Energy Technology Innovation Strategy: Brown Coal Research and Development

Final report for

Brown Coal Innovation Australia (BCIA)

Latrobe Valley Post-Combustion Carbon Capture (LVPCC): CO2CRC-IPRH Stream (Carbon Dioxide Capture Technologies for Brown Coal Power Generation)

CONFIDENTIAL

Abdul Qader and Barry Hooper

March 2012 | CO2CRC Report No: RPT11-2962

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1. Executive Summary

The CO2CRC H3 Capture Project represents a world first in demonstrating post combustion capture (PCC) using three different separation technologies (solvents, membranes and adsorption) in parallel in a real power plant setting. The work, led by the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), in partnership with International Power Hazelwood (IPRH), was funded under the Victorian Government's ETIS program for three years commencing in 2007. The learning associated with operation of such a facility linked to the R&D from evaluating three novel capture techniques is unique. The benefit to the Brown Coal generation community is significant in terms of providing a high-level development and assessment of novel PCC technology for use within current Latrobe Valley power plants.

Key objectives of the project were to:

a. Test solvent, adsorbent and membrane post-combustion capture (PCC) techniques with real power plant flue gas
b. Reduce the technical risk and cost of capturing CO_2 from post combustion sources
c. Identify the most cost effective technologies for Victorian use
d. Provide large scale designs for all technologies and compare their technical and economic performance

The project met its objectives with successful demonstration of the three capture technologies. It produced valuable new information on heat integration, large scale simulation and economic evaluation; and provided new insights into the capture opportunities for existing power plants.

Major breakthroughs in understanding the likely energy penalties for Australian power plants with retrofit PCC plants have been made as a result of the project's findings on heat integration. Traditionally the nominal parasitic energy penalty (the lost power output of the plant) attributed to retrofitting capture to power plants is 30% and over. Through sophisticated heat integration incorporating the power plant and PCC capture plant Australian coal fired power plant parasitic losses have the potential to be reduced to between 15% and 20% with the brown coal plants being at the low end of that range.

New methodologies and techniques to optimise the flowsheet performance for PCC processes have been developed and used to produce feasible large scale integrated designs. These designs, based on moderately heat integrated configurations, resulted in the technical performance noted in the table below. The most energy efficient design (22.3 % energy penalty) is that based on the CO2CRC solvent IP, referred to as UNO Mk 3, a development using potassium carbonate solvent in a precipitating mode. The adsorption based capture process (23.8 % energy penalty) was next best in performance.

Summary of PCC Technology Alternatives

	Units	Base	MEA	Generic GJ\t*	UNO Mk3*	Polaris*	Adsorption*
Gross Electricity	MW	520	355	463	462	542	542
Auxiliary Power	MW	20	75	90	72	202	161
Net Power	MW	500	280	373	390	340	381
Net Cycle Efficiency (HHV)	%	28.6	16.0	21.3	22.3	19.5	21.8
Energy Penalty	%	-	44	25.4	22.3	32.0	23.8
Cooling Water Usage	t/MWh	2.41	-	6.21	5.9	6.3	6.0

* All processes with moderate heat integration

These initial designs offer valuable comparisons between the technologies but further optimisation is recommended for all designs with considerable improvement expected. A further point to note from the table is the water usage. All capture designs result in increased water usage and further work on the use of air cooling to reduce these figures will be necessary.

As part of the economic analysis the alternative capture technologies are compared to the conventional solvent Mono-Ethanolamine (MEA) in a relatively un-integrated configuration. This was chosen as the baseline for its status as the ‘standard configuration’ for most such studies worldwide.

The estimated costs per tonne avoided to capture CO_2 as a retrofit to a Brown Coal equivalent power station range from approximately A$53 to over A$108 per tonne CO_2 avoided.

The technology with the lowest specific cost of CO_2 avoided ($53 per tonne) is solvent absorption capture using the potassium carbonate based UNO Mk 3 process. The low energy penalty coupled with the moderate capital costs (A$622 million) compared to the other technologies are the major contributory factors.

The technology with the highest estimate cost is the baseline MEA solvent process at A$108 per tonne CO_2 avoided. The higher cost estimate is primarily due to the high energy consumption of the process and the high capital costs (over A$806 million).

The adsorption process also results in a low capture cost of A$55 per tonne CO_2 avoided, once again driven by the lower energy penalty and lower capital cost than other more expensive options.

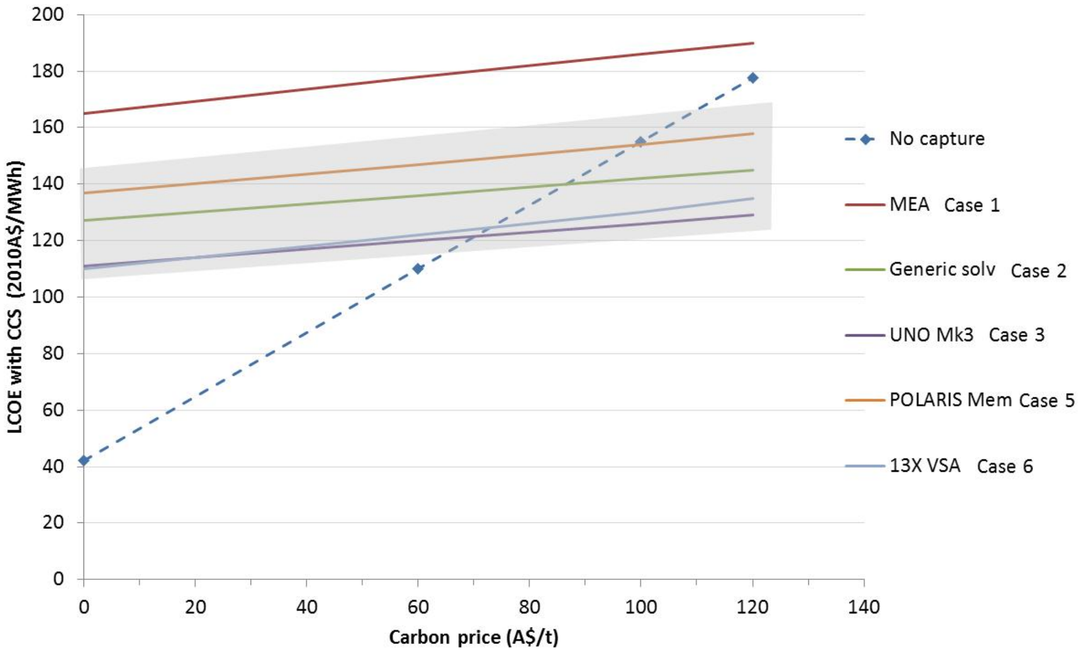
The results show the capital costs for the capture technologies to be in the range of A$620 to A$880 million.

Breakdown of the captures costs and the sensitivities to key cost variables are provided in this report, along with broad bands of uncertainties for both the resulting levelised cost of electricity (LCOE) and capture cost.

The graph below shows the change in LCOE (based on net electricity generated) for the different capture technologies with increasing carbon prices. The LCOE includes estimates of offshore transportation and storage costs for a Latrobe Valley/offshore Gippsland source-sink match. It should be noted that these costs are highly project specific and should be treated as indicative only. Below A$70/t carbon price, the results show that paying the price on unabated carbon would result in lower LCOE than implementing any of the capture technologies reviewed in this project. Above this price, implementation of capture results in lower LCOE.

The studies show that different low emissions technology retrofit configurations can provide a range of LCOE outcomes. These LCOEs are at the low end of a range of studies. This reinforces the view that retrofit should be considered when examining low emissions outcomes from Australian power plants, and particularly brown coal fired power plants given their location adjacent to attractive storage sites in the Gippsland Basin.

It is important to note that the outcomes of this study are largely indicative and based on well thought out but un-optimised designs. Further studies and detailed review with proponents may result in revision to the current findings. Any preferred approach will have to be fully designed to determine the final project cost estimate.



R&D Outcomes

The specific outcomes from the project and particularly the trials at Hazelwood on the three technologies are:

- Successful management of a complex multi-party, multi-technology, multi-objective carbon capture demonstration project.
- Confidence and skill development in construction, commissioning and operation of capture plants on a power plant site using real flue gas.
- Gathering of valuable information to facilitate technology development for three pre-combustion techniques (solvent absorption, membranes and adsorption) resulting in substantial reduction in technical risk and cost for all three technologies.
- Large scale design development

The specific learnings for each of the research areas are as follows:

Solvent absorption

The Hazelwood Carbon Capture plant has successfully demonstrated the operation of solvent capture at considerable scale and provided an insight into the issues for larger scale demonstrations.

Research and trialing on the UNO liquid K_2CO_3 system has led to the development of the significantly lower energy alternative process, UNO Mk3, utilising precipitating carbonate technology.

Large scale design evaluations have identified the CO2CRC UNO Mk 3 process to be a highly competitive post combustion technology through both the energy reduction of the precipitating system and it's inherent sulphur and nitrogen removal capability - obviating the need for supplemental or new gas treatment facilities such as FGD and deNOx.

Membrane

The trials provided valuable information about performance of membrane capture and with real power plant flue gas including selectivity over time and the effects of competitive sorption. There was little evidence of ash build up on the membrane during the trials in the current plant configuration.

Considerable work has been completed on the impact of impurities (including water) on suitable membrane materials along with some development of process designs for large scale applications.

Adsorption

Stable operation with minimal intervention has been demonstrated on a Zeolite 13X vacuum swing adsorption (VSA) treating power plant flue gas. Water management protocols have been established proving that no expensive pre-treatment steps will be necessary for VSA operation with the CO2CRC designed process while achieving high degrees of separation.

The adsorbent system offered the equal lowest cost alternative for retrofit thus warranting further analysis of the cycles, materials alternatives and importantly the capital equipment requirements.

Heat integration

A multi-objective optimisation tool for CO_2 capture from power stations has been developed by CO2CRC as part of the CO2CRCs ETIS post- and pre-combustion projects. It enabled the creation of highly integrated designs that minimise energy usage and reduce costs.

Energy penalty targets for Australian power plants have been established using comprehensive heat integration of capture plant into power cycles. This demonstrates the significant opportunity for retrofit PCC to Australian power plants at much lower energy penalties than previously considered possible. In particular the brown coal fired power plants have the additional opportunity of innovative pre-drying as potential add-on to capture plant without pursuing the full scale deep drying technologies.

Our heat integration studies have identified that considerable amounts of post-combustion capture (40-50% capture) can be done with minimal impact on the Net Power from any given plant. This may offer interesting implementation opportunities in the transition to full capture. Energy penalties for full scale (90% capture) could be further reduced both by an optimisation procedure targeting process parameters and through more aggressive, but still manageable, heat integration strategies.

Economics

The sensitivity results show that cost estimates are strongly affected by the discount rate. Doubling the discount increases the capture cost by up to 30% of the baseline cost. The effect of increasing the energy penalty, the capital cost and energy price by 20% had less impact, with increases in the capture cost observed to be up to 10%.

Intellectual Property

Intellectual property has been developed/tested in the following areas:

- Knowledge in designing and operating plant & process for removing CO_2 from gas streams using;
    - Solvents
    - Gas-liquid membrane contactors
    - Gas separation membranes
    - CO_2 adsorption systems and adsorbents
- Large scale designs for these systems
- Heat & Process Integration methodologies for reduced parasitic load.

Communications

Communications, publications, awards, collaborations and skills development have been important components of this project and this area has resulted in the following outcomes:

- The project has been visited by more than fifty groups from Australia and overseas, raising the profile of CO_2 capture researchers and industry collaborators.
- At least 53 publications including 27 refereed journal articles, a book chapter, media releases, news/web articles, interviews and public lectures have been produced related to this project. They have enhanced public and scientific knowledge and awareness of CO_2 capture.

More than 20 researchers and higher degree research students have been involved in the project. Their involvement with the industrial partners has assisted in developing high caliber R&D skills for the Brown Coal industry in Victoria. The capabilities of our researchers has been formally acknowledged by the awarding of a Fulbright scholarship in 2009 to one of our postdoctoral fellows, Dr Colin Scholes, which provided the opportunity to collaborate with one of the leading international gas separation membrane researchers at The University of Texas at Austin, USA.

Recommendations

As a result of this work it is recommended that:

- Further engagement between CO2CRC and International Power be pursued to formalize the project findings in terms of potential designs and commercialisation issues for the range of capture technologies;

- Optimisation of the process designs be carried out, in particular for the membrane and adsorption technologies. This will provide greater confidence in the comparisons and subsequent selections of technologies for more detailed study;
- Continue to run targeted tests on membranes and adsorbents at the Hazelwood site to gather additional information under the CO2CRC program;
- Targeted R&D resulting from the evaluation of different separation technologies be initiated and potential future pilot facilities be identified as required. In particular work on UNO Mk3, membranes and adsorbents should be investigated;
- The learning developed from the pilot facilities in this project be incorporated in any future development facility;
- Further economic assessments targeting implementation pathways for retrofit and including more detailed assessment of transport and storage should be undertaken;
- Ongoing communication of the project findings be provided to local and international stakeholders to demonstrate the potential for low emissions power as retrofits to existing plants. The opportunities for formal heat integration studies for CCS projects should be highlighted.

2. Introduction

2.1 ETIS Brown Coal Research and Development

Victoria is facing significant environmental challenges to the economic advantages it derives from utilisation of its very low-cost brown coal resources. The State accounts for 22 % of Australia's greenhouse gas emissions, and approximately 52 % of these arise from the use of brown coal for electricity generation in the State. The Victorian Government has committed to a substantial reduction in greenhouse gas emissions by 2020. Its Department of Primary Industry (DPI) initiated the Energy Technology Innovation Strategy (ETIS) that has provided more than $12 million to low emissions coal research and development projects. These projects covered a broad range of research topics including carbon capture, combustion, gasification and dewatering and involved working with researchers and industry, to ensure successful progression of new, low-emission energy technologies through their innovation processes.

The single objective of ETIS is to drive prospective sustainable energy technologies down their respective cost curves and, in so doing, ensure that a portfolio of low cost, low emissions technologies are available for commercial deployment to minimise the economic impact of a cost on carbon. A key feature of initiatives under ETIS is that Victoria’s investments support those technologies that industry would choose as the most practical, commercial, cost effective and attractive to Australian Government and private investment.

The ETIS Brown Coal Research and Development Grants Program builds on the significant achievements of the brown coal industry and academia over several decades, continuing the Victorian Government's commitment to investing in brown coal science, technology and innovation. Investment in R&D in any sector plays a major role in maintaining, retaining and growing the skills and knowledge base.

This current project, known as the CO2CRC-IPRH H3 Capture Project (as it tests three capture technologies at Hazelwood – H3) and covered by this Volume 1, is a part of the broader Latrobe Valley Post-Combustion Capture (LVPCC) project. The LVPCC was the result of DPI’s grant under the ETIS R&D program of $2.5 million, details of which are provided in Section 2.3.3 below.

Following the success of the ETIS Brown Coal R&D Grants program, Brown Coal Innovation Australia (BCIA) was established in 2009 with $16 million funding from the Victorian Government to continue to fund new low emissions coal research and development in Victoria. BCIA is an independent company that has a clear mandate to co-invest with industry and research entities in skills development and R&D projects in new high quality brown coal technologies and in adaptation of existing low-emissions technologies to Victorian brown coal. BCIA co-ordinates all brown coal R&D in Australia in conjunction with the Commonwealth's Australian National Low Emissions Coal (ANLEC) R&D organisation. This project has been funded by BCIA since July 2010 with an extension grant of $0.481 million.

This report covers the research completed under funding from both the original ETIS R&D grant and the BCIA extension grant.

2.2 Technology Options for CO_2 Capture

It is now well accepted that CCS is an essential part of the portfolio of technologies that is needed to achieve substantial global emissions reduction [*CO2CRC web page*]. IEA reported that CCS will deliver one-fifth of the lowest-cost GHG reduction solution in 2050 and it also stipulated that in the absence of CCS, the overall cost to achieve a 50 % reduction in CO_2 emissions by 2050 will increase by 70 % [*IEA, 2010*]. As a result, R&D activities and interests in the CCS area are increasing around the world.

Reducing the cost of the three main elements in the CCS chain (CO_2 capture, CO_2 transport and CO_2 storage) is critical to the effective demonstration and large-scale deployment of CCS. Among them, capture has the most potential for cost reduction due to its sheer size in the chain in terms of cost of deployment (60 % to 80 %). Various capture technologies have been tested and deployed at a range of scales around the world. The main challenges faced by the capture technologies are:

a) Reducing the capital cost of the equipment;

b) Reducing the energy penalty (i.e., the additional power generation required to compensate for the losses in output due to capture);

c) Reducing the total cost by heat and process integration; and

d) Addressing scale up issues.

There are four main areas where capture technologies are applicable. These are:

1. Post-combustion capture (PCC): Carbon dioxide (CO_2) is separated out from flue gases after combustion of fossil fuels in air. The CO_2 concentration in the flue gases is usually around 10 – 12%.
2. Pre-combustion capture: Fossil fuel gasification plants produce syngas, which is a mixture of hydrogen (H_2) and carbon monoxide (CO) under high pressure and temperature. The syngas is shift reacted to convert CO into CO_2, which is separated from the mixture. The relatively pure H_2 is combusted in a turbine in an Integrated Gasification Combined Cycle (IGCC) plant. The CO_2 concentration in the gases sent to the capture unit can be up to 60% on a dry basis.
3. Oxyfuel combustion capture: Combustion of fossil fuels occurs in the presence of pure (or enriched) oxygen leading to the production of CO_2 and steam from which the CO_2 is then separated. Because combustion occurs in a stream depleted of nitrogen, the concentration of CO_2 in the resulting flue gas is higher, typically over 60%.
4. Other industrial process gas capture: This includes capturing CO_2 from process streams that contain significant concentrations of CO_2 such as in purification of natural gas; production of synthesis gas for manufacturing ammonia, alcohols and synthetic liquid fuels; cement manufacture; steel production; and, fermentation processes for food and drink production. CO_2 could be captured from all these streams using techniques that are common to pre-combustion capture, post-combustion capture and/or oxyfuel combustion capture.

Technologies that have been trialled for one or more of these applications include:

i. Solvent absorption;
ii. Membrane separation;
iii. Adsorption;
iv. Cryogenics;
v. Hydrate formation;
vi. Chemical Looping;
vii. Mineralisation via aqueous precipitation;
viii. Enzyme-based capture; and
ix. Algae-based capture.

Details of these technologies are readily available in the published literature, e.g., the IPCC Special Report [IPCC, 2005], Global CCS Institute [GCCSI-a, 2010], Electric Power Research Institute [EPRI, 2007], the RECCS study by the Wuppertal Institute [WI 2010] and the International Energy Agency's "Technology Roadmap – Carbon capture and storage" [IEA, 2010]. Since this project deals with post-combustion capture, only technologies suited for this application are summarised below. Despite low CO_2 concentration in the flue gas making post-combustion capture equipment large and potentially expensive, post-combustion processes are considered to have the highest short- to medium-term achievable potential for CO_2 reduction. Due to the ability for application to both existing emissions sources and other industrial applications, PCC is suitable for retrofitting onto existing power plants, which cause around two thirds of CO_2 emissions in the electricity sector [Figueroa et al. 2008]. Furthermore, post-combustion processes are the most developed technological path to CO_2 capture, with similar scrubbing processes already in use in other branches of industry. Some of the leading suppliers include Mitsubishi Heavy Industries (MHI, Japan), Cansolv (Canada), Fluor (USA), HTC Purenergy (Canada) and Aker Clean Carbon (Norway) [WI 2010]. Other players include RWE, who in conjunction with Linde and BASF, have launched a pilot plant in Germany. RWE is also involved in developing two other pilot plants in USA under the auspices of the Electric Power Research Institute (EPRI) and the American Electric Power (AEP). Vattenfall Europe is another player who is implementing their technology in a lignite-fired power plant in Lusatia, Germany. A compiled document [Appendix 1] shows the current status of worldwide commercial scale post-combustion capture facilities [GCCSI-b, 2010].

Solvent absorption is the leading technology in this area. Although hindered amines (Mitsubishi Heavy Industry) and tertiary amines (Cansolv's DC 101) have been successfully deployed in large scale gas-fired power plants, use in coal fired power plants is only now being trialled at large scale. The University of Texas, The University of Regina and The University of Waterloo are currently conducting laboratory tests on blended piperazines (PZ) with other amines and carbonates (Potassium Carbonate). The chilled ammonia process, originally developed by Nexant but now licensed by Alstom, is being tested by American Electric Power in New Haven, West Virginia and by E.On in a pilot plant in Sweden [WI 2010]. This process has also been under testing in Australia by CSIRO in a power plant in NSW. Other solvents currently undergoing laboratory-scale testing include ionic liquids and biphasic solvents. While solvents are already available for post-combustion capture, more research is needed to develop solvents with improved characteristics, such as reduced energy requirements, rate promotion, lower solvent loss rates and reduced corrosion. In all cases defining the large scale equipment design issues is also a challenge. With these challenges in mind, the current study involves a potassium carbonate process patented by CO2CRC (The University of Melbourne), which has been developed from reviewing an old technology for this new application. This is described in Section 5.1.

Membrane separation technologies utilise high pressure drops across the membrane to achieve separation streams. While gas separation membranes are already available for natural gas and oxygen separation, membranes suited to CO_2 PCC separation have received less attention until recently. Various polymeric, ceramic and metal-based membranes are currently under R&D investigations to evaluate their CO_2 removal characteristics including selectivity, permeability and the resulting economic performance. The challenge is to develop a membrane with high CO_2 selectivity and permeability that is also tolerant to impurities found in flue gas streams such as NOx and SOx. Several institutions, including the University of New Mexico, the New Mexico Institute of Mining and Technology, the Membrane Technology and Research (MTR) and the University of Texas are carrying out research into alternative membrane designs. CO2CRC (The University of Melbourne) has been active in this area carrying out testing at both laboratory and pilot plant scale as described in Section 5.2.

Adsorption technology, which removes CO_2 through the interaction between gases and solids, is another candidate for PCC. Considerable focus has been on zeolites (13x) due to their high porosity and a crystalline molecular structure that shows relatively high selectivity for CO_2 and N_2. CO_2 capture using zeolites was tested by Tokyo Electric Power Company (TEPCO) in the 1990s, at the Carnegie Mellon University and at CO2CRC (Monash University). Metal-organic frameworks (MOFs) and amine loaded mesoporous silicates are also under research at the US Department of Energy (DOE), the University of Phoenix (UOP) and CO2CRC (Monash University). The current study involved zeolites, including a modified version developed by CO2CRC (Monash University) as detailed in Section 5.3.

General overviews of CO2CRC's capture technologies applied in this PCC project are given in the following section.

2.3 Project Development

The International Power Hazelwood (IPRH) components of the broader post-combustion project were completed by CO2CRC and International Power personnel. The project was originally a stand-alone submission to ETIS R&D with CO2CRC as the proponent. However, after requests from the DPI, a combined project in conjunction with Loy Yang Power and CSIRO resulted in the LVPCC with CO2CRC and Loy Yang Power as joint proponents. The following section outlines the prospects and technologies for CO2CRC-IPRH H3 component and the interaction with LVPCC.

2.3.1 CO2CRC and Capture Research

CO2CRC has, since 2003 (see figure 2.1), pursued research into technologies that can be applied to electricity generation as well as other industrial CO_2 sources such as natural gas production. The aim is to develop new, and improve existing, technologies to significantly reduce the cost of CO_2 capture. An important part of the strategy is to ensure that the research does not duplicate work being conducted elsewhere. To achieve its aim, CO2CRC partners with leading international companies and researchers at Australian and international Universities to develop CO_2 capture research that spans from laboratory-scale through to plant-based test facilities.

The laboratory facilities together with the pilot scale industrial demonstration facilities and the large scale design resources provide a unique multi-scale, multi-technology, multi-site capture R&D capability to drive research outcomes towards commercialization. More details of these capabilities are provided below.

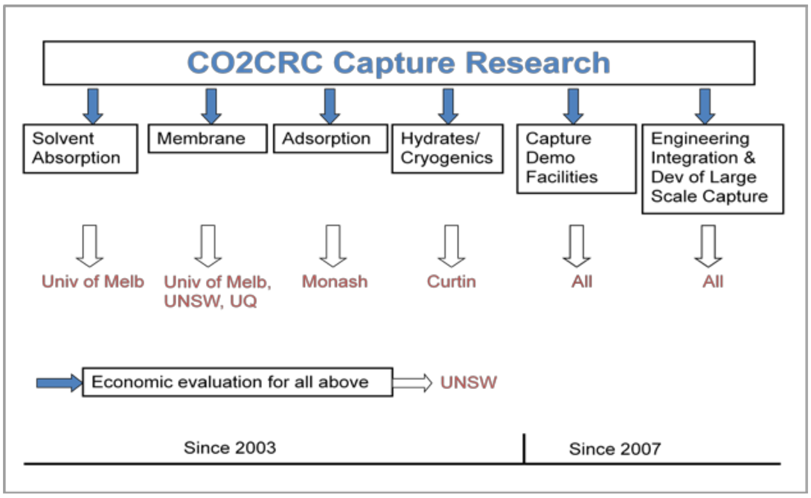


Figure 2.1 CO2CRC Capture research at a glance

2.3.1.1 Solvent Absorption

Solvent absorption (Fig 2.2) is the traditional method for removing CO_2 from flue gas. After feed gas enters the absorption column, it contacts the solvent and the CO_2 is absorbed. The other gases leave the absorption column, and the “rich” solvent containing the CO_2 is pumped to another column, variously called a desorber, a stripping column or a regenerator. The “rich” solvent is heated to release the CO_2 from the solvent. The CO_2 emerges at the top of the desorber where it is cooled to remove water and then captured. The water is returned to the desorber and the “lean” solvent is pumped back to the absorber. On the way, the hot, lean solvent passes through a heat exchanger with the rich solvent leaving the absorber column. This cools the lean solvent and heats the rich solvent on its way to the desorber.

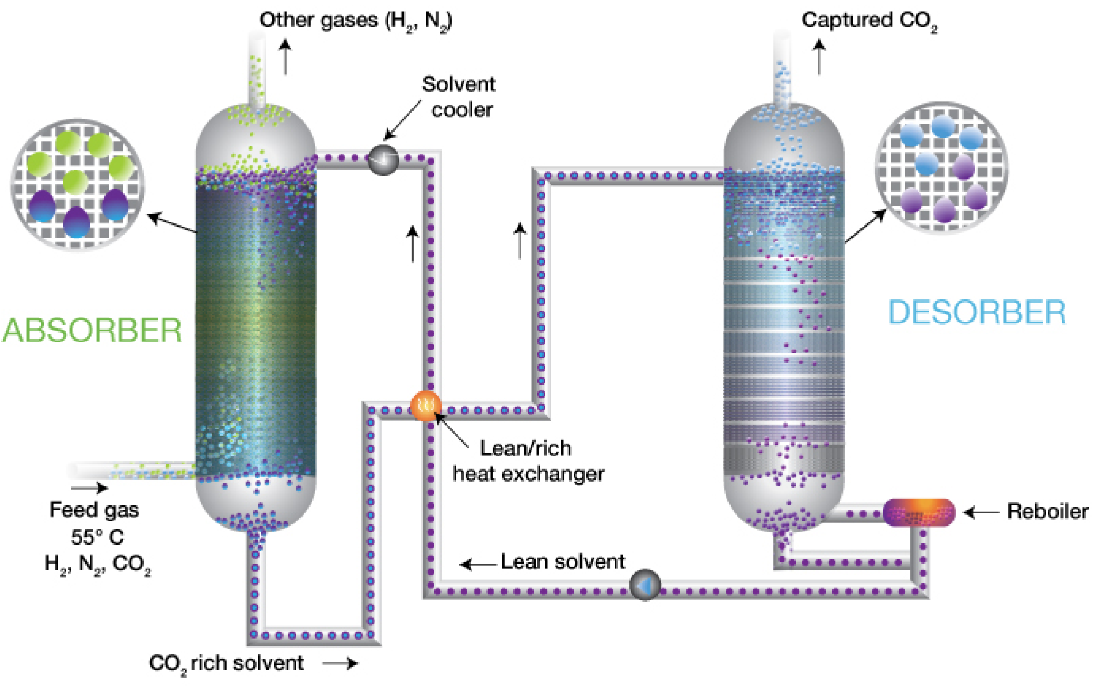


Figure 2.2 Schematic diagram of solvent capture process

2.3.1.2 Membranes

Relative to absorption or adsorption technologies, membrane technology is a ‘new’ technology that has the potential to provide significant capture cost reductions. Membranes can be used to separate CO_2 from other gases (gas separation membranes) or to allow CO_2 to be absorbed from a gas stream into a solvent (membrane gas absorption).

Gas Separation Membranes

CO_2 can selectively pass through gas separation membranes (Fig. 2.3), to be removed from the feed gas. These membranes separate gases based on their sizes. They are better suited for separations at higher pressures and higher CO_2 concentrations.

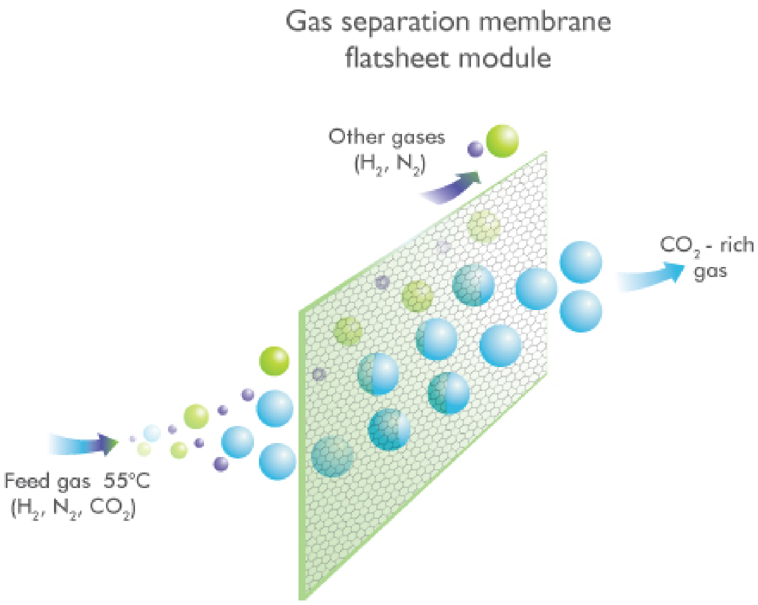


Figure 2.3 Gas Separation Membranes

Membrane Gas Absorption

In membrane gas absorption a membrane separates the feed gas from the liquid solvent (Fig 2.4). The CO_2 is absorbed into the solvent via pores in the membrane, while the other gases are not. The CO_2 is removed from the solvent as for solvent absorption.

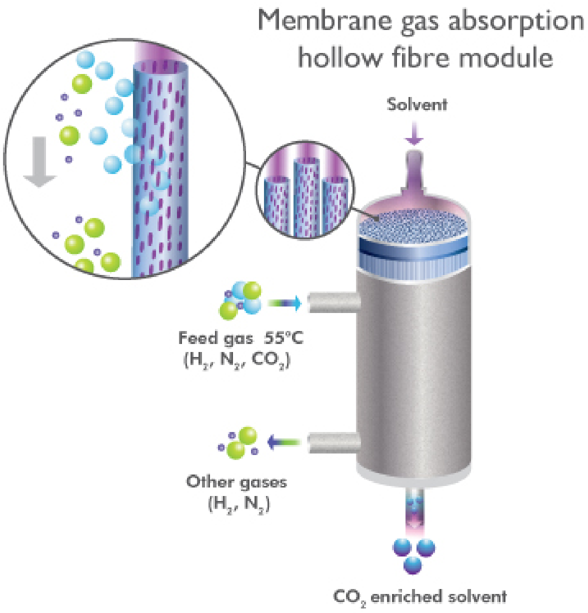


Figure 2.4 Membrane gas absorption

2.3.1.3 Adsorption Technology

Adsorbents are solids that have the capacity to capture CO_2 on their surface and can be reused in a cyclical process. When the CO_2 is released from the adsorbent by reducing the pressure, this is known as Pressure Swing Adsorption (PSA) (Fig 2.5). Alternatively, the CO_2 can be released using Vacuum Swing Adsorption (VSA), usually for post-combustion capture, Temperature Swing Adsorption (TSA) or in a combination mode. A multi-layered adsorption column (Fig. 2.6) can provide staged separation of multiple gas components.

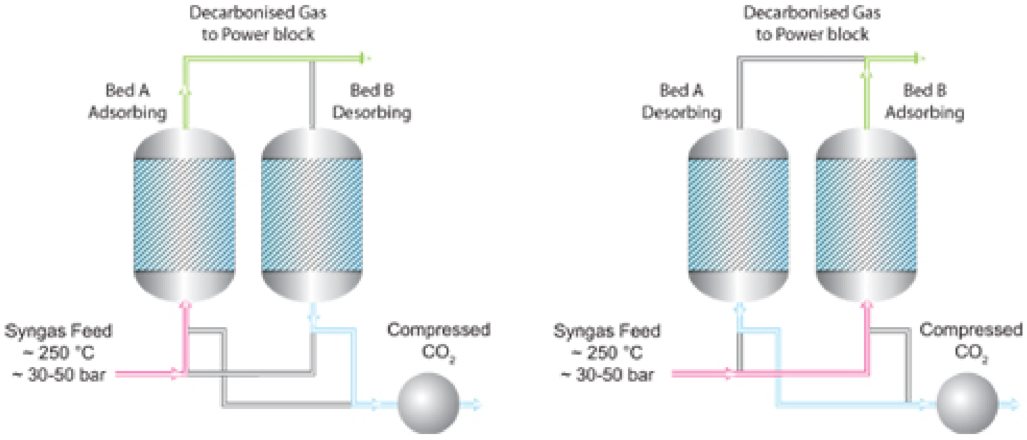


Figure 2.5 Adsorption Process

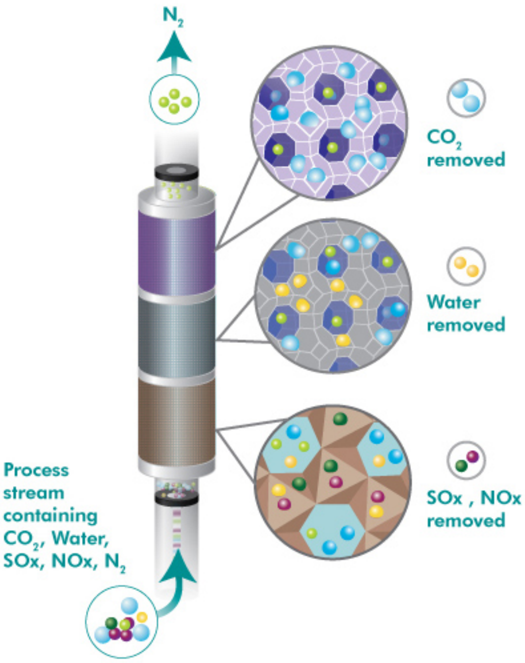


Figure 2.6 Multi-layer Adsorption Column

2.3.1.4 Cryogenics/Hydrates Systems

Cryogenic/hydrate systems, though not investigated as part of the ETIS/BCIA funded research, are believed to be attractive for pre-combustion capture and are being pursued in the CO2CRC capture research portfolio. Its application in the post-combustion field as a hybrid technology is under consideration though not through this project.

2.3.1.5 Capture Demonstration Facilities

Under BCIA/ETIS funding, we have established pilot plants for three of our capture technologies (solvent, membrane and adsorption) for both pre-combustion at Mulgrave (HRL) and post-combustion at the International Power Hazelwood (IPRH) power plant.

2.3.1.6 Engineering Development / Process Integration for CO_2 Capture

The translation of CO2CRC IP from research through to large scale commercial application is critical. The Engineering team undertakes studies particularly in relation to heat and energy integration and practical equipment issues likely to lead to significant reduction in CO_2 capture costs for large-scale plant.

2.3.1.7 Economic Evaluation

A major decision metric for large-scale engineering projects is the commercial viability. The CO2CRC economics team is at the forefront of developing such evaluation methodologies nationally and internationally. These tools help to drive the direction of the research and facilitate decision making for large scale CCS application all the way along the CCS chain.

2.3.2 International Power

International Power plc is an international electricity generator formed in 2000 by the demerger of National Power. International Power entered into the Australian energy industry in 1996 with the purchase of Hazelwood power station and the associated mine in 1996 [now called International Power Hazelwood (IPRH)]. It has grown to become Australia’s largest private generators of electricity. International Power Australia owns and operates 3,723 MW (gross) of renewable, gas-fired and brown coal-fired generating plants in Victoria, South Australia and Western Australia. In February 2011, International Power combined with GDF SUEZ’s Energy International Business Areas outside Europe and certain assets in the UK and Turkey, with more than 70 GW of power generation (gross) in operation and 17 GW gross capacity under construction.

Together with power generation, International Power plc is actively involved in:

1. Wholesale production of fresh water through seawater desalination;
2. LNG terminals and distribution;
3. Production and distribution of steam;
4. Electricity retail business;
5. Open-cast coal mining;
6. Gas transportation and distribution;
7. Renewable energy; and
8. Developing measures to reduce greenhouse gas emissions, e.g., carbon capture.

As part of its drive to cut down CO_2 emissions, IPRH has designed and built a relatively large size (50 tpd design capacity) solvent-based PCC plant with support from the Federal Government's Low Emissions Technology Demonstration Fund (LETDF) and ETIS LSDP. This is known as the "Hazelwood Carbon Capture Project" (see Figure 2.7). Under the current H3 project agreement as part of LVPCC, IPRH provided that plant for CO2CRC to conduct tests on solvent technology and supported the installation and testing of the other capture technologies (membrane and adsorption) at Hazelwood power plant.

The large scale PCC plant was supplied by the Process Group (a supporting participant of CO2CRC) and installed by Alstom under contracts directly with IPRH. Process Group also built and supplied the adsorbent and membrane test rigs.

2.3.3 Development of the CO2CRC-IPRH H3 Capture Project

As indicated in Section 2.1, the Victorian Government's ETIS initiative in 2006 drove the development of the collaborative framework for the carbon capture demonstration activities in the heart of the Latrobe Valley. The LVPCC project (Fig. 2.7) combined the facilities and expertise of Loy Yang Power (LYP), International Power Hazelwood (IPRH), the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) and the Commonwealth Scientific and Industrial Research Organisation (CSIRO) to conduct research and pilot scale deployment of prospective technologies for the post combustion capture (PCC) of carbon dioxide from the flue gases of brown coal fired power stations. This is an essential step on the roadmap to large scale abatement of greenhouse gases by carbon dioxide capture and storage.

The LVPCC has two research streams (Fig. 2.7) - one is the CSIRO-LYP stream led by CSIRO and based at Loy Yang Power Plant to investigate solvent capture technology ($1.475 million ETIS funding); the other is the CO2CRC-IPRH stream, i.e., the current project, also known as the "CO2CRC-IPRH H3 Capture Project" led by CO2CRC and based at IPRH power plant at Hazelwood (ETIS funding of $1.025 million).

In addition to reducing the cost of existing solvent based post-combustion CO_2 capture technology, the aim of the H3 capture project was also to investigate other emerging technologies (namely, membrane and adsorption) that are likely to prove cheaper in the long term.

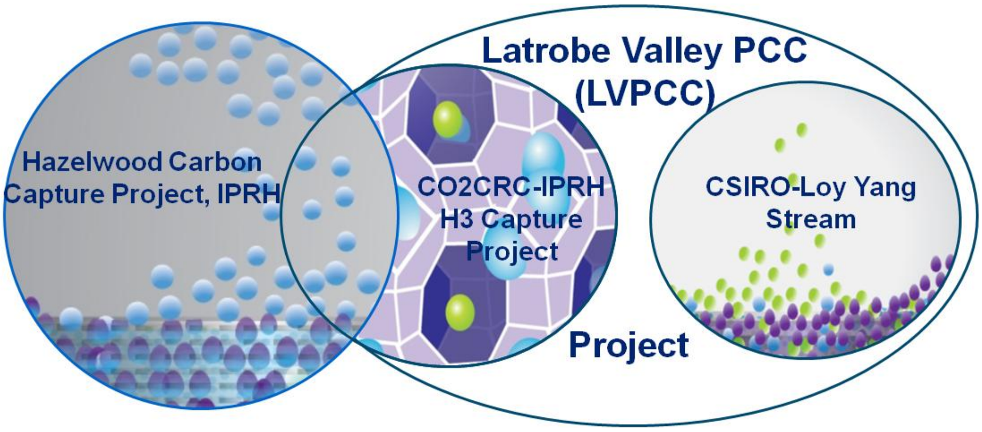


Figure 2.7 Post-combustion Capture Demonstration projects in Victoria

The research summarised in this Volume 1 of the report is for the H3 Capture Project which was a joint project undertaken cooperatively by CO2CRC and IPRH. It is interlinked with both the Hazelwood Carbon Capture Project by using their solvent plant and LVPCC as explained above and also shown schematically in Figure 2.7. The report for CSIRO-LYP Stream is provided in Volume 2 of the LVPCC. The LVPCC provided a globally unique multi-site, multi-scale and multi-technology facility for CO_2 capture research.

In view of the global significance of the Victorian brown coal resource and the availability of significant close storage locations in the Gippsland Basin, the aims of the H3 project were to:

1. Design, install, commission and test three capture technologies in a real (post-combustion) power plant setting for brown coal;
2. Advance the knowledge base regarding the capabilities of post-combustion capture for brown coal;
3. Evaluate the suitability of existing and emerging technologies for post-combustion capture for brown coal at different points in the process chain; and
4. Evaluate the opportunities to significantly drive down the cost of post-combustion capture for brown coal through technology improvements as well as heat and process integration.

CO2CRC's selection of the three technologies to be trialled in the facility was based on the fact that the work would not only focus on traditional solvent options but also on the emerging membrane and adsorbent technologies. All three plants have been commissioned and have been in full operation since early 2009. The outcomes of this research are not only vital to the brown coal sector in Victoria and other parts of the world where brown coal is a significant fuel or feedstock (Canada, USA, Germany, and the Netherlands), but also for CO_2 capture in general.

2.4 References

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3. Overview of the CO2CRC-IPRH H3 Capture Project

3.1 Objectives of the CO2CRC-IPRH H3 Capture Project

The key objective of this project was to reduce the technical risk and cost of post-combustion capture for Victorian coal-fired stations. The program was executed in line with the agreed plan. For each of the three capture technologies (namely, solvent absorption, membrane and adsorption), the more specific objectives were to:

- Identify and quantify the effects of operating parameters of CO_2 concentration, moisture content, gas temperature, SOx and NOx concentration and fly ash properties on the behaviour of sorbent systems and novel separation technologies using flue gases at Hazelwood Power Plant.;
- Optimise process operating parameters;
- Develop engineering solutions at a scale at which confidence can be established for full scale plant design and assessment;
- Assess the post-combustion capture process and energy integration options; and
- Review the technical and economic viability of the commercial use of post-combustion capture for Victorian brown-coal fired power stations.

3.2 Solvent Trials

Technologies for amine solvent post-combustion CO_2 capture have been extensively investigated in recent years. Although, the aqueous alkanolamines such as monoethanolamine (MEA) or diethanolamine (DEA) have gained widespread attention due to their effectiveness for removing CO_2 from flue gas streams, they have some limitations. One of the biggest issues is corrosion resulting in the need for expensive materials of construction. MEA has a high theoretical absorption capacity for CO_2 however it suffers significant degradation problems. Most amine solvents like MEA will degrade at high temperatures and particularly so in the presence of oxygen, leading to high solvent losses or expensive reclaiming equipment. MEA can also react irreversibly with gas impurities resulting in the formation of heat stable corrosive salts that also lead to solvent degradation and foaming problems. MEA has a high vapour pressure which leads to high solvent losses in both the absorber and regenerator, requiring the inclusion of wash sections. Finally MEA has a high energy requirement for regenerating the solvent in the stripping column. For these reasons, a significant amount of research is being conducted to examine alternative solvents and processes with reduced energy consumption for solvent regeneration as well as methods that reduce or avoid solvent degradation.

Australian power stations, in particular those in Victoria, have no flue gas scrubbing for the removal of SOx (i.e: flue gas desulphurisation or FGD) and NOx compounds prior to discharge to the atmosphere. While this is due to relatively low levels of sulphur in Australian coals even these levels are too high for amine based CO_2 solvents. If such solvents are used then an FGD wash will be needed, thus adding to the cost. Consequently the development of a direct/one-step capture process is considered both desirable and advantageous, with an anticipated reduction in net capture cost (capital and operating). This would provide a true “bolt-on” greenhouse gas emission solution for existing Australian power plants.

The CO2CRC has researched and patented a scrubbing system based on cheap potassium carbonate (K_2CO_3) solvent, which offers advantages over the conventional MEA solvent by avoiding the need for separate Flue Gas Desulphurisation (FGD) facilities. It is non-volatile, oxygen tolerant and hence suffers little thermal degradation, is potentially more environmentally friendly, reacting with flue gas impurities to produce usable by-products such as fertilisers and, in modified configurations, is expected to offer lower energy requirements.

Potassium carbonate for carbon dioxide removal has been known for many years. Over time many variations to the basic process have been developed including operating the absorber column at higher temperatures, improving the contacting performance in the absorber and regenerator columns and searching for heat integration designs in the high pressure application areas. In this project, the main aims were to investigate the process, chemistry, equipment and heat integration aspects of the potassium carbonate solvent in PCC configuration and then to validate simulation models against plant data. New design concepts were also to be developed that offer to drive down costs.

3.3 Membrane Trials

There is a range of membranes with considerable potential for post-combustion capture. The key selection criteria are suitably high permeability and high selectivity with high resistance to compaction, plasticization and contamination.

Polyimide and cellulose acetate membranes are currently used commercially for the removal of CO_2 from natural gas streams and are likely to be suitable as gas separation membranes for post-combustion capture. Surface treated polypropylene membranes are likely to be a cheap alternative for post-combustion membrane gas absorption because of their ability to retain hydrophobicity on exposure to amine solutions. These membranes warranted assessment at the pilot scale and were included in the H3 research program.

3.4 Adsorption Trials

Although there has been considerable international focus on development of adsorbents for CO_2 capture from flue gas, there has been limited testing of adsorption processes on real flue gas streams from power plants. The trials undertaken at the Hazelwood power plant were designed to test adsorption processes on real flue gas streams. In particular, the role of high levels of water and impurities on the performance of the adsorption process were unknown prior to testing. Cycle and adsorbent testing were therefore of paramount importance to confirm the technical feasibility of the process and to identify engineering obstacles on the path to commercialization.

4. Project Management and Related Issues

4.1 Management Structure and Collaboration

The two streams of the LVPCC project operated largely independently in a research sense, however, Loy Yang Power liaised with the Victorian Government/BCIA and collated reports from the two streams.

The participant organisations in the H3 project were CO2CRC, International Power Hazelwood (IPRH), The University of Melbourne, Monash University, the University of New South Wales (UNSW) and Process Group (PG). Some contractual work was performed by ALSTOM based at Hazelwood Power Plant. CO2CRC managed and coordinated the overall H3 project. Although the project was fully managed by CO2CRC, it was the collaborative effort by all participating bodies that made this project successful. Figure 4.1 shows the project management structure.

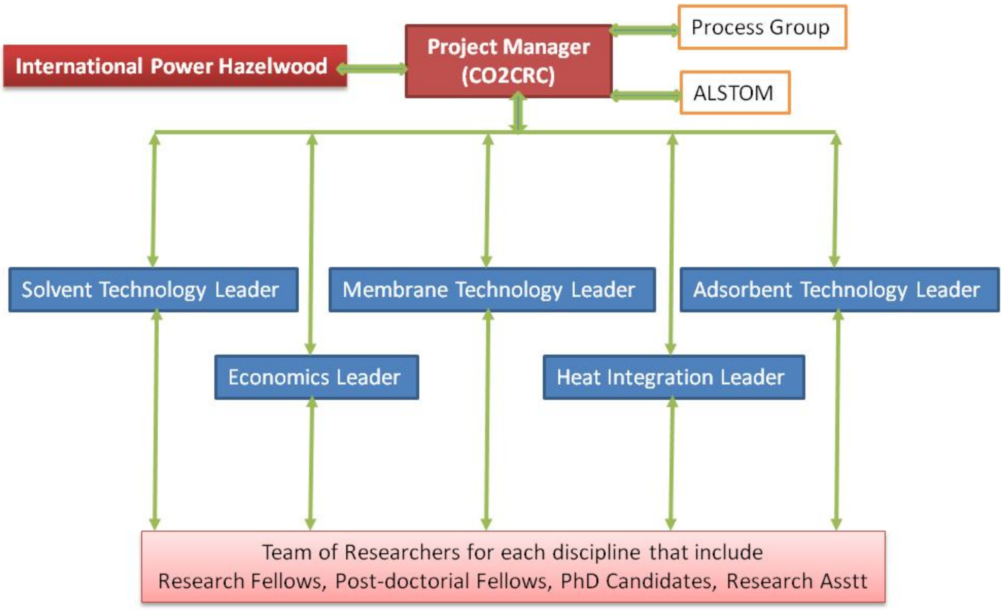

Figure 4.1 Project Management Structure

IPRH managed the operational aspects within the power plant in coordination with CO2CRC. The University of Melbourne was responsible for the solvent and membrane R&D while Monash University was responsible for the adsorption technology. CO2CRC and Monash University were responsible for the heat and process integration. UNSW was responsible for the economic evaluation. CO2CRC engaged two local engineering companies, namely, PG and ALSTOM, with PG being responsible for the design, construction and commissioning of the membrane and adsorption rigs while ALSTOM was responsible for tie up connections at the power plant.

4.2 Strategies to Meet the Objectives of the Project

A range of strategies were adopted to ensure the success of the project as shown in Table 4.1, targeted to achieve:

- Quality and effectiveness of the R&D program;
- Progress of the research along the innovation chain to commercial application; and
- Efficient resource utilization.

Table 4.1 Strategies at different phases of the project

Project Phase	Strategies	Leading/ Most Involved Party
Initiation	1. Map out a detailed research plan with strict time frames outlining the tasks for all parties involved.	CO2CRC and Discipline Leaders
	2. Arrange recruitment of postdoctoral personnel and research assistants from both local and international sources.	
Physical implementation	3. Bring together the process engineering party (PG) and technology groups to complete detailed design for each pilot plant. Tasks involved were: • Review literature and existing work to confirm the best potential post-combustion capture techniques, and required operating conditions; • Use modelling and laboratory trials to define expected process design, degradation, corrosion, chemical interaction and predicted response time, heat and energy load, and power consumption; • Identify likely and possible barriers to implementation both technical and economic; • Design two rigs in accord with these parameters to suit the flue gas conditions at IPRH's Hazelwood power plant including sufficient instrumentation for data acquisition.	CO2CRC, PG, IPRH and Melbourne & Monash University technology groups
	4. Construct, fabricate, install and commission the plants at Hazelwood.	CO2CRC, IPRH, PG and ALSTOM
	5. Liaise with all parties on a repeated basis to check process, equipment and logistics to comply with requirements of all participants but without compromising project objectives.	CO2CRC and IPRH

Project Phase	Strategies	Leading/ Most Involved Party
Test Program and Data Collection	6. Liaise and coordinate with IPRH and with technology groups from Melbourne and Monash Universities to operate the capture plants under a range of conditions as per the test campaign programs. Ensure all required safety measures and auxiliary supplies are in place.	CO2CRC, IPRH and Melbourne & Monash University technology groups
	7. Data collection for each rig during the campaigns.	IPRH, Melbourne & Monash University technology groups
	8. In parallel with plant based tests, continue laboratory research and evaluation of test data to reformulate and redirect the test program as required.	
Techno-economic evaluations	9. Acquire tools for techno-economic studies.	CO2CRC
	10. Ongoing work on heat integration and economic evaluation throughout the program. Ensure information exchange between the technology, heat integration and economic researchers through virtual and real workshops and meetings.	CO2CRC, Monash University and UNSW
Keeping project on track	11. Manage various interest groups (university researchers, government, industry, CO2CRC core participants). Tasks involved were: • Obtain regular updates from technology, heat integration and economics researchers; • Monitor safety, process and equipment procedures and performance; • Resolve day-to-day site and laboratory issues; • Maintain adequate human resources; • Attend periodic Latrobe Valley Brown Coal R&D Stakeholders meetings; • Coordinate and prepare progress reports.	CO2CRC and IPRH
Collaboration activities	12. Establish and maintain procedures for participants to seek collaboration (through CO2CRC) with relevant local and international organizations.	CO2CRC
Dissemination activities	13. Liaise with researchers, IPRH and LVPCC coordinators to report project outcomes to funding bodies, government and CO2CRC. Six-monthly reports were submitted to VIC DPI apart from separate six-monthly reports to CO2CRC	CO2CRC, IPRH and all research groups
	14. Facilitate preparation and approval of publications and presentations for journals, seminars, workshops, conferences, public lectures etc. in order to publicise project outcomes as well as enhance CCS awareness.	CO2CRC, IPRH and Lead Researchers
	15. Host visits by local and international groups to research facilities to enhance CCS awareness.	CO2CRC and IPRH

4.3 Risk Assessment and Mitigation

The strategies outlined in Section 4.2 were carefully chosen to minimise the risks listed in Table 4.2. The biggest risk to the project has been the supply of flue gas for the 3 capture plants.

Table 4.2 Risks and mitigation measures

Risk	Mitigation Measure
Availability of funding at the right time: There was a delay in releasing DPI's funds after the announcement due to the time taken for signing the contract	CO2CRC started the project on time with injection of funds from its core resources
Flue gas readiness: Since it involved installation of a pipe line branch from the existing stack and connecting to the inlet of the solvent plant, there was a risk of not being ready on time for the first trials	1. PG, IPRH and CO2CRC discussed this issue at length and 2. Adequate resources (manpower and auxiliaries organized) to ensure commissioning in time for the first trials.
Delay in construction and commissioning of the three CO2CRC post-combustion rigs	Strategies used to mitigate this risk included: 1. Developed detailed schedule and dates for key deliverables, including long lead items; 2. Included sub-contractor late penalties in contracts; 3. Organised regular team meetings to assess progress against schedule; 4. Identified and sourced additional resources / measures when needed.
Safety issues	1. The site was certified for installation of two rigs. 2. HAZOPs were conducted for all three rigs after detailed design and recommended measures were undertaken accordingly. Pre-commissioning checks were also performed. Special safety meetings were organized involving experts and representatives from PG, IPRH and CO2CRC to establish safe working procedures. 3. Operational training was organized and delivered. 4. Rules and procedures were updated as required. 5. Strict safety regulatory measures were in place for operators while on site, with clear instructions for incident reporting. 6. A working day always started with reporting to the IPRH site management team including checking of protective tools and equipment. Other safety rules of the power plant were also enforced.
Availability of personnel to work on-site for CO2CRC plants	1. Schedules were prepared and regularly updated and coordinated to maximise staff availability.

5. Pilot Plant Activities

5.1 Solvent

As explained in sections 2.3.2 and 2.3.3, the solvent absorption CO_2 capture plant, also known as "Carbon Capture Plant" (CCP), at International Power's Hazelwood Power Station in the Latrobe Valley Victoria, was built under the "Hazelwood 2030 Project". Under the CO2CRC stream of the LVPCC, International Power Hazelwood (IPRH) provided that plant for CO2CRC to conduct tests on solvent technology. The basis of design for the CCP was the capture of 25 tonnes/day (expandable to 50 tonnes/day) of CO_2 from Unit 8 flue gas utilizing BASF's PuraTreat^{TM} F solvent. The operation of this plant for the CO2CRC H3 Capture Project, utilizing both the PuraTreat^{TM} F solvent and a potassium carbonate solvent, is the focus of this report.

In addition to the construction of the CO_2 capture plant, modifications have been made by IPRH to an existing plant that neutralises ash water produced on site. In this modification CO_2 is injected via Venturi nozzles into the ash water pond. Calcium carbonate (which sequesters the CO_2) is produced in mineral form (Figure 5.1.1). Approximately 16 tonnes per day of CO_2 is required for pH neutralisation replacing the need for a mineral acid (Hooper, Innocenzi et al. 2009).

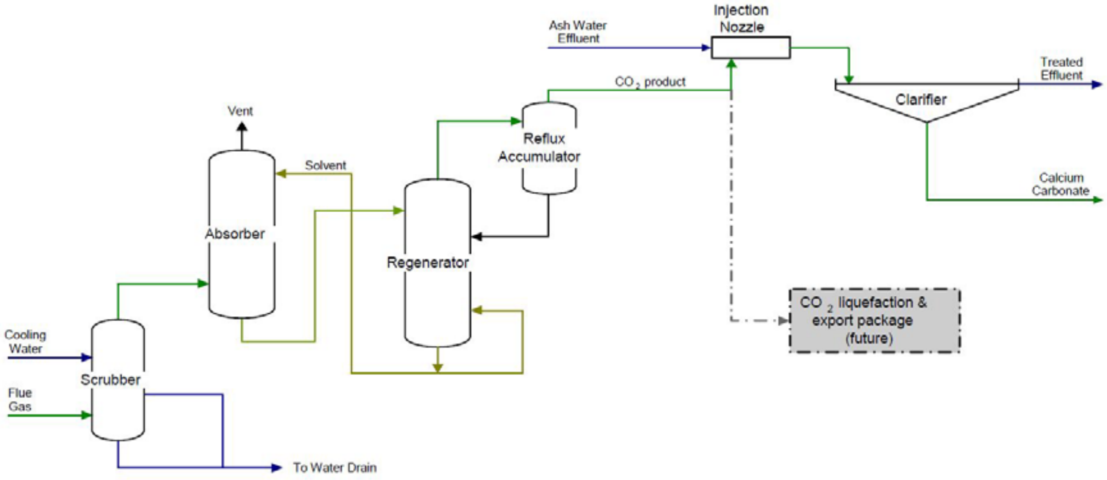

Figure 5.1.1 CCP Process Flow Diagram (Hazelwood Carbon Capture Project)

5.1.1 Process Description

Solvent absorption is currently the preferred option for removing CO_2 from industrial waste gas and for purifying natural gas. This process involves passing the flue gas through a liquid chemical that can absorb the CO_2 (in an absorber) and then releasing the CO_2 at an elevated temperature in a regenerator or stripper (further details are in the sections below).

The post combustion solvent absorption plant was designed and commissioned using PuraTreat^{TM} F, a commercially available amino-acid based solvent produced by BASF. After operating for a considerable time with PuraTreat™ and demonstrating the plant performance, tests with CO2CRC solvent were conducted. The solvent was drained, the system flushed and filled with a potassium carbonate (K_2CO_3) based solvent. The CO_2 absorbed from the flue gas stream with either solvent is released to atmosphere or used for ash water neutralisation.

5.1.1.1 BASF PuraTreat^{TM} F solvent system

PuraTreat^{TM} F is an amino acid based solvent marketed by BASF as a high performance solvent for the selective removal of H_2S and CO_2, specifically in gas streams containing olefins and oxygen. In addition to high stability in the presence of olefins and oxygen, the use of PuraTreat^{TM} F is associated with negligible vapour pressure which will minimize solvent losses. The product also offers lower hydrocarbon solubility than water and high H_2S selectivity, depending on process conditions. PuraTreat^{TM} F contains no ethanolamines and is environmentally friendly, non-toxic and biodegradable which results in easy product handling. It is reported to have low maintenance costs due to its non-corrosive nature and requires lower capital expenditure because of high acid gas loading capacity at low CO_2 partial pressures. As PuraTreat^{TM} F is a patented solvent, little information regarding its chemical composition, thermodynamics and reaction sequences is publicly available or supplied to CO2CRC.

5.1.1.2 Potassium Carbonate solvent system

Hot potassium carbonate solutions have been used commercially for acid gas absorption for many years. The process is commonly known as the Benfield process (Benson, Field et al. 1954) and was originally developed by the U.S. Bureau of Mines in 1954 to reduce the costs of synthesis gas purification for the production of liquid fuel from coal. The process was designed for a gas process stream that had high temperatures and high partial pressures. Due to the high temperature in the absorber, it was therefore not necessary to further heat the solution to the stripping temperature required in the stripping process. This resulted in a lower process energy requirement and eliminated the need for heat exchange equipment between the absorber and the regenerator columns. Furthermore, the operation at such high temperatures increases the solubility of the bicarbonate species, so the Benfield process can operate with highly concentrated solutions.

In more recent years aqueous alkanolamines such as monoethanolamine (MEA) or diethanolamine (DEA) have gained widespread attention for capture of CO_2. Although amine solvents are effective for removing CO_2 from flue gas streams, they have some serious limitations. One of the biggest issues is corrosion resulting in the need for expensive materials of construction. MEA has a high theoretical absorption capacity for CO_2 however it rarely achieves these levels in practice due to degradation problems. Most amine solvents like MEA will degrade at high temperatures as well as in the presence of oxygen leading to high solvent losses or expensive reclaiming equipment. MEA can also react irreversibly with minor gas components resulting in the formation of heat stable corrosive salts which also lead to solvent degradation and foaming problems. MEA has a high vapour pressure which leads to high solvent losses in both the absorber and regenerator. Finally MEA has a high energy requirement for regenerating the solvent in the stripping column. For these reasons, a significant amount of research is being conducted to examine alternative solvents and processes with reduced energy consumption for solvent regeneration as well as methods that reduce or avoid solvent degradation.

Potassium carbonate has a number of advantages over the amine based solvents with one of the most important being that absorption can occur at high temperatures making the regeneration process more efficient and economical. Potassium carbonate also has a low cost, is less toxic and is less prone to degradation effects that are commonly seen with amines at high temperatures and in the presence of oxygen and other minor gas components. The biggest challenge associated with using potassium carbonate as a solvent is that it has a low rate of reaction resulting in poor mass transfer performance. Promoters are often added to the solvent to improve the mass transfer rates. Traditionally promoters such as piperazine (Cullinane and Rochelle 2004), diethanolamine (Rahimpour and Kashkooli 2004) and arsenic trioxide (Sharma and Danckwerts 1963) have been used but these are known to be toxic and hazardous to the environment. A number of less-toxic promoters such as boric acid have been used in the past and are currently being investigated for today's applications (Ahmadi, Gomes et al. 2008; Ghosh, Kentish et al. 2009).

The overall reaction for the absorption of carbon dioxide using a potassium carbonate, K_2CO_3, solution is described as follows:

$$CO_2 + K_2CO_3 + H_2O \rightleftharpoons 2KHCO_3 \qquad \textbf{Equation 1}$$

Since potassium carbonate and bicarbonate are strong electrolytes, it can be assumed that the metal is present only in the form of K^+ ions and reaction (1) can be represented as:

$$CO_2 + {CO_3}^{2-} + H_2O \rightleftharpoons 2{HCO_3}^{-} \qquad \textbf{Equation 2}$$

Reaction (2) proceeds according to the following sequence of elementary steps:

$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \qquad \textbf{Equation 3}$$

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad \textbf{Equation 4}$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \textbf{Equation 5}$$

Reactions (3) and (4) are both followed by subsequent instantaneous reactions as follows:

$$H^+ + CO_3^{2-} \rightleftharpoons HCO_3^- \qquad \textbf{Equation 6}$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^- \qquad \textbf{Equation 7}$$

The reaction sequence (3), (5) and (6) is known as acidic mechanism (Bishnoi and Rochelle 2000). The contribution of the acidic mechanism to the overall rate is negligible unless the pH of the liquid solution is very low. Almost all cases of industrial absorption are performed at high pH (generally, pH>8). Hence the acidic mechanism can be neglected. Reaction (4) is the rate controlling step for absorption of CO_2 into hot potassium carbonate solution as reactions (5) and (7) are instantaneous reactions.

5.1.2 Design basis

The solvent plant consisted of three main columns: a Direct Contact Cooler (DCC) (to cool the flue gas), an absorber (to remove CO_2 from the flue gas via dissolution into the solvent) and a regenerator (to remove CO_2 from the solvent through addition of heat). A photo of the solvent plant located at Hazelwood Power Station is presented in Figure 5.1.2. The solvent plant (CCP) was designed to be used with BASF PuraTreat^{TM} F solvent.

The following information was used as the basis of design for the solvent plant:

- Flue gas flow rate: 6,400 kg/hr
- Gas Temperature: 240 °C
- Gas Composition:

    - Carbon dioxide, CO_2: 13.0 mol%
    - Nitrogen, N_2: 62.0 mol%
    - Oxygen, O_2: 3.5 mol%
    - Water, H_2O: 20.5 mol%
    - Argon, Ar: 0.8 mol %
    - Nitrate, NO_x, 151 ppmV (dry basis)
    - Sulfate, SO_x, 212 ppmV (dry basis)

- Solvent flow rate: 45,700 kg/hr
- Absorber Details:
    - Diameter: 1.5 m
    - Packing Type: Sulzer Nutter Rings No. 0.7
    - Packing Height: 2 x 7 m
    - Pressure: 10 kPag

- Stripper Details
    - Diameter: 1.4 m
    - Packing Type: Sulzer Nutter Rings No. 0.7
    - Packing Height: 2 x 6 m
    - Pressure: 40 kPag

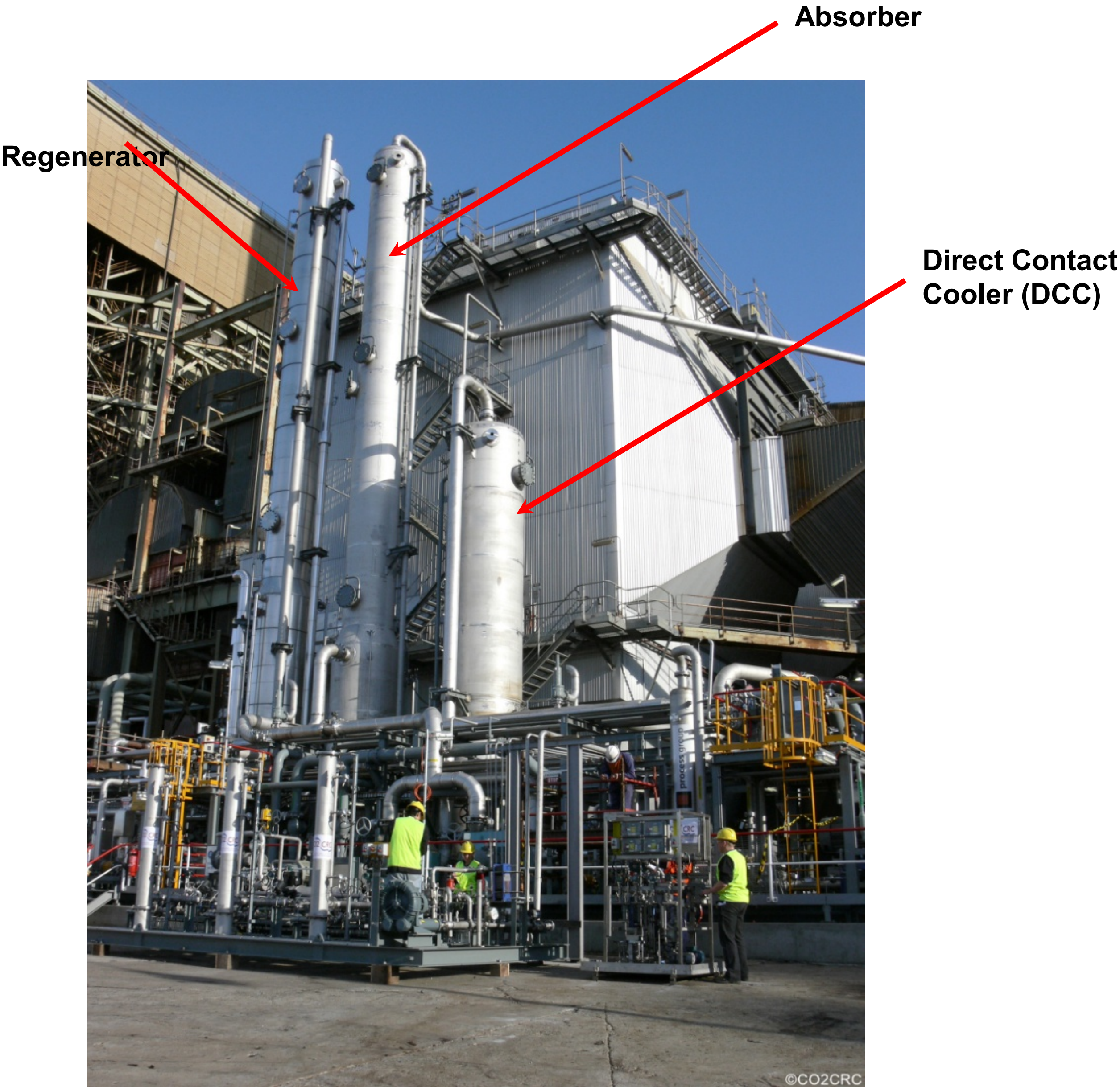

Figure 5.1.2 Photo of the Carbon Capture Plant located at Hazelwood Power Station

5.1.3 Construction, commissioning & operation

Construction and commissioning of the CCP was completed by the Process Group (PG) in July 2009, and very limited input was required from CO2CRC since it was under the Hazelwood Carbon Capture Project. After the commissioning, a series of performance tests were conducted with first PuraTreat^{TM} F and then the potassium carbonate solvent. Table 5.1.1 shows the schedule of performance tests with the gas analysis completed by the three groups: AECOM (Buckland, Taljaard et al. 2009), HRL Technology Pty Ltd (Steeman, Mikecz et al. 2009) and the CO2CRC.

Table 5.1.1 Plant operational summary

Solvent	Test Completion Date	Group	Notes
PuraTreat^{TM} F	4 June 2009	AECOM	24 hr test
PuraTreat^{TM} F	6 Nov 2009	HRL	12 hr test
PuraTreat^{TM} F	26 Feb 2010	CO2CRC	
PuraTreat^{TM} F	4 Mar 2010	CO2CRC	
K_2CO_3	28 Sept 2010	CO2CRC	

The requirement for four performance tests for PuraTreat^{TM} F was because:

1. Contractual arrangements between Process Group and International Power required a 24 hour test to be undertaken with a NATA accredited laboratory monitoring the gas composition;
2. The gas analysis of the regenerator outlet stream obtained by AECOM was deemed unsuitable by International Power and Process Group, therefore requiring additional testing by a NATA accredited laboratory;
3. CO2CRC wanted to investigate the changes in performance over time.

The results obtained during operation are discussed in the following sections.

5.1.4 Testing and Data Collection with Operating Issues & Learning

5.1.4.1 Sample points

Six sample points were incorporated into the solvent plant design to ensure the process performance could be adequately monitored during performance trials. Four gas sample points and two liquid sample points were selected as follows:

1. Flue gas inlet to DCC
2. Flue gas exit from DCC
3. Treated gas exit from Absorber
4. CO_2 rich gas stream exiting Regenerator
5. Lean Solvent exiting lean solvent pump
6. Rich Solvent exiting rich solvent pump

5.1.4.2 Data Collection and Operational Reliability

General plant data collected continuously while the plant was operating. Stream information such as flow rate, pressure and temperature was continuously logged online via a PLC connected to individual transmitters. The operational data was downloaded on a weekly basis at 1 hour intervals.

Analysis of gas composition for the inlet flue gas and for the flue gas out of the Direct Contact Cooler was performed on-site by others using a variety of methods. Please refer to consultant reports (Buckland, Taljaard et al. 2009; Steeman, Mikecz et al. 2009) for methods used in their work. CO2CRC utilized a Horiba PG250 Gas Analyser, e.g., in Runs 3 and 4 (Table 5.1.2). This analyser enabled the concentration of CO_2, O_2, SO_2 and NO_x to be measured on a dry basis. The moisture content of the gas stream was measured using a HT-305 Humidity meter. The gas composition of the CO_2 gas product stream exiting the regeneration process was determined using a Varian CP-800 Gas Chromatograph.

Analysis of solvent concentration and Loading were performed by following standard methods. As dissolved acid gases can influence the sample solution, each sample was degassed by boiling the solution before the density was measured. This analysis was performed throughout the performance testing period. The Chittick carbon dioxide apparatus provided a measurement of the amine solvent concentration and the amount of CO2 absorbed into the solvent.

Table 5.1.2 Gas stream compositions

Gas Stream		Run 1 (Jun-2009)	Run 2 (Nov-2009)	Run 3 (Feb-2010)	Run 4 (Mar-2010)
Flue gas to DCC	CO_2,%	13.1	11.4	n/a	n/a
	O_2,%	6.8	8.4	n/a	n/a
	SO_2,ppmv	44.3	47	n/a	n/a
Gas into Absorber	CO_2,%	13.1	7.1	11.99	11.69
	O_2,%	6.8	12.8	7.06	7.40
	SO_2,ppmv	16	18	1.3	2.7
Gas out of absorber	CO_2,%	1.1	n/a	0.77	2.50
	O_2,%	9.8	n/a	7.78	8.03
	SO_2,ppmv	0	n/a	n/a	0.29
CO_2 product stream	CO_2,%	89	96.1	n/a	95.3*
	O_2,%	7.2	0.7	n/a	n/a
	SO_2,ppmv	3.19	0	n/a	n/a

*Gas composition obtained via gas chromatography, n/a: not available

5.1.4.2.1 BASF PuraTreatTM F Solvent

The solvent capture plant was operated from June 2009 to April 2010 under steady state conditions for a cumulative total of > 1840 hours using PuraTreat^{TM} F solvent. During this period the stability or reliability of the plant was studied by closely monitoring the process stream data via an online logging system. The feed gas flow rate from the blower into the absorber column and the waste gas out of the absorber were found to fluctuate significantly, however the temperature of the feed gas stream was relatively constant at 45°C. The lean and rich solvent flow rates were relatively constant throughout the testing period at approximately 46 ton/h. Finally the temperature at which the regenerator operated was also constant throughout the testing period at approximately 110°C.

During the testing period the plant was shut down numerous times and on occasion for extended periods to complete a variety of tasks. These included maintenance tasks (cleaning process line and transmitters, etc) and resolving a number of operational problems (including solvent pump failure, DCC failure, steam valves leakage and corrosion of demister pads). These delays reflected that equipment of this type had not been used at Hazelwood previously. Therefore significant skill development was required and achieved by Hazelwood engineering, maintenance and operations staff.

5.1.4.2.2 Potassium Carbonate Solvent

The solvent capture plant was operated from June 2010 till September 2010 using potassium carbonate solvent with on and off shut down of the unit for various reasons including plant maintenance, Unit 8 shut downs etc. As previously stated the carbon dioxide capture plant at Hazelwood Power Station was specifically designed to be operated with BASF PuraTreat^{TM}F solvent. Comprehensive simulations of the potassium carbonate system were conducted prior to undertaking the trial to ensure that the plant could be operated efficiently. However, throughout the course of the trial it became apparent that there were areas of the plant which were unable to meet the operating conditions desired and so modifications were made.

The high temperature gas entering the carbon capture plant first passes through the Direct Contact Cooler (DCC) for cooling before entering the Absorber. The Absorber feed gas had a fairly stable oxygen concentration of ~ 8.5 wt%. The concentration of CO_2 in the cooled flue gas entering the Absorber had a larger variation during the initial trials, possibly related to the instability in the gas flow rate to the plant, but attained fairly stable levels of 16 wt%. The pressure drop across the absorber packing was also reasonable and did not show a significant change over the course of the trial, indicating that little, if any, fouling or flooding occurred. Calculation of the expected pressure drop, based on the generalised pressure drop correlation, agreed well with the observed values and was well below that for flooding.

The reboiler temperature had to be restricted to a maximum temperature of 116°C. At temperatures above this, the amount of water vapour exiting the top of the regenerator column was beyond the cooling capacity of the condenser at the top of the regenerator (max. set point of 50°C), resulting in column instability and plant trip. Options such as reducing the solvent volume, reducing the solvent flow rate, altering the regenerator pressure were all considered. It was decided to insist on a reduction in the solvent flow rate from an initial 60 to 45 tonnes/h and place an upper limit of 116°C on the reboiler outlet temperature for a period until the plant settled. Stability was achieved when these changes were made. In addition to tripping the plant, the high vapour flow rate at the outlet of the regenerator also resulted in a significant flow of water exiting in the rich CO_2 vapour stream. This water condensed in the line returning the product vapour to the Unit 8 stack, subsequently blocking the non-return valve and causing a lack of control of the regenerator pressure. In response to this a drain valve was installed in the pipe work. The pressure drop across the packing in the regenerator, similar to the absorber, indicated no evidence of fouling or flooding.

The mass flow rate of CO_2 entering the Absorber varied greatly which is a reflection of the variation of gas flow into the system. Due to the unreliability of flue gas flow rate data, it is more accurate to rely on the solvent loadings to estimate the CO_2 absorbed. On a relatively stable day of operation, the flow of CO_2 entering the Absorber was ~1000 kg/h of which ~200 kg/h has been captured, resulting in a capture rate of approximately 20 %.

Detailed data collections enabled us to record the followings during the operation periods:

1. Flue gas flow rate out of the Absorber
2. Feed flue gas temperature into the Absorber
3. Rich solvent flow rate
4. Lean solvent flow rate
5. Lean solvent flow rate
6. Regenerator temperature
7. Variation of solvent loading and solvent flow rate with time
8. Solid precipitations build up and analysis
9. Impurities build up and analysis

5.1.4.3 Results and Discussions

5.1.4.3.1 BASF PuraTreat^{TM} F Solvent

The plant was designed to be operated with a solvent concentration of 35% PuraTreat^{TM} F. The process operation resulted in a variable water balance thereby affecting the solvent concentration. Therefore during plant operation it was important to monitor the solvent concentration to ensure that it was kept within the target range of 35 ± 3% PuraTreat^{TM} F, to ensure optimal operation and prevent solvent precipitation. The regenerator performance results for PuraTreat^{TM} F are shown in Table 5.1.3.

Table 5.1.3 Performance results for the Regenerator (for PuraTreat^{TM} F)

Plant Data	Run 2	Run 3	Run 4	Design
CO_2 Produced based on 95 % purity (dry basis); (*kg / h*)	1015	620	860	964
Energy Usage; (*GJ/t CO_2 captured*) (corrected, assuming 50% saturated steam)	6.00	6.25	4.75	6.6

Flue gas components such as SO_x can react with the solvent to form heat stable salts that build up in the solvent potential to a level that can affect the absorption and regeneration efficiency of the solvent and cause operational problems (Uyanga and Idem 2007). Within the BASF operational procedures, change out of a percentage of the solvent each year is recommended due to this reason, and a potassium hydroxide dosing tank was installed for solvent addition. Due to the effect that sulphur can have on the performance of the system, the concentration was monitored during the performance testing and results are shown in Figure 5.1.3. It can be seen that the sulphate concentration increased throughout the testing period and after 8 months the sulphate concentration was approximately 6 times the initial concentration.

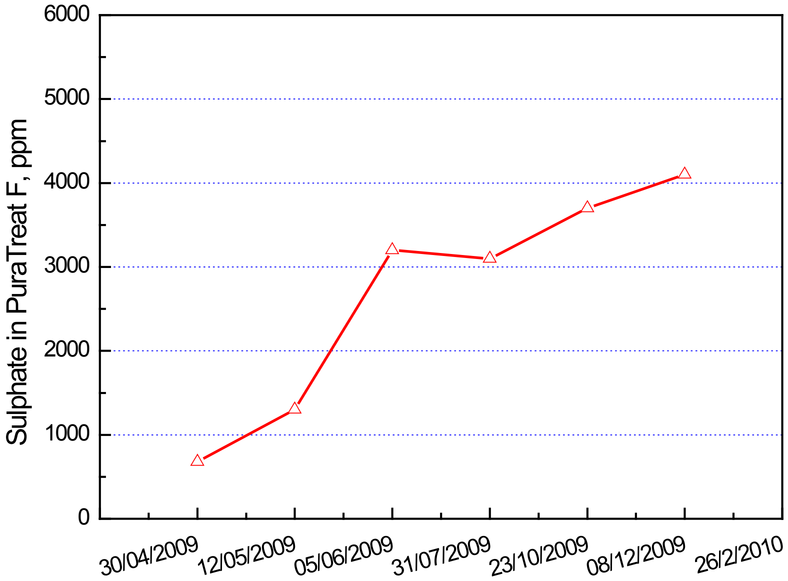

Figure 5.1.3 Sulphur concentration in solvent over performance testing period

5.1.4.3.2 Potassium Carbonate Solvent

A nominal solvent concentration of 30 wt% K_2CO_3 was initially used as the lean solvent in the absorber. Figure 5.1.4 shows the variation of solvent concentration with time. It can be seen that the solvent concentration decreased gradually from an initial 30 wt% to ~ 20 wt% during the testing period. This can be attributed to the dilution of the stripped solvent by makeup water during the cleaning of level transmitters, pump strainers and repairs to the reboiler, as well as solvent losses. The Figure 5.1.4 shows that there seems to be no significant change in solvent loading due to the change in solvent concentration. It was also observed that solvent flow rate also did not affect the CO_2 absorption into the solvent.

Throughout the trials with potassium carbonate solvent, precipitation of solids in various parts of the plant resulted in operating problems. The precipitation of $KHCO_3$ in the solvent is dependent on the solvent temperature and the CO_2 loading, for a given initial concentration of K_2CO_3, as shown in Figure 5.1.5. The yellow highlighted band shows the operating area, within (average) lean and rich solvents loadings of 0.17 and 0.23 respectively. The initial solvent concentration ranged from 27-28 wt% K_2CO_3, corresponding to a $KHCO_3$ precipitation temperature of ~ 5°C. As the trials were run during a Victorian winter, when the overnight temperatures frequently decreased to this level, $KHCO_3$ precipitation was observed, particularly during plant shutdown.

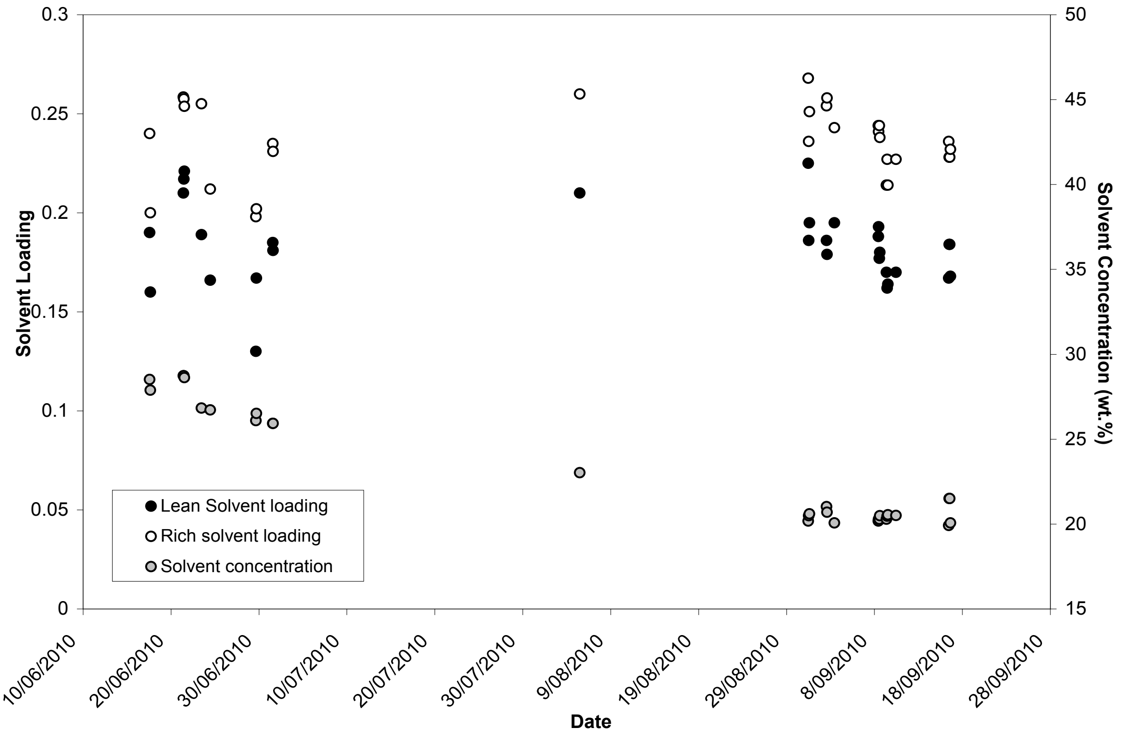

Figure 5.1.4 Variation of solvent loading and solvent concentration with time

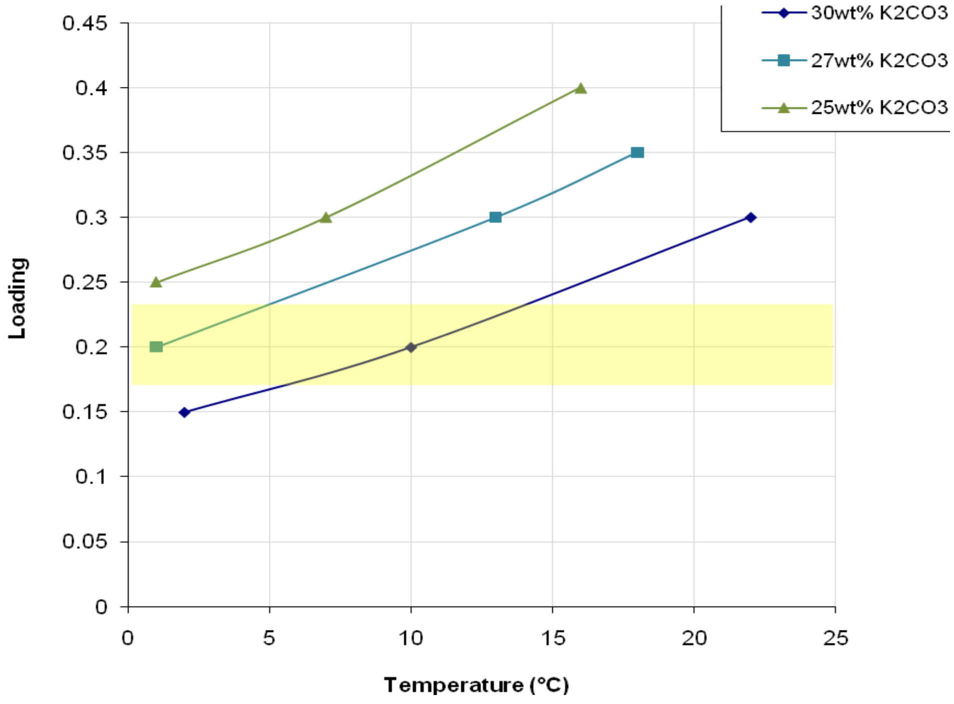

Figure 5.1.5 Solubility of $KHCO_3$ as a function of temperature and solvent concentration

It must be restated that the current carbon capture plant was not designed for K_2CO_3 solvent but for PuraTreat^{TM} F. Therefore, no provisions were made for the correct thermal operation for K_2CO_3, such as heat tracing and cladding. None of the columns in the capture plant was insulated; therefore, the temperature gradients from the column centres to the walls were high during the runs with K_2CO_3. This resulted in the cooling of the solvent at the walls of the column, and the resulting increase in $KHCO_3$ precipitation.

However, the latter half of the trials was run at a lower solvent concentration of 20 – 21 wt% K_2CO_3. Even at the highest observed solvent loading of 0.23, it is not expected that $KHCO_3$ will precipitate. Nevertheless, after a few weeks of operation at this low solvent concentration, solid precipitation issues were still observed. Analysis of solvent samples, including the solid precipitates, was carried out in the CO2CRC laboratory at the University of Melbourne. The solvent samples taken for analysis were seen to precipitate when stored overnight. The crystals were heated at 65 °C for 3 hours but a small proportion of the crystals did not dissolve, suggesting that they were not K_2CO_3/$KHCO_3$ crystals. Acid was added to remove K_2CO_3 and $KHCO_3$ (Figure 5.1.6), and the crystals were washed with water and ultrasonically dissolved with HCl prior to analysis by ICP. This process found that the extracted crystals were of > 90% potassium sulphate. This confirmed simulation models on the formation of this potential by-product from flue gas impurities when using UNO solvent.

Figure 5.1.6 Dried crystals of potassium sulphate

The low capture rate (~20%) observed in these trials can be primarily attributed to:

1. operation at low temperature and low CO_2 partial pressures, thereby reducing reaction kinetics.
2. insufficient packing area for the operating conditions
3. low concentration of K_2CO_3

The rich K_2CO_3 solvent was analysed for nitrate/nitrite content using the Dionex ICS-1000 ion chromatograph using a AS14A analytical column and AG14 guard column along with a suppressor. The analysis showed that the nitrite content in solution was twice that of the nitrate concentration, showing that the nitrites were stable in solution even after several months in storage at room temperature. A mass balance around the absorber also showed that the N_2 concentration in the rich solvent was far greater than that which is present in the flue gas. This confirms that there is a build up of nitrate and nitrite in the solvent over time. As the solubility of nitrates/nitrites is far greater than the corresponding sulphates, no significant nitrate/nitrite precipitation was observed.

The high temperature of the flue gas entering the Direct Contact Cooler (DCC) resulted in the CO2CRC personnel only being able to evaluate the performance of the Carbon Dioxide Capture Plant (CCP) at the gas entry point to the absorber. And as such, unlike for the PuraTreat^{TM} F trials, no evaluation of the performance of the DCC in terms of sulphate removal could be conducted. However, because the DCC operating conditions were similar to that for the PuraTreat^{TM} F, it is reasonable to assume that even in the case of the carbonate trials, ~ 90 % of the SOx from the flue gas was absorbed by the cooling water.

The Reboiler energy usage under the conditions noted varied from 20 to 55 GJ per tonne of CO_2 captured which matched the ASPEN model predictions. While not economic at these levels it provided confidence that optimized designs can be achieved for purpose built facilities.

Analysis of the gas stream exiting the regenerator concluded that the product purity was above 95 % CO_2.

5.1.4.4 Performance of the geopolymer composites

Geopolymer concrete is being proposed as a potential large-scale infrastructure construction material, with its aluminosilicate chemistry suggested to provide the possibility of withstanding the harsh chemical environments and elevated temperatures found in post-combustion capture solvent columns. Geopolymers also offer ~80% reduction in CO_2 emissions relative to traditional cementing systems and utilise industrial wastes such as fly ash, which can bring appealing synergies in carbon capture applications. Geopolymer concretes are synthesised by reacting industrial wastes (coal fly ash and/or metallurgical slags) with an alkali source to form the binder, which is blended with aggregates (sand and rocks) in a manner similar to that of traditional concretes. The chemical resistance of the geopolymer binder has previously been highlighted in laboratory testing due to the nature of cross linked alumino silicate geopolymer gel. Four previously prepared (aged ~2 years) fly ash/ground granulated blast furnace slag (GGBFS) geopolymer concrete sections were installed in the solvent rig for the duration of the trial: two sections were exposed to the rich (average temperature of 112 °C) and two to the lean (average temperature of 46 °C) K_2CO_3 solvents. One of each set was oriented vertical to the solvent flow, and one horizontal.

Figure 5.1.7 shows photographs of the samples following removal from the rig. There was significant corrosion of the geopolymer binder exposed to the rich, hotter solvent, leaving exposed aggregate in the concrete. The surface was eroded by ~1 to 3 mm. The binder exposed to the lean, cooler solvent appears to have withstood exposure. The corrosion observed in the rich solvent stream is likely to be due to the enhancement of alkali attack on the geopolymer binder phase at high temperature, with the ingress of aggressive agents facilitating the removal of the surface binder phases. There is likely to be alteration of the Al-substituted calcium silicate hydrate (C-(A)-S-H) gel binder phase, formed due to the Ca present in the GGBFS component, with removal of Ca through carbonation due to the high concentration of carbonate species in both solvents. However, the damaging effects observed in the rich solvent streams cannot be attributed to the extra CO_2 alone; the temperature effect appears to be most significant here, and will become the focus of further research.

Corrosion in alkaline solvents is temperature dependent, and further durability studies will examine this effect. However, long term solvent exposure to unprotected geopolymer surfaces may prove infeasible, particularly at higher temperature. The possibilty of attaching a protective polymer or stainless steel coating to the exposed surface will be investigated in future testing, as will the effects of extended periods of exposure to elevated temperature, with and without solvent attack (i.e. simulating uncoated and coated geopolymer surfaces).

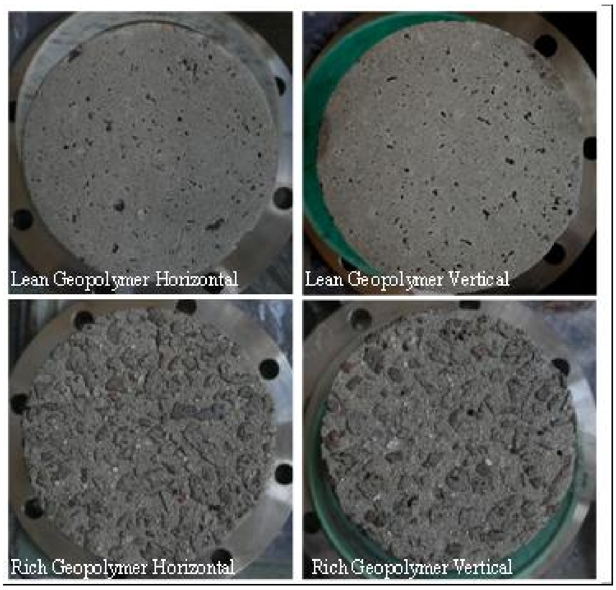

Figure 5.1.7 Geopolymer samples following solvent exposure

5.1.5 Performance Evaluation and Results as against Simulation

5.1.5.1 BASF PuraTreat^{TM} F

Data collected from the plant during performance Run 3 (26 Feb 2010) has been compared with simulation results (Table 5.1.4). The simulation results were taken from the Process Flow Diagram prepared by Process Group in consultation with BASF. Further process optimisation cannot be completed as CO2CRC does not have copies of this simulation or the thermodynamic properties associated with BASF's solvent PuraTreat^{TM} F that is required to develop appropriate process simulations.

Table 5.1.4: Comparison between plant data and simulation results (plant data 26 Feb 2010-Run 3)

Unit	Stream	Parameter	Plant Data	Simulation Result	% difference
Direct Contact Cooler (DCC)	Flue Gas Inlet	Temperature, °C	185	240	-29.7
		Pressure, kPag	-.0.1	1	-
		Flow rate, kg/h	n/a	6,400	-
	Cooling water inlet	Temperature, °C	29.7	35	-17.8
		Flow rate, kg/h	22,250	20,000	10.1
	Cooling water outlet	Temperature, °C	50	65.1	-30.2
		Flow rate, kg/h	22,340	20,500	8.2
Absorber	Blower feed gas inlet	Temperature, °C	44.7	50	-11.9
		Pressure, kPag	1.7	10	-
		Flow rate, kg/h	5,640	5,700	-1.1
	Treated gas out of absorber	Temperature, °C	41.8	41.5	0.7
		Pressure, kPag	0.03	10	-
		Flow rate, kg/h	n/a	4,556	-
	Lean solvent inlet	Temperature, °C	41.6	40	3.8
		Flow rate, kg/h	45,920	45,700	0.5
	Rich solvent outlet	Temperature, °C	50.5	52.2	-3.4
		Flow rate, kg/h	46,100	46,950	-1.8
Regenerator	Column	Temperature, °C	109.1	110	-0.8
	Rich solvent inlet	Temperature, °C	n/a	107	-
	Lean solvent outlet	Temperature, °C	n/a	117	-
	Vapour overheads outlet	Temperature, °C	102.1	104	-1.9
		Pressure, kPag	48.25	38	21.2
		Flow rate, kg/h	n/a	1,989	-
Reflux accumulator	Reflux stream outlet	Flow rate, kg/h	834.9	1,173	-40.5
	CO_2 product outlet	Temperature, °C	44	44	0.0
		Pressure, kPag	47.5	30	36.8
		Flow rate, kg/h	n/a	1018	-
Reboiler	Solvent inlet	Temperature, °C	113	117	-3.5
		Flow rate, kg/h	n/a	48,123	-
	Solvent outlet	Temperature, °C	115.7	117	-1.1
	Steam supply inlet	Temperature, °C	179.9	180.1	-0.1
		Pressure, kPag	871	899	-3.2
		Flow rate, kg/hr	3,657	2,750	24.8
	Condensate outlet	Temperature, °C	125.4	179.6	-43.2
Lean-rich exchanger	Lean solvent inlet	Temperature, °C	n/a	117	-
	Lean solvent outlet	Temperature, °C	71	62.4	12.1
	Rich solvent inlet	Temperature, °C	50.5	52.2	-3.4
	Rich solvent outlet	Temperature, °C	110	107	2.7

n/a: not available due to faulty transmitter

5.1.5.2 Potassium Carbonate Solvent

The absorption of CO_2 with amine or potassium carbonate solvents has been used extensively for the removal of CO_2 from flue gas produced by coal combustion. Numerous investigators have investigated the solubility and reaction rate of CO_2 in aqueous potassium carbonate (Benson, Field et al. 1954; Benson, Field et al. 1956; Tosh, Field et al. 1959) . These studies have shown that potassium carbonate has a low heat of regeneration, but its rate of reaction is slow compared to amines. Understanding the thermodynamics and the ability to model the behavior of the potassium carbonate solvent is of great importance for process development, design and optimization.

The plant data chosen for comparison with simulation data from ASPEN Plus^{TM} were those on the most stable days of operation, namely 24 June, 8 September and 16 September 2010.

Performance Indicators

The following performance indicators have been used in the analysis.

$$\%\boldsymbol{CO_2\ Removed}_{(\boldsymbol{Regenerator})} = \frac{\boldsymbol{CO}_{2(\boldsymbol{Regenerator\ out})}}{\boldsymbol{CO}_{2(\boldsymbol{Feed})}} \qquad \textbf{Equation 8}$$

$$\boldsymbol{Energy\ Usage}\ (\boldsymbol{kJ} / \boldsymbol{kg}) = \frac{\boldsymbol{Q_{Reboiler}}}{\boldsymbol{CO}_{2\ \boldsymbol{RegeneratorOut}}} \qquad \textbf{Equation 9}$$

where:

CO_{2Feed}	CO_2 mass flow rate in the flue feed stream (kg / h)
$CO_{2AbsorberOu\ t}$	CO_2 mass flow rate in the Absorber Overhead stream (kg / h)
$CO_{2RegneratorOut}$	CO_2 mass flow rate in the Regenerator Overhead stream (kg / h)
$Q_{Reboiler}$	energy of the Reboiler (kJ/ h)

The values of these performance indicators for the days selected above have been calculated from the simulation and are presented in Table 5.1.5. Calculation using plant measurements was not feasible due to the problems associated with the reboiler and lack of accuracy in the plant instrumentation, which led to insufficient information for calculating the energy usage. Therefore, energy usage analysis has been determined solely from the simulation results.

The energy usage values are higher than work conducted by other investigators (3 to 4.5 kJ / kgCO_2) (Furukawa and Bartoo 2003; Feron 2008). This is due to the low CO_2 absorption in the absorber, resulting in “loss” of energy in the regenerator.

Table 5.1.5 Summary of Performance Indicators from selected days of stable operation

CASE	Feed Flow	CO_2 Removed	Heat Efficiency (Allowing For Heat Loss)
	kg / h	%	MJ / kg CO_2
24/6/2010 1115AM	5602	22	35
08/9/2010 1320PM	6617	20	37
16/9/2010 1530PM	4740	23	38

5.1.5.2.1 Simulation Development

Simulation of the post-combustion pilot plant was completed using ASPEN Plus (Version 7.1). Within ASPEN Plus, the Electrolyte-NRTL (ENRTL) model was chosen as most appropriate for modelling aqueous solutions of ions such as potassium carbonate.

ASPEN Plus uses a resistance model based upon film theory to determine the overall amount of CO_2 transferred from the gas phase to the liquid phase. Film theory (as shown schematically in Figure 5.1.8) assumes that there is gas film and liquid film at the interface, which provide resistance to the absorption of CO_2 from the gas into the liquid as shown in Equation 10.

$$r_A = \frac{1}{gas\ film\ resistance + liquid\ film\ resistance + liquid\ bulk\ resistance}(p_A - p_A^*) \qquad \textit{Equation 10}$$

where:

r_A	rate of absorption of component A (CO_2) from gas to liquid
p_A	concentration of component A (CO_2) in the bulk gas
p_A*	equilibrium concentration of component A (CO_2) in the liquid

As discussed in Section 5.1.1.2, the absorption of CO_2 into potassium carbonate is known to be rate-limited by Equation 4, which is slow and in the liquid phase. Therefore it can be assumed that the gas film resistance is negligible. Equation 10 is then solved using vapour-liquid equilibrium data for p_A*, liquid phase mass transfer coefficients for the liquid film and liquid bulk resistances. The reaction kinetics are taken into account by way of an enhancement in the liquid film transport.

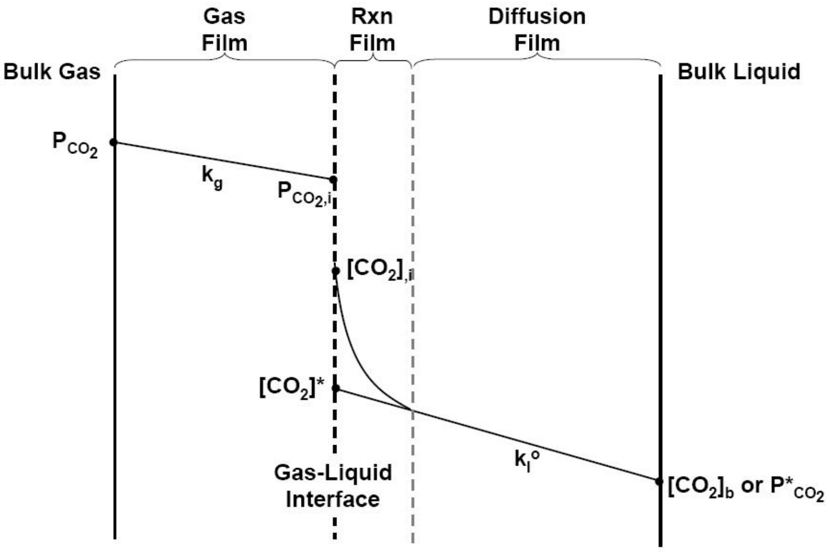

Figure 5.1.8 Mass transfer of CO_2 into bulk liquid phase with chemical reaction (Cullinane 2005)

Vapour-Liquid Equilibrium

The vapour-liquid equilibrium data built-in to ASPEN Plus for potassium carbonate is based upon the original work completed by Tosh (Tosh, Field et al. 1959). More recently, Cullinane and Rochelle (Cullinane and Rochelle 2004) improved upon the accuracy of the binary interaction parameters for the potassium carbonate system. These so called “Cullinane Parameters” have also been included in the ASPEN model.

Liquid Phase Mass Transfer

There are various correlations available for the prediction of the mass transfer coefficient. The Onda correlation (Onda, Takeuchi et al. 1968) was selected as it can be applied to a wide range of packing including Sulzer Nutter Ring.

Reaction Kinetics

As discussed in Section 5.1.1.2, Equation 4 is rate limiting. This is taken into account in the ASPEN model by selecting the rate-based approach in the RadFrac unit operation used for modelling the absorber and the regenerator columns.

The rate expression is an Arrhenius type equation as shown in Equation 11.

$$\boldsymbol{k = k_0 exp\left(\frac{-E_a}{RT}\right)}$$

Equation 11

Where:

k	rate Constant (M^{-1} s^{-1})
k_0	pre-exponential factor (M^{-1} s^{-1})
E_a	activation energy (J / mol)
R	gas constant = 8.314 (J / mol.K)
T	temperature (K)

The default values of Ea (55350 J / mol) and k0 (4.3154 x 1013 M-1 s-1) were used as they compare well with the values obtained experimentally by the CO2CRC (Guo and al 2011).

ASPEN Factors

The two other user variables within ASPEN that impact upon the simulation results are the (a) reaction condition factor and (b) the interfacial area factor.

The reaction condition factor is a weighting factor that is used for calculating the reaction rate based on the conditions of the bulk liquid or the interface. It is expressed in the following equation:

$$\mathbf{Conditions\ used = factor * bulk\ condition + (1 - factor) * interface\ condition}$$

Equation 12

Therefore, when the reaction condition factor is set to 1, the conditions of the bulk are used. When the reaction condition factor is set to 0, the conditions of the interface are used. The default value is 0.5.

In order to set the reaction factor, it is necessary to understand the relative contributions of mass transfer and reaction rate to the absorption of CO_2 into the liquid. For example, if the reaction rate is slow relative to mass transfer of CO_2 through the film, the reaction will occur in the bulk and as such the reaction condition factor should be set to 1.

A quantitative method for determining the relative contributions of mass transfer and reaction rate is through calculating the Hatta number (M_H) as described in Equation 13 below. The Hatta number is the ratio of the maximum possible conversion in the film over the maximum diffusion transport through the film. If the Hatta number is > 1, the reaction occurs exclusively in the film and the interfacial area controls the amount of absorption. If the Hatta number is < 1, the reaction occurs in the bulk and the bulk liquid volume controls the amount of absorption. The Hatta number calculated for the conditions of the post-combustion pilot plant is ~ 2. This implies that there is little enhancement of mass transfer due to the chemical reaction, ie, the reaction is more likely to take place in the bulk than in the film. A value close to 1 would then be chosen as the reaction condition factor.

$$M_H^2 = \frac{k C_B D_{AL}}{k_{AL}^2} \qquad \textit{Equation 13}$$

Where:

k	Rate Constant ($M^{-1}\ s^{-1}$)
C_B	Concentration of Component B (OH^-) (M)
D_{AL}	Molecular Diffusion Coefficient of Component A in the Liquid (m^2 / s)
k_{AL}	Mass Transfer Coefficient of Component A in the Liquid (m^3 / m^2.s)

The interfacial area factor is a multiplier to the interfacial area calculated by an inbuilt correlation. An interfacial area factor < 1 would be used if fouling or channeling is suspected, and therefore underperforming. An interfacial area > 1 would be used if there were uncertainties in the packing parameters used and the applicability of the inbuilt correlation or increased surface area from column conditions such as foaming. The packing used in the plant was Sulzer Nutter Rings. A packing factor of 1 is used because no fouling was observed during the major inspection at the end of the trial period.

The pilot plant results were matched with a reaction condition factor close to 1 and a packing factor of 1. This suggests that the values selected for both factors respectively are valid and reasonable.

Plant Input Data

The inputs to the simulation from the plant data were chosen in a manner that is representative of what could be controlled on the actual plant making the simulation a true operating model. Therefore, the following parameters were fixed in the ASPEN simulation.

- Feed gas temperature, pressure, flow and composition as per the selected operating days
- Lean Solvent inlet temperature, pressure and flow into the absorber
- Lean solvent CO_2 loading
- Regenerator pressure and vapour overheads flow
- Condenser outlet temperature
- Rich/lean heat exchanger cold outlet temperature
- Packing dimensions and properties.

5.1.5.2.2 Simulation Results

Simulation was done for all stable runs, the results for 8 September data are shown in Table 5.1.6 as an example. In general the model predicts the performance well (within ± 5 %). The exceptions to this can be explained as follows. The gas temperatures in the absorber and regenerator determined by ASPEN are slightly higher because the simulation model does not directly account for heat loss. The difference in the measured loading and that determined by ASPEN is attributed to errors in the experimental technique used to determine the loading and the timing of taking the samples not exactly correlating with the time period used for the modelling.

Table 5.1.6 Summary of ASPEN Simulation Results from 8 September 2010 13:20PM

Unit	Stream	Parameter	Plant data	Simulation result	% difference
Absorber	Blower feed gas inlet	Temperature, °C	42	Input	N/A
		Pressure, kPag	3	Input	N/A
		Flow rate, kg / h	6617	Input	N/A
	Treated gas out of absorber	Temperature, °C	45.7	47.1	-3.1
		Pressure, kPag	0.4	0	+100.0
		Flow rate, kg / h	5182	6478	-25.0
	Lean solvent inlet	Temperature, °C	46.8	Input	N/A
		Flow rate, kg / h	45030	Input	N/A
	Rich solvent outlet	Temperature, °C	46.5	46.6	-0.2
		Flow rate, kg / h	44400	45169	-1.7
Regenerator	Column	Temperature, °C	112.8	111.6	+1.1
	Rich solvent inlet	Temperature, °C	112	104.2	+7.0
	Lean solvent outlet	Temperature, °C	-	112.2	-
	Vapour overheads outlet	Temperature, °C	109.1	111.1	-1.8
		Pressure, kPag	41.7	44.1	-5.9
		Flow rate, kg / h	2639	Input	N/A
Reflux accumulator	Reflux stream outlet	Flow rate, kg / h	2629	2168	+17.5
	CO_2 product outlet	Temperature, °C	-	46.1	-
		Pressure, kPag	-	44.1	-
		Flow rate, kg / h	-	230	-
Reboiler	Solvent inlet	Temperature, °C	113.2	-	-
		Flow rate, kg / h	103600	-	-
	Solvent outlet	Temperature, °C	114.5	-	-
	Steam supply inlet	Temperature, °C	178.9	-	-
		Pressure, kPag	813.4	-	-
		Flow rate, kg / h	4747	-	-
	Condensate outlet	Temperature, °C	124	-	-
Lean-rich exchanger	Lean solvent inlet	Temperature, °C	-	112.2	-
	Lean solvent outlet	Temperature, °C	46.8	53.7	-14.7
	Rich solvent inlet	Temperature, °C	46.5	46.6	-0.2
	Rich solvent outlet	Temperature, °C	112	104.2	+7

5.1.5.2.3 Large scale post combustion simulation

A large scale post-combustion CO_2 capture plant using 30 wt% potassium carbonate as the solvent has been simulated in ASPEN Plus. The inlet feed conditions used in the simulation are provided in Table 5.1.9. The absorber and stripper were modeled with standard industrial packing (Nutter Ring, Sulzer). The height of the packing in both columns was adjusted to meet a removal efficiency of 90 % and the diameter of the column was set based on the gas velocity. The solvent flow rate was set such that the liquid to gas (L/G) ratio was 6. The column packing height was set at 17.5 m in order to bench-mark it against a standard amine-based solvent plant.

Table 5.1.9 Inlet conditions of feed stream to full scale post-combustion capture plant

Parameter	Units	Value
Vapour Fraction		1
Temperature	°C	50
Pressure	kPag	7
Mass Flow	tonnes / h	2988
Gas Composition		
H_2O	Mass %	7.5
CO_2	Mass %	18.9
N_2	Mass %	67.8
O_2	Mass %	4.9
Ar	Mass %	0.9

Given the low operating temperature and pressure of the absorber, CO_2 absorption in the absorber is limited by the slow reaction rate. This is translated into poor CO_2 removal by the absorber column. In this large scale study, 90% CO_2 removal is set as the desired performance and piperazine is used as a rate promoter. Therefore in this analysis two scenarios are under investigation: the un-promoted rate (Scenario 1) and rate promoted using piperazine (Scenario 2).

The piperazine promoted process has a better energy usage in the reboiler per kg of CO_2 removed than the un-promoted process. This is because the absorber column absorbs 90% of the CO_2 entering the system; hence more CO_2 is captured with the same amount of reboiler energy used in the regenerator column. The reboiler energy usage between the two scenarios differs by a factor of 5. This shows that the un-promoted process is uneconomic and hence will not be used in large scale. A detailed summary of the sizing results for both the rate promoted and un-promoted scenarios is given in Table 5.1.10.

Table 5.1.10 Summary of the results for the full scale post-combustion capture plant

Parameter	Units	Scenario 1 (un-promoted)	Scenario 2 (rate promoted)
CO_2 Removed	tonnes / h	48.8	508.4
Reboiler Energy	MW	210	425.6
Reboiler Energy Usage	GJ / tonne CO_2	15.5	3
Solvent Rate	tonnes / h	17931	17931
Absorber Height	m	17.5	17.5
Absorber Diameter	m	22.5	22.5
Regenerator Height	m	15	15
Regenerator Diameter	m	22.5	22.5

5.1.6 Other Outcomes (communications, collaborations, skills development, etc)

The solvent absorption pilot plant performance has been reported at the following conferences in either presentation or poster formats:

- 9th International Conference on Greenhouse Gas Technologies 2008, Washington DC, USA
- CO2CRC Symposium 2008, Queenstown, New Zealand
- CO2CRC Symposium 2009, Coolum, Australia
- Twenty Sixth International Pittsburgh Coal Conference 2009, Pittsburgh, USA
- CO2CRC Symposium 2010, Melbourne, Australia
- 10th International Conference on Greenhouse Gas Technologies 2010, Amsterdam, Netherlands

The following publications (journal papers and conference presentations) have been produced as a result of this research:

Journal Papers

5 Khan, A.A., Wappel, D., Joswig, S., Smith, K.H., Kentish, S.E., Shallcross, D.C., Stevens, G.W. (2010) The solubility of sulfur dioxide and carbon dioxide in an aqueous solution of potassium carbonate, (In preparation)

6 Zhao, X., Smith, K.H., Simioni, M.A., Tao, W. Kentish, S.E., Fei, W. & Stevens, G.W. (2010). Comparison of several packings for CO_2 chemical absorption in a packed column, (In preparation)

7 Zhao, X., Simioni, M.A., Smith, K.H., Kentish, S.E., Fei, W. & Stevens, G.W. (2009). Study on the interaction between NOX and K_2CO_3 during CO_2 absorption, *Energy Fuel*, 23, 4768–4773

8 Smith, K., Ghosh, U., Khan, A., Simioni, M., Endo, K., Zhao, X., Kentish, S., Qader, A., Hooper, B., Stevens, G. (2009). Recent developments in solvent absorption technologies at the CO2CRC in Australia, *Energy Procedia,* 1, 1549–1555

Conference Papers

Smith, K, Ghosh, U, Khan, A, Simioni, M, Endo, K, Zhao, X, Kentish, S, Qader, A, Hooper, B and Stevens, G, (2008). Recent developments in solvent absorption technologies at the CO2CRC in Australia. Poster presented at the 9th International Conference on Greenhouse Gas Control Technologies (GHGT-9), Washington DC, 16-20 November.

Smith, K, Zhao, X, Tao, W, Kentish, S and Stevens, G, (2008). Solvent Absorption Column Performance Trials with Potassium Carbonate Solvent. In: Program and Abstracts, CO2CRC Research Symposium 2008, Queenstown, New Zealand, 1-4 December. CO2CRC, Canberra, pp. 67. (oral presentation)

Khan, A, Anderson, C, Smith, K, Tao, W, Shallcross, D, Kentish, S and Stevens, G, (2009). Modelling and analysis of CO2 removal from a gasifier flue gas stream using brown coal with an aqueous potassium carbonate solvent in a pilot scale. In: Program and abstracts, CO2CRC Research Symposium, Coolum, Australia, 1 December - 3 November. CO2CRC, Canberra, pp. 95. (poster presentation)

Smith, K, Mumford, K, Anderson, C, Ghosh, U, Khan, A, Simioni, M, Endo, K, Zhao, X, Kentish, S, Qader, A, Hooper, B and Stevens, G, (2009). Commercial Technologies for Capture Research. In: Program and abstracts, CO2CRC Research Symposium, Coolum, Australia, 1-3 December. CO2CRC, Canberra, pp. 39. (oral presentation)

Hooper, B, Innocenzi, T and Dugan, C, 2009. The Hazelwood/H3 Capture Demonstration Project. In: Proceedings of the Twenty Sixth International Pittsburgh Coal Conference [CD-ROM], Pittsburgh, USA, 20-23 September.

Qader, A, Hooper, B, Innocenzi, T, Stevens, G, Kentish, S, Scholes, C, Smith, K, Webley, P, Mumford, K and Zhang, J, 2010. Novel Post-Combustion Capture Technologies on a Lignite Fired Power Plant — Results from the CO2CRC/H3 Capture Project . *Poster presented at the 10th International Conference on Greenhouse Gas Control Technologies (GHGT-10),* Amsterdam, The Netherlands, 19-23 September.

Mumford, K, Smith, K, Shen, S, Anderson, C, Suryaputradinata, Y, Tao, W, Endo, K, Thee, H, Kentish, S and Stevens, G, 2010. Results from the Solvent Pilot Plant for Post-Combustion Capture at Hazelwood Power Station. Oral presentation given at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.

Mumford, K, Smith, K, Shen, S, Anderson, C, Suryaputradinata, Y, Tao, W, Endo, K, Thee, H, Kentish, S and Stevens, G, 2010. Results from the Solvent Pilot Plant for Post-Combustion Capture at Hazelwood Power Station. Oral presentation given at CO2CRC Research Symposium 2010, Melbourne, Australia, 1-3 December.

Along with interactions at the numerous international and national conferences listed above, continuous collaboration occurred between the solvent capture group and the following organisations/universities:

- Process Group
- International Power
- Tsinghua University, Beijing

The skills and knowledge developed through this project have made the CO2CRC solvent research group one of the world leading experts in operating K_2CO_3 solvent based capture plants under post-combustion conditions. This includes developing the skills of the following people in solvent post-combustion capture:

- 2 postgraduate students
- 2 research assistants
- 4 research fellows

5.1.7 Conclusions and Recommendations

The solvent absorption CO_2 capture plant has been successfully capturing CO_2 from Hazelwood power plant flue gas for 10 months. The plant has undergone successful commissioning, start-up, steady state and shutdown operations with no safety incidents. Calculation of energy consumption was limited due to uncertainty associated with calculating steam consumption. Standard operating and safety procedures have been developed onsite and numerous personnel are now trained in the operation of the CO_2 capture plant.

Using ***BASF PuraTreat^{TM} F solvent*** the plant has operated at a CO_2 capture capacity of 20 - 25 tonnes of CO_2 per day resulting in 80 – 90 % of the CO_2 being removed from the waste flue gas stream. The purity of the captured CO_2 was around 95 %. The plant operated for approximately 1850 hours.

Using ***potassium carbonate*** solvent of 20 – 30 wt% solvent concentration, the plant has operated for several months. As the plant was not designed for this solvent, the conditions were not optimal for CO_2 capture, resulting in only 20 – 25 % of the CO_2 being removed from the flue gas, corresponding to a nominal capture rate of 4 - 5 tonnes per day.

Overall, operation of the solvent absorption CO_2 capture plant enabled the following to be achieved:

- Demonstrate long term operation of a CO_2 capture plant
- Determine the performance of the amino acid based solvent BASF PuraTreat^{TM} F
- Obtain useful operational information for potassium carbonate solvent
- Compare the absorption efficiency and energy consumption of the plant with the design case
- Gain a preliminary understanding into the interaction of the solvents with minor gas components such as SO_x and how these contaminants effect the quality and performance of the solvent
- Gain valuable experience in operating a large scale CO_2 capture plant
- Verify simulations against operating data

The following recommendations are considered to be important for completing further analysis of the solvent capture plant:

- Improve steam consumption measurements so that a comprehensive analysis of the energy usage can be completed
- Gain a better understanding of the vapour-liquid-equilibrium relationship between the PuraTreat^{TM} F solvent and CO_2 so that extensive process simulations can be developed in order to optimize the overall performance of the plant
- Further investigate the operational effects related to the accumulation of sulfur or nitrogen components in the solvents
- Improve reliability of fault temperature, flow and pressure transmitters
- Develop promoters for K_2CO_3 solvent to enhance the reaction kinetics, especially at low temperatures
- Use heat tracing and cladding of the solvent capture plant when using concentrated solutions of K_2CO_3 to prevent operational issues associated with solids precipitation
- Investigate methods to increase the partial pressure of CO_2 in the feed gas, to increase the driving force for CO_2 absorption

5.1.8 References

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5.2 Membranes

5.2.1 Process Description

The purpose of the CO2CRC H3 Project Membrane Pilot Plant was to trial gas separation membranes and membrane gas-solvent absorption contactors to remove CO_2 from flue gas, with the overall objective to determine which membrane technology had the most potential for successful post-combustion carbon capture.

To achieve this objective, the membrane pilot plant was designed and constructed by Process Group Pty Ltd (PG), to CO2CRC requirements. The plant was designed to separate approximately 15 tonne of CO_2 per annum from flue gas, based on expected membrane performance.

Two membrane separation processes were tested in parallel (Figures 5.2.1 and 5.2.2):

- A gas separation membrane (M-101), where the membrane is a nonporous polymer selective for CO_2 and the permeate stream is under vacuum.
- A membrane gas-solvent absorption contactor (M-102), which is a hybrid technology of solvent absorption and membrane separation, where CO_2 separation was achieved by absorption into a solvent (from the solvent pilot plant), with the interaction area between the flue gas and solvent rigidly controlled by a porous membrane.

The separation performance criteria used to asses each technology were as follows:

- Good CO_2 selectivity relative to N_2.
- Good CO_2 permeability (i.e. flux) through the membrane
- Separation performance stability under process conditions

The membrane technology that demonstrates these three criteria has potential for implementation in post-combustion capture. To fully quantify performance, the permeability of minor components in the flue gas, specifically SOx, NOx, CO as well as O_2 and water were measured.

5.2.1.1 Feed Gas pre-treatment

Flue gas was taken from after the blower discharge of the Solvent capture plant (after the direct contact cooler), with the main feed pipe work shared with the Adsorption Pilot Plant. The flue gas pressure was increased via feed booster to ~150 kPa_{abs}, and subsequently cooled through a plate heat exchanger to ambient conditions. A separator vessel removed the condensed water. The flue gas was then reheated to ~45^{o}C through trace heating on the pipe work. The two membrane units were in parallel and could run simultaneously. To control the feed gas pressure, a control valve on the feed line was present with the discharge to the bypass line that returns to the Solvent capture plant feed blowers suction line.

5.2.1.2 Gas Separation Membrane Module

The gas separation membrane is a hollow fibre module (Air Products PRISM membrane) with the retentate flow rate controlled and the feed flow rate measured (See Figure 5.2.2). The permeate stream was under vacuum (water sealed), with the permeate discharge into a separator vessel for removal of water. The vacuum was varied, with recycle present to ensure minimum flow through the pump.

Figure 5.2.2 H3 Capture Project Membrane Pilot Plant, Gas separation membrane is on the right with the gas-solvent contactor unit on the left.

5.2.1.3 Membrane Gas-Solvent Contactor Module

The membrane gas-solvent contactor is a hollow fibre module (Membrana Liqui-cell X50), operating in counter-current mode with the solvent on the shell side and gas on the lumen side. The gas flow rate through the contactor was controlled on the retentate side. The solvent was drawn directly from the Solvent Plant’s lean solvent circuit. Lean solvent passed through a pressure control valve to reduce it to the range 115-255 kPa_{abs}, which was greater than the flue gas pressure. The enriched solvent was returned to the Solvent plant on the rich Solvent pump suction side. The differential pressure between the solvent and gas streams was monitored via two pressure gauges.

5.2.1.4 Exit Gas treatment

All permeate, retentate and bypass streams discharged into the same header line from where the processed gases were returned to the blower suction of the Solvent Capture Plant.

5.2.1.5 Gas and Solvent Sampling

Sample points were isolated via a manual needle valve and were present at appropriate locations for discrete sampling of gas streams. All gas samples were analysed by gas chromatography for carbon dioxide, nitrogen and oxygen. The minor components present were evaluated qualitatively, for CO and NOx by portable gas meters. Solvent samples, both PuraTreat™ F and Potassium Carbonate, were analysed by standard methodology covered in the solvent section of this report.

5.2.2 Testing and Data Collection with Operating Issues and Learning

5.2.2.1 Operational Issues

The plant was installed at International Power Hazelwood site in June 2009 and commissioned in July 2009. The Plant was operated intermittently from July 2009 until November 2010. In total the pilot plant was operated for 55 hours, with the membrane gas-solvent contactor operated over this entire time period and the gas separation membrane operated for 32 hours.

A number of major delays in operating the plant were related to operational issues. One of the reasons was due to corrosion of the feed blower made from carbon steel. The delay period was prolonged due to another stainless steel based feed blower being sourced and installed. During this delay period the membrane gas-solvent contactor was operated for a time, given that feed gas pressure in this system is not a critical parameter for performance. The next major delay period occurred between April 2010 and June 2010 and was caused by solvent change over in the solvent plant to potassium carbonate solvent from PuraTreat^{TM}, F shutting down the membrane and adsorbent rigs. The last major delay period between July 2010 and August 2010 was due to the shut-down of unit 8 of the power plant for maintenance, shutting down the H3 capture project.

The operation of the Membrane Pilot Plant had two key learnings. Firstly, the materials of construction needed to be able to handle the acidic conditions of wet flue gas, as demonstrated from the corroded carbon steel blower. Secondly, the operational status of both the solvent plant and adsorption pilot plant had a severe impact on the performance of the membrane plant.

5.2.2.2 Gas Separation Membrane

The gas separation membrane stream tested an Air Products PRISM membrane hollow fibre module. The module was of length 600 mm and diameter 55 mm, with the feed gas on the lumen side and operated in a counter-current mode. The membrane material is a derivative of polysulfone. It should be noted that the Air Products membrane was chosen as it was available commercially in a size and format suitable for the pilot plant. This membrane material is optimised for oxygen/nitrogen separation and is not designed specifically for carbon dioxide separation. Hence, laboratory work was also conducted with a variety of other membrane materials more suited to carbon capture, to support the pilot plant work.

The sealed hollow fibre nature of the membrane meant the surface area and thickness were unknown, and therefore the permeability of gases through the membrane could not be defined in standard units. Instead, the gas permeance through the membrane was determined as a volumetric rate, normalized by the partial pressure driving force across the membrane. This allowed comparison between the different gases, given both the membrane thickness and area are common.

The CO_2 normalized flux through the membrane over the trial period is provided in Figure 5.2.3. This shows an initially high flux of almost 3 cm^3(STP)/s cmHg, which rapidly drops over the first 3 hours of operation to ~1.25 cm^3(STP)/s cmHg. This is attributed to the build up of other flue gas components in the membrane, especially water. These will compete with CO_2 for transport through the membrane.

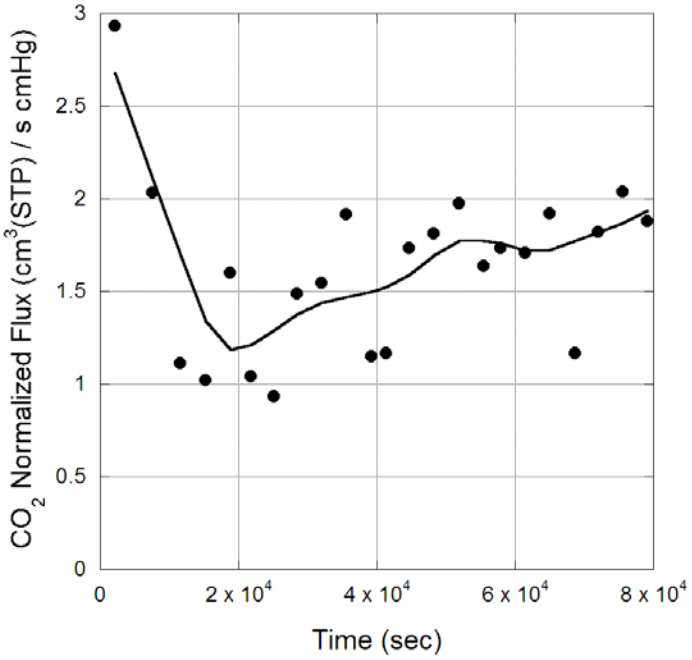

Figure 5.2.3 CO_2 Normalized Flux (cm^3(STP)/s cmHg) through gas separation membrane as a function of accumulated time, with average performance line.

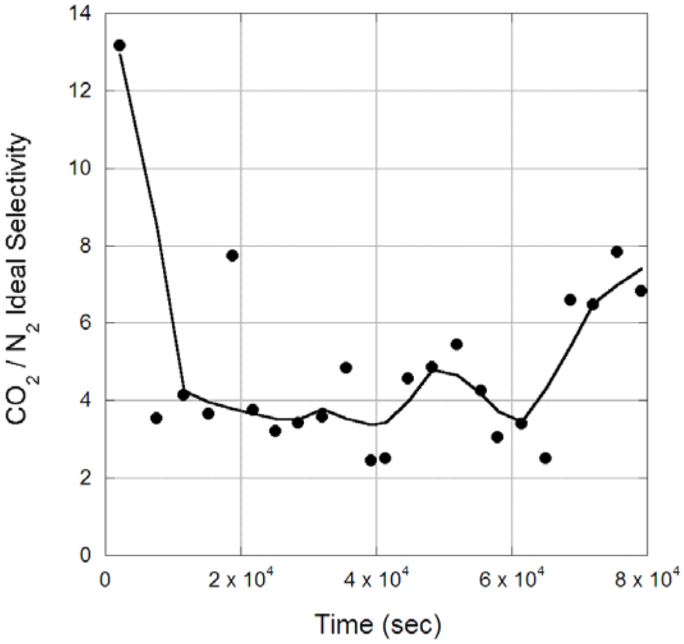

Figure 5.2.4 CO_2/N_2 Ideal Selectivity for Gas separation membrane as a function of accumulated time, with average performance line.

The CO_2/N_2 ideal selectivity of the membrane is provided in Figure 5.2.4, which is the ratio of the CO_2 and N_2 permeances. The decrease in selectivity suggests that water is more strongly competing with CO_2 for flux through the membrane compared to N_2.

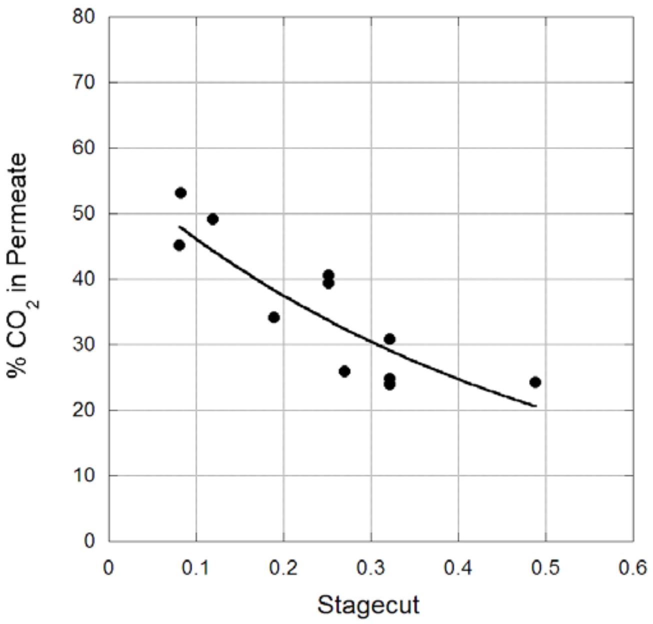

Figure 5.2.5 % CO_2 in Permeate stream (dry basis) as a function of stage-cut, on a dry basis.

The effect of stage-cut (the ratio of permeate flow rate to retentate flow rate) on the %CO_2 in the permeate can be seen in Figure 5.2.5 for the Air Products PRISM membrane, on a dry basis. Increasing the stage cut across the membrane decreases the %CO_2 in the permeate stream, which is attributed to falling CO_2 concentration along the contactor's length. Hence, this reduces the relative flux of CO_2 compared to N_2 though more of both gases is recovered from the feed. Importantly, 50% CO_2 in the permeate stream (from ~8.5% in the feed) can be achieved at very low stage-cuts. However, this is less than the 95% purity target of the USA Department of Energy, and indicates multiple membrane stages will be required to achieve this level of purity with this membrane material.

Water

The presence of water in the flue gas clearly has a strong influence on the performance of the membrane. It leads to a very strong water flux through the membrane which results in the permeate stream being supersaturated with water. This will have serious implications for larger scale facilities, where dealing with the liquid water content of the permeate gas will become a major process issue.

Oxygen

The normalized flux of oxygen through the Air Products PRISM membrane was on average 0.37 cm^3(STP)/s cmHg. This is a quarter of the CO_2 flux (towards the end of the trial period) and indicates the selectivity of the membrane for CO_2 over O_2. This normalized flux is very similar to the average N_2 normalized flux of 0.39 cm^3(STP)/s cmHg, and implies that under flue gas conditions the membrane has similar permeance of both N_2 and O_2. This is in contrast to the PRISM's membrane design purpose of separating O_2 from air.

Minor Components

The low concentration of the minor components in the flue gas, specifically CO, NOx and SOx, coupled with the low gas flow rates has meant quantitative determination of the permeance through the membrane was not possible. Qualitative measurements were undertaken to determine the percentage of each minor component that is transferred to the permeate stream, and these are provided in Table 5.2.1.

The results show that only a small amount of CO transferred through the membrane to the permeate stream. Therefore, the majority of CO remained in the retentate stream. In contrast, most of the NOx and SOx transferred to the permeate stream. This indicates that both minor component gas classes have high permeances, possibly greater than CO_2, and will enrich the permeate stream. This is expected because of the condensability of these gases (especially, NO_2, SO_2 and SO_3), which for glass polymeric membranes, like polysulfone, strongly correlates with gas permeability [5].

Table 5.2.1 Percentage of minor components in the feed gas that transfer to the permeate stream.

CO	13 ± 2
NOx	82 ± 16
SOx	87 ± 12

There was no evidence of ash build up in the membrane fibres or module.

5.2.2.3 Membrane Gas-Solvent Contactor

The membrane gas-solvent contactor utilises a solvent to remove CO_2 from the flue gas, with a non-selective porous membrane providing the contact area between the gas and solvent. In this manner, the membrane provides a high degree of surface area and allows for control of the solvent flow. The solvent ensures high selectivity for CO_2. The membrane gas-solvent contactor module is a Liqui-cel contactor with a polypropylene membrane, having a surface area of 8.1 m^2, porosity of ~40% and hollow fibre internal diameter of 220 µm. In the process, the flue gas is on the lumen side of the contactor while the solvent is on the shell side. The lean solvent was drawn directly from the solvent plant, and therefore either PuraTreat^{TM} F (BASF) or 30 wt% Potassium Carbonate (CO2CRC). The gas-solvent contactor unit was trialled with PuraTreat™ F solvent (BASF) from July 2009 until April 2010, and from June 2010 until November 2010 with 30 wt% potassium carbonate solvent (CO2CRC), corresponding to the trial periods of the solvent plant.

The overall mass transfer coefficient for CO_2 with PuraTreat™ F and K_2CO_3 solvents are shown in Figure 5.2.6 and 5.2.7 respectively, as a function of solvent flow rate. It is immediately clear that the PuraTreat™ F mass transfer coefficient is two orders of magnitude greater than that observed for unpromoted K_2CO_3. and similar to that reported in the literature [6]. Unpromoted K_2CO_3 is poor at removing CO_2 from flue gas. This is in keeping with low kinetics for K_2CO_3 at the pressure and temperature of the process [7].

The overall mass transfer coefficient for PuraTreat^{TM} F and K_2CO_3 increases with solvent flow rate. This is associated with the influence of solvent flow rate on the solvent-side mass transfer boundary layer resistance as the captured CO_2 transgresses this region. Increasing the solvent flow rate decreases the boundary layer thickness, reducing the mass transfer resistance and leading to an increase in overall mass transfer coefficient.

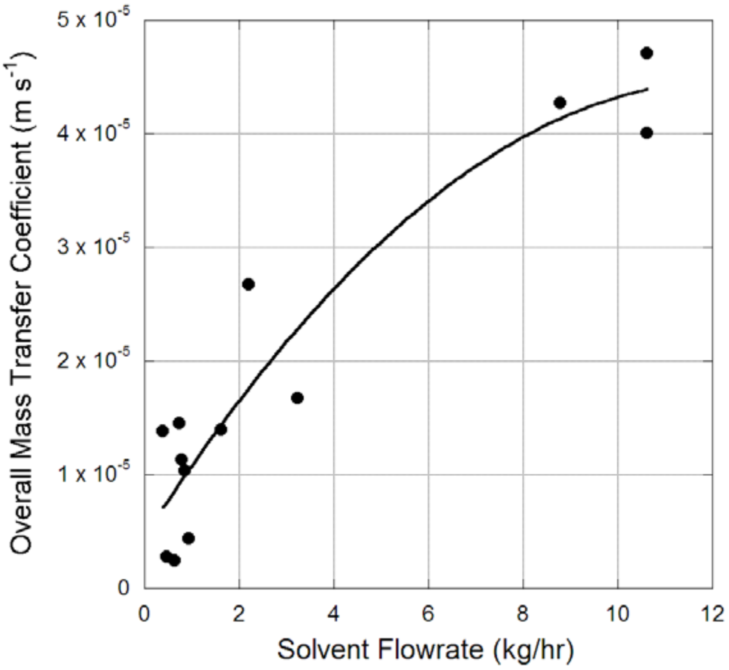

Figure 5.2.6 Overall CO_2 Mass Transfer coefficient (ms^{-1}) for PuraTreat^{TM} F and the polypropylene contactor.

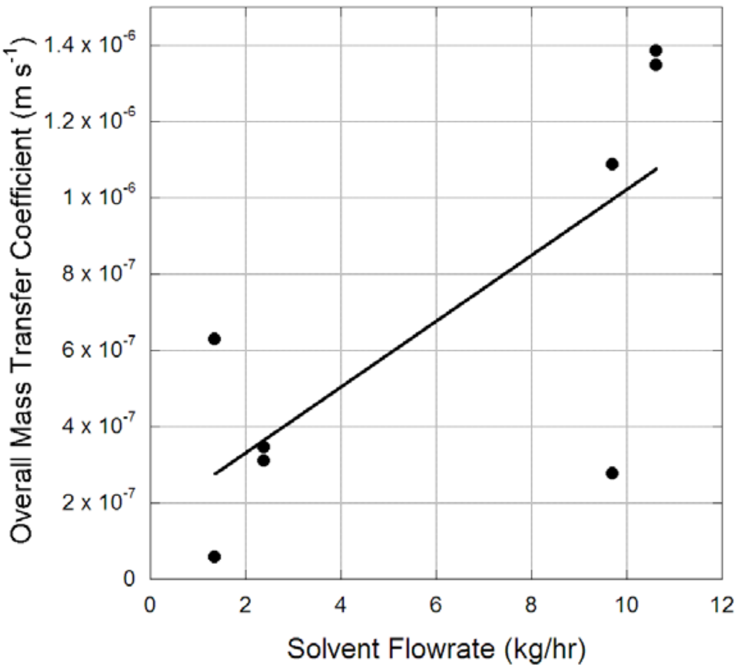

Figure 5.2.7 Overall CO_2 Mass Transfer coefficient (ms^{-1}) for 30 wt% K_2CO_3 and the polypropylene contactor.

An increasing solvent flow rate also results in a shorter residence time in the contactor and hence the solvent loading (mols of CO_2 absorbed per mol of solvent) should fall. This is most evident for the PuraTreat™ F data, where there is a clear trend of decreasing solvent loading with increase in the solvent to gas ratio (Figure 5.1.2.8). In addition, reasonable CO_2 loadings where obtained for PuraTreat™ F at low solvent to gas ratios, meaning that the amount of solvent required for the process can be minimized. In contrast, K_2CO_3 had very low CO_2 loadings across the solvent to gas flow rate ratio range. The low solvent loading, as well as low overall mass transfer coefficient, meant it was very hard to establish a trend in the data as a function of K_2CO_3 flow rate (Figure 5.2.9).

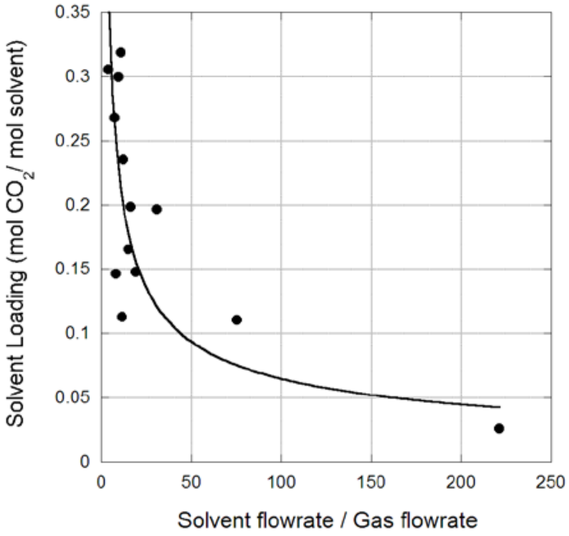

Figure 5.2.8 Solvent loading as a function of solvent flow rate to gas flow rate ratio for PuraTreat™ and polypropylene contactor.

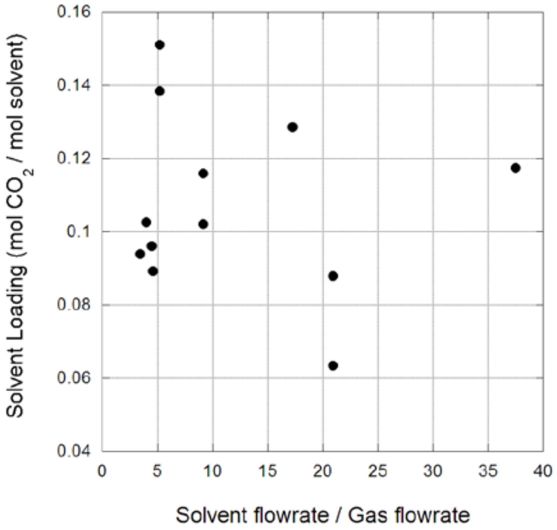

Figure 5.2.9 Solvent loading as a function of solvent flow rate to gas flow rate ratio for 30 wt% K_2CO_3 and polypropylene contactor.

Oxygen and Minor Components

The low flow rate of the flue gas in the contactor (as most results were obtained without an operational blower), coupled with the low concentration of the minor components in the flue gas, specifically CO, NOx and SOx, meant quantitative determination of their transfer across the membrane, along with O_2, was not possible. Qualitative measurements were undertaken to determine the percentage of each minor component that is transferred to the solvent, and these are provided for both PuraTreat^{TM} F and K_2CO_3 in Table 5.2.2. It should be highlighted that determination of SOx concentration was extremely difficult and no valid measurement for either solvent system was possible. However, based on the solvent plant data for K_2CO_3, it is expected that significant amounts of SOx will react with the solvent.

For both O_2 and CO, an average reduction of 8.5% was observed between the feed and retentate streams across both solvents. Within the error of the measurement this suggests very little preferential absorption of either O_2 or CO occurs for PuraTreat™ F or K_2CO_3. Alternatively, for NOx there is significant reduction across the contactor, especially for K_2CO_3, and indicates that there is a reaction with the solvent. This is expected given the similar chemistry of NO and NO_2 with CO_2 [8].

Table 5.2.2 Percentage of minor components in the feed gas that transfer to the solvent through the contractor.

	PuraTreat^{TM} F	30 wt% K_2CO_3
O_2	8 ± 2	10 ± 6
CO	4.5 ± 3.5	12 ± 4
NO_x	55 ± 12	78 ± 14

The cumulated trial time of the membrane gas-solvent contactor was 55 hours, of which 20 hours was with PuraTreat™ F and the remainder with K_2CO_3. For the whole 20 hours with PuraTreat™ F no change in the flow rate performance was observed, however for K_2CO_3, a decrease in solvent flow rate was monitored towards the end of the plant operation run. Hence, this is obviously a significant problem we faced when operating with the K_2CO_3 solvent, which can be considered as a limitation and addressed in improving future test conditions.

Ash, Solvent Breakthrough and Crystals

The polypropylene contactor has some ash build up at the entrance to the membrane fibres after being exposed to the flue gas for 55 hours. This is only a minor build up of ash and suggests the upstream direct contact cooler and knock-out pot prevents most ash particles from reaching the contactor. Solvent breakthrough is a significant issue, caused when the solvent penetrates the porous structure of the membrane. This results from a combination of high transmembrane pressures and low interfacial tension. This drives solvent through the membrane pores and into the gas stream and subsequently reduces the overall mass transfer coefficient. There is a suggestion of some solvent breakthrough as indicated by a discolouration of the membrane fibres at the gas exit end. The colour of this residue suggests PuraTreat™ is the breakthrough agent. No evidence was found for K_2CO_3 breakthrough. However, for K_2CO_3 there is clear indication of carbonate crystal formation on the shell side, and indeed upon the membrane fibre bundle. Hence, there is evidence that carbonate crystal build-up in the contactor is responsible for the dramatic decrease in solvent flow rate towards the end of the operation of the unit.

5.2.3 Laboratory Results

In support of the pilot plant work, a large range of laboratory experiments have been conducted. These focused on polysulfone, which was the membrane material used in the pilot plant trials but also on two polyimides, Matrimid 5218, (3,3'-4, 4'-benzophenone tetracarboxylic – dianhydride diaminophenylindane) and 6FDA-TMPDA(2-2'-bis(3,4'-dicarboxyphenyl) hexafluoropropane dianhydrid-2,3,5,6-tetramethyl-1,4-phenylenediamine). These polyimides are more prospective membranes for large scale carbon capture, but were unavailable as a membrane module of sufficient size for testing in the pilot plant.

5.2.3.1 Nitrogen Oxide and Carbon Monoxide Permeation

Full details of this work can be found in Scholes *et al*. [9]. In summary, the permeability of NO was measured in the laboratory for three glassy membrane materials - polysulfone, Matrimid 5218 (Huntsman Chemicals) and 6FDA-TMPDA (manufactured in house). This permeability was compared to that of N_2, CO and CO_2.

There was a clear trend of increasing gas permeability coinciding with increasing gas critical temperature in the order $N_2 < CO < NO < CO_2$. This is a product of the increased solubility affinity of each gas for the polymeric matrixes.

Under mixed gas conditions, the permeabilities of CO_2 and N_2 in polysulfone and 6FDA-TMPDA are reduced from the pure gas case, indicative of competitive sorption. Upon exposure to 1000 ppm CO, a further reduction in both permeabilities was observed. The decrease in CO_2/N_2 selectivity implies that CO has a stronger competitive sorption effect on CO_2 within these two membranes than N_2. Within experimental error, the permeability loss for polysulfone is the same at all the temperatures tested. However, for 6FDA-TMPDA, the permeability loss is smaller at higher temperatures, reflecting the stronger contribution of Langmuir sorption at lower temperatures [11].

The average activation energy for permeation is -2.5 kJ/mol, which is consistent with previous literature reports for CO_2 permeation in this polymer [11, 12].

5.2.3.2 The Impact of Water on Carbon Dioxide and Nitrogen Permeation

Full details of this work can be found in Scholes *et al*. [13]. In summary, the sorption of the light gases CH_4, N_2, CO_2 as well as water into polymer films prepared from a commercial sample of Matrimid 5218 were measured. For water, sorption behaviour was similar to rubbery polymers, that of significant adsorption into the polymeric matrix and was modeled by Henry's law exclusively.

5.2.3.3 Plasticisation of Polysulfone Membranes

Full details of this work can be found in Scholes *et al*. [16].

It is well known that plasticization of gas separation membranes by carbon dioxide can permanently alter their performance and increase the possibility of membrane failure. This is amplified in ultra-thin composite membranes of the type used commercially, where the active polymeric layer is less than 2 µm. Here, the plasticization influence of CO_2 is measured on ultra-thin polysulfone composite membranes for a range of active layer thicknesses, at four temperatures. The resulting permeability – pressure isotherms demonstrated that plasticization occurs for all thicknesses at pressures lower than has been reported for dense membranes.

These isotherms were quantitatively fitted with an expanded dual-sorption model that takes into account plasticization of the membrane. The plasticization potential of CO_2 for polysulfone was found to increase with reduced active layer thickness. Similarly, the plasticization potential of CO_2 was found to decrease with temperature. These results are consistent with similar research that shows that thin films behave differently to dense membranes.

5.2.4 Performance Evaluation and Results as against Simulation

The performance data determined from the pilot plant was used as the basis for simulation studies for large scale membrane based capture plants from flue gas.

The design basis for these simulations is provided in Table 5.2.3.

Table 5.2.3 Flue gas conditions for the design of large scale membrane capture plant.

Flow rate (kg/hr)	6400
Temperature (°C)	240
Pressure (kPag)	10
Composition (mol%)	
CO_2	13.0
N_2	62.2
O_2	3.5
Water	20.5
Ar	0.8

5.2.4.1 Gas Separation Membrane

Based on power consumption minimisation for similar separation performance, both Ho *et al.* [17] and Merkel *et al.* [2] have determined that a vacuum on the permeate side is a better option than a compressor on the feed side. This is mainly due to the low CO_2 content of the feed gas, meaning a compressor is required to compress a significant amount of inert N_2, while a vacuum pump operates on a smaller flow rate because of the CO_2-rich permeate. In terms of membrane flow configuration, Merkel [2] found that a counter-flow mode utilised the minimal energy demand, compared to either a cross-flow or co-current-flow regime. Hence, the Aspen HYSYS design simulation (CO2CRC internal module) for the post-combustion gas separation capture plant [18], is based on a vacuum driven counter-current flow model, using the feed gas specifics provided in Table 5.2.3. The membrane simulation performance utilises the Air Products PRISM results, with the permeability of Argon assumed to be 0.421 barrer [19].

90% CO_2 Recovery

To obtain a 90% CO_2 recovery in a single stage membrane unit, as per USA Department of Energy guidelines, the Air Products PRISM membrane requires an area of 1.59×10^7 m^2, for a stage cut of 40%. For a feed pressure of 111 kPa_{abs} and vacuum pressure of 22 kPaa [2], the permeate flow rate is 2543 kg/h (78 kmol/hr), with the permeate composition provided in Table 5.2.4. The cooling duty on the system is 864kW with the vacuum pump duty of 83 kW.

Table 5.2.4 Permeate composition (mol%) of one stage membrane unit from simulations, based on pilot plant performance data.

CO_2	34
N_2	46
H_2O	12
O_2	7
Ar	1

It is clear that to recover 90% of CO_2, the permeate composition is still dominated by N_2. This is because of the low selectivity of the membrane for CO_2/N_2 separation, and therefore given the stage cut a considerable amount of the N_2 passes into the permeate stream. Importantly, the high amount of water flux through the membrane leads to supersaturated conditions at atmospheric conditions. Therefore a considerable amount of water would be removed in a subsequent separating vessel, substantially reducing the water content of the permeate gas. This single membrane stage is only able to concentrate the CO_2 level 2.6 times.

While this concentration is clearly inadequate for sequestration purposes, such a membrane separation might provide a first stage concentration step prior to an absorption or cryogenic separation step.

95% CO_2 purity

It is difficult to obtain a CO_2 stream of 95% purity, as per USA Department of Energy guidelines, with only the Air Products PRISM membrane in series abel to achieve this purity. A simple simulation design scheme uses three membranes in series, for a feed pressure of 111 kPa_{abs} to each membrane unit and a vacuum of 22 kPa_{abs}, with intermediate separation vessels to remove condensed water. The compositions and flow rates of the permeate stream of each membrane system is shown in Table 5.2.5. The corresponding membrane area and stage cut across the membrane are provided in Table 5.2.6. The cooling demands and vacuum duty of each membrane unit is provided in Table 5.2.7. This design is focused on achieving the desired purity and not recovery; hence no recycle streams are present.

Table 5.2.5 Permeate flow rate and composition determined by Aspen HYSYS simulation of a post-combustion gas separation membrane capture plant.

	Membrane 1	Membrane 2	Membrane 3
Total Flow rate (kg/hr)	280	13	0.55
CO_2 (mol %)	55.1	87.9	93.5
N_2	31.9	3.2	0.2
H_2O	5.1	5.1	5.1
O_2	7.2	3.7	1.2
Ar	0.7	0.1	0.0

By operating at very low stage cuts, the CO_2 content in the permeate stream is able to be concentrated by each consecutive membrane unit, until a concentration of 93.5% is obtained after the third membrane. However, the flow rate of purified CO_2 is very small and the net recovery very low.

The low stage cut results in low N_2 flux through the first membrane unit and therefore a reduced mol% is observed in the permeate compared with the first simulation based on 90% recovery. Importantly, the high water permeance means a significant amount of water passes into the permeate, and for all three membranes units at atmospheric conditions the permeate is supersaturated. Removing the liquid water leads to saturated conditions at this temperature of 5.1%. Thus, it is not possible to achieve a CO_2 purity of 95% on a wet gas basis. To achieve the desired purity, it is necessary to operate below saturation conditions, either by removing significant amounts of water by initial cooling (<10 ^{o}C), or removing the water from the process via another method. Again, integration with a cryogenic process might prove useful in this case.

Table 5.2.6: Area and stage-cut determined by Aspen HYSYS simulation of a post-combustion gas separation membrane capture plant.

	Membrane 1	Membrane 2	Membrane 3
Area (m^2)	$1.12x10^6$	$9.77x10^9$	$2.34x10^8$
Stage cut	0.05	0.05	0.05

Table 5.2.7: Cooling and vacuum duty determined by Aspen HYSYS simulation of a post-combustion gas separation membrane capture plant.

	Membrane 1	Membrane 2	Membrane 3
Cooling Duty (kW)	890	1.2	0.05
Vacuum Duty (kW)	10	0.4	0.02

The reducing flow rate of the feed to each membrane unit in series is responsible for the reduction in cooling and vacuum duty down the series. However, to achieve both recovery and purity requirements significant amounts of recycle streams around each membrane stage will be required leading to significant greater cooling and vacuum duties, especially for Membrane 2 and 3.

These poor results reflect the use of the polysulfone membrane in the pilot plant trials. As indicated previously, this membrane material was chosen as it was available as a commercial module of reasonable scale. Ongoing trials will focus on membranes that are more optimum for this application.

Merkel *et al*. (2010) [2] have developed a range of potential gas separation membrane processes for post-combustion capture. In one such scenario (Figure 5.2.10), two membrane stages are used to reduce the CO_2 concentration of the flue gas from 11.6 to 1.8% CO_2. The first membrane step produces a permeate containing 50% CO_2 and 29% water. The CO_2-depleted residue leaving this membrane unit is sent to a second membrane stage. The permeate from the second membrane stage is recompressed and recycled to the front of the membrane process. The CO_2-enriched permeate from the first membrane step is compressed in stages to 25 bar and cooled to ambient temperature, which removes the bulk of the water in the gas. The dry gas is then cooled to −20 ◦C and sent to a short fractionating condenser column that produces CO_2 liquid of greater than 95% purity as a bottoms product. The liquid CO_2 can then be pumped to 140 bar and sent for sequestration as a supercritical fluid. A third small membrane unit is used to recycle the bulk of the CO_2 in the overhead gas to the front of the condensing column. The residue stream is then recycled to the flue gas feed. Overall, this process achieves 90% CO_2 capture. The total energy usage is about 24% of the power plant output. In addition, about 3.0 million m^2 of the membrane would be used, which combined with the power usage, results in a capture cost of about US$39/ton CO_2.

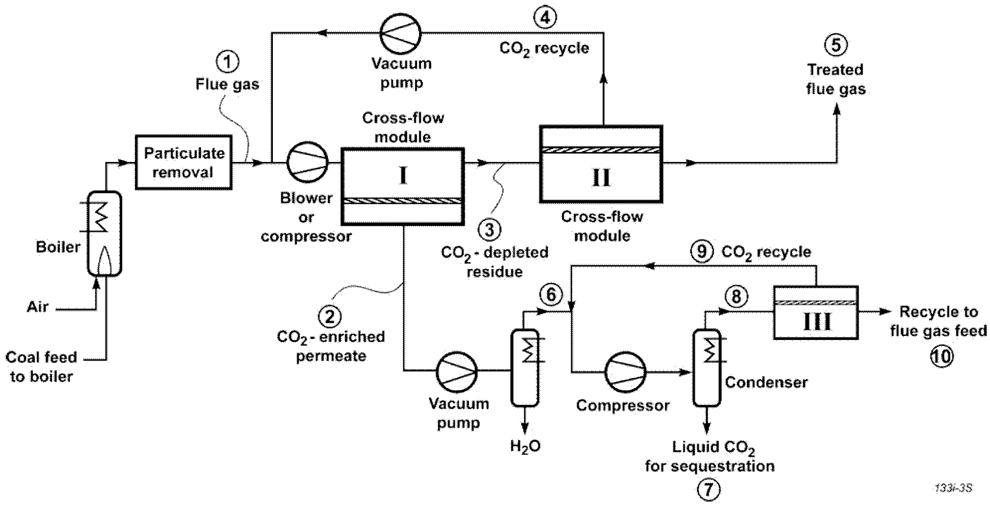

Figure 5.2.10: A two stage vacuum membrane process designed by Merkel et al. (2010) [2] to meet the US DOE guidelines of 90% recovery and 95% purity.

Merkel *et al*. (2010) [2] also present an alternative scenario in which the feed air to the boiler is first used as a sweep gas (Figure 5.1.2.11). In this scheme, a vacuum pump is used on the permeate side of the first membrane stage. The residue gas leaving this stage still contains about 7% CO_2. This gas passes on one side of a second membrane. All or a portion of the feed air to the boiler passes on the permeate side of this membrane as a sweep stream. Some CO_2 permeates through this second membrane and is recycled with the feed air to the boiler. After the bulk of the water has been removed by condensation, the permeate gas from the first stage contains about 83% CO_2. This gas is sent to a compression-condensation-membrane loop similar to that described in the previous design. Overall, at 90% CO_2 capture, this approach uses 16% of power generated by the plant to produce supercritical CO2 ready for sequestration. About 1.3 million m^2 of membrane is used, which combined with the power usage, results in a capture cost of about US$23/ton CO_2.

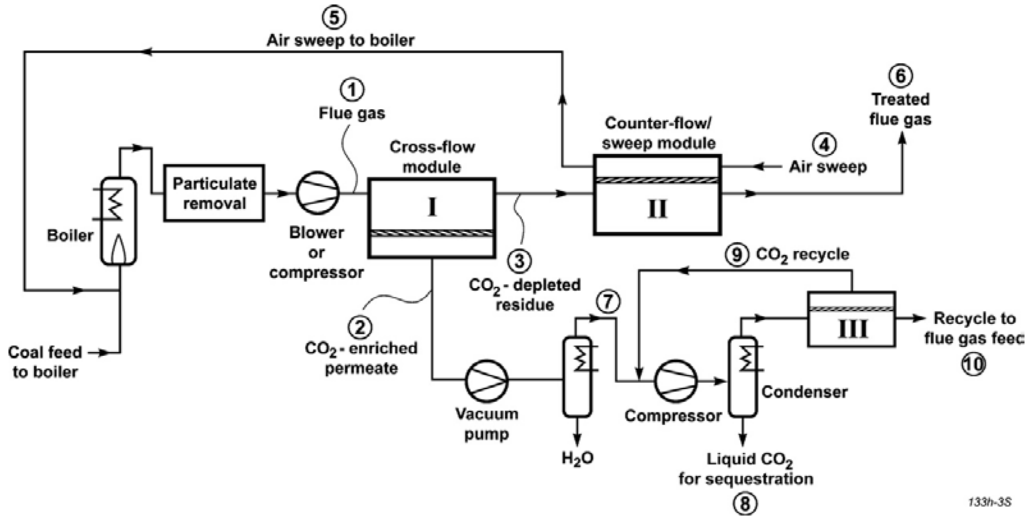

Figure 5.2.11: A two stage counter-flow/sweep membrane process designed by Merkel et al. (2010) [2] to meet the US DOE guidelines of 90% recovery and 95% purity.

5.2.4.2 Membrane Gas-Solvent Contactor

The membrane gas-solvent contactor is required to remove 26.5 kmol/hr of CO_2, at 10 kPag to achieve 90% recovery. For the large scale plant simulation, the overall mass transfer coefficient for both PuraTreat^{TM} F and 30 wt% K_2CO_3 was based on that observed for 9 kg/hr solvent flow rate in the pilot plant trials. This is a sufficiently high solvent flow rate to minimise the boundary layer resistance for both solvents, and represents a realistic overall mass transfer coefficient for the process. The membrane contactor area calculated to achieve the 90% recovery is provided in Table 5.2.8. It is clear that PuraTreat^{TM} F requires two orders of magnitude less area than K_2CO_3 because of the higher mass transfer coefficient. Furthermore, the high solvent loadings that would be achieved at this flow rate means that less PuraTreat^{TM} F solvent will also be required. Therefore, PuraTreat^{TM} F clearly represents the best solvent for the membrane contactor in terms of solvent loading and area required.

Table 5.2.8: Membrane gas-solvent contactor area required to capture 90% of CO_2 in large scale simulation.

	Area (m^2)
PuraTreat^{TM} F	4.2×10^6
30 wt% K_2CO_3	8.6×10^8

5.2.5 Other outcomes (communications, collaboration, skills development etc)

The membrane pilot plant performance has been reported at the following conferences in either presentation or poster formats:

- 9th International Conference on Greenhouse Gas Technologies 2008, Washington DC, USA
- CO2CRC Symposium 2008, Queenstown, New Zealand
- 5th Conference of the Aseanian Membrane Society 2009, Nagoya, Japan
- 8th World Congress of Chemical Engineering 2009, Montreal, Canada
- CO2CRC Symposium 2009, Coolum, Australia
- CO2CRC Symposium 2010, Melbourne, Australia
- 20th Annual Meeting of the North American Membrane Society 2010, Washington DC, USA
- 10th International Conference on Greenhouse Gas Technologies 2010, Amsterdam, Netherlands
- 6th Conference of the Aseanian Membrane Society 2010, Sydney, Australia
- International Chemical Congress of Pacific Basin Societies (Pacifichem) (2010) Honolulu, Hawaii, USA, December 15-20, 2010

The following peer-reviewed journal papers have been produced as a result of this research:

- R. Hasan, C. A. Scholes, G. W. Stevens, S. E. Kentish '*Effect of Hydrocarbons on the Separation of Carbon Dioxide from Methane through a Polyimide gas separation membrane*' Industrial & Engineering Chemical Research (2009) 48: 5415-5419
- C. A. Scholes, S. E. Kentish, G. W. Stevens *'Effects of Minor Components in Carbon Dioxide capture using polymeric gas separation membranes' Separation & Pur*ification Reviews (2009) 38: 1-44
- C. A. Scholes, S. E. Kentish, G. W. Stevens *'Carbon Dioxide Separation through Polymeric Membrane Systems for Flue Gas Applications'* Recent Patents on Chemical Engineering (2008) 1: 52-66.
- C. A. Scholes, W. X. Tao, S. E. Kentish, G. W. Stevens ' *Sorption of Gases and Water in Matrimid 5218*' Journal of Applied Polymer Science (2010) 117: 2284-2289
- C. A. Scholes, G. Q. Chen, G. W. Stevens, S. E. Kentish '*Plasticization of ultra-thin polysulfone membranes by carbon dioxide*' Journal of Membrane Science (2010) 346: 208-214
- C. A. Scholes, G. Q. Chen, S. E. Kentish, G. W. Stevens '*Nitric oxide and carbon monoxide in glassy polymeric membranes for carbon dioxide separation*' Chemical Engineering Research and Design (2011) in review

The following book chapter has been produced as a result of this research:

- C. A. Scholes, S. E. Kentish, G. W. Stevens '*The effects of minor components on the gas separation performance of polymeric membranes for carbon capture'* Membrane Gas Separation, Eds. B. Freeman, Y. Yampolskii (2010) Wiley, Singapore, pp201-226

The following peer-reviewed conference papers have been produced as a result of this research:

- C. A. Scholes, S. E. Kentish, G. W. Stevens '*Minor components effects on membrane gas separation for carbon capture*' 8th World Congress of Chemical Engineering (2009)

The following non-peer-reviewed journal papers have been produced as a result of this research:

- C. A. Scholes, G. Q. Chen, W. X. Tao, J. Bacus, C. Anderson, S. E. Kentish, G. W. Stevens '*The effects of minor components on the gas separation performance of membranes for carbon capture*' Energy Procedia (in press)
- B. Hooper, A. Qader, T. Innocenzi, G. Stevens, S. Kentish, C. Scholes, K. Mumford, K . Smith, P. Webley, J. Zhang '*Novel post-combuation capture technologies on a lignite fired power plant – results of the CO2CRC/H3 capture project*' Energy Procedia (in press)
- C. A. Scholes, G. Chen, W. Tao, G. W. Stevens, S. E. Kentish, A. Qader, B. N. Hooper '*Membrane based carbon capture pilot plant trials*' 5th Conference on Aseanian Membrane Society (2009)
- C. A. Scholes, S. E. Kentish, G. W. Stevens '*The effect of condensable minor components on the gas separation performance of polymeric membranes for carbon dioxide capture*' Energy Procedia (2009) 1: 311-317
- C. A. Scholes '*Capturing carbon with membranes*' Australiasian Science (2010) November: 33-35
- C. A. Scholes '*Capturing carbon from waste gases*' Issues (2010) 92: 14-17

The following collaborations have been made:

- Department of Environmental Engineering and Biotechnology, Myongji University, South Korea
- EcoTechnologies Proprietary Limited

The skills and knowledge developed through this project have made the CO2CRC Membrane research group one of the leaders in polymeric membranes and membrane gas-solvent contactors for carbon capture from post-combustion scenarios. This includes developing the skills of the following in membrane post-combustion capture:

- 2 research assistants
- 1 research fellow
- 2 PhD Students

5.2.6 Conclusion

- The Membrane Pilot Plant was successfully constructed, commissioned and operated to achieve its design aim of operating two processes, gas separation membranes and gas-solvent contactors. For gas separation membranes, an Air Products PRISM membrane was trialled and was able to concentrate CO_2 in the permeate stream, with concentrations approaching 50% only possible at very low stage cuts. The high permeance of water was a significant problem, and simulations of large scale plants demonstrated that the water content of the flue gas would need to be reduced to enable high purity CO_2 could be produced. It was found that O_2 had low permeance through the membrane, on par with N_2, while NO_x and SO_x both preferentially went to the permeate stream.
- The relatively poor results achieved with the gas separation membrane reflect the decision to trial a membrane material that is not optimised for CO_2 capture. This membrane was chosen because it was available commercially in a size and format suitable for the pilot plant trials. The very limited runtime achieved on the pilot plant, due to a range of operability issues have prevented the use of alternate membrane materials to date.
- Further work using membrane better adapted for CO_2 capture has been identified. It is hoped that one of these identified materials can approach the membrane performance prescribed by Merkel *et al.* [2]. as necessary to meet the US Department of Energy guidelines of 90% recovery at 95% CO_2 purity. These authors have reported that a membrane material of at least 1000 GPU and CO_2/N_2 selectivity of 50, coupled with a novel process configuration can achieve these targets, using about 16% of plant energy at a cost of US$23/ton CO_2. This leads to the recommendation for further work in this direction.
- For the membrane gas-solvent contactor, a porous polypropylene contactor with PuraTreat^{TM} (BASF) as the solvent achieved the highest overall mass transfer coefficients and good solvent loadings. It was determined that NO_x interacted with both solvents and was removed from the gas, while O_2 and CO remained with the flue gas.

A major outcome of the H3 Project Membrane Pilot Plant has been the training of students and researchers (5 in total) in carbon capture technologies and the communication of information and skills learnt, as well as collaborations established, with parties interested in the carbon capture and storage field.

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5.3 Adsorption

5.3.1 Process Description and Scope

This project applied state-of-the-art vacuum swing adsorption technology to capture flue gas CO_2 emitted from a coal-fired power station – International Power Hazelwood, Victoria. In this project, a pilot-scale vacuum swing adsorption rig was designed, fabricated and deployed to capture CO_2 from flue gas. The rig (Figure 5.3.1) comprises of three columns loaded with adsorbents, a feed gas booster, a recycle compressor, a vacuum pump pack, manifolds etc. The adsorber column was multiple-layered with adsorbents considering the complex composition of flue gas. Water-selective adsorbents were included to remove water in the flue gas and acidic gas resistant adsorbents were also utilized to tackle SOx and NOx. The majority of the adsorbents in the adsorber column were CO_2-selective adsorbents to adsorb CO_2 in an adsorption step and release CO_2 in a desorption step in a cyclic manner. The flue gas (120°C ~250°C) from the power station stack induced draught fan was sent to a direct contact cooler (DCC), where it was cooled down to ~40°C with some Sox and NOx removal. The cooled flue gas (10-15% CO_2, saturated with water vapor, N_2, O_2, and other ppm level impurities) was then pressurised through a feed gas booster to 130-150kPa$_{abs}$ and cooled by a plate heat exchanger before entering the columns. In the feed/adsorption step, CO_2 was selectively adsorbed onto the adsorbents with CO_2-lean gas leaving the top of the column and directed to the stack. After several additional bed to bed interaction steps, the column was evacuated by a vacuum pump to around 1kPa$_{abs}$ in the desorption step and the CO_2-rich product gas (110kPa$_{abs}$) was ready for compressing and sequestration, though in this specific project this gas stream was sent back to the inlet of the general feed gas blower. The adsorption and desorption processes were operated in a cyclic manner and the whole process was automatically controlled by Allen-Bradley PLC with real-time data acquisition. The effects of impurities, flue gas temperature and layer ratios on the performance of the vacuum swing adsorption process over a sustained period were investigated. Also, the durability of key adsorption process components eg. valves, compressors, vacuum pump, etc. were studied. In addition, this project conducted economic assessment of the potential of adsorption technology to post-combustion capture, and identified engineering and equipment obstacles for large scale carbon capture deployment.

5.3.2 Design Basis

The following design basis is provided to summarize the process engineering activities for a qualitative and quantitative understanding of the project.

Input conditions

Flue gas flow rate: 100 - 300 Nm^3/hr

Flue gas temperature: 192°C

Flue gas temperature after direct contact cooler: 30 - 40°C

Temperature of flue gas entering adsorption rig: 30 - 80°C

Flue gas compositions:

Composition	mole % (wet basis)
N_2	62.0
O_2	3.9
CO_2	11.0
H_2O	22.5
Ar	0.6
NOx	151 ppmv (dry basis)
CO	13.9 ppmv (dry basis)
SO_2	211 ppmv (dry basis)
SO_3	0.5 ppmv (dry basis)

Output conditions

Product gas pressure: 110 kPa$_{\text{abs}}$

CO$_2$ flow: 0.5 -1.0 TPD

CO$_2$ purity: 70 – 95%

For sequestration purposes, the product is further compressed and cooled.

Pressure: 150 bar(a)

Temperature: 50ºC

The specifications above reflect a range of operating conditions which were incorporated in the testing processes. The adsorption rig produced high purity CO$_2$ gas suitable for compression and liquefaction for transport and geo-sequestration.

Key technologies - Process novelty

An innovative vacuum swing adsorption process utilizing multiple-layered adsorption columns was developed and tested in this project. The major difference of this process from other previous adsorption-based technologies is that it processed all the gas components simultaneously and eliminated the needs for pre-treatment or guard bed. Such configuration greatly reduces CAPEX and OPEX of a capture plant. However, due to the complexity of flue gas, the engineering realisation/control of such process is sophisticated and requires relevant knowledge, experience and skills which formed as parts of the important objectives to achieve from the project.

Operation & Control

The adsorption rig was designed to run continuously and automatically. The rig was installed with Allen-Bradley PLC (Compact Logix) and a few types of I/O for process control and supervision. Factory Talk View and Citect-SCADA/HMI were used together to control the process and collect real-time data for analysis. The rig was interconnected with the main solvent plant which gave a digital signal indicating solvent process running status. The adsorption rig could only operate when the solvent plant was running, until a bypass line was installed at a later stage in the project to permit operation of the adsorption rig independently. All the flow ON/OFF functions were performed by pneumatic solenoid valves. A few control valves were also included to perform flow rate control, pressure control etc. Pressure, temperature, gas purity, flow rate were recorded continuously by the PLC and stored on a local hard drive. Remote wireless connection was established on the local control computer to enable remote access to the rig from the Melbourne office. The PLC has built in safety functions to automatically shut down the plant when certain safety conditions occur. Proper start-up and shutdown sequences, as well as control loops were incorporated in the PLC program. The high degree of automation minimized human attendance/interference, and to a large extent, ensured continuous operation of the rig. The history of data acquisition and storage capacity enabled maximum data collection and ensured good observation of the process.

Utilities

Cooling water

Cooling water was needed for the heat exchanger and the liquid ring vacuum pump. Both were once-through design and the used water was returned to the major cooling water return line after re-pressurising to 14bar.g. The total cooling water required was around 1.5 m^3/hr. As water vapour from the flue gas condensed in the liquid ring pump, the process was actually recovering water from flue gas.

Electricity

3-phase 415V, 50 Hz power was supplied to operate the blowers and pumps. The total maximum power requirements of the electric motors were 21 kW. The PLC system, instrumentation system and lighting also required small amount of power (<5kW).

Pneumatic air

Compressed air (4-6 bar.g) was required for pneumatic valve control and such air was supplied by the power station.

Liquid/solid handling

The waste water was pressurized to 14 bar.g and sent back to the cooling water return without direct manual handling. Proper operating, storage and safety procedures were developed and documented for adsorbent solids handling. Such solids handling activity was performed by International Power contractors with the supervision of CO2CRC personnel.

5.3.3 Construction, Commissioning and Operation

The design was finalized and approved in the first half of 2008 and thereafter went into fabrication stage. Before the rig left the workshop, a pre-commission check was performed by CO2CRC resulting in modification requests to the fabricator. The rig was shipped to the test site at International Power Hazelwood in the first half of 2009 and site preparation/pipeline work was performed by International Power contractors (Fig. 5.3.4). Though commissioning of the membrane and adsorption rigs started in July 2009, the adsorption rig commissioning was only officially finished in January 2010. However, CO2CRC personnel gained full control access to the rig from then onwards. As mentioned previously, the rig was highly automated and once started up, the operator had to observe the process for a couple of hours only before leaving the rig running on its own. Due to various reasons, the rig operation was interrupted from time to time. From January 2010 to September 2010, a few long continuous runs were realized and valuable data were collected. Rig operation was stopped mid-September 2010 due to scheduled power station unit shutdown. A simple cycle was tested during those operations (as shown in Figure 5.3.5). A complex cycle with a recirculation of product gas (Figure 5.3.6) designed to product high purity CO_2 (>=95%) was not tested due to various reasons but it was investigated by computer simulation and further investigation will be performed experimentally.

Figure 5.3.4 Adsorption rig installed at International Power Hazelwood, Victoria, Australia

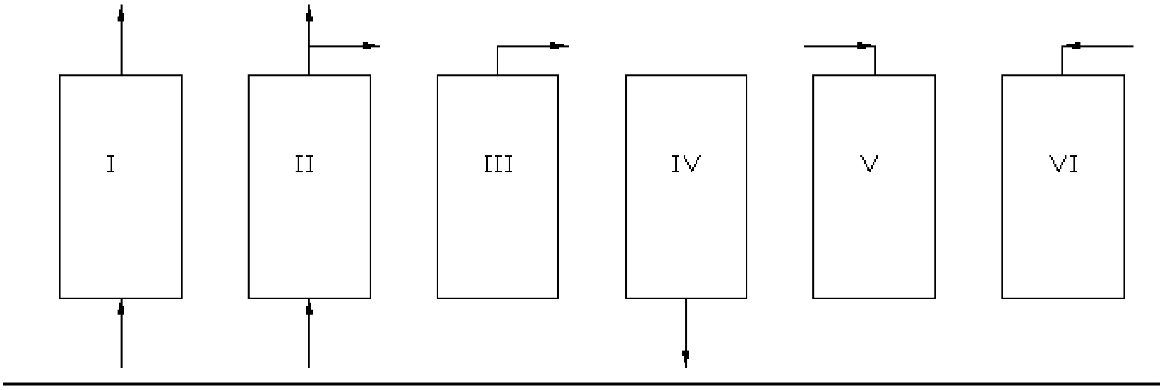

Figure 5.3.5 Adsorption cycle-1

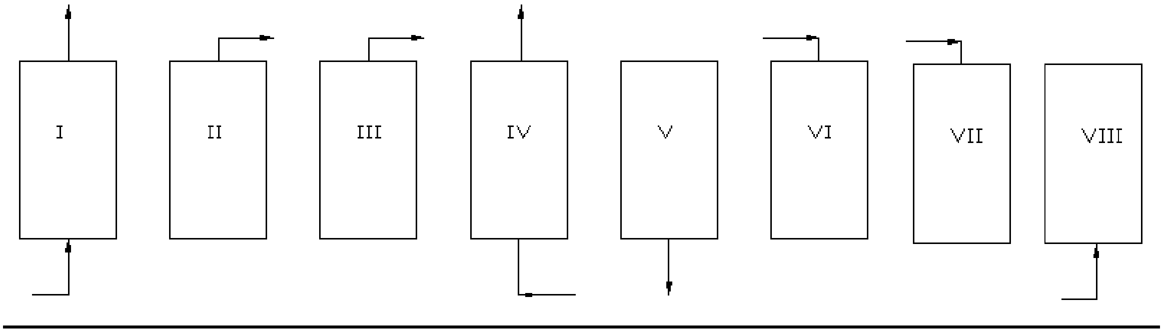

Figure 5.3.6 Adsorption cycle-2

5.3.4 Testing and Data Collection with Operating Issues and Learning

In addition to operation of the facility at Hazelwood, supporting pilot experiments and extensive numerical simulations were performed in the lab at Monash University . These helped in troubleshooting and scale-up calculations. Detailed characterisation of the adsorbent materials were also completed in support of the project.

5.3.4.1 Adsorbent properties

The adsorbent is the key media to perform the gas separation in this process. Isotherms provide the basic level of understanding of adsorption behavior of the adsorbates in the flue gas. We measured H_2O isotherms on SorbeadWS, F-200(BASF),NaY and NaX(UOP) and CO_2/N_2 isotherms on NaX to enable interpretation of data from the Hazelwood facility and aid in process simulation. Water isotherms are represented by a BET model and the CO_2/N_2 adsorption was represented with a dual-site Langmuir model. The capacity maximum, the isotherm shape, and adsorption dependence on temperature are all indicated by the gas adsorption isotherms under different temperatures. A study of those isotherms generated the actual process configuration, especially regeneration methods, and the operating pressure window. Fundamental adsorption experiments were performed, investigating the adsorption property of major gas components in the flue gas.

The results indicate that 13X,SorbeadWS and F-200 Alumina all have adequate water adsorption capacity though Sorbead and F-200 Alumina have greater capacity than 13X at higher humidity levels. The CO_2 and N_2 isotherms briefly indicate good capacity and selectivity.

5.3.4.2 Lab scale trial experiments

5.3.4.2.1 Water effects

NaX, as a widely used commercial adsorbent, was tested under different humidity conditions. Various temperature profiles with cyclic swing for 6-step and 9-step cycles were constructed to investigate water front movement, its effect on 13X zeolite capacity of CO_2 adsorption/desorption, breakthrough points, CO_2 recovery and purity. The 6-step cycle and 9-step cycle experiments indicated that with proper purge, product purity can be increased and the water front can be controlled with proper layering, though the purge gas needs to be optimized in terms of purge ratio and purge pressure. To help understanding of the process, detailed adsorption simulations were utilized in this study. Different cycles and conditions were simulated typical of operation in the field. The results are summarized in Table 5.3.2.

Table 5.3.2 Simulation performances

Temperature	*35°C*	*35°C*	*45°C*
Cycle	6-step without purge	9-step with purge	9-step with purge
Adsorbents	F-200, zeolite 13X	F-200, zeolite 13X	F-200, zeolite 13X
Feed pressure,kPa.a	1.4	1.4	1.4
Vacuum pressure,kPa.a	3	3	3
Inlet compositions	CO2-13% H2O-0.05%	CO2-13% H2O-0.05%	CO2-13% H2O-0.07%
CO2 in waste gas	3.85%	4.25%	3.36%
Product purity	89.63%	98.90%	98.90
Recovery	74.9%	78.5%	82.7%
Power, kW/TPD	8.43996	6.57668	7.62

The data indicated great improvement in the optimization of the process. From those results, it was found that with a layer of F-200 in the adsorber column (40% of the total packing), the water front could be stabilized within the alumina layer at 3 kPa and the process produced reasonable purity and recovery even at a high feed humidity level.

5.3.4.2.2 SO2/NO experiments

In this study, breakthrough experiments (20°C) were performed on 13X zeolite (5LPM, 90ppm SO_2, 45ppm NO) and CDX adsorbent (10LPM, 50ppm SO_2, 250ppm NO) which were the main CO_2 layer and pre-layer, respectively. The SO_2/NO concentrations were not high in this study as the target flue gas was assumed to have passed through a water washing tower to knock out SO_2. Results indicated that overall, SO_2/NO could be adsorbed and desorbed under ambient conditions and confirmed the applicability of multiple layer columns to tackle flue gas with $CO_2/H_2O/O_2/N_2/SO_2$/NO although further long term studies are needed to determine the life time of the adsorbent system.

Through continuous full cycle experiments and simulation, it was found that the water front could be well managed by using a combination layer of alumina and 13X, and reasonably good performance was observed at steady state. A single adsorbent, such as 13X and NaY, could not stabilize the water front under high humidity. The vacuum level was also found be one of the most important factors in controlling the counter current flow and equilibrium desorption of water. A vacuum level lower than 3 kPa_{abs} was preferred so as to obtain good process performance. The water front was indicated by thermal profiles in experiments and detailed axial water concentration profile was produced in our simulations. It was seen that wet product gas purge had little effect on the purge process as the humidity level for this stream was low. With proper management of the purge ratio, good product purity (>95%) and recovery (86%) can be achieved with a power consumption of ~13-16 kW/TPD CO_2.

In gas breakthrough experiments with a SO_2/NO mixture, it was found that H_2O has roll-up effects for SO_2 and O_2 for both 13X and CDX alumina. Such an effect may also have contributed to the quick breakthrough of SO_2 in the adsorbents studied. NO desorption was closely related to O_2 concentration in the gas mixture. Also it was found that SO_2 desorption was slow due to its great capacity and chemical adsorption while NO could be desorbed fairly quickly. However, more fundamental work needs to be done to better understand the mechanism of those interactions and more cycle work needs to be done to test the long term running effects of those gases on process performances and adsorbent structures.

5.3.4.3 Hazelwood rig testing results

5.3.4.3.1 Pre-running test

After the adsorption testing rig was installed at Hazelwood power station, a comprehensive system testing was conducted. The purpose of this testing was to check the functionality of system components, including solenoid valves, control valves, flow meters, heat exchangers, blower, vacuum pump etc. It was found that all system components were in good operating condition except the columns. The columns were firstly pumped down to a very low pressure (<8 kPa_{abs}) and then all the valves connected to the columns were closed. The pressure changes during this period were recorded. It was found that two of the columns could not hold vacuum very well indicating significant leaks (shown Figure 5.3.19). A few measures were taken to remedy such problem, such as checking gasket, tightening bolts/nuts, etc. Eventually, columns leakage was reduced to acceptably low levels. The persistence of minor leaks might be due to angle valve seating contamination from fine particles affecting its seal. Also, some improper pipe sizing in the cooling water line resulted in hammering during plant shutdown and startup period. After extensive and prolonged preliminary testing/ commissioning, the rig was run continuously.

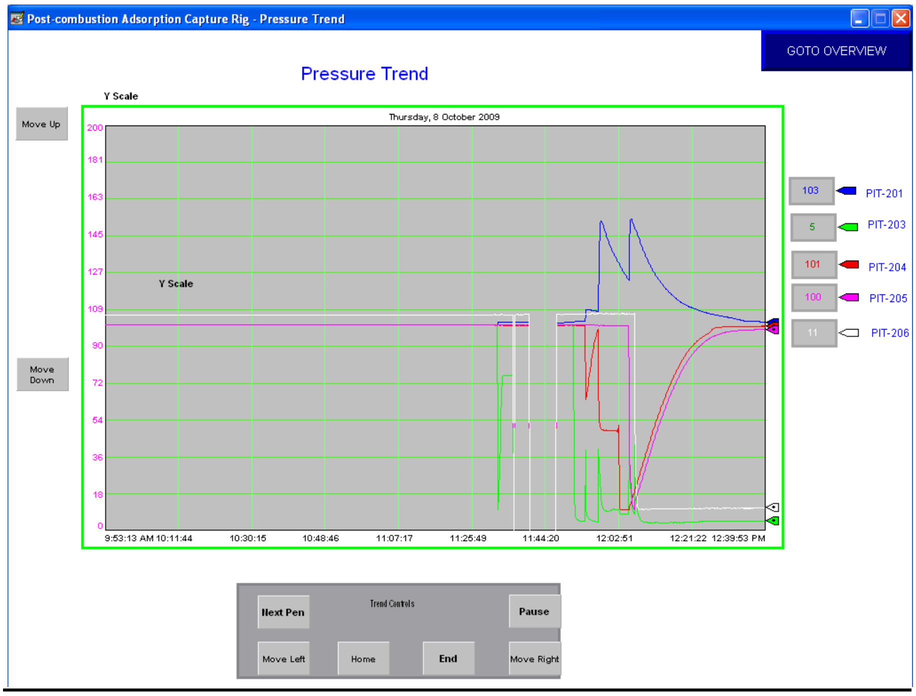

Figure 5.3.19 Pressure profile during leak tests

5.3.4.3.2 Pressure profiles of adsorption columns

One of the most important parameters of a pressure swing process is the column pressure. PSA is a batch operation arranged in a cyclic manner to realize continuous gas processing. A good pressure swing is an indication of a smoothly running gas separation process. The SCADA/HMI system was set properly to record such pressure profiles. As shown in Figure 5.3.20, the pressure swing of each column was quite symmetric. The stable flat line at 120kPa$_{abs}$ indicated a good feed gas stream and smooth adsorption process. The rapid pressure drop during a desorption step indicated good pumping and quick desorption. The pressures of two columns equalized very quickly which saved pumping energy, increased purity and increased productivity by cutting short cycle time.

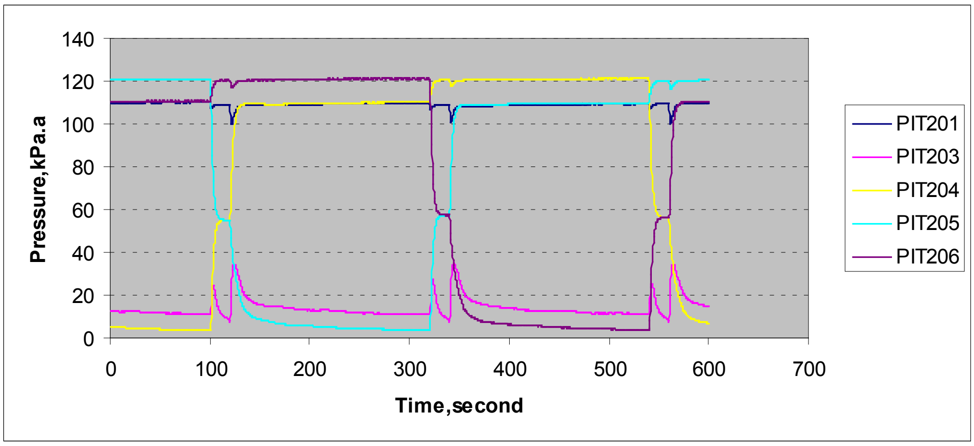

Figure 5.3.20 Pressure profiles during cyclic adsorption process

5.3.4.3.3 Temperature swing

The purpose of installing thermocouples into the adsorption columns at various axial locations was to monitor the gas adsorption front according to temperature changes/swing. As is well known, adsorption is an exothermic process and desorption is a highly endothermic process. When heat is released when gas is being adsorbed, the temperature increase with time indicates the adsorption amount and adsorption kinetics. The same principle applies to the desorption process, where the system absorbs heat to support the desorption process resulting in a temperature drop of the adsorption columns. The temperature swings at different positions tell process controllers when to stop the adsorption/desorption and also indicates how much gas is being adsorbed/desorbed. Simple thermocouple provides significant information of the process status and eliminates the need for installing expensive gas detectors/analysers along the adsorption columns. Another important function of observing the temperature swing is to help judge the accomplishment of cyclic steady state. Adsorption is a batch, cyclic process. When it reaches cyclic steady state, the same location at the same cyclic time will have the same states. An identical cyclic temperature profiles is normally an good indication of reaching cyclic steady state and the adsorption system is running well. Figure 5.3.21 is one good example of temperature swing profile. This figure includes the temperature profiles of two columns. As shown in the figure, a local temperature swing of ~10℃ was achieved which indicated good adsorption and desorption. The observed repeatable temperature swing behaviour also suggesting a steady cyclic running process.

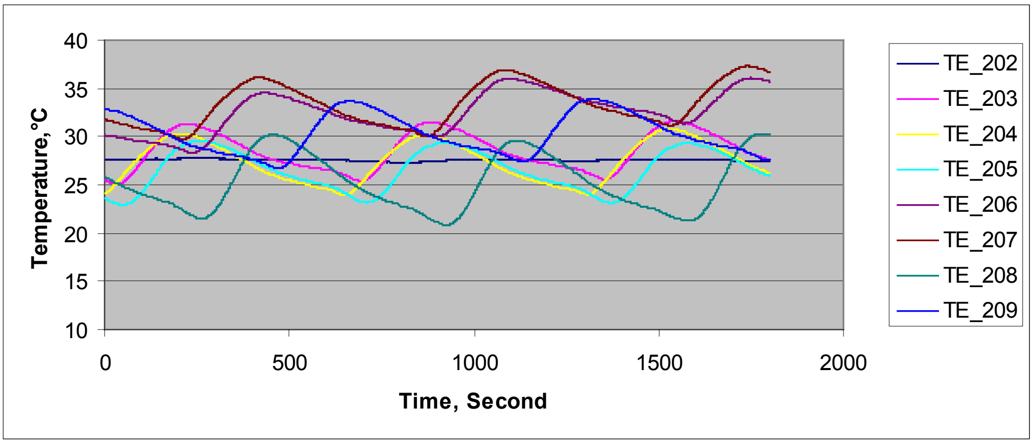

Figure 5.3.21 Temperature profile during cyclic adsorption processes

5.3.4.3.4 Purity profile

Figure 5.3.22 shows the steady gas purity profiles. With a simple cycle, a CO_2 purity of 75% was reached while it was calculated that with a complex cycle, a CO_2 purity of >95% could be achieved. It was found that purity and recovery are often needed to be properly balanced. The target purity and recovery number should take the downstream compression cost into account for the whole CCS analysis. Higher CO_2 purity means less energy consumption on the N_2/O_2 during the compressing stage but it also means more energy in the separation stage. A trade-off has to be found for a specific system as compression and transportation costs of CO_2 vary greatly from case to case. After all, it is noteworthy that the adsorption system is able to produce high purity carbon dioxide for downstream processing.

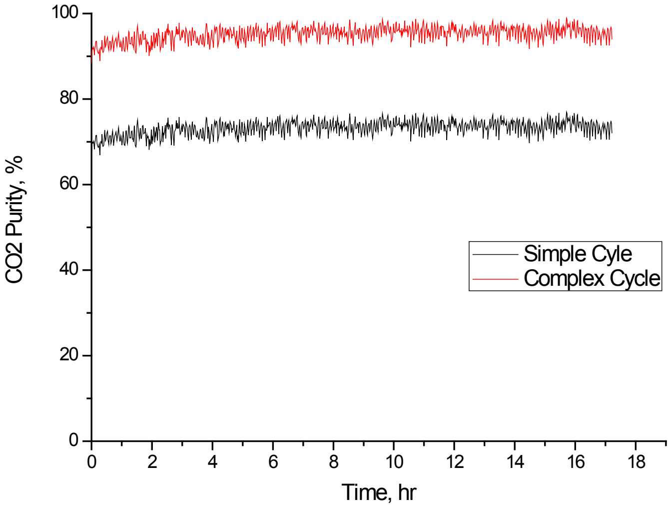

Figure 5.3.22 CO_2 product purity (Simple cycle: Hazelwood experiment; Complex cycle: simulation based on simple cycle Hazelwood experiments)

Water vapour

One of the biggest barriers for the application of adsorption to flue gas carbon dioxide capture is that flue gas comprises a high level (~12% by volume) of water vapour, which is detrimental to many CO_2-adsorbing adsorbents. To avoid the expensive pre-treatment for such a large amount of water vapour, a multiple-layering strategy was developed and tested in the field experiments. A few adsorption layering configurations were tried. After long term experiments at Hazelwood power station, adsorbent samples were taken out from different axial locations and TGA analysis were performed in the laboratory. Results indicated that with the 25% pre-layer configuration, the adsorbent retained its working capacity for carbon dioxide. Used adsorbents exhibit similar behaviour as fresh 13X adsorbents. However, a 10% pre-layer proved to be inadequate to contain the water in the pre-layer. Eventually water vapour was broken through the entire column and the adsorbents lost CO_2 working capacity as indicated by the small/flat temperature profile. Although those layering ratio numbers are quite case-specific, its consequences for the whole process are significant as it not only proves the success of multiple-layering strategy but also provides a methodology for proper engineering design of gas separation processes in the presence of high humidity feed gas. For an unknown high humidity gas separation system, numerical simulations and bench top experiments should be used to determine the engineering design parameters. Also, it is very important that when the process is not running, the whole system should be kept free from liquid water condensates, especially from any directly connected pipeline. It was found that during a prolong shutdown period, condensed liquid water would slowly get adsorbed, penetrate the whole column and eventually deactivate the adsorbents.

For future large scale engineering design, adequate sweeping and inerting procedures have to be included in the shutdown sequence to make sure the system is free from liquid water to save cost and timing in regenerating those adsorbents.

SOx and NOx

Two important impurities in flue gas are SO_X and NOx. Though these are only at ppm levels in the flue gas, their high acidity and high corrosiveness when in contact with liquid water are extremely detrimental to the adsorbents and equipment. Engineering costs increased significantly when choosing acid resistant steel materials for key equipment. SS316/304 equipment is normally 4-5 times the price of carbon steel equipment. Proper trade-off between durability and price should be considered. Analysis of used 13X revealed that sulphur components were adsorbed onto the adsorbent at the bottom layer, mostly in the form of SO_2. It also indicated little NO presence on the adsorbents. During experiments, it was observed that NO did not adsorb on to the material and directly flowed through the column without much impact. Experiments revealed that the system in use had certain reversible SO_2 working capacity and desorbed SO_2 entering the liquid ring pump with portion absorbed by the liquid in the pump and the rest passing with the CO_2 product. Due to the multiple layering protection, the main CO_2 adsorption layer was well protected. The XRD picture compared fresh zeolite 13X and used 13X. It was found that the two samples have almost identical XRD pattern which suggests no impact of impurities on the crystal structure of the zeolite. The SEM scanning image also confirmed that the zeolite crystals have remained intact. Those results and analysis suggested that the zeolite material was well protected from the acidic gas during the running period. However, much longer term running (> 1000 hours) has to be performed to confirm those effects.

On the other hand, one piece of key equipment in the system, the feed gas blower, was slightly corroded by the acidic gas. The blower was made of aluminium due to budget limitations. After running for a certain period, solid particle precipitates were found on the chamber wall and the propeller. The blower was jammed by those particles as the clearance between the propeller edge and the wall is very small. Analyses were conducted on the particles (salt crystals formed on the propeller) and the results clearly indicated the existence of sulphur and oxygen elements in those particles. It has been suggested that aluminium sulphate hydrates ($Al_2(SO4)_3 \cdot nH_2O$) might have been formed. Such phenomena can be eliminated by using a stainless steel blower or implementing a sweep for the blower with low humidity air for a significant period of time during shutdown.

5.3.4.3.5 Void space and fluidization

Void space is inevitable in any system. For continuous flow systems, void space is not important. However, for batch systems such as PSA, additional voids are detrimental to performance since work must be done to fill and empty these voids and no separation is done by adsorbent-free voids. It is important therefore to keep the ratio of the void space relative to the effective working volume as small as possible. In this project, the column and pipe design generated too much void volume and resulted in a purity drop of 5-10%, as proved by numerical simulations. The gas in the large void volume might have also disturbed the normal running of the process as some abnormal temperature swing profiles were observed during testing experiments. In future design, the system should minimize its void volume effects on the process performance.

Another technical issue encountered during the testing experiments is the unexpected fluidization of the adsorption columns. As mentioned above, the system adopted multiple-layering strategy to perform different gas separation functions. When fluidization occurred, all the adsorbents were mixed up and the multiple-layering was destroyed. Steady operation was disturbed which was reflected by the undifferentiated temperature profiles along the column. Figure 5.3.30 shows the mixed adsorbents due to fluidization. The reasons for such fluidization were found to be related to a design fault. The top suppressing mesh disc and the internal column wall had a gap of >3mm which allowed some beads to flow out. The bottom support mesh disc also had the same problem. When adsorbent beads left the column, the column became loose and were subjected to fluidization at certain stages of the cycle (high velocity) and eventually the performance was compromised. Future fabrication of adsorption columns must take adequate measures to keep the adsorbents tightly compressed and keep adsorbent beads from escaping the column.

Figure 5.3.30 Mixed adsorbents due to fluidization

5.3.5 Performance and Evaluation against Simulation

On the basis of experiments and numerical simulation for the adsorption process (described earlier), a process flow diagram (PDF) was developed for the whole capture process. The process model was constructed in ASPEN HYSYS. In this PDF, the flue gas was firstly cooled off by direct contact cooling tower and then compressed slightly by a feed gas blower. The discharged gas may be subject to a controllable heat exchanger to manage the temperature of the gas entering the vacuum swing adsorption unit depending the actual adsorbent and process. At the CO2VSA unit, the CO_2 lean gas is emitted back to atmosphere and the CO_2 rich gas was pumped out of the system before entering the multi-stage compressing stations. The calculation from HYSYS indicated that for a 500 MW power station, a water consumption of >5000 t/hr is needed to cool the flue gas down to <60°C. An increase of the discharge flue gas temperature would greatly reduce the amount of cooling water.

Several scenarios were simulated in HYSYS.

Table 5.3.2 HYSYS simulation results

Case: 130kPaabs feed gas pressure, capturing 12,000 ton CO_2/day			
Vacuum Pressure, kPa	1	10	30
Feed blower, MW	23.96	23.96	23.96
Vacuum Blower, MW	141.90	55.82	26.67
Total power, MW	165.86	79.78	50.03
Specific power, MJ/kg CO_2	1.19	0.61	0.38

The model in HYSYS is not a dynamic model and a fixed vacuum pressure is used in calculating the vacuum pump power. It has to be noted that, in an adsorption process, an ultimate vacuum pressure of 1 kPa_{abs} does not mean the pressure at suction side of the vacuum pump is always at 1 kPa_{abs}. Actually, from Figure 5.3.32, it can be seen that most of the gas molecules are removed at much higher pressure than the ultimate vacuum pressure. The point here is that using HYSYS to calculate vacuum pump energy consumption is very conservative and may overestimate the energy consumption. The adsorption system consumes electric energy of 0.38 – 1.19 MJ/kg CO_2, which could indicate a great energy advantage.

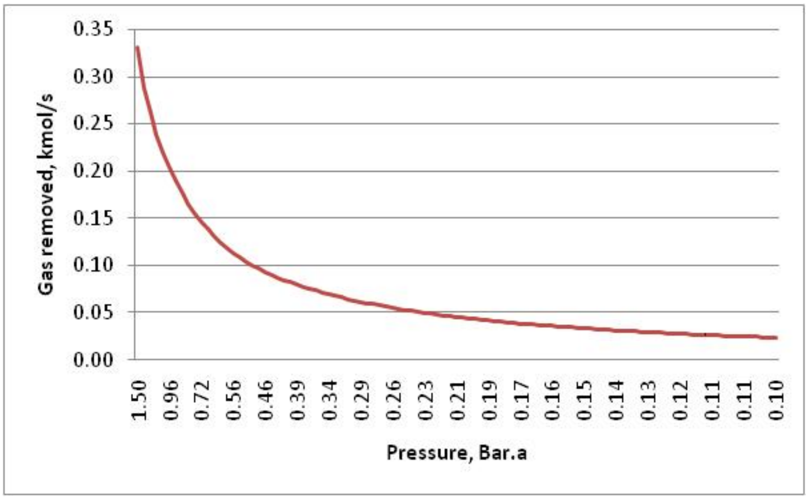

Figure 5.3.32 Typical pump down curve

According to the experimental data and HYSYS calculations, a preliminary engineering scale-up was performed. It is estimated that to capture the carbon dioxide emitted from a 500 MW power station, ~4,416 ton adsorbent materials are needed. A total of 12 adsorption columns (each with a external diameter of 6 m) are needed. Considering the large scale of process and industry state-of-the-art practice, it is recommended that radial structured column be used in such application due to its high throughput capacity. Although a detailed costing for large scale engineering design has been discussed in Chapter 6, a simple cost estimation is shown below (only for understanding of a large scale system and not to be quoted as real plant cost).

• Inlet gas blower, 130 kPa_{abs} , 3.5 million Am^3/hr,	US$30 million
• Vacuum pump/blower, 10 kPa_{abs}, 5.67 million Am^3/hr	US$50 million
• Adsorber column, 56 m X 6 m *12	US$50 million
• Adsorbent, 5000 ton	US$30 million

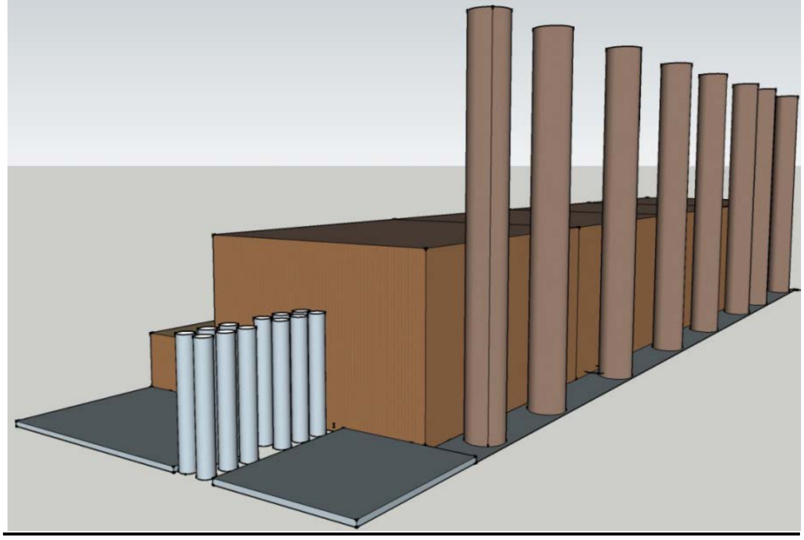

Figure 5.3.33 Preliminary blueprint for a 500MW capture plant, Victoria

A simple sum of those key equipment/materials amounts to US$160million. Valves, instrumentation, utilities etc will significantly increase the project costs. The main purpose of this exercise is to present a simple picture of the costing for a large scale carbon capture using adsorption technology. A preliminary blueprint design is shown in Figure 5.3.33. It is seen that the adsorption capture plant footprint is relatively small compared with the power station.

Key equipment availability

Procuring off-the-shelf equipment will be difficult due to the very large scale of gas flow. Large solenoid controlled ON/OFF valves (ID>25 inches) are not very economical, therefore special butterfly valves may be used instead to provide million m^3/hr flow while minimizing pressure drop across the valves. This is a situation frequently used in large scale hydrogen (H2PSA) removal plant. Blowers and vacuum pumps with a capacity of million m^3/hr magnitude are already in use in steel industry, synchrotrons etc. Large scale radial adsorption columns are used in many large scale air separation plant (>4,000 TPD oxygen). The design and fabrication costs of such column are extremely high but the simplicity of the system would definitely decrease the overall project costs. The affirmation of the availability/potential availability of these key equipment items is of paramount significance for the deployment of large scale carbon capture and storage.

5.3.6 Other Outcomes (communications, collaboration, skills development etc)

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Conference Proceedings

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5.3.7 Conclusion

Through systematic pilot plant experiments, lab experiment and numerical simulations, we have gained significant knowledge/know-how in carbon capture from flue gas using adsorption technology. The project has proven the feasibility of adsorption technology application in carbon dioxide capture from flue gas in a brown coal-fired plant.

The strategy of eliminating an expensive pre-treatment facility for flue gas by using multiple layer adsorption columns has been proved to be successful. During the continuous testing experiments, we were able to control the water vapour penetration front and achieve significant working capacity of water. The water vapour contained in the flue gas was eventually recovered in the vacuum pump system and such water was in fairly clean condition, only containing a small amount of carbonic acid and sulphuric acid. Such recovered water may, with minimal treatment, be able to be used as cooling water. The adsorption system in discussion also demonstrated the SOx/NOx impurities tolerance. Most NOx, in the form of NO, passed through the adsorption column without impacting the process. SOx, on the other hand, was adsorbed and desorbed reversibly, eventually being removed from the system together with product carbon dioxide. The multiple-layer strategy proved to be technical feasibile and potentially offers great cost savings (CAPEX/OPEX).

Experiments under different temperatures indicated that higher temperature processing achieved better performance in terms of purity, recovery and energy consumption. More importantly, under high temperature, water adsorption was reduced and its isotherm showed a tendency to “flatten out” which made the water removal more efficient. Adsorption cycles have been designed and tested by experiments/numerical simulations. Using a simple cycle, a purity of 75% was achieved and a purity of >95% was achieved with a complex cycle. With the innovative cycle, a recovery of >86% and a purity of >95% is achievable. For the adsorption system, energy is mostly consumed by the feed gas blower, recycle blower and vacuum pump. The electric energy penalty is around 1.19 MJ/kg CO_2 captured.

Throughout the duration of the project, various technical issues were incurred, identified and solved. The complexity and the corrosiveness of flue gas brought great challenges to the adsorption process and equipment. Material selection (such as 304SS or 316SS) is important for specific locations in the plant. These have to be identified. Scheduled or unexpected shutdowns must have the proper shutdown sequence to ensure the system is not in any way adversely affected by the residual gas in the system. Proper measures must be taken to ensure the durability of key rotary equipment.

Experimental trials and numerical evaluations have adequately equipped us with preliminary engineering design data for large scale designs which are details in section 7. An electric energy penalty of less than 1.0 MJ/kg CO_2 captured is expected through utilizing better adsorbent materials and process configurations.

It is encouraging to see that carbon capture using adsorption process appears feasible in terms of technology capability, processes and equipment, though high cost may be a factor. However, there is still scope for improvement in many areas, such as solid adsorbent material, process integration and optimization and in utilities such as cooling water. Larger scale continuous pilot plant is recommended before any full scale engineering implementation.

6. Heat and Process Integration Studies

6.1 Introduction

The heat and process integration studies aims to develop each capture technology into flowsheets for their large scale use in the power stations. The process includes both ