

Post-combustion CO₂ Capture with Chemical Absorption: A State-of-the-art Review

M. Wang^{a*}, A. Lawal^a, P. Stephenson^b, J. Sidders^b, C. Ramshaw^a and H. Yeung^a

^aProcess Systems Engineering Group, School of Engineering, Cranfield University, UK.

^bRWE npower, UK.

* Corresponding author. Tel: +0044 1234 754655; Fax: +0044 1234 754685; Email address: meihong.wang@cranfield.ac.uk

Abstract

Global concentration of CO₂ in the atmosphere is increasing rapidly. CO₂ emissions have an impact on global climate change. Effective CO₂ emission abatement strategies such as Carbon Capture and Storage (CCS) are required to combat this trend. There are three major approaches for CCS: Post-combustion capture, Pre-combustion capture and Oxyfuel process. Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to implement as a retrofit option (to existing power plants) compared to the other two approaches. Therefore, post-combustion capture is probably the first technology that will be deployed. This paper aims to provide a state-of-the-art assessment of the research work carried out so far in post-combustion capture with chemical absorption. The technology will be introduced first, followed by required preparation of flue gas from power plants to use this technology. The important research programmes worldwide and the experimental studies based on pilot plants will be reviewed. This is followed by an overview of various studies based on modelling and simulation. Key issues such as energy consumption and plant flexibility will be included. Then the focus is turned to review development of different solvents and process intensification. Based on these, we try to predict challenges and potential new developments from different aspects such as new solvents, pilot plants, process heat integration (to improve efficiency), modelling and simulation, process intensification and government policy impact.

Keywords: Carbon Capture and Storage (CCS), CO₂ Capture, Chemical Absorption, Power Plant, Modelling and Simulation, Pilot Plant, Post-combustion, Process Intensification, Review

1. Introduction

1.1 Background

CO₂ is the main greenhouse gas. CO₂ emissions have an impact on global climate change. Global concentrations of CO₂ in the atmosphere have increased from pre-industrialisation levels of approximately 280 parts per million by volume (ppmv) in around 1860 to approximately 316 ppmv in 1958 and rapidly to approximately 369 ppmv today (UNEP, 2005). Global CO₂ concentration is predicted to rise to above 750 ppmv by 2100 if no action is taken to address the current situation.

Power generation from fossil fuel-fired power plants (e.g. coal and natural gas) is the single largest source of CO₂ emissions (Freund, 2003). However, fossil fuel fired power plants play a vital role in meeting energy demands. For instance, coal-fired power plants could be operated flexibly in meeting with varying demand. With growing concerns over the increasing atmospheric concentration of anthropogenic greenhouse gases, effective CO₂ emission abatement strategies such as Carbon Capture and Storage (CCS) are required to combat this trend.

CCS is a "process consisting of the separation of CO₂ from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere." (IPCC, 2005). From this definition, CCS consists of three basic stages: (a) Separation of CO₂; (b) Transportation and (c) Storage. There are

three major approaches for CCS: Post-combustion capture, Pre-combustion capture and Oxyfuel process (IPCC, 2005).

Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to implement as a retrofit option to existing plants compared to the other two approaches. The advantage comes at the expense of the efficiency of the power generation process. The separation stage (*i.e.* CO₂ capture) is energy intensive and as such largely determines the cost of the CCS process. It represents about 75-80% of the total cost of CCS (Davison, 2007).

A number of separation technologies could be employed with post-combustion capture. These include: (a) adsorption; (b) physical absorption; (c) chemical absorption; (d) cryogenics separation and (e) membranes (see, for example, IPCC, 2005). Figure 1 shows classification of various separation technologies available for post combustion capture. A brief introduction of these technologies will set the background of this review paper.

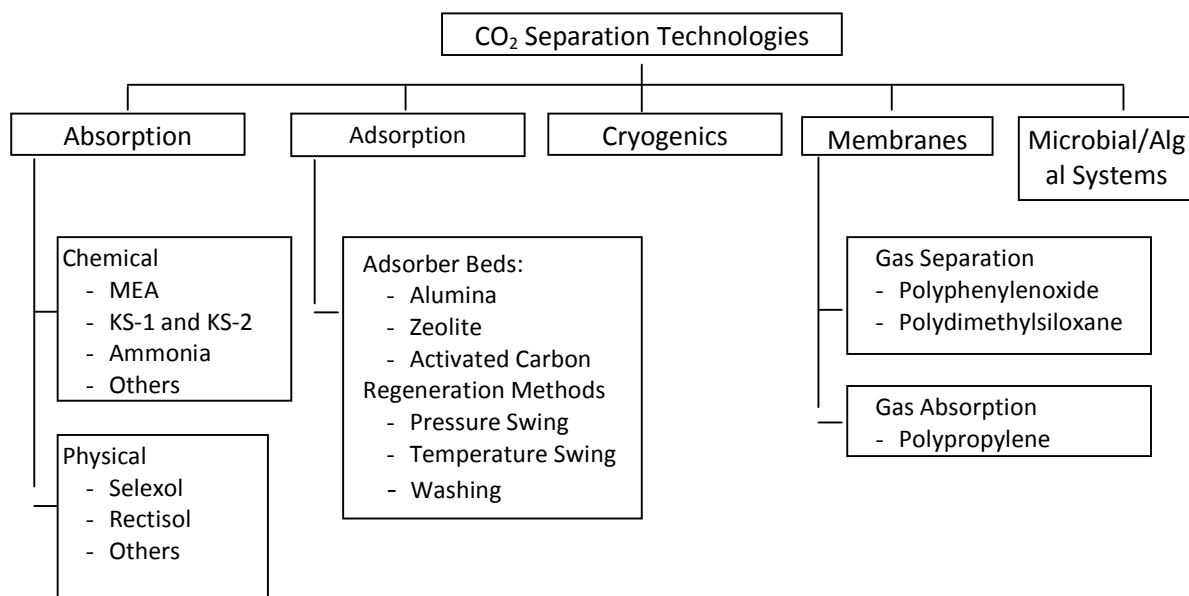


Figure 1 Process technologies for post combustion CO₂ capture adapted from (Rao and Rubin, 2002)

1.1.1 Adsorption

Adsorption is a physical process that involves the attachment of a gas or liquid to a solid surface. The adsorbent is regenerated by the application of heat (temperature swing adsorption, TSA) or the reduction of pressure (pressure swing adsorption, PSA). Adsorbents which could be applied to CO₂ capture include activated carbon, alumina, metallic oxides and zeolites (IEA GHG, 1993, Zhao et al, 2007).

Current adsorption systems may not be suitable for application in large-scale power plant flue gas treatment. At such scale, the low adsorption capacity of most available adsorbents may pose significant challenges. In addition, the flue gas streams to be treated must have high CO₂ concentrations because of the generally low selectivity of most available adsorbents. For instance, zeolites have a stronger affinity for water vapour. (IEA 2004, IEA 2007, Zhao et al, 2007)

1.1.2 Physical absorption

This involves the physical absorption of CO₂ into a solvent based on Henry's law. Regeneration can be achieved by using heat, pressure reduction or both. Absorption takes place at high CO₂ partial pressures. As such, the main energy requirements originate from the flue gas pressurization. Physical absorption is therefore not economical for gas streams with CO₂ partial pressures lower than 15vol% (Chakravati et al, 2001, IEA, 2004). Typical solvents are Selexol (dimethyl ethers of polyethylene glycol) and Rectisol (methanol) (IEA GHG, 1993).

1.1.3 Cryogenics separation

Cryogenics separation separates CO₂ from the flue gas stream by condensation. At atmospheric pressure, CO₂ condenses at -56.6°C (IEA GHG, 1993). This physical process is suitable for treating flue gas streams with high CO₂ concentrations considering the costs of refrigeration. This is also used for CO₂ capture for oxyfuel process.

1.1.4 Membrane absorption

When membranes are used in gas absorption, membranes act as contacting devices between the gas stream and the liquid solvent. The membrane may or may not provide additional selectivity. These offer some advantages over the conventional contacting devices such as packed columns as they are more compact and are not susceptible to flooding, entrainment, channelling or foaming. They, however, require that the pressures on the liquid and gas sides are equal to enable CO₂ transport across the membrane. Their separation efficiency depends on the CO₂ partial pressure. As such, they are suitable for high CO₂-concentration applications (well above 20vol%) such as flue gas streams from oxyfuel and IGCC processes. (Favre 2007, IEA GHG 1993, IPCC, 2005).

1.1.5 Membrane-based separation

In membrane-based separation, selectivity is provided by the membranes themselves. These usually consist of thin polymeric films and separate mixtures based on the relative rates at which constituent species permeate. Permeation rates would differ based on the relative sizes of the molecules or diffusion coefficients in the membrane material. The driving force for the permeation is the difference in partial pressure of the components at either side of the membrane. However, the selectivity of this separation process is low and thus a fraction of the CO₂ is captured. In addition, the purity of the captured CO₂ is low for the same reason (IEA, 2004, IEA GHG, 1993). Multistage separation is employed to capture a higher proportion of CO₂ incurring extra capital and operating cost (Chakravati et al, 2001, IEA, 2004, IEA GHG, 1993).

1.1.6 Chemical absorption

Chemical absorption involves the reaction of CO₂ with a chemical solvent to form a weakly bonded intermediate compound which may be regenerated with the application of heat producing the original solvent and a CO₂ stream (IPCC, 2005). The selectivity of this form of separation is relatively high. In addition, a relatively pure CO₂ stream could be produced. These factors make chemical absorption well suited for CO₂ capture for industrial flue gases. More details will be described in Section 2.

1.2 Aim of this paper and its novelty

This paper aims to provide a state-of-the-art assessment of the research work carried out so far in post-combustion capture with chemical absorption. For beginners, this paper will give an introduction to the technology and a summary of literatures. For experienced researchers, this paper will review the recent progress and predict the future research directions based on the available achievements.

The differences between this paper and previous review reports such as IPCC (2005) and Davidson (2007) are: (a) This paper is to provide an update of important research programs worldwide and major pilot plant studies; (b) This paper is to provide a critical review of research activities in modelling and simulation; (c) This paper is to draw the readers' attention on process intensification for post-combustion capture with chemical absorption; (d) This paper tries to predict challenges and future breakthroughs.

1.3 Outline of the paper

In Section 2, the technology is introduced. Then major research programs worldwide and experimental studies based on pilot plants are reviewed in Section 3. This is followed by an overview of various studies based on modelling and simulation in Section 4. Section 5 is a survey of various solvents and relevant problems such as degradation. Section 6 discusses new development in process intensification for post-combustion CO₂ capture. In Section 7, we try to predict challenges ahead and potential new developments from different aspects such as new solvents, pilot plants, heat integration (to improve efficiency), modelling and simulation, and process intensification. Conclusions are drawn in the end.

2. Post-combustion CO₂ Capture with Chemical Absorption

Post-combustion CO₂ Capture means that CO₂ is removed after combustion of the fossil fuel. In other words, CO₂ is captured from flue gases at power plants or other large point sources. The most commonly used solvent is monoethanolamine (MEA).

2.1 Preparation of the flue gas to use the technology

Prior to absorption, other acid gases such as SO₂ and NO₂ must be removed as they affect the performance of the system by forming heat stable salts with solvent such as MEA. SO₂ concentrations of less than 10ppm are recommended (Davidson, 2007). SO₂ removal is usually achieved in a Flue Gas Desulphurization (FGD) unit. NO_x is removed using Selective Catalytic Reduction (SCR), Selective Noncatalytic Reduction (SCNR) or low NO_x burners. Particulate matter such as fly ash is removed by either electrostatic precipitators (ESP) or bag house filters otherwise they would cause foaming in the absorber and regenerator columns decreasing their performance.

The presence of oxygen increases the likelihood of corrosion in equipment. In addition, alkanolamines like MEA can easily be degraded in the presence of oxygen (Davidson, 2007). Oxygen levels of less than 1ppm are recommended for use with MEA when corrosion inhibitors are not employed (IEA GHG, 1993). The Fluor Daniel ECONAMINE™ Process makes use of inhibitors (IPCC, 2005).

Flue gases to the CO₂ absorber must be cooled between 45–50°C (Rao et al. 2007, Ramezan et al. 2007). This would improve absorption of CO₂ and minimize solvent losses due to evaporation. This is achieved in a direct contact cooler (DCC) where the flue gas is cooled by a spray of water, this in addition saturates the flue gas to the absorber and thereby helps the water balance.

2.2 Process description

The conventional MEA absorption process is displayed in Figure 2 (IPCC, 2005). The cooled flue gas is contacted counter-currently with the lean solvent usually of CO₂ loading of about 0.1–0.2 mol CO₂/mol MEA yielding a rich solvent of about 0.4–0.5 mol CO₂/mol MEA loading (Freguia and Rochelle, 2003). The scrubbed gas is then water washed of solvent and vented to the atmosphere. The lean solvent gradually heats up as it absorbs CO₂. The temperature inside the absorber is typically between 40°C and 60°C. The rich solvent is heated in a cross heat exchanger by regenerated lean solvent from the Stripper (or regenerator). It is then pumped to the top of the Stripper where it is regenerated at elevated temperatures (100°C–120°C) and at slightly higher than atmospheric pressure (1.5 – 2 atm) (IPCC, 2005). Heat is supplied via the reboiler which is the major energy penalty of the process. The regenerated solvent is then pumped back to the Absorber via the cross heat exchanger to reduce the temperature.

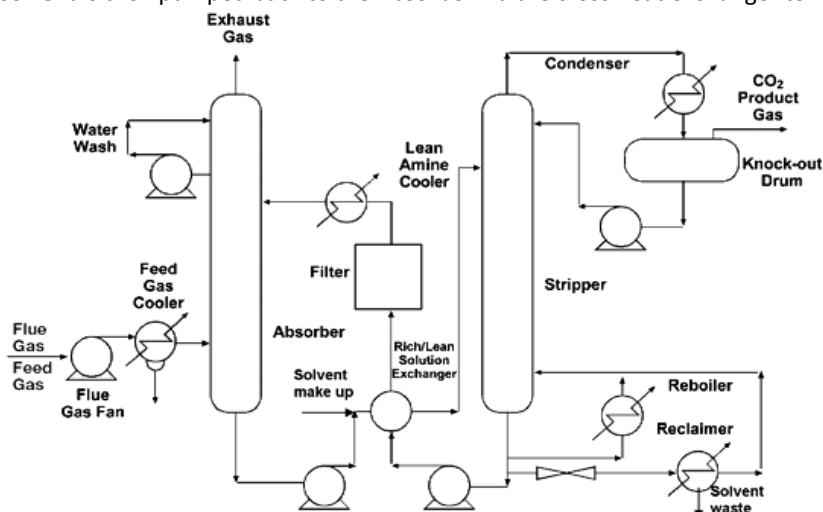


Figure 2 Process flow diagram for CO₂ capture from flue gas by chemical absorption (IPCC, 2005)

Amine solvents like MEA degrade on contact with certain impurities such as excess oxygen, sulphur dioxide or nitrous oxides to form substances including heat stable salts. Part of the bottoms product from the stripper is sent to a reclaimer unit where the solvent is evaporated and returned leaving the non-volatile solvent wastes which are purged from the system.

3. Important Research Programmes worldwide & Pilot Plants

This section seeks to give an overview of important research programs worldwide in post-combustion CO₂ capture.

3.1 Luminant Carbon Management program

3.1.1 Participants and Purpose

The Luminant Carbon Management Program led by Professor Gary Rochelle in the Department of Chemical Engineering, University of Texas at Austin (USA) focuses on the technical obstacles to the deployment of post-combustion CO₂ separation from flue gas by alkanolamine absorption/stripping and integrating the design of the capture process with aquifer storage/enhanced oil recovery processes (Rochelle, 2010)

3.1.2 Description of facilities

The schematic of the pilot plant facility is shown in Figure 3. Both the absorber and stripper columns are packed columns with internal diameters of 0.427m and total column height of 11m. Columns consist of two 3.05m packed bed sections with a collector plate and redistributor between the beds. Both random and structured packings were used alternatively in the two columns. The facility has a capacity to process approximately 3 tons of CO₂ per day (Dugas, 2006). The flue gas stream is prepared since it is not obtained directly from a power plant.

3.1.3 Activities

At this university pilot plant, several studies are carried out where research looks into CO₂ rate kinetics and solubility measurements (Bishnoi and Rochelle, 2000), degradation of solvents (Chi and Rochelle (2002), Davis and Rochelle (2009)), systems modelling (Freguia and Rochelle (2003), Ziaii et al. 2009), pilot plant testing (Dugas (2006), Chen et al. (2006)) amongst others.

One of the main projects carried out was the Carbon Dioxide Capture by Absorption with Potassium Carbonate. This project ran from 2002 to 2007 with the aim to improve the process for CO₂ capture by alkanolamine absorption/stripping by developing an alternative solvent, aqueous Potassium Carbonate (K₂CO₃) promoted by piperazine (NETL, 2008). Accomplishments include evaluation of three solvents – MEA, and two variants of the piperazine-promoted K₂CO₃. It was shown that the requirements for one of the piperazine promoted K₂CO₃ solvents was much less than the conventional MEA due to increased absorption capacity and rates, as well as reduced heat of absorption – implying reduced regeneration requirements. A number of studies were also carried out on the process performance in terms of packing performance and absorber/stripper configurations among others. A rate-based model of the absorber unit was developed. Absorber intercooling was found to improve absorption performance especially for high absorption capacity solvents. (NETL, 2008)

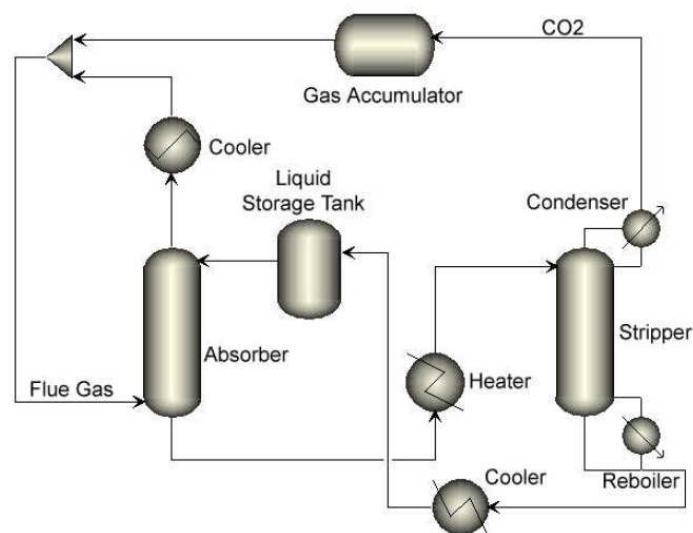


Figure 3 Schematic of CO₂ capture pilot plant from (Dugas, 2006)

3.2 International Test Centre (ITC) for CO₂ capture

3.2.1 Participants and Purpose

The ITC is formed by the collaboration of University of Regina (Canada) led by Professor Malcolm Wilson

and a consortium of government, industrial partners and its aim is to explore and develop new cost effective technologies for CO₂ capture.

3.2.2 Description of facilities

Infrastructure in the ITC consists of bench-scale CO₂ separation units as well as a multi-purpose pilot plant unit (1 ton of CO₂ per day) at the University of Regina. A 250kW steam boiler is used to generate the flue gas which is then treated in a CO₂ absorption unit. The absorption column is composed of three 0.3 m-diameter sections for a total height of 10 m.

In 2000, the ITC re-commissioned a semi-commercial (4 ton of CO₂ per day) demonstration unit adjacent to SaskPower's 875 MW Boundary Dam power station. The unit captures CO₂ from part of the flue gas from this coal-fired power plant (Wilson et al, 2004). This facility consists of three units in series as shown in Figure 4:

- i. A baghouse unit for flyash removal
- ii. A scrubbing unit for removal of SO₂ down to 2ppm.
- iii. Chemical absorption-based CO₂ recovery unit (Fluor's Econamine FGSM technology).

