setup and troubleshooting of the plant (Chen and Rochelle, 2004, 2005). Dugas and others (2006) have reported results from an MEA campaign which was conducted as a baseline to compare CO_2 absorption and stripping performance with campaigns using

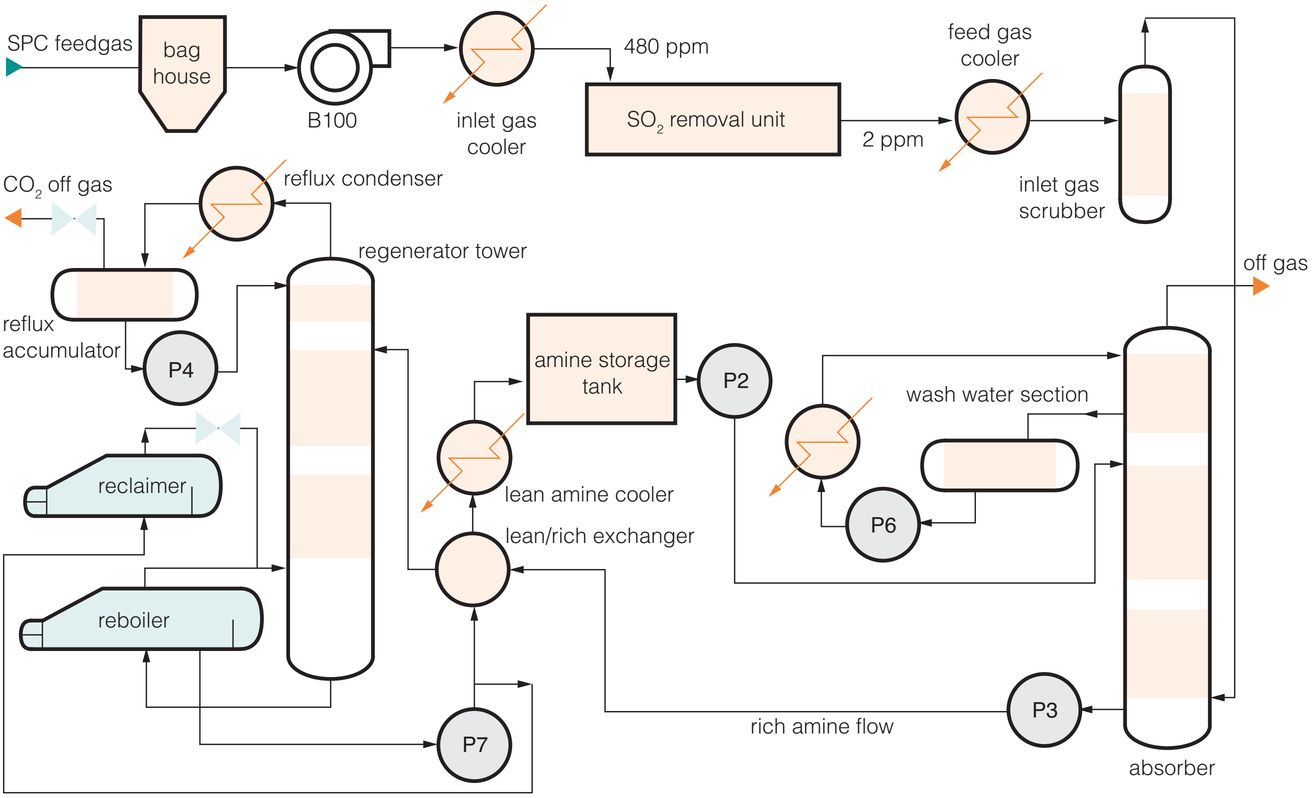


Figure 15 Process flow diagram of the Boundary Dam CO_2 extraction pilot plant (Wilson and others, 2003a)

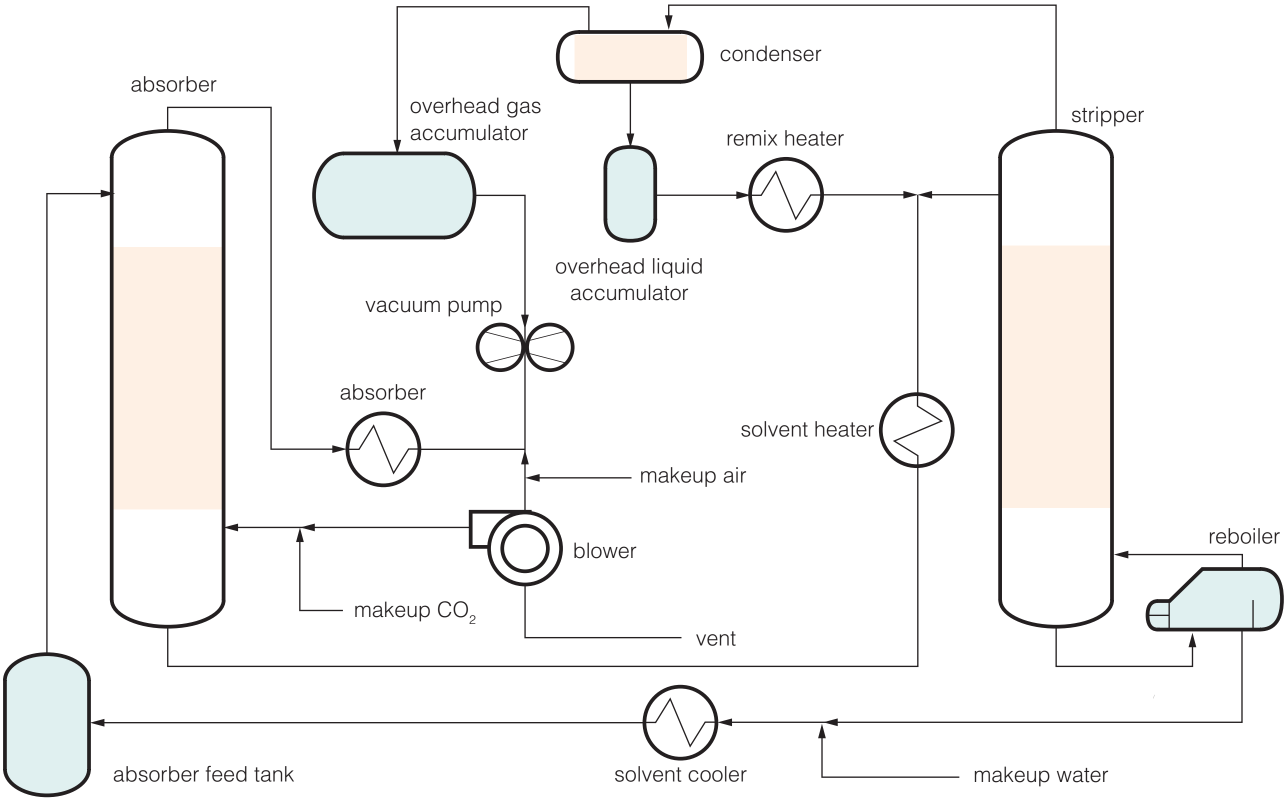


Figure 16 University of Texas pilot plant schematic (Chen and Rochelle, 2005)

an experimental potassium carbonate/piperazine solvent. Experimental results from the three pilot plant campaigns using aqueous piperazine/potassium carbonate have been presented by Chen and others (2006; *see also* Chen and Dugas, 2005). These campaigns successfully demonstrated reliable operation in an absorber/stripper system although temperature bulges in the absorber were significant. At high CO_2 concentrations, the temperature bulge varied from 18 to 33°C.

A 2 t CO_2/d pilot plant has been constructed near unit 5 of the natural gas fired Seoul thermal power plant in Korea (Eum and others, 2005). It uses MEA as the absorbent and real flue gas.

A 1 t CO_2/d pilot plant has been constructed in the MHI Hiroshima R&D centre to demonstrate CO_2 capture from coal fired flue gas and carry out various tests for the treatment of impurities. The plant uses the sterically hindered amine KS-1 solvent developed by KEPCO/MHI and special proprietary equipment (Iijima and others, 2005; Yagi and others, 2005). It is claimed that, compared with the MEA method the KEPCO/MHI technology can reduce the CO_2 capture energy by 20% and reduce the deterioration of the solvent to approximately 1/50. Although, in the 2 t CO_2/d pilot plant at the natural gas fired Nanko power plant in Osaka (Yagi and others, 2006), the new improved KM-CDR (Kansai-Mitsubishi proprietary Carbon Dioxide Recovery) process had a steam consumption 15% less than the conventional MEA process. The KS-1 solvent has been used commercially but not in coal fired plant. The Hiroshima pilot plant incorporates MHI's experience in commercial FGD plants to remove flue gas impurities prior to CO_2 capture. The process flow of the MHI pilot plant is shown in Figure 17.

The CO_2 recovery system incorporates a rinse tower for a high level of sulphur dioxide removal using caustic soda, a cooling tower for cooling the cleaned flue gas, an absorbing tower for capturing CO_2 with the KS-1 solvent, and a regenerating tower for stripping CO_2 by heating the solvent absorbing the CO_2 with steam. The regeneration of the KS-1 solvent can be carried out at low pressures and temperatures of 110–120°C. In the pilot test, Australian coal was used and two tests were run, one with <1 ppm (dry) of SO_2 at the inlet of the CO_2 absorber and the other with 30 ppm of SO_2, other conditions remained the same.

The higher level of SO_2 had no apparent effect on the CO_2 recovery performance. On the other hand, although the concentration of heat stable salts, particularly sulphates, in the form of deteriorated products in the solvent increased with the higher concentration of SO_2, it was as low as 1 wt% of the KS-1 or less. The purity of the CO_2 captured from the flue gas was approximately 99.8% (dry). The major impurities being nitrogen (0.14%) and oxygen (0.04%). SO_2 was not detected in the captured CO_2 even in the high SO_2 case. No heavy metals were detected.

MHI has constructed a plant to demonstrate what is now called the 'Kansai-Mitsubishi proprietary Carbon Dioxide Recovery process' (KM-CDR process). The demonstration plant has the capacity to recover 10 tons of CO_2 per day using flue gas containing 14.1 vol% CO_2 taken at a rate of 1750 Nm^3/h from a coal fired boiler of J-POWER's Matsushima power plant at Saikai City, Nagasaki, Japan (Ohishi and others, 2006; Modern Power Systems, 2006a). Starting in July 2006 with more than 3000 hours of operation planned, the plant is designed to demonstrate:

- the actual mass balance of substances which require long

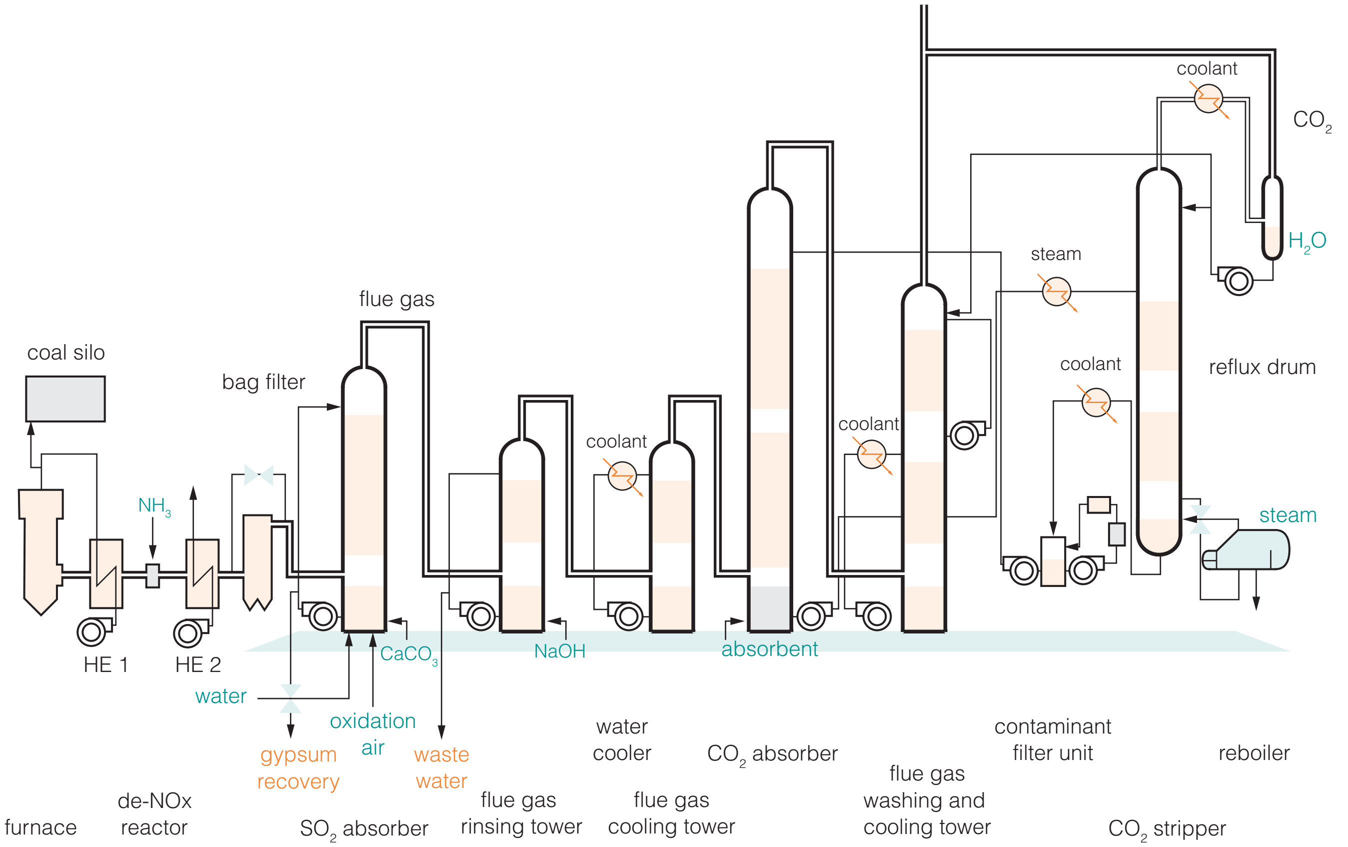


Figure 17 Process flow of MHI pilot plant (Iijima and others, 2005)

periods to accumulate in the absorber; and

- the gradual change with the passage of time of parameters such as deterioration of absorbent and corrosion;
- optimisation of the impurities pre-removal system will be carried out based on the evaluation of the results from 1 and 2.

As part of the Australian Low Emissions Technology Demonstration Fund (LETDF), two post-combustion capture projects are being built. One is a natural gas combined cycle plant powered by coalbed methane, the other is a 25 t/d capture plant on International Power's 1600 MW Hazelwood brown coal pf plant in Victoria's Latrobe Valley. Some further details can be found at http://www.greenhouse.gov.au/demonstrationfund/. The project, to be built with the assistance of funds from the Victorian State Government's Energy Technology Innovation Strategy (ETIS) fund, will use proprietary solvent technology with the CO_2 being minerally sequestered. The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) will provide technology support for this project. In an associated project, funded by the ETIS brown coal R&D fund, the CO2CRC will, as well as the solvent absorption system, test a full suite of separation technologies including adsorption, gas absorption membranes and gas separation membranes in these power plant conditions. Also in Australia, CSIRO has developed a 1000 t/y transportable pilot plant operating on slip streams from operating power plants (Wibberley, 2005, 2006; Brockway and Wibberley, 2006; Puxty, 2007).

A pilot plant has been constructed in the Netherlands based on a patented working method using polyolefin membrane gas absorption and dedicated absorption liquids (CORAL) based on mixtures of salts and amino acids (Feron and ten Asbroek, 2005a,b). The flowsheet is shown in Figure 18.

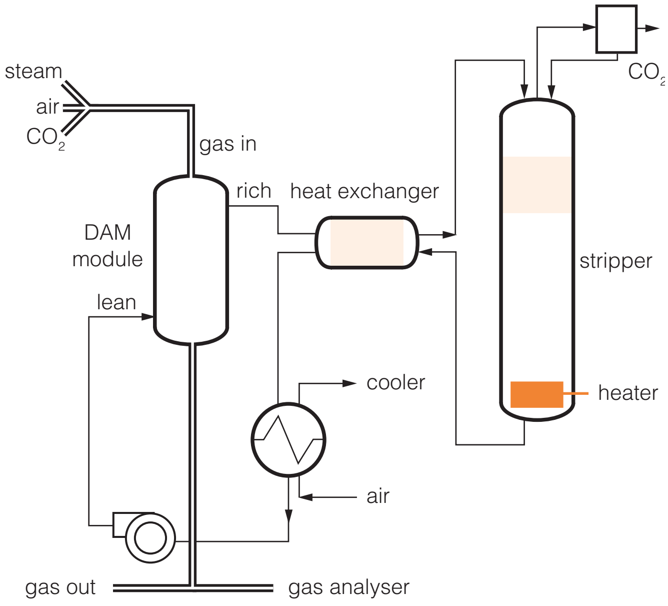


Figure 18 CORAL pilot plant flow diagram (Feron and ten Asbroek, 2005b)

A mini plant has been built at the Institute of Thermodynamics and Thermal Process Engineering at the University of Stuttgart as part of the CASTOR integrated EU project (Notz and others, 2006, 2007) to screen new solvents for further testing in the larger CASTOR pilot plant. This has

Table 5 Design specifications of CASTOR pilot plant (Knudsen and others, 2006)

Flue gas capacity	5000 = Nm^3/h 0.5% of Esbjerg plant flue gas flow
CO_2 production (at 12 vol% CO_2)	1000 kg/h
Absorption degree	90%
Maximum solvent flow	2500 kg/h (3.5 bar)
Maximum reboiler steam flow	2 bar
Flue gas conditions	47°C (sat), <10 ppm SO_2, <65 ppm NOx, <10 mg/Nm^3 dust

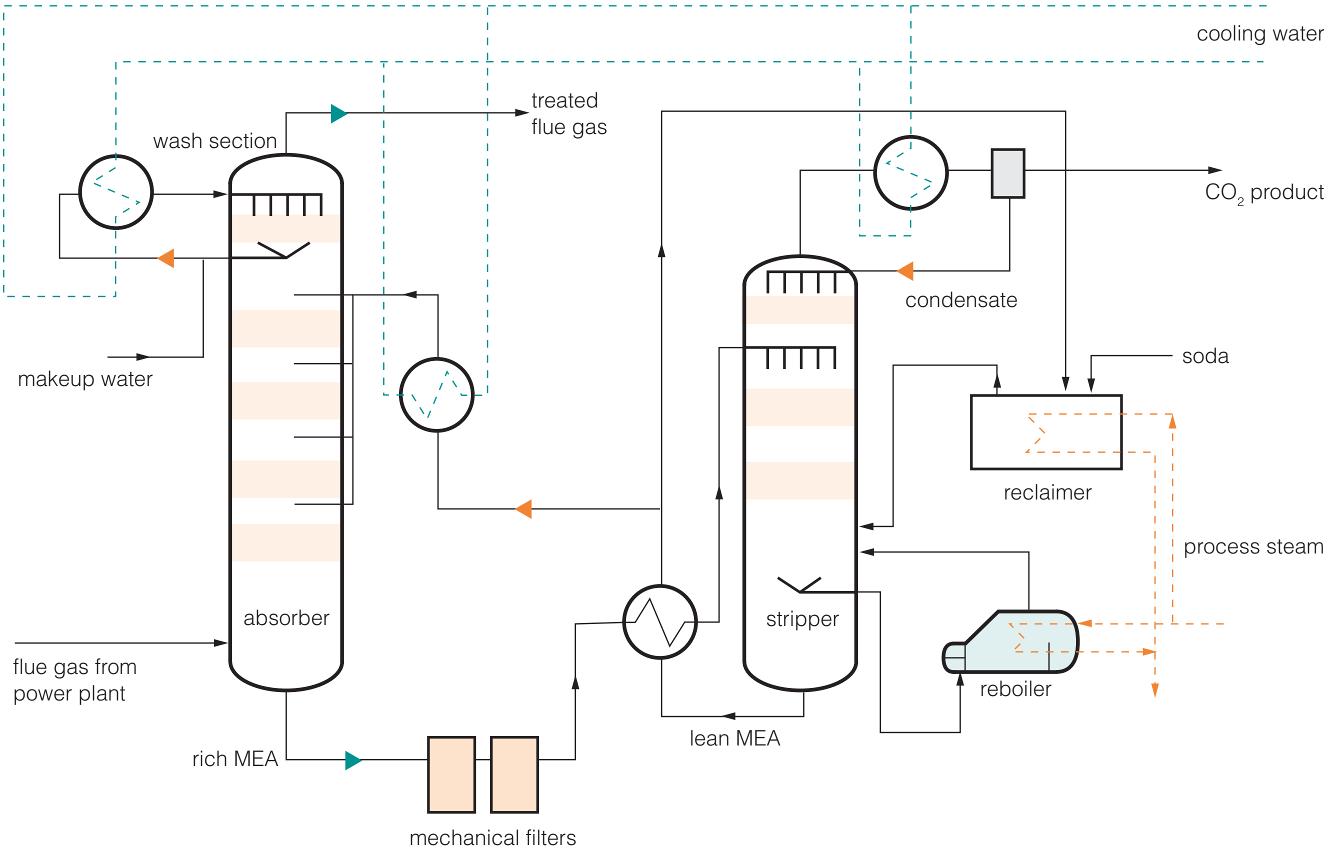


Figure 19 Flow diagram of the CASTOR pilot plant at the Esbjerg coal fired power plant (Knudsen and others, 2006)

been constructed at the Esbjerg power station in Denmark (Le Thiez and others, 2006; www.co2castor.com). The test facility, launched on 15 March 2006, has a capacity of 1 t CO_2/hour and will be operated for two years with real flue gas and uses a 30% aqueous MEA solution but other solvents will be tested. In fact, prior to the official opening, in January-February 2006, a 1000 hours test campaign on 30% MEA was conducted at the pilot plant (Biede and Knudsen, 2006; Knudsen and others, 2006, 2007a; Feron and others, 2007). The key design and performance figures for the pilot plant are shown in Table 5 and a flowsheet in Figure 19. The flue gas purity criteria were defined in order to avoid excessive solvent degradation or other adverse impact on the pilot plant operation, for example, foaming and fouling. In daily practice, the NOx level is allowed to rise significantly above 65 ppm, whereas high SO_2 concentrations will cause plant shutdown.

During the test campaign the pilot plant was operating at 93% CO_2 removal efficiency, producing approximately 850 kg/h of CO_2. Thus, the CO_2 removal efficiency had been above the target value of 90%. This early operation experience also indicated that controlling the water balance and dealing with SO_2 and particulates from the coal flue gas may be a challenge. Indications were found that the MEA solvent consumption rate (2.5 kg/t CO_2) might be higher than the rate known from industrial CO_2 plants operating on flue gases derived from gaseous or oil fuels. The steam requirement was found to be 4000 MJ/t CO_2. Some experimental data from the first MEA campaign were also reported by Tobiesen and others (2006b). A second 1000 hours campaign using 30% MEA has been conducted at the pilot plant (Knudsen and others, 2007b). The campaign indicated that:

- stable operation on coal derived flue gas is possible;
- it is possible to operate at neutral water balance but neutral water balance may increase emissions;
- for MEA the specific steam consumption was 3.75 GJ/ton CO_2 at 90% removal;
- ‘optimal’ operating conditions with respect to energy consumption may not be optimal in daily practice; and
- slipstream filtration may be the best method to remove gypsum and fly ash particles.

In Italy, ENEL has almost completed the design of a 2.25 t CO_2/h slipstream pilot plant to be installed at the Brindisi Sud power station (La Marca and others, 2007). The pilot plant will use a 20 wt% MEA solution and should be in operation by the end of 2008.

As noted in Section 5.4, Alstom (2006), in collaboration with EPRI, has announced that a 5 MW pilot plant is planned in the USA which will use chilled ammonia (Modern Power Systems, 2006b; Rhudy, 2006, 2007; Douglas, 2007). The US$10 million pilot plant will capture about 100 t CO_2/d from a portion (~1%) of the flue gas at the We Energies’ Pleasant Prairie coal fired power plant in Kinosha, WI. Also, AEP (2007) announced plans on 15 March 2007 to begin capture of up to 100,000 t CO_2/y at its coal fired Mountaineer plant in West Virginia.

