

Cranfield University

Adekola Lawal

**STUDY OF POST-COMBUSTION CO₂ CAPTURE FOR
COAL-FIRED POWER PLANT THROUGH MODELLING
AND SIMULATION**

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PhD. THESIS

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AND SIMULATION**

Supervisors: Dr. Meihong Wang and Prof. Hoi Yeung

December 2010

This thesis is submitted in fulfilment of the requirements for the
degree of Doctor of Philosophy

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Abstract

Fossil-fuel power plants are the largest single source of carbon dioxide (CO₂) emissions. Post-combustion capture through monoethanolamine-based absorption is viewed as the most mature technology proposed for mitigating CO₂ emissions from such power plants. Despite its advantages, several design and operational challenges arise in the application of this technology. The amount of flue gas to process is much greater than current applications. As a consequence, there will be a large thermal energy requirement for solvent regeneration. There are also concerns about how post-combustion CO₂ capture would affect the flexibility and operability of coal-fired power plants. Though expensive pilot plant studies exist worldwide, they are still on a much smaller scale than what would be required commercially. This thesis provides useful insights for the design and operation of pilot and commercial plants through modelling and simulation.

Dynamic models of the chemical absorption process were developed in gPROMS[®] using the rate-based approach. Based on the two-film theory, mass transfer rates were calculated using the Maxwell-Stefan formulation. Chemical reactions were assumed to attain equilibrium. Steady state and dynamic validations were carried out at pilot plant scale. Process analysis at pilot plant scale indicated that rate-based models give more accurate predictions than their equilibrium-based counterparts. In addition, CO₂ capture performance is more dependent on the liquid to gas mass flow ratio than on their absolute flow rates. It is also important to maintain proper water balance control.

The dynamic model was subsequently scaled up to treat flue gas from a 500 MWe sub-critical coal-fired power plant. A 500 MWe sub-critical power plant dynamic model developed by RWE npower was modified for integration with the post-combustion CO₂ capture plant model. The manner in which the models were linked was described. Dynamic analyses show that the CO₂ capture plant has slower dynamics than the power plant. Possible interactions of controllers in the post-combustion CO₂ capture plant and the power plant were also reported. Case studies on the integrated model show the influence of absorber packing height on the performance and economics of the process.

Keywords: Post-combustion CO₂ capture, coal-fired power plants, dynamic modelling and simulation

Acknowledgements

I wish to extend my sincere gratitude to Dr. Meihong Wang who was indeed more than a supervisor to me. Meihong, this project benefited greatly from your guidance, your excellent grasp of what was important and your attention to detail. You were always available when I needed help and your support and encouragement kept me going through the tough times. I would also like to appreciate the guidance and support of my industrial supervisor, Dr. Peter Stephenson from RWE npower. This work greatly benefited from your professionalism and commitment to excellence. Our meetings were always effective and your advice was always helpful. Thank you for always being eager to take the time out to help. Prof. Hoi Yeung could spot a problem a hundred miles off! I greatly appreciate your advice and all the support you gave.

I am especially grateful to all the staff at Process Systems Engineering group who were supportive during the course of my work. Thank you, Prof. Colin Ramshaw for taking out the time to answer my many questions. Dr. Yi Cao, your advice and comments were indeed very useful. Dr. Ossama Badr, I really appreciate your support and availability. Thank you for the useful materials and information you provided. How can I forget you, Sam Skears – you're my angel!

I would not have been able to cope without the excellent support from the staff at Process Systems Enterprise Ltd. Georgios, thanks for all the help not just with technical issues but also for your advice regarding finishing a PhD with one's sanity intact! Praveen, you were always helpful when I had a question and your support cannot be forgotten. Bart, your support was excellent and got me through some difficult times. Costas, I still remember our meeting in Cranfield and your advice then still inspires me.

The models in this thesis were validated with the results from pilot plant studies of the Separations Research Program at the University of Texas at Austin led by Prof. Gary Rochelle. I would like to thank him and his team for all the support they gave me. Thank you, Ross Dugas and Frank Seibert for really helpful answers to my questions and for providing relevant data and information. From my research I have come to

appreciate the challenges with such pilot plant studies and I think you do an excellent job.

I gained practical insight into the operation of post-combustion pilot plants from the support given by the staff at RWE npower's Combustion Test Facility. Thank you, Jonathan Marriott, Richard Mather, Jing Tian for all the help with the tour of the pilot plant, process diagrams and PROMAX simulations.

I can't say enough to thank my family and friends who have been so supportive. Dad, thank you for your confidence in me and your constant encouragement. Mum, thanks for caring and taking out time to spend with me. Nike, Funmi and Ayo, I could not ask for better siblings. Thanks for all the calls, texts, and good fun. God bless you and your families. Mrs Bakare, you have been like a mother to me, thanks for your kindness, care and all those excellent soups! To my cousins Olu and Ayo, thanks for a fantastic holiday – I really needed it!

To my 'hit men' – Yinka, Chet and Tunde (in no particular order, Chet) – thanks for making this time great fun. Thank you to the Ubadikes – my second family! Words are not enough! Dan, Group Capt. Paul, Gareth, Chet, Victoria and Solomon, thank you for proofreading my work. Crispin, you have continued to be an inspiration. Thank you for all the help and support. Ogonna, we go a long way. Thank you for your support and prayers despite your busy schedule. Gareth and Roberta, thank you for all the good times, late nights and good food! John Shotade, thank you for the encouragement and inspiration you constantly bring. God bless you and your family. To my colleagues in the office – Patricia, Edith, Jing, Isaac, Chet and Michael – I will always cherish the good times we had.

To everyone at Holding Forth the Word Ministries – I am grateful for the friendship, support and great community you provided. Thank you Pastor 'Biyi and Esther for your care, prayers and advice.

My Cranfield experience would not have been the same without the CSA. Thanks everyone, you are all life savers! Thank you, Mina, Sue, Glenda, Paddy, Stewart and Rachel. I was fortunate to work with great students in office – Sami, Amu, Steven, Martin, Lefteris, Dimitrios, Varvara, Anietie, Shahab, Bipin, Sujay, Sunil, James, Anthony, Riki, Ashkan, Abdul-Aziz, Lukasz, Nishi, Abrar, Harriet, Crispin, Przemyslaw and Luismi – it was an absolute pleasure working with you.

Lastly, but certainly not least, to my dear Victoria. Thank you for loving me the way you do. You were relentless in your support and understanding and helped me through really tough times. I am truly lucky to have met you.

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Nomenclature

A	Cross sectional area (m^2)
c_t	Total molar concentration (mol/m^3)
f	Fugacity coefficient
F_i	Component mass flow rate (kg/s)
F_H	Enthalpy flow rate (J/s)
F_{LV}	Flow parameter of packing dependent on L/G ratio
g	Acceleration due to gravity (m^2/s)
G_T	Temperature gradient
$\dot{G}$	Gas flowrate (m^3/s)
H	Heat flux (J/m^2)
h	Specific enthalpy (J/kg); packing height (m)
h_i^M	Specific molar enthalpy of component, i (J/mol)
HL	Heat loss to surroundings (J/m^3)
ht	Height (m)
K	Empirical constant
K_4	Pressure drop parameter
L	Height of column section (m)
$\dot{L}$	Liquid flowrate (m^3/s)
L_W^*	Liquid mass flowrate per unit cross sectional area ($\text{kg}/\text{m}^2 \cdot \text{s}$)
M	Mass holdup (kg/m^3)
m	Mass flowrate (kg/s)
mw	Molecular weight (kg/mol)
n	Number of years
N	Molar flux ($\text{mol}/\text{m}^2 \cdot \text{s}$)
nc	Number of components
P	Pressure (Pa), proportional (controller)
P_{dev}	Percentage deviation (%)
P_{OPEX}	Plant operating cost per year ($\text{€}/\text{year}$)
P_{FUEL}	Plant fuel costs per year ($\text{€}/\text{year}$)
PI	Proportional–integral (controller)
ICo	Installed cost (€)
Q	Heat flow (J/s)
R	Universal gas constant ($\text{J}/\text{mol} \cdot \text{K}$)
Sp	Specific area (m^2/m^3)
T	Temperature (K)
U	Energy holdup (J/m^3)
V	Volume (m^3)
V_W^*	Gas mass flowrate per unit cross sectional area ($\text{kg}/\text{m}^2 \cdot \text{s}$)
x	Mass fraction
x_i^M	Molar fraction
y	Axial position
z	Film position

Greek Symbols

β	Constant for estimating effective gas temperature
---------	---

δ	Film thickness (m)
λ	Thermal conductivity (W/m·K)
ρ	Density (kg/m ³)
σ	Stefan-Boltzmann constant
μ	Viscosity (Pa·s)
ω	Wetted area ratio
χ	Diffusivity (m ² /s)
γ	CO ₂ loading (mol CO ₂ /mol MEA)

Subscripts

<i>abs</i>	Absorption
<i>ad</i>	Adiabatic
<i>ave</i>	average
<i>DC</i>	Downcomer
<i>DCB</i>	Downcomer bottom
<i>eff</i>	effective
<i>evap</i>	evaporative
<i>FW</i>	Feed water
<i>g</i>	gas
<i>H</i>	Enthalpy
<i>i</i>	Component number
<i>Liq</i>	Liquid
<i>MR</i>	Riser tube metal
<i>pil</i>	Pilot plant measurement
<i>R</i>	Riser
<i>s</i>	Steam
<i>sim</i>	Simulation
<i>TD</i>	Total (drum)
<i>tfr</i>	Thrown-forward radiation
<i>WDC</i>	Water in downcomer
<i>WR</i>	Water in riser
<i>WRO</i>	Water out of riser
<i>Vap</i>	Vapour

Superscripts

<i>Cond</i>	Conduction
<i>Conv</i>	Convection
<i>I</i>	Interface
<i>L</i>	Liquid
<i>Lb</i>	Liquid bulk
<i>Lf</i>	Liquid film
<i>M</i>	Molar
<i>R</i>	Reference
<i>V</i>	Vapour
<i>Vb</i>	Vapour bulk
<i>Vf</i>	Vapour film

Abbreviations

ARA	Amsterdam, Rotterdam and Antwerp ports
BERR	Department for Business, Enterprise and Regulatory Reform
CCS	Carbon capture and storage
CIF	Cost insurance and freight
CIAB	Coal Industry Advisory Board
EIA	Energy Information Administration
ESRL	Earth System Research Laboratory
GCV	Gross calorific value
IEA	International Energy Agency
IEAGHG	International Energy Agency Greenhouse Gas Programme
IMTP	INTALOX [®] metal tower packing
IP/LP	Intermediate pressure / low pressure
IPCC	Intergovernmental Panel on Climate Change
L/G	Liquid to gas mass flow rate
MEA	Monoethanolamine
NAE	Number of axial elements
NCV	Net calorific value
NETL	National Energy Technology Laboratory
NGCC	Natural gas combined cycle
ppmv	Parts per million by volume
UNEP	United Nations Environment Program

Chapter 1 Introduction

1.1 Background

The continued increase in the atmospheric concentration of greenhouse gases is suggested to contribute to the greenhouse effect (IPCC, 2005). This phenomenon is predicted to result in global temperature rise and climate change. Carbon dioxide (CO₂) is the main greenhouse gas. 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 389.7 ppmv in December 2010 (ESRL, 2011). They are predicted to rise above 750 ppmv by 2100 if no action is taken to address the current situation (UNEP, 2005).

Power generation from fossil fuel-fired power plants is the largest single source of CO₂ emissions (Freund, 2003). However, fossil-fuel fired power plants play a vital role in meeting energy demands as they can be operated flexibly to satisfy varying demand. In addition, they act as backup capacity for intermittent renewable power generation or unplanned plant outages (Chalmers et al., 2006). Coal and natural gas are common fuels in many large-scale power generation plants. Coal-fired power plants emit twice as much CO₂ as their natural gas counterparts per unit of electricity generated (Lawal et al., 2009a). The natural gas combined cycle (NGCC) plants operate at higher efficiencies when compared with most coal-fired power plants. However, coal's peculiar attributes of availability, affordability, reliability and its stabilising effect on world energy markets continue to make it an economic choice for electricity generation (CIAB, 2005) when compared with other fossil fuels.

Coal-fired power plants are projected to supply 44% of the global power generation by 2030 (IEA, 2010). Coal would, therefore, remain the dominant fuel in the power sector for a considerable period. Figure 1.1 illustrates this trend especially due to its continued use in emerging economies such as India and China. Between 2004 and 2030, global electricity demand is expected to double. During this period, about 1400 GW of new

coal-fired power capacity would be required worldwide (Zanganeh et al., 2006; Bohm et al., 2007). This is expected to result in a 75% increase in CO₂ emissions from coal combustion in 2030 in the business-as-usual scenario compared with 2004 levels (EIA, 2007).

With growing concerns over the increasing atmospheric concentration of anthropogenic greenhouse gases, effective CO₂ emission abatement strategies must be developed and implemented. These strategies, however, must be implemented with minimal loss of plant performance.

1.1.1 Options for CO₂ emissions abatement

Gerlagh and Van der Zwaan (2006) discussed some physical and policy instrument options available in making deep reductions in CO₂ emissions. The physical options discussed are:

- Reduction in the use of fossil fuels.
- Replacement of the use of high carbon-content fuels (such as coal) with lower carbon-content fuels (such as natural gas).
- Replacement of fossil fuel power generation technologies by “carbon-free alternatives” such as renewables (wind or solar energy), hydro or nuclear energy sources.
- Enhancement of natural sinks of CO₂ such as forests.

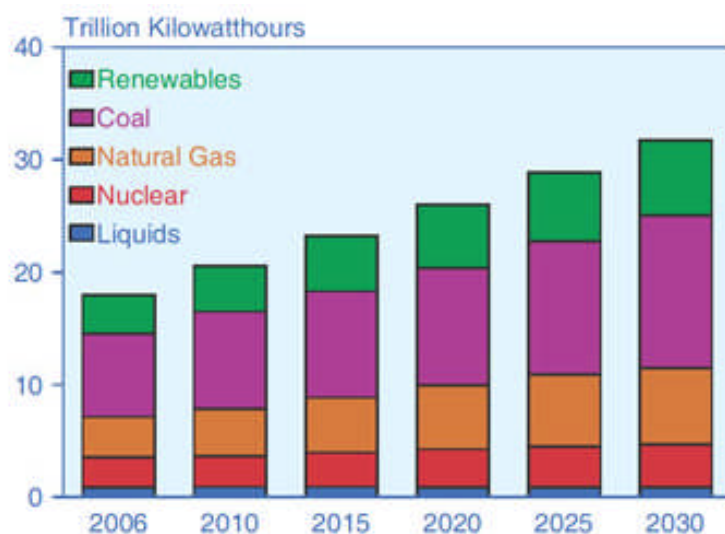


Figure 1.1 World electricity generation by source, 2006-2030 (EIA, 2006)

- Carbon capture (before or after the combustion of fossil fuels) and storage (in geological formations or for reuse).

In addition, they listed some policy instruments to address the problem such as (Gerlagh and Van der Zwaan, 2006):

- Carbon taxes.
- Fossil fuel taxes.
- Renewable energy subsidies.
- Portfolio standards for carbon intensity of energy production or relative or absolute use of renewable energy sources.

Gerlagh and Van der Zwaan (2006) concluded that, though carbon capture and storage (CCS) technology may not be sufficient to stabilize atmospheric CO₂ concentrations at desired levels, it could relax the requirement on the deployment of carbon-free alternatives. In view of growing energy demand as well as the urgent need for emission abatement, CCS could preserve the diversity of fuel sources while allowing the necessary cuts in CO₂ emissions (Freund, 2003). With the current shift towards employing more renewable energy sources for power generation, there would be increased demand for technologies that could operate flexibly to balance the intermittent supply from sources such as wind energy. Coal-fired power plants traditionally play such a role in the power grid. Effective policy instruments such as carbon taxes can only be determined with realistic predictions of the additional cost of integrating CO₂ capture in power generation.

1.1.2 Carbon capture and storage

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)

As such CCS consists of three basic stages:

- Separation of CO₂.
- Transportation to storage location.

- Storage.

The separation stage (CO₂ capture) is the most energy intensive and as such largely determines the cost of the CCS process. Davidson (2007) reports that separation represents about 75-80% of the total cost of CCS.

1.1.3 Carbon capture approaches

There are three major approaches to CCS, which are illustrated in Figure 1.2:

- Post-combustion capture.
- Pre-combustion capture.
- Oxyfuel process.

1.1.3.1 Post-combustion capture

When CO₂ is separated from the mixture of flue gases produced after combustion of fuels in air, the capture process is referred to as post-combustion capture (IPCC, 2005). This approach has been applied in industry but not at the scale applicable in power generation (Audus, 2006).

Commonly associated with this approach is chemical absorption of CO₂. This process can effectively separate CO₂ at low partial pressures. In a conventional pulverised fuel power plant, flue gases are released at about atmospheric pressure with CO₂ partial pressures ranging from 10-15 kPa (IPCC, 2005).

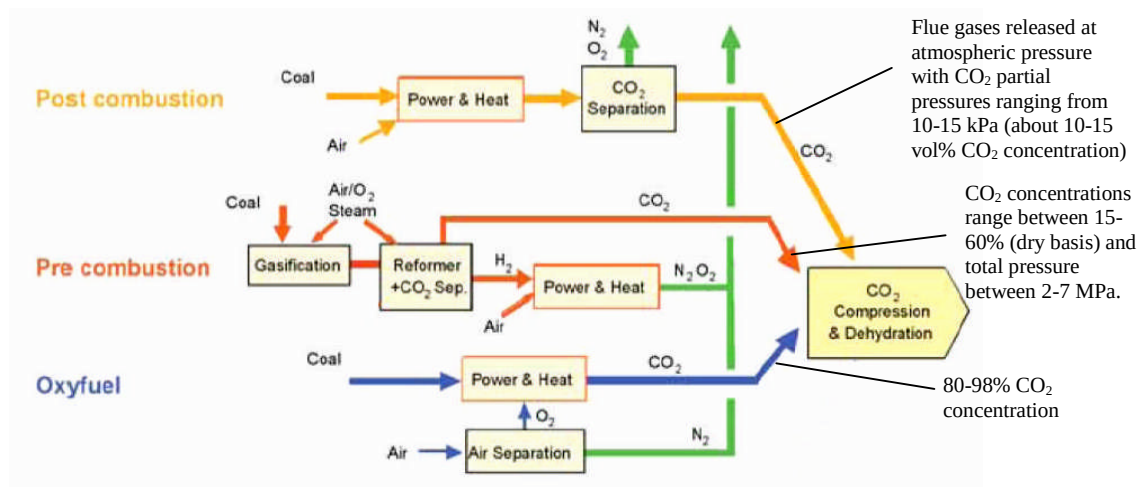


Figure 1.2 CO₂ capture approaches (IPCC, 2005)

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 compared with the other two approaches. However, this advantage comes at the expense of the efficiency of the power generation process, which, in some occasions, may be prohibitive (Audus, 2006).

1.1.3.2 Pre-combustion capture

This involves the separation of CO₂ before the combustion process. The fuel is reacted with oxygen or air and/or steam to produce synthesis gas, composed of carbon monoxide and hydrogen. In a catalytic reactor called a Shift Converter, carbon monoxide is reacted with steam to give CO₂ and more hydrogen. CO₂ concentrations range between 15-60 vol% (dry basis) and total pressure between 2-7 MPa (IPCC, 2005). CO₂ is separated at this stage leaving a hydrogen-rich fuel available for combustion and other applications (IPCC, 2005). For solid fuels such as coal, the process of producing synthesis gas is referred to as gasification. This is obtainable in the Integrated Gasification Combined Cycle (IGCC) power plants. Figure 1.3 illustrates a block flow diagram of such a plant.

In these plants, the heat required to generate steam is not obtained directly from the combustion of coal. Through gasification, synthetic gas (syngas) is produced, which consists of carbon monoxide (CO) and hydrogen (H₂) gas. Gasification is basically a partial oxidation process that makes high-value products such as clean synthetic fuels and electricity from low-value solid feedstocks like coal.

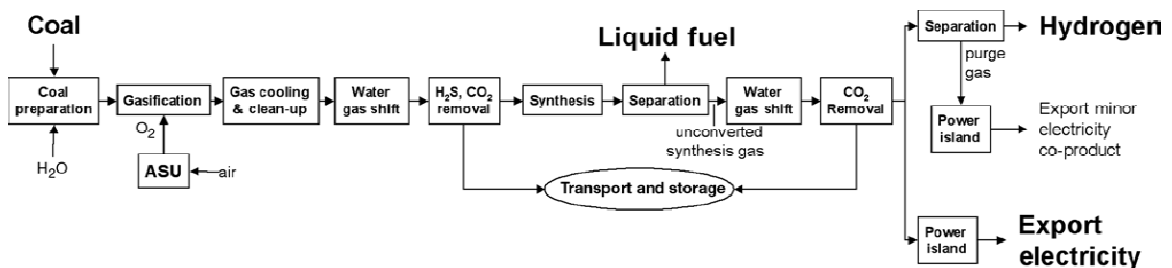


Figure 1.3 IGCC Process with CO₂ capture and storage (IPCC, 2005)

The syngas produced is cleaned of contaminants such as hydrogen sulphide, particulate matter etc and burned to produce electricity via a gas-turbine/steam-turbine combined cycle. The IGCC draws its advantage from the use of the high efficiency combined cycle. Power generation efficiencies could be as high as 56% (net calorific value (NCV)) (IPCC, 2005). In addition, CO₂ is released at higher partial pressures in the flue gas, making capture easier. IGCC plants, however, have higher capital costs than pulverised fuel plants. There are also availability (reliability) concerns about their operation as all integrated units must function simultaneously (IPCC, 2005).

1.1.3.3 Oxyfuel process

In this process, almost pure oxygen is used for combustion instead of air. After combustion, the flue gas will consist mainly of CO₂, H₂O and any excess oxygen (used to ensure complete combustion). Oxygen is usually produced by cryogenic air separation. This requires a significant amount of energy to operate. Combustion of fuels in oxygen occurs at about 3500°C, which is beyond the capacity of current power plant materials. Some flue gas has to be recycled to the combustor to reduce these temperatures to about 1900°C (IPCC, 2005; Rodewald et al., 2005). The flue gas is cooled to condense the water vapour present leaving a gas stream consisting of 80-98% CO₂ depending on the fuel used. The large concentration of CO₂ in the flue gas makes further separation easier (if required).

Issues encountered in oxyfuel process include:

- The large energy requirement to separate oxygen from air.
- Air leakage into the combustion system.
- Unknown effects on the radiative heat transfer in the furnace due to the recycled flue gas among others.

1.1.3.4 Summary

Amongst the various approaches to CCS, post-combustion capture by chemical absorption using monoethanolamine (MEA) solvent is currently the only commercial technology for large scale CO₂ capture for coal-fired power plants (Lawal et al., 2010a). It offers advantages over other CO₂ capture approaches as it is a suitable technology for

retrofitting of existing power generation plants. It is also well suited for treating flue gas streams with low CO₂ partial pressures typical of coal-fired power plants.

This study focuses on the post-combustion capture process. Despite the level of development of the chemical absorption process, there has never been any such plant applied at the scales required for commercial coal-fired power plants (FLUOR, 2004). There are therefore several unknowns about the design and operation of coal-fired power plants integrated with carbon capture. This work aims to study and address some of these.

1.2 Motivation for the study

Design and operational studies of new processes are typically carried out with pilot and larger scale demonstration plants. Current pilot plant studies worldwide are on a much smaller scale than would be required for CCS (typically less than 5 MWe). Once built, these plants are limited in the range of studies that could be carried out. For instance, the pilot plant may be built to study a certain characteristic or a certain system configuration. Even at this scale, the cost of construction for these facilities typically runs up to several million dollars (Herzog et al., 2009). Full scale demonstration projects are estimated to cost over a billion dollars (Herzog et al., 2009). Many useful insights could be derived from accurate dynamic models of the post-combustion capture process at a much lower cost. Such information would be useful in the design of demonstration plants and full-scale commercial plants.

Most process models developed to study cost and performance implications of CCS are steady state models that cannot account for the various disturbances and transients associated with the power generation process. As such these models are limited in their ability to study how power plants with CCS would operate. Such studies are especially important for coal-fired power plants, which typically operate flexibly (Chalmers and Gibbins, 2007). The resulting transients as well as those occurring during plant start-up and shutdown operations can only be studied using dynamic models of the process.

Operational problems could be further compounded if there are tight restrictions on CO₂ emissions, meaning the downstream absorption plant may have to closely follow load changes. This study could also, therefore, help contribute to policy making on emission regulation. Finally, to improve overall efficiency, increased process integration of the power generation process and capture process would be required (Abu-Zahra et al., 2007b). This would likely further complicate the operation of the integrated facility. Insights into the integrated plant operation could also be provided through studies using dynamic modelling and simulation.

1.3 Project aims and objectives

This work is aimed at providing insights into the design and operation of a 500 MWe sub-critical coal-fired power plant with post-combustion capture through modelling and simulation.

This project seeks to achieve the following objectives:

- a) Develop dynamic models of CO₂ chemical absorption process with MEA solvent.
- b) Carry out steady state and dynamic validation of the developed models at pilot plant scale.
- c) Scale-up of the model of the chemical absorption plant to process the flue gas from a 500 MWe sub-critical coal-fired power plant.
- d) Link the scaled-up CO₂ chemical absorption model with a 500 MWe power plant model to form the integrated plant model to carry out relevant studies.
- e) Carry out dynamic analyses on the integrated plant model to identify the possible operational challenges of the integrated plant.
- f) Carry out studies towards the design and operation of coal-fired power plant with post-combustion CO₂ capture.

1.4 Research methodology and tools used for the study

1.4.1 Research methodology

The integration of post-combustion CO₂ capture with the power generation process has not been applied commercially. There are a number of unknowns about the concept.

The research methodology illustrated in Figure 1.4 shows how the research objectives were achieved.

1.4.2 Software tools used for the study

1.4.2.1 gPROMS[®]

gPROMS[®] (general **PRO**cess **MO**delling **SYS**tem) is developed by Process Systems Enterprise Limited. It is an equation-based modelling system that enables the user to develop accurate process models from first principles. These models could then be used to perform various activities including steady state or dynamic simulation and optimisation. Through the CAPE-OPEN interface, gPROMS[®] could be used with other compatible process modelling tools such as the physical property methods and models of Aspen Properties[®].

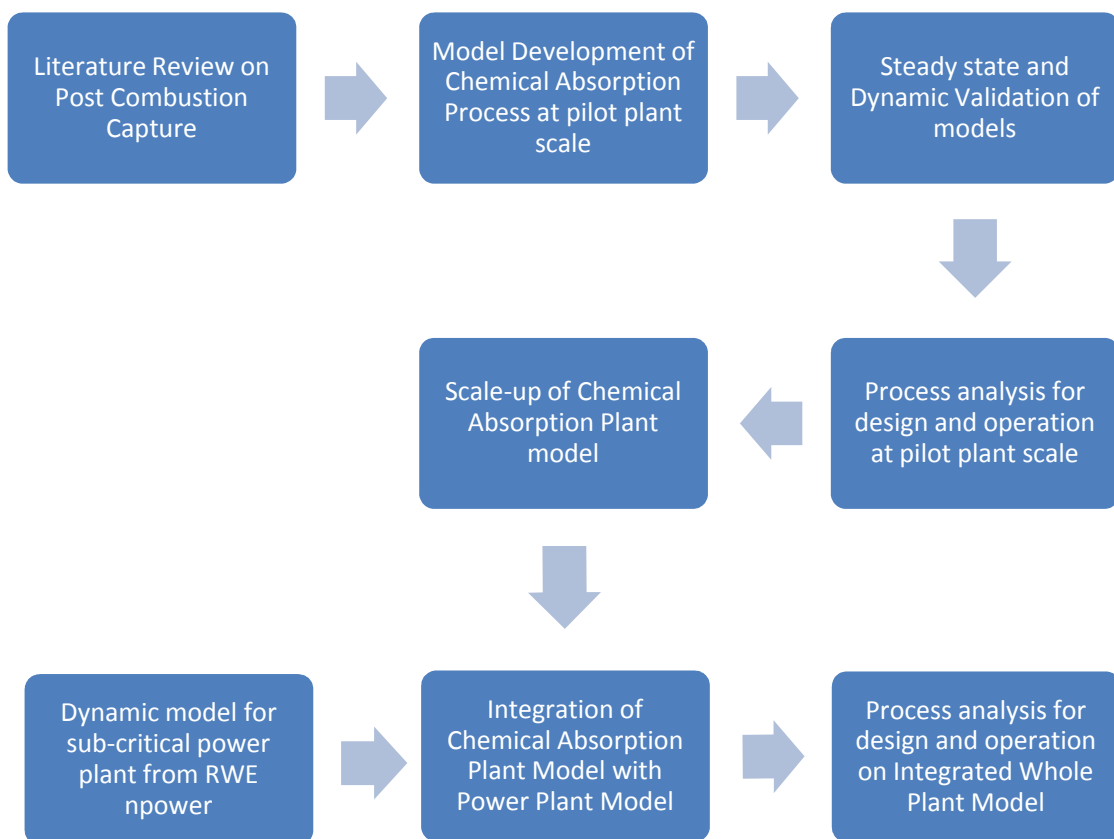


Figure 1.4 Overview of research methodology

1.4.2.2 Aspen Engineering suite

Four application software were used from the Aspen Engineering suite – Aspen Plus[®], Aspen Properties[®], Aspen Process Economic Analyser[®] and Aspen HYSYS[®].

Aspen Plus[®] is a process modelling and simulation tool that includes model libraries of various unit operations. In addition, it is equipped with a relatively large physical property database via Aspen properties[®]. It is referred to in Chapter 4 in the development of the equilibrium-based model.

Aspen properties[®] provides an interface for stand-alone property calculations. It could also be used to generate property packages that contain physical property methods and models (such as Peng-Robinson or Electrolyte-NRTL) as well as chemical components. These packages could be exported and used by other software through the CAPE-OPEN interface. The rate-based and equilibrium-based models reported in Chapters 4 to 6 use Aspen properties[®].

Aspen Process Economic Analyser[®] is a tool that could be used to estimate the costs of process equipment in a project. The tool utilises comprehensive design-based installation models rather than capacity-factored curves for equipment pricing (Aspentech, 2008a). Version V7.2.1 was used, which has a 1st Quarter 2009 pricing basis. This software is used to estimate costs of process equipment as discussed in Chapter 6 and Appendix C.

Aspen HYSYS[®] is a process modelling tool used for conceptual design, process optimisation, and performance monitoring for various process industries. It was used to estimate the properties of streams. Aspen HYSYS[®] is used for various calculations in Appendix B.

1.5 Outline of the thesis

Chapter 1 describes the background, motivation, project aims and objectives. An overview of the research methodology and tools used for the study is also given.

Chapter 2 introduces post-combustion CO₂ capture technologies and focuses on the chemical absorption process. The chemical absorption CO₂ capture process is described giving its operational requirements. Various process designs and various chemical solvents are discussed. The reaction kinetics of MEA solvent is described.

Chapter 3 focuses on the progress in research activities towards demonstrating post-combustion CO₂ capture for power plants with emphasis on chemical absorption technology. Different pilot plant studies and research programs are discussed. Research activities in terms of modelling and simulation of the power plant and the post-combustion CO₂ capture plant are also discussed. Finally various approaches towards optimising the post-combustion capture process are discussed.

Chapter 4 describes the model development of the post-combustion CO₂ capture process. The accuracy of the equilibrium-based and rate-based approaches is compared. The rate-based model is selected and used to model stand-alone absorber and regenerator columns. The two columns are subsequently linked together and validated using steady state and dynamic data. Steady state and dynamic analyses are carried out on the post-combustion CO₂ capture process model to gain insights useful for its design and operation.

In Chapter 5, the methods used to scale up the post-combustion CO₂ capture process model from pilot plant scale to the scale required to process flue gas from a 500 MWe sub-critical power plant are discussed.

Chapter 6 describes the 500 MWe sub-critical power plant model used and the methods used in linking this model to the full-scale post-combustion CO₂ capture process model. The performance of the integrated plant is studied with steady state and dynamic case studies. Costs of electricity and CO₂ avoidance are estimated and used to select an appropriate absorber packing height.

Chapter 7 provides conclusions for the study and recommendations for future work.

Chapter 2 Post-combustion CO₂ capture

2.1 Introduction

Post-combustion CO₂ capture enables CO₂ separation from flue gases with minimal modification to the combustion process. This chapter introduces different options for CO₂ separation for this carbon capture approach. The chemical absorption CO₂ separation process is selected based on its ability to process flue gases with low partial pressures of CO₂. The process is described giving its operational requirements, various process designs and various chemical solvents are discussed. The reaction kinetics of MEA solvent are finally described.

2.2 Separation technologies for post-combustion CO₂ capture

Figure 2.1 gives a summary of process options available for post-combustion CO₂ capture. In the following subsections, an overview of these technology options is given.

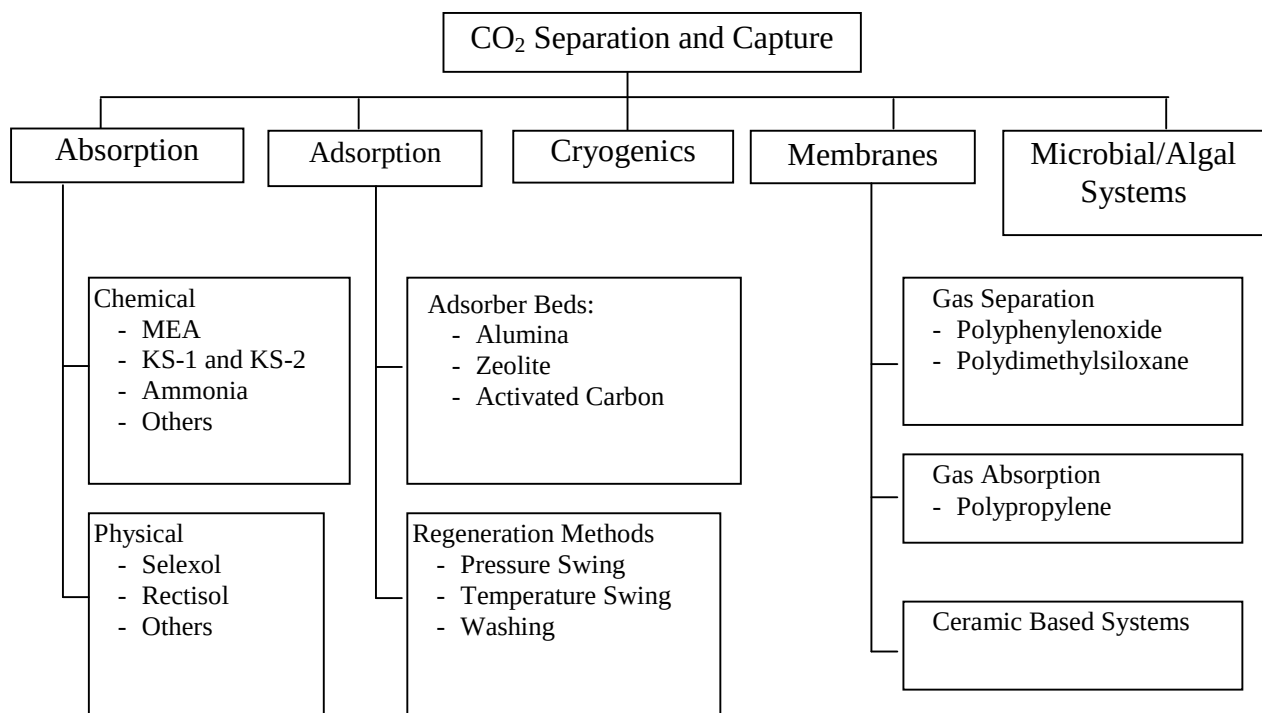


Figure 2.1 Process options for post-combustion CO₂ capture adapted from Rao and Rubin (2002)

2.2.1 Chemical absorption

Chemical absorption involves the reaction of CO₂ with a chemical solvent to form a weakly bonded intermediate compound that may be regenerated with the application of heat producing the original solvent and a CO₂ stream (IEAGHG, 1993; IPCC, 2005). The most commonly used solvent for CO₂ absorption is MEA. Other solvents include the sterically-hindered amines (KS-1, KS-2 and KS-3) developed by the Kansai Electric Power Company (Davidson, 2007). The latter are claimed to offer lower energy consumption and solvent loss (Audus, 2006). These solvents however, have higher costs (Reddy et al., 2003).

Chemical absorption offers the advantage of being able to operate at low CO₂ partial pressures obtainable in flue gas streams of conventional pulverised fuel power plants (IPCC, 2005; IEAGHG, 1993). However, the relatively large amount of energy required to regenerate the solvent would have severe implications on the power plant performance (IEAGHG, 1993; Mimura et al., 1997; Freguia and Rochelle, 2003; IPCC, 2005; Abu-Zahra et al., 2007a; Abu-Zahra et al., 2007b; Davidson, 2007; Davison, 2007; Ramezan et al., 2007; Rubin et al., 2007;).

2.2.2 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. Physical absorption requires high CO₂ partial pressures. As such the main energy requirements originate from the flue gas pressurisation. Physical absorption is therefore not economical for gas streams with CO₂ partial pressures lower than 15 vol% (Chakravati et al., 2001; IEA, 2004). This is the case especially with large scale power generation that are associated with large volumetric flows of flue gas. Typical solvents are Selexol (dimethyl ethers of polyethylene glycol) and Rectisol (methanol) (IEAGHG, 1993).

2.2.3 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 (IEAGHG, 1993; IEA, 2004; Zhao et al., 2007).

Current adsorption systems may not be suitable for application in large-scale power plant flue gas treatment. At such scales, the low adsorption capacity of most available adsorbents would make the amounts required prohibitive. 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; Zhao et al., 2007; IEA, 2007).

2.2.4 Membrane technology

Membrane technology was first developed for water treatment applications. In recent years, it has been demonstrated as a technology that could be applied in CO₂ capture. Two basic forms of this technology can be used:

- Gas separation membranes.
- Gas absorption membranes.

In gas separation membranes, separation is based on Knudsen diffusion. Flue gas stream components are separated based on their ability to permeate through 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 only a fraction of the CO₂ is captured. In addition, the purity of the captured CO₂ is low for the same reason (IEAGHG, 1993; IEA, 2004). Multistage separation is employed to capture a higher proportion of CO₂ incurring extra capital and operating cost (IEAGHG, 1993; Chakravati et al., 2001; IEA, 2004).

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 is dependent on the CO₂ partial pressure. As such, they are suitable for high CO₂-concentration applications (well above 20 vol%) such as flue gas streams from oxyfuel and IGCC processes (IEAGHG, 1993; IPCC, 2005; Favre, 2007). Davidson (2007) discusses recent developments in gas absorption membranes.

2.2.5 Cryogenic separation

This method involves separation of CO₂ from the flue gas stream by condensation. At atmospheric pressure, CO₂ condenses at -56.6°C (IEAGHG, 1993). This physical process is suitable for treating flue gas streams with high CO₂ concentrations (such as those from the oxyfuel process) considering the costs of refrigeration. In addition, the gas stream must be dried to prevent the formation of ice and must also be free from other condensable materials (IEAGHG, 1993; BERR, 2000; Freund, 2003). An advantage of the process is that it directly produces liquefied CO₂, which may be required for certain means of transportation such as shipping (BERR, 2000).

2.3 The CO₂ chemical absorption process

Chemical absorption with MEA is preferred for post-combustion capture of CO₂ from pulverised fuel power plants because it is suitable for CO₂ capture from dilute streams. The solvent is relatively cheap and the process is backed up by commercially available and proven technology (Rao et al., 2004).

Commercially available process technologies for MEA absorption include the Fluor Daniel® ECONAMINE™ process and the Kerr-McGee/ABB Lummus Crest Process (Rao et al., 2004; IPCC, 2005). Differences in the technologies are based on the concentration of the lean amine solvent solution as well as the manner of heat integration. The former employs 30 wt% (weight percentage) MEA solution with oxygen inhibitors to reduce solvent degradation as well as corrosion. The latter employs 15-20 wt% MEA solution without inhibitors but requires larger equipment due to the lower solvent concentration (Rao et al., 2004; IPCC, 2005). An advanced MEA absorption process is proposed for the latter technology that uses 30 wt% MEA solution (Ramezan et al., 2007).

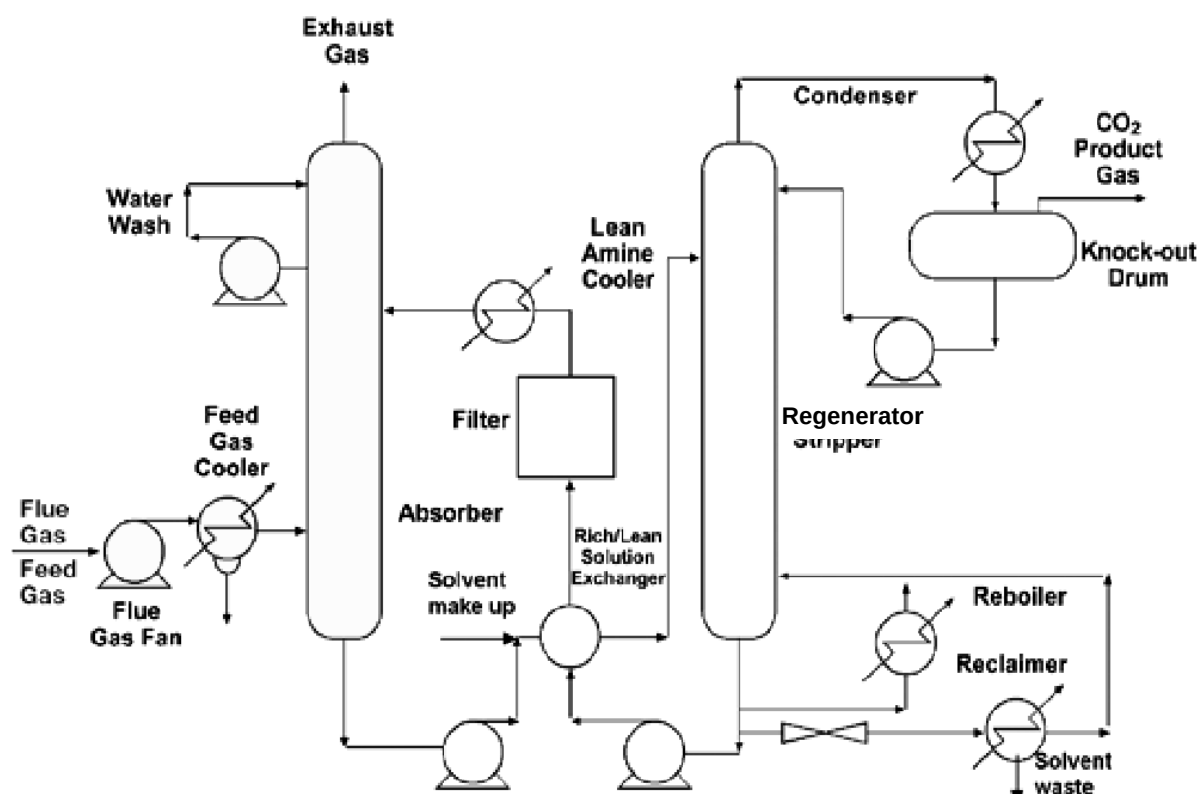


Figure 2.2 Process flow diagram for CO₂ recovery from flue gas by chemical absorption from IPCC (2005)

The conventional (based on the Fluor Daniel® ECONAMINE™ process) MEA absorption process is displayed in Figure 2.2 (IPCC, 2005). 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 MEA. SO₂ concentrations of less than 10 ppmv are recommended. SO₂ removal is usually achieved in a Flue Gas Desulphurization (FGD) unit. NO_x could be removed using Selective Catalytic Reduction (SCR) or Selective Noncatalytic Reduction (SCNR). Particulate matter such as fly ash is removed by either electrostatic precipitators or baghouse filters.

Flue gases to the CO₂ absorber must be cooled between 45–50°C (Rao et al., 2004; Ramezan et al., 2007). This would improve absorption of CO₂ and minimise 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 (Rao et al., 2004). A blower is used to overcome the pressure drop across the absorber. The flue gas is contacted counter-currently with the lean solvent usually of CO₂ loading of about 0.1–0.3 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 washed of solvent and vented to the atmosphere. The lean MEA heats up gradually as it absorbs CO₂. To maintain water balance in the process, the temperature of the lean solvent should be maintained as close as possible to that of the flue gas. If the flue gas comes in at a significantly higher temperature than the lean solvent, it cools down and loses moisture, which would condense in the absorber and dilute the solvent. If the flue gas is significantly colder than the lean solvent, it would heat up in the tower and pick up extra moisture that is carried out of the system resulting in a water deficiency. As such accurate control of both flue gas and lean solvent temperatures is essential (Ramezan et al., 2007).

The rich solvent is heated in a cross heat exchanger by regenerated lean solvent from the regenerator, also referred to as ‘stripper’. It is then pumped to the top of the regenerator where it is regenerated at elevated temperatures (100°C-140°C) and at slightly higher than atmospheric pressure (IPCC, 2005). Heat is supplied via the reboiler to release the chemically bound CO₂. This serves as the major energy penalty of the process. Some steam is recovered in the condenser and fed back to the reboiler. The regenerated solvent is then pumped back to the absorber via the cross heat exchanger.

Some additional equipment displayed in Figure 2.2 is used to maintain solution quality by preventing the accumulation of products of solvent degradation and of corrosion as well as the presence of particulates. These are the filter and reclaimer. The filters prevent the accumulation of particulates, which could result in erosion, solvent degradation and equipment fouling. The thermally operated reclaimer distills the MEA solution thus separating it from degradation products (Davidson, 2007).

2.3.1 Operational requirements for chemical absorption

Due to certain operational requirements associated with the operation of packed columns and the specific solvents involved, some pre-processing of the flue gas sent to the absorber columns is required.

2.3.1.1 Removal of SO₂ and NO_x

The presence of other acid gases such as sulphur dioxide (SO₂) and nitrogen oxides (NO_x) affect the performance of CO₂ capture systems. Chemical solvents tend to form heat stable salts with SO₂ and NO_x that cannot be regenerated leading to excessive solvent loss. With chemical solvents such as MEA, SO₂ levels of less than 10 ppmv are recommended (Ramezan et al., 2007; Rao et al., 2004). NO_x levels should be less than 20 ppmv (Audus, 2006). SO₂ is captured in a flue gas desulphurization (FGD) units while NO_x levels are reduced by means of selective catalytic (and non-catalytic) reactors (SCR and SNCR) or with low-NO_x burners (IEAGHG, 1993; IPCC, 2005; Davidson, 2007; Ramezan et al., 2007). There are claims that high lean MEA CO₂ loadings (e.g. 0.25 mol CO₂/mol MEA) could act as a degradation inhibitor because it would reduce the amount of SO₂ and O₂ that could enter into the aqueous MEA (Davidson, 2007).

2.3.1.2 Removal of particulates

The presence of particulates in the flue gas stream (in CO₂ scrubbing systems for instance) may lead to erosion, solvent degradation, fouling of equipment and may build up in heat exchangers and tower bottoms. Particulate build-up in the solvent loop of CO₂ scrubbing systems could also lead to foaming in towers thus increasing pressure drops and reducing mass transfer. The build-up could also lead to the formation of sludge or scale in equipment and subsequent plugging of equipment as well as crevice corrosion (IEAGHG, 1993; IPCC, 2005).

2.3.1.3 Removal of oxygen

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 1 ppmv are recommended for use with MEA when corrosion inhibitors are not employed (IEAGHG, 1993). The Fluor Daniel ECONAMINETM Process makes use of inhibitors (IPCC, 2005).

2.3.1.4 Flue gas temperature

The flue gas temperature is generally preferred as low as possible. For instance, the

solubility of CO₂ in solvents reduces with temperature increase. High flue gas temperatures could also lead to high solvent loss due to vaporisation (Rao et al., 2004). In addition, high temperatures could damage equipment such as the membranes of gas absorption membrane systems.

2.3.2 Alternative process designs

Kohl and Nielson (1997) discuss various modifications to the basic flow scheme of the conventional chemical absorption process. The following subsections describe some options for increased performance.

2.3.2.1 Increased number of lean amine feed points

One minor modification aimed at reducing the capital costs in the absorber column (Kohl and Nielson, 1997) is to use several lean amine feed points (illustrated in Figure 2.3). Kohl and Nielson (1997) described a case where most of the lean solvent is fed near the midpoint of the column to remove the bulk of CO₂ while a smaller stream is fed at the top to complete the clean-up. Because of the reduced solvent and gas flows, the top portion of such an absorber could be smaller in diameter.

Multiple
absorber feed
locations

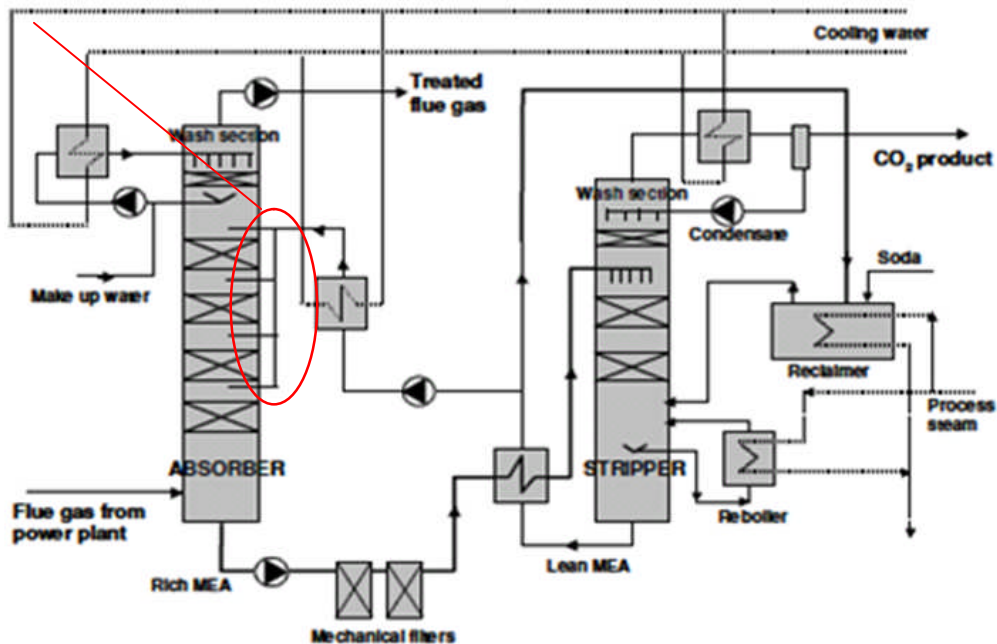


Figure 2.3 Pilot plant at CASTOR pilot plant at Esbjergværket with multiple absorber feed locations (Knudsen et al., 2009)

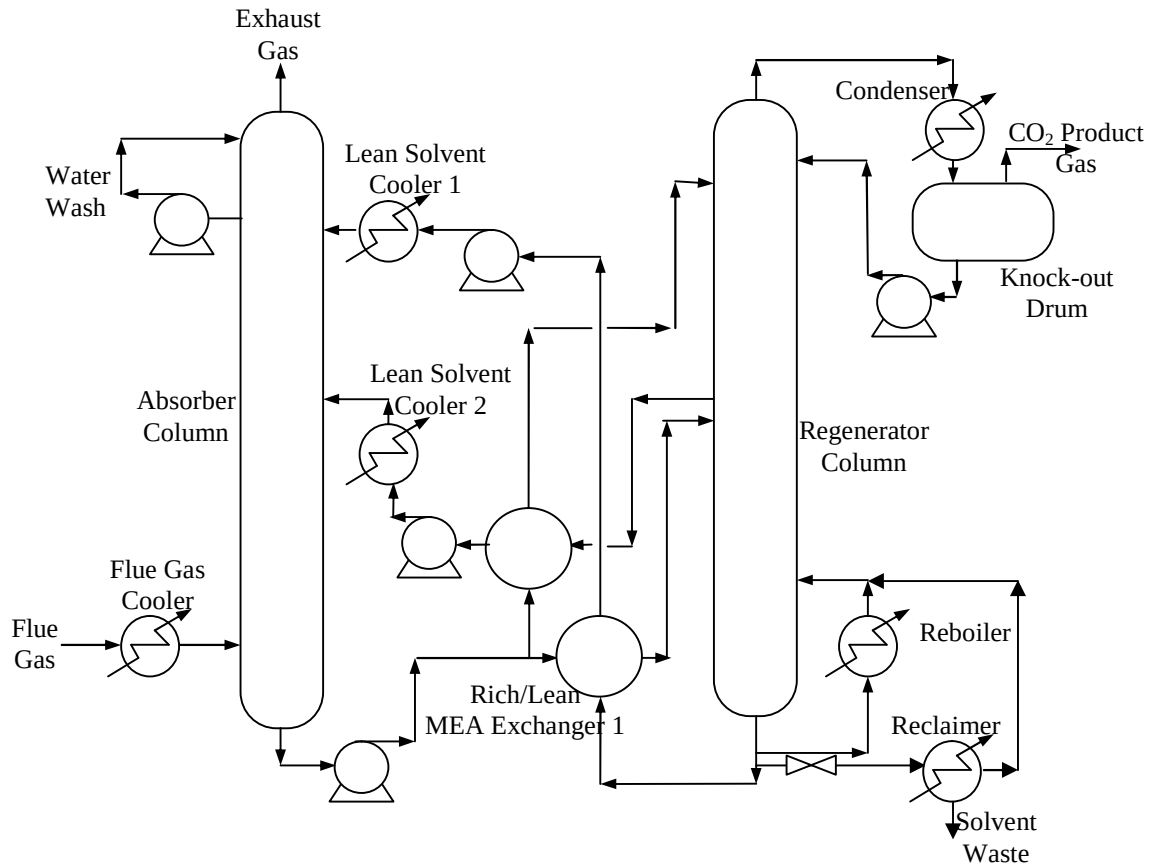


Figure 2.5 Split-stream configuration adapted from Kohl and Nielson (1997)

and completes the absorption of CO_2 from the flue gas. A process flow diagram of this configuration is shown in Figure 2.5.

2.4 Solvents for the chemical absorption of CO_2

Chemical absorption of CO_2 is achieved with chemical solvents in a reactive absorption process. Chemical absorption of CO_2 is preferred for post-combustion capture of CO_2 from pulverised fuel power plants because it is able to capture CO_2 at low partial pressures.

The ideal chemical solvent would possess (Davidson, 2007):

- Low regeneration cost requirements – based on a low heat of reaction with CO_2 .
- High absorption capacity – which directly influences solvent circulation flow rate requirements.

- High reactivity with CO_2 – which would reduce height requirements for the absorber and/or reduce solvent circulation flow rates.
- Low solvent costs – should be easy and cheap to produce. High thermal stability and reduced solvent degradation – reduced solvent waste due to thermal and chemical degradation.

Low toxicity of solvent.

The following describe various types of chemical solvents suitable for capturing CO_2 .

2.4.1 Amine-based solvents

2.4.1.1 Types of 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 amines, based on the degree of substitution of hydrogen atoms of the amine group. 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 $(\text{C}_2\text{H}_4\text{OH})\text{NH}_2$. 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 $(\text{C}_2\text{H}_4\text{OH})_2\text{NH}$. In the same way, triethanolamine (TEA) is a tertiary amine $(\text{C}_2\text{H}_4\text{OH})_3\text{N}$ (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 $(\text{C}_2\text{H}_4\text{OH})_2\text{N}(\text{CH}_3)$ (Booth, 2005).

Primary and secondary alkanolamines react rapidly with CO_2 to form carbamates. Equation (2.1) shows the reaction of a primary alkanolamine (represented by RNH_2) with CO_2 to form a carbamate. Tertiary alkanolamines (R_3N) do not possess a hydrogen atom attached to the nitrogen atom. They, therefore, facilitate the CO_2 hydrolysis reaction to form bicarbonates (equation (2.2)). 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 heat duty requirements. Examples include 2-Amino-2-methyl-1-propanol and 2-piperidineethanol (Vaidya and Kenig, 2007) and KS-1, KS-2 and KS-3 developed by the Kansai Electric Power Company (Davidson, 2007). These solvents are claimed to offer lower energy consumption and solvent loss. These solvents, however, have higher costs (Reddy et al., 2003).

MEA solvent is relatively cheap, and chemical absorption process with MEA is backed up by commercially available and proven technology (Rao et al., 2004). On the other hand, Davidson (2007) highlighted some problems encountered using MEA as a solvent such as (a) degradation of solvents in the oxidising environment of flue gas; (b) high energy consumption for regeneration of solvents; (c) corrosion. In order to be of practical interest, alternative solvents to MEA should have higher capacity for CO₂ capture and lower energy consumption.

2.4.1.2 Degradation of alkanolamines

Davidson (2007) discussed three main degradation routes for alkanolamines:

- (a) Carbamate polymerisation.
- (b) Oxidative degradation.
- (c) Thermal degradation.

Carbamate polymerisation of alkanolamines is insignificant at temperatures below 100 °C and thus would typically occur in the regenerator (Rochelle et al., 2001; Davidson, 2007). This form of degradation requires high CO₂ loadings of solvent - as such it is more prevalent at the rich end of the regenerator (Rochelle et al., 2001). At high

temperatures and with MEA solvents, the carbamate formed from the absorption of CO₂ is converted to a five-member ring, 2-oxazolidone, via a reversible reaction (Rochelle et al., 2001). The oxazolidone could revert back to the carbamate or degrade irreversibly in the presence of another molecule of MEA to form 1-(2-hydroxyethyl) imidazolidone-2. This product could hydrolyze to form the second degradation product, N-(2-hydroxyethyl) ethylenediamine (Rochelle et al., 2001).

Thermal degradation takes place at temperatures above 205 °C. As a result, it is the least well studied since it occurs at temperatures much higher than the operating temperatures of the absorption process (Rochelle et al., 2001).

Oxidative degradation comes from the presence of oxygen in the flue gas (Rochelle et al., 2001). 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. Neither high CO₂ loading or high temperature is needed in this case for degradation to occur (Rochelle et al., 2001). Since flue gases typically contain about 5 vol% O₂, this type of degradation may be significant (Rochelle et al., 2001).

Sexton and Rochelle (2009) described catalysts and inhibitors for MEA oxidation. They carried out studies at 55°C and found that dissolved metals catalyse 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. Formaldehyde, for instance, reacts with primary amines to form imines (Rochelle et al., 2001),

Davis and Rochelle (2009) focused on the regeneration in the regenerator unit. At 135°C the degradation rate (the amount of MEA lost to solvent degradation) varies from 2.5% to 6% per week via carbamate degradation. 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.

2.4.1.3 Effects of sulphur dioxide (SO₂) and nitrous oxides (NO_x)

Since amines are moderate bases, they react with acidic compounds to form salts. SO₂ and NO_x react with MEA to form heat stable salts. By varying the SO₂ concentrations in the range of 6 – 196 ppmv, 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 had an inhibition effect on 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). SO₂ levels should be kept below 10 ppmv while NO_x levels should be kept below 20 ppmv (FLUOR, 2004; Audus, 2006; Ramezan et al., 2007).

2.4.1.4 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 with 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).

2.4.2 Blended solvents

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 (Aroonwilas and Veawab, 2007; Davidson, 2007).

Aroonwilas and Veawab (2007) studied the performance of different amine blends such as MEA and MDEA for coal-fired power plants. It was found that, when MEA and MDEA are mixed at the appropriate ratio and used as solvent for CO₂ capture, the

energy consumption for regenerating CO₂ is reduced significantly. Compared with using MEA only, the thermal efficiency of the whole power plant with CO₂ capture using an MEA/MDEA blend increased by around 3% (Aroonwilas and Veawab, 2007).

2.4.3 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 (on a weight-by-weight basis) compared with 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., 2009; Kozak et al., 2009).

In the Chilled Ammonia Process (CAP), CO₂ is absorbed in the absorber at low temperatures. This would minimise solvent losses since ammonia is more volatile than amine solvents. The flue gas is first cooled to 0 to 20°C (preferably 0 – 10°C), it is then contacted in the absorber with lean solvent typically composed of 28 wt% ammonia, with a CO₂ loading between 0.25 and 0.67 mol CO₂/mol ammonia and water (Darde et al., 2009). The CO₂ loading in the lean solvent should be high enough to prevent excessive solvent evaporation and low enough to maximise the capture efficiency of the plant (Darde et al., 2009). The CO₂ rich stream is typically a slurry as solid products (typically of ammonium bicarbonate) are formed (Darde et al., 2009).

The desorber operating temperature ranges from 50 to 200°C (preferably 100 to 150°C) and the operating pressure from 2-138 bar (Darde et al., 2009). 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).

2.4.4 Piperazine-promoted K_2CO_3

The promotion of potassium carbonate (K_2CO_3) with amines appears to be a particularly effective way to improve overall solvent performance. K_2CO_3 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 at 160 kPa regenerator pressure and with a 5°C temperature approach in the lean/rich amine heat exchanger when compared with MEA (Davidson, 2007).

2.4.5 Concentrated, aqueous piperazine

Concentrated, aqueous piperazine (PZ) has been investigated as a novel amine solvent for CO_2 chemical absorption. The CO_2 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).

2.5 Reaction kinetics of chemical absorption using MEA solvent

Vaidya and Kenig (2007) reviewed the reaction kinetics of CO_2 absorption in alkanolamines and described three mechanisms:

- Zwitterion mechanism.
- Termolecular mechanism.
- Base-catalyzed hydration mechanism.

MEA being a primary amine reacts with CO_2 to produce carbamate via sets of liquid phase reactions (Davidson, 2007; Kucka et al., 2003). The reaction of CO_2 with primary, secondary and sterically hindered amines is usually described by the zwitterion mechanism (Vaidya and Kenig, 2007).

The zwitterion mechanism is a two-step mechanism that suggests that the reaction between CO_2 and the amine (denoted as $RR'NH$) involves the formation of a zwitterion as an intermediate. The forward and reverse reaction rate coefficients are k_1 and k_2 respectively (Danckwerts, 1979; Glasscock et al., 1991; Vaidya and Kenig, 2007):



The zwitterion subsequently undergoes deprotonation by a base (B) forming carbamate:



The rate of reaction of CO_2 in aqueous amine solution was expressed as (Vaidya and Kenig, 2007):

$$r = \frac{k_1[\text{CO}_2][\text{RR}'\text{NH}]}{1 + \frac{k_2}{k_B[B]}} \quad (2.5)$$

The base, B , may be the amine itself, H_2O , a hydroxide ion present or a combination of bases. Thus $k_B[B]$ represents the sum of the rates of all occurring deprotonation reactions (Vaidya and Mahajani, 2005).

When deprotonation is almost instantaneous compared with the zwitterion formation ($k_2 \ll k_B[B]$), the latter is rate limiting and equation (2.5) becomes:

$$r = k_1[\text{CO}_2][\text{RR}'\text{NH}] \quad (2.6)$$

Thus a first order reaction with respect to the amine and CO_2 is observed. Hikita et al. (1977) gave the following expression for the rate constant:

$$\log(k_1) = 10.99 - \frac{2152}{T} \quad (2.7)$$

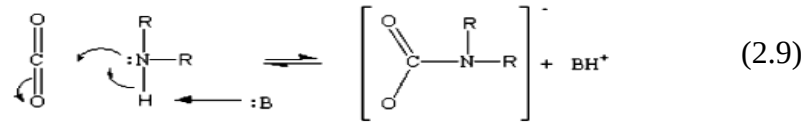
On the other hand, if the deprotonation step is rate limiting ($k_2 \gg k_B[B]$), equation (2.5) becomes:

$$r = \frac{k_1 k_B[B]}{k_2} [\text{CO}_2][\text{RR}'\text{NH}] \quad (2.8)$$

In this case, the contribution of the amine to the zwitterion deprotonation is significant and a fractional reaction order between one and two with respect to the amine is observed.

Several studies report the absorption of CO₂ by MEA as first order with respect to both reactants (Hikita et al., 1977; Danckwerts, 1979; Mahajani and Joshi, 1988; Glasscock et al., 1991; Freguia and Rochelle, 2003; Rao et al., 2004; Vaidya and Mahajani, 2005). However, there are conflicting estimations of the reaction rate coefficients in literature (Aboudheir et al., 2003; Vaidya and Kenig, 2007). Aboudheir et al (2003) explained these discrepancies as being due to (among other factors) the assumption of a pseudo-first order reaction. It was further illustrated that this assumption is valid for low MEA concentrations or high CO₂ loadings but is inaccurate otherwise (Aboudheir et al., 2003). This is illustrated in the Table 2.1.

Studies suggest that the termolecular mechanism provides better description of the absorption process (Aboudheir et al., 2003; da Silva and Svendsen, 2004). This mechanism is similar to the second case of the zwitterion mechanism (where the deprotonation step is rate limiting). This mechanism assumes that the bond formation between the amine and CO₂ takes place simultaneously with the proton transfer to the base rather than in two steps as the zwitterion mechanism suggests. This is represented in the equation (2.9) (da Silva and Svendsen, 2004):



The rate of the forward reaction is given by Aboudheir et al. (2003) and da Silva and Svendsen (2004):

$$r = k_{app}[\text{CO}_2] \quad (2.10)$$

where

$$k_{app} = k_{RNH_2} [\text{RNH}_2]^2 + k_{H_2O} [\text{H}_2\text{O}] [\text{RNH}_2] \quad (2.11)$$

Table 2.1 Apparent reaction order and rate constant for CO₂ absorption into MEA solutions ($r = k_{app}[\text{CO}_2]$, where $k_{app} = k[\text{MEA}]^n$) (Aboudheir et al., 2003)

$T(^{\circ}\text{K})$	Series A: $[\text{CO}_2]_{\text{in}} \sim 18 \text{ mol/dm}^3$ and $[\text{MEA}] = 0.193 - 3.875 \text{ mol/dm}^3$		Series B $[\text{CO}_2]_{\text{in}} \sim 0.6 \text{ mol/dm}^3$ and $[\text{MEA}] = 1.405 - 5.498 \text{ mol/dm}^3$	
	n (reaction order)	k ($\text{dm}^3/\text{mol s}$)	n (reaction order)	k ($\text{dm}^3/\text{mol s}$)
293	1.04	4615	1.29	5338
303	1.08	6674	1.37	7691
313	1.15	10,119	1.42	11,643
323	1.21	12,479	1.45	17,141
333	1.31	19,635	1.36	27,706

2.6 Summary

For flue gases with less than 15 vol% CO₂, the chemical absorption process is currently the most economical option for post-combustion capture. Therefore, it would be the preferred option for CO₂ separation in pulverised coal-fired power plants and natural gas fired power plants. The various operational requirements for the process were discussed. The process has the drawback of high heat requirement for the thermal regeneration of solvent. In order to address this issue, alternative process designs and alternative chemical solvents have been developed. Three alternative process designs were discussed. These improve the efficiency of the process at the cost of increased process complexity. MEA is the most popular solvent choice for chemical absorption. Significant efforts have been made worldwide towards developing improved chemical solvents. Many solvents perform better than MEA in terms of regeneration requirements; however, other factors such as absorption capacity or cost of production may make them less desirable.

Chapter 3 Research activities towards demonstrating post-combustion CO₂ capture

3.1 Introduction

This chapter focuses on the progress achieved by recent research activities towards demonstrating post-combustion CO₂ capture for power plants. Firstly, a number of research programs involving pilot plant studies on post-combustion CO₂ capture are discussed. Research activities in terms of modelling and simulation of the power plant and the post-combustion CO₂ capture plant are then described. Finally, various approaches towards optimising the post-combustion capture process are outlined.

3.2 Important research programmes worldwide

This section aims to give an overview of important research programmes worldwide in post-combustion CO₂ capture based on pilot plant studies. A more comprehensive review of such research programs is presented in Wang et al. (2010).

3.2.1 Luminant carbon management programme

3.2.1.1 Participants and purpose

The Luminant Carbon Management Programme led by Professor Gary Rochelle in the Department of Chemical Engineering, University of Texas at Austin (USA) focuses on tackling 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).

3.2.1.2 Description of facilities

The schematic of the pilot plant facility is shown in Figure 3.1. Both the absorber and regenerator columns are packed columns with internal diameters of 0.427 m and total column height of 11 m. Columns consist of two 3.05 m 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 tonnes of CO₂ per day (Dugas, 2006). The flue gas stream is prepared

since it is not obtained directly from a power plant. Once the plant is in operation, the separated CO₂ gas is mixed with the treated gas and returned to the absorber to as shown in Figure 3.1.

3.2.1.3 Activities

At the pilot plant, several studies are carried regarding CO₂ rate kinetics and solubility measurements (Bishnoi and Rochelle, 2002), 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) amongst others.

One of the main projects carried out was the CO₂ capture by absorption with potassium carbonate. This project ran from 2002 to 2007 with the aim to improve the process for CO₂ capture by absorption/stripping via the development of an alternative solvent, namely 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 energy 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/regenerator configurations among others. A rate-based model of the absorber unit was developed.

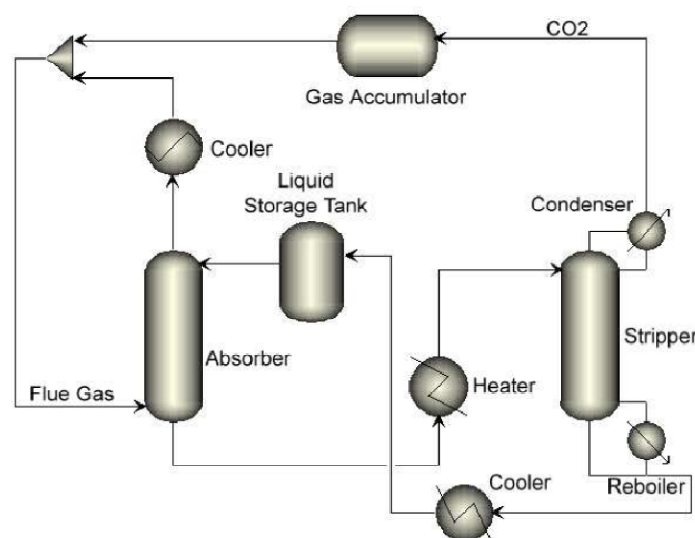


Figure 3.1 Schematic of CO₂ capture pilot plant from Dugas (2006)

Absorber intercooling was found to improve absorption performance especially for high absorption capacity solvents (NETL, 2008).

3.2.2 International Test Centre (ITC) for CO₂ capture

3.2.2.1 Participants and purpose

The ITC is formed by the collaboration of University of Regina with government and industrial partners. It is led by Professor Malcolm Wilson and aims at exploring and developing new cost effective technologies for CO₂ capture.

3.2.2.2 Description of facilities

Infrastructure in the ITC consists of bench-scale CO₂ separation units as well as a multi-purpose pilot plant unit (1 tonne of CO₂ per day) at the University of Regina. A 250 kW 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, with a total height of 10 m.

In 2000, the ITC re-commissioned a semi-commercial (4 tonne of CO₂ per day) demonstration unit adjacent to SaskPower's 875 MWe 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 3.2:

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

3.2.2.3 Activities

Kinetics of the reactive absorption of CO₂ in high CO₂-loaded, concentrated aqueous MEA solutions were studied by Aboudheir et al. (2003) experimentally. Kinetics of the reactive absorption of CO₂ with mixed solvents MEA and MDEA were again studied by Edali et al. (2009).

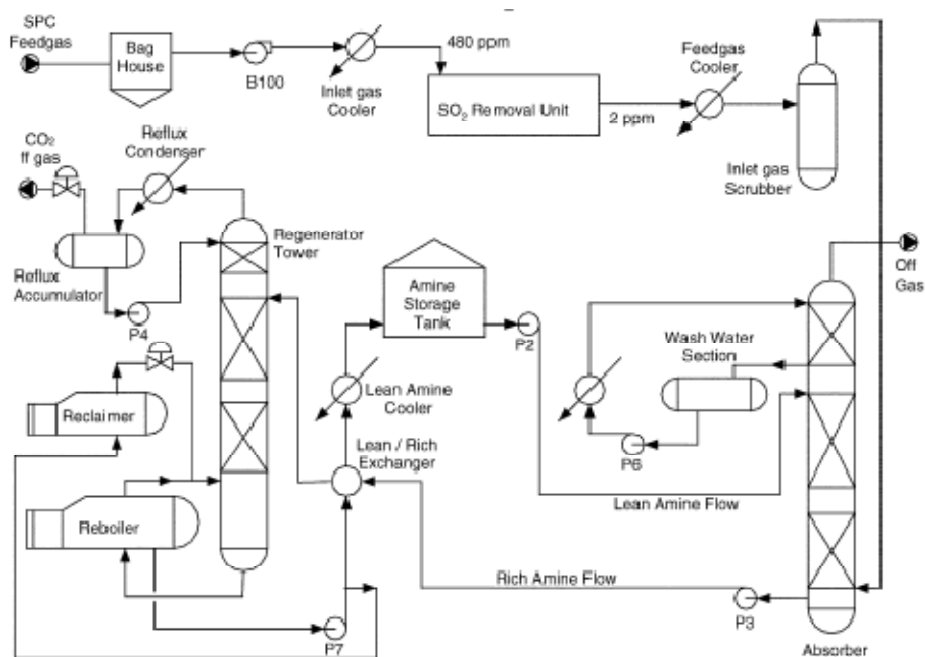


Figure 3.2 Schematic of Boundary Dam CO₂ pilot plant (Wilson et al., 2004)

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.

3.2.3 CASTOR

3.2.3.1 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 programme and has members from 11 EU countries, including: (a) 16 industrial firms (including Dong Energy, Vattenfall, Repsol, Statoil, Gaz de France, Rohoel, Alstom power and RWE); (b) 12 research institutes (including IFP, BGRM, Imperial College, TNO and BGS). The CASTOR project had a total budget of €15.8 million with a

contribution of €8.5 million from European Commission (FP6 – Sixth Framework programme) (IEAGHG, 2010).

The project's stated goals involved halving the cost of capturing and separating CO₂ (from €40-60/tonne CO₂ to €20-30/tonne 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.

3.2.3.2 Description of facilities

A gas-fired mini plant with full absorption/desorption cycle was built at the University of Stuttgart. This facility consists of an absorber with 0.125 m diameter absorber column and 4 m packing height and a regenerator column with 2.5 m packing height (Notz et al., 2007). An industrial-scale pilot plant facility (Figure 3.3) was launched alongside a power plant run by Dong Energy (formerly ELSAM) in Esbjerg, Denmark on 15 March 2006. This plant has a capacity to capture about 24 tonnes of CO₂ per day (Knudsen et al., 2009). It consists of an absorber with 4 consecutive packed bed of 4.25 m packing height each. The regenerator consists of two 5 m packing height sections. Both columns have an internal diameter of 1.1 m (Knudsen et al., 2009).

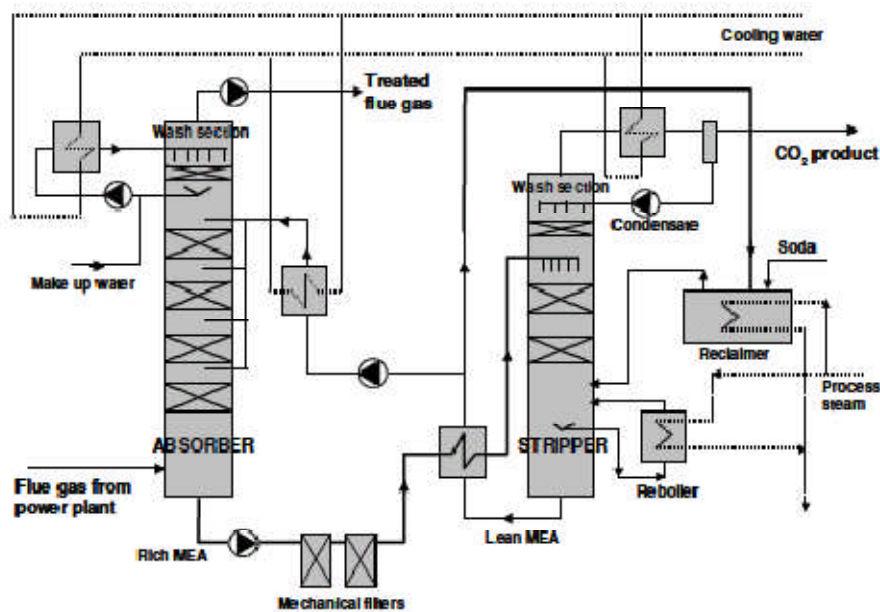


Figure 3.3 Simplified flow diagram of the CASTOR pilot plant at Esbjergværket (Knudsen et al., 2009)

3.2.3.3 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 March 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 30 wt% 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. An achievement of a cost of €35-37/tonne CO₂ was reported (Le Thiez, 2008). 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).

3.2.4 CESAR

3.2.4.1 Participants and purpose

This 4-year long project, funded by FP7 (Seventh Framework Programme), 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 that 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 €/tonne CO₂. The consortium consists of 3 research organizations, 3 universities, 1 solvent supplier, 1 membrane producer, 3 equipment suppliers, 2 oil and gas companies and 6 power generators (CO₂CESAR, 2010).

3.2.4.2 Description of facilities

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

3.2.4.3 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.

3.2.5 The Cooperative research centre for greenhouse gas technologies (CO₂CRC)

3.2.5.1 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, and 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 systems.

3.2.5.2 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 in the Latrobe Valley, Victoria, Australia. 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).

3.2.5.3 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), is a \$5.6 million post-combustion capture 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 (CO₂CRC, 2009a). Research is still ongoing especially with regards the improved heat integration of the process.

3.2.6 Investigations at Mitsubishi Heavy Industries

3.2.6.1 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 lower 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 that recover CO₂ from flue gas from natural gas fired power plant. 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).

3.2.6.2 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 that recover CO₂ from flue gas from natural gas-fired power plant (Kishimoto et al., 2009).

A 1 tonne 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 tonnes 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).

3.2.6.3 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.

3.2.7 Summary

Although many research programmes 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 5.0 MWe). Consequently, the packed column sizes are modest in size (up to 1.1 m in diameter) (Dugas, 2006; Feron et al., 2007). Current pilot plant studies worldwide are on a much smaller scale than would be required for CCS. Even at such scales (typically less than 5 MWe), the cost of construction for these facilities typically runs up to several million dollars (Herzog et al. 2009). Once built, these plants are limited in the range of studies that could be carried out. Full scale demonstration projects are estimated to cost over a billion dollars (Herzog et al., 2009). Useful insights for the design and operation of power plants with post-combustion CO₂ capture plants could be obtained through dynamic modelling and simulation.

3.3 Research through modelling and simulation

Although computer modelling and simulation cannot completely eliminate the necessity of building demonstration plants, a lot of useful insights could be derived from accurate models of the post-combustion capture process at a much lower cost. The approaches and principles for modelling the chemical absorption process are first discussed. The

development in dynamic modelling of the chemical absorption and power generation processes, which could be used for operational studies, then follow.

3.3.1 Level of complexity in modelling

In modelling the chemical absorption process, 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). In the rate-based approach, actual rates of multi-component mass and heat transfer as well as chemical reactions are considered directly (Noeres et al., 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 3.4 (Kenig et al., 2001).

Starting from Model 1 in Figure 3.4, the packed column is modelled as a column containing different equilibrium stages. Moving towards the right (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 3.4), 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 CO_2 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.

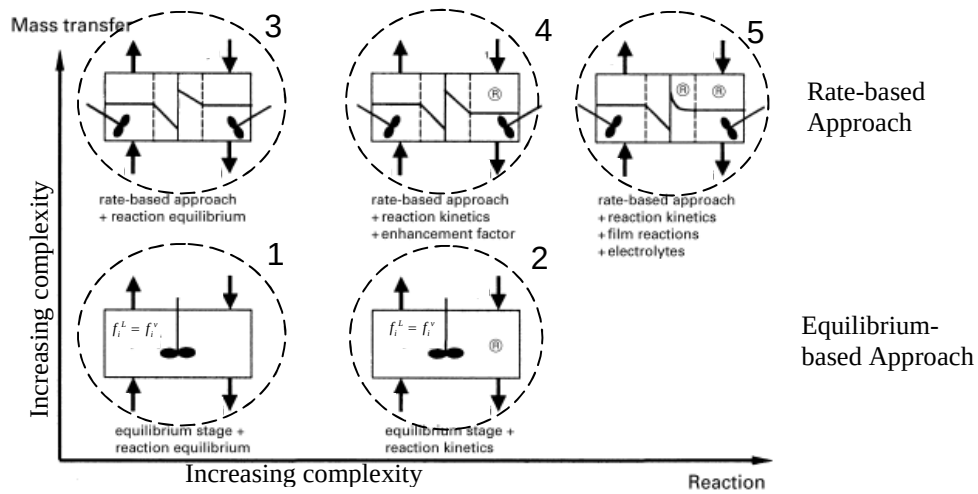


Figure 3.4 Different levels of reactive absorption model complexity (Kenig et al., 2001)

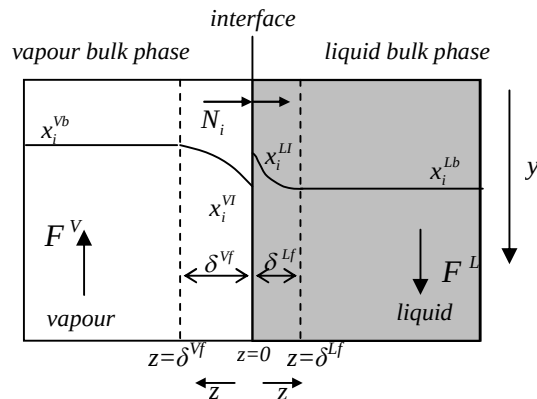


Figure 3.5 Modelling the conventional process based on the two-film theory

3.3.2 Modelling mass transfer

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 3.5, the model will include ideally mixed vapour and liquid bulk phases and two film regions adjacent to the interface.

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 rest of the bulk liquid and vapour is assumed to have a uniform composition based on agitation. There is no convection in

the film, and dissolved gases cross these regions by molecular diffusion alone (Danckwerts, 1970). The rate of mass transfer is affected by the film thickness, which in turn depends on the liquid agitation, geometry, and physical properties (Danckwerts, 1970). Although the model theory is not very realistic, its predictions are usually remarkably similar to those based on more sophisticated models (Danckwerts, 1970 & 1979).

Mass transfer in the two-film theory model could be described based on Fick's law or Maxwell-Stefan formulation. Fick's law is not suitable for this application because its assumptions are valid only for (Krishna and Wesselingh, 1997):

- Binary mixtures or dilute components in a multicomponent mixture – chemical absorption of CO₂ in MEA is from a multicomponent mixture where CO₂ concentrations may reach significant levels.
- Diffusion in the absence of electrostatic force fields – amine solvents are ionic and as such electrostatic force fields exist.

The Maxwell-Stefan formulation is well suited for modelling mass transfer under these conditions (Krishna and Wesselingh, 1997).

The penetration theory 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 (Danckwerts, 1970). 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).

3.3.3 Operational studies of the chemical absorption post-combustion capture process through dynamic modelling and simulation

The performances of the absorber and the regenerator, the two major components in the conventional CO₂ capture process, have been studied by a number of researchers through 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 MWe supercritical coal-fired power plants. The model was based on an integration of several sub-models which account for the liquid flow distribution, mass transfer process with enhancement factors and vapour-liquid equilibrium (Aroonwilas and Veawab, 2007). 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. This corresponded to an increase of up to 3% thermal efficiency in the power plant when compared with using MEA solvent only. 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 was assumed that simple relationships could be used to represent the CO₂ capture efficiency penalty across all loads. It was pointed out that further work is required to better understand transient behaviour of power plants with CO₂ capture especially during load changes using more detailed whole plant models as well as pilot plant studies (Chalmers and Gibbins, 2007).

Few studies with dynamic process models have been carried out. In Lawal et al. (2009a), a dynamic rigorous model was developed for the absorber. Various approaches for modelling the chemical absorption process were described. Validation results showed that the rate-based approach gives better predictions of pilot plant measurements than the equilibrium-based approach. The rate-based approach, with the assumption that chemical reactions attain equilibrium (Model 3), was used. Process analysis based on this model found that the absorber performance (including the CO₂ capture level) 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 3.4). 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 regenerator and heat exchange units) is required to evaluate different operational challenges.

In Lawal et al. (2009b), a dynamic model for the regenerator 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 regenerator. In Ziaii et al. (2009), only the regenerator was modelled dynamically using rate-based mass transfer and assuming reaction at equilibrium (Model 3 in Figure 3.4). This model was subsequently used to minimise the energy consumption of the regenerator.

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

In Lawal et al. (2010a), dynamic models for the absorber and regenerator columns were developed (Model 3 in Figure 3.4). 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 (Lawal et al., 2010a). These disturbances include an increase in flue gas flow to the absorber column as well as reduction in reboiler heat duty. The dynamic effects of these on CO₂ removal rate and energy requirements of the process are described. A time constant for the process was estimated to be 57 minutes. The effect of poor water balance on the capture plant performance was also shown (Lawal et al., 2010a).

The integrated operation of the post-combustion CO₂ capture plant with a coal-fired power plant was studied by Lawal et al. (2010b). The scale-up of the post-combustion

CO₂ capture plant model from pilot plant scale to one sufficient to process flue gas from a 500 MWe sub-critical coal-fired power plant was described (Lawal et al. 2010b). It was estimated that two absorber columns would be required for this purpose. A dynamic model of the sub-critical power plant was developed (Lawal et al. 2010b). Here, Lawal et al. (2010b) described the development of component models for the furnace, downcomer, riser, steam drum of the power plant. The paper describes how the power plant model was linked to the CO₂ capture plant model to form the integrated plant model. The flue gas from the power plant are first cooled then supplied to two absorber columns for CO₂ capture. Steam is drawn from the IP/LP crossover to supply heat for solvent regeneration in the regenerator's reboiler. The condensate from the reboiler is returned to the low pressure feedheater of the power plant. Both steady state and dynamic analyses were carried out on this model to study the performance of the plant (Lawal et al. 2010b).

All the above models were developed based on the two-film theory (for mass transfer calculations). Tobiesen et al. (2007) 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.

Kvamsdal et al. (2010a) 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 12 MPa. Another key issue of water balance for the whole CO₂ capture process. This was achieved primarily by controlling the temperature of the flue gas at the top of the absorber column (Kvamsdal et al., 2010a).

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. A good approach for the model development of such a process is to model the individual columns of the process and subsequently link them up with recycle. Coal-fired power plants traditionally operate flexibly to satisfy varying

electricity demands (Chalmers and Gibbins, 2007). As a result, the downstream post-combustion CO₂ capture plant may be subjected to various disturbances, which may complicate operation. Previous studies suggest that these disturbances would include variation of flue gas mass flow to the absorber column with changes of the power plant's power output, possible disruption of steam supply to the reboiler and improper water balance in the absorber column.

3.3.4 Power plant dynamic modelling

A number of studies explored the dynamic response of power plants. Lu (1999) combined a dynamic model with steady state correlations to simulate power plant component dynamics in MATLAB/SIMULINK. The components could be linked to form a power plant. The dynamic model developed was not validated, although some simulation results for a whole plant were shown. Åström and Bell (1999) derived a model from first principles to describe the drum, downcomer, and riser components of a natural circulation drum-boiler. Bhambare et al. (2009) modelled from first principles a 250 MW coal-fired natural circulation boiler. The boiler system was divided into seven submodels: downcomer, riser, waterwall, drum, superheater and reheater, steam attemperator, and furnace. Chaibakhsh et al. (2007) developed a dynamic model of a sub-critical once-through Benson-type boiler based on the experimental data obtained from a complete set of field experiments. Genetic Algorithm (GA) was executed to estimate the model parameters and fit the models response on the real system dynamics. Stephenson et al. (2009) developed dynamic models of a sub-critical coal-fired power plant in gPROMS[®] and validated the results with plant data. Power plant models described by these authors do not include integration with a CO₂ capture plant.

3.3.5 UK grid code and system frequency response requirements

System frequency in a grid is determined by a balance in system demand and total power generation. When the demand rises above the power generated, the frequency drops and vice versa. The UK Grid Code demands relatively strict minimum requirements for primary frequency response in power generation. In particular, power plants are required to be able to increase their output by 10% over a 10 second period. Secondary response refers to the requirement of output increase between 30 seconds and

30 minutes (E.ON UK, 2008). One reason why sub-critical power plants can meet the UK Grid requirements is that they have boiler drums and as such have a large amount of stored energy. Higher efficiency supercritical boilers do not have drums and therefore it may be harder for them to meet Grid Code requirements. There are therefore concerns that these supercritical plants may not be able to meet the primary response requirement of the UK Grid Code (E.ON UK, 2008). In such a situation, some benefits may accrue from addition of a post-combustion plant downstream the power plant as the steam supplied to the reboiler could be reduced to make more steam available for power generation thus aiding primary response. It is, therefore, important to understand the behaviour of the absorption process with such a reduction. Temporary storage of rich amine solvent could enable this to be done without a drop in CO₂ capture rates. In addition, the flue gas supplied to the absorption process may vary in flow rate or composition as the power plant operates in varying load conditions.

3.4 Techno-economic studies of power generation with CO₂ capture

Several studies assessing different CCS options have been carried out (Rao and Rubin, 2002; IPCC, 2005; Abu-Zahra et al., 2007b; Davidson, 2007; Davison, 2007). These studies, in general, compare different CCS options based on the cost of CO₂ avoided. The cost of electricity is estimated for a reference case with no CO₂ capture and for the capture case. The cost of electricity (*COE*) is obtained by dividing the total annualised plant cost (€/yr) by the net electricity generated (kWh/yr). The difference in CO₂ emission levels of both cases is estimated as the mass flow of CO₂ captured (tonnes). The cost of CO₂ avoided is evaluated as follows (Davidson, 2007):

$$\text{Cost of CO}_2 \text{ avoided (€/tonne)} = \frac{COE_{CCS} - COE_{Ref}}{\text{Mass flow of CO}_2 \text{ captured}} \quad (3.1)$$

3.5 Performance improvement of chemical absorption process for power generation

Many authors have approached the challenge of the performance improvement of post-combustion CO₂ capture from three basic perspectives:

- The minimisation of heat requirements for solvent regeneration. This could be achieved through the:
 - o Use of solvents with lower heats of absorption (Davidson, 2007; MacDowell et al., 2010).
 - o Use of improved process configurations with concepts such as intercooling, split flow configuration and supply of lean solvent to multiple feed locations in the absorber (Kohl and Nielson, 1997; Aroonwilas and Veawab, 2007).
- Improved heat and process integration of the chemical absorption process with the power generation process (Aroonwilas and Veawab, 2007; Pfaff et al., 2010).
- Determining the optimal operating conditions for the chemical absorption process (Ziaii et al., 2010).

Kvamsdal et al. (2010) added an additional constraint of maintaining a neutral water balance in the process that was specifically important to the application considered (offshore operation).

Dynamic optimisation of the process has rarely been considered. Ziaii et al. (2010) recently published a paper regarding the optimum design and control of the process. The study used multivariable optimisation tools in Aspen Custom Modeller[®] to maximise the hourly profit of a 100 MWe coal-fired power plant. Optimization was carried out as a function of a price ratio (CO_2 price / electricity price). Dynamic optimisation was carried out to determine the optimum setpoints for reboiler steam rate, solvent circulation loops and stripper pressure control loops in response to two partial load scenarios – reboiler steam load reduction and power plant boiler load reduction. It should be noted that an approximate steady state model of the steam turbine was used as well as general performance curves for the multi-stage CO_2 compressor and pumps therefore, there may be some inaccuracies in the obtained results (Ziaii et al., 2010). In addition, an assumption is made that the work done by the steam is only a function of the total steam rate in the cycle, which is simplistic since, with steam extraction, the steam pressures to the LP turbine would change (Cooke, 1985; Ziaii et al., 2010).

The objective function for both steady state and dynamic optimisation cases carried out by Ziaii et al. (2010) was as follows:

$$\begin{aligned} Profit(\$ / year) = & (Electricity\ price(\$ / kWh) \times Electricity\ generated\ (kWh / year)) \quad (3.2) \\ & + (CO_2\ price(\$ / tonne) \times removed\ CO_2\ (tonne / year)) \end{aligned}$$

3.5.1 Use of solvents with lower heats of absorption

The use of alternatives solvents to MEA has been considered by various authors (Davidson, 2007; Kishimoto et al., 2009; Oexmann and Kather, 2010; Rochelle, 2010). Oexmann and Kather (2010) stated that focusing on just the heat of absorption of the solvents may be misleading. They described the heat requirement of the process as being dependent on three contributors:

- The sensible heat to raise the solvent to the reboiler temperature.
- The heat of evaporation required to produce the part of the stripping steam in the reboiler.
- The heat of absorption associated with the solvent.

3.5.2 Use of improved process configurations

Kohl and Nielson (1997) as well as Aroonwilas and Veawab (2007) describe alternative configurations of the chemical absorption process such as the split flow configuration. These lead to higher complexity of such systems. Other solutions such as intercooling (Seibert et al., 2010) and use of multiple feed locations for lean solvent supply to the absorber column could be simpler in this regard (Knudsen et al., 2009; Feron et al., 2007).

3.5.3 Improved heat and process integration

Pfaff et al. (2010) described the possibilities of optimized design of post-combustion CO₂ capture systems in newly built power plants. Particular focus is put on optimized de-superheating of reboiler steam and heat recovery from the condenser of the regenerator column. A lot of heat is available but at low quality. Thus these heat sources could be used to heat the combustion air and the condensate heat sinks.

3.5.4 Selecting optimal operating conditions

Abu-Zahra et al. (2007a) considered the technical and economic performance of MEA CO₂ absorption plants for power plants. By optimising the lean solvent loading, the amine solvent concentration as well as the regenerator operating pressure, they obtained a minimum CO₂ avoidance cost of €33 per tonne of CO₂ avoided. These results were for a steady state operation. Cifre et al. (2009) optimized the regenerator operating pressure, the solvent circulation rate and the height of the absorber packing.

3.6 Summary

Although the chemical absorption process has been employed for CO₂ separation for several years, it has never been applied at the scale required for post-combustion capture in large power plants. Numerous research programs have carried out studies regarding the design and operation of such plants. Currently, these pilot plants are at a relatively small scale, and full scale demonstration is required. Building such demonstration plants would be very expensive. Studies carried out through modelling and simulation could provide useful insights into the design and operation of future plants, especially with regards to comparing different process technologies or solvents. Various steady state models have been developed to study the post-combustion capture process. However, transients such as start-up, shut down and disturbances from the upstream power plant can only be studied using accurate dynamic models. The developments in the dynamic modelling and simulation of the power plant and the post-combustion CO₂ capture process were discussed.

Chapter 4 Model development for post-combustion CO₂ capture process

4.1 Introduction

This chapter describes the model development of the post-combustion CO₂ capture process – specifically the chemical absorption process. The main process units are the absorber and regenerator columns. Dynamic models of the entire process are developed systematically. The accuracy of the equilibrium- and rate-based approaches is compared in modelling the absorber column. The rate-based model is selected and used to model stand-alone absorber and regenerator columns. The two columns are subsequently linked together and validated using steady state and dynamic data. Steady state and dynamic analyses are carried out with the post-combustion CO₂ capture process model to gain useful insights for its design and operation.

4.2 Equilibrium-based absorber model development

The equilibrium-based approach to the chemical absorption of CO₂ in aqueous monoethanolamine solution was discussed in Section 3.3. This approach assumes theoretical stages, in which liquid and vapour phases are at equilibrium and perfect mixing occurs. By so doing, mass transfer resistances are ignored. The equilibrium-based approach was implemented in Aspen Plus based on its Radfrac column model. This model was steady state and assumes perfect mixing occurs (Aspentech, 2010).

In the Radfrac model, the physical property method used is the Electrolyte Non-Random-Two-Liquid (NRTL) model with electrolyte inserts for MEA. This insert includes new parameters and Henry's constant for CO₂ in MEA (Aspentech, 2010).

MEA electrolyte solution chemistry is used to predict the equilibrium mass fractions in the liquid and vapour phases. The following are the set of equilibrium reactions describing this chemistry (Aspentech, 2008b):





4.3 Rate-based absorber model development

In the rate-based approach, actual rates of multi-component mass and heat transfer as well as chemical reactions are considered directly (Noeres et al., 2003). The process is described using the two-film theory and mass transfer rates are calculated using the Maxwell-Stefan formulation. Heat and mass transfer resistances are modelled in the liquid and vapour films.

The rate-based model was developed based on the Gas-Liquid Contactor model in Process Systems Enterprise's Advanced Model Library for Gas/Liquid Contactor (AML:GLC) using the process modelling tool, gPROMS[®]. With gPROMS[®], accurate dynamic models of processes can be developed as it is equation-based.

The models were based on the two-film theory (Figure 3.5). As such the models structure is as follows:

- Liquid and Vapour Bulk Models.
- Liquid and Vapour Film Models.
- Interface Model between Liquid and Vapour Films.

The following assumptions were used in developing this dynamic model:

- Plug flow regime.
- Linear pressure drop along the column.
- No accumulation in liquid and vapour films as well as in the bulk vapour.
- Phase equilibrium at interface between liquid and vapour films.
- Negligible solvent degradation.
- Oxygen is considered inert and all inert species are represented by nitrogen.
- Negligible heat loss to the surroundings.
- Liquid phase equilibrium reactions.

Important equations in each of the model are described and explained in the following subsections.

4.3.1 Liquid bulk model

The liquid bulk model mainly describes the mass/energy balances as well as the flow of liquid (and its components) in the column.

$$\text{Mass Balance: } \frac{\partial M_i}{\partial t} = \frac{-1}{L \cdot A} \frac{\partial F_i^L}{\partial y} + N_i \cdot Sp \cdot mw_i \cdot \omega \quad (4.6)$$

In equation (4.6), the change in component mass holdup, M_i , per unit volume with respect to time is determined by the differential change of the component mass flow

along the vertical axis of the column $\frac{\partial F_i^L}{\partial y}$ and the estimated component molar fluxes,

N_i , to and from the liquid bulk. N_i is estimated in the liquid film model whilst calculating mass transfer rates (equation (4.12)). Sp is the specific area of packing, mw_i is the molecular weight of component, i and ω is the wetted area ratio, which compares the surface area available for mass transfer to the total surface area of packing. y represents the spatial domain along the vertical axis of the column, which is discretized into 15 equal elements.

$$\text{Energy Balance: } \frac{\partial U}{\partial t} = \frac{-1}{L \cdot A} \frac{\partial F_H^L}{\partial y} + Sp \cdot \omega \cdot (H_{liq}^{cond} + H_{liq}^{conv} + H_{abs}) \quad (4.7)$$

In the energy balance, the change in energy holdup with respect to time, $\frac{\partial U}{\partial t}$, is

determined by the differential change of ‘energy flow’ along the vertical axis of the

column, $\frac{\partial F_H^L}{\partial y}$ and the liquid heat fluxes at the liquid film-liquid bulk interface due to

conduction, H_{liq}^{cond} , convection, H_{liq}^{conv} which are both estimated in the liquid film model (equations (4.16) and (4.17) respectively) as well as the heat flux due to chemical absorption of CO_2 , H_{abs} .

$$\text{Heat of absorption (or desorption): } H_{abs} = N_{\text{CO}_2} \cdot h_{abs} \quad (4.8)$$

$$h_{abs} = R \cdot \left(-14281 - \left(\frac{1092554 \cdot \gamma^2}{T} \right) - \left(\frac{6800882 \cdot \gamma}{T} \right) + 32670.01 \cdot \gamma \right) \quad (4.9)$$

The specific heat of absorption, h_{abs} , was estimated based on the temperature, T , the CO₂ loading of the solvent, γ and R is the universal gas constant. This equation applies to both the absorber and regenerator columns.

4.3.2 Vapour bulk model

$$\text{Mass Balance:} \quad 0 = \frac{-1}{L \cdot A} \frac{\partial F_i^V}{\partial y} - N_i \cdot Sp \cdot mw_i \cdot \omega \quad (4.10)$$

$$\text{Energy Balance:} \quad 0 = \frac{-1}{L \cdot A} \frac{\partial F_H^V}{\partial y} + Sp \cdot \omega \cdot (H_{vap}^{cond} + H_{vap}^{conv}) \quad (4.11)$$

In the vapour bulk, it is assumed that the rate of change of mass and energy holdups with time are negligible. This was assumed because the residence time of the vapour phase in the absorption system is relatively small compared with that of the circulated liquid phase solvent. The composition and temperature would change along the vertical axis direction of the column. Chemical absorption of CO₂ is assumed to take place only via liquid phase reactions; therefore, the heat of absorption is included only in the liquid bulk energy balance (cf. equation (4.7)).

4.3.3 Vapour and liquid film models

$$\text{Maxwell-Stefan Formulation:} \quad \frac{1}{\delta} \frac{\partial x_i^M}{\partial z} = \frac{1}{c_t} \sum_{k=1}^{nc} \left(\frac{x_i^M N_k - x_k^M N_i}{\chi_{i,k}} \frac{\mu^R}{\mu} \frac{T}{298.15} \right) \quad (4.12)$$

Mass transfer rates are determined using the Maxwell-Stefan formulation (Krishna and Wesselingh, 1997). Corrections are made to the formulation for different viscosities, μ (relative to the reference viscosity μ^R) as well as for different temperatures (T) relative to the reference temperature of 298.15 K. z represents the spatial domain along the thickness of the vapour or liquid film. The liquid film is discretized into 10 equal elements while the vapour film has 3 equal elements. It is discretized in this way because the mass transfer resistances in the former are more important.

The diffusivity (χ) of CO₂ in the liquid phase was based on expressions provided by Vaidya and Mahajani (2005) . The diffusivity (χ) of CO₂ and other components in the vapour phase was estimated using Fuller's equation (Reid et al., 1977). Mass transfer coefficients in the liquid and vapour films were determined by correlations given by Onda et al. (1968) which, in turn, set the value for the film thickness, δ .

In the mass balance, it is assumed that there is no accumulation of mass in the film. Therefore, the molar fluxes, N_i , appearing in equation (4.12), are independent of the position, z . The energy balance is given in equation (4.13). For a film of thickness δ ,

$$\frac{1}{\delta} \left(\frac{\partial(\lambda G_T)}{\partial z} \right) - \frac{1}{\delta} \left(\frac{\partial H_{flux}}{\partial z} \right) = 0 \quad (4.13)$$

where, λ is the thermal conductivity of the fluid and the temperature gradient, G_T , is defined as:

$$G_T = \frac{1}{\delta} \left(\frac{\partial T}{\partial z} \right) \quad (4.14)$$

The heat flux, H_{flux} across the film thickness is defined as:

$$H_{flux} = \sum_{i=1}^{nc} N_i h_i^M \quad (4.15)$$

where h_i^M is the specific molar enthalpy of pure component, i , and N_i is the component molar flux.

At the vapour film-vapour bulk as well as the liquid film-liquid bulk interface (where $z=1$), the heat fluxes due to conduction and convection given in equations (4.7) and (4.11) are estimated as follows:

$$H^{cond} = \frac{-\lambda}{\delta} \frac{\partial T}{\partial z} \Big|_{z=1} \quad (4.16)$$

$$H^{conv} = H_{flux} \Big|_{z=1} = \sum_{i=1}^{nc} N_i \Big|_{z=1} h_i^M \Big|_{z=1} \quad (4.17)$$

4.3.4 Interface model

$$f_i^L \cdot x_i^{M,L} = f_i^V \cdot x_i^{M,V} \quad (4.18)$$

Phase equilibrium between liquid and vapour phases is assumed at the interface. The equilibrium molar compositions of the components in the vapour and liquid

phases, $x_i^{M,V}$ and $x_i^{M,L}$ are estimated based on the vapour and liquid fugacity coefficients, f_i^V and f_i^L respectively.

4.3.5 Physical property estimation

Physical property estimations for viscosities, enthalpies and densities were determined using a physical property package, Multiflash[®], while the fugacity coefficients and flash calculations in the reboiler and condenser were determined using the Electrolyte Non-Random-Two-Liquid (NRTL) model in Aspen Properties and accessed through the CAPE-OPEN Thermo interface. The fugacity coefficients are estimated based on additional features in the property model referred to as “electrolyte inserts” for MEA. These are data packages that use electrolyte capabilities, but also take into consideration equilibrium reactions of CO₂ in the liquid phase (given in Equations (4.1) to (4.5)) (Aspentech, 2010). The predictions from these “inserts” are valid up to 50 wt% MEA concentration and 120°C. Without these “inserts”, the Vapour-Liquid Equilibrium (VLE) predictions would be inaccurate. As such the VLE predictions from Multiflash are inaccurate and would require a separate model to account for the liquid phase reactions.

4.4 Steady-state validation of the absorber model

The absorber model was validated using pilot plant studies from the Separations Research Programme at the University of Texas at Austin (Dugas, 2006) (this program is briefly described in Section 2.5.1). The absorber column of the pilot plant is a packed column with a diameter of 0.427 m and total packing height of 6.1 m. This column consists of two 3.05 m packed bed sections with a collector plate and redistributor between the beds (Dugas, 2006). Out of the 48 experimental cases carried out in the research programme, two cases (Cases 32 and 47) were selected for steady state validation purposes. These two cases were selected because of their relatively high and low liquid to gas (L/G) mass flow rate ratios respectively. In addition, the regenerator pressures in Case 32 and Case 47 are above and below atmospheric pressure respectively. In the model validation the temperature profile predicted by the model is compared with the temperature measurements from the pilot plant. Figure 4.1 shows the location of temperature measurements in the absorber column. The bottom of the lower

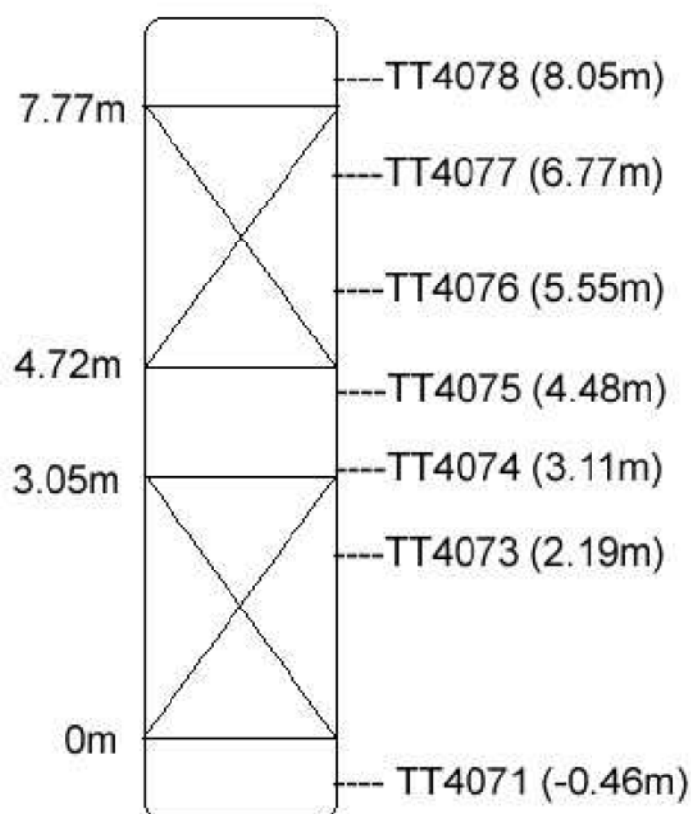


Figure 4.1 Absorber temperature measurement locations (Dugas, 2006)

packing bed in the column is used as the reference point (0 m). Therefore, the temperature measurement below the packing bed has a negative position value as shown in Figure 4.1. It should be noted that Dugas (2006) had reported a number of issues with the measurements in the pilot plant study. One of particular relevance is the measurement of the flow rate of gas to the absorber column that was reported to be inaccurate by Dugas (2006) and Kvamsdal et al. (2009). Attempts were made to acquire additional data for validation from other pilot plant studies which would have made the validation exercise more robust. These attempts were, however, unsuccessful. Emphasis was, therefore, placed on whether the models provided accurate qualitative predictions of the pilot plant measurements and not necessarily their absolute values. Features such as the shape of the temperature profile and the location of the maximum temperature in the columns were considered important.

For simulation of the equilibrium-based model, the specifications presented in Table 4.1 were used with the Aspen Plus[®] Radfrac column model.

Table 4.2 shows the inlet process conditions for the lean MEA and flue gas streams to the absorber while Table 4.3 shows some absorber column and packing specifications used in the rate-based absorber model.

Simulation results were validated using the temperature profile of the absorber column measured in the pilot plant (Dugas, 2006). In addition, the measured CO₂ loadings of the amine solvent taken at different positions were compared with values obtained from simulation. The rate-based absorber model topology in gPROMS[®] is shown in Figure 4.2.

Table 4.1 Specifications for equilibrium-based model

Description	Value
Number of equilibrium stages	7
Type of packing	IMTP
Packing material	Metal
Packing Dimension (m)	0.038
Packing height (m)	6.1
Condenser	None
Reboiler	None
Physical Property Method	Electrolyte NRTL

Table 4.2 Inlet process conditions for absorber in Case 32 and Case 47

	Case 47		Case 32	
Stream ID	FLUE GAS	LEAN MEA	FLUE GAS	LEAN MEA
Temperature (K)	332.3	313.3	319.7	313.8
Total flow (kg/s)	0.158	0.642	0.13	0.72
L/G ratio	4.1		5.5	
Mass fraction				
H ₂ O	0.0193	0.6334	0.0148	0.6334
CO ₂	0.2415	0.0618	0.2520	0.0618
MEA	0.0000	0.3048	0.0000	0.3048
N ₂	0.7392	0.0000	0.7332	0.0000

Table 4.3 Absorber column and packing specifications

Description	Value
Column inside diameter (m)	0.427
Height of packing (m)	6.1
Nominal packing size (m)	0.0381
Specific area (m^2/m^3)	145

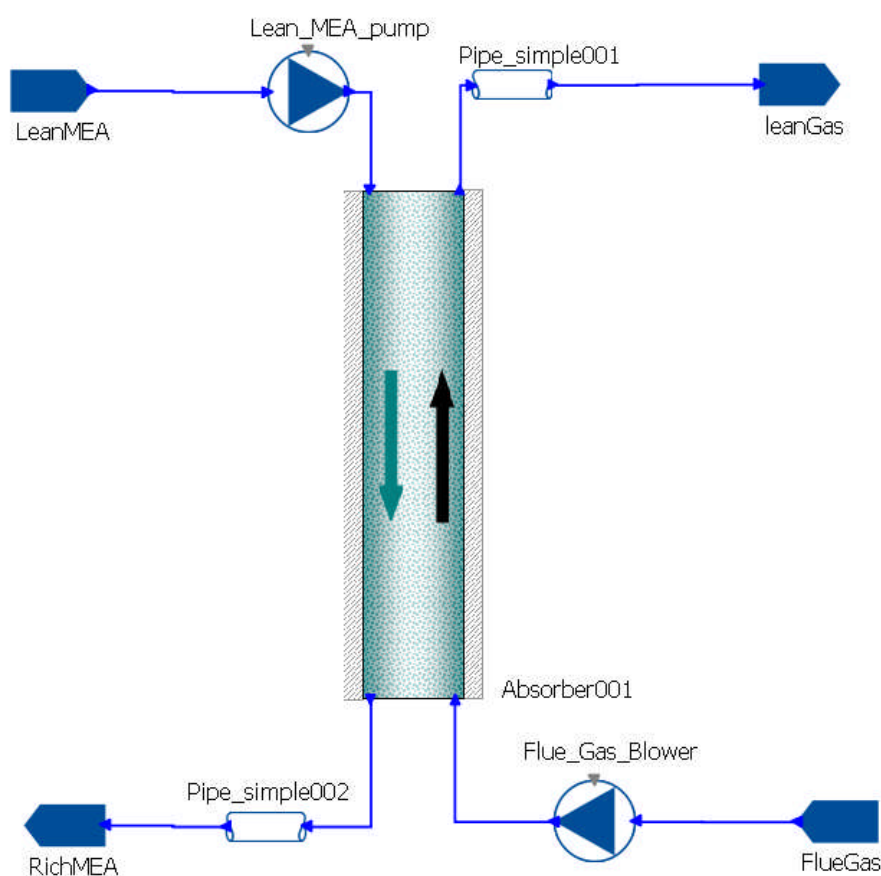


Figure 4.2 Absorber rate-based model topology in gPROMS®

4.4.1 Validation results - Case 32

The validation results for Case 32 are shown in Table 4.4, Figures 4.3 and 4.4. With the original flue gas mass flow rate of 0.13 kg/s, the model predicted a capture level less than what was measured. In addition, the shape of temperature profile did not match the reported shape. To correct for the errors, the flue gas mass flow rate was adjusted to obtain a similar capture level as reported in the pilot plant study. This was done in a similar fashion as described by Kvamsdal et al. (2009) for the same case.

Table 4.4 Case 32 process conditions and validation results

	Pilot plant measurements	Equilibrium- based model	Rate-based model	Equilibrium- based model	Rate-based model
Flue gas flow rate (kg/s)	0.13	0.12*	0.12*	0.11*	0.11*
L/G ratio (kg solvent/kg flue gas)	5.5	6	6	6.5	6.5
Lean solvent loading mol CO ₂ /mol MEA	0.279	0.279	0.279	0.279	0.279
Rich solvent loading mol CO ₂ /mol MEA	0.428	0.469	0.464	0.456	0.456
CO ₂ absorption level (%)	95.0	97.8	94.4	99.6	99.5

*Adjusted flue gas flow rate

It was found that 0.12 kg/s flue gas mass flow rate gave good agreement with pilot plant measurements of capture level (Table 4.4). However, both the rate-based and equilibrium-based models gave poor predictions of the temperature profile as shown in Figure 4.3. With reduction in the inlet flue gas rate to 0.11 kg/s, closer predictions of the temperature profile were observed as shown in Figure 4.4. However, the models in this case predicted higher CO₂ capture levels than what was measured in the pilot plant (Table 4.4). Some deviations (as seen in Table 4.4) may be due to the assumption that the reactions between CO₂ and MEA are at equilibrium as calculated by the electrolyte solution chemistry. A model with kinetically controlled reactions may therefore provide better predictions of the trend. The accuracy of the rate-based and equilibrium-based models was calculated (for the 0.11kg/s inlet flue gas rate case) by estimating the average percent deviation of the temperature predictions along the height of the column. The estimation is described in Appendix A and Section A.1. The average percent deviation calculated was 2.0% for the rate-based model and 3.1% for the equilibrium-based model.

For both cases, the rate-based model gives a better prediction of the absorber temperature profile (Figure 4.3 and Figure 4.4) compared with the equilibrium-based model results from Aspen Plus. The equilibrium-based model predicts higher

temperatures than those measured in the pilot plant study. In addition, with 0.12 kg/s flue gas flow, it predicts higher CO₂ capture levels (97.8%) compared with what was measured (95%). By comparing Figures 4.3 and Figure 4.4, it could be observed that the predictions of the temperature profile from the equilibrium-based model hardly change despite the change in flue gas mass flow rate. This could be due to its assumption of phase equilibrium which would overestimate mass transfer rates.

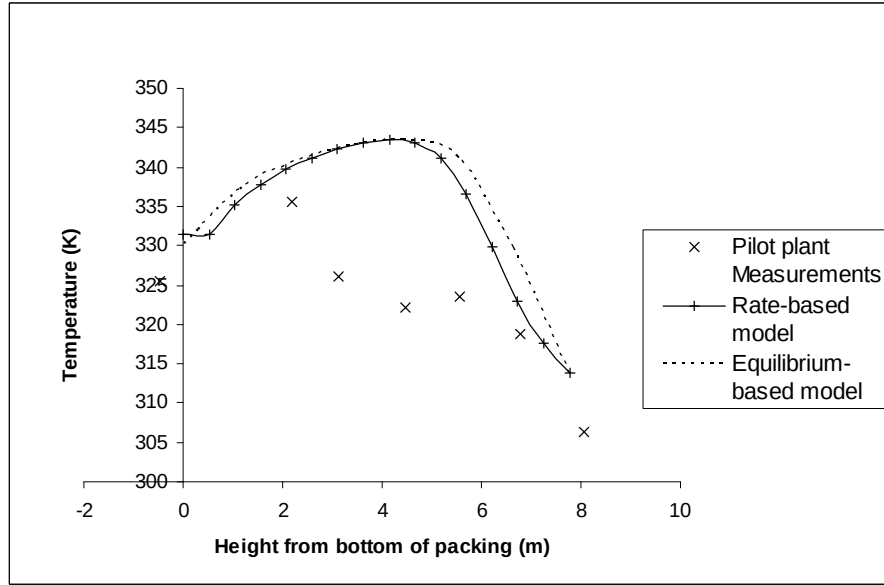


Figure 4.3 Validation results based on absorber liquid temperature profile for Case 32 with flue gas mass flow rate = 0.12 kg/s

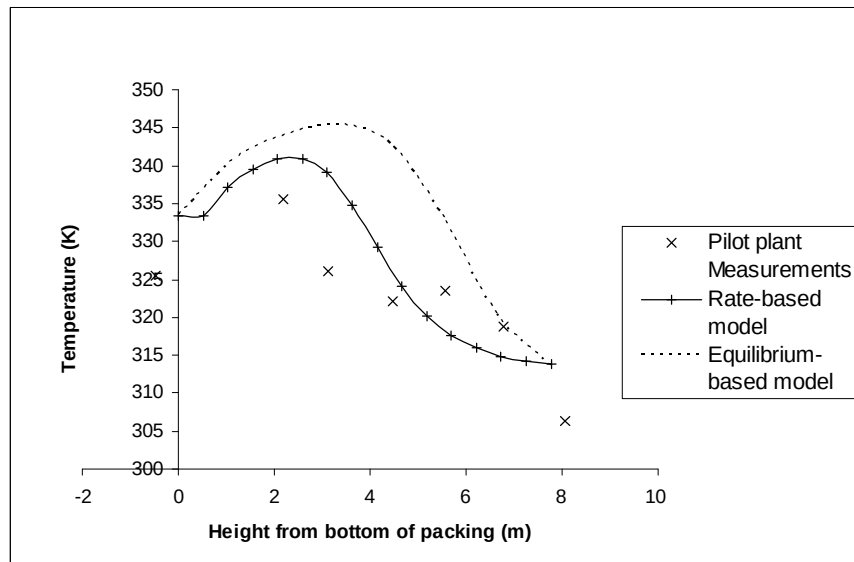


Figure 4.4 Validation results based on absorber liquid temperature profile for Case 32 with flue gas mass flow rate = 0.11 kg/s

The temperature profile of the absorber column reveals a “temperature bulge” (maximum temperature) close to the bottom of the absorber packing (Kvamsdal and Rochelle, 2008). The chemical absorption of CO₂ is an exothermic process. Therefore, the temperature of the liquid solvent rises as it flows down the column. As temperatures rise, the rate of evaporation of water from the liquid solvent increases as well. Close to the top of the column, water vapour in the vapour stream will condense as it contacts the cooler liquid solvent whilst close to the bottom of the column, water will evaporate from the hotter solvent. These effects are responsible for the “temperature bulge” typically observed in the absorber columns of the chemical absorption process (Kvamsdal and Rochelle, 2008). Kvamsdal and Rochelle (2008) explain that the magnitude and location of the temperature bulge depend on several factors including the L/G ratio. The rate-based model predicts this location better. Dugas (2006) reports that for the experimental cases conducted, the bulge was located at the top of the absorber with L/G ratio less than 5 kg solvent/kg flue gas and at the bottom of the absorber with L/G ratio greater than 6 kg solvent/kg flue gas. Based on the reported measurements, the L/G ratio in Case 32 was between 5 and 6 kg solvent/kg flue gas. This might explain the big shift in temperature predictions observed when changing the flue gas mass flow rate. At 0.11kg/s flue gas mass flow, the L/G ratio becomes 6.5 kg solvent/kg flue gas.

4.4.2 Validation results - Case 47

The validation results for Case 47 are shown in Table 4.5 and Figure 4.5. This case involved a relatively low liquid to gas (L/G) ratio, thus a lower CO₂ capture level. Once again, because of the reported inaccuracy in the flue gas flow measurement (Dugas, 2006; Kvamsdal et al., 2009), its value was adjusted to match reported capture levels as shown in Table 4.5. Both the equilibrium-based and rate-based models predicted lower rich solvent loading than what was measured while the absorption levels are virtually the same as measured. The reason for this discrepancy is not clear.

The temperature profile in the absorber was used to validate the two models as shown in Figure 4.5. Both models generally predict the absorber temperature profile fairly well. The rate-based model gives a better prediction as the equilibrium-based model predicts generally lower temperatures than what was measured. The average percent deviation

was estimated in Appendix A, Section A.2 as 2.3% for the rate-based model and 3.1% for the equilibrium-based model. The “temperature bulge” reported by Kvamsdal and Rochelle (2008) is located close to the top of the absorber packing in this case.

Table 4.5 Case 47 process conditions and validation results

	Pilot plant measurements	Equilibrium-based model	Rate-based model
Flue gas flow rate (kg/s)	0.158	0.172*	0.172*
L/G ratio (kg solvent/kg flue gas)	4.1	3.7	3.7
Lean solvent loading (mol CO ₂ /mol MEA)	0.281	0.281	0.281
Rich solvent loading (mol CO ₂ /mol MEA)	0.539	0.500	0.487
CO ₂ absorption level (%)	69.0	68.8	69.2

*Adjusted flue gas flow rate

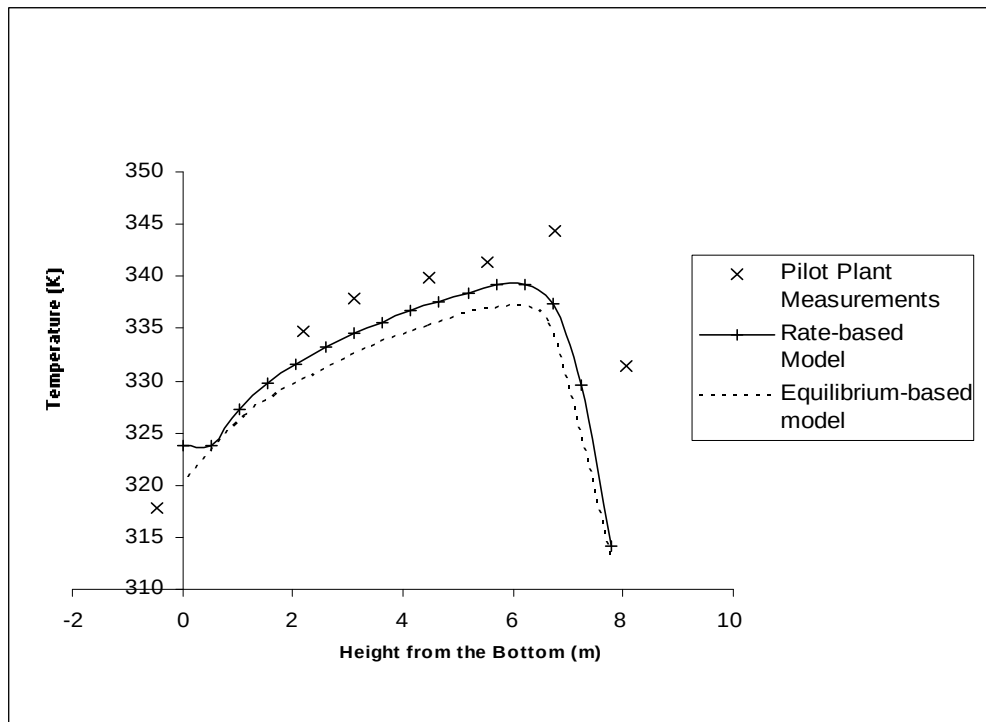


Figure 4.5 Validation results based on Absorber liquid temperature profile for Case 47

4.5 Rate-based regenerator model development

The packed column section of the regenerator model was modelled in a similar fashion to that described in Sections 4.3.1 – 4.3.5 except for a modification in the liquid energy balance. This is so because the regenerator operates at higher temperatures than the absorber and thus heat loss to the surroundings would become more important.

As a result, the energy balance presented in equation (4.7) becomes:

$$\text{Energy Balance: } \frac{\partial U}{\partial t} = \frac{-1}{L \cdot A} \frac{\partial F_H^L}{\partial y} + Sp \cdot \omega \cdot (H_{liq}^{cond} + H_{liq}^{conv} + H_{abs}) + HL \quad (4.19)$$

$$\text{Heat Loss (HL)} = \frac{131.64 \times \text{Column Surface Area} \times (T_{regen_bottom} - T_{ambient})}{\text{Height} \times \text{Cross Sectional Area}} \quad (4.20)$$

The Heat Loss (*HL*) is calculated in the regenerator column model alone. The value is calculated based on the temperature difference between the regenerator bottoms temperature (T_{regen_bottom}) and the ambient temperature ($T_{ambient}$). It is calculated per unit volume and distributed evenly along the axial length of the column. The constant value of $131.64 \frac{W}{m^2 K}$ was derived from a correlation from the University of Texas at Austin test results (Dugas, 2006). Dugas (2006) reported a correlation obtained from experimental studies at pilot plant scale. This correlation was extrapolated based on the increased surface area of the column at commercial scale. The heat losses to the surroundings are fully accounted for in the liquid phase, so this term is not repeated in the vapour bulk energy balance.

The regenerator model was completed by adding condenser and reboiler models to the packed column section model. These models were developed based on the flash drum model in the Process Model Library in gPROMS[®]. The flash drum model describes the flash separation of vapour and liquid phases (Process Systems Enterprise, 2009). The flash drum is modelled as an equilibrium stage where vapour-liquid equilibrium is predicted using the Electrolyte NRTL property package described in Section 4.3.5. Heating and cooling duties could be specified in the model to depict the level of heat addition (in the reboiler) and removal (in the condenser). For simplification, in the stand-alone regenerator model, absolute values of reboiler and condenser heat duties are

supplied directly. Figure 4.6 shows the model topology of the regenerator stand-alone model. Two P-controllers are employed to control the levels of liquid in the condenser and reboiler respectively.

4.6 Steady-state validation of regenerator model

Validation is only performed for the rate-based regenerator model. The feed conditions to the regenerator for Cases 32 and 47 are shown in Table 4.6. In Case 47, the regenerator is operated at a pressure below atmospheric whilst in Case 32 it is conducted above atmospheric pressure. The composition of the feed to the regenerator was estimated based on the results from stand-alone absorber model simulations for the respective cases.

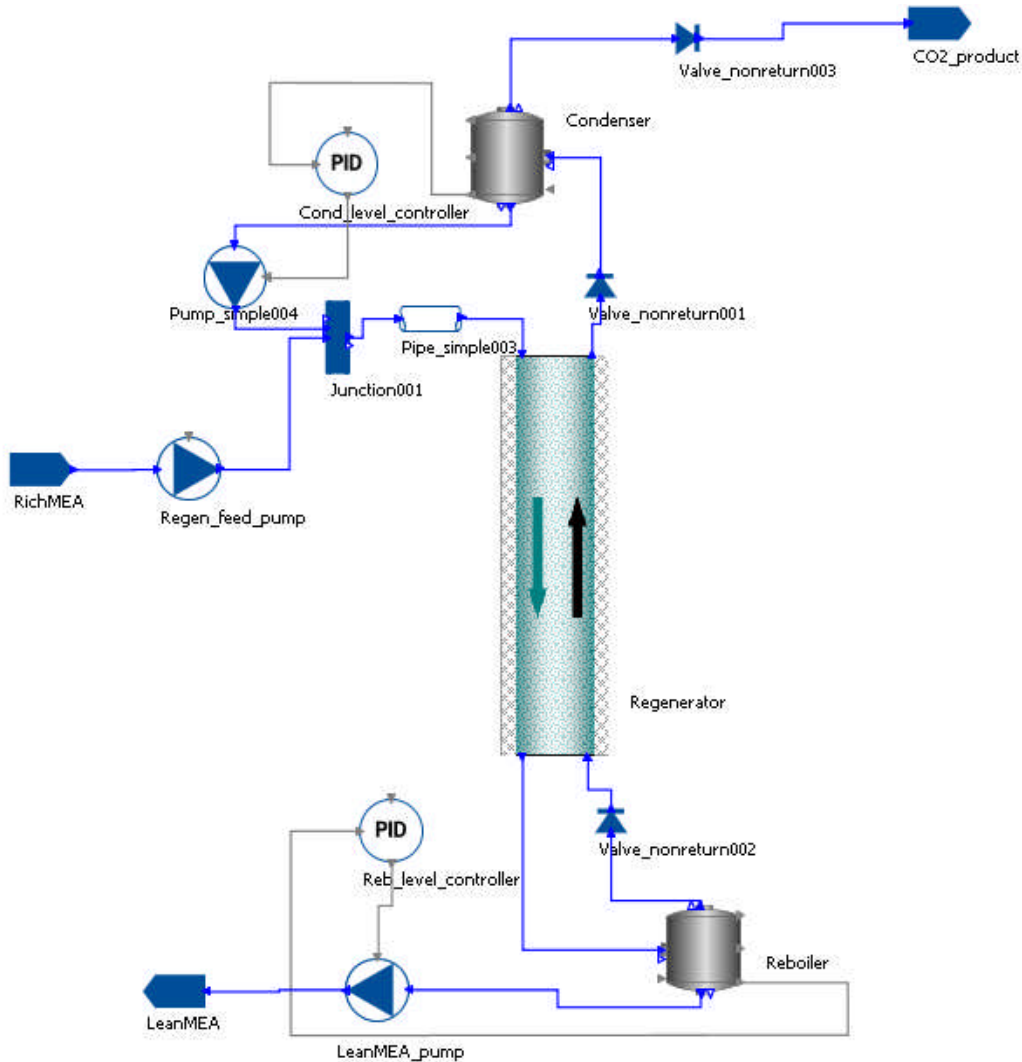


Figure 4.6 Regenerator rate-based model topology in gPROMS®

Table 4.6 Process conditions for regenerator in Cases 32 and 47

	Case 47	Case 32
Stream ID	RICH MEA	RICH MEA
Temperature (K)	356	358
Pressure (10^5 Pa)	0.690	1.630
Regenerator feed flow (kg/s)	0.746	0.745
Reboiler Duty (W)	205,000	152,222
Condenser Duty (W)	134,168	10,000
Mass fraction		
H ₂ O	0.6085	0.6122
CO ₂	0.0966	0.0971
MEA	0.2943	0.2901

Table 4.7 Regenerator column and packing specifications

Description	Value
Column inside diameter (m)	0.427
Height of packing (m)	6.1
Nominal packing size (m)	0.0381
Specific area (m^2/m^3)	420

4.6.1 Validation results - Case 32

Temperature profiles predicted by the rate-based model were compared with the measurements from the pilot plant and shown in Figure 4.7. The results show a fairly good prediction of the pilot plant measurements especially with regard to the shape of the profile. There are, however, quite significant differences in the absolute temperature predictions. This could be due to the fact that the feed process conditions for the regenerator (Table 4.6) are obtained from the simulation results of the rate-based absorber model. Errors in the results of that simulation would therefore be propagated to the regenerator simulation. Better predictions of the feed conditions would give better results. The average percent deviation was estimated in Appendix A, Section A.3 as 3.1%.

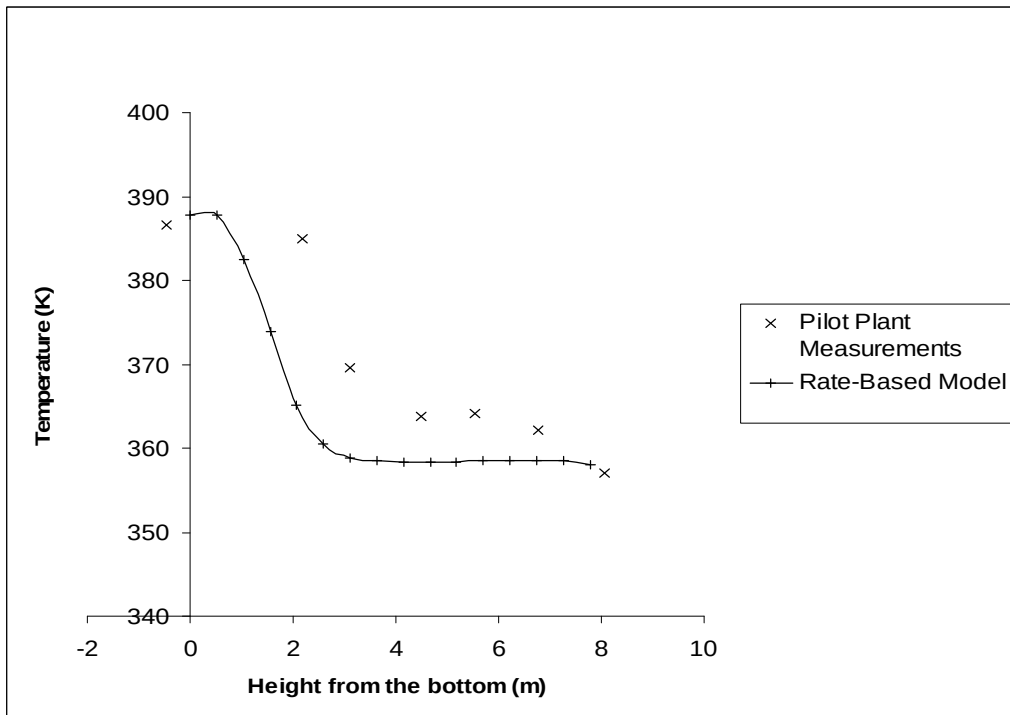


Figure 4.7 Validation results based on regenerator liquid temperature profile for Case 32

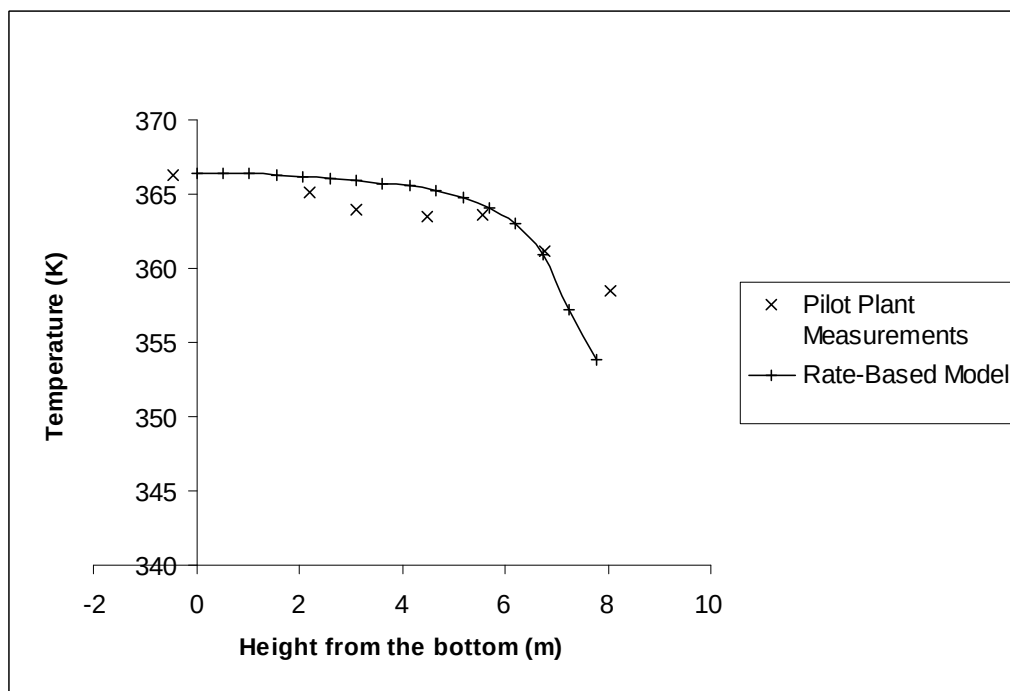


Figure 4.8 Validation results based on regenerator liquid temperature profile for Case 47

4.6.2 Validation results - Case 47

Temperature profiles predicted by simulation were compared with the measurements from the pilot plant and shown in Figure 4.8. These results show good agreement between the predictions and the measurements. The average percent deviation was estimated in Appendix A, Section A.4 as 0.8%. The temperatures in Case 47 are significantly lower than those in Case 32. This is because higher temperatures are required to regenerate the solvent at the higher pressures found in Case 32 compared with Case 47 thus a maximum solvent temperature of about 389 K in the former compared with 366 K in the latter.

At first glance, the higher reboiler duty in Case 47 is unexpected since regenerator temperatures are far lower. However, by observing the condenser duties (Table 4.6) some insight to why this occurs is obtained. In Case 47, the lower regenerator operating pressure and the corresponding lower regenerator temperatures mean that larger quantities of stripping vapour are required for regeneration. To produce such quantities of vapour, a large heating duty is demanded in the reboiler. The condenser cooling duty also increases as it has to condense a lot more vapour (the vapour mass flow rate into the condenser is over twice that recorded in Case 32). It is likely due to this increased mass flow rates of stripping vapours that there is a difference in regenerator temperature profile for Case 47 compared with Case 32. In Case 32, the relatively small mass flow rates of the stripping vapours would increase solvent temperatures close to the bottom of the column while the inlet temperature of the solvent dictates the temperature of the rest of the column. In Case 47, the higher mass flow rates of stripping vapours would raise the temperature of the solvent over a greater height from the bottom of the column.

The simulation results of the rate-based model in both cases are generally in agreement with the pilot plant measurements especially with regards to the shape of the profile in the two different cases.

4.7 Rate-based amine plant model

Linking the absorber to the regenerator column (including recycle) involves the inclusion of a number of auxiliaries as shown in Figure 4.9:

- Rich MEA pump.
- Lean/Rich MEA Heat Exchanger.
- Lean MEA Storage Tank.
- Lean MEA Cooler.

4.7.1 Rich amine pump (“Rich_MEA_from_abs_pump”)

The rich amine pump delivers the rich MEA solvent to the regenerator column via the Lean/Rich MEA exchanger. The regenerator may operate at a higher pressure than the absorber as seen in Case 32.

4.7.2 Lean/rich MEA heat exchanger (“Cross_exchanger”)

The lean/rich MEA heat exchanger is used to reduce the heat requirement of the process. The rich MEA from the absorber is heated using the lean MEA stream from the regenerator, which would naturally be at a higher temperature. It should be noted that the study by Dugas (2006) did not include this equipment – rather there was a combination of heater and cooler used to achieve the required process conditions.

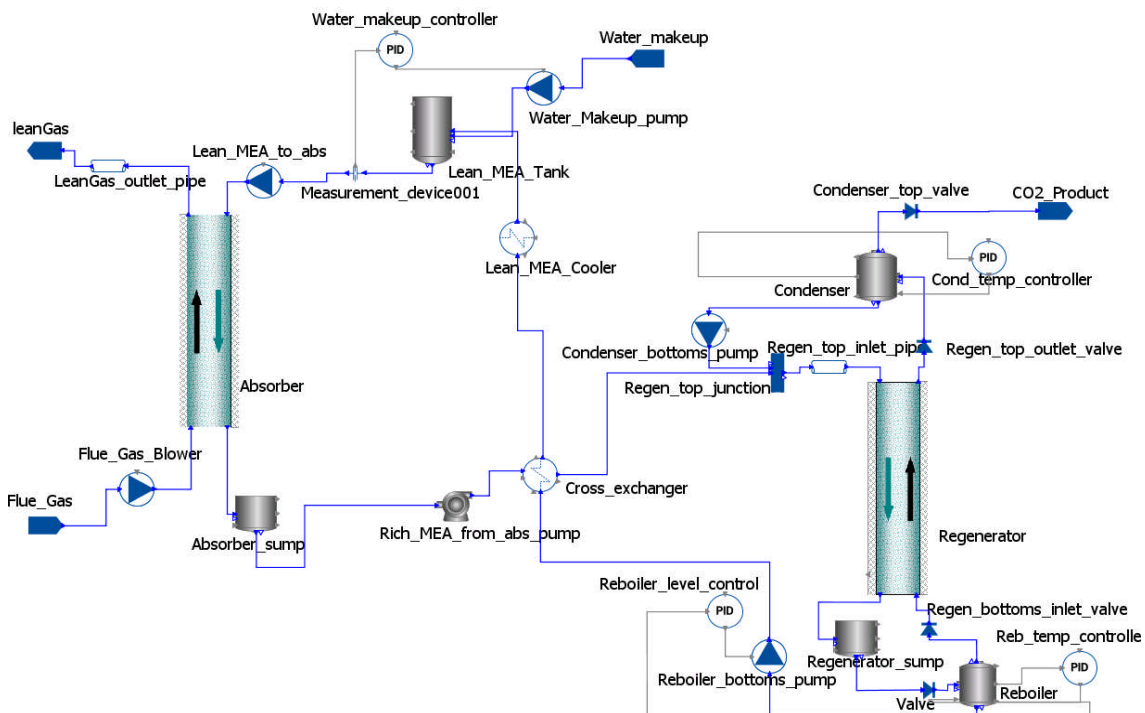


Figure 4.9 Amine plant model topology in gPROMS®

Table 4.8 Process controllers in amine plant model

	Controlled Variable	Setpoint	Manipulated Variable
Condenser Temperature Controller	Condenser temperature	320 K	Condenser heat duty
Reboiler Temperature Controller	Reboiler temperature	387 K	Reboiler heat duty
Reboiler Level Controller	Reboiler level	50%	Reboiler bottoms flow rate
Water Makeup Controller	Water mass fraction in lean solvent	0.6334	Water Makeup flow
Capture Level Controller	CO ₂ capture level in absorber	97%	Lean MEA solvent flow

4.7.3 Lean MEA storage tank

The lean MEA storage tank serves as a buffer in the amine plant model. In addition, it provides an avenue for measuring and maintaining water balance in the system. In a full scale plant where operation would continue for extended periods and the degradation of the solvent being used becomes more important, this tank could also be used to makeup MEA concentration in the solvent.

4.7.4 Lean MEA cooler

The lean MEA stream from the lean/rich MEA heat exchanger is hardly cool enough for ideal operation in the absorber (roughly about 40°C). An additional cooler is used to achieve the required temperature levels.

4.7.5 Controllers for the process

Control schemes are illustrated in Figure 4.9 and listed in Table 4.8. The PI controllers are used for temperature control of the regenerator column. The temperatures of the top and bottom of the regenerator are manipulated using the condenser and reboiler heat duties. The temperature of the regenerated solvent determines its CO₂ loading and thus affects its absorption capacity. Therefore, the temperature of the solvent from the regenerator bottoms must be maintained at desired levels. The reboiler level was

controlled using a P controller by manipulating the reboiler bottoms flow rate.

The temperature and capture level setpoints given correspond to what was reported for Case 32. Water balance is achieved by controlling the water mass fraction in the lean solvent with the water makeup flow rate used as manipulated variable. A typical composition of the lean MEA stream consists of 30.48 wt% MEA, 6.18 wt% CO₂, which leaves a 63.34 wt% H₂O. The setpoint for the mass fraction of water in the lean solvent was therefore set as 0.6334. The level in the reboiler was assumed to be controlled at 50%.

The percentage of CO₂ captured in the absorber column is measured and controlled by manipulating the lean MEA solvent flow rate. The cross heat exchanger allows for the exchange of heat between the lean MEA solvent from the regenerator and the rich MEA solvent from the absorber. The cooler upstream of the lean MEA tank is specified to have a constant outlet temperature. The pressure of the partial condenser is controlled by a non-return valve as shown in Figure 4.9 (“condenser_top_valve”) to maintain the regenerator column operating pressure. The rich MEA from absorber pump is specified to add the required head to enable flow between the absorber and regenerator including the pressure drops of the equipment in between.

4.7.6 Assumptions for model topology

The following are the assumptions and simplifications made in building the model topology:

- a. No water wash section in the absorber and regenerator columns. The water wash section minimizes the loss of solvent through evaporation in the column. In addition, it would help control the temperature of the flue gas leaving the absorber that is required for adequate water balance. However, the pilot plant study used to validate the model developed does not include a water wash section in the absorber as well as the regenerator. In the study, it was assumed that a similar topology as the pilot plant was maintained.
- b. To control water balance in the absorber, an idealistic case was assumed where a controller maintained the water composition in the lean solvent being circulated.

The lean amine solvent from the regenerator is fed into the lean MEA tank where water is made up before being pumped to the absorber. The water balance would likely be controlled by the temperature of the gas leaving the absorber.

- c. The absorber and regenerator sumps are modelled as simple tanks through which the bottom products flow as shown in Figure 4.9.

4.8 Steady state validation of rate-based amine plant model

Figure 4.10 shows the validation results for the absorber and regenerator columns when they are linked together with recycle as shown in Figure 4.9 and compares them with predictions from the stand-alone column models. The process conditions used are those of Case 32. The results show a different prediction of the temperature profile in the integrated model especially in the regenerator because of the limitations discussed in Section 4.6.1. In general, the integrated model gives a better prediction of the observed temperature profile. This is expected as the pilot plant consists of columns linked together with recycle and not stand-alone. As a result the two-way interaction between the two columns would be better predicted.

4.9 Dynamic validation of rate-based amine plant model

Kvamsdal et al. (2010b) discussed the dynamic validation of an absorber model with an absorber of 5.4 m packing height using Mellapak 2X structured packing. The dynamic

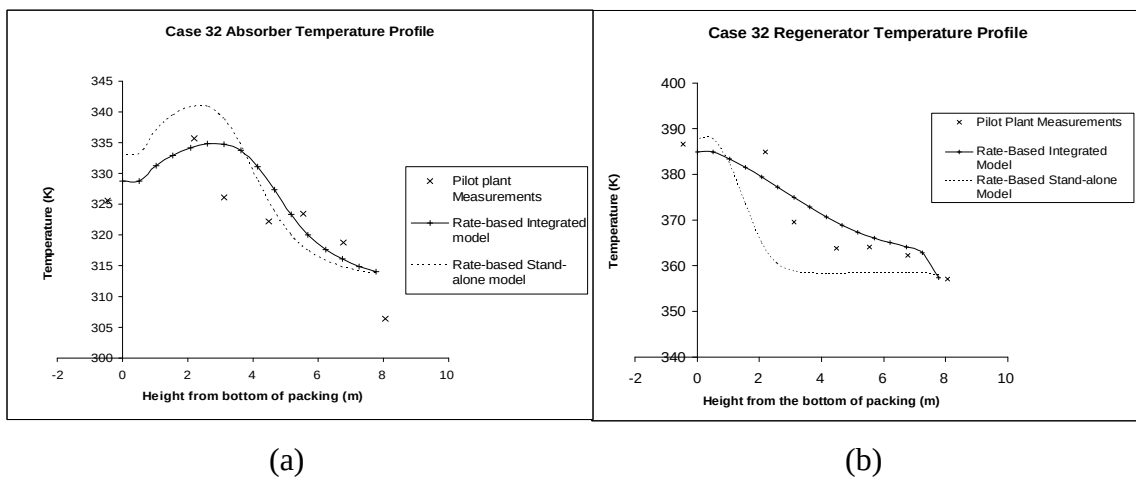


Figure 4.10 (a) Absorber and (b) Regenerator temperature profile for Case 32 from stand-alone and integrated model

response to a change in CO₂ content in the inlet flue gas stream was considered. The validation discussion was quite brief – only the CO₂ removal rates and the rich loading were compared. During the course of the test, the model predicted CO₂ removal rates that were about 10% higher than the measured values. The CO₂ loading of the rich solvent was also overestimated.

In Section 4.8, steady state validation was carried out using the pilot plant study at the University of Texas at Austin (Dugas, 2006). A similar dynamic validation study based on logged measurements from the pilot plant study at the University of Texas at Austin (Dugas, 2006) is carried out in this section.

4.9.1 Dynamic validation methodology

The dynamic validation was also carried out using logged data from the Separation Research Programme at the University of Texas at Austin (Dugas, 2006). None of the tests were meant to be strictly dynamic tests. However, a few steady state tests were carried out consecutively and certain conditions were changed from one steady state value to the next to achieve this. Logged data of the MEA campaign was obtained and the most suitable case for dynamic validation was chosen. This case was selected based on the following criteria:

- Significant change in the plant input that would affect CO₂ capture performance.
- Minimal number of additional disturbances in other inputs.

Based on these criteria, the selected case corresponds to the transition away from Case 25 (process conditions given in Table 4.9). There are three main disturbances in this test. The first involves the slow decrease in lean solvent flow to the absorber consisting of several small step reductions as shown in Figure 4.11(a). A constant reboiler temperature setpoint was assumed and a controller adjusts the reboiler heat duty to maintain this. The composition and temperature of the inlet gas stream to the absorber were found to vary significantly as shown in Figure 4.11(b) and (c) respectively and constitute the other disturbances.

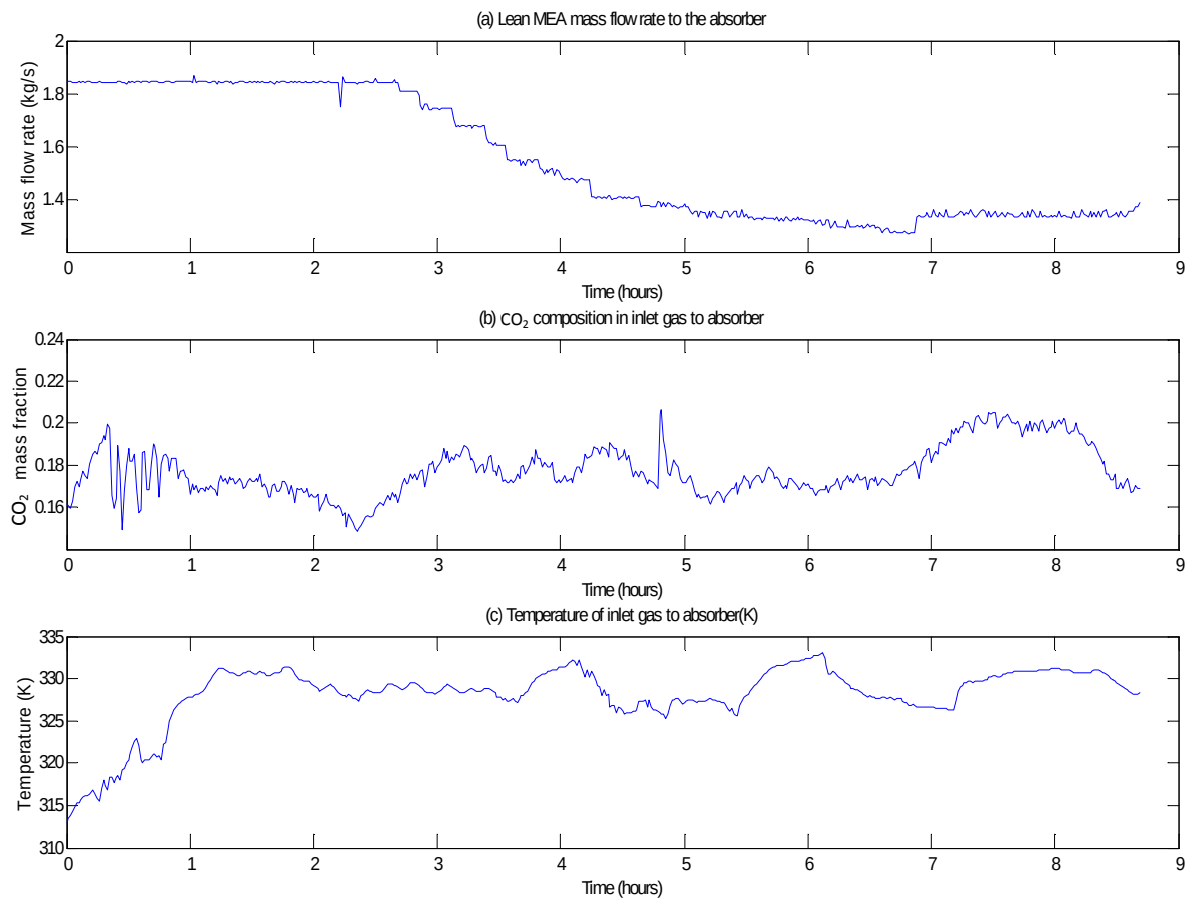


Figure 4.11 Changes in process conditions in dynamic validation test case

Table 4.9 Initial process conditions for dynamic test (Case 25)

Stream ID	FLUE GAS	LEAN MEA
Temperature (K)	313	316
Pressure (10^5 Pa)	1.05	1.05
Total flow (kg/s)	0.235	1.840
Mass fraction		
H ₂ O	0.015	0.633
CO ₂	0.159	0.059
MEA	0.000	0.308
N ₂	0.826	0.000

Other variables were either constant or could be assumed to have negligible effect on the validation results. Table 4.9 shows the process conditions used at the onset of the

dynamic test. The same column specifications for the absorber and regenerator given in Table 4.3 and Table 4.7 apply for the dynamic validation test.

To account for the changes in inputs (i.e. disturbances) to the plant, a gPROMS[®] / Microsoft Excel foreign process interface was developed, which enabled gPROMS[®] to read off a time sequence of the input values for the lean MEA mass flow, the inlet gas CO₂ and nitrogen compositions of the gas (water vapour content was assumed to be constant) as well as the inlet gas temperature to the absorber from a Microsoft Excel spreadsheet. With the assumption of constant water vapour content, the nitrogen composition could be estimated based on the CO₂ composition.

4.9.2 Dynamic validation results

The results of the dynamic validation are shown in Figures 4.12(a-e). Figures 4.12 (a-c) compare the logged plant measurements and dynamic model predictions of absorber temperature at various locations. Figure 4.12(d) compares these two for the treated gas CO₂ mass fraction as it leaves the absorber, which indicates the level of CO₂ captured. The reboiler duty values are compared in Figure 4.12(e).

The changes in temperature with time around the top (6.77 m above bottom of packing), middle (4.48 m above the bottom of packing) and bottom (2.05 m above the bottom of packing) in the absorber were compared with the corresponding predictions from the dynamic model. The model predicts these changes without much deviation from pilot plant measurements especially at the earlier part of the test (before the 7-hour mark). Between the 7-hour and 8-hour marks, a temperature rise is observed throughout the column. This is followed by a reduction in temperature between the 8-hour and 9-hour mark. This appears to correspond to the rise CO₂ mass fraction and temperature of the inlet gas to the absorber as shown in Figure 4.11(b) and (c). Though the model predicts this trend well, the magnitude of the changes predicted by the model do not match those measured as well as they did before the 7-hour mark.

The dynamic model appears to overestimate the quantity of CO₂ captured/absorbed in the column. From Figure 4.12(d), throughout the test, the values of the CO₂ mass

fraction in the treat gas are much lower in the model compared with those measured in the pilot plant study. Again, the trend of fluctuations was well predicted by the model including the effect of the peak in CO₂ concentration in the inlet gas (Figure 4.11(b)). The difference in magnitude could be as a result of the assumption of all chemical reactions attaining equilibrium inherent in the dynamic model.

The dynamic model also appears to overestimate the heat duty required in the reboiler for solvent regeneration. A fairly good prediction of the trend is observed, however, there are differences in the magnitude of the heat duty predicted and measured especially after the ramp in solvent circulation rate (or lean solvent mass flow rate to the absorber – Figure 4.11(a)). This could be because of the higher level of CO₂ absorption predicted by the dynamic model – resulting in higher heat duty required to regenerate the solvent.

4.10 Process analysis at pilot plant scale

Dynamic analysis was carried out with the post-combustion CO₂ capture process model to gain insights on its operation. Analyses carried out include:

- A ramped increase in flue gas mass flow rate to the absorber column.
- A step decrease in reboiler duty.
- A step decrease in lean solvent mass flow rate to the absorber.

4.10.1 Increasing flue gas flow rate to the absorber

A dynamic case study was carried out to investigate the effect of an increase in the flue gas flow rate to the absorber. It is assumed that its composition is maintained during this process. The process was simulated with the base-load conditions (Case 32 in Table 4.2 and Table 4.6) for two hours afterwards a ramp corresponding to a 10% increase flue gas flow rate over a period of 10 minutes was carried out. The simulation was then left to run for just under eight hours. In Case 1, the solvent circulation rate was kept constant while in Case 2, the circulation rate was correspondingly increased to maintain the molar L/G ratio (Figure 4.13).

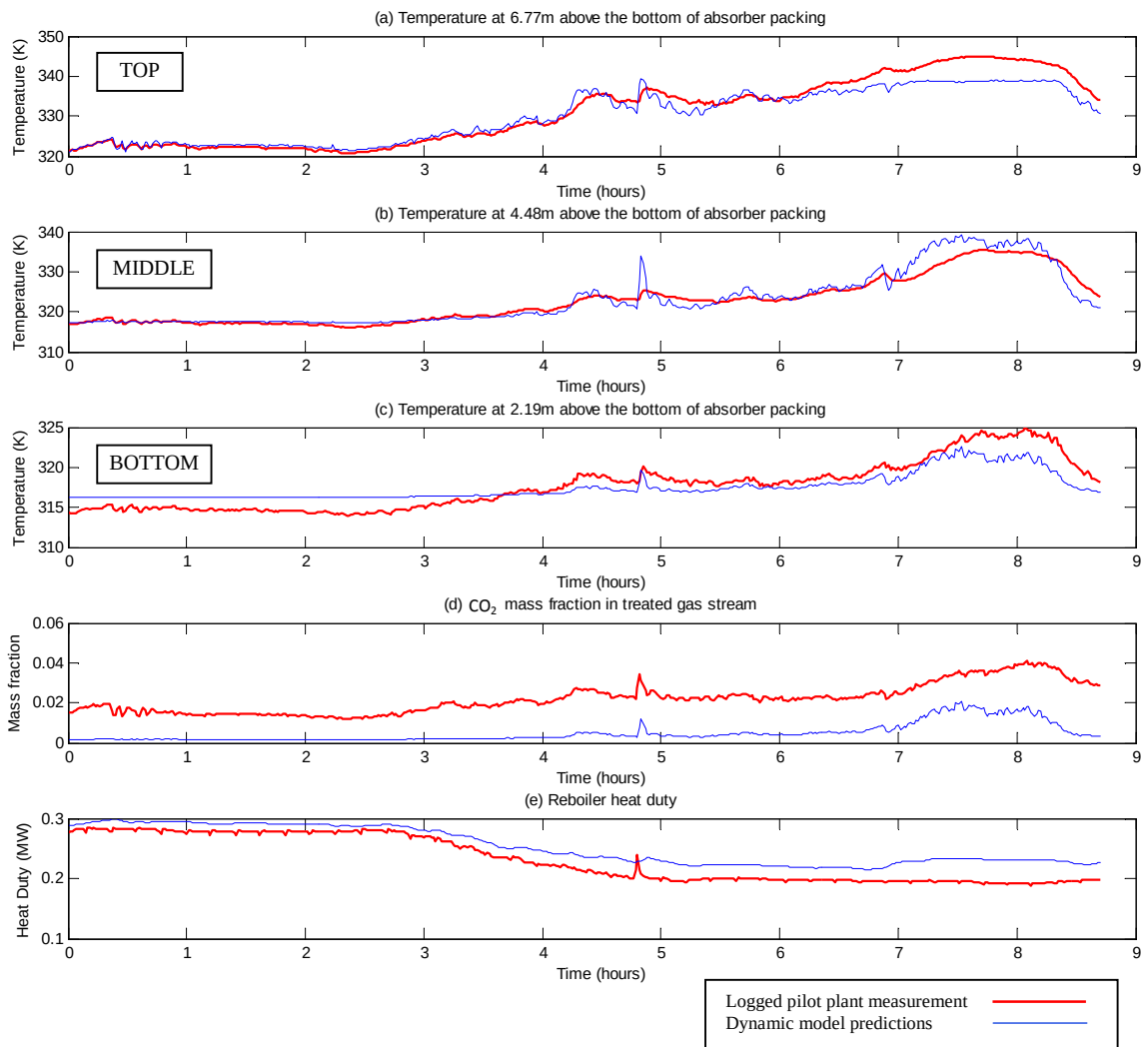


Figure 4.12 Comparison of logged plant measurements and dynamic model predictions

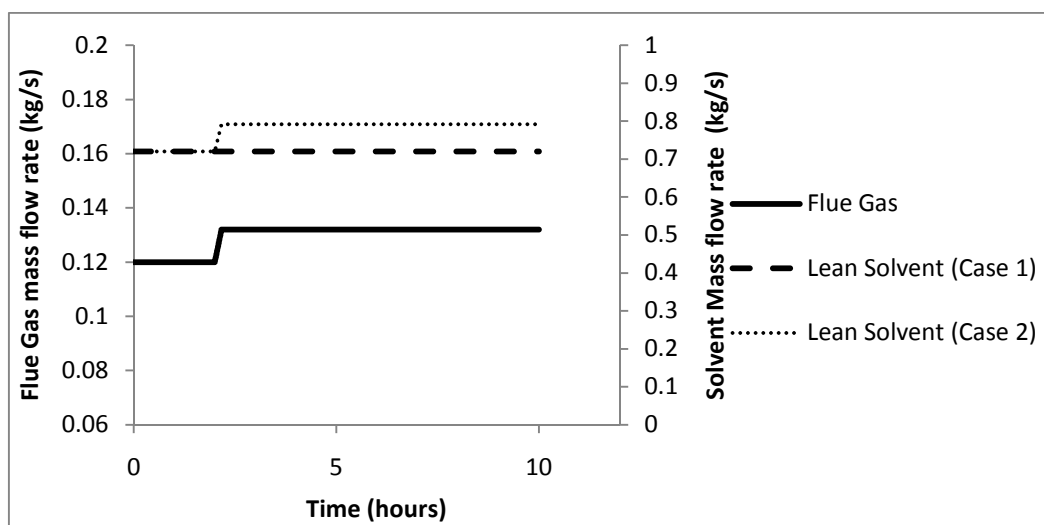


Figure 4.13 Flue gas and Lean MEA flow rate while increasing power plant load

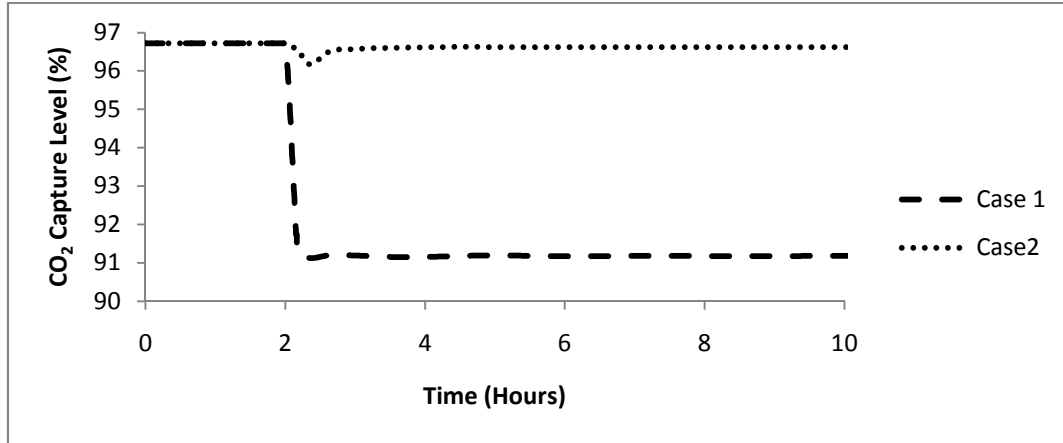


Figure 4.14 CO₂ capture level with increasing power plant load (Case 1 and Case 2)

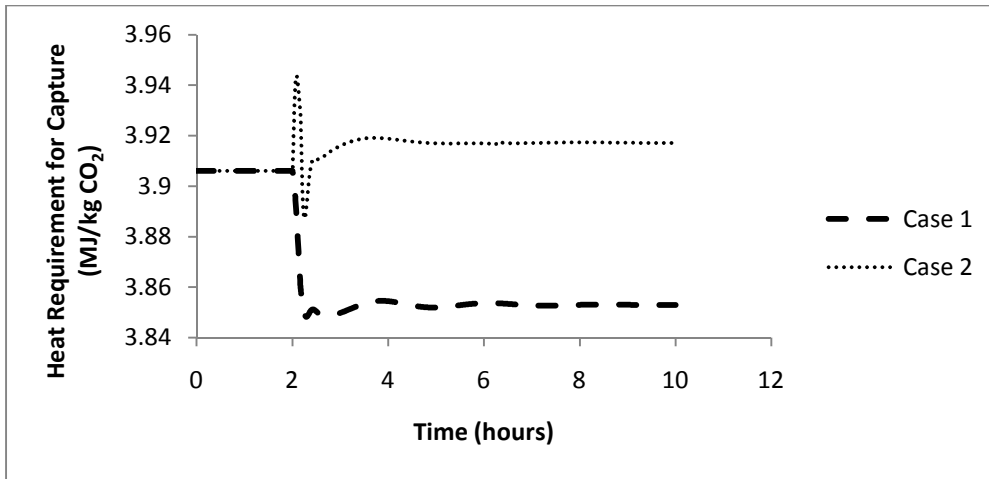
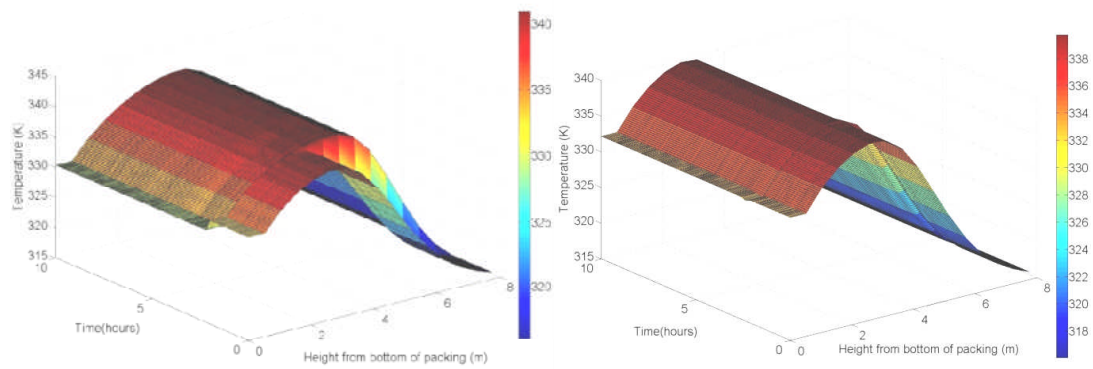


Figure 4.15 Heat requirement with increasing power plant load (Case1 and Case2)

Figure 4.14 shows a significant decrease in CO₂ capture levels at the onset of the disturbance for Case 1 and virtually the same capture level maintained for Case 2 after a slight drop. This is however at the cost of increased heat requirement for capture (Figure 4.15). The heat requirement for capture corresponds to the reboiler heat duty required to capture 1 kg of CO₂. In Case 1, its value drops because the lean solvent had the capacity to capture more CO₂ at the same circulation rate and attain a higher rich loading with the disturbance. The heat requirement for capture in Case 2 is higher than that of Case 1, but is maintained at almost the same level as before the disturbance. The oscillations observed are likely due to controller action. From Figure 4.16(a and b), it is shown that the temperature profile is virtually constant in Case 2 as compared with Case 1 where there are significant changes in temperature.



(a) 10% increase in flue gas flow
(L/G ratio varies)

(b) 10% increase in flue gas flow with
corresponding increase in lean solvent flow
(L/G ratio constant)

Figure 4.16 Absorber temperature profile with increasing power plant load for Case 1

(a) and Case 2 (b)

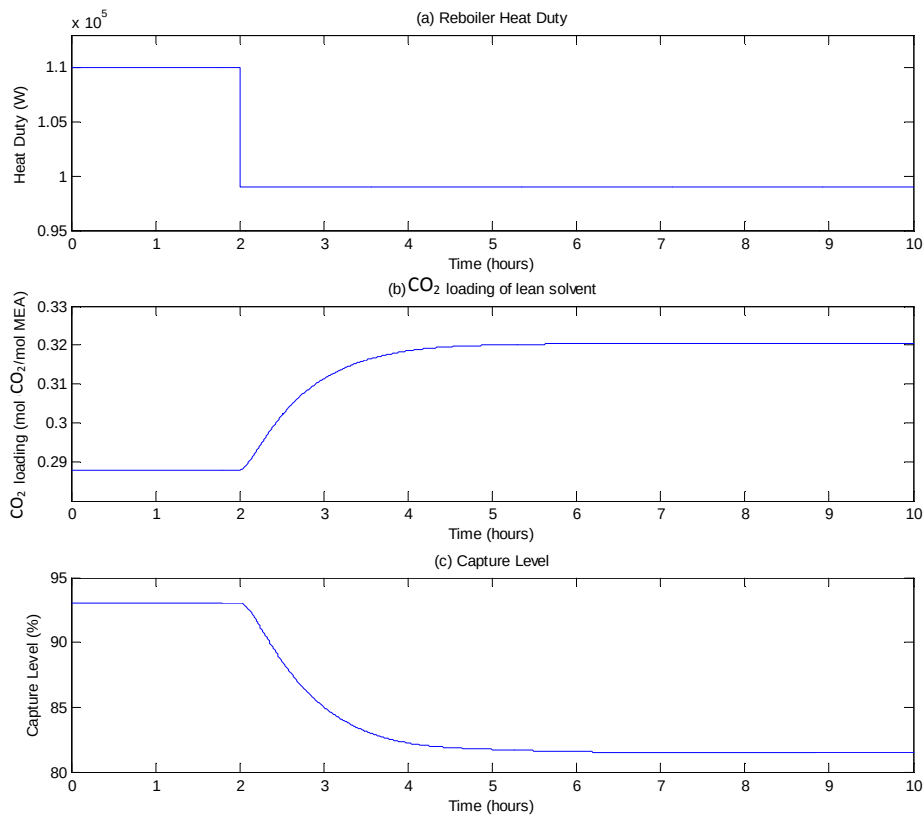


Figure 4.17 Reducing reboiler heat duty

4.10.2 A step decrease in reboiler heat duty

This case investigates the effect of a decrease in reboiler heat duty. This required heat duty for regeneration is supplied from the power generation process. Base conditions were maintained for a period of two hours (Case 32 in Table 4.2 and Table 4.6). A 10%

reduction in reboiler duty was implemented over 10 seconds (Figure 4.17(a)). Conditions were maintained for just under eight hours. A significant increase in CO₂ loading is observed of the lean solvent (Figure 4.17(b)) resulting from reduced reboiler temperature. This also had a significant effect on the absorption levels in the absorber column (Figure 4.17(c)).

Since the change is carried out over a relatively short period of time, Figure 4.17(b) could be viewed as a step response and a time constant could be estimated. The time constant estimated for the process was 3420 seconds or 57 minutes. It should be noted that the holdup of solvent in the absorber and regenerator sumps, lean MEA storage tank and reboiler would contribute to such a big time constant. It should be noted that in this model, transport delay has not been accounted for.

4.10.3 A step decrease in lean solvent supply to the absorber

This case investigates the effect of a decrease in lean solvent flow to the absorber. Essentially the solvent circulation rate is being reduced. The lean solvent flow to the absorber was directly manipulated to investigate the step response of the absorber to disturbances. Base conditions were maintained for a period of four hours (Case 32 in Table 4.2 and Table 4.6). A 10% reduction in lean solvent mass flow rate was implemented over 10 seconds (Figure 4.18(a)). Conditions were maintained for eight hours. The response of the CO₂ capture level (observed in Figure 4.18(c)) is as a result of two separate phenomena. The first is the relatively fast response of the absorber CO₂ capture level to the initial reduction in lean solvent mass flow rate at the same composition. However, this is accompanied by the second phenomenon where the loading of the lean solvent decreases slowly (as shown in Figure 4.18(b)). This decrease is because less solvent is circulated in the system and with the same heat duty maintained in the reboiler, the temperature of the lean solvent in the reboiler increases and slowly attains a new steady state as shown in Figure 4.18(d). The significant holdup of liquid in the reboiler and the lean MEA tank would contribute to the slow reduction in lean solvent CO₂ loading observed. The reduction in CO₂ loading of the lean solvent ultimately increases the CO₂ capture level back to and even beyond the original level before the disturbance (Figure 4.18(c)).

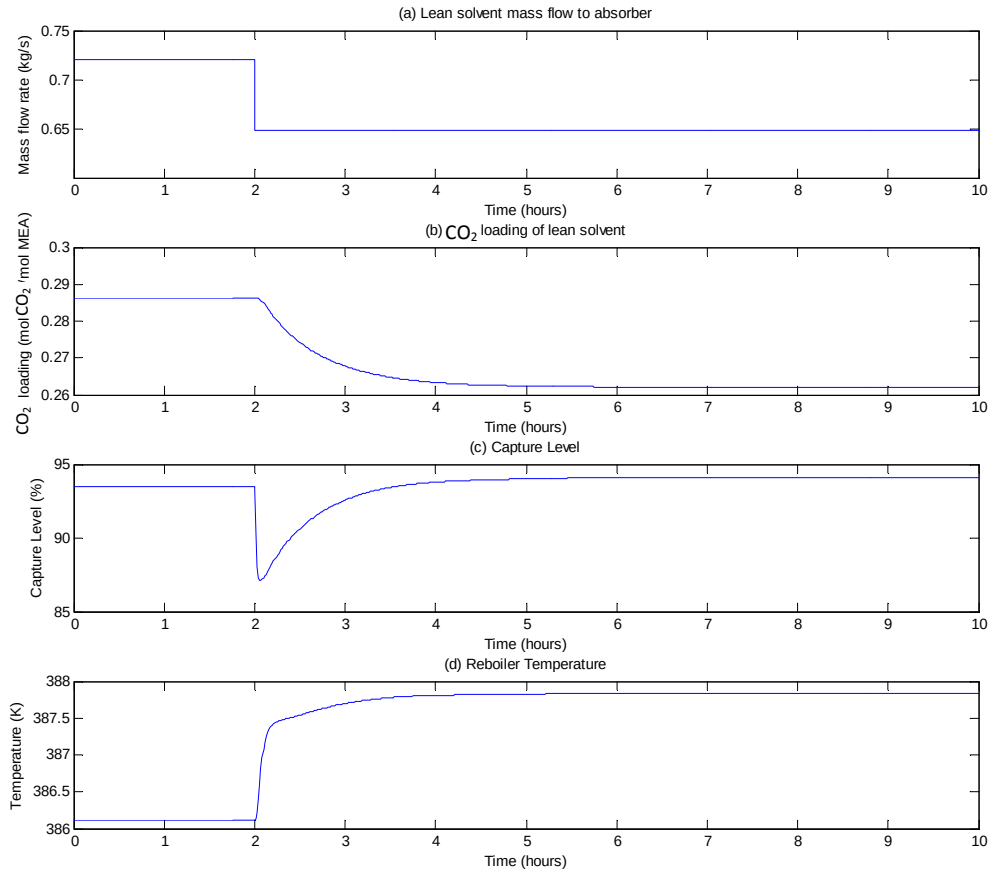


Figure 4.18 Reducing lean solvent mass flow to the absorber

The results in the analyses carried out in this Section and Section 4.10.2 show a generally slow plant response to disturbances. In particular, this Section suggests that the response of the absorber column to disturbances is faster than the rest of the plant. This difference could be as a result of the larger liquid holdups used in the regenerator column especially contained in the condenser and reboiler systems of the column. In addition, in the absorber column, the residence time of the gas in the column is relatively small. In the regenerator, changes to the lean solvent loading appear to be generally slow (Figure 4.18(b)) despite the rapid rise in reboiler temperature (Figure 4.18(d)). The lean MEA storage tank in between the two columns would also play a part in determining the dynamics of the system because of the delay it introduces.

4.11 Summary of insights gained through analyses at pilot plant scale

Based on the analyses described in Section 4.10 as well as the steady state and dynamic validation studies of Section 4.8 and 4.9 respectively, a number of insights could be

derived, which would be useful for the design and operation of a post-combustion CO₂ capture plant. These insights include:

- Accuracy of steady state and dynamic models.
- The importance of water balance control.
- Absorber performance sensitivity to L/G ratio.
- Absorption process dynamics.

4.11.1 Accuracy of steady state and dynamic models

Steady state and dynamic validation of the amine plant are discussed in Sections 4.6 to 4.9. From the steady state validation results, the rate-based modelling approach was shown to give better predictions than the equilibrium-based approach. This is likely because the equilibrium-based approach assumes the mass transfer resistances in the liquid and vapour films are negligible. This has been shown to be inaccurate. The difference appears to increase with increasing L/G ratio (from Figures 4.3 and 4.4). In Case 32, with high L/G ratio, the difference in temperature profile of the equilibrium-based model and the pilot plant measurements appears worse than Case 47, which has a relatively low L/G ratio. This suggests that at high L/G ratios, which are required for attaining high CO₂ capture levels of 90% and above, mass transfer limitations become increasingly important.

It is also likely that non-equilibrium reaction kinetics become significant at higher L/G ratios. The rate-based model used assumes reactions attain equilibrium. It appears the model provides more accurate predictions for Case 47 (with lower L/G ratio) than Case 32. For this case, the model predicts higher CO₂ capture levels than what was measured as shown in Table 4.4. The assumption of equilibrium reactions attained in the column would be valid if the liquid solvent and flue gas were in contact for an infinite period of time. Since the residence time of the flue gas in the column is relatively short, this assumption would be inaccurate despite the relatively fast kinetics of the reactions between MEA and CO₂ compared with other similar chemical solvents (Davidson, 2007).

It was seen from the validation results that the conditions of the inlet gas to the absorber are very important. In Section 4.4.1, it is shown that a small change in flue gas flow rate has a significant effect on the temperature profile of the column. The accuracy of the models developed was very sensitive to accurate inlet gas conditions.

Chemical absorption of CO₂ in MEA is an exothermic process. The temperature profiles measured in the pilot plant and predicted by the models show the significance of this phenomenon in plant operation. The difference between maximum and minimum column temperatures was over 20°C in both Case 32 and Case 47. Kvamsdal and Rochelle (2008) explained this phenomenon and how it could have a detrimental effect on absorber performance.

4.11.2 The importance of water balance control

It is important to keep control of the water balance in the process because the phenomenon would introduce additional disturbances to the system. Kvamsdal and Rochelle (2008) explained that if the flue gas stream to the absorber is not saturated with water, there is a tendency that some water would be evaporated from the solvent in the column yielding a saturated stream at the top of the column and concentrating the solvent. This could also occur if the temperature of the flue gas significantly increases as it passes through the column. On the other hand, if the temperature of the flue gas reduces significantly as it passes through the column, some water vapour would condense and thus dilute the solvent (Kvamsdal and Rochelle, 2008). Water balance is therefore a key control issue in the process.

Figure 4.19 illustrates some of the effects poor water balance could have. The same conditions for Case 32 were maintained for the integrated model as described in Section 4.7. In this case, however, all the controllers in Table 4.8 were active except the water makeup controller. Without any disturbances introduced, the CO₂ capture level varies significantly (Figure 4.19(c)). As the water mass fraction in the lean solvent reduced fairly steadily (Figure 4.19(a)), the effect was an initial increase in the CO₂ loading of the lean solvent (Figure 4.19(b)). A maximum loading is reached followed by a subsequent reduction with a resulting increase in CO₂ capture levels (Figure 4.19(c)).

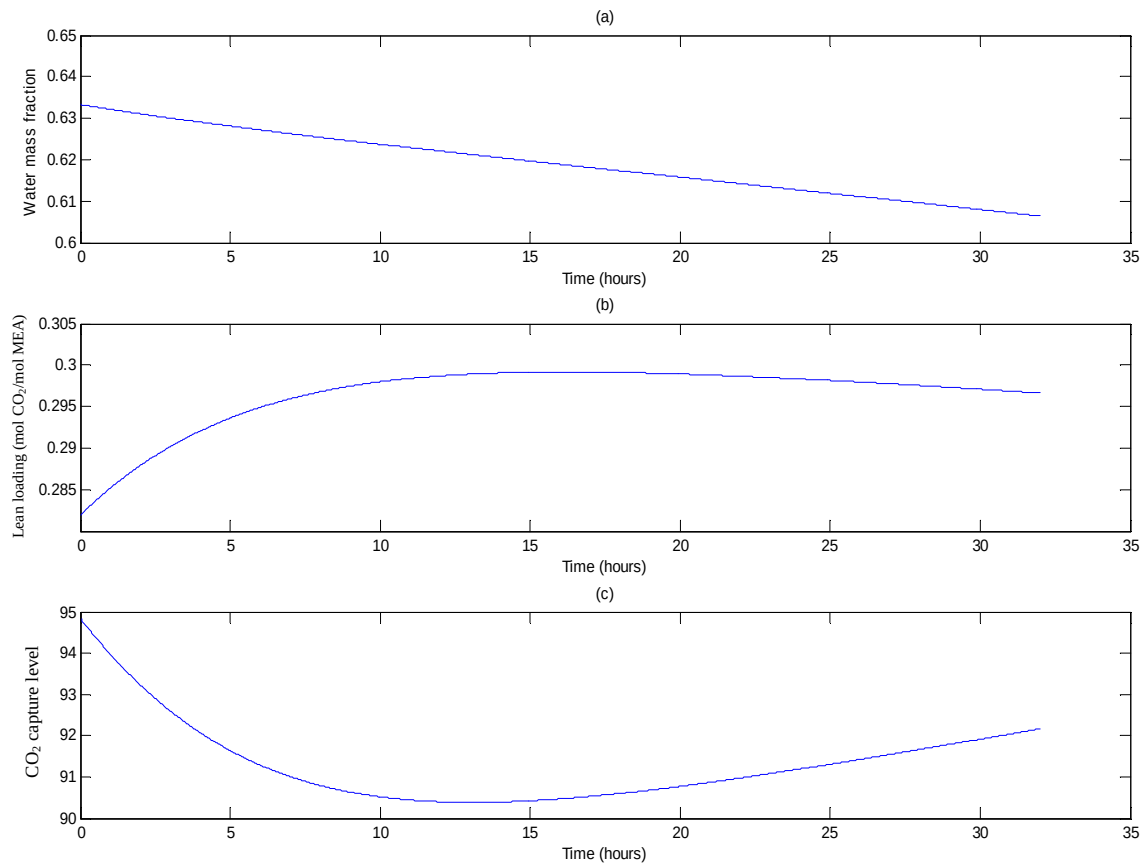


Figure 4.19 Effects of poor water balance in CO₂ absorption process

The water mass fraction in the lean solvent reduced because some water vapour would have been lost through the treated gas stream. This process could lead to severe operational problems especially with regards to corrosion due to the high concentrations of MEA and CO₂ in the solvent.

4.11.3 CO₂ capture performance vs L/G ratio

The performance of the absorber appears to be more sensitive to the L/G ratio rather than to the absolute flows of liquid and gas. Dugas (2006) reported that, in the experimental cases he carried out, the “temperature bulge” is located at the top of the absorber for L/G ratios less than 5 kg solvent/kg flue gas. It is located at the bottom for L/G ratios greater than 6 kg solvent/kg flue gas. Both the temperature profile (Figure 4.16) and the capture level (Figure 4.14) are essentially maintained whilst maintaining

the L/G ratio. This suggests that ratio control could be used to control the absorber performance to tackle disturbances of varying flue gas flow rates. Such disturbances could be common with coal-fired power plants operating flexibly in order to meet varying electricity demand. There are indeed limits to which the absolute flows of liquid and gas could be varied. These flows must be within the operating range of the column.

4.11.4 Process dynamics

The CO₂ capture process via chemical absorption has relatively slow dynamics compared with the power generation process (E.ON UK, 2008; Pearmine et al., 2007). In the pilot plant study, a time constant of over 57 minutes was estimated for a step change in regenerator reboiler duty. The absorber dynamics appear faster than those of the regenerator (Section 4.10.3). The absorber is also very sensitive to flue gas conditions as seen in the dynamic validation study (Section 4.9).

4.12 Summary

In order to model the chemical absorption process, stand-alone absorber and regenerator column models were first developed and validated. The rate-based approach to modelling the absorption process is shown to be more accurate than the equilibrium-based approach. The two columns were subsequently linked together and validated using steady state and dynamic data. Both steady-state and dynamic validation at pilot plant scale show that the rate-based model gives good predictions of the plant performance.

Steady state and dynamic analyses are carried out on the post-combustion CO₂ capture process model to gain insights useful for its design and operation. It is shown that the performance of the absorber is very sensitive to the flue gas conditions. The temperature profile of the absorber column was such that the maximum temperature (or temperature bulge) could be located at different locations along the column height. The differences between the maximum and minimum temperatures in the absorber column were significant in the cases considered. The importance of water balance in chemical absorption process plants was demonstrated – such problems could not be effectively studied with steady-state models. The performance of the chemical absorption process

was shown to be more sensitive to the L/G ratio of the absorber column than to the absolute mass flow rates of liquid or gas for small changes (10%) in flue gas mass flow. In addition, the dynamics of the chemical absorption process are shown to be relatively slow compared with those of the power plant.

Chapter 5 Scale-up of post-combustion CO₂ capture plant

5.1 Introduction

In Chapter 4, a dynamic model of the post-combustion CO₂ capture plant was developed. The model was validated at steady state and dynamically at pilot scale. In this chapter, based on the experience gained from pilot plant studies and using chemical engineering principles, the CO₂ capture plant is scaled to process the flue gas from a 500 MWe sub-critical power plant. The system was designed to capture 90% of the CO₂ from 600 kg/s of flue gas from the power plant. This would be achieved using a 30 wt% MEA solution. A framework for design of the CO₂ capture plant is presented and the analysis of the design of various components of the plant is presented.

Assumptions

- a. The lean solvent loading of 0.29 mol CO₂/mol MEA, used in the pilot plant study, is used at full scale.
- b. The rich solvent loading was assumed to be 0.49 mol CO₂ / mol MEA. The difference between the rich and lean solvent loading was used to calculate the solvent circulation rate.
- c. The effect of oxygen on MEA was assumed to be negligible. For simplification, the oxygen composition was included in the final nitrogen composition since oxygen was assumed to be inert.
- d. There is no water wash section in the absorber.
- e. Water balance achieved via an idealised makeup control system.

Scaling up the pilot plant scale model was found to be fairly complicated because of the interdependency of various design parameters. To simplify this process, a framework for the scale-up methodology was developed and is shown in Figure 5.1. This methodology is similar to that described by Kohl and Nielson (1997). Although this methodology would not necessarily result in optimal sizes of process equipment, it

would suffice for conceptual studies and would minimise the iterations needed to develop a scaled-up model.

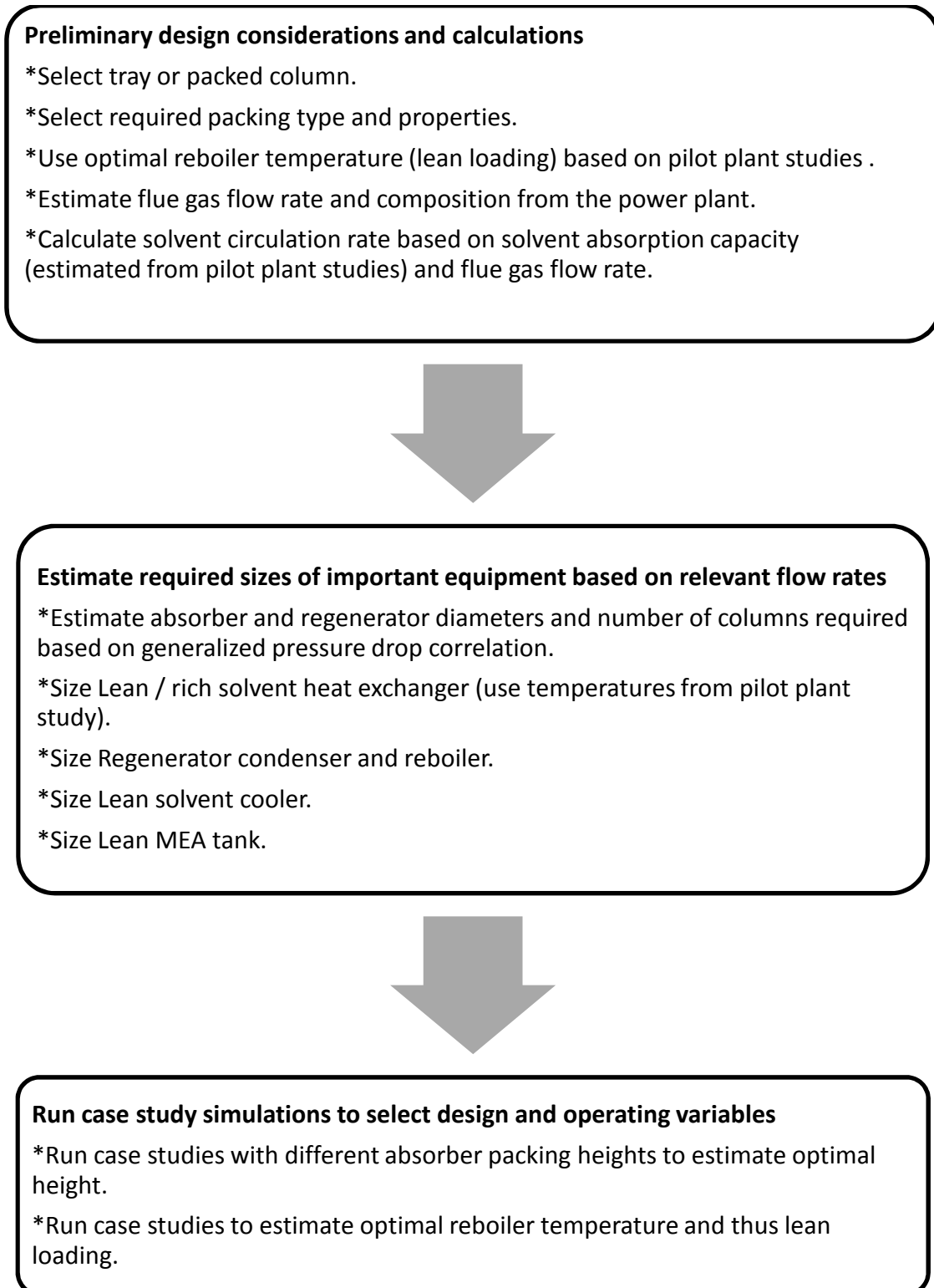


Figure 5.1 Scale-up methodology framework

5.2 General considerations for absorber and regenerator column design

The following describes the rationale behind the selection process for some of the process equipment used.

5.2.1 Tray vs. packed column

Generally, for gas purification purposes, both packed and tray columns could be designed to meet specific requirements. However, in CO₂ separation applications where separation efficiencies are important and high CO₂ removal rates are required, packed columns are usually preferred over tray columns. This is essential because a significant number of trays (usually greater than 20 in number) would be required for separation leading to excessively tall column designs. Tray columns are also not advantageous because of the significant effects of pressure drop involved in this application due to the large volume of flue gas being processed and the tendency for foaming and corrosion to occur with amine solvents (Kister, 1992; Kohl and Nielson, 1997).

5.2.2 Structured vs. random packing

Structured packing has higher specific areas and separation efficiency but is more expensive and sensitive to plugging by suspended particles in solution than random packing (Kohl and Nielson, 1997). Kister (1992) suggests that structured packing could cost 3 to 10 times more than their random counterparts per unit volume. However, since their mass transfer performances are better than those of random packing, some balance could be achieved through the reduced volume of packing required for mass transfer.

The relative performance of packing types should not be judged by comparing their specific areas alone. Dugas (2006) confirms this in his pilot plant studies. His study compared the performance of Flexipac structured packing and IMTP #40 (random packing). Although the former had a specific area three times that of the latter, his findings showed that the structured packing outperforms the random packing only by a factor of 1.5 – 2.

Perry (1999) suggests that the advantages (in terms of efficiency and capacity) of structured packing over random packing could be estimated based on a flow parameter, F_{LV} , defined as:

$$F_{LV} = \frac{L_W^*}{V_W^*} \sqrt{\frac{\rho_v}{\rho_L}} \quad (5.1)$$

The flow parameter is proportional to the L/G ratio used in the process. For values of this parameter between 0.02 and 0.1, the structured packing efficiency is about 1.5 times that of random packing. Closer to 0.02, the structured packing also has a capacity advantage (of a factor of 1.3-1.4) over random packing. This advantage disappears as the value of 0.1 is approached. With parameter values from 0.1 to 0.3, the efficiency of structured packing compared with random packing diminishes from a factor of 1.5 to 1.2. For the scaled up case, the estimate for this parameter is about 0.17 (Appendix B in Section B.2). This translates roughly to a maximum of 40% improvement in performance.

5.3 Diameter of absorber column

Ramezan et al. (2007) suggests that column diameters should not exceed 12.2 m (40 feet). Absorber columns with larger diameters would be faced with increased liquid and gas maldistribution. As a consequence, and in order to process the large volumes of flue gas from power plant, more than one absorber column would be required. Having multiple absorber columns could also help improve the turndown ratio of the process (regarding processing power plant flue gas at full and part load). Coal-fired power plants traditionally operate flexibly to meet varying demand. Since many renewable energy sources (such as wind turbines) that contribute to the grid are intermittent in nature, it would be of advantage if coal-fired power plants fitted with post-combustion CO₂ capture could continue to operate flexibly to balance the intermittency. To achieve this, the CO₂ capture process should be designed to accommodate a large turndown ratio. This could be easier to achieve with more than one absorber column.

On the other hand, Abu-Zahra et al. (2007b) reports that the absorber would most likely be the largest equipment in the capture plant since it would process huge volumes of

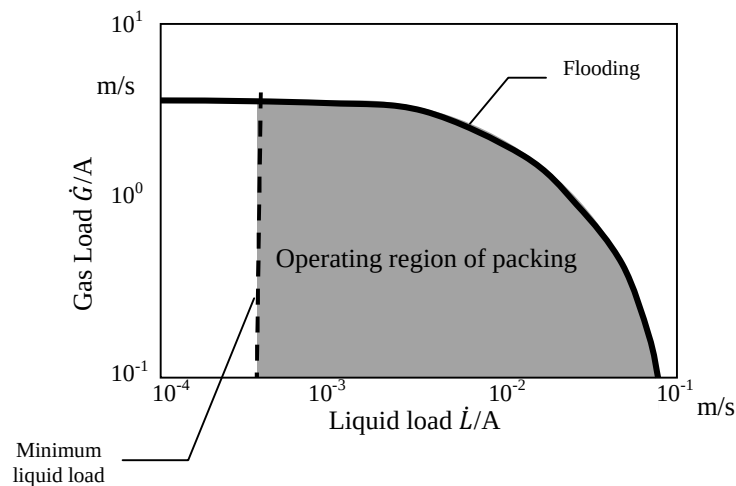


Figure 5.2 Operating region of a packed column adapted from Stichlmair and Fair (1998)

flue gas. To provide a balance, therefore, the minimum number of columns required should be selected to keep capital costs down and minimise footprint requirements. The capacity of the absorber is largely based on its cross sectional area. The column is usually designed to operate at the highest economical pressure drop to ensure good liquid and gas distribution (Sinnott et al., 2005).

The operating region of the packed column is limited by two main mechanisms: flooding and minimum liquid load (Stichlmair and Fair, 1998). Flooding sets the upper capacity of limit of the packed column. At this point, the pressure drop of the gas flow increases to an extent that the liquid is no longer able to flow downward against the gas flow (Stichlmair and Fair, 1998). The minimum liquid load refers to the lowest liquid flow rate required to ensure sufficient mass transfer. Beyond this point, only a small proportion of the packing surface is wetted (Stichlmair and Fair, 1998). Figure 5.2 illustrates these limits.

The required solvent flow rate (liquid load) was estimated based on the nominal conditions specified in Table 5.1. Details of calculations are given in Appendix B in Section B.1. Flue gas compositions and mass flow rate of 600 kg/s were derived from simulations of the dynamic model of the sub-critical coal-fired power plant. This model will be described in Section 6.2.

Sinnott et al. (2005) gives the recommended pressure drop per metre packing for absorbers and regenerators as 15 to 50 mm of water per metre of packing height typically away from the flooding line (Figure 5.3). 42 mm of water per metre of packing height was used for the design of both the absorber and regenerator columns.

Table 5.1 Calculation of required lean solvent flow

Description	Value
Flue gas mass flow rate (kg/s)	600
Flue gas mass fraction (N ₂)	0.740
Flue gas mass fraction (CO ₂)	0.215
Flue gas mass fraction (H ₂ O)	0.045
Lean solvent mass fraction (MEA)	0.3048
Lean solvent mass fraction (CO ₂)	0.0618
Lean solvent mass fraction (H ₂ O)	0.6334
Estimated required lean solvent mass flow (kg/s)	2940

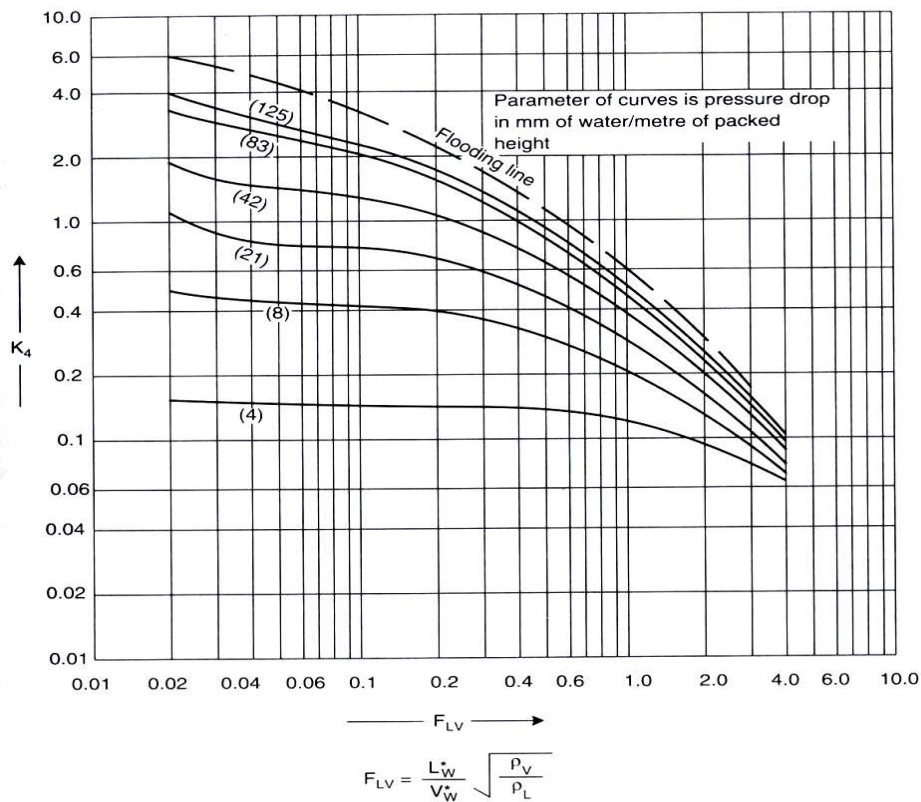


Figure 5.3 Generalized pressure drop correlation (Sinnott et al., 2005)

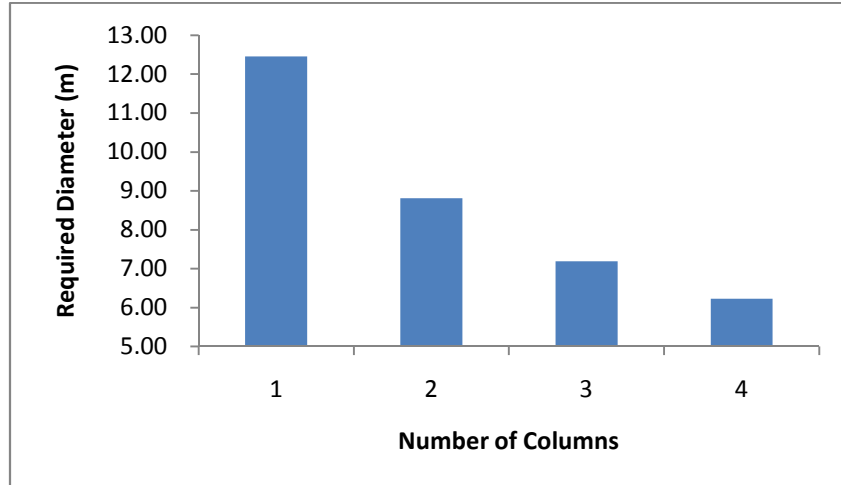


Figure 5.4 Required absorber diameter based on the number of columns

F_{LV} is the flow parameter given by equation (5.1) while K_4 is a modified gas load (Stichlmair and Fair, 1998). Based on the estimated flow parameter and the pressure drop parameter value chosen, the K_4 value is obtained from Figure 5.3:

$$K_4 = \frac{13.1(V_w^*)^2 \cdot F_p \cdot \left(\frac{\mu_L}{\rho_L}\right)^{0.1}}{\rho_v \cdot (\rho_L - \rho_v)} \quad (5.2)$$

μ_L = Liquid viscosity

F_p = Packing factor (dependent on the packing size and type)

The V_w^* term is estimated from equation (5.2) and is then used to estimate the required cross sectional area of the column and thus the diameter. These values were used to estimate required column diameters for the process. A sample calculation is presented in Appendix B in Section B.2.

The estimated absorber diameters required for 1 to 4 absorber columns in parallel are displayed in Figure 5.4. As can be seen, one absorber column would require a diameter of over 12 m, which would exceed 40 feet. Although some authors claim that it is possible to have absorber columns with diameters between 40 – 50 feet (Reddy et al., 2003), it would be wise to select more than one column to add operational redundancy in the integrated process. In the event of a failure in one absorber column, the power

generation process could be operated at part-load. In addition, the turndown ratio of a single column would be significantly limited, which may restrict the flexibility of the upstream power plant. The number of columns selected was two each with a diameter of 9 m. Selecting three or four columns may not provide significant returns in comparison with the large capital cost and footprint requirements this would demand. Ramezan et al. (2007) estimated that 2 trains are required – 2 absorber and 2 regenerator columns. Each absorber had a diameter of 34 feet or 10.36 m.

5.4 Diameter of regenerator column

Earlier simulation studies have shown that the regenerator processes much less volumetric vapour flow than the absorber; thus, a single column could be used. From the generalized pressure drop correlation method used in Section 5.3, the regenerator diameter was estimated as 8.39 m, thus a single 9 m diameter column would suffice.

5.5 Sizing of other equipment items

Apart from the two column units, the following equipment items are required (as shown in Figure 4.9):

- Lean/Rich amine heat exchanger.
- Regenerator Reboiler and Condenser.
- Lean MEA cooler.
- Storage tank for lean amine.
- Pumps.

The aim of this section is not to provide the detailed design of these units. Rather, some preliminary design parameters are estimated that are relevant to their dynamic simulation in gPROMS[®].

5.5.1 Sizing of lean/rich amine heat exchanger

This heat exchanger serves as an ‘economiser’ and exchanges heat between the hotter lean solvent from the regenerator and the cooler rich solvent from the absorber column. It is possible to raise the temperature of the rich solvent by over 30 K in this heat exchanger. Considering the volumetric flow of fluids being processed and the large temperature difference to be attained, a large heat transfer area is required.

The heat exchange area required to achieve the required temperature differences was estimated in Appendix B in Section B.3. The stream conditions were provided based on the pilot plant studies (temperatures, pressures and compositions) as well as the estimates for the scaled up process (for mass flow rates of the corresponding streams). The total heat transfer area required was 6000 m².

5.5.2 Sizing of regenerator condenser and reboiler

In order to provide the necessary information for the dynamic model, the capacities of the regenerator's condenser and reboiler must be estimated. In gPROMS[®], these equipment were modelled as flash drums with allowances for heat input or removal. This is a simplification of what would likely be used. For this purpose, a thermosyphon reboiler has been used for the reboiler (Ramezan et al., 2007; Knudsen et al., 2009). A combination of a heat exchanger and a reflux drum was used for the condenser in the Esbjerg pilot plant described in Section 3.2.3. Thermosyphon reboilers typically have higher heat-transfer coefficients than kettle reboilers because of liquid circulation (Sinnott et al., 2005). Kettle reboilers also have a longer residence times and thus may not favour thermally sensitive fluids such as MEA, which is prone to thermal degradation (Walas, 1990).

The rule of thumb used to size the condenser and reboiler is that they must have the capacity for 5 minutes holdup time whilst being 50% full. As these equipment were specified as flash drums with heat input specifications, the heat transfer areas required were not estimated. The condenser capacity was thus sized as 20 m³ and the reboiler capacity was 1800 m³.

5.5.3 Lean amine cooler

The lean amine cooler cools the lean MEA solvent from the cross heat exchanger (about 350 K) down to the temperature required in the absorber column (about 313 K). A compact heat exchanger is also recommended for this purpose due to the large volumetric flow of liquid required as well as the substantial temperature difference desired. The total heat exchange area of about 3000 m² was estimated in Appendix B in Section B.4.

5.5.4 Lean MEA tank

The lean MEA tank was sized to store a holdup time of 10 minutes. Based on the estimated solvent circulation rate (Table 5.1) and the estimated density of the lean solvent, the required capacity of the lean MEA tank was estimated as 1860 m³. 2000 m³ was selected to account for variations in circulation rates. Details of the estimation are provided in Appendix B in Section B.5.

5.6 Case study on absorber packing heights

Different packing heights of the absorber columns were tested to study the effect of increasing absorber packing height on the performance of the system. The parameter used to assess the performance of each case was the heat requirement for CO₂ capture – the amount of heat required to separate 1 kg of CO₂ from the flue gas mixture. The preliminary design parameters summarized in Table 5.2 were used. Absorber packing heights ranging from 17 to 37 m were tested.

Table 5.2 Summary of preliminary design parameters for chemical absorption plant

Description	Value
Design flue gas mass flow rate (kg/s)	600
CO ₂ mass fraction in flue gas	0.21
CO ₂ capture level (%)	90
Number of absorber columns	2
Absorber diameter (m)	9
Number of regenerator columns	1
Regenerator column diameter (m)	9
Absorber operating pressure (10 ⁵ Pa)	1.01
Regenerator operating pressure (10 ⁵ Pa)	1.62
Lean solvent mass fraction (MEA)	0.3048
Lean solvent CO ₂ loading (mol CO ₂ /mol MEA)	0.29

Cifre et al. (2009) estimated that the absorber column design should be performed with a minimum height of 17 m for the random packing (IMTP50) considered. For each case, the capture level controller was set to capture 90% of the CO₂ in the flue gas. The results are presented in Figure 5.5.

Significant savings of about 0.7 MJ/kg CO₂ could be achieved when increasing absorber packing heights from 17 to 25 m. There appears to be diminishing returns in the reduction of heat requirement over the range (which corresponds to the decrease in solvent circulation rates required to achieve 90% CO₂ capture). Relatively marginal savings could be achieved from 27 m and above. The capital cost of the absorber column would increase with increased absorber packing height. However, there could be considerable operational savings with higher packing heights that would compensate for the additional capital costs required. A trade-off is required. Another consideration is the use of process intensification (such as replacing the conventional packed column with a rotating packed bed), which would significantly decrease the size of equipment required for the process (Wang et al., 2010).

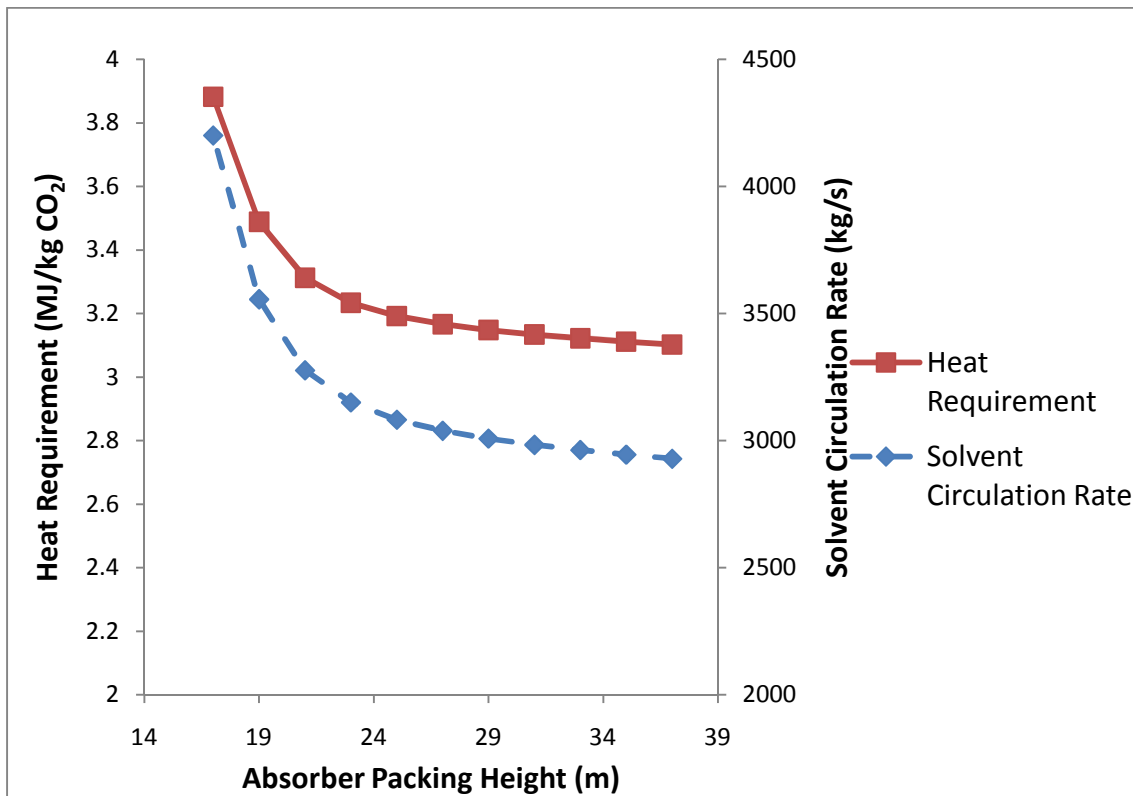


Figure 5.5 Plant performance with different absorber packing heights

Cifre et al. (2009) stated that the regenerator height does not affect the heat requirement as much as the absorber height does.

5.7 Case study on the solvent circulation rate with various reboiler temperatures

The solvent circulation rate required for a given flow rate and composition of flue gas mainly depends on the lean MEA solvent loading. The loading in turn depends on the level of regeneration in the regenerator. At constant regenerator operating pressure, the level of regeneration depends on the reboiler temperature. A case study was therefore carried out to study the effect of reboiler temperature setpoint on the heat requirement for CO₂ capture. In all cases, the CO₂ capture level was set to achieve 90% in the absorber. The absorber and regenerator heights were assumed to be 27 m and 20 m respectively. The temperature setpoint of the reboiler was varied from 382 K to 389 K with steps of 1 K. The steady state solvent circulation rates and corresponding heat requirement for CO₂ capture were then obtained and plotted in Figure 5.6. The latter was obtained by dividing the required reboiler heat duty by the amount of CO₂ captured.

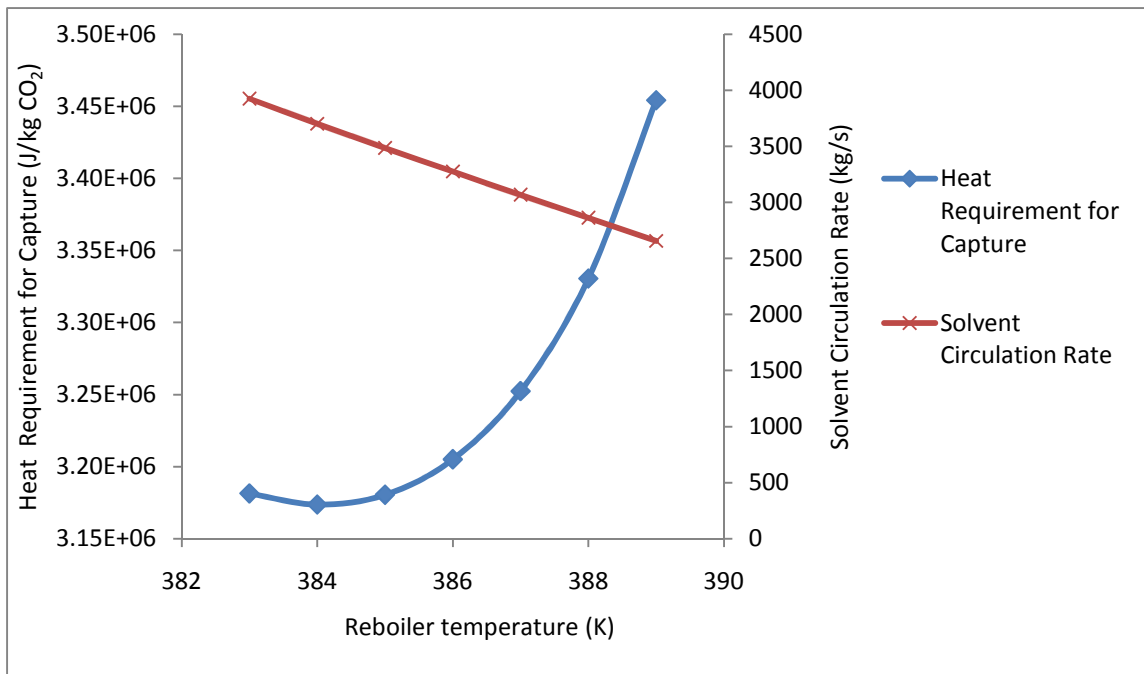


Figure 5.6 Case study on the effect of reboiler temperature on absorption performance.

From Figure 5.6, the minimum heat duty was achieved at 384 K corresponding to a circulation rate of 3700 kg/s. Below 373 K, it was impossible to attain the requirement of 90% CO₂ capture with the system configuration.

5.8 Summary

This chapter presents a design analysis for a CO₂ capture plant that would process the flue gas of a 500 MWe sub-critical coal-fired power plant. It is estimated that this plant would also be sufficient to process the flue gas from a 600 MWe supercritical coal-fired power plant. The diameters of the absorber and regenerator columns are estimated using the generalized pressure drop parameter. Two absorber columns are selected as a result of structural limitations and to improve the flexibility of operation of the plant through benefits such as operational redundancy and increased turndown ratio. Only one regenerator column is required. The sizing of other equipment such as the lean/rich MEA heat exchanger, reboiler, condenser, lean MEA cooler and lean MEA tank are also presented. In general, large capacity equipment would be required that may necessitate the use of more than one unit in parallel.

The absorber is the largest equipment in the plant and also the most expensive. A trade-off is required in selecting the height of the column – higher packing heights would improve the process efficiency driving down operating costs at the expense of increased capital costs and vice versa. A case study shows how the heat requirement and solvent circulation rate vary with increase in absorber packing height.

Chapter 6 Integrated plant model – linking the capture plant with the power plant

6.1 Introduction

This chapter describes the integrated plant model – the post-combustion CO₂ capture plant model linked with the 500 MWe sub-critical power plant model. The power plant model and its components are described briefly. Subsequently, the integration of the two models is discussed. Essentially the two models are linked via:

- i. the flue gas stream from the power plant to the absorber column,
- ii. the steam drawn off from the power plant's IP/LP crossover to the reboiler of the regenerator, and
- iii. the condensate return from the regenerator's reboiler to the power plant's low pressure feed-water heater.

The linked dynamic model is then used for performance studies and dynamic analysis. The base case using 30 wt% MEA is described. The steady state performance of the power plant with three MEA concentrations is then discussed in a case study. A number of dynamic case studies are also presented based on the operation of the integrated plant.

6.2 Dynamic model for sub-critical coal-fired power plant model

The dynamic model of the 500 MWe sub-critical power plant was developed by RWE. Some modifications to the model were necessary for its integration with a CO₂ capture plant. The power plant model is described briefly.

6.2.1 Model description

Dynamic models for the furnace, boiler, steam turbines (HP, IP and LP), condenser and feed-water system have been developed and dynamically validated using plant data (Stephenson et al., 2009).

The block flow diagram of the power plant model is shown in Figure 6.1.

NCV (Stephenson et al., 2009). Heat is transferred to the riser and tube banks of the boiler via convection and radiation. It should be noted that this model does not account for flue gas leakage.

6.2.1.2 Downcomer, riser and drum models

The mass flow rate of water in downcomer was modelled as being proportional to the pressure drop in the downcomer. Mass and energy balances of fluid in the riser and drum are also modelled based on Sidders (1989).

6.2.1.3 Heat exchanger-type models (superheater and reheater)

A transient heat exchanger model was used to model convective heat transfer in the superheater and reheater. The superheater platens and secondary superheater models also accounted for radiative heat transfer. These models generally account for changes on the steam side as well as on the gas side (Stephenson et al., 2009).

6.2.1.4 Important control systems

Superheater temperatures are controlled using spray water atomizers. These essentially mix the steam streams with controlled flows of spray water to achieve required temperatures. Reheater temperatures are controlled by using rear gas pass bypass dampers that control the flow of flue gas along the divided rear pass. The fuel burn rate and governor valve both control power plant power output. The target power plant output is directly controlled by the governor valve; this target also sets the target drum pressure. The drum pressure is controlled by the fuel burn rate.

6.2.1.5 Steam turbine models

These models apply generally to the high, intermediate and low pressure steam turbines and are described in Sidders (1989).

6.2.1.6 Validation of power plant model

The power plant model in gPROMS[®] was validated on a steady state and dynamic basis. The steady state simulation results were compared with the plant design data and satisfactory agreement was observed (Stephenson et al., 2009).

A comparison between plant data and power plant model predictions for the transients is given in Stephenson et al. (2009) showing that the gPROMS[®] model predicted flows fairly well through the course of the test. Details of the validation are discussed in Stephenson et al. (2009). RWE validated their dynamic model against an in-house steady-state model that is near to design conditions and against recent dynamic plant data. The current plant thermal efficiency is lower than the design value, in view of the age of the plant (Stephenson et al., 2009).

6.3 Linking the CO₂ capture plant to the sub-critical power plant model

Three main links are included between the power plant and the CO₂ capture plant, as follows.

- a. The flue gas stream from the power plant to the absorber column.
- b. The steam draw-off from the power plant used to regenerate solvent in the reboiler.
- c. The condensate return from the reboiler to the power plant.

The linked power plant and CO₂ capture plant model is subsequently referred to as the integrated plant model.

6.3.1 Flue gas pre-processing

Flue gas from the power plant must be cooled down to between 40 – 50°C for best absorption performance in the absorber. Gases like sulphur oxides and nitrous oxides form heat stable salts with MEA solvent (which cannot be regenerated). Particulates in the flue gas could clog the column packings and lead to problems due to foaming. Particulate matter such as fly ash is removed by either electrostatic precipitators or baghouse filters.

In the integrated plant model, it is assumed that all the SO₂ and NO_x is removed upstream of the absorber and a Direct Contact Cooler (DCC) reduces the flue gas temperature to 40 to 50°C. All the particulate matter is assumed removed. In addition, the effect of oxygen in the degradation of MEA solvent is neglected. Thus oxygen is considered inert and its mass fraction is simply incorporated in the nitrogen mass

fraction (Figure 6.2). A blower adds the required head necessary to feed the flue gas to the absorber at just above atmospheric pressure. A splitter splits the flue gas flow into two equal streams that feed the two identical absorber columns as shown in Figure 6.2.

6.3.2 Steam draw-off

Steam is drawn off at the IP/LP crossover as recommended by Ramezan et al. (2007) and Lucquiaud and Gibbins (2009) amongst other authors. Due to the reduced flow through the turbine, the pressure upstream of the LP turbine drops with the draw-off as shown in Figure 6.3. This drop in pressure could be estimated by Stodola's Ellipse law (Cooke, 1985). The floating IP/LP crossover pressure configuration was employed (Lucquiaud and Gibbins, 2009; Sanpasertparnich et al., 2010). This would accommodate a variable flow rate of steam draw-off. A throttling valve between the steam draw-off point and the LP turbine adds an additional pressure drop to raise the crossover pressure by about 1 bar (Figure 6.3). This ensures that the pressure across the IP/LP crossover does not drop below the required pressure needed in the reboiler (at least 3 bar). To employ this configuration, it is assumed that the IP turbine can accommodate the reduced exit pressures encountered with the steam draw-off (Lucquiaud and Gibbins, 2009).

A temperature controller measures the temperature of the lean solvent stream from the reboiler and controls the amount of steam drawn-off for regeneration. A water spray is used to cool down the steam temperature to just above saturation. It is assumed that there is no loss of total enthalpy in the process as the additional sensible heat is converted to latent heat of the vaporized spray water. This stream is then supplied to the reboiler where it exchanges heat with the solvent. It is assumed that all the steam supplied condenses in the reboiler leaving saturated liquid condensate at the outlet. It is assumed that there are no heat losses and all the latent heat of vaporisation is transferred to the reboiler fluid.

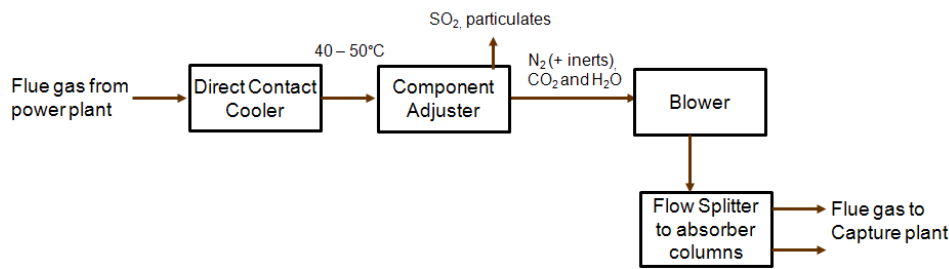


Figure 6.2 Linking the flue gas from the power plant with the CO₂ capture plant

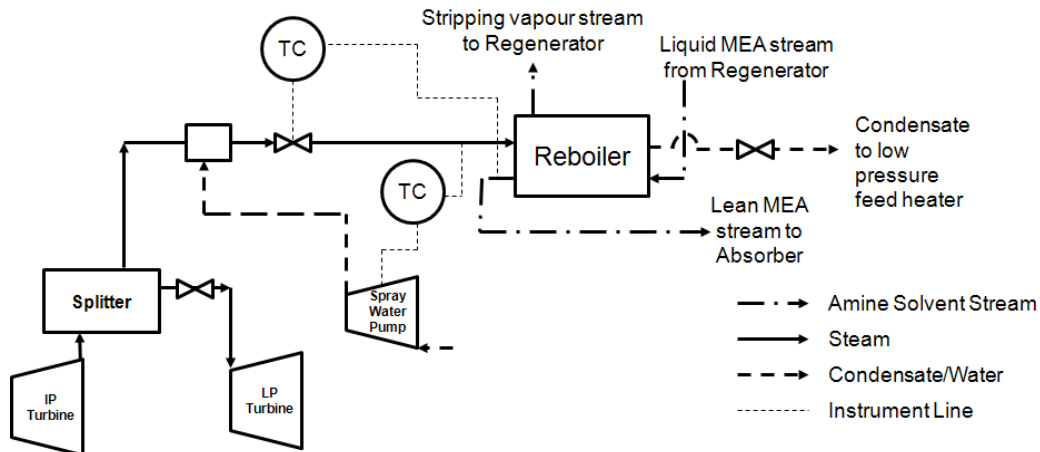


Figure 6.3 Steam draw-off and condensate return

6.3.3 Condensate return

The condensate is returned to the low pressure feed heater before being sent to the boiler feed pump. These two links between the power plant and CO₂ capture plant are shown in Figure 6.3. Part of this stream could be used as water spray to cool down the steam to the reboiler.

6.3.4 Integrated plant model topology

The integrated plant model topology is shown in Figure 6.4. Important streams and equipment are labelled. The various types of streams are also described in the legend. Flue gas from the power plant is passed through a black box (component adjuster) described in Section 6.3.1 that removes the SO₂, NO_x and includes the O₂ composition in the N₂ component. It is then cooled in the Direct Contact Cooler and subsequently supplied to the two absorber columns by the flue gas blower. In each absorber column, the gas is contacted with lean MEA solvent to achieve the target level of CO₂ capture (typically 90%). The lean solvent is obtained from the lean amine tank where water and MEA could be added to makeup required solvent concentrations. Lean MEA chemically

absorbs CO₂ to form Rich MEA, which is pumped from the absorber bottoms through the lean/rich amine heat exchanger. Regenerated lean solvent is used to heat up the rich solvent from the absorber to reduce the reboiler required heat duty in the regenerator column. This heat duty is required to strip CO₂ from the solvent giving a CO₂ product via the condenser. The regenerated lean solvent is pumped back to the absorber column via the lean/rich amine heat exchanger, the lean amine cooler and the lean MEA tank. The regenerated lean solvent is pumped back to the absorber column via the lean/rich amine heat exchanger, the lean amine cooler and the lean MEA tank.

Steam required in the reboiler is drawn from the IP/LP crossover at a controlled flowrate. The flowrate required is determined by the reboiler temperature controller. To ensure the superheated steam from the IP/LP crossover does not thermally degrade the MEA solvent, some condensate is sprayed into the steam to reduce the temperature to just above saturation. This activity is controlled by the steam desuperheater control system. The steam is assumed completely condense and the latent heat of vaporisation is transferred to the solvent for regeneration in the reboiler. The condensate is returned to the low pressure feed heater in the power plant.

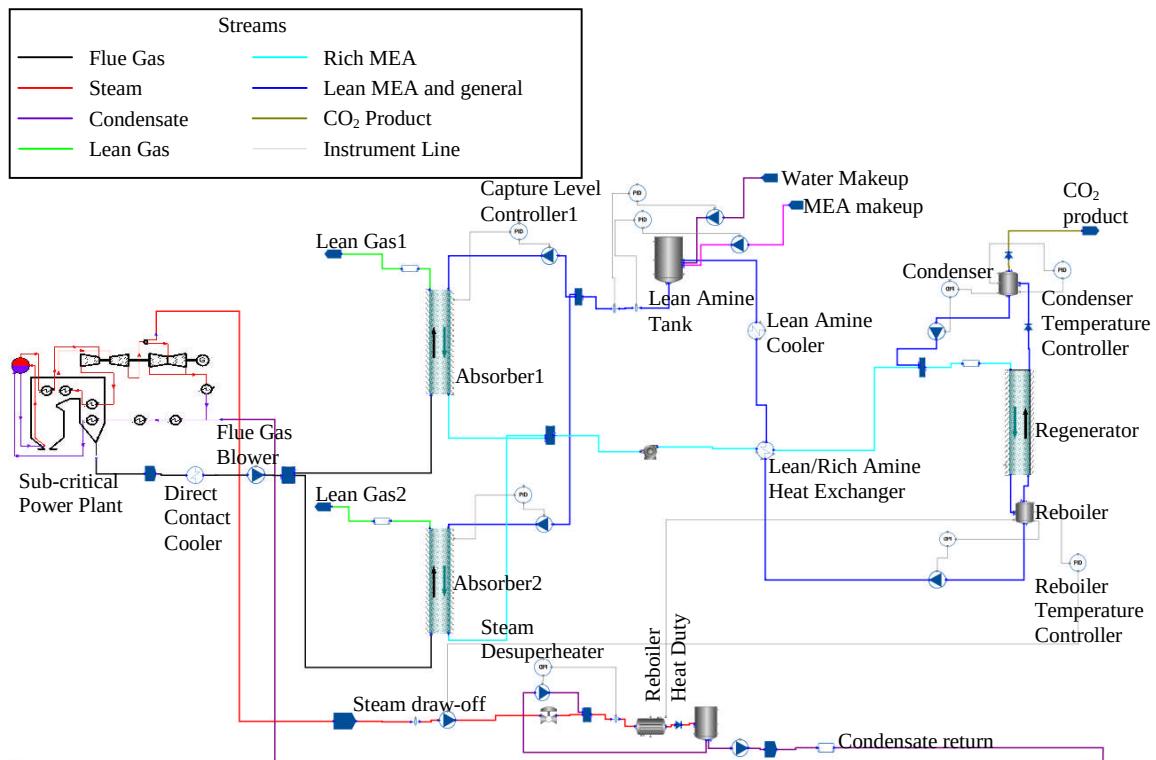


Figure 6.4 Integrated plant model topology in gPROMS®

Table 6.2 Summary of base case parameters for CO₂ capture plant for 500 MWe sub-critical coal-fired power plant

Description	Value
CO ₂ capture level setpoint (%)	90
Number of absorber columns	2
Absorber Diameter (m)	9
Absorber Packing Height (m)	27
Number of regenerator columns	1
Regenerator Column Diameter (m)	9
Regenerator Packing Height (m)	20
Absorber operating pressure setpoint (10 ⁵ Pa)	1.01
Regenerator operating pressure setpoint (10 ⁵ Pa)	1.62
Lean solvent mass fraction setpoint (MEA)	0.3048
Lean solvent CO ₂ loading setpoint (mol CO ₂ /mol MEA)	0.29

6.4 Performance of power plant integrated with CO₂ capture

The performance of the power plant integrated with the post-combustion CO₂ capture process is investigated in this section. The power requirements for compressing the CO₂ leaving the regenerator to a pressure suitable for pipeline transmission to a storage site are not included in this Section. Three case studies are considered. One involves investigating the effect of using three different MEA solvent concentrations in the CO₂ capture plant. The next case investigates the dynamic response of the integrated plant with a decrease in target power output. This is important because coal-fired power plants could operate flexibly in order to meet varying electricity demands. As such part-load operation may not be uncommon. The last case study investigates the effect of increasing the CO₂ capture level setpoint from 90% to 95%.

6.4.1 Base case

Process conditions obtained for the base case simulation are shown in Figure 6.5. The huge heating duty requirements in the reboiler – about 352 MWth can clearly be seen. In addition, there are significant cooling duties such as 338 MWth in the lean MEA cooler, which returns the lean solvent to favourable temperatures for CO₂ absorption in

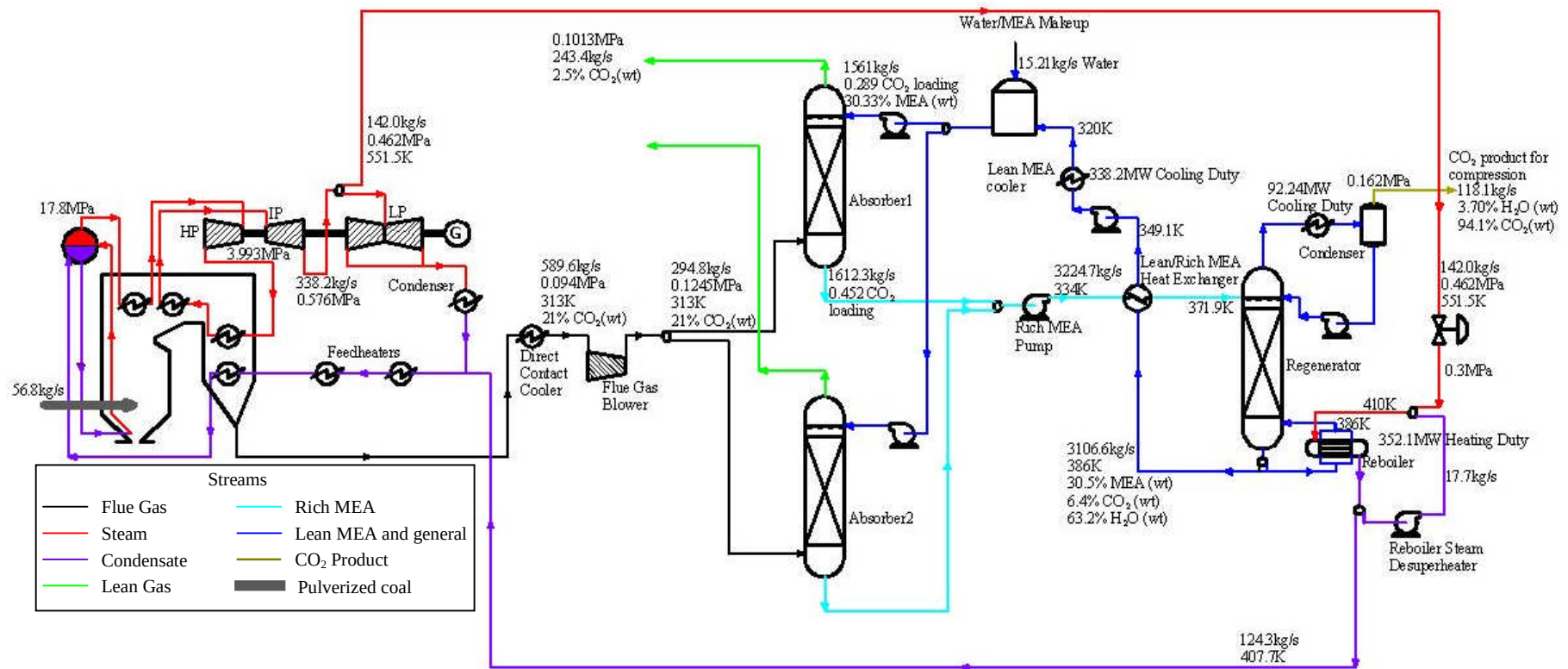


Figure 6.5 Process flow diagram showing base case process conditions

the absorber and 92 MWth for the condenser of the regenerator column. A summary of the base case design parameters are given in Table 6.2.

To develop the base case with CO₂ capture, the power plant model was simulated to achieve a net power output of 500 MWe. The fuel burn rate required for this output level was used as a fixed value for the base case with CO₂ capture. Here, not all the steam generated in the boiler is used to produce electricity. Some steam is drawn off for solvent regeneration, thus, the net power output drops below 500 MWe.

6.4.2 Case study I: Steady state effects of different MEA concentrations

The integrated plant performance with different concentrations of MEA is shown in Table 6.3 and compared with the base case without CO₂ capture. As discussed in Section 6.2.1.4, the fuel burn rate in the power plant is manipulated to control the drum pressure. The setpoint of the drum pressure is set to achieve a certain power output. The fuel burn rate was fixed at 56.8 kg/s, which is the value required to achieve a net power output of 500 MWe in the case without CO₂ capture. With steam drawn off for regeneration in the CO₂ capture cases, the net power output drops below 500 MWe and the actual power plant output depends on the amount of steam drawn off.

Power plant efficiency (NCV basis), η , is calculated as follows:

$$\eta = \frac{\text{net power output}}{\text{fuel burn rate} \times \text{NCV}} \quad (6.1)$$

The net power output was estimated by accounting for the power consumption of the various auxiliaries (estimated as 15 MWe (P. Stephenson, pers. comm.)). This power output corresponds to the electrical power generated.

With carbon capture, the power plant efficiency drops from 37.2% to the values given in Table 6.3. It should be noted that the power requirement for CO₂ product compression, the electrical duty of solvent circulation pumps and flue gas blowers are not considered in this study.

In summary, an increase in MEA concentration leads to reduced solvent regeneration duties and lower requirement for steam draw-off. The power plant efficiency increases with MEA concentration. 30 wt% MEA is typically employed in the chemical absorption process. 20 wt% concentration would necessitate relatively higher solvent circulation rates that would increase the heat duty demanded by the reboiler to raise the temperature of the circulated solvent to the setpoint. On the other hand, this configuration required the least amount of pure MEA solvent (about 727 kg/s) and at 20 wt% concentration, would pose the least challenge in terms of corrosion. 40 wt% MEA concentration would require the most solvent (1149 kg/s compared with 912 kg/s at 30 wt%) and would have the most severe corrosion challenges (refer to Section 2.4.1.4). With increased MEA concentration, more heat of reaction is released whilst absorbing CO₂ with less solvent circulation. As a result, the maximum absorber temperature increases as shown in Table 6.3 and the efficiency of the absorption process thus reduces. Some savings could be achieved if temperatures are lowered in the column through techniques such as inter-cooling, especially at higher concentrations of MEA solvent. The cooling duty requirement of the lean MEA cooler in the 20 wt% case is 19% higher than in the 30 wt% case. The 40 wt% case has a cooling duty that is 6% lower than the 30 wt% case value. This trend is due to the different solvent circulation rates in each case. For the remaining case studies (in Section 6.4.3), only 30 wt% MEA is used.

6.4.3 Case study II: Dynamic effect of reducing target power output

This case simulates the effect of a decrease in target power output. Target power output was ramped down from 440 MWe to 415 MWe over a period of 10 minutes. The net power output is determined by the power output controllers (described in Section 6.2.1.4), which manipulate the fuel burn rate and governor valve opening to meet the target power output. The capture level controller setpoint was maintained at 90%. Base case conditions were maintained for 4 hours before the disturbance was introduced. The integrated plant model was then simulated for another 10 hours. Results of the simulation are shown in Figures 6.6 and 6.7.

Table 6.3 Summary of parameters for the integrated plant model with and without CO₂ capture and at different MEA concentrations

Description	Without CO₂ Capture	With CO₂ Capture (20 wt% MEA)	With CO₂ Capture (30 wt% MEA)	With CO₂ Capture (40 wt% MEA)
CO ₂ capture level (%)	0	90	90	90
Solvent Circulation Rate (kg/s)	0	3,663	3,122	2,964
Flue gas flow rate (kg/s)	589.6	589.6	589.6	589.6
Net Power Output (MWe)	500	437	453	467
Fuel burn rate (kg/s)	56.8	56.8	56.8	56.8
Power Plant efficiency	37.2	30.0	31.1	32
Steam draw-off flow rate (% of steam flow rate from IP turbine exit)	N/A	54	42	34
Maximum absorber temperature (K)	N/A	335	338	340
Lean MEA cooler cooling duty (MWth)	N/A	401.4	338.2	316.9

Figure 6.6(a) shows the drop in net power output with time. The fuel burn rate is adjusted to achieve this drop (Figure 6.6(b)). With a reduced fuel burn rate, the flue gas produced reduces correspondingly and thus the flow of gas to the absorber column reduces.

With less gas to process in the absorber, a smaller solvent circulation is required (Figure 6.6(d)). The heat duty required in the reboiler to regenerate solvent thus decreases correspondingly and there is therefore a reduced demand for steam from the power generation process (Figure 6.6(c)). The power plant efficiency (Figure 6.6(e)) shows some initial perturbations before settling down to roughly the same steady state value. The CO₂ capture level (Figure 6.6(f)) also oscillates and steadies at the controller's setpoint of 90%.

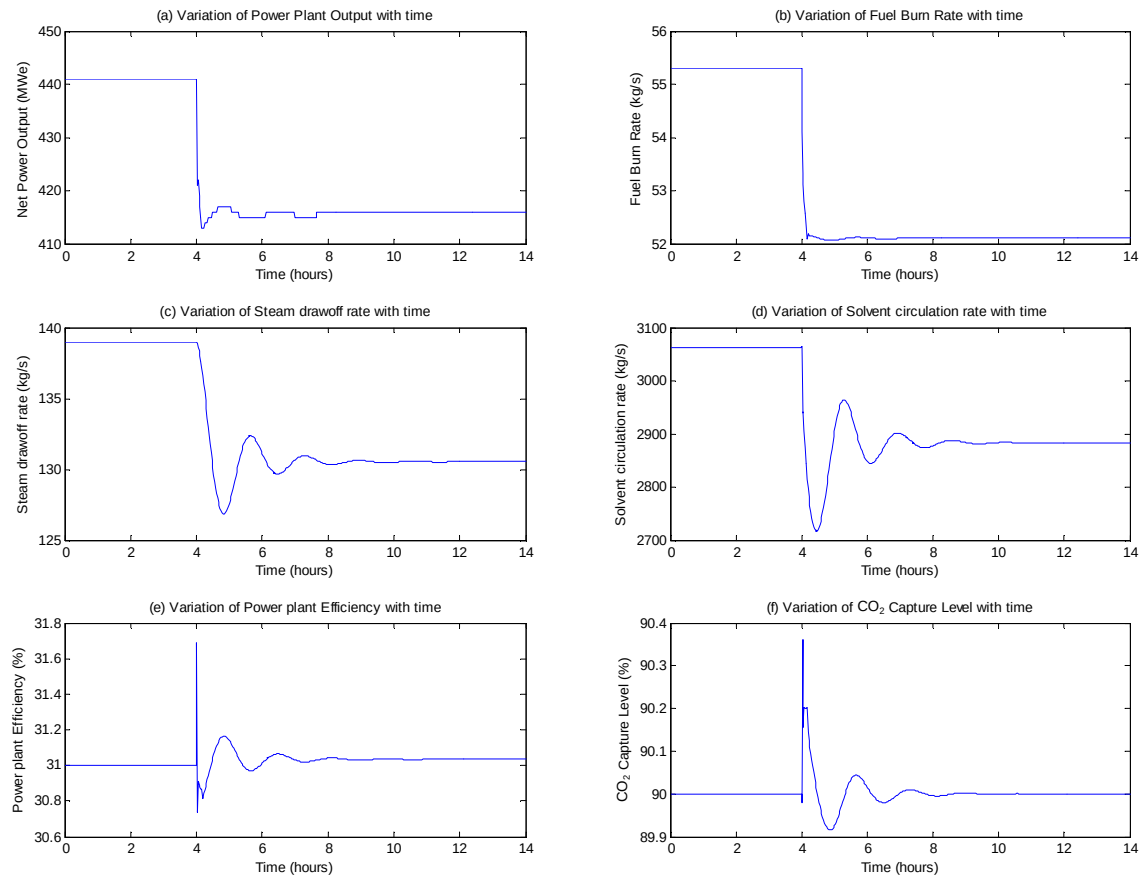


Figure 6.6 Effects of decreasing target power plant output

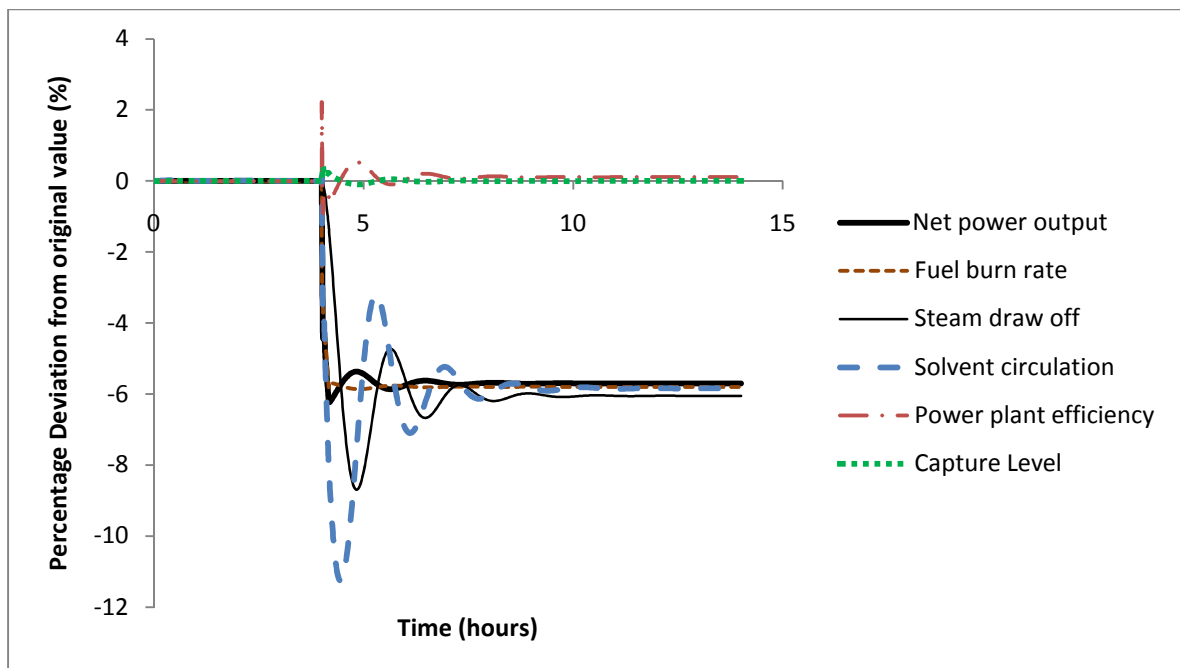


Figure 6.7 Percentage deviations with decreasing target power plant output

Figure 6.7 shows the same results in terms of their percentage deviation from their original values (before onset of the disturbance). By close observation, certain features become more apparent. For instance, the solvent circulation rate shows the largest deviation perhaps because its settings provide tight control of the capture level. Also from Figure 6.7, the capture level does not vary much. Even as such, there are periods where the capture level is above the setpoint and more importantly below the setpoint as well. If emission regulations are such that the capture level must not go below a certain value at any point in time, it is advisable to operate the capture plant sufficiently above the minimum value so that disturbances from the power plant do not drop the capture level below it. From Section 6.4.3.2, it is shown that achieving higher capture levels becomes increasingly difficult as 100% capture is approached so care must be taken to select appropriate operating capture levels.

In addition, because of the tight controls on capture level and the resulting oscillations in solvent circulation rates, the power plant power output oscillates in response to changing steam draw-off rates from the IP/LP crossover. From Figure 6.6(a) and 6.7, the power plant output drops below the setpoint and takes a while to settle at the setpoint making it difficult to achieve steady power output levels quickly. In this case, it appears that the tight control on capture level interacts with the power plant power output control.

The response of the power plant to operational changes is relatively fast. From the onset of the disturbance (reducing the power plant output), the change in fuel burn rate and subsequently flue gas flow rate is relatively fast. In addition, the capture level and solvent circulation rates also change soon after this disturbance is introduced. However, the response of the amine plant is much slower. For instance, with a reduction in the solvent circulation rate, a lower heat duty is demanded in the reboiler. However, as can be seen in Figure 6.7, there is a delay in the response of the steam draw-off rate compared with that of the solvent circulation rate. This shows that the process dynamics of CO₂ capture plant is relatively slow compared with that of the power plant. The manipulation of solvent circulation rate (and subsequently steam draw-off rate) in turn imposes some disturbances on the power generation process. It is therefore, not

advisable to have such tight control on the capture level considering the interaction of this control loop with the power plant power output control.

6.4.4 Case study III: Dynamic effect of increasing capture level setpoint from 90% to 95%

This case simulates the change in CO₂ capture level setpoint in the capture level controller from the base case value of 90% to 95%. Power output targets were maintained. Base case conditions were maintained for 4 hours before the disturbance was introduced. The integrated plant model was then simulated for another 10 hours. Results of the simulation are shown in Figures 6.8 and 6.9.

Figure 6.8(a) shows the power plant power output changes with time. Roughly, a 1.8% reduction in power plant output is observed after the disturbance (Figure 6.9). The fuel burn rate increases to compensate for the loss in power output and attempt to return to the setpoint (Figure 6.8(b)). It then steadies at a slightly higher value than before the disturbance. Increasing the capture level setpoint would imply increased solvent circulation rates (Figure 6.8(d)). This increases up to a maximum of 34% of the value prior to the disturbance (Figure 6.9) before it steadies at a value 16% higher although the CO₂ capture level was increased by only 5% points (Figure 6.8(f)). This confirms that as 100% capture level is approached, CO₂ capture becomes increasingly difficult. This is clearly seen from Figure 6.8(g) where there is an increase in heat requirement for CO₂ capture after the disturbance was introduced. This value measures how much heat is required to separate 1 kg of CO₂. It increases by just over 5% and appears to correspond to the increase in capture level at steady state (Figure 6.9).

The power plant efficiency (NCV basis) reduces by almost 2.5% before attaining a steady state value 1.7% less than original due to the disturbance (Figure 6.8(e) and 6.9). From observing Figures 6.8(c) and 6.8(e), it could be concluded that the efficiency reduction follows the response of the steam draw-off.

Both dynamic case studies show possible negative effects that a poor control system or strategy could have on the integrated operation of a post-combustion capture plant. Better process control could be achieved with improved controller tuning.

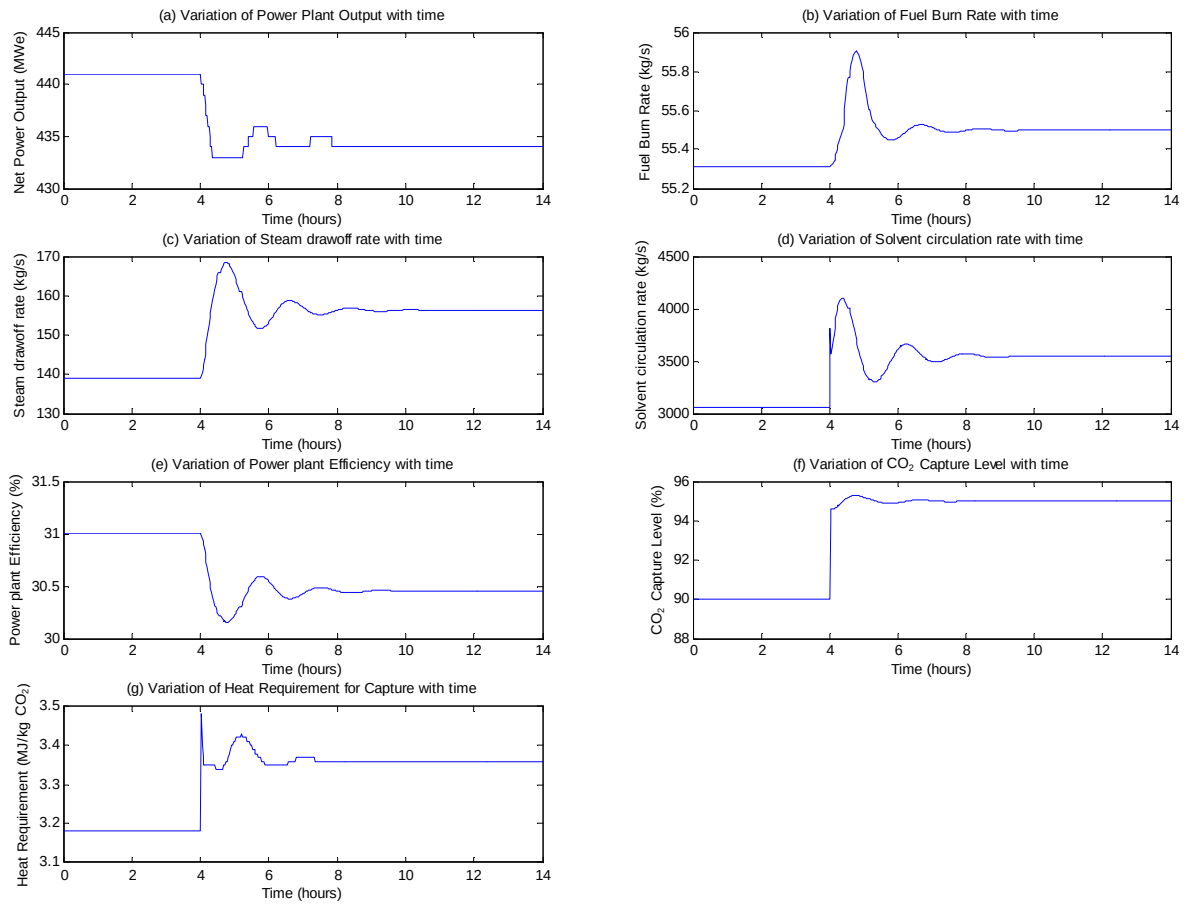


Figure 6.8 Effects of increasing CO₂ capture level setpoint

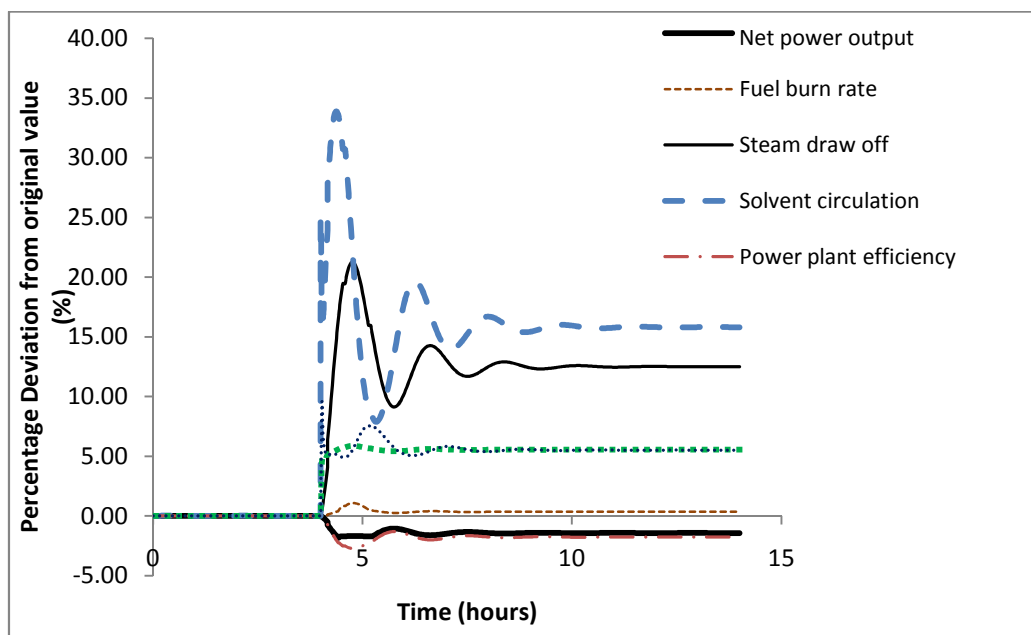


Figure 6.9 Percentage deviations with increasing CO₂ capture level setpoint

6.5 Selecting absorber packing height based on cost of electricity

6.5.1 Background

The absorber column is one of the largest pieces of equipment in the post-combustion CO₂ capture process. It also accounts for about 55% of the total capital cost of the facility (Abu-Zahra et al., 2007a). The capital cost of the absorber column increases with the height of packing in the column. On the other hand, there are operational benefits associated with higher packing heights. One significant benefit is the reduced L/G ratio required to capture the same amount of CO₂ and as a result reduced heat requirements for solvent regeneration. This would reduce the operating costs of the plant. A trade-off is therefore required. A case study to show the effect of varying the absorber packing height was given in Section 5.6. This was carried out using only the CO₂ capture plant, which made it difficult to ascertain the best absorber packing height as the heat requirement for capture did not reach a minimum value with increasing absorber packing heights (Figure 5.5). It is, therefore, necessary to take a more holistic view of capital and operating costs when selecting the appropriate packing height.

The estimated cost of electricity with CO₂ capture was used to select the packing height. This cost reflects the total expenditure (both capital and operating) needed to produce a unit of electricity. To estimate this cost, the integrated plant model described in Section 6.4.1 was used. A PI controller ensures that the amount of solvent supplied to the absorber is such that it is possible to attain 90% CO₂ capture in the absorber. A constant fuel burn rate in the furnace is assumed. As a result, there is constant flue gas feed from the power plant. The CO₂ compression unit was not modelled explicitly, but estimates of its requirements were calculated. Based on the preliminary design, two absorber columns of 9 m diameter each were required (refer to Section 5.3) to process flue gas from a 500 MWe sub-critical power plant. Each absorber column would have the same packing height.

Abu-Zahra et al. (2007a) carried out an economic analysis of MEA CO₂ capture for a 600 MWe supercritical coal-fired power plant. A 600 MWe supercritical coal-fired power plant would release roughly the same amount of flue gas as a 500 MWe sub-critical coal-fired power plant (Lawal et al., 2010b). Therefore, it could be assumed that the cost estimates from Abu-Zahra et al (2007a) are applicable for this study. This study

provides in addition an analysis of how the absorber packing height selection affects the economics of the power plant with post-combustion CO₂ capture process. It also provides an up-to-date cost estimation of the integrated process.

6.5.2 Estimating the cost of electricity

6.5.2.1 Assumptions

- Basis taken for cost estimation is 1st Quarter 2010.
- Costs of equipment in the chemical absorption plant are similar to those reported by Abu-Zahra et al. (2007a). No basis for the costs was given, so it was assumed that these costs were for 4th Quarter 2006.
- Inlet flue gas conditions to the absorber column remain constant (temperature and composition).
- CO₂ compression cost is assumed to be fixed.
- Plant life time, $n = 25$ years (Abu-Zahra et al., 2007a).
- Equipment salvage value = 0 (Abu-Zahra et al., 2007a).
- Coal price (CIF ARA – 25 MJ/kg NCV) was seen to vary greatly (€46.98/tonne in May 2009 and €65.60/tonne in Jan 2010) so the average of the two values was taken and used as the 1st Quarter 2010 price – €56.29/tonne (Platts, 2009; Platts, 2010).
- Plant operating hours per year – 7500 hr/year (Abu-Zahra et al., 2007a).
- Lean solvent CO₂ loading is assumed fixed at 0.289 mol CO₂/ mol MEA.
- Fuel burn rate is assumed constant.

The simulations were carried out with the following conditions:

- CO₂ capture level, $\eta_{CO_2} = 90\%$. This is achieved using a PI controller in the process.
- Lean solvent temperature from the regenerator reboiler, $T_{lean} \leq 120^\circ\text{C}$ (393 K).
- CO₂ product purity ≥ 93 wt%.

6.5.2.2 Developing the cost function

The cost of electricity was estimated as follows:

$$\text{Cost of electricity} = \left[\frac{PICO}{n} + \frac{ICo(h)}{n} + P_{OPEX} + P_{FUEL} \right] / MWh(h) \quad (6.2)$$

$PICO$ is the installed cost of the power plant and capture plant excluding the two absorber columns. The specific investment for the supercritical coal-fired power plant

reported by Abu-Zahra et al. (2007a) were found to be within the range reported for a sub-critical coal-fired power plant by Lowe (2007). For simplification, therefore, the power plant investment costs used by Abu-Zahra et al. (2007a) were used here as well. $PICo$ is assumed constant and is estimated from Abu-Zahra et al. (2007a) by subtracting the installed cost of the absorber column from the total capital investment cost of the integrated plant. This value is determined in Appendix C in Section C.2. $ICo(h)$ is the installed cost of the two absorber columns expressed as a function of absorber packing height, h . This was obtained using Aspen Process Economic Analyser V7.2.1 with a cost basis of 1st Quarter 2009. Estimates were obtained for different absorber packing heights ranging from 15 to 40 m. The polynomial trendline obtained for predicting these costs is described in Appendix C in Section C.1 and is given by:

$$ICo(h) = (1.2988E+05 \times h + 1.3614E+06) \times 2 \quad (6.3)$$

P_{OPEX} refers to the plant operating cost for one year including cooling water duty and electrical utility of the solvent circulation pumps, CO₂ compression cost, the cost of chemicals such as MEA makeup costs, taxes, plant overhead, general expenses etc and is obtained from Abu-Zahra et al. (2007a). The estimation of this value is shown in Appendix C in Section C.3. It is assumed constant.

P_{FUEL} is the fuel costs for a year (the cost of pulverised coal-fired in the furnace). Since a constant fuel burn rate is assumed, this value is also constant. The value is estimated in Appendix C in Section C.4. The fuel costs were not lumped with the rest of the operating costs since it appears there was a significant change in the coal prices since Abu-Zahra et al. (2007a) was published.

Since the fuel burn rate in the power plant furnace is assumed constant, varying absorber packing height would result in different net power outputs. This is the case because of the different solvent circulation rates that would lead to different steam draw-off mass flow rates to the reboiler.

Since the integrated plant model does not account the electrical duties of the various, pumps, blowers and the CO₂ compression system, an estimate for these was obtained

based on Ramezan et al. (2007). The total electrical duty required was subtracted from the power generated to give an updated net power output. Ramezan et al. (2007) considered a post-combustion CO₂ capture plant that would capture 90% of CO₂ from the flue gas from an existing sub-critical 434 MWe power plant. The total auxiliary power demanded by the capture plant was about 55 MWe. A linear relationship was assumed between the power plant total output and the auxiliary power demanded by the CO₂ capture plant. Based on this, the electrical duty was estimated as 63 MWe for this case. The value of this electrical duty was assumed to have negligible variation with the absorber packing height. The solvent circulation pumps would deliver different flow rates of solvent with different absorber packing heights. However, considering that the electrical duty of the solvent circulation pumps constitute about 5% of the total additional electrical duty (Ramezan et al., 2007), it was assumed that this change could be neglected.

6.5.3 Results and discussion

The cost of electricity given by Equation (6.2) was plotted for different absorber packing heights to find the height with the least cost of electricity. This is shown in Figure 6.10. An absorber packing height of 27m gave the minimum cost of electricity of €57.77/MWh. This is slightly higher than the value reported by Abu-Zahra et al. (2007a). This is likely due to the higher fuel costs (based on recent increases in coal prices). The minimum point represents a good trade-off between the increased installed cost of the absorber column and reduced net power output of the power plants shown in Figure 6.10. The variation of net power output with absorber packing height is also shown. The net power output in this case accounts for the auxiliary power demanded by the CO₂ capture plant (unlike that reported in Table 6.3). The power plant efficiency drops to 26.8% when auxiliary power is accounted for, corresponding to a 10.4% drop in power plant efficiency.

The cost of CO₂ avoided was estimated as €32.96/tonne based on equation (3.1). Details of the calculation are given in Appendix C in Section C.5. This was lower than the value reported in Abu-Zahra et al. (2007a) (€39.3/tonne). This is likely due to the lower heat requirement

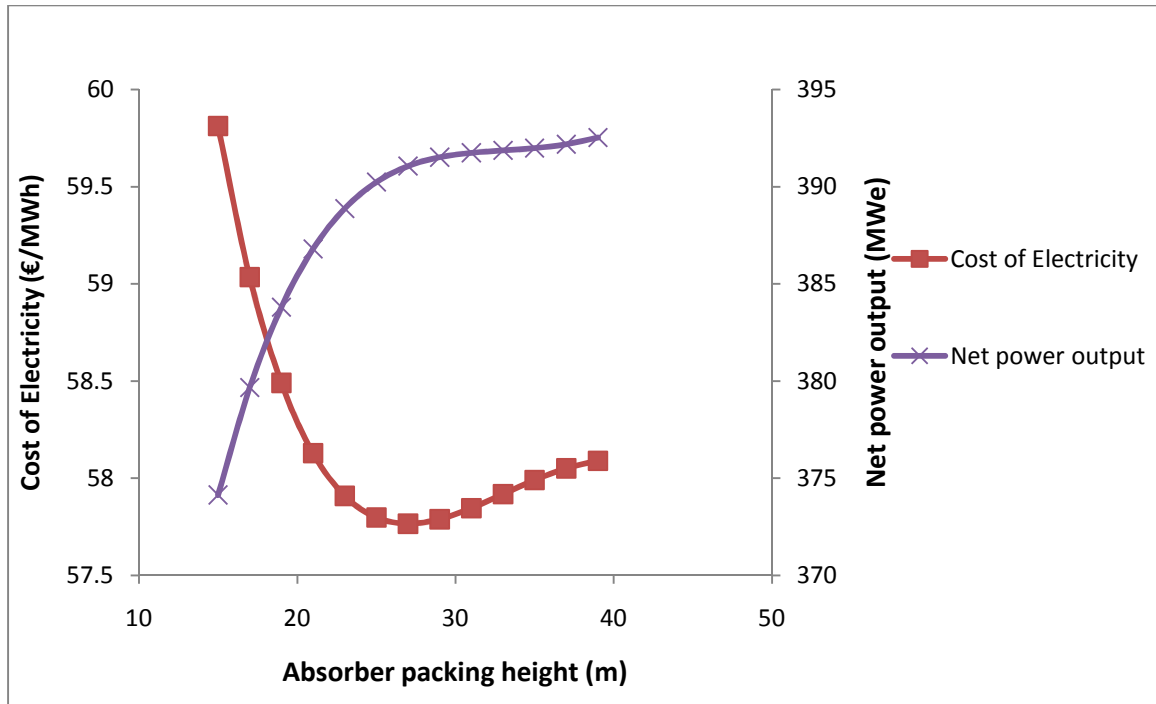


Figure 6.10 Cost of electricity and net power output with absorber packing height

for CO₂ capture used in this study (about 3.2GJ/tonne CO₂) compared with (3.9GJ/tonne CO₂) reported in Abu-Zahra et al. (2007a).

6.6 Summary

This chapter described the integrated plant model – the post-combustion CO₂ capture plant model linked with the 500 MWe sub-critical power plant model. The power plant model and its components were described briefly. Subsequently, the integration of the two models is discussed. Essentially the two models are linked via the flue gas stream from the power plant to the absorber column, the steam drawn off from the IP/LP crossover to the reboiler of the regenerator, and the condensate return from the reboiler to the low pressure feed heater. The base case using 30 wt% MEA is described. About 42% of the steam mass flow from the IP turbine was drawn off for solvent regeneration in the base case.

A number of case studies were considered. The steady state performance of the power plant using solvent with three different MEA concentrations is compared. Dynamic case studies investigated the effect of reducing the target power output of the power plant as

well as increasing the CO₂ capture level setpoint. Both cases demonstrated the slower response of the capture plant compared with the power plant. In addition, it was shown that there could be issues with the interaction of the control loops in the capture plant and power plant especially via the amount of steam drawn off for solvent regeneration.

The power plant efficiency drops to 26.8% corresponding to a 10.4% drop. Estimates of requirements for CO₂ compression were included. With an absorber packing height of 27m, the cost of electricity with CO₂ capture was estimated as €57.77/MWh with CO₂ capture. The cost of CO₂ avoided was estimated as €32.96/tonne CO₂.

Chapter 7 Conclusions and recommendations for future work

7.1 Conclusions

This work studies the design and operation of a post-combustion CO₂ capture for a 500 MWe sub-critical coal-fired power plant through modelling and simulation. The chemical absorption process using MEA solvent is considered as it is the most mature technology for CO₂ separation from flue gases with low CO₂ partial pressures.

Recent activities carried out worldwide towards demonstrating post-combustion CO₂ capture, involving both pilot plant studies and studies through modelling and simulation were reviewed revealing the current gaps in knowledge. In particular, it was observed that no accurate dynamic model of a coal-fired power plant integrated with CO₂ post-combustion capture had been reported.

Dynamic models of the CO₂ chemical absorption process with MEA solvent were developed using a rate-based modelling approach based on finite rates of mass and heat transfer between liquid and vapour. Stand-alone columns of the absorber and regenerator were developed and validated using data from the Separations Research Program at the University of Texas at Austin. The rate-based modelling approach was shown to be more accurate than the equilibrium-based approach. Analysis of steady state validation results showed the rate-based model predicted temperature values in the absorber and regenerator columns with average percent deviations of the up to 3.1%. The two column models were linked together with recycle to form the post-combustion CO₂ capture plant model. Steady state and dynamic validation studies were carried out at pilot plant scale. The temperature profile of the absorber and regenerator columns, CO₂ capture levels in the absorber, rich solvent loading in the absorber and regenerator reboiler duties were used as bases for comparing the predictions of the dynamic model with the measurements from the pilot plant. The results show that the dynamic models gave reasonably good predictions of the plant behavior on both steady state and dynamic bases.

Insights into the design and operation of the post-combustion CO₂ capture plant were derived through process analysis at pilot plant scale. The temperature profile of the absorber column was shown to have a maximum temperature (or “temperature bulge”) that could be located at different locations along the column height. The differences between the maximum and minimum temperatures in the absorber column were significant in the cases considered. The effect of poor water balance in the absorber column was demonstrated. This effect would not be observed using a steady state model. The performance of the absorption process was shown to be more sensitive to the L/G ratios in the absorber than the absolute mass flow rates of the solvent or flue gas. Finally, the chemical absorption CO₂ capture process was shown to have relatively slow dynamics in comparison with the power plant. Using a step reduction in reboiler heat duty, a process time constant of 57 minutes was estimated. This suggests that with disturbances from the coal-fired power plant, the CO₂ capture plant will require a longer period of time to find a new steady state.

The post-combustion CO₂ capture plant was scaled up to process the flue gas from a 500 MWe sub-critical power plant. A scale-up methodology framework was presented, which should minimise the number of iterations needed to develop scaled-up post-combustion CO₂ capture plant. The important units of the CO₂ capture plant were selected and sized. Case studies carried out show the effect of varying absorber packing heights and lean solvent loading on plant performance.

A dynamic model of 500 MWe sub-critical power plant was developed by RWE and modified for integration with the post-combustion CO₂ capture plant model. The links between the two models were primarily the flue gas stream from the power plant to the absorber, the steam drawn off from the IP/LP crossover to the reboiler for solvent regeneration, and the condensate return from the reboiler to the low pressure feed heater. The base case using 30 wt% MEA solution was described. 42% of the steam mass flow from the IP turbine outlet was drawn off for solvent regeneration. A case study was carried out investigating the effects of using 20, 30 and 40 wt% MEA solution for CO₂ capture. The power plant efficiency was highest with the 40 wt% case

though increased absorber temperatures were observed. It was concluded that further improvements could be made by application of inter-cooling in the absorber. At higher solvent concentrations, more quantities of corrosion inhibitors would be required.

Dynamic case studies on the integrated plant model were carried out. The first case investigated the effect of decreasing the target power output of the power plant – a typical practice for coal-fired power plants in meeting varying electricity demand. The CO₂ capture plant shows a slower response compared with the power plant. In addition, with poorly designed control systems in the CO₂ capture plant, interaction between the CO₂ capture level (solvent circulation) control and power plant output control loops would result in unsteady operation. It was recommended that tight control should be avoided on the CO₂ capture level control. In the second case study, the magnitude of disturbances with increasing CO₂ capture level buttresses the importance of appropriate controller tuning in the plant.

Based on the assumptions made in this study, it was estimated that the cost of electricity with CO₂ capture was €57.77/MWh. This is comparable with values reported elsewhere in the literature. The cost of CO₂ avoided was estimated as €32.96/tonne CO₂. A 10.4% drop in power plant efficiency was estimated.

7.2 Recommendations for future work

The dynamic models were developed using the rate-based approach. However, these models included the assumption that all chemical reactions attained equilibrium, which is a simplification that may not always be accurate. With the inclusion of reaction kinetics (moving from Model 3 to Model 5 as discussed in Section 3.3.1), the accuracy of dynamic models could be improved.

The current studies involved linking the post-combustion CO₂ capture plant with a sub-critical coal-fired power plant. The reduction in power plant efficiency to about 26.8% would typically make this option unattractive. It is likely that most post-combustion CO₂ capture plant units would be linked with supercritical power plants, which have higher plant efficiencies. It is therefore recommended that similar design and

operational studies are conducted with a post-combustion CO₂ capture plant model linked to a supercritical power plant model.

The cost of CO₂ avoided estimated in this study is €32.96/tonne CO₂. This is lower than the reported value by Abu-Zahra et al. (2007a) but still much higher than the target of recent research activities of €15/tonne CO₂ (CO₂CESAR, 2010). The cost improvements achieved are due to the higher absorber packing heights employed. Further improvements could be made to the process as outlined in Section 3.5. These include the use of inter-cooling in the absorber, use of improved solvents and employing more efficient process configurations such as the split flow configuration, amongst others. Base case simulation results reveal that there are significant heat duties as well as cooling duties. The significant cooling duties in the condenser and lean MEA cooler provide opportunities for better heat integration with the power plant. A pinch analysis on the integrated plant could provide options for better heat integration.

Optimization studies could be carried out on the integrated plant using formal optimization techniques. This would allow the consideration of additional optimization decision variables such as lean solvent loading, regenerator packing height, absorber L/G ratio, the inlet temperatures of the lean solvent and flue gas to the absorber among others. In addition, if intercooling is employed, the optimal position of the intercooler could be estimated to derive maximum benefits. If a split-flow configuration is employed, the optimal positions of the splits in the absorber and regenerator columns should be determined. In terms of optimal operation, the optimal regenerator pressure could be determined. To study this, a CO₂ compression model would be needed as well to provide accurate information on the benefits of operating at higher pressures. The optimal reboiler temperature (corresponding to the optimal lean solvent CO₂ loading) should also be considered. Using more than one absorber feed location could provide a simple (in terms of design) improvement to the system performance. The relative flows at the feed locations could be optimized.

Dynamic analyses in Section 6.4.3 reveal the importance of well-tuned control systems. The analyses should be repeated with better tuned control systems to investigate the

degree of improvement. There could be huge benefits from investigating dynamic optimisation on the whole process.

Solvent degradation has been ignored in this thesis. The effect of varying compositions of O_2 , SO_2 and NO_x should be investigated. SO_2 and NO_x could be separated from the flue gas using available technologies. However, it would be difficult to remove the excess O_2 from the flue gas. The effect of this should be studied as it may be necessary to modify the power generation process to minimise the level of degradation from excess oxygen.

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APPENDICES

Appendix A Estimating the accuracy of developed model

This section provides the detailed calculations for the estimation of the accuracy of the models based on validation results presented in Chapter 4.

The average percent deviation was used as a basis for evaluating the accuracy of the model for each validation case. This was carried out in a similar fashion as described by Tobiesen et al. (2007).

The location of the pilot plant measurements along the axis of the column did not match the locations predicted by the dynamic model because the position of the predicted values from the model along the height of the packed column was determined by the discretization used. To resolve this issue, trendlines of the predicted temperatures from the model were developed and their corresponding equations were used to determine the value the model would predicted at the exact location of the pilot plant measurement.

Based on these estimates, the percent deviation of the predictions from the pilot plant measurements were estimated and an average value was calculated for all the measurements. The trendlines are shown in Figure A.1 below whilst the determination of the absolute percent deviation is given in Table A.1.

The trendlines are given on the various figures in the form:

$$T_{sim} = f(ht)$$

where,

T_{sim} is the model (simulation) trendline prediction at the pilot plant measurement location;

ht is the height from the bottom of packing and f is a polynomial function with coefficient of determination (R^2).

The percent deviation ($Pdev$) was obtained by comparing the trendline prediction, T_{sim} with the pilot plant measurement, T_{pil} :

$$Pdev = \frac{|T_{pil} - T_{sim}|}{T_{pil}} \times 100\%$$

The accuracy of the model is then represented by the average percent deviations for all the measurement locations (which are n in number) on the column and is estimating as follows:

$$\text{Average percent deviation} = \frac{1}{n} \sum_{i=1}^n |Pdev_i|$$

A.1 Case 32 Absorber validation

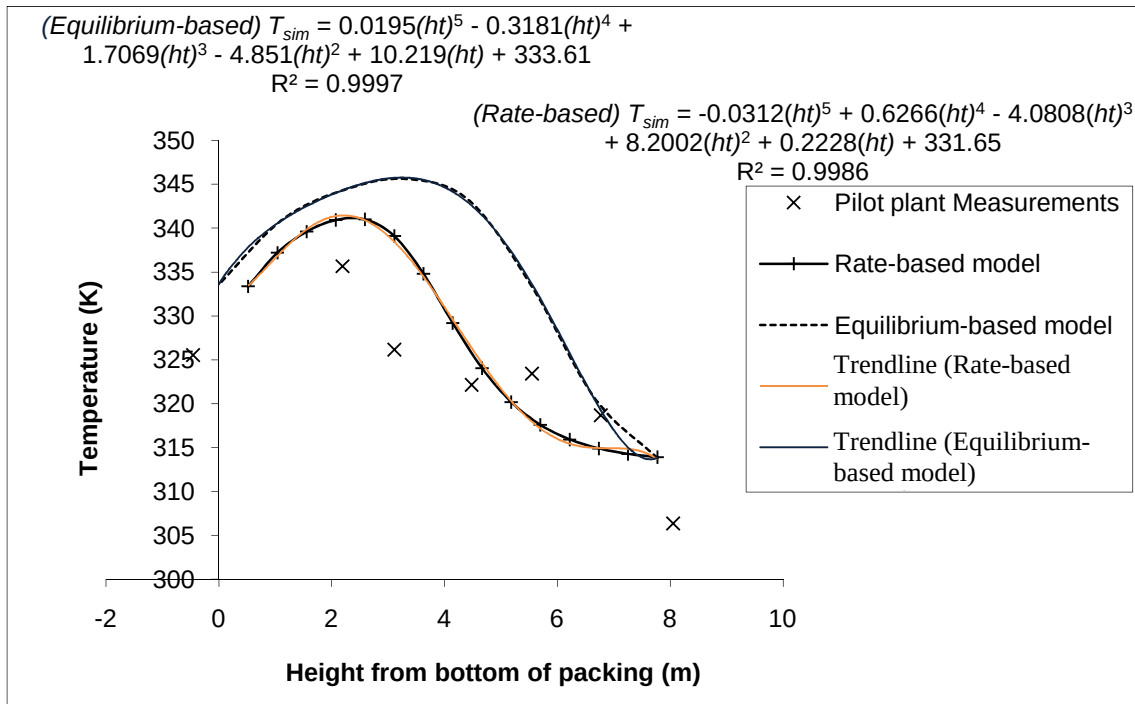


Figure A.1 Validation results based on absorber liquid temperature profile for Case 32 with polynomial trend lines for model predictions

Table A.1 Estimation of the average percent deviation for the rate-based and equilibrium-based models for Case 32

ht (m)	T_{pil} (K)	T_{sim} (Rate-based model) (K)	T_{sim} (Equilibrium-based model) (K)	$Pdev$ (Rate-based model) (%)	$Pdev$ (Equilibrium-based model) (%)
-0.46	325.54	333.71	327.70	2.51	0.66
2.19	335.66	341.45	344.32	1.72	2.58
3.11	326.16	338.45	345.73	3.77	6.00
4.48	322.16	326.41	342.56	1.32	6.33
5.55	323.42	318.07	333.58	1.66	3.14
6.77	318.69	315.33	319.19	1.05	0.16
8.05	306.36	312.66	315.32	2.05	2.92
			AVERAGE	2.01	3.11

A.2 Case 47 Absorber validation

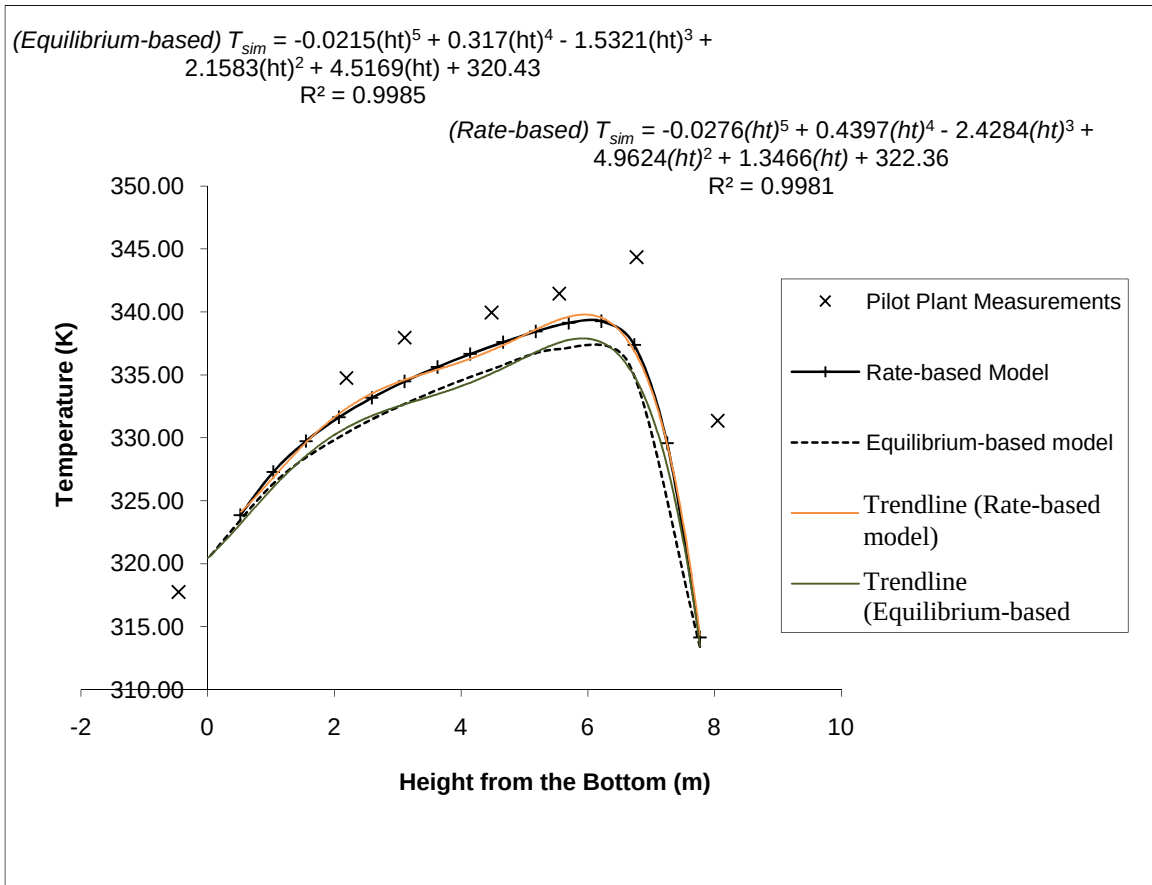


Figure A.2 Validation results based on absorber liquid temperature profile for Case 47 with polynomial trend lines for model predictions

Table A.2 Estimation of the average percent deviation for the rate-based and equilibrium-based absorber models for Case 47

ht (m)	T_{pil} (K)	T_{sim} (Rate-based model) (K)	T_{sim} (Equilibrium-based model) (K)	$Pdev$ (Rate-based model) (%)	$Pdev$ (Equilibrium-based model) (%)
-0.46	317.75	323.05	318.97	1.67	0.38
2.19	334.75	332.33	330.79	0.72	1.18
3.11	337.95	334.60	332.67	0.99	1.56
4.48	339.95	336.95	335.12	0.88	1.42
5.55	341.45	339.39	337.61	0.60	1.12
6.77	344.35	336.56	334.68	2.26	2.81
8.05	331.35	301.42	301.81	9.03	8.91
			AVERAGE	2.31	2.49

A.3 Case 32 Regenerator validation

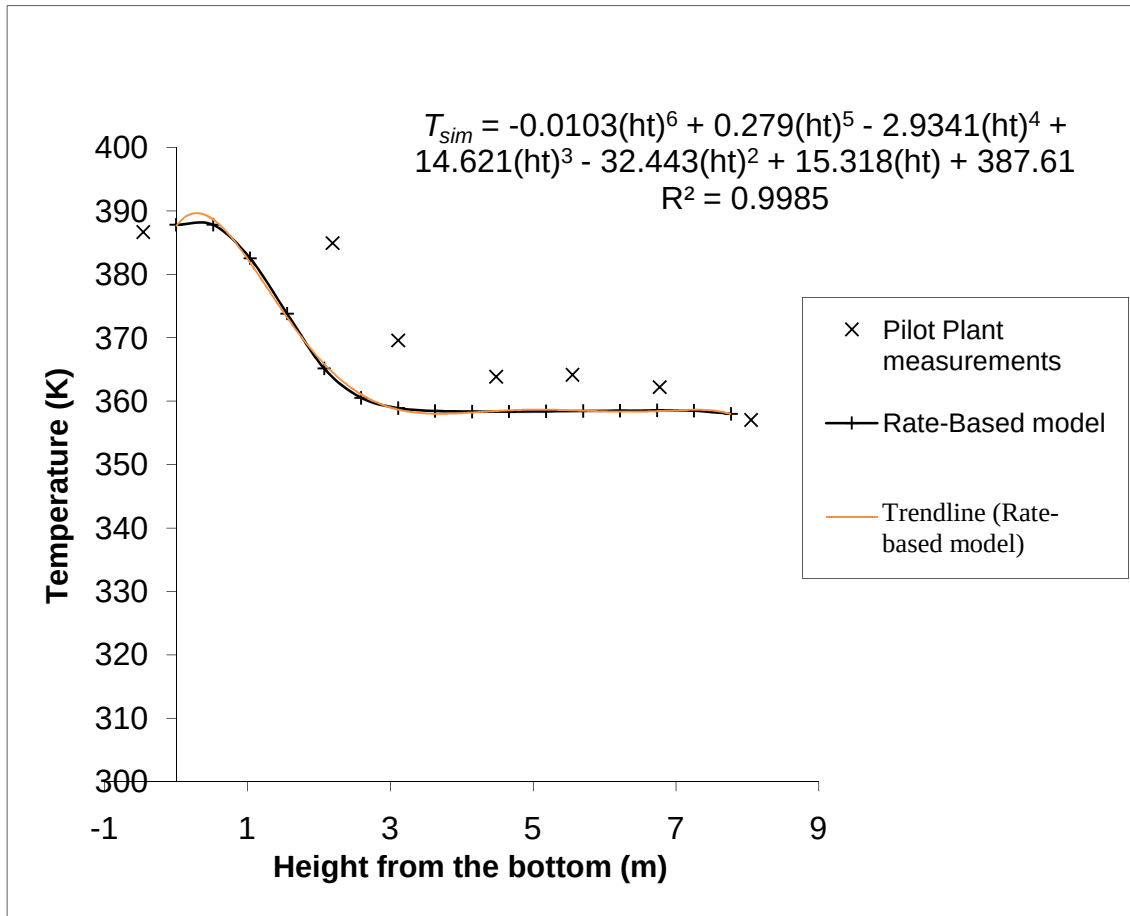


Figure A.3 Validation results based on regenerator liquid temperature profile for Case 32 with polynomial trend lines for model predictions

Table A.3 Estimation of the average percent deviation for the rate-based regenerator model for Case 32

ht (m)	T_{pil} (K)	T_{sim} (Rate-based model) (K)	$Pdev$ (Rate-based model) (%)
-0.46	386.68	372.14	3.76
2.19	384.93	364.55	5.29
3.11	369.59	358.63	2.97
4.48	363.84	358.05	1.59
5.55	364.15	357.10	1.94
6.77	362.21	353.66	2.36
8.05	357.04	343.00	3.93
		AVERAGE	3.12

A.4 Case 47 Regenerator validation

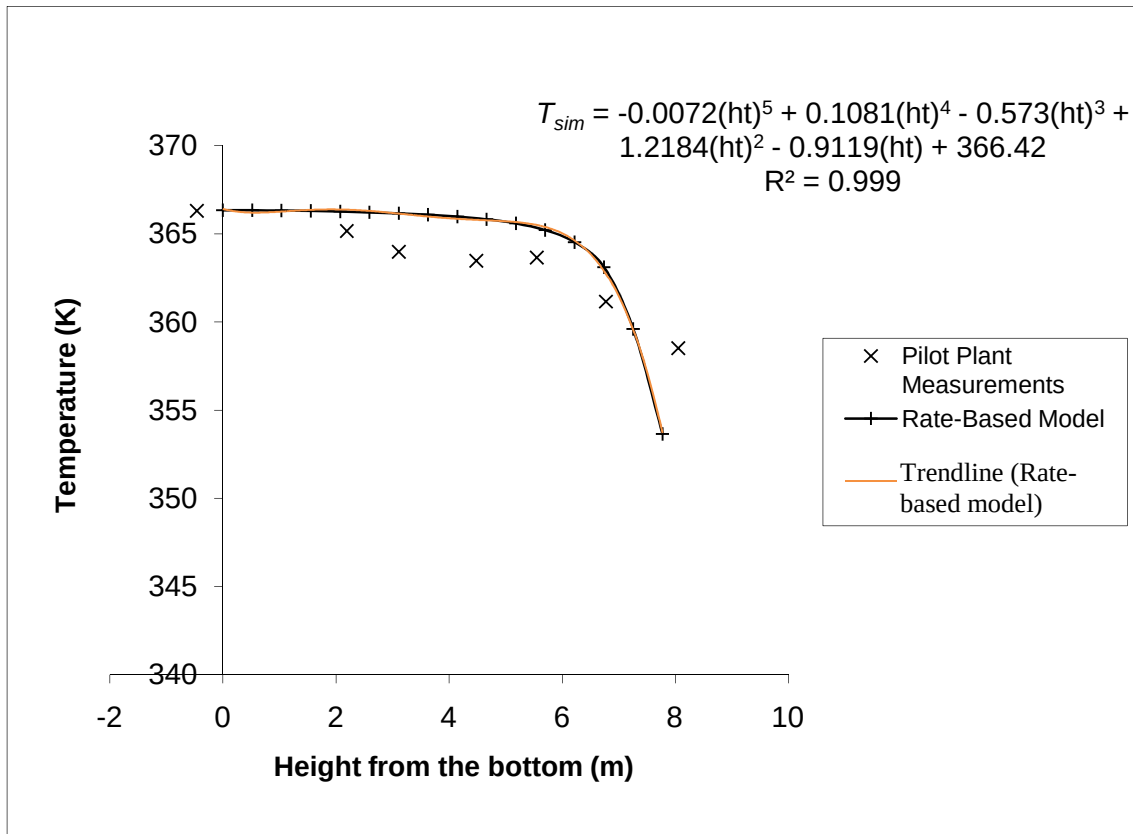


Figure A.4 Validation results based on regenerator liquid temperature profile for Case 47 with polynomial trend lines for model predictions

Table A.4 Estimation of the average percent deviation for the rate-based and equilibrium-based regenerator models for Case 47

ht (m)	T_{pit} (K)	T_{sim} (Rate-based model) (K)	$Pdev$ (Rate-based model) (%)
-0.46	366.30	367.16	0.23
2.19	365.16	366.37	0.33
3.11	363.98	366.15	0.60
4.48	363.47	365.82	0.65
5.55	363.65	365.58	0.53
6.77	361.16	362.98	0.51
8.05	358.51	349.68	2.46
		AVERAGE	0.76

Appendix B Scale-up calculations

This section provides the detailed calculations of variables used in Chapter 5.

B.1 Required solvent circulation rate

From values given in Table 5.1,

Estimated maximum flue gas mass flow rate = 600 kg/s

Estimated CO₂ mass fraction = 0.215

$$\text{Molar flow of CO}_2 = \frac{600 \frac{\text{kg}}{\text{s}} \times 0.215}{44 \frac{\text{kg}}{\text{kgmol}}} = 2.93 \text{ kgmol/s}$$

From assumptions (Section 5.1), MEA solvent absorption capacity = $0.2 \frac{\text{mol CO}_2}{\text{mol MEA}}$

Mass flow of MEA solution required (30.48 wt% MEA)

$$\begin{aligned} &= \frac{2.93 \frac{\text{kgmol}}{\text{s}}}{0.2 \frac{\text{mol CO}_2}{\text{mol MEA}}} \times 61.08 \frac{\text{kg}}{\text{kgmol}} \div 0.3048 \frac{\text{kg MEA}}{\text{kg solution}} = 2936 \text{ kg/s} \\ &\approx 2940 \text{ kg/s} \end{aligned}$$

B.2 Sample calculation of absorber diameter

Typical stream densities and viscosities were obtained using Aspen HYSYS®

Typical density of vapour in column = 1.3 kg/m³

Typical density of liquid in column = 1066.65 kg/m³

Liquid viscosity = 0.00187 Ns/m²

Packing factor = 310 m⁻¹ (Sinnott et al., 2005)

The $\frac{L_W^*}{V_W^*}$ ratio is equivalent to the L/G ratio = $\frac{2940}{600} = 4.9$

$$F_{LV} = 4.9 \times \sqrt{\frac{1.3}{1066.65}} = 0.171$$

From Figure 5.3 and with $F_{LV} = 0.171$ and 42 mm of water/metre packing height parameter, $K_4 = 1.149$

From Equation (5.2),

$$V_W^* = \sqrt{\frac{1.149 \times 1.3 \times (1066.65 - 1.3)}{13.1 \times 310 \times \left(\frac{0.00187}{1066.65}\right)^{0.1}}} = 1.21 \text{ kg/(m}^2\text{s)}$$

$$\text{Cross sectional area of column} = \frac{600 \frac{\text{kg}}{\text{s}}}{1.21 \frac{\text{kg}}{\text{m}^2\text{s}}} = 494 \text{ m}^2 \text{ (for one column)}$$

$$\text{Diameter } (\pi \text{ is } \frac{22}{7}) = \sqrt{\frac{494 \times 7}{22}} = 12.5 \text{ m}$$

For two columns, V_W^* is constant and the mass flow to the column is halved. The diameter then becomes 8.9 m. This was rounded up to 9 m.

B.3 Sizing of lean/rich amine heat exchanger

From pilot plant studies, typical values of the relevant variables of the heat exchanger were obtained.

Overall heat transfer coefficient of heat exchanger is assumed to be $5000 \text{ W/(m}^2\text{K)}$. This was the maximum amine/amine coefficient for a compact heat exchanger reported by Perry (1999).

Lean MEA inlet temperature = 386.0 K

Lean MEA outlet temperature = 349.1 K

Rich MEA inlet temperature = 334 K

Rich MEA outlet temperature = 371.9 K

$$\text{The log mean temperature difference} = \frac{(349.1 - 334) - (386 - 371.9)}{\ln\left(\frac{349.1 - 334}{386 - 371.9}\right)} = 14.6 \text{ K}$$

The specific heat capacity of the rich solvent was obtained from Aspen HYSYS[®] as 3880 J/(kg.K) .

The rich MEA mass flow rate was assumed equal to the solvent circulation rate.

Thus the rate of heat transfer in the heat exchanger

$$= 2940 \frac{\text{kg}}{\text{s}} \times 3880 \frac{\text{J}}{\text{kg.K}} \times (371.9 - 334) \text{ K} = 432.33 \text{ MW}$$

$$\text{The total heat transfer area required for such heat transfer} = \frac{432.33 \times 10^6 \text{ W}}{5000 \frac{\text{W}}{\text{m}^2\text{K}} \times 14.6 \text{ K}} = 5922 \text{ m}^2$$

6000 m^2 total heat transfer area was selected.

B.4 Sizing of lean amine cooler

Temperature of lean solvent to cooler = 349.1 K

Cooler outlet temperature = 313 K

Cooling water available at 293 K

Estimated cooling water outlet temperature = 308 K

Lean solvent flow rate assumed equal to estimated solvent circulation rate

Heat transfer rate in the cooler =

$$2940 \frac{kg}{s} \times 3880 \frac{J}{kgK} \times (349.1 - 313)K = 411.80 MW$$

$$\text{The log mean temperature difference} = \frac{(349.1-308) - (313-293)}{\ln\left(\frac{(349.1-308)}{(313-293)}\right)} = 29.3 \text{ K}$$

Assuming an overall heat transfer coefficient of 5000W/m²K,

$$\text{Total heat transfer area required for the lean MEA cooler} = \frac{411.80 \times 10^6 W}{5000 \frac{W}{m^2 K} \times 29.3 K} = 2811 \text{ m}^2$$

3000 m² total heat transfer area was selected

B.5 Lean MEA tank sizing

Solvent circulation rate = 2940 kg/s

Lean solvent density (estimated from Aspen HYSYS[®]) = 935.7 kg/m³

Holdup time required is 10 minutes or 600 seconds

$$\text{Required Lean MEA tank size} = \frac{2940 \times 600}{935.7} = 1885 \text{ m}^3$$

Appendix C Absorber packing height estimation

This section shows the details of the calculations used to estimate the absorber packing height in Section 6.5.

C.1 Installed cost of the absorber column

Inputs to the Aspen Process Economic analyzer V7.2 software include the absorber packing type, absorber packing height, the vessel tangent to tangent height and vessel diameter.

The height of liquid redistributor in large diameter columns is 2.5 m. Maximum feasible distance before redistribution is 6 to 8 m (Stichlmair and Fair, 1998).

A 27 m high packing in the column would require 4 redistributors – the total height would be $27 + (4 \times 2.5) + (2 \times 2.5 \text{ for top and bottom and water wash, } 5 \text{ m})$ – about 47 m.

The purchased cost of a single column is plotted in Figure B.1 as a function of absorber packing height, h . The cost values had been updated by the Marshall and Swift equipment cost index to give updated 1st Quarter 2010 prices. A linear trendline was obtained from the plot in Microsoft Excel. This is given as:

$$\text{Purchased Cost} = 132510 \times h + 1389000$$

The coefficient of determination (R^2) was obtained as 0.998 showing good fit of the data.

Table C.1 Marshall and Swift equipment cost indices used

1 st Quarter 2010 (Lozowski, 2010)	1448.3
1 st Quarter 2009 (Lozowski, 2009)	1477.7
4 th Quarter 2006 (Lozowski, 2007)	1353.8

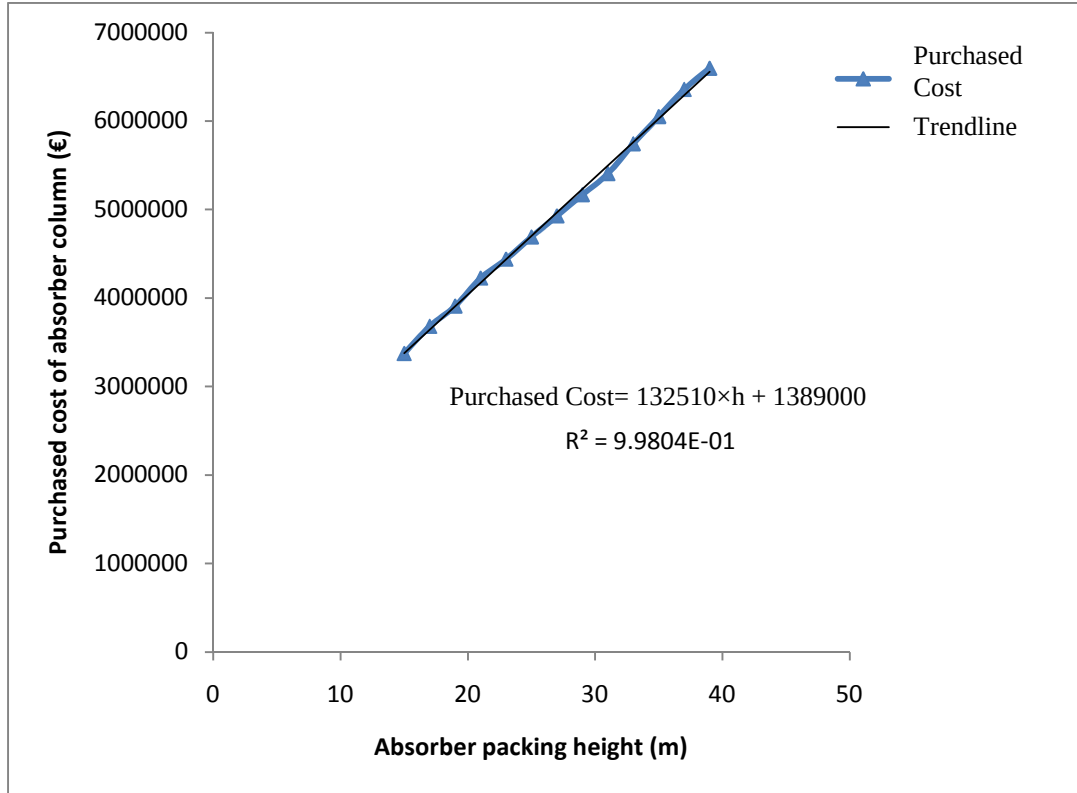


Figure C.1 Purchased cost of absorber as function of absorber packing height

Abu-Zahra et al. (2007a) reported factors for estimating installed cost from purchased cost: Installed cost = 171% of purchased cost.

At 27 m absorber packing height, the installed cost of the two absorber columns (ICo) would be:

$$\text{ICo}(h) = 2 \times 4,966,770 \times 171\% = \text{€}16,986,353$$

This is comparable with the value of the installed cost for the absorber reported by Abu-Zahra et al. (2007a).

C.2 Installed cost of the power plant and capture plant excluding the two absorber columns (PICO)

PICO was estimated based on the reported value of the total specific investment (€/kW) of the power plant with CO₂ capture by Abu-Zahra et al. (2007a) (given as €1855/kW). This value was also within the range proposed by IPCC (2005).

$$\text{Total investment} = \text{€}1855/\text{kW} \times 500,000 \text{ kW} = \text{€}927,500,000.$$

Purchased equipment cost of absorber (Abu-Zahra et al., 2007a) = €10.94×10⁶

Installed cost factors (Abu-Zahra et al., 2007a) = 171% of purchased cost.

From Abu-Zahra et al. (2007a), Investment cost of absorber = 10.94 × 10⁶ × 1.71 = €18,710,000

Therefore, PICo = €927,500,000 - €18,710,000 = €908,790,000

For the 1st Quarter 2010, PICo = €908,790,000 × $\frac{1448.3}{1353.8}$ = €972,226,737

C.3 Estimate of operating cost of plant

From Abu-Zahra et al. (2007a) the operating cost of the power plant and CO₂ capture plant excluding fuel costs per unit MWh is given as €13.9/MWh.

Thus the total operating cost per year (P_{OPEX})

$$P_{OPEX} = 13.9 \left(\frac{\text{€}}{\text{MWh}} \right) \times 7500 \left(\frac{\text{hr}}{\text{year}} \right) \times 500 \text{ MW} = \text{€}52,125,000/\text{year}$$

C.4 Estimate of plant fuel costs

Coal price (CIF ARA – 25 MJ/kg NCV) was seen to vary greatly (€46.98/tonne in May 2009 and €65.60/tonne in Jan 2010) so the average of the two values was taken and used as the 1st Quarter 2010 price – €56.29/tonne (Platts, 2009; Platts, 2010)

The fuel burn rate was fixed at 56.8 kg/s. Thus the fuel costs (P_{FUEL}) would be

$$P_{FUEL} = \frac{56.8 \left(\frac{\text{kg}}{\text{s}} \right) \times 3600 \left(\frac{\text{s}}{\text{hr}} \right) \times 7500 \left(\frac{\text{hr}}{\text{year}} \right) \times 56.29 \left(\frac{\text{€}}{\text{tonne}} \right)}{1000 \left(\frac{\text{kg}}{\text{tonne}} \right)} = \text{€}86,326,344/\text{year}$$

The total operating expenditure per year = €138,451,344/year.

C.5 CO₂ avoidance cost

Based on Equation (3.1), the CO₂ avoidance cost was estimated. The reference cost of €31.4/MWh for the power plant was obtained from Abu-Zahra et al. (2007a).

$$\text{Cost of CO}_2 \text{ avoided} = \frac{(57.77 - 31.4) \frac{\text{€}}{\text{MWh}} \times 500 \text{ MW}}{400 \left(\frac{\text{tonnes}}{\text{hour}} \right)} = \text{€}32.96/\text{tonne}$$

Appendix D Peer-reviewed publications

Peer-reviewed journal papers

1. Wang M., Lawal A., Stephenson P., Sidders J., Ramshaw, C. (2010). Post-combustion CO₂ Capture with Chemical Absorption: A State-of-the-art Review, *Chemical Engineering Research and Design*, doi:10.1016/j.cherd.2010.11.005
2. Lawal A., Wang M., Stephenson P., Obi O. (2010). Demonstrating full-scale post-combustion CO₂ capture for coal-fired power plants through dynamic modelling and simulation, *FUEL*, doi:10.1016/j.fuel.2010.10.056
3. 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*, 89, (10), pp 2791–2801.
4. Lawal A., Wang M., Stephenson P. and Yeung H., (2009). Dynamic modelling of CO₂ absorption for post-combustion capture in coal-fired power plants, *FUEL*, 88, (12), pp 2455-62.

Peer-reviewed conference papers

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