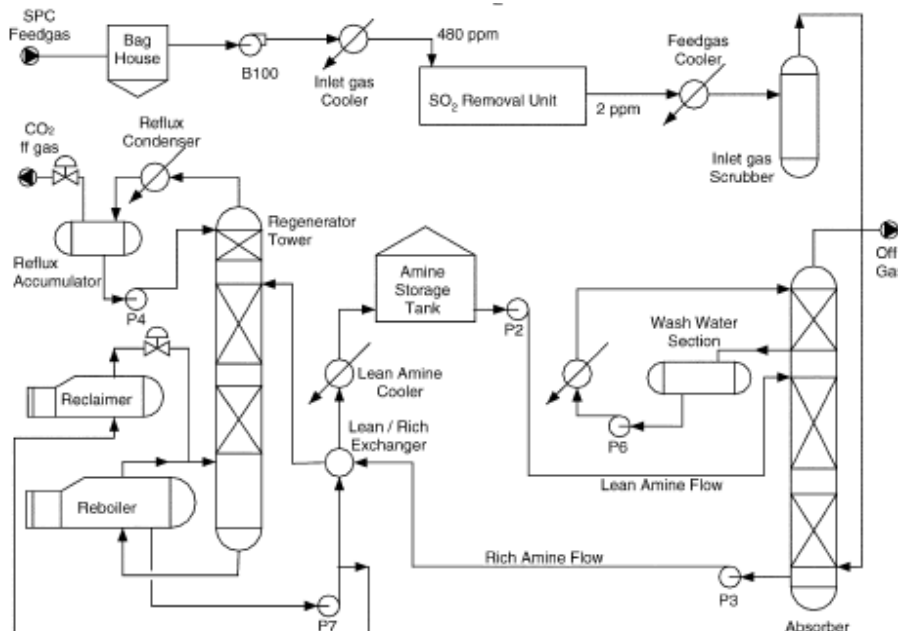


Figure 4 Schematic of Boundary Dam CO₂ Pilot Plant (Wilson et al, 2004)

3.2.3 Activities

Kinetics of the reactive absorption of carbon dioxide in high CO₂-loaded, concentrated aqueous MEA solutions were studied in Aboudheir, et al. (2003) by experiments. Kinetics of the reactive absorption of carbon dioxide with mixed solvents MEA and MDEA were again studied in Edali et al. (2009). Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the Boundary Dam CO₂ capture demonstration plant were compared in Idem et al. (2006). Uyanga and Idem (2007) studied the degradation of solvent MEA in the presence of SO₂. Kittel et al. (2009) studied corrosion of MEA unit for CO₂ capture through pilot plant experiment.

3.3 CASTOR

3.3.1 Participants and Purpose

This European Commission-funded and IFP-run project involves capturing and providing geological storage for 30% of the emissions released by large industrial facilities around Europe (conventional power stations, principally), i.e. for 10% of Europe's CO₂ emissions. CASTOR, which started in February 2004, was

a 4-year program and counts members from 11 EU countries, including: (a) 16 industrial firms (Dong Energy, Vattenfall, Repsol, Statoil, Gaz de France, Rohoel, Alstom power, RWE, etc); (b) 12 research institutes (IFP, BGRM, Imperial College, TNO, BGS, IFP, etc.). The CASTOR project had a total budget €15.8 million with a contribution of €8.5 million from European Commission (FP6 – sixth framework program) (IEAGHG, 2010).

Its specific goals involve halving the cost of capturing (from €40-60/ton CO₂ to €20-30/ton CO₂) and separating CO₂, developing the geological-storage concept's efficiency, safety and security while limiting its environmental impact, and testing it in real-life, industrial-scale facilities.

3.3.2 Description of facilities

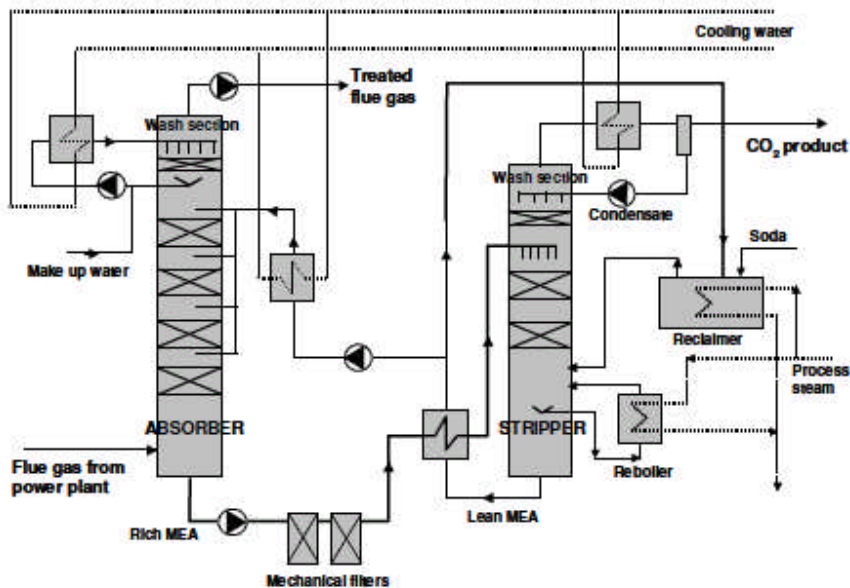


Figure 5 Simplified flow diagram of the CASTOR pilot plant at Esbjergværket (Knudsen et al, 2009)

A gas-fired mini plant with full absorption/desorption cycle was built at the University of Stuttgart. This facility consists of an absorber with 0.125m diameter absorber and 4m height and a 2.5m high stripper. An industrial-scale pilot plant facility (Figure 5) was launched alongside a power plant run by Dong Energy (formerly ELSAM) in Esbjerg, Denmark on 15 Mar. 2006. This plant has a capacity to capture about 24tonnes of CO₂ per day.

3.3.3 Activities

Studies were carried out on the selection of solvents as well as solvent degradation for the larger CASTOR pilot plant (Notz et al, 2007). Since Mar. 2006, four 1000-hour test campaigns have been carried out with MEA solvent and new proprietary solvents – CASTOR-1 and CASTOR-2. In January to February 2006, a 1000-hour preliminary test campaign was conducted using 30wt% MEA being the reference solvent. Another 1000-hour test was repeated from mid December 2006 to February 2007 to improve on certain problems encountered in the first test whilst collecting data (Knudsen et al, 2009). Results show that it is possible to run the post combustion plant continuously whilst achieving roughly 90% CO₂ capture levels. In addition, one of the proprietary solvents, CASTOR-2, operated with lower steam requirement and L/G ratio than the conventional MEA solvent.

From CASTOR project, it was concluded that future investigations would involve tests of solvents developed in the EU CESAR project. In addition, the effect of process modifications on steam requirements as well as environmental effects would be investigated (Knudsen et al, 2009).

3.4 iCap

iCap is a 4-year project supported by the European Commission under the 7th Framework Program. It consists of a consortium of 15 partners including eight Research & Technical Development providers and six power companies as well as an Australian research institute and a Chinese university. The project started on January 1, 2010.

iCap aims to remove barriers that cause bottlenecks in post-combustion and pre-combustion CO₂ capture. Targets include halving the efficiency penalty of CO₂ capture for power plants and reducing the associated CO₂ avoidance cost to 15€/tonne CO₂. These aims should accelerate the commercial development of large scale near zero emission power generation technology based on CCS (*iCap*, 2010).

3.5 CAPRICE

CAPRICE is funded by the European Union and was scheduled to last two years. This project began on 1 January 2007. TNO, a Dutch organization, is running it. CAPRICE stands for CO₂ capture using Amine Process International Cooperation and Exchange and involves pooling information and research findings on amine-enabled CO₂ capture with non-European CSLF countries.

More specifically, findings from the European CASTOR project's MEA chapter will be compared with those of the ITC at the University of Regina (Canada). It counts: (a) 10 research centres (University of Regina, Alberta Research Council, ITC, Energy Inet, IFP, Trondheim University, Stuttgart University, Tsinghua University, Topchiev Institute of Petrochemical Synthesis, and Salvador University); (b) 3 power generation companies (E-ON, Dong Energy and Vattenfall) (CAPRICE, 2010).

3.6 CESAR

3.6.1 *Participants and Purpose*

This 4-year long FP7 (Seventh Framework Programme)-funded project was launched in 2008 and aims for a breakthrough in the development of low-cost post-combustion CO₂ capture technology to provide economically feasible solutions for both new power plants and retrofit of existing power plants which are responsible for the majority of all anthropogenic CO₂ emissions. CESAR focuses on post-combustion as it is the only feasible technology for retrofit and current power plant technology. The primary objective is to decrease the cost of capture down to 15 €/ton CO₂. The consortium consists of 3 research organizations, 3 universities, 1 solvent supplier, 1 membrane producer (SME), 3 equipment suppliers, 2 oil and gas companies and 6 power generators (= industrial commitment) (CO2cesar, 2010).

3.6.2 *Description of facilities*

This project employs the Esbjerg pilot plant used in the CASTOR project.

3.6.3 *Activities*

Novel activities and innovations CESAR focuses at are (CO2cesar, 2010):

- Novel (hybrid) solvent systems
- New high flux membranes contactors
- Improved modelling and integration studies on system and plant level
- Testing of new solvents and plant modifications in the Esbjerg pilot plant. In the Esbjerg Pilot Plant novel technologies are assessed and compared with mainstream techniques to provide a fast track towards further scale-up and demonstration.

3.7 The joint UK-China Near Zero Emissions Coal (NZE) initiative

The project is managed by UK consultants AEA (for the Department Energy and Climate Change in the UK), in partnership with the Administrative Centre for China's Agenda 21 (ACCA21), and involves a consortium of 28 industrial and academic partners from the UK and China. Its objectives are (a) knowledge sharing and capacity building; (b) future technology perspectives; (c) case studies for carbon dioxide capture; (d) carbon dioxide storage potential; and (5) policy assessment. The Project started in 2007 and was finished at the end of 2009 (NZE, 2009).

3.8 The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC)

3.8.1 *Participants and Purpose*

CO2CRC comprises participants mainly from Australia and New Zealand. CO2CRC works through 3 main research programmes in CCS: Capture research, Storage research, Demonstration and pilot projects. The programme commenced in July 2003 and was expected to last 7 years. It has since been extended up till 2015 (CO2CRC, 2009a). Capture research involves a number of post combustion capture technologies such as solvent-based systems, innovative membrane systems and pressure swing adsorption (PST) systems.

3.8.2 *Description of facilities*

CO2CRC employs a 28-metre high absorber column in its International Power Capture Plant built at the Hazelwood coal-fired power station. The plant can capture up to 50 tonnes of CO₂ per day and is the largest post-combustion capture plant at a power plant in Australia (CO2CRC, 2009a).

3.8.3 *Activities*

The Latrobe Valley (post-combustion capture) project involving CO2CRC, Loy Yang Power, International Power and Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) consists of a \$5.6 million PCC research project with the aim of reducing CO₂ emissions from brown coal power stations. Research on three post combustion capture technologies – solvents, membranes and adsorbents is being carried out.

The CO2CRC H3 Capture Project, based at Hazelwood power station, utilises the International Power Capture Plant. At present, new solvents (such as BASF PuraTreat™) (CO2CRC, 2009b) are being researched with studies conducted at industrial scale. These studies generally relate to investigating process and energy efficiency improvements. The International Power Capture plant is used for these studies and can capture up to 50 tonnes of CO₂ per day. (CO2CRC, 2009a)

3.9 Investigations at Mitsubishi Heavy Industries, Hiroshima R&D Centre Japan

3.9.1 *Participants and Purpose*

The Mitsubishi Heavy Industries (MHI) in conjunction with the Kansai Electric Power Company (KEPCO) has conducted research and development of capturing CO₂ since 1990 (Kishimoto et al, 2009). They have developed a sterically hindered amine KS-1 solvent which has been shown to have less heat requirements than the conventional MEA solvent as well as reduced solvent degradation. This solvent is used in their proprietary KM-CDR process (Kishimoto et al, 2009). MHI has deployed four commercial CO₂ recovery plants which recover CO₂ from natural gas fired flue gas. Tests have been carried out on a 1 tonne CO₂/day as well and recently on a 10 tonne CO₂/day pilot plant to demonstrate that the process is applicable to coal-fired power plants as well (Davidson, 2007, Kishimoto et al, 2009).

3.9.2 *Description of facilities*

MHI has successfully deployed four commercial CO₂ capture plants, currently operating in Malaysia, Japan and two locations in India. The latter two plants have the highest capacity of 450 tonnes CO₂/day. These plants operate in the chemical and fertilizer industries which recover CO₂ from natural gas fired flue gas (Kishimoto et al, 2009).

A 1 ton CO₂/day pilot plant has been constructed in the MHI Hiroshima R&D centre to demonstrate CO₂ capture from coal-fired flue gas and to carry out various tests for the treatment of impurities (Davidson, 2007).

In Japan, a testing plant capable of recovering 10 tons of CO₂ per day using MHI's KM-CDR process was reported to have operated at a coal-fired power generation plant in Nagasaki – the Matsushima Thermal Power Station of Electric Power Development Co., Ltd. (J-POWER) for over 4000 hours (Kishimoto et al, 2009).

3.9.3 *Activities*

Currently, MHI is working to resolve certain key issues it has identified with the deployment of post combustion CO₂ capture (Kishimoto et al, 2009):

1. Reduction in energy consumption of such plants
2. Efficient integration with other environmental control systems
3. Minimizing the decrease in net electrical output of the power plant

3.10 Summary

Although many research programs or investigations have been carried out globally, all the pilot plants for post-combustion CO₂ capture with MEA are small scale (for power plants up to 2.0 MWe). Consequently, the packed column sizes are modest in size (up to 1.1 m in diameter) (Feron et al., 2007, Dugas, 2006). Therefore, post-combustion CO₂ capture with chemical absorption (although viewed as best technology available) has still not been fully demonstrated.

4. Modelling, Simulation and relevant studies

4.1 Level of complexity in modelling

In modelling absorbers and stripper, two approaches are commonly used: the equilibrium-based approach and the rate-based approach. The former approach assumes a theoretical stage in which liquid and gas phases attain equilibrium and the performance of each stage is adjusted using a tray efficiency correction factor (Schneider et al., 1999). This is usually sufficient to model non-reactive systems. In amine absorption, chemical reactions are involved and such equilibrium is rarely attained. As such, the rate-based approach is more appropriate. In the rate-based approach, actual rates of multi-component mass and heat transfer as well as chemical reactions are considered directly (Noeres, 2003).

To model such a reactive absorption process, simple or complex representations can be used for mass transfer and reaction aspects. Differences between various forms of models are indicated in Figure 6 (Kenig et al., 2001).

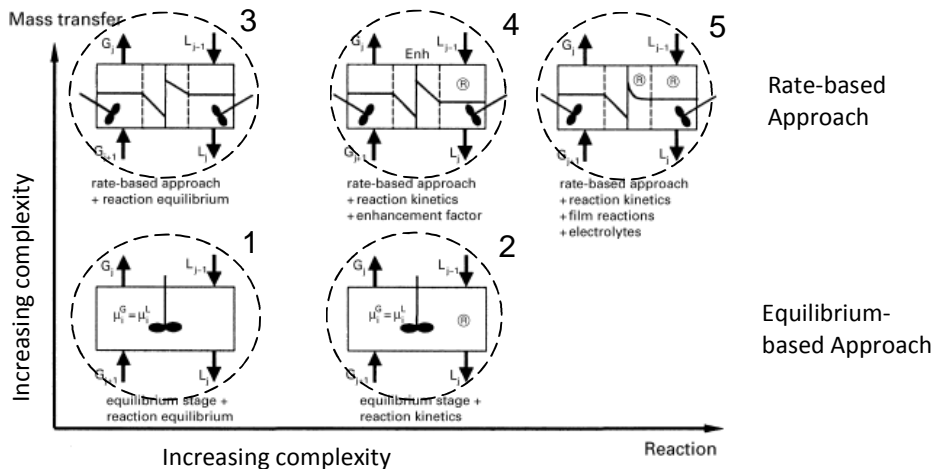


Figure 6 Different levels of reactive absorption model complexity (Kenig et al., 2001)

Starting from Model 1 in Figure 6, the packed column is modelled as a distillation column containing different equilibrium stages. Moving rightwards (Model 2), the model accuracy is increased by considering the bulk phase reaction kinetics. Moving upwards (Models 3, 4 and 5), the mass transfer rate is considered. Thus, the models are called rate-based models. The mass transfer across the gas-liquid interface can be described using the two-film theory. At its lowest level of complexity (Model 3 in Figure 6), the chemical reactions of the rate-based model are assumed to be at equilibrium. Model 3 can be accurate only when the reaction rate between CO₂ and the solvent is very fast. In Model 4, an enhancement factor is used to estimate actual absorption rates. However, the enhancement factor used is strictly valid for the pseudo first-order reaction regime (Kucka et al., 2003). Chemical reactions are assumed to be completed in the liquid film while the bulk fluid remains in chemical equilibrium. Model 5, the most complex of all, considers mass transfer resistances, electrolyte thermodynamics, the reaction system as well as the column configurations. With Model 5, the acceleration of mass transfer due to reactions in the liquid film is taken into account (Kucka et al., 2003). Therefore, Model 5 is the most accurate and will give more realistic predictions.

4.2 Basic Theory behind modelling - Two-film theory and Penetration theory

To describe such a process accurately, it is necessary to develop mathematical models taking into account the column hydraulics, mass transfer resistances and reactions. The influence of chemical reactions on mass

transfer cannot be neglected. From Figure 7, the model will include ideally mixed vapour and liquid bulk phases and two film regions adjacent to the interface.

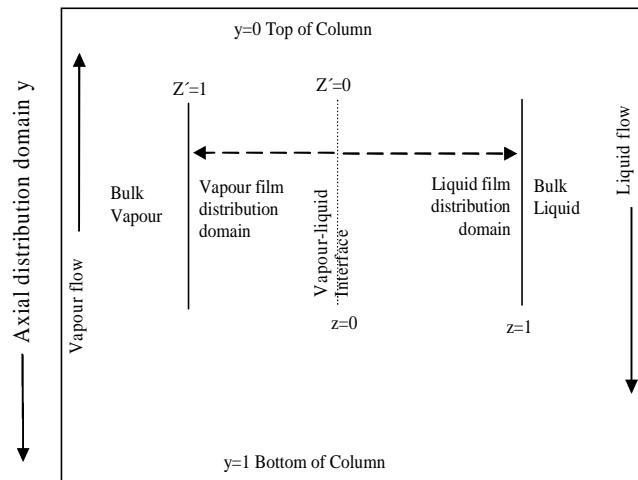


Figure 7 Modelling the conventional process based on the two-film theory

The two-film theory assumes that the liquid and vapour phases both consist of film and bulk regions. Heat and mass transfer resistances are assumed to be restricted to these laminar film regions (Danckwerts, 1970). The penetration theory originally proposed by Higbie assumes that every element on the surface of the liquid is exposed to the vapour phase for the same length of time, before it is replaced by liquid of the bulk composition. The exposure time encompasses the effects of the hydrodynamic properties of the system and is used to define their effect on the mass transfer coefficient (Danckwerts, 1970).

4.3 Current status of modelling Post-combustion with CO₂ capture

The performances of the Absorber and the Stripper, the two major components in the conventional CO₂ capture process, have been studied by a number of researchers through modelling and simulation.

In Lawal et al. (2009a), a dynamic rigorous model was developed for the Absorber. This assumed rate-based mass transfer with reactions at equilibrium (Model 3). Process analysis based on this model found that the Absorber performance can be maintained during part load operation by maintaining the ratio of the flowrates of the lean solvent and flue gas to the Absorber. In Kvamsdal et al. (2009), the Absorber was modelled dynamically assuming rate-based mass transfer and counting the impact of reaction with an enhancement factor (Model 4 in Figure 6). The dynamic model of Absorber was then used to investigate two transient operation scenarios: start-up and load-reduction. The authors also pointed out that a dynamic model for the whole CO₂ capture process (i.e. with the stripper and heat exchange units) is required to evaluate different operational challenges.

In Lawal et al. (2009b), a dynamic model for the Stripper was developed. This assumed rate-based mass transfer and reaction at equilibrium (Model 3). It was used to analyse the impact of the reboiler duty on the CO₂ loadings in the solvent at the bottom of the Stripper. In Ziaii et al. (2009), only the Stripper was modelled dynamically using rate-based mass transfer and assuming reaction at equilibrium (Model 3 in Figure 6). This model was subsequently used to minimise the energy consumption of the Stripper.

The limitation of the publications so far (Lawal et al. (2009a), Kvamsdal et al. (2009), Ziaii et al. (2009) and Lawal et al. (2009b)) is that process dynamic analysis was carried out with individual dynamic models for Absorber or Stripper independently without considering their possible interaction when operation together as a plant.

In Lawal et al. (2010), dynamic models for the absorber and regenerator columns were developed (Model 3 in Figure 6). The gPROMS (Process Systems Enterprise Ltd.) advanced process modelling environment was used. These models were then linked together with recycle (including heat exchanger). A study of the dynamic responses of a post-combustion CO₂ capture plant was carried out based on modelling and simulation. The study gives insights into the operation of the absorber-regenerator combination with possible disturbances arising from integrated operation with a power generation plant. The importance of appropriate water balance in the absorber column is shown.

All the above models were developed based on the two-film theory (for mass transfer calculations). Tobiesen et al. (2010) developed a rigorous absorber model based on penetration theory (for mass transfer calculation). Experimental data from a laboratory pilot plant absorber were used for model validation. The model is fairly accurate.

In summary, an accurate dynamic model of the whole CO₂ capture process is required to study the start-up, shutdown and operation under different power plant loads and process disturbances.

4.4 Studies based on modelling and simulation

Based on modelling (the two-film theory) and simulation, Aroonwilas and Veawab (2007) studied the performance of different amines such as MEA, MDEA and mixture of MEA/MDEA for CO₂ capture in a 500 MW supercritical coal-fired power plants. It was found that when the MEA and MDEA are blended at the appropriate ratio and used as solvent for CO₂ capture, the energy consumption for regenerating CO₂ is reduced significantly. Compared with MEA only, the whole power plant with CO₂ capture can improve thermal efficiency around 3%. However, this study was carried out at steady state and when power plant is operated at full load.

Chalmers and Gibbins (2007) studied post-combustion CO₂ capture with MEA for pulverised coal power plant under part load operating conditions. This study was again carried out at steady state based on simplified models. It pointed out that further work is required to better understand transient behaviour of power plants with CO₂ capture especially from one load changing to another.

Kvamsdal et al. (2010) studied a 450 MWe natural gas combined cycle (NGCC) sea floating power plant (for offshore use) with post-combustion CO₂ capture with MEA. It is concluded that the NGCC plant will have 9% efficiency penalty due to adding CCS with 90% CO₂ captured and compression of CO₂ to 1.47 MPa. Another key issue of water balance for the whole CO₂ capture process was solved by adjusting operating or design conditions.

4.5 Commercial products and studies based on commercial products

Aspen Plus® provides two rigorous multistage separation models for modelling absorber and regenerator (or stripper). These are RadFrac and RateFrac sub-models (Aspentech, 2008). RadFrac model is equilibrium stage column model (equivalent as Model 2 in Figure 6). RateFrac model considers actual multi-component heat and mass transfer (equivalent as Model 3 or Model 5 in Figure 6 depending upon whether reaction kinetics is used).

Freguia and Rochelle (2003) used RateFrac to simulate the absorber and stripper. These were linked with heat exchanger to form a whole CO₂ capture process. In the absorber, the reactions involving CO₂ were described with kinetics. In the stripper model, all the reactions were set to equilibrium due to higher operating temperature. Effects of process design and operating variables (such as solvent circulating rate, absorber height, stripper height and stripper pressure) on energy requirement were studied. Intercooling in the absorber was also explored and found that the reboiler duty was reduced by 3.8% for inlet stream with 10 vol% CO₂.

Kvamsdal and Rochelle (2008) used Aspen RateSep™ in Aspen Plus® process simulator (a second generation rate-based multistage separation unit operation) and a dynamic rate-based gPROMS model (Model 4 in Figure 6) to study the position of temperature bulge (which is caused by combining chemical absorption and water vaporisation) in the absorber and its impact on absorption of CO₂.

Zhang et al. (2009) used Aspen RateSep™ in Aspen Plus® again for simulation study. Experimental data from the pilot plant tests in the University of Texas at Austin were used for model validation of the absorber only (Dugas, 2006). These experimental data include 48 runs at 24 operating conditions since two runs were executed at each operating condition. It also discussed the importance of film discretisation.

Dugas et al. (2009) used Aspen RateSep™ in Aspen Plus® to simulate the absorber. Experimental data from pilot plant tests in CASTOR project were used for model validation. It claimed that the model successfully represented both gas phase temperature and CO₂ profiles in the absorber.

5. Solvents

The ideal chemical solvent possesses (Davidson, 2007):

- High reactivity with respect to CO₂ – which would reduce height requirements for the absorber and/or reduce solvent circulation flow rates.
- Low regeneration cost requirements –based on a low heat of reaction with CO₂

- High absorption capacity – which directly influences solvent circulation flow rate requirements.
- High thermal stability and reduced solvent degradation – reduced solvent waste due to thermal and chemical degradation
- Low environmental impact
- Low solvent costs – should be easy and cheap to produce

5.1 Amine-based solvents

Amines have been used for around 75 years for the treatment of industrial gas streams with the alkanolamines being the most popular group of solvents (Booth, 2005). Amines could be classified as primary, secondary or tertiary based on the degree of substitution of the nitrogen atom. MEA consists of one alkanol chain and two hydrogen atoms bonded to a nitrogen atom and thus it is classified as a primary amine with the molecular formula $(C_2H_4OH)NH_2$. Diethanolamine (DEA) consists of two alkanol chains and one hydrogen atom bonded to the nitrogen atom and is a secondary amine with the molecular formula $(C_2H_4OH)_2NH$. In the same way, triethanolamine (TEA) is a tertiary amine $(C_2H_4OH)_3N$ (Booth, 2005).

A variety of ethanolamine derivatives can be produced by replacing one or more of the ethanol groups by other hydrocarbon groups. An example of this is the tertiary amine methyldiethanolamine (MDEA) where a methyl group replaces one of the ethanol groups. MDEA has the molecular formula $C_2H_4OH)_2N(CH_3)$ (Booth, 2005).

Primary and secondary alkanolamines react rapidly with CO_2 to form carbamates. Tertiary alkanolamines do not possess a hydrogen atom attached to the nitrogen atom. They therefore facilitate the CO_2 hydrolysis reaction to form bicarbonates. The heat of reaction involved with bicarbonate formation is lower than that of carbamate formation and thus tertiary amines like MDEA are often blended with primary or secondary amines to reduce solvent regeneration costs (Vaidya and Kenig, 2007).

Sterically hindered amines are primary and secondary amines modified to reduce regeneration costs. Examples include 2-Amino-2-methyl-1-propanol and 2-piperidineethanol (Vaidya and Kenig, 2007).

MEA and popular alternative solvents for chemical absorption are discussed.

5.2 MEA

Chemical absorption of CO_2 is preferred for post combustion capture of CO_2 from pulverized fuel power plants because it is able to capture CO_2 in low partial pressures. MEA solvent is relatively cheap and chemical absorption process with MEA is backed up by commercially available and proven technology (Rao et al., 2004).

Davidson (2007) highlighted some problems encountered using MEA such as (a) degradation of solvents in the oxidising environment of flue gas; (b) energy consumption for regeneration of solvents; (c) corrosion. Alternative solvents to MEA should have higher capacity for CO_2 capture and lower energy consumption.

5.2.1 Reaction kinetics of the reactive absorption of CO_2

Vaidya and Kenig (2007) reviewed the reaction kinetics of CO_2 absorption in alkanolamines. In the paper it was shown that there have been varied predictions of the reaction rate coefficients for absorption with MEA. Aboudheir et al. (2003) explained that these discrepancies are due to (among other factors) the assumption of a pseudo-first order reaction with respect to both CO_2 and MEA. More detailed reaction mechanisms are needed to accurately describe the kinetics. Three mechanisms were described in Vaidya and Kenig (2007):

- Zwitterion mechanism
- Termolecular mechanism
- Base-Catalyzed Hydration Mechanism

5.2.2 Degradation of MEA solvent

Davidson (2007) discussed three main degradation routes: (a) carbamate polymerisation; (b) oxidative degradation; (c) thermal degradation.

Carbamate polymerisation is insignificant at temperatures below 100 °C. Thermal degradation takes place at temperatures above 205 °C. Most degradation comes from the presence of oxygen in the flue gas. Davidson (2007) explains that four carboxylic acids (formate, glycolate, oxalate and acetate) are major amine degradation products while nitrites, nitrates and ethylenediamine were also found in significant quantities.

Sexton and Rochelle (2009) described catalysts and inhibitors for MEA oxidation. They carried out studies at 55°C and found that dissolved metals catalyze the oxidation process in the order copper > chromium/nickel > iron > vanadium. They also identified effective degradation inhibitors such as ethylenediaminetetracetic acid (EDTA) and explained that some expected inhibitors such as formaldehyde, formate and sodium sulphite actually increased MEA losses.

Davis and Rochelle (2009) focused on the regeneration in the stripper unit. At 135°C the degradation rate is 2.5 to 6% per week. CO₂ loading of the solvent was found to have a first order effect and amine concentration had a slightly higher than first order effect on increasing the degradation rate. The paper also suggests that MEA degradation is significantly reduced if temperatures are kept below 110°C.

5.2.3 Effects of Sulphur Dioxide (SO₂)

SO₂ reacts with MEA to form heat stable salts. By varying the SO₂ concentrations in the range of 6 - 196ppm, Uyanga and Idem (2007) demonstrated that an increase in SO₂ concentration would result in an increase in MEA degradation. Their study also suggests that an increase in CO₂ loading in the liquid phase produced an inhibition effect to MEA degradation because this would reduce the amount of SO₂ and O₂ that could react with the MEA solution to induce degradation. It may therefore be of advantage to operate the absorption process with higher lean CO₂ loading. However, in doing so, consideration has to be made regarding the corrosive effect of more CO₂ in the system (Davidson, 2007).

5.2.4 Corrosion of MEA solvent

Davidson (2007) explained that factors that influenced corrosion rates in amine plants include CO₂ loading, amine type and concentration, temperature, solution velocity and degradation products. MEA is quite corrosive compared to the secondary or tertiary amines used for gas treating. (Kittel et al, 2009). Corrosion is found to reduce in the following order MEA>AMP>DEA>MDEA (Davidson, 2007).

5.3 MEA and MDEA Blends

Other solvents used for CO₂ chemical absorption include methyldiethanolamine (MDEA). MEA can react more quickly with CO₂ than MDEA can, but MDEA has a higher CO₂ absorption capacity and requires lower energy to regenerate CO₂ (Davidson, 2007, Aroonwilas and Veawab, 2007).

Aroonwilas and Veawab (2007) studied the performance of different amines such as MEA and MDEA for coal-fired power plants. It was found that when the MEA and MDEA is mixed at the appropriate ratio and used as solvent for CO₂ capture, the energy consumption for regenerating CO₂ is reduced significantly. Compared with MEA only, the whole power plant with CO₂ capture can improve thermal efficiency around 3%. However, this study was carried out at steady state and when power plant is operated at full load.

Other solvents include the sterically-hindered amines (KS-1, KS-2 and KS-3) developed by the Kansai Electric Power Co. (Davidson, 2007). These solvents are claimed to offer lower energy consumption and solvent loss. These solvents however, have higher costs (Reddy et al., 2003).

5.4 Ammonia

Ammonia has been identified as a possible alternative to MEA solvent as it has a number of desirable characteristics. It is a relatively cheap solvent that is commercially available. It has a relatively high CO₂ absorption capacity compared to most other solvents based (among other factors) on its low molecular weight. It absorbs CO₂ with a low heat of reaction and thus the regeneration energy requirements are also low. It is not as corrosive as MEA and has a lower susceptibility to degradation in the presence of oxygen and other contaminants when compared with MEA (Davidson (2007), Darde et al. (2010), Kozak et al. (2009).

The Chilled Ammonia Process (CAP) is being developed for CO₂ capture. In this process, CO₂ is absorbed in the absorber at low temperatures. This would minimize solvent losses due to its relatively volatile compared with the amine solvents. First the flue gas is cooled to 0 to 20°C (preferably 0 – 10°C) it is then contacted in the absorber with lean solvent typically composed of 28wt% ammonia, CO₂ loading between 0.25 and 0.67mol CO₂/mol ammonia and water (Darde et al, 2010). The CO₂ loading in the lean solvent should be high enough to prevent excessive solvent evaporation and low enough to maximize the capture efficiency of the plant (Darde et al, 2010). The CO₂ rich stream is typically a slurry as solid products (typically of ammonium bicarbonate) are formed. (Darde et al, 2010)

The stripper operating temperature ranges from 50 to 200°C (preferably 100 to 150°C) and the operating pressure from 2-136atm..This produces a high pressure stream rich in CO₂. Water vapour and ammonia

could be recovered by cold washing possibly with a weak acid for higher efficiency. Energy requirements for regeneration are significantly lower than those for MEA absorption.

The Aqua Ammonia Process is another process that employs ammonia solvent and is proposed to capture SO₂, NO_x and CO₂ from the flue gas (Davidson, 2007).

5.5 Piperazine promoted K₂CO₃

The promotion of potassium carbonate (K₂CO₃) with amines appears to be a particularly effective way to improve overall solvent performance. K₂CO₃ in solution with catalytic amounts of piperazine (PZ) has been shown to exhibit a fast absorption rate comparable to 30% wt% MEA. Heat of absorption is significantly lower than that for aqueous amine systems (Cullinane and Rochelle, 2005). This could translate to 29-33% regeneration energy savings for certain conditions when compared with MEA (Davidson, 2007).

5.6 Concentrated aqueous piperazine

Concentrated, aqueous piperazine (PZ) has been investigated as a novel amine solvent for CO₂ chemical absorption. The CO₂ absorption rate of aqueous PZ is much faster than MEA. Thermal degradation is negligible in concentrated aqueous PZ up to a temperature of 150 °C. This is a significant advantage over MEA systems. Industrial study showed that PZ will use 10 to 20% less energy than MEA (Freeman et al., 2010).

6. Process intensification (PI)

6.1 Motivations for using process intensification in post-combustion chemical absorption

It should be recognised that the flue gas volumetric flowrate involved for a typical coal-fired power plant is extremely large. For example, an electrical output of 500 MWe corresponds to a combustion rate of roughly 1500 MWh. Assuming that coal's calorific value is based on the heat of formation of CO₂ and with 10% excess air, the flue gas flow is roughly 550m³/s. Hence, with a flue duct velocity of 15 m/s in order to limit flue pressure drops to reasonable values, the duct cross sectional area must be substantial (around 65m²). The CO₂ chemical absorption system need only be a fairly crude affair which would provide, say, the equivalent of 2 to 3 transfer units which corresponds roughly to a 10 fold CO₂ reduction. This is based on the assumption of a low CO₂ partial pressure over the CO₂ rich solvent flowing to the stripper system.

With respect to the absorption stage, as shown above, large gas ducts are needed whether or not carbon capture is involved. It is, therefore, worth considering the installation of a simple liquid spray system to implement the absorption stage. This leaves us with the issue of the stripping duty and the lean/rich solvent cross heat exchanger where PI may be employed to good effect.

6.2 Principles and benefits

Process intensification can be achieved with a novel technology called Hige (an abbreviation for high gravity). This was first proposed by Ramshaw and Mallinson (1981) when they invented a rotating packed bed (RPB) to enhance distillation and absorption efficiencies. It takes advantage of centrifugal fields through RPB to generate high gravity, and therefore boosts the mass transfer coefficients, resulting in an order of magnitude reduction in equipment size.

PI is a strategy of making major (i.e. orders of magnitude) reductions in the volume of processing plant without compromising its production rate. This is achieved by reducing individual process elements and, where possible, combining process functions in multi-functional modules. In order to achieve this, new technology is exploited, often where high centrifugal acceleration fields and fine channels are used to intensify heat and mass transfer rates as described below.

The benefits of this approach are potentially profound:

1. Piping and structural support costs can be dramatically reduced, leading to lower installation factors and reduced capital costs.
2. Process inventories are slashed, giving improved intrinsic safety when toxic or flammable material is being treated.
3. Residence times are reduced to seconds rather than the hours encountered in conventional plant. As a consequence, plant response times are much faster. This can be particularly important for reactors because it facilitates rapid grade changes and just-in-time production. This may allow cost savings to be realised by reducing warehouse inventories of a multi-grade product.

4. The improvement in heat/mass transfer coefficients may be used to reduce thermodynamically parasitic differences in temperature/concentration so that the process thermodynamic efficiency is improved.
5. In some situations, a much smaller plant may be more compatible with the environment.

Approximately two thirds of process unit operations involve the contact of two or more phases. Thus we have boilers, condensers, absorbers and distillation columns etc. For these unit operations, the fluid dynamic intensity is controlled by the interfacial slip velocity which is dependent on the buoyancy force $\Delta\rho.g$ where $\Delta\rho$ is the interfacial density difference and g is the applied acceleration. For a given system, this implies that higher levels of acceleration can result in greater flooding rates, enhanced settling and greater heat/mass coefficients. This key idea suggests that the operation of many process units in a centrifugal acceleration environment such as RPB or a spinning disc, could be a powerful means of realising PI. This has indeed proved to be the case, as has been shown in many publications (Ramshaw and Mallinson, 1981). Thus distillation or absorber heights of $\sim 1.5\text{cm}$ (gas film controlled) and 4 to 6cm (liquid film controlled) can be realised in a RPB while achieving very high mass fluxes in view of the enhanced flooding rates. Gas-liquid reactions can be performed in seconds on spinning discs provided the chemical kinetics are not limiting. Stripping and evaporation can be operated in one rotating element as they both benefit from the high acceleration field. This is a good example of a multi-functional application. This latter example is particularly relevant to the stripper stage of a carbon capture process.

When the process operation does not involve multiple phases and with relatively clean systems, it may be possible to exploit laminar flow in narrow (0.1 to 2 mm) channels as exemplified by the printed circuit heat exchanger/reactor marketed by Heatric Ltd. Very high transfer coefficients can be achieved in view of the short conduction lengths involved. As the narrow channels also permit large specific areas, the space-time performance of these units is impressive.

6.3 Recent progress

A recent laboratory study by Lin and Liu (2007) of CO_2 absorption has shown that the height of transfer unit (HTU) for an 8 cm diameter RPB was 1 – 4 cm, at modest rotational speed of less than 1,000 rpm. The inlet CO_2 concentration was 1% mole fraction of $\text{CO}_2\text{-N}_2$ mixture and NaOH (0.2 kmol/m^3) was the absorbent. This compares with the 10-60 cm of conventional packed beds for similar ratings. In a more recent study by Cheng and Tan (2009) using high voidage packed beds, similar findings were reported with amine solutions. These studies indicate that process intensification technology has the potential to reduce the size of CO_2 capture plants and reduce both the capital and operating costs.

The standard concentration of the MEA solution used for carbon capture in conventional equipment is 30wt%. This is largely determined by the need to limit solution viscosity and the corrosion potential with carbon steel construction. However, recent work by Jassim et al. (2009) using a RPB and stronger solutions, has shown that much more efficient absorption can be achieved despite the higher solution viscosity. This effect is probably due to the accelerated chemical kinetics associated with MEA solution concentrations in the range 50-100wt%. A further advantage of this approach is that the CO_2 loading/ m^3 of solvent solution is much higher, thereby resulting in lower liquid flows between the absorber and stripper. In order to overcome corrosion problems, the rotating stripper (including reboiler) would have to be fabricated in stainless steel. However, this would not present too much of a cost penalty in view of the small size of the unit compared to the carbon steel conventional columns. A comparison of the size of rotating units with their equivalent columns is shown in Figure 8 (Trent, 2004).



Figure 8 Three very small size RPBs equivalent to one large packed column (photo courtesy of The Dow Chemical Company)

7. Challenges ahead and potential breakthroughs

7.1 Solvents

The characteristics of an ideal solvent are presented in Section 5. In the same section, recent developments in new solvents are also reviewed. The most commonly used solvent MEA in post-combustion chemical absorption of CO₂ has the following disadvantages (Resnik et al., 2004):

- Low carbon dioxide loading capacity (kg CO₂ absorbed per kg solvent)
- Solvent degradation due to SO₂ and O₂ in flue gas
- High equipment corrosion rate
- High energy consumption

Development of new solvents has achieved some progress such as ammonia (Darde et al., 2010), piperazine promoted K₂CO₃ (Cullinane and Rochelle, 2005), and concentrated aqueous piperazine (Freeman et al., 2010). Future efforts should be directed towards developing better solvents. Future progress in solvents should be (a) to reduce energy consumption; (b) to avoid damage to environment and human being (when it is vented with treated gas); (c) solvent degradation and corrosion to the packed column acceptable. More important is to combine all these in one solvent.

7.2 Pilot plants - the roadmap to commercial scale

A number of pilot plant scale studies have been carried out. Although these projects have so far been below 10MWe scale, their costs usually run to millions of dollars (Herzog et al, 2009). Processing flue gas from real fossil fuelled power plants has been carried out in a number of plants by treating a slip stream of the flue gas produced. However, to evaluate the effect of the significant energy requirements of post combustion process, demonstration projects, with scales of 100s of MWe and likely costing over a billion dollars, are required (Herzog et al, 2009).

The first demonstration project may be in the UK resulting from the government's CCS competition (Herzog et al, 2009). The UK government CCS competition has finalised in Mar. 2010 that E.ON UK and Scottish Power will share a £90 million pot (BBC News, 2010). These two firms now compete to build the UK's first CCS coal-fired power plant. The undisclosed amount of money each firm won, which has been drawn from the £90 million pot, will support engineering and design work for the CCS projects.

7.3 Modelling and Simulation

7.3.1 Dynamic validation

Currently all the dynamic models reported were only validated at steady state (rather than dynamically). This is mainly due to lack of experimental data for CO₂ capture pilot plants running at transient conditions. The dynamic validation is vital to gain understanding for operation and control design of such a process.

7.3.2 Use of commercial software for simulation study

Several studies were reported to study the post-combustion CO₂ capture process for process design and operation (Freguia and Rochelle (2003), Kvamsdal and Rochelle (2008), Zhang et al. (2009), Dugas et al. (2009)). These studies were all conducted by experts in modelling and simulation. The challenge is how to make these commercial tools easy to use by practising engineers.

7.4 Process Intensification

As described in Section 6, it will be seen that PI has the potential to make large cost savings in a carbon capture process. It is recommended that the development of a rotating unit which combines the function of stripper including reboiler is actively considered.

7.5 To reduce energy consumption of CO₂ capture

7.5.1 By developing new solvents

Generally for a given solvent, it can only save less than 10% of energy consumption by optimising design and operating conditions (Freguia and Rochelle, 2003). However, a new solvent has a potential to save 20 to 30% (even more) of energy consumption (Darde et al., 2010).

7.5.2 By process heat integration

When the temperature profile inside the absorber is plotted, it is easy to find a temperature bulge, which is caused by combining chemical absorption and water vaporisation. The temperature bulge is not helpful for CO₂ chemical absorption. Freguia and Rochelle (2003) indicated that when the absorber deals with 3 vol% CO₂ in the flue gas and MEA solvent is used, the temperature bulge is not significant. On the other hand, when the absorber deals with 10 vol% CO₂ in the flue gas, the temperature bulge is significant. Intercooling means to take away heat from middle of the absorber to the reboiler in stripper (which has no effect on the rich end of the column). For the case with 10 vol% CO₂ in the flue gas, reboiler duty reduced 3.8% (Freguia and Rochelle, 2003). Plaza et al. (2010) carried out a similar simulation study with Piperazine-promoted Potassium Carbonate as solvent which is intercooling in the absorber with different configurations. It is also found that the effect of intercooling is related to the position of the temperature bulge.

Another way to reduce energy consumption of CO₂ capture can be achieved by better process integration of CO₂ capture plant with the power generation plant. Lucquiaud and Gibbins (2009) studied effective integration between these two parts and pointed out that with different solvent used in CO₂ capture plant, there will be different requirements to steam pressure, temperature and flowrate extracted from the crossover pipe between the intermediate pressure and low pressure turbines.

7.6 Simultaneous removal of SO₂ and CO₂

Resnik et al. (2004) carried out an experimental study to use ammonia as solvent to capture CO₂, SO₂ and NO_x simultaneously from flue gas. The benefits are: (a) A single process to capture all the acidic gases is expected to reduce the total cost and complexity of emission control systems; (b) The CO₂ loading capacity by NH₃ can approach 1.20 kg CO₂ / kg NH₃, while CO₂ loading capacity by MEA is only 0.4 kg CO₂ / kg MEA. In other words, ammonia's CO₂ loading capacity is three times that of MEA; (c) Cycling tests results demonstrated that a 64% reduction in regeneration energy is possible due to higher CO₂ loading capacity of aqueous ammonia solution and lower heat of reaction.

7.7 Policy impact

It is sensible to assume that the government will legislate at some point so that retrofitting combined cycle gas turbine (CCGT) plant with CO₂ capture technologies is mandatory (The Press and Journal, 2010). Although capture efficiencies are low compared with coal fired applications, it begs the question of flue gas re-cycling on gas turbines to increase CO₂ concentration and reduce NO_x.

8. Conclusions

Post-combustion capture with chemical absorption is probably the first technology that will be deployed. A state-of-the-art assessment of the research work carried out so far in post-combustion capture with chemical absorption is provided in this paper. These include important research programs globally, experimental studies with pilot plants, and studies through modelling and simulation. The use of process intensification has also been discussed. Based on these recent developments, we tried to predict future challenges and potential breakthroughs. More efforts in the future should be directed to reduce energy consumption in post-combustion CO₂ capture with chemical absorption. Another concern is the solvent's damage to the environment when it is vented with treated gas. The impact of government policies cannot be ignored before this post-combustion CO₂ capture with chemical absorption process can be commercialised.

References:

- Aboudheir, A., Tontiwachwuthikul, P., Chakma, A. and Idem, R. (2003), Kinetics of the reactive absorption of carbon dioxide in high CO₂-loaded, concentrated aqueous monoethanolamine solutions, *Chemical Engineering Science*, 58: 5195-5210.
- Aroonwilas A, Veawab A. (2007), Integration of CO₂ 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*, 1:143-150.
- Aspentech (2008), New feature to Aspen Plus 2006.5: Rate-based model of the CO₂ capture process by MEA using Aspen Plus, www.support.aspentech.com (accessed in May 2009).
- Bishnoi, S., Rochelle, G.T. (2002), "Thermodynamics of Piperazine/Methyldiethanolamine/Water/Carbon Dioxide," *Ind. Eng. Chem. Res.*, 41: 604-612.
- BBC News (2010), Firms gets Kingsnorth carbon capture design funding, <http://news.bbc.co.uk/1/hi/england/kent/8565225.stm> (accessed in May 2010).
- Booth N.J. (2005), Secondment to the International Test Centre for CO₂ Capture (ITC), University of Regina, Canada; January- March 2005 Report No COAL R303 DTI/Pub URN 06/798.
- CAPRICE (2010), CO₂ Capture using Amine Processes International Cooperation and Exchange, www.caprince-project.eu, (Accessed in April 2010).
- Chalmers, H. and Gibbins, J. (2007), Initial evaluation of the impact of post-combustion capture of carbon dioxide on supercritical pulverised coal power plant part load performance, *Fuel*, 86:2109-2123.
- Chakravati S, Gupta A, Hunek B. (2001), Advanced technology for the capture of carbon dioxide from flue gases. 1st National Conference on Carbon Sequestration, Washington DC.
- Chen, E., Rochelle, G. T. and Seibert, F. (2006), Pilot plant for CO₂ capture with aqueous piperzine/potassium carbonate, GHGT-8, Trondheim, Norway.
- Cheng, H.H. and Tan, C.S. (2009), Carbon Dioxide Capture by blended Alkanolamines in Rotating Packed Bed, *Energy Procedia*, 925-932.
- Chi, S. and Rochelle, G. T. (2002), Oxidative degradation of monoethanolamine, *Ind. Eng. Chem. Res.*, 41:4178-4186.
- CO2cesar (2010), CO2cesar, 7th Framework Program – CO₂ enhanced separation and recovery, www.co2cesar.eu, (Accessed in April 2010).
- CO2CRC (2009a), CO2CRC Annual Report 2008-2009. www.co2crc.com.au/dls/annreps/09/research_CO2CRC_Annual0809.pdf (accessed in April 2010)
- CO2CRC (2009b), The International Capture Plant. www.co2crc.com.au/dls/factsheets/CO2CRC_factSheet_18.pdf (accessed in April 2010)
- Cullinane, J. T. and Rochelle, G. T. (2005), Thermodynamics of aqueous potassium carbonate, piperazine, and carbon dioxide, *Fluid Phase Equilibria*, 227: 197-213.
- Danckwerts, P. V. (1970), *Gas-Liquid Reactions*, McGraw-Hill, New York, U.S.A
- Darde, V., Thomsen, K., van Well, W. J. M. and Stenby, E. H. (2010), Chilled ammonia process for CO₂ capture, *International Journal of Greenhouse Gas Control*, 4:131-136.
- Davis J. and Rochelle G. (2009), Thermal degradation of monoethanolamine at stripper conditions, *Energy Procedia* 1 (1): 327-333.

- Davison J. (2007), Performance and costs of power plants with capture and storage of CO₂, *Energy*, 32:1163-1176.
- Davidson, R. M. (2007), Post-combustion carbon capture from coal fired plants - solvent scrubbing, IEA Clean Coal Centre, CCC/125.
- Dugas, E.R. (2006), *Pilot plant study of carbon dioxide capture by aqueous monoethanolamine*, MSc Thesis, University of Texas at Austin, USA.
- Dugus, R., Alix, P., Lemaire, E., Broutin, P. and Rochelle, G. (2009), Absorber model for CO₂ capture by monoethanolamine – application to CASTOR pilot results, *Energy Procedia*, p103-107.
- Edali, M., Aboudheir, A. and Idem, R. (2009), Kinetics of carbon dioxide absorption into mixed aqueous solutions of MDEA and MEA using a laminar jet apparatus and a numerically solved 2D absorption rate/kinetics model, *International Journal of Greenhouse Gas Control*, 3:550-560.
- Feron, P.H.M., Abu-Zehra, M., Alix, P., Biede, O., Broutin, P., Jong Hans (2007), Development of post-combustion capture of CO₂ within the CASTOR Integrated Project: First results from the pilot plant operation using MEA, *3rd International Conference on Clean Coal Technologies for our Future*, Italy.
- Favre E. (2007), Carbon dioxide recovery from post-combustion processes: Can gas permeation membranes compete with absorption? *Journal of Membrane Science*, 294:50-59.
- Freeman, S.A., Dugus, R., Van Wagener, D. H., Nguyen, T., Rochelle, G. T. (2010), Carbon dioxide capture with concentrated, aqueous piperazine, *International Journal of Greenhouse Gas Control*, 4:119-124.
- Freguia, S. and Rochelle, G.T. (2003), Modeling of CO₂ capture by aqueous monoethanolamine, *AIChE Journal*; 49:1676-1686.
- Freund P (2003), Making deep reductions in CO₂ emissions from coal-fired power plant using capture and storage of CO₂. *Proc Inst Mech Eng Part A J Power Eng*.217:1-8
- Herzog, H., Meldon, J., Hatton, A. (2009), Advanced Post Combustion CO₂ Capture, <http://web.mit.edu/mitei/docs/reports/herzog-meldon-hatton.pdf> (accessed in May 2010)
- iCap (2010), iCap News and Highlights. www.icapco2.org/news_1.html (accessed in April 2010)
- Idem, R., Wilson, M., Tontiwachwuthikul, P., Chakma, A. Veawab, A., Aroonwilas, A. And Gelowitz, D. (2006), Pilot plant studies of the CO₂ capture performance of aqueous MEA and mixed MEA/MDEA solvents at the University of Regina CO₂ capture technology development plant and the Boundary Dam CO₂ capture demonstration plant, *Ind. Eng. Chem. Res.*, 45:2414-2420.
- IEA (2007), World energy outlook 2007 - China and India insights: Executive summary. Paris, France: OECD/IEA;
- IEA (2004), Prospects for CO₂ capture and storage. Paris, France: OECD/IEA.
- IEAGHG (2010), Project details: CASTOR, "CO₂ from Capture to Storage". www.co2captureandstorage.info/project_specific.php?project_id=124 (accessed in April 2010)
- IPCC (2005), Intergovernmental Panel on Climate Change (IPCC) special report on carbon dioxide capture and storage, Cambridge University press, Cambridge, UK.
- IEA GHG(1993), The capture of carbon dioxide from fossil fuel fired power stations. Cheltenham, UK: IEA GHG; IEA GHG/SR2.
- Jassim, M.S., Rochelle, G., Eimer, D., Ramshaw, C. (2009), Carbon dioxide absorption and desorption in aqueous monoethanolamine solutions in a rotating packed bed, *Ind. Eng. Chem. Res.*, 46:2823-2833.
- Kenig, E. Y., Schneider, R. and Górak, A. (2001) Reactive absorption: Optimal process design via optimal modelling, *Chemical Engineering Science*, 56:343-350.
- Kishimoto, S., Hirata, T., Iijima, M., Ohishi, T., Higaki, K. and Mitchell, R. (2009), Current status of MHI's CO₂ recovery technology and optimization of CO₂ recovery plant with a PC fired power plant, *Energy Procedia*, 1:1091-1098.
- Kittel, J., Idem, R., Gelowitz, D., Tontiwachwuthikul, P., Parrain, G. and Bonneau, A. (2009), Corrosion in MEA units for CO₂ capture: Pilot plant studies, *Energy Procedia*, 1(1): 791-797.
- Kozak, F., Petig, A., Morris, E., Rhudy, R. and Thimsen, D. (2009), "Chilled ammonia process for CO₂ capture", *Energy Procedia*, 1(1):1419-1426.

Knudsen JN, Jensen JN, Vilhelmsen P, Biede O. (2009), Experience with CO₂ capture from coal flue gas in pilot-scale: Testing of different amine solvents. *Energy Procedia*;1(1):783-90.

Kucka, L., Müller, I., Kenig, E.Y. and Górak, A.(2003), On the modelling and simulation of sour gas absorption by aqueous amine solutions, *Chemical Engineering Science*, 58:3571-3578.

Kvamsdal H.M., Rochelle G.T. (2008), Effects of the temperature bulge in CO₂ absorption from flue gas by aqueous monoethanolamine. *Ind Eng Chem Res*; 47(3):867-75.

Kvamsdal, H.M., Jakobsen, J.P. and Hoff, K.A. (2009), Dynamic modelling and simulation of a CO₂ absorber column for post-combustion CO₂ capture, *Chemical Engineering and Processing: Process Intensification*, Vol. 48, p135-144.

Kvamsdal HM, Hetland J, Haugen G, Svendsen HF, Major F, Karstad V, Tjellander G.(2010), Maintaining a neutral water balance in a 450MWe NGCC-CCS power system with post-combustion carbon dioxide capture aimed at offshore operation. *Int. J. Greenhouse Gas Control*; 2010, doi:10.1016/j.ijggc.2010.01.002

Lawal, A., Wang, M., Stephenson, P. and Yeung, H. (2009a), Dynamic modelling of CO₂ absorption for post combustion capture in coal-fired power plants, *Fuel*, Vol. 88, Issue 12, p2455-2462.

Lawal, A., Wang, M., Stephenson, P. and Yeung, H. (2009b), Dynamic modeling and simulation of CO₂ chemical absorption process for coal-fired power plants, *10th International Symposium on Process Systems Engineering – PSE '09, Brazil*.

Lawal, A., Wang, M., Stephenson, P., Koumpouras, G. and Yeung, H. (2010), Dynamic Modelling and Analysis of Post-Combustion CO₂ Chemical Absorption Process for Coal-fired Power Plants, *Fuel* (accepted).

Lin, C.C. and Liu, W.T (2007), Mass Transfer Characteristics of a High-voidage Rotating Packed Bed, *J. Ind Eng. Chem.*, vol 13, No. 1, 71-78.

Lucquiaud, M. and Gibbins, J. (2009), Retrofitting CO₂ capture ready fossil plants with post-combustion capture. Part 1: requirements for supercritical pulverized coal plants using solvent-based flue gas scrubbing, *Proceedings IMechE Part J: Journal of Power and Energy*, 213-226.

NETL (2008), Carbon Dioxide Capture by Absorption with Potassium Carbonate. www.netl.doe.gov/publications/factsheets/project/Proj280.pdf (accessed April 2010)

Noeres C, Kenig EY, Górak A (2003), Modelling of reactive separation processes: Reactive absorption and reactive distillation. *Chemical Engineering and Processing*, 42:157-178.

Notz R, Aspiron 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

NZEC (2009), The joint China-UK Near Zero Emissions Coal (NZEC) Initiative: Summary Report. www.nzec.info/en/assets/Reports/China-UK-NZEC-English-031109.pdf (accessed April 2010)

Plaza, J.M., Chen, E. and Rochelle, G.T. (2010), Absorber intercooling in CO₂ absorption by Piperazine-promoted Potassium Carbonate, *AIChE Journal*, 56:905:914.

Rao A.B, Rubin E.S. (2002), A technical, economic, and environmental assessment of amine-based CO₂ capture technology for power plant greenhouse gas control. *Environmental Science and Technology*, 36:4467-4475.

Rao A.B., Rubin E.S., Berkenpas M.B. (2004), An integrated modeling framework for carbon management technologies. Pittsburgh, Pennsylvania: Carnegie Mellon University.

Ramezan M, Skone T. J. and Nsakala N. (2007), Carbon dioxide capture from existing coal-fired power plants, National Energy Technology Laboratory; DOE/NETL-401/110907.

Ramshaw, C. and Mallinson, R.H. (1981), Mass transfer process, US Patent No 4 283 255.

Reddy S, Scherffius J, Freguia S. Fluor's econamine FG Plus_{SM} technology. 2003

Rochelle, G.T. (2010), The Rochelle Lab, The University of Texas at Austin: CO₂ capture, www.che.utexas.edu/rochelle_group/index.html (accessed in April 2010).

Resnik, K.P., Yeh, J.T. and Pennline, H.W. (2004), Aqua ammonia process for simultaneous removal of CO₂, SO₂ and NO_x, *Int. J. Environmental Technology and Management*, 4:89-104.

Rochelle, G.T., S. Bishnoi, Chi, S., Dang, H., Santos, J. (2001), Research Needs for CO₂ Capture from Flue Gas by Aqueous Absorption/Stripping, www.che.utexas.edu/rochelle_group/Pubs/DOE_Literature_Review_2001.pdf (accessed in April 2010)

Schneider, R., Kenig, E.Y. and Górak A. (1999), Dynamic modelling of reactive absorption with the maxwell-stefan approach, *ICHEME Part A: Chemical Engineering Research and Design*, 77:633-638.

- Sexton A.J. and Rochelle G., (2009), Catalysts and Inhibitors for MEA Oxidation, *Energy Procedia* 1(1): 1179 – 1185.
- The Press and Journal (2010), Plea for £600m carbon-capture rethink, <http://www.pressandjournal.co.uk/Article.aspx/1601369?UserKey&UserKey> (accessed May 2010).
- Tobiesen, F. A., Svenden, H. F. and Juliussen, O. (2007), Experimental validation of a rigorous absorber model for CO₂ post-combustion capture, *AIChE Journal*, 53:846-865.
- Trent, D.L. (2004), *Chemical processing in high-gravity fields*, from *Re-engineering the chemical processing plant: Process Intensification*, edited by Stankiewicz, A. and Moulijn (2004), Marcel Dekker, Inc.
- UK Government Budget Report (2009), http://www.hm-treasury.gov.uk/d/Budget2009/bud09_chapter1_237.pdf (accessed in Jul. 2009).
- UNEP (2005), *United Nations Environment Program, Introduction to climate change*, <http://www.grida.no/climate/vital/06.htm> (accessed in Mar. 2010).
- Uyanga I J, Idem R O (2007) Studies of SO₂- and O₂- induced degradation of aqueous MEA during CO₂ capture from power plant flue gas streams. *Ind. Eng. Chem. Res.*, Vol 46 (8); 2558-2566
- Vaidya P.D., Kenig E.Y. (2007), CO₂-alkanolamine reaction kinetics: A review of recent studies. *Chemical Engineering and Technology*, 30:1467-1474.
- Wilson, M., Tontiwachwuthikul, P., Chakma, A., Idem, R., Veawab, A., Aroonwilas, A., Gelowitz, D., Barrie, J., Mariz, C. (2004), Test results from a CO₂ extraction pilot plant at Boundary Dam Coal-fired power station, *Energy*, 29:1259-1267.
- Yi, F., Zou, H.K., Chu, G.W., Shao, L. and Chen, J.F. (2009), Modelling and experimental studies on absorption of CO₂ by Benfield solution in rotating packed bed, *Chemical Engineering Journal*, 145: 377-384.
- Zhao Z, Cui X, Ma J, Li R. (2007), Adsorption of carbon dioxide on alkali-modified zeolite 13X adsorbents. *International Journal of Greenhouse Gas Control*, 1:355-359.
- Ziaii, S., Rochelle, G.T. and Edgar, T.F. (2009), Dynamic modelling to minimise the energy use for CO₂ capture in power plant aqueous monoethanolamine, *Ind. Eng. Chem. Res.*, Vol. 48, 6105-6111.
- Zhang, Y., Chen, H., Chen, C.-C., Plaza, J.M., Dugas, Ross and Rochelle, G.T. (2009), Rate-based process modelling study of CO₂ capture with aqueous monoethanolamine solution, *Ind. Eng. Chem. Res.*, 48:9233-9246.