The IEA Greenhouse Gas R&D Programme has suggested that a full-scale demonstration plant for CO_2 capture by amine solvents be commissioned (Topper, 2005). This would probably be stand-alone but it could be one stream on a large unit. The size would need to be at least 300 MWe to justify supercritical operation and high efficiency SO_2 and NOx clean-up would also be required. Approximately 6000 t CO_2/d should be captured.

10 National and international R&D programmes

This section will be limited to coordinated programmes operating within individual countries or internationally. There are many carbon capture and storage programmes but this chapter will be limited to those in which solvent scrubbing represents a major part.

Australia

Australia has a Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC). This centre researches capture and geological storage of CO_2 and has a mandate to demonstrate both aspects of CCS technology. Overview of the capture programme have been provided by Kentish (2005), Hooper and Murray (2006), and Webley (2007). Further details can be found at http://www.co2crc.com.au/. The work of the centre in the first three years of operation has identified several potentially cost effective post-combustion capture techniques. The first is using carbonate absorption of flue gases in local power plants – this utilises the fact that Australian power plants have limited NOx and SO_2 removal facilities. These contaminants will be removed for fertilizer usage along with bulk CO_2 removal. This, along with other solvent and separation process testing, will be demonstrated in the LETDF/ETIS funded projects, discussed in Chapter 9. While solvent absorption will have a significant role to play in post-combustion capture of CO_2 the CO2CRC has identified and tested parameters that would make adsorbent and membrane processes competitive with solvent absorption systems.

A National Post Combustion Capture (NPCC) programme is being proposed in Australia, incorporating a research programme (AU$20 M) led by CSIRO (Wibberley, 2005, 2006; Brockway and Wibberley, 2006; Puxty, 2007). The research component provides a focus for applied research, laboratory and pilot testing of sorbents and technologies, for Australian specific PCC requirements. Testing will include use of a 1000 t/y transportable pilot plant operating on slip streams from operating power plants. For PCC to be implemented in Australia, plants will require retrofit of deNOx and deSOx equipment which will reduce the advantages of PCC. This situation requires that new sorbents and new process designs be developed to minimise the effect of NOx and SOx. Without cost effective PCC, in a carbon constrained future, many of the current 40 GW of pf plant could become stranded assets. Many Australian plants are located in areas of high sunshine, and these could utilise some lower grade heat. PCC is particularly suitable for using solar thermal energy, and new sorbents with lower regeneration temperature (as distinct from regeneration energy) could further improve the cost benefits of this integration. PCC can also provide a means for offsetting peak load, and can therefore assist in the integration of intermittent renewables into the grid.

Canada

Canada's *National Initiative on CO_2 Capture and Storage* was presented by Legg and others (2001). One of its three working groups is a CO_2 capture group to target topics such as absorption, O_2/CO_2 combustion, and membrane and cryogenic separation. Up-to-date information can be found at http://www.nrcan.gc.ca/es/etb/cetc/combustion/co2network/htmldocs/aboutus_e.html.

The *Canadian Clean Power Coalition* was formed in 2001 by power generators and coal suppliers representing over 90% of Canada's coal fired power generation (Campbell and Richards, 2002; Stobbs and Barrie, 2004; Stobbs and Clark, 2005). A summary of its work on CO_2 capture and storage was produced by the IEA Clean Coal Centre (Morrison, 2004) and can be found at http://www.iea-coal.org.uk/publishorsystem/component_view.asp?PhyDocId=5602&LogDocId=81216.

Up-to-date information can be found at http://www.canadiancleanpowercoalition.com/Customer/ccpc/ccpcwebsite.nsf.

A compendium of all Canada's participation in carbon dioxide capture and storage activities has been produced by Natural Resources Canada (2006; Bulut and Dell, 2007). It is also available at http://www.nrcan.gc.ca/es/etb/cetc/combustion/co2network/pdfs/ccs_canadian_compendium_e.pdf.

European Union

A listing of European Union research programmes carried out as part of the 6th Framework programme (2003-2006) has been provided by Feron (2003b). From the point of view of amine scrubbing, the most relevant is the CASTOR project: *CA*pture and *STOR*age of CO_2. Further details have been provided by Le Thiez (2004), Feron (2005), Biede and Knudsen (2006), Le Thiez and others (2006), Svendsen (2007), and can also be found at www.co2castor.com.

Japan

In 2004, three Japanese companies formed the Cost Saving CO_2 Capture System (COCS) Project to study chemical absorption processes and to develop novel absorbents with high absorption rates and low reaction energies (Shimizu and others, 2006). Two new but un-named high-performance absorbents have been identified from fundamental experiments. Solvent A has a feature of much higher CO_2 capture capacity than MEA and Solvent B shows preferable characteristics in absorption/desorption rate and reaction heat.

The Netherlands

The Government of the Netherlands supports the CATO programme, implemented by a consortium of Dutch companies, research, universities, and environmental organisations, led by the Utrecht Centre for Energy Research. The aim of CATO is to identify whether and how CO_2 capture and storage (CCS) can contribute to a sustainable energy system in the Netherlands, from an economical, technical, social and ecological point of view and under which conditions this option could be implemented in the energy system. The programme began in 2004 and will run to 2008.

The total budget amounts to €25.4 million of which €12.7 million is a Dutch government subsidy (Lysen and others, 2005). Post-combustion capture of CO_2 is work package 2.1 of the programme. Up-to-date information can be found at http://www.co2-cato.nl/.

As part of the CATO programme, KEMA has performed a baseline study in which a number of CO_2 capture processes have been evaluated (Ploumen, 2006).

Connected with the CATO programme, CAPTECH is a research programme of six Dutch consortium partners. The programme runs from 2006 until 2009 and is coordinated by the Energy research Centre of the Netherlands (ECN). The aim of the consortium is the development of CO_2 capture technologies with power plant efficiency losses of less than 5 percentage points, resulting in capture costs not higher than 20–30 €/t CO_2 depending on fuel type. The budget of the programme is €2.5 million per year, and is financial supported by the Dutch government. Part of the programme involves advanced solvents: new advanced chemical and hybrid solvents with low regeneration energy consumption for post- and pre-combustion CO_2 capture.

More details can be found at http://www.co2-captech.nl.

United Kingdom

The UK Carbon Capture and Storage Consortium Project was started in June 2005 by a group of 14 UK universities and research institutions with funding from the UK Research Councils' Towards a Sustainable Energy Economy (TSEC) Programme. The mission of the consortium is: 'to promote an understanding of how options for decoupling fossil fuel use from carbon emissions through the use of carbon capture and storage could be used to assist the UK in achieving an energy system which is environmentally sustainable, socially acceptable and meets energy needs securely and affordably' (Gibbins and others, 2006c). Further details can be found at http://www.co2capture.org.uk/UKCCSC/.

USA

An overview of the US *Carbon Sequestration R&D Program* was presented by Schmidt and Beecy (2001). In 2000, the funding was $9.2 million and one of the five pathways of the programme was 'Separation and capture'. Up-to-date information can be found at http://www.fossil.energy.gov/programs/sequestration/index.html and http://www.netl.doe.gov/technologies/carbon_seq/index.html. There is also a database of 'carbon sequestration' projects but few are directed specifically at solvent scrubbing http://www.fossil.energy.gov/fred/feprograms.jsp?prog=Carbon+Sequestration.

11 Environmental aspects

Recently, some attention has been paid to the possible adverse environmental impacts of CO_2 capture by solvents. Direct environmental impacts could result from the emission of solvent and its degradation products and indirectly by the production and transport of solvent and additives and the final waste as a result of disposal of solvent and degradation products. The environmental impacts of solvent processes have been studied for the IEA GHG (2006e) by van Gijlswijk and others (2006, 2007) using a life cycle assessment (LCA) methodology. The environmental impacts are influence primarily by the increased fuel use. Figure 20 gives the environmental impact ‘spider graph’ for the ultra supercritical pulverised coal fired power plant (USCPF) without and with CO_2-capture. The graph shows the impacts on various environmental ‘themes’. The decrease of SO_2 and NOx emissions is clearly visible as a dent on the left side of the figure in the acidification and photochemical oxidation themes. The high impact on human toxicity is almost fully caused by the production of MEA. The graph indicates a need for more energy efficient solvents and solvents whose consumption in the process is less. It should be noted that, although the ‘spokes’ in Figure 20 are of equal length, this does not mean that all the impact categories are of equal importance. It is easy to be misled by such diagrams.

It is pointed out that large scale deployment of amine scrubbing in power plants would need alkanolamine production to increase by at least a factor of 10 compared with the estimated current production. Although the amount of waste reclaimer sludges would be large, the amounts are small compared with the fuel use and they are also still smaller than the consumption of limestone in coal firing. These sludges can also be considered to be environmentally manageable (IEA GHG, 2006e).

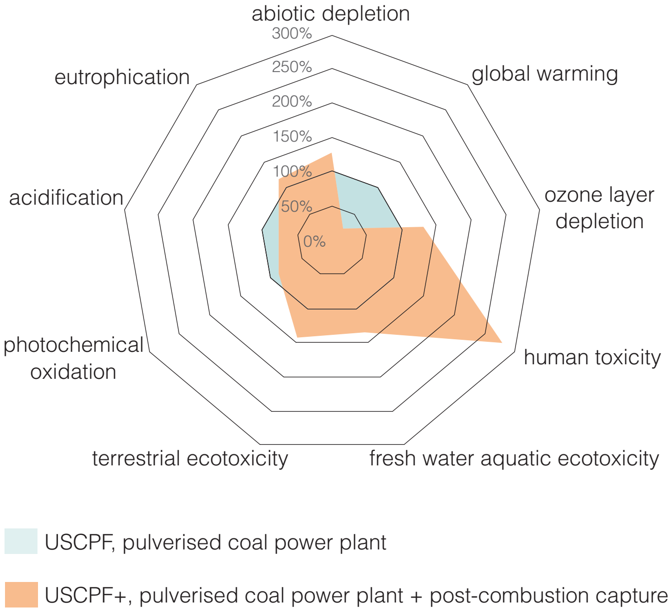


Figure 20 Environmental impact spider graph for ultra supercritical pulverised coal plant (van Gijlwijk and others, 2006)

Thitakamol and others (2006, 2007) point out that CO_2 capture units integrated into coal fired power plants may create mild, unintentional and potential burdens to the human health and the environment through four pathways including treated gas, process wastes (liquid, solid and vapour), fugitive emissions, and accidental emissions. Among the first three pathways, reclaimer waste is the largest in quantity and contributes the highest impacts due to the presence of heavy metal corrosion inhibitors and heat-stable salts. Treated gas contributes less because it contains amine solvents and some types of degradation products but not corrosion inhibitors. Fugitive emissions are the smallest and contribute the least to the environmental impacts. The impacts can be predetermined and properly mitigated through a well-established environmental management program and mitigation measures. Use of more environmentally friendly chemicals, especially as corrosion inhibitors and other additives, is also encouraged.

The Norwegian pollution authorities have classified MDEA and piperazine as ‘red’ chemicals which means that they have to be replaced by ‘green’ or ‘yellow’ alternatives for *offshore* application (Hoff and others, 2007). However, it is not unreasonable to suspect that the regulations might extend to onshore applications some time in the future. Using the EC-50 test many amines, including MEA, MDEA, AMP, and piperazine are not considered toxic but on biochemical oxygen demand considerations, MDEA and piperazine are considered to be ‘red’ but MEA is ‘yellow’. None of the tested chemicals were considered to be bioaccumulating. Most tertiary and sterically hindered amines are considered to be ‘red’. In future, the ecological impacts of amine solvents may prove to have an impact on the choice of solvent.

At present, there are few data concerning the environmental impacts of solvent scrubbing of CO_2. Thus, it is not possible to quantify these potential impacts with any degree of accuracy.

12 Conclusions

If we consider that there are over 2000 coal fired power plants in existence then, other than shutting them down, or substituting natural gas for coal, the best option for CO_2 emission abatement is to retrofit as many as possible with carbon capture systems. At present, the lead contending technology would appear to be solvent scrubbing using amine solvents. Some of the advantages of amine scrubbing for post-combustion capture can be listed, the process:

- can be retrofitted to some existing power plants in suitable locations;
- has been proven on a small scale;
- may offer flexibility if it can be switched between capture and no capture,
- offers potential cost reductions if it proves to be analogous to other technologies; and
- has a strong research base which should lead to better solvents and processes.

Nevertheless, the difficulties in retrofitting post-combustion capture must not be underestimated. There is little point in retrofitting plants of low thermal efficiency since the efficiency losses would render the plant uneconomic. Also, if the views of Ducroux and Jean-Baptiste (2005) that only limited evolution is expected in solvent development are correct, then CO_2 capture by solvents may be superseded by other processes. These, such as solid sorbents and membranes, will be the topic of a future IEA Clean Coal Centre report.

However, flue gas from coal fired power plant should be viewed as a fairly difficult material for amine solvents to deal with, so some challenges remain:

- the cost of electricity will increase;
- more coal is needed for the same power generation capacity;
- it is likely that the FGD systems will need to be improved; and
- there is no experience with CO_2 capture in coal fired plant at full power plant scale.

There are other problems, such as the degradation products formed by solvent reaction with flue gas from coal and the associated corrosion problems. It is likely that these could be avoided by the use of stainless steel components in the CO_2 capture equipment but this would increase the capital cost.

The reason that the cost of electricity increases and more coal is needed is the reboiler heat duty, the energy that is needed to regenerate the solvent by driving off the captured CO_2. Efforts to reduce this heat duty are at the heart of reducing the total costs of solvent scrubbing. There has been much work directed at finding alternative solvents to MEA that could result in the overall energy demand being reduced.

Some of the energy demand can be reduced by improved design of the contactors which provide the area on which the gas and liquid phases interact.

There is hope that the economics of CO_2 capture will improve; analogous technologies have seen considerable cost reductions as a result of ‘learning by doing’ and many experts believe that significant improvements are possible in the next decade. Certainly, if new power plants are to be built, it makes sense to build them ‘capture ready’ if possible. Despite many well planned national and international R&D programmes and the existence of some pilot and demonstration plants, as yet there is no full-scale demonstration plant. One is sorely needed.

A potential problem is that, in capturing CO_2 with solvents, environmental problems are shifted elsewhere. It is likely that any environmental impacts can be properly mitigated but they certainly should not be ignored.

Finally, the main challenge still remains: how to reduce the costs of capture.

13 References

Aaron D, Tsouris C (2005) Separation of CO_2 from flue gas: a review. *Separation Science and Technology*; **40** (1/3); 321-348 (Jan 2005)

Aboudheir A, Tontiwachwuthikul P, Chakma A (2001) CO_2-MEA absorption in packed columns: comprehensive experimental data and modeling results. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 217-222 (2001)

Aboudheir A, Tontiwachwuthikul P, Idem R (2006) Rigorous model for predicting the behaviour of CO_2 absorption into AMP in packed-bed absorption columns. *Industrial and Engineering Chemistry, Research*; **45** (8); 2421-2429 (12 Apr 2006)

Abu-Zahra M R M, Niederer J P M, Feron P H M, Versteeg G F (2006) The technical and economical analysis of CO_2 capture based on an absorption/desorption process using mono-ethanolamine. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_04_05.PDF, 6 p. (2006) CD-ROM

Abu-Zahra M R M, Schneiders L H J, Niederer J P M, Feron P H M, Versteeg G F (2007a) CO_2 capture from power plants. Part I. A parametric study of the technical performance based on monoethanolamine. *International Journal of Greenhouse Gas Control*; **1** (1); 37-46 (Apr 2007)

Abu-Zahra M R M, Schneiders L H J, Niederer J P M, Feron P H M, Versteeg G F (2007b) CO_2 capture from power plants. Part II. A parametric study of the economical performance based on mono-ethanolamine. *International Journal of Greenhouse Gas Control*; **1** (2); 135-142 (Apr 2007)

AEP (2007) *AEP to install carbon capture on two existing power plants; company will be first to move technology to commercial scale***.** Press release (15 Mar 2007) http://www.aep.com/newsroom/newsreleases/default.asp?dbcommand=displayrelease&ID=1351

Al-Juaied M, Rochelle G T (2006) Absorption of CO_2 in aqueous diglycolamine. *Industrial and Engineering Chemistry, Research*; **45** (8); 2473-2482 (12 Apr 2006)

Alie C (2005) A generalized framework for scheduling the operation of power plants incorporating CO_2 capture. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 110-130 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Alie C, Croiset E, Douglas M, Douglas P (2002a) Simulating CO_2 from pulverized coal fired power plants: model assumptions. Assessment of MEA-CO_2 processes using AspenPlus. In: *International Test Network for CO_2 Capture: report on 3rd workshop,* Apeldoorn, the Netherlands, 16-17 May 2002. Report PH4/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 247-282 (Jul 2002) http://www.co2captureandstorage.info/docs/PH4-11%20ApeldoornWorkshop.pdf

Alie C, Croiset E, Douglas M, Douglas P (2002b) Assessment of MEA-CO_2 processes using AspenPlus. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 22 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Alie C, Douglas P, Croiset E (2006a) Simulation and optimization of a coal-fired power plant with integrated CO_2 capture using MEA scrubbing. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_08.PDF, 6 p. (2006) CD-ROM

Alie C, Douglas P, Croiset E, Elkamel A (2006b) A generalized framework for evaluating the performance of CO_2 capture processes. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_06_07.PDF, 6 p. (2006) CD-ROM

Alix P, Raynal L (2006) Liquid distribution and liquid hold-up in a high capacity structured packing. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_04.PDF, 6 p. (2006) CD-ROM

Alstom (2006) *ALSTOM to build pilot plant in the US to demonstrate its unique CO_2 capture process.* Press release (2 Oct 2006) http://www.power.alstom.com/pr_power/2006/october/27531.EN.php?languageId=EN&dir=/pr_power/2006/oc tober/&idRubriqueCourante=2727

Aresta M, Dibenedetto A (2003) New amines for the reversible absorption of carbon dioxide from gas mixtures. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1599-1602 (2003)

Aroonwilas A (2005) Evaluation of split-flow scheme for CO_2 absorption process using mechanistic mass- transfer and hydrodynamic model. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1841-1844 (2005)

Aroonwilas A, Veawab A (2004) Characterization and comparison of the CO_2 absorption performance into single and blended alkanolamines in a packed column. *Industrial and Engineering Chemistry, Research*; **43** (9); 2228-2237 (28 Apr 2004)

Aroonwilas A, Veawab A (2006a) Cost, energy consumption and performance of CO_2 capture process using MEA-MDEA and DEA-MDEA. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_04_06.PDF, 6 p. (2006) CD-ROM

Aroonwilas A, Veawab A (2006b) Integration of CO_2 capture unit using single- and blended-amines into supercritical coal-fired power plants: implications for emission and energy management. In: 8th *international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_09.PDF, 6 p. (2006) CD-ROM

Aroonwilas A, Veawab A (2006c) Cost structure and performance of CO_2 capture unit using split-stream cycle . In: 8th *international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_26.PDF, 5 p. (2006) CD-ROM

Aroonwilas A, Veawab A (2007) Integration of CO_2 capture unit using single- and blended-amines into supercritical coal-fired power plants: implications for emission and energy management. *International Journal of Greenhouse Gas Control*; **1** (2); 143-150 (Apr 2007)

Aroonwilas A, Tontiwachwuthikul P, Chakma A (2001) Effects of operating and design parameters on CO_2 absorption in columns with structured packings. *Separation and Purification Technology*; **24** (3); 403-411 (2001)

Aroonwilas A, Chakma A, Veawab A, Tontiwachwuthikul P (2003a) New column design concept for CO_2 absorbers fitted with structured packings. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd (Pergamon), Volume II, pp 1587B1590 (2003)

Aroonwilas A, Chakma A, Tontiwachwuthikul P, Veawab A (2003b) Mathematical modelling of mass- transfer and hydrodynamics in CO_2 absorbers packed with structured packings. *Chemical Engineering Science*; **58** (17); 4037-4053 (Sep 2003)

Audus, H (2001) Leading options for the capture of CO_2 at power stations. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 91-96 (2001)

Barrie J (2002a) Update of activities: Boundary Dam CO_2 pilot plant. In: *International Test Network for CO_2 Capture: report on 2nd workshop,* Calgary, Canada, 12-13 Nov 2001. Report PH4/4, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 8 p. (Jan 2002)
http://www.co2captureandstorage.info/docs/PH4-4%202nd%20CO2-Calgary.pdf

Barrie J (2002b) International Test Centre for CO_2 capture. In: *International Test Network for CO_2 Capture: report on 3rd workshop,* Apeldoorn, the Netherlands, 16-17 May 2002. Report PH4/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 6 p. (Jul 2002)
http://www.co2captureandstorage.info/docs/PH4-11%20ApeldoornWorkshop.pdf

Barrie J (2002c) Update of activities: Boundary Dam CO_2 pilot plant. In: *International Test Network for CO_2 Capture: report on 3rd workshop,* Apeldoorn, the Netherlands, 16-17 May 2002. Report PH4/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 6 p. (Jul 2002)
http://www.co2captureandstorage.info/docs/PH4-11%20ApeldoornWorkshop.pdf

Barrie J (2003) Boundary Dam CO_2 pilot plant. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 174-179 (Jul 2003)
http://www.co2captureandstorage.info/docs/PH4-22.pdf

Barrie J, Wilson M (2000) Practical R&D needs. In: *International Test Network for CO_2 Capture: report on a workshop,* Gaithersburg, MD, USA, 11-12 Oct 2000. Report PH3/33, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 5 p. (Dec 2000)
http://www.co2captureandstorage.info/docs/Ph3_33%20CO2%20capture%20workshop%20report%20.pdf

Bello A, Idem R O (2005) Pathways for the formation of products of the oxidative degradation of CO_2-loaded concentrated aqueous monoethanolamine solutions during CO_2 absorption from flue gases. *Industrial and Engineering Chemistry, Research*; **44** (4); 945-969 (16 Feb 2005)

Bello A, Idem R O (2006) Comprehensive study of the kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous monoethanolamine (MEA) with and without sodium metavanadate during CO_2 absorption from flue gases. *Industrial and Engineering Chemistry, Research*; **45** (8); 2569-2579 (12 Apr 2006)

Biede O, Knudsen J (2006) Carbon dioxide capture and storage activities in Denmark. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 26-86 (Jun 2006)
http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Bishnoi S, Rochelle G T (2000) Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chemical Engineering Science*; **55** (22); 5531-5543 (Nov 2002)

Bishnoi S, Rochelle G T (2002a) Thermodynamics of piperazine/methyldiethanolamine/water/carbon dioxide. *Industrial and Engineering Chemistry, Research*; **41** (83); 604-612 (6 Feb 2002)

Bishnoi S, Rochelle G T (2002b) Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine. *AIChE Journal*; **48** (12); 2788-2799 (Dec 2002)

Booth N J (2005) *Secondment to the International Test Centre for CO_2 capture (ITC), University of Regina, Canada; January-March 2005.* Report COAL R303 DTI/Pub URN 06/798, London, UK, Department of Trade and Industry, 94 p. (May 2005)

Brockway D, Wibberley L (2006) Post combustion capture program in Australia. In: 8th *international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_03_01.PDF, 6 p. (2006) CD-ROM

Broutin P, Kittel J, Pasquier D, Ropital F (2005) Corrosion experiments for CO_2 solvent. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 260-280 (Nov 2005)
http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Brouwer J P, Feron P H M, ten Asbroek N A M (2006) CO_2 absorption using precipitating amino acids in a spray tower. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 87-104 (Jun 2006) http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Bulut D, Dell L (2007) Clean coal: a compendium of Canada's engagement. In: *CCT2007: Third international conference on clean coal technologies for our future*, Cagliari, Italy, 15-17 May 2007. Davidson R M (ed.) London, UK, IEA Clean Coal Centre, 7 p. (2007) CD-ROM

Campbell B, Richards W H (2002) The Canadian Clean Power Coalition CO_2 extraction demonstration project: an update. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 521 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Carrette P-L, Cadours R, Boucot P, Mougin P, Gibert A, Jacquin M (2007) New solvent for CO_2 capture with low energy of regeneration. In: *International Test Network for CO2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 263-275 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Chalmers H, Gibbins J (2007) Initial evaluation of the impact of post-combustion capture of carbon dioxide on supercritical pulverised coal power plant part load performance. Article in press in *Fuel.*

Chalmers H, Chen C, Lucquiaud M, Gibbins J, Strbac G (2006) Initial evaluation of carbon capture plant flexibility. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_04_02.PDF, 6 p. (2006) CD-ROM

Chen E, Dugas R (2005) Pilot plant for CO_2 capture. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 192-216 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Chen E, Rochelle G T (2004) Pilot plant for CO_2 capture using aqueous piperazine/potassium carbonate. In: *International Test Network for CO_2 Capture: report on 7th workshop,* Vancouver, BC, Canada, 10 Sep 2004. Report PH4/34, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 268-295 (Oct 2004) http://www.co2captureandstorage.info/docs/PH4-34%20Capture%20network%207th%20Workshop.pdf

Chen E, Rochelle G T (2005) Pilot plant for CO_2 capture with aqueous piperazine/potassium carbonate. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1821-1824 (2005)

Chen E, Rochelle G T, Seibert F (2006) Pilot plant for CO_2 capture with aqueous piperazine/potassium carbonate. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_04.PDF, 6 p. (2006) CD-ROM

Chi S, Rochelle G T (2002) Oxidative degradation of monoethanolamine. *Industrial and Engineering Chemistry, Research*; **41** (17); 4178-4186 (21 Aug 2002)

Cullinane J T, Rochelle G T (2003) Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1603-1606 (2003)

Cullinane J T, Rochelle G T (2004) Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. *Chemical Engineering Science*; **59** (17); 3619-3630 (Sep 2004)

Cullinane J T, Rochelle G T (2005a) Thermodynamics of aqueous potassium carbonate, piperazine, and carbon dioxide. *Fluid Phase Equilibria*; **227** (2); 197-213 (25 Jan 2005)

Cullinane J T, Rochelle G T (2005b) Concentrated potassium carbonate/piperazine mixtures for an improved carbon dioxide capture process. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1825-1829 (2005)

Cullinane J T, Rochelle G T (2006) Kinetics of carbon dioxide absorption into aqueous potassium carbonate and piperazine. *Industrial and Engineering Chemistry, Research*; **45** (8); 2531-2545 (12 Apr 2006)

Cullinane J T, Oyenekan B A, Lu J, Rochelle G T (2005) Aqueous piperazine/potassium carbonate for enhanced CO_2 capture. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 63-71 (2005)

da Silva E, Svendsen H F (2004) Ab initio study of the reaction of carbamate formation from CO_2 and alkanolamines. *Industrial and Engineering Chemistry, Research*; **45** (13); 3413-3418 (2004)

da Silva E F, Svendsen H F (2005) The chemistry of CO_2 absorption in amine solutions studied by computational chemistry. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1891-1895 (2005)

da Silva E F, Svendsen H F (2006a) Study of the carbamate stability of amines using ab initio methods and free-energy perturbations. *Industrial and Engineering Chemistry, Research*; **45** (8); 2497-2504 (12 Apr 2006)

da Silva E F, Svendsen H F (2006b) Chemistry of solvents for CO_2-capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_01.PDF, 6 p. (2006) CD-ROM

da Silva E F, Svendsen H F (2007) Computational chemistry study of reactions, equilibrium and kinetics of chemical CO_2 absorption. *International Journal of Greenhouse Gas Control*; **1** (2); 151-157 (Apr 2007)

da Silva E F, Pereira F S, González E P (2006) Experimental characterization and computational chemistry study on novel solvents for CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier

Ltd., paper P01_01_11.PDF, 4 p. (2006) CD-ROM

Dang H, Rochelle G T (2003) CO_2 absorption rate and solubility in monoethanolamine/piperazine/water. *Separation Science and Technology*; **38** (2); 337-357 (2003)

Dave N C, Duffy GJ, Edwards J H, Lowe A (2001) Economic evaluation of capture and sequestration of CO_2 from Australian black coal-fired power stations. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 173-178 (2001)

Davison J (2007) Performance and costs of power plants with capture and storage of CO_2. *Energy*; **32** (7); 1163-1176 (Jul 2007)

deMontigny D (2004) Comparing packed columns and membrane absorbers for CO_2 capture. In: *International Test Network for CO_2 Capture: report on 7th workshop,* Vancouver, BC, Canada, 10 Sep 2004. Report PH4/34, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 296- (Oct 2004) http://www.co2captureandstorage.info/docs/PH4-34%20Capture%20network%207th%20Workshop.pdf

deMontigny D, Tontiwachwuthikul P, Chakma A (2001) Parametric studies of carbon dioxide absorption into highly concentrated monoethanolamine solutions. *Canadian Journal of Chemical Engineering*; **79** (1); 137- 142 (Feb 2001)

deMontigny D, Tontiwachwuthikul P, Chakma A (2003) Carbon dioxide absorption contactors: hollow fibre membranes and packed absorption columns. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1583-1586 (2003)

deMontigny D, Tontiwachwuthikul P, Chakma A (2005) Absorption of carbon dioxide using packed columns and membrane contactors. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1933-1936 (2005)

deMontigny D, Aboudheir A, Tontiwachwuthikul P, Chakma A (2006a) Using a packed-column model to simulate the performance of a membrane absorber. *Industrial and Engineering Chemistry, Research*; **45** (8); 2580-2585 (12 Apr 2006)

deMontigny D, Aboudheir A, Tontiwachwuthikul P, Chakma A (2006b) Modelling the performance of a CO_2 absorber containing structured packing. *Industrial and Engineering Chemistry, Research*; **45** (8); 2594- 2600 (12 Apr 2006)

Derks P W J, Dijkstra H B S, Hogendoorn J A, Versteeg G F (2005) Solubility of carbon dioxide in aqueous piperazine solutions. *AIChE Journal*; **51** (8); 2311-2327 (Aug 2005)

Derks P W J, Kleingeld T, van Aken C, Hogendoorn J A, Versteeg G F (2006) Kinetics of absorption of carbon dioxide in aqueous piperazine solutions. *Chemical Engineering Science*; **61** (20); 6837-6854 (Oct 2006)

Dibenedetto A, Aresta M, Narracci M (2002) Carbon dioxide capture by amines: increasing the efficiency by amine structure modification. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **47** (1); 53-54 (Spr 2002)

Dibenedetto A, Aresta M, Girardi R (2003) New amines for carbon dioxide separation from gas-mixtures. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **48** (1); 167-168 (Spr 2003)

Douglas J (2007) The challenge of carbon capture. *EPRI Journal*; 14-21 (Spr 2007)

Draxler J, Stevens G, Kentish S (2005) Criteria for the selection of reagents for CO_2 absorption. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1879-1882 (2005)

Ducroux R, Jean-Baptiste P (2005) Technologies, methods and modelling for CO_2 capture. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1835-1839 (2005)

Dugas R E, Rochelle G T, Seibert F (2006) CO_2 capture performance of a monoethanolamine pilot plant. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_02.PDF, 6 p. (2006) CD-ROM

Dugas R, Hilliard M, Sexton A, Davis J, Mathur N (2007) 7m MEA & 7m MEA/2m PZ: kinetics, thermodynamics & degradation. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 41-71 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Epp B, Fahlenkamp H, Pieper B, Stankewitz C, Erich E, Vogt M (2007) Tail-end CO_2 capture as convincing opportunity for retrofitting of coal-fired power stations and related R&D objectives. *VGB PowerTech*; **87** (5); 106-116 (2007)

EPRI (2000) *Evaluation of innovative fossil fuel power plants with CO_2 removal.* Report 1000316, Palo Alto, CA, USA, EPRI, 396 p. (Dec 2000) Available from: http://www.netl.doe.gov/technologies/carbon_seq/Resources/Analysis/pubs/EPRICO2Study.pdf

Eum H-M, Kim J-H, Jang K-R, Ahn Y-M (2005) CO_2 recovery pilot plant. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1929- 1932 (2005)

Falk-Pederson O, Dannström H, Grønvold M, Stuksrud D-B, Rønning O (2001) Gas treatment using membrane gas/liquid contactors. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 115-120 (2001)

Féraud A, Marocco L, Howard T (2006) CASTOR study of technological requirements for flue gas clean-up prior to CO_2-capture. In: *8th international conference on greenhouse* *gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_06.PDF, 6 p. (2006) CD-ROM

Feron P H M (2002) CO_2 capture from flue gas. In: *International Test Network for CO_2 Capture: report on 3rd workshop,* Apeldoorn, the Netherlands, 16-17 May 2002. Report PH4/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 6 p. (Jul 2002) http://www.co2captureandstorage.info/docs/PH4-11%20ApeldoornWorkshop.pdf

Feron P H M (2003a) CO_2 capture using membrane gas absorption - status report. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp180-201 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Feron P H M (2003b) CO_2 capture and storage: EU project initiatives. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 344-352 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Feron P H M (2004) New solvents based on amino-acids for CO_2 cpature from flue gases; their use in the DECAB process. In: *International Test Network for CO_2 Capture: report on 6th workshop,* Trondheim, Norway, 8-9 Mar 2004. Report PH4/28, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 301-320 (May 2004) http://www.co2captureandstorage.info/docs/PH4-28%20Capture%20network%206th%20Workshop.pdf

Feron P H M (2005) CASTOR: CO_2 from capture to storage. "A project overview and tasting." In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 301-336 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Feron P H M, ten Asbroek N (2005a) Developments in CO_2-capture using amino-acid salt solutions and novel processes. In: *8th international conference on energy for a clean environment*: *Cleanair 2005*, Lisbon, Portugal, 27-30 Jun 2005. Lisbon, Portugal, Instituto Superior Tecnico, Paper 01.2_N.Asbroek.pdf, 15 p. (2005)

Feron P H M, ten Asbroek N (2005b) New solvent based on amino-acid salts for CO_2 capture from flue gases. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 1, pp 1153-1158 (2005)

Feron P H M, Abu-Zahra M, Alix P, Biede O, Broutin P, de Jong H, Kittel J, Knudsen J, Raynal L, Vilhelmsen P-J (2007) Development of post-combustion capture of CO_2 within the CASTOR integrated project: results from the pilot plant operation using MEA. In: *CCT2007: Third international conference on clean coal technologies for our future*, Cagliari, Italy, 15-17 May 2007. Davidson R M (ed.) London, UK, IEA Clean Coal Centre, 15 p. (2007) CD-ROM

Freguia S, Rochelle G T (2002) Modeling of CO_2 absorption/stripping with monoethanolamine. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 26 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Freguia S, Rochelle G T (2003) Modeling of CO_2 capture by aqueous monoethanolamine. *AIChE Journal*; **49** (7); 1676-1686 (Jul 2003)

Gabrielsen J, Michelsen M L, Stenby E H, Kontogeorgis G M (2006) Modelling of randomly packed CO_2 absorber using an alkanolamine solution. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_01.PDF, 4 p. (2006) CD-ROM

Gibbins J (2006) Making new power plants 'capture ready'. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 205-226 (Jun 2006) http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Gibbins J, Crane B, Cooper P (2002) Integration of absorber system with steam cycle for energy optimisation, exergy optimisation, economic optimisation, economic + economic risk optimisation. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 19 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Gibbins J, Crane R, Lambropoulos D, Man C, Jingbo Z (2004) Making pulverised coal plant 'capture ready': methods and benefits. In: *International Test Network for CO_2 Capture: report on 7th workshop,* Vancouver, BC, Canada, 10 Sep 2004. Report PH4/34, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 67-83 (Oct 2004) http://www.co2captureandstorage.info/docs/PH4-34%20Capture%20network%207th%20Workshop.pdf

Gibbins J R, Crane R I, Lambropoulos D, Booth C, Roberts C A, Lord M (2005) Maximising the effectiveness of post combustion CO_2 capture systems. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 139-146 (2005)

Gibbins J, Li J, Liang X (2006a) Capture ready fossil fuel plants: a critical stage in tackling climate change. In: *The 7th European Gasification conference*, Barcelona, Spain, 25-27 Apr 2006. Rugby, UK, Institution of Chemical Engineers, 9 p. (2006)

Gibbins J, Lucquiaud M, Li J, Lord M, Liang X, Reiner D, Sun S (2006b) Capture ready fossil fuel plants: definitions, technology options and economics. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_04_03.PDF, 6 p. (2006) CD-ROM

Gibbins J, Haszeldine S, Holloway S, Pearce J, Oakey J, Reiner D, Turley C (2006c) interim results from the UK Carbon Capture and Storage Consortium project. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_03_05.PDF, 6 p. (2006) CD-ROM

Goff G S, Rochelle G T (2003a) Oxidative degradation of aqueous monoethanolamine in CO_2 capture systems under absorber conditions. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume I, pp 115-120 (2003)

Goff G S, Rochelle G T (2003b) Oxidative degradation of aqueous monoethanolamine in CO_2 capture. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 202-222 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Goff G S, Rochelle G T (2004a) Monoethanolamine degradation: O_2 mass transfer effects under CO_2 capture conditions. *Industrial and Engineering Chemistry, Research*; **43** (20); 6400-6408 (29 Sep 2004)

Goff G S, Rochelle G T (2004b) Oxidative degradation of monoethanolamine: O_2 mass transfer & degradation inhibitors. In: *International Test Network for CO_2 Capture: report on 7th workshop,* Vancouver, BC, Canada, 10 Sep 2004. Report PH4/34, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 229-251 (Oct 2004) http://www.co2captureandstorage.info/docs/PH4-34%20Capture%20network%207th%20Workshop.pdf

Goff G S, Rochelle G T (2005) Oxidative degradation of monoethanolamine in CO_2 capture: O_2 mass transfer. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1831-1834 (2005)

Goff G S, Rochelle G T (2006) Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO_2 capture processes. *Industrial and Engineering Chemistry, Research*; **45** (8); 2513- 2521 (12 Apr 2006)

Habaki H, Perera J, Kentish S, Stevens G W (2006) Absorption behaviour of a CO_2-MEA system in a packed column with a novel packing. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_13.PDF, 6 p. (2006) CD-ROM

Hakka L (2007) Integrated regenerable SO_2 and CO_2 capture. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 156-173 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Han K, Park S, Lee J, Nam S, Min B (2006) A study about absorption rate and capacity of CO_2 in aqueous mixture of AMP and HMDA. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_14.PDF, 4 p. (2006) CD-ROM

Herzog H, Falk-Pederson O (2001) The Kværner membrane contactor: lessons from a case study in how to reduce capture costs. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 115-120 (2001)

Hilliard M D, Rochelle G T (2005) Thermodynamics of aqueous piperazine/potassium carbonate/carbon dioxide characterized by the electrolyte non-random two-liquid model in Aspen Plus. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1975-1978 (2005)

Hilliard M D, Kim I, Rochelle G T, Svendsen H F, Hoff K A (2006) Thermodynamics of carbon dioxide in aqueous piperazine/potassium carbonate systems at stripper conditions. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_05.PDF, 6 p. (2006) CD-ROM

Ho M T, Wiley D E, Allinson G W (2006) Reducing the cost of post-combustion CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_05_04.PDF, 6 p. (2006) CD-ROM

Hoff K A, Mejdell T, Juliussen O, Børresen E, Lauritsen K G, Semb H T, Svendsen H F (2006) Solvents selection for a post combustion CO_2 capture process. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_08.PDF, 6 p. (2006) CD-ROM

Hoff K A, da Silva E F, Brakstad O G, Sørheim K R (2007) Reducing the Environmental impact of Acid gas Control Technologies - REACT. In: I*nternational Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 174-190 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Hoggart S (2006) The Capital Letter Challenge. *The Guardian*; 16 (12 Jul 2006)

Hooper B, Murray L (2006) Overview of the CO2CRC capture program. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 03_03_01.PDF, 6 p. (2006) CD-ROM

Huttenhuis P J G, van Elk E O, Versteeg G F (2007) Performance of aqueous MDEA blends for CO_2 removal from flue gases. In: *International Test Network for CO2 Capture: report on 10th workshop, Lyon*, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 96-116 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Idem R, Wilson M, Tontiwachwuthikul P, Chakma A, Veawab A, Aroonwilas A, Gelowitz D (2006a) Pilot plant studies of the CO_2 capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina capture technology development plant and the Boundary Dam CO_2 capture demonstration plant. *Industrial and Engineering Chemistry, Research*; **45** (18); 2414-2420 (12 Apr 2006)

Idem R, Wilson M, Tontiwachwuthikul P, Veawab A, Aroonwilas A, Gelowitz D (2006b) Capturing carbon in Canada. *Modern Power Systems*; **26** (4); 28-29 (Apr 2006)

IEA GHG (2000) *International Test Network for CO_2 Capture: report on a workshop,* Gaithersburg, MD, USA, 11-12 Oct 2000. Report PH3/33, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, vp. (Dec 2000) http://www.co2captureandstorage.info/docs/Ph3_33%20CO2%20capture%20workshop%20report%20.pdf

IEA GHG (2004a) *Canadian Clean Power Coalition studies on CO_2 capture and storage.* Report PH4/27, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 63 p. (Mar 2004)

IEA GHG (2004b) *Improvement in power generation with post-combustion capture of CO_2.* Report PH4/33, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 272 p. (Nov 2004)

IEA GHG (2006a) *CO_2 capture in low rank coal power plants.* Report 2006/1, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 617 p. (Jan 2006)

IEA GHG (2006b) *Estimating the future trends in the cost of CO_2 capture technologies.* Report 2006/6, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 104 p. (Feb 2006)

IEA GHG (2006c) *CO_2 capture as a factor in power station investment decisions.* Report 2006/8, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 144 p. (May 2006)

IEA GHG (2006d) *Near zero emission technology for CO_2 capture from power plant.* Report 2006/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 114 p. (Oct 2006)

IEA GHG (2006e) *Environmental impact of solvent scrubbing of CO_2.* Report 2006/14, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 153 p. (Nov 2006)

IEA GHG (2007a) *Capturing CO_2.* Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 19 p. (May 2007)

IEA GHG (2007b) CO_2 capture ready plants. Report 2007/4, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 127 p (May 2007)

Iijima M, Ishida K, Takashina T, Tanaka H, Hirata T, Yonekawa T (2005) Carbon dioxide capture technology for coal fired boiler. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1781-1785 (2005)

Imai N (2002) Flue gas CO_2 capture (CO_2 capture technology of KS-1). In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 20 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Imai N, Ishida K (2005) Economic study on CO_2 capture and sequestration from PCF flue gas. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 147-154 (2005)

IPCC (2005) *IPCC special report on carbon dioxide capture and storage.* Metz B, Davidson O, de Coninck H, Loos M, Meyer L (eds.) New York, NY, USA, Cambridge University Press, 440 p. (2005) http://www.ipcc.ch

Jang K-R, An Y-M, Kim J-H, Eum H-M, Min B-M (2005) Solubility of carbon dioxide inaqueous solutions of 2 2-amino-2-ethyl-1,3-propanediol. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1865-1868 (2005)

Jassim M S, Rochelle G T (2006) Innovative absorber/stripper configurations for CO_2 capture by aqueous monoethanolamine. *Industrial and Engineering Chemistry, Research*; **45** (8); 25465-2472 (12 Apr 2006

Kentish S (2005) CO2CRC: capturing CO_2 down under. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 2415-446 (2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Kim I, Ma'mun S, Tobiesen F A, Svendsen H (2006) Determination of absorption of CO_2 in the aqueous solutions of MEA, MDEA, and AEEA. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_07.PDF, 6 p. (2006) CD-ROM

Kittel J, Pasquier D, Ropital F, Boudou C, Bonneau A (2006) Corrosion experiments for CO_2 solvents. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paperP01 01_27_.PDF, 6 p. (2006) CD-ROM

Knudsen J N, Vilhelmsen P-J, Biede O, Jensen J N (2006) CASTOR 1 t/h CO_2 absorption pilot plant at the Elsam Kraft A/S Esbjerg power plant - first year operation experience. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_01, 6 p. (2006) CD-ROM

Knudsen J N, Vilhelmsen P-J, Jensen J N, Biede O (2007a) First year operating experience with a 1 t/h CO_2 absorption pilot plant at Esbjerg coal-fired power plant. *VGB PowerTech*; **87** (3); 57-61 (2007)

Knudsen J N, Jensen J N, Vilhelmsen P-J, Biede O (2007b) CASTOR pilot plant - results and implications for scale up. In: *International Test Network for CO_2 Capture: report on 10th workshop,* Lyon, France, 24-25 May 2007. Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 17%p. (2007) To be published. http://www.co2captureandstorage.info/networks/capture_workshops.htm

Knuutila H, Anttila M, Børresen E, Juliussen O, Svendsen H F (2006) CO_2 capture with sodium carbonate. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_16.PDF, 6 p. (2006) CD-ROM

La Marca C, Malloggi S, Politi M, Rossi N (2007) CO2 post combustion capture - the ENEL's demonstration project. In: *Power-Gen Europe*, Madrid, Spain, 26-28 Jun 2007. Upshire, UK, PennWell Corp., paper ID 187, 17 p. (2007) CD-ROM

Lawal A O, Idem R O (2006) Kinetics of oxidative degradation of CO_2 loaded and concentrated aqueous MEA-MDEA blends during CO_2 absorption from flue gas streams. *Industrial and Engineering Chemistry, Research*; **45** (8); 2601-2607 (12 Apr 2006)

Lawal O, Bello A, Idem R (2005) Pathways and reaction products for the oxidative degradation of CO_2 loaded and concentrated aqueous MEA and MEA/MDEA mixtures during CO_2 absorption from flue gases. In: *Proceedings of* *the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 1, pp 1159-1164 (2005)

Le Thiez P (2004) CASTOR - CO_2 from capture to storage: a European initiative. In: *International Test Network for CO_2 Capture: report on 6th workshop,* Trondheim, Norway, 8-9 Mar 2004. Report PH4/28, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 386-406 (May 2004) http://www.co2captureandstorage.info/docs/PH4-28%20Capture%20network%206th%20Workshop.pdf

Le Thiez P, Lindeberg E, Feron P, Zweigel P (2006) CASTOR, CO_2 capture to storage: overview of results obtained after 2 years. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_01.PDF, 6 p. (2006) CD-ROM

Legg J, McDonald M, Wilson M (2001) Canada's National Initiative on CO_2 Capture and Storage. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 1056-1061 (2001)

Lysen E, Faaij A, Hendriks C (2005) The CATO programme in the Netherlands on CO_2 capture, transport and storage. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1849-1852 (2005)

Majchrowicz M, Niederer J P M, Versteeg G F, Velders A H (2006) Precipitation in amino salt CO_2 absorption systems. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_18.PDF, 6 p. (2006) CD-ROM

Ma'mun S, Svendsen H, Hoff K A, Juliussen O (2005) Selection of new absorbents for carbon dioxide capture. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 45-53 (2005)

Ma'mun S, Jakobsen J P, Svendsen H, Juliussen O (2006a) Experimental and modeling study of the solubility of carbon dioxide in aqueous 30 mass % 2-((2-aminoethyl)amino)ethanol solution. *Industrial and Engineering Chemistry, Research*; **45** (8); 2505-2512 (12 Apr 2006)

Ma'mun S, Juliussen O, Hoff K A, Svendsen H (2006b) Absorption of carbon dioxide using aqueous 30 mass % 2-((2-aminoethyl)amino)ethanol solution**.** In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_21.PDF, 6 p. (2006) CD-ROM

Ma'mun S, Svendsen H, Hoff K A, Juliussen O (2007) Selection of new absorbents for carbon dioxide capture. *Energy Conversion and Management*; **48** (1); 251-258 (Jan 2007)

Mimura T, Matsumoto K, Iijima M, Mitsuoka S (2001) Development and application of flue gas carbon dioxide recovery technology. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 138-142 (2001)

Mimura T, Nojo T, Iijima M, Yoshiyama T, Tanaka H (2003) Recent developments on flue gas CO_2 recovery technology. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1057-1061 (2003)

Modern Power Systems (2006a) MHI attacks CO_2 capture on two fronts. *Modern Power Systems*; **26** (4); 31 (Apr 2006)

Modern Power Systems (2006b) Chilling news for carbon capture. *Modern Power Systems*; **26** (12); 17,19 (Dec 2006)

Morrison G F (2004) *Summary of Canadian Clean Power Coalition work on CO_2 capture and storage.* London, UK, IEA Clean Coal Centre, 23 p. (Aug 2004) Available from http://www.iea-coal.org.uk/publishor/system/component_view.asp?PhyDocId=5602&LogDocId=81216

Muramatsu E, Iijima M (2003) Life cycle assessment for CO_2 capture technology from exhaust gas of coal power plant. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume I, pp 57-62 (2003)

Natural Resources Canada (2006) Carbon dioxide capture and storage: a compendium of Canada's participation. Ottawa, Canada, Natural Resources Canada, 245 p. (2006) CD-ROM http://www.nrcan.gc.ca/es/etb/cetc/combustion/co2network/pdfs/ccs_canadian_compendium_e.pdf

Notz R, Asprion N, Clausen I, Hasse H (2006) Selection of solvents for post combustion CO_2 capture and mini plant experiments with MEA. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_10.PDF, 6 p. (2006) CD-ROM

Notz R, Asprion N, Clausen I, Hasse H (2007) Selection and pilot plant tests of new absorbents for post- combustion carbon dioxide capture. *Chemical Engineering Research & Design*; **85** (A4); 510-515 (Apr 2007)

Ohishi T, Iwasaki S, Tanaka H, Hirata T, Iijima M, Ishida K, Yonekawa T (2006) Long term testing of the capture of CO_2 from a coal-fired boiler. Paper presented to: *8th international conference on greenhouse gas control technologies: GHGT-8*, Trondheim, Norway, 19-22 Jun 2006. 6 p. (2006) http://www.ghgt8.no/ [Paper not on CD-ROM] https://events.adm.ntnu.no/ei/viewpdf.esp?id=24&file=d%3A%5CAmlink%5CEVENTWIN%5Cdocs%5Cpdf%5C950Final00324%2Epdf

Okabe K, Nakamura M, Mano H, Teramoto M, Yamada K (2006) Separation and recovery of CO_2 by membrane/absorption hybrid method. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_08.PDF, 6 p. (2006) CD-ROM

Oyenekan B A, Rochelle G T (2005a) Stripper models for CO_2 capture by aqueous solvents. In: *Proceedings of the seventh international conference on greenhouse gas control* *technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1861-1864 (2005)

Oyenekan B A, Rochelle G T (2005b) Modeling of innovative stripper concepts. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 131-151 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Oyenekan B A, Rochelle G T (2006a) Energy performance of stripper configurations for CO_2 capture by aqueous amines. *Industrial and Engineering Chemistry, Research*; **45** (8); 2457-2464 (12 Apr 2006)

Oyenekan B A, Rochelle G T (2006b) Alternative stripper configurations to minimize energy for CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_03.PDF, 6 p. (2006) CD-ROM

Panesar R, Lord M, Simpson S, White V, Gibbins J, Reddy S (2006) Coal-fired Advance Supercritical Boiler/Turbine retrofit with CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_03_01.PDF, 6 p. (2006) CD-ROM

Park S-Y, Min B-M, Lee J-S, Nam S-C, Han K-H, Hyun J-S (2004) Absorption characteristic of continuous CO_2 absorption process. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **49** (1); 249-250 (Spr 2004)

Park S, Lee J, Min B, Jang K, Eum H (2005) Absorption rates of CO_2 into aqueous mixtures of MDEA (methyldiethanolamine) and HMDA (hexamethylenediamine). In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1901-1905 (2005)

Park H, You J K, Hong W H, Kim J-N, Ko C H, Park J (2006) Absorbent based on ammonia for removal of carbon dioxide. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **51** (1); 115-117 (Spr 2006)

Plasynski S I, Chen Z-Y (2000) Review of CO_2 capture technologies and some improvement opportunities. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **45** (4); 644-649 (Aug 2000)

Ploumen P (2006) Retrofit of CO_2 capture at coal-fired power plants in the Netherlands. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_05_06.PDF, 6 p. (2006) CD-ROM

Poplsteinova J, Svendsen H F, Krane J (2005) Modeling VLE for CO_2-H_2O-alkanolamine systems and NMR study on the liquid phase composition. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1869-1872 (2005)

Puxty G (2007) Current CO_2 PCC research and development activity, CSIRO Energy Technology, Australia. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 447-478 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Ramezan M, Nsakala N, Liljedahl G (and others) (2006) *Carbon dioxide capture from existing coal-fired power plants.* DOE/NETL-401/120106, Pittsburgh, PA, USA, National Energy technology Laboratory, 255 p. (Dec 2006) http://www.netl.doe.gov/energy-analyses/pubs/CO2%20Retrofit%20-%20Internet%20Draft%20Final.pdf

Rao A B, Rubin E S (2002) A technical, economic, and environmental assessment of amine-based CO_2 capture technology for power plant greenhouse gas control. *Environmental Science & Technology*; **36** (20); 4467-4475 (15 Oct 2002)

Rao A B, Rubin E S (2006) Identifying cost-effective CO_2 control levels for amine-based CO_2 capture systems. *Industrial and Engineering Chemistry, Research*; **45** (8); 2421-2429 (12 Apr 2006)

Rao A B, Rubin E S, Morgan M G (2003) Evaluation of potential cost reductions from improved CO_2 capture systems. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 65-86 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Rao A B, Rubin E S, Keith D W, Morgan M G (2006) Evaluation of potential cost reductions from improved amine-based CO_2 capture systems. *Energy Policy*; **34** (18); 3765-3772 (Dec 2006)

Rhudy R (2006) CO_2 testing program: an industry, EPRI initiative to develop CO_2 capture and storage test capabilities. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 351-367 (Jun 2006) http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Rhudy R (2007) Chilled ammonia process update. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 215-236 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Roberts C A, Gibbins J, Panesar R, Kelsall G (2005) Potential for improvement in power generation with post-combustion capture of CO_2. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 155-163 (2005)

Rochelle G (2000) Research needs for CO_2 capture by aqueous absorption/stripping. In: *International Test Network for CO_2 Capture: report on a workshop,* Gaithersburg, MD, USA, 11-12 Oct 2000. Report PH3/33, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 4 p. (Dec 2000) http://www.co2captureandstorage.info/docs/Ph3_33%20CO2%20capture%20workshop%20report%20.pdf

Rochelle G T (2003) Innovative stripper configurations to reduce the energy cost of CO_2 capture. Paper presented to: *2nd annual carbon sequestration conference*, Alexandria, VA, USA, 5-8 May 2003. 13 p. (2003)

Rochelle G, Bishnoi S, Chi S, Dang H, Santos J (2001) *Research needs for CO_2 capture from flue gas by aqueous absorption/stripping.* DE-AF26-99FT01029, Pittsburgh, PA, USA, Federal Energy Technology Center, 154 pp (17 Jan 2001)

Rochelle G T, Goff G S, Cullinane J T, Freguia S (2002) Research results for CO_2 capture from flue gas by aqueous absorption/stripping. Paper presented to: *Laurance Reid gas conditioning conference*, Oklahoma City. OK, USA, 25-27 Feb 2002. 21 p. (2002)

Rubin (2003) Update on IECM development. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 60-64 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Rubin E S (2005) Estimating future costs of CO_2 capture systems. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 73-109 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Rubin E S, Rao A B (2002a) A plant-level model of CO_2 capture and storage options. In: *International Test Network for CO_2 Capture: report on 3rd workshop,* Apeldoorn, the Netherlands, 16-17 May 2002. Report PH4/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 11 p. (Jul 2002) http://www.co2captureandstorage.info/docs/PH4-11%20ApeldoornWorkshop.pdf

Rubin E S, Rao A B (2002b) Reducing the costs of CO_2 capture. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 20 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Rubin E S, Rao A B, Chen C (2004) IECM comparisons of PC, NGCC and IGCC plants: current technology and the potential for cost reductions through "learning". In: *International Test Network for CO_2 Capture: report on 6th workshop,* Trondheim, Norway, 8-9 Mar 2004. Report PH4/28, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 58-100 (May 2004) http://www.co2captureandstorage.info/docs/PH4-28%20Capture%20network%206th%20Workshop.pdf

Rubin E S, Yeh S, Antes M, Berkenpas M, Davison J (2007a) Use of experience curves to estimate the future cost of power plants with CO_2 capture. *International Journal of Greenhouse Gas Control*; **1** (1); 188-197 (Apr 2007)

Rubin E S, Chen C, Rao A B (2007b) Cost and performance of fossil fuel power plants with CO_2 capture and storage. Article in press in *Energy Policy*.

RWE npower (2007a) *RWE npower outlines plans for over £1bn clean coal power station in Essex.* Press release (13 Mar 2007) http://www.npowermediacentre.co.uk/Content/Detail.asp?ReleaseID=1142&NewsAreaID=2

RWE npower (2007b) *RWE npower begins environmental study into new Blyth Power Station*. Press release (11 May 2007) http://www.npowermediacentre.co.uk/Content/Detail.asp?ReleaseID=1236&NewsAreaID=2

Sakwattanapong R, Aroonwilas A, Veawab A (2005) Behavior of reboiler heat duty for CO_2 capture plants using regenerable single and blended alkanolamines. *Industrial and Engineering Chemistry, Research*; **44** (12); 4465-4473 (8 Jun 2005)

Schmidt C, Beecy D (2001) Overview of the U.S. Carbon Sequestration Program. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 1044-1049 (2001)

Seibert F, Wilson I, Lewis C, Rochelle G (2005) Effective gas/liquid contact area of packing for CO_2 absorption/stripping. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1925-1928 (2005)

Sexton A, Alawade A, Rochelle G T (2006) Oxidation products of amines in CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_04.PDF, 6 p. (2006) CD-ROM

Shimizu S, Onoda M, Goto K, Yamada K, Mimura T (2006) Novel absorbents for CO_2-capture from gas stream. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_03.PDF, 6 p. (2006) CD-ROM

Simbeck D R, McDonald M (2001) Existing coal power plant retrofit CO_2 control options analysis. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 103-108 (2001)

Singh P, Niederer J P M, Versteeg G F (2006) Structure and activity relationships for amine based CO_2 absorbents. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_02.PDF, 6 p. (2006) CD-ROM

Singh P, Niederer J P M, Versteeg G F (2007) Structure and activity relationships for amine based CO_2 absorbents - I. *International Journal of Greenhouse Gas Control*; **1** (1); 5-10 (Apr 2007)

Skoropad D, Gelowitz D, Idem R, Stobbs B, Barrie J (2003) Challenges of recommissioning a CO_2 capture pilot plant in Saskatchewan, Canada. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1575-1578 (2003)

Srinivasan P, Veawab A (2006) synergistic effect of multi heat-stable salts on corrosion in alkanolamine-based CO_2 capture unit. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_25.PDF, 5 p. (2006) CD-ROM

Stobbs B, Barrie J (2004) CCPC summary - amine scrubbing study. In: *International Test Network for CO_2 Capture: report on 6th workshop,* Trondheim, Norway, 8-9 Mar 2004. Report PH4/28, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 116-128 (May 2004) http://www.co2captureandstorage.info/docs/PH4-28%20Capture%20network%206th%20Workshop.pdf

Stobbs R, Clark P (2005) Canadian Clean Power Coalition: the evaluation of options for CO_2 capture from existing & new coal-fired power plants. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 1, pp 1187-1192 (2005)

Strazisar B R, Anderson R R, White C M (2002) Degradation of monoethanolamine used in CO_2 capture from flue gas of a coal-fired electric power generating station. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **47** (1); 55-56 (Spr 2002)

Strazisar B R, Anderson R R, White C M (2003) Degradation pathways for monoethanolamine in a CO_2 capture facility. *Energy and Fuels*; **17** (4); 1034-1039 (Jul/Aug 2003)

Supap T, Aroonwilas A, Veawab A, Chakma A, Tontiwachwuthikul P, Kybett B D (2001a) An investigation of solvent stability in amine based systems used to capture CO_2. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 211-216 (2001)

Supap T, Idem R, Veawab A, Aroonwilas A, Tontiwachwuthikul P, Chakma A, Kybett B D (2001b) Kinetics of the oxidative degradation of aqueous monoethanolamine in a flue gas treating unit. *Industrial and Engineering Chemistry, Research*; **40** (16); 3445-3450 (8 Aug 2001)

Supap T, Idem R, Tontiwachwuthikul P, Saiwan C (2006) Analysis of monoethanolamine and its oxidative degradation products during CO_2 absorption from flue gases: a comparative study of GC-MS, HPLC-RID, and CE-DAD analytical techniques and possible optimum combinations. *Industrial and Engineering Chemistry, Research*; **45** (8); 2437-2451 (12 Apr 2006)

Svendsen H F (2007) Learning from CASTOR: solvent, pilot plant and modeling work. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 394-417 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Tanthapanichakoon W, Veawab A (2003) Heat stable salts and corrosivity in amine treating units. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1591- 1594 (2003)

Tanthapanichakoon W, Veawab A, McGarvey B (2006) Electrochemical investigation on the effect of heat- stable salts on corrosion in CO_2 capture plants using MEA. *Industrial and Engineering Chemistry, Research*; **45** (8); 2586-2593 (12 Apr 2006)

Teramoto M, Ohnishi N, Takeuchi N, Kitada S, Matsuyama H, Matsumiya N, Mano H (2003) Separation and enrichment of carbon dioxide by capillary membrane module with permeation of carrier solution. *Separation and Purification Technology*; **30** (3); 215-227 (1 Mar 2003)

Teramoto M, Kitada S, Ohnishi N, Matsuyama H, Matsumiya N (2004) Separation and concentration of CO_2 by capillary-type facilitated transport membrane module with permeation of carrier solution. *Journal of Membrane Science*; **234** (1/2); 83-947 (1 May 2004)

Thitakamol B, Veawab A, Aroonwilas A (2006) Environmental impacts of the integration of CO_2 capture unit into coal-fired power plants. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_24.PDF, 5 p. (2006) CD-ROM

Thitakamol B, Veawab A, Aroonwilas A (2007) Environmental impacts of absorption-based CO_2 capture unit for post-combustion treatment of flue gas from coal-fired power plant. *International Journal of Greenhouse Gas Control*; 1 (3); 318-342 (Jul 2007)

Tobiesen F A, Svendsen H F (2004) Desorber performance in MEA based absorption plant. In: *International Test Network for CO_2 Capture: report on 7th workshop,* Vancouver, BC, Canada, 10 Sep 2004. Report PH4/34, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 179-202 (Oct 2004) http://www.co2captureandstorage.info/docs/PH4-34%20Capture%20network%207th%20Workshop.pdf

Tobiesen F A, Svendsen H F (2006) Study of a modified amine-based regeneration unit. *Industrial and Engineering Chemistry, Research*; **45** (8); 2489-2496 (12 Apr 2006)

Tobiesen F A, Svendsen H F, Hoff K A (2005a) Desorber energy consumption amine based absorption plants. *Journal of Green Energy*; **2** (2); 201-215 (2005)

Tobiesen A, Juliussen O, Svendsen H F (2005b) Experimental validation of a model for CO_2 post-combustion capture using monoethanolamine (MEA). In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 234-259 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Tobiesen A, Juliussen O, Svendsen H F (2006a) Experimental validation of a model for simulating the desorber and connected unit operations for a CO_2 post-combustion capture system using monoethanolamine (MEA). In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_05_05.PDF, 6 p. (2006) CD-ROM

Tobiesen A, Mejdell T, Svendsen H F (2006b) A comparative study of experimental and modeling performance results from the CASTOR Esbjerg pilot plant. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_22.PDF, 6 p. (2006) CD-ROM

Tontiwachwuthikul P (2002a) Multi-purpose process technology development pilot plant units at University of Regina: an update. In: *International Test Network for CO_2 Capture: report on 2nd workshop,* Calgary, Canada, 12-13

Nov 2001. Report PH4/4, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 15 p. (Jan 2002) http://www.co2captureandstorage.info/docs/PH4-4%202nd%20CO2-Calgary.pdf

Tontiwachwuthikul P (2002b) International Test Centre for CO_2 capture (ITC). An update - October 2002. In: *International Test Network for CO_2 Capture: report on 4th workshop,* Kyoto, Japan, 5 Oct 2002. Report PH4/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 58 p. (Nov 2002) http://www.co2captureandstorage.info/docs/PH4-13.pdf

Tontiwachwuthikul P, Aroonwilas A (2002) Mass-transfer in CO_2 absorption systems: experimental data and comprehensive modeling. In: *International Test Network for CO_2 Capture: report on 2nd workshop,* Calgary, Canada, 12-13 Nov 2001. Report PH4/4, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, 20 p. (Jan 2002) http://www.co2captureandstorage.info/docs/PH4-4%202nd%20CO2-Calgary.pdf

Topper J M (2003) International CO_2 Capture Test Network. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1543-1546 (2003)

Topper J M (2005) Wrap up session. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 447-471 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Uyanga I J, Idem R O (2007) Studies of SO_2- and O_2-induced degradation of aqueous MEA during CO_2 capture from power plant flue gas streams. *Industrial and Engineering Chemistry, Research*; **46** (8); 2558-2566 (11 Apr 2007)

van der Vaart R, Beckers M, de Jong H, Feron P H M (2006) Membrane contactors for post-combustion CO_2 capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P01_01_03.PDF, 6 p. (2006) CD-ROM

van Gijlswijk R, Feron P H M, Davison J (2006) Environmental impact of solvent processes for CO_2-capture. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_09.PDF, 6 p. (2006) CD-ROM

van Gijlswijk R, Feron P H M, Davison J (2007) Environmental impact of CO_2 capture in power plants. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 191-214 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

van Holst J, Politiek P P, Niederer J P M, Versteeg G F (2006) CO_2 capture from flue gas using amino acid solutions. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_06_07.PDF, 6 p. (2006) CD-ROM

van Loo S, van Elk E P, Versteeg G F (2007) The removal of carbon dioxide with activated solutions of methyl-diethanol-amine. *Journal of Petroleum Science and Engineering*; **55** (2); 135-145 (Jan 2007)

Veawab A (2003) Corrosion in CO_2 capture unit for coal-fired power plant flue gas. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1595-1598 (2003)

Veawab A, Aroonwilas A (2002) Identification of oxidizing agents in aqueous amine-CO_2 systems using a mechanistic corrosion model. *Corrosion Science*; **44** (5); 967-987 (May 2002)

Veawab A, Aroonwilas A (2005a) Cost-saving opportunity for CO_2 capture by blended-alkanolamines. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1845-1848 (2005)

Veawab A, Aroonwilas A (2005b) CO_2 capture by blended alkanolamines: experiments, modeling & simulation, cost analysis. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 152-191 (Nov 2005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Veawab A, Aroonwilas A (2006) Energy requirement for solvent regeneration in CO_2 capture plants. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 26-86 (Jun 2006) http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Veawab A, Tontiwachwuthikul P, Chakma A (1999) Corrosion behaviour of carbon steel in the CO_2 absorption process using amine solutions. *Industrial and Engineering Chemistry, Research*; **38** (10); 3917-3924 (Oct 1999)

Veawab A, Tontiwachwuthikul P, Chakma A (2001) Investigation of low-toxic organic corrosion inhibitors for CO_2 separation process using aqueous MEA solvent. *Industrial and Engineering Chemistry, Research*; **40** (22); 4771-4777 (2001)

Veawab A, Aroonwilas A, Tontiwachwuthikul P (2002) CO_2 absorption performance of aqueous alkanolamines in packed columns. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **47** (1); 49-50 (Spr 2002)

Veawab A, Tontiwachwuthikul P, Aroonwilas A, Chakma A (2003) Performance and cost analysis for CO_2 capture from flue gas streams: absorption and regeneration aspects. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume I, pp 127-132 (2003)

Wang S (2007) Ammonia scrubbing technology for CO_2 capture. In: *International Test Network for CO_2 Capture: report on 10th workshop, Lyon*, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 237-262 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Webley P (2007) Overview of the CO2CRC capture program. In: *International Test Network for CO_2 Capture: report on 10th workshop*, Lyon, France, 24-25 May 2007. Report 2007/08, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 328-371 (Jul 2007) http://www.co2captureandstorage.info/docs/capture/2007-810thCaptureMtg_FinalReport.pdf

Wheeldon J, Booras G, Holt N (2006) Re-evaluation of post-combustion CO_2-capture from pulverized coal plants. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper 01_04_04.PDF, 6 p. (2006) CD-ROM

Wibberley L (2005) PCC demonstration program in Australia. In: *International Test Network for CO_2 Capture: report on 8th workshop,* Austin, TX, USA, 3-4 Oct 2005. Report 2005/13, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 403-414005) http://www.co2captureandstorage.info/docs/2005-13%208th%20capture%20network%20meeting.pdf

Wibberley (2006) Australian national post combustion capture and storage demonstration project. In: *International Test Network for CO_2 Capture: report on 9th workshop,* Copenhagen, Denmark, 16 Jun 2006. Report 2006/11, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 227-242 (Jun 2006) http://www.co2captureandstorage.info/networks/capture_workshops_copenhagen.htm

Wilson M (2003) International Test Centre for CO_2 capture. In: *International Test Network for CO_2 Capture: report on 5th workshop,* Pittsburgh, PA, USA, 2-3 Jun 2003. Report PH4/22, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp129-173 (Jul 2003) http://www.co2captureandstorage.info/docs/PH4-22.pdf

Wilson (2004) Test results from CO_2 extraction pilot plants: Boundary Dam station and University of Regina facilities. In: *International Test Network for CO_2 Capture: report on 6th workshop,* Trondheim, Norway, 8-9 Mar 2004. Report PH4/28, Cheltenham, UK, IEA Greenhouse Gas R&D Programme, pp 147-169 (May 2004) http://www.co2captureandstorage.info/docs/PH4-28%20Capture%20network%206th%20Workshop.pdf

Wilson M, Tontiwachwuthikul P, Chakma A (2001) International Test Centre for carbon dioxide (CO_2) capture. In: *Proceedings of the fifth international conference greenhouse gas control technologies: GHGT-5*, Cairns, Qld., Australia, 13-16 Jun 2000. Williams D J, Durie R A, McMullan P, Paulson C A J, Smith A (eds.) Collingwood, Vic., Australia, CSIRO Publishing, pp 87-90 (2001)

Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, Gelowitz D, Barrie J, Mariz C (2003a) Test results from a CO_2 extraction pilot plant at Boundary Dam coal-fired power station. In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume I, pp 31-36 (2003)

Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, Gelowitz D (2003b) The International Test Centre for carbon dioxide capture (ITC). In: *Proceedings of the sixth international conference on greenhouse gas control technologies: GHGT-6*, Kyoto, Japan, 1-4 Oct 2002. Gale J, Kaya Y (eds.) Oxford, UK, Elsevier Science Ltd. (Pergamon), Volume II, pp 1547-1550 (2003)

Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, Gelowitz D, Barrie J, Mariz C (2004) Test results from a CO_2 extraction pilot plant at Boundary Dam coal-fired power station. *Energy*; **29** (9/10); 1259-1267 (Jul/Aug 2004)

Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, Gelowitz D, Stobbs R (2005a) Evaluation of the CO_2 capture efficiency of the University of Regina CO_2 technology development plant and the Boundary Dam CO_2 demonstration plant. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Rubin E S, Keith D W, Gilboy C F (eds.) Oxford, UK, Elsevier Ltd., Volume I, pp 55-61 (2005)

Wilson M, Tontiwachwuthikul P, Chakma A, Idem R, Veawab A, Aroonwilas A, Gelowitz D, Henni A, Mahinpey N (2005b) The International Test Centre for carbon dioxide capture (ITC). In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 2, pp 1807-1810 (2005)

Yagi Y, Mimura T, Iijima M, Ishida K, Yoshiyama R, Kamijo T, Yonekawa T (2005) Improvements of carbon dioxide capture technology from flue gas. In: *Proceedings of the seventh international conference on greenhouse gas control technologies: GHGT-7*, Vancouver, Canada, 5-9 Sep 2004. Wilson M, Morris T, Gale J, Thambimuthu K (eds.) Oxford, UK, Elsevier Ltd., Volume II - Part 1, pp 1139-1145 (2005)

Yagi Y, Mimura T, Yonekawa T, Yoshiyama R (2006) Development and improvement of CO_2-capture system. In: *8th international conference on greenhouse gas control technologies*, Trondheim, Norway, 19-22 Jun 2006. Oxford, UK, Elsevier Ltd., paper P02_01_14.PDF, 6 p. (2006) CD-ROM

Yeh J T, Pennline H W, Resnik K P (2000) Study of CO_2 absorption and desorption in a packed column. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **45** (4); 650-654 (Aug 2000)

Yeh J T, Resnik K P, Pennline H W (2004) Regenerable Aqua Ammonia Process for CO_2 sequestration. *Division of Fuel Chemistry, American Chemical Society - Preprints of Symposia*; **49** (1); 247-248 (Spr 2004)

Yeh J T, Resnik K P, Pennline H W (2005) Semi-batch absorption and regeneration studies for CO_2 capture by aqueous ammonia. *Fuel Processing Technology*; **86** (14/15); 1533-1546 (Oct 2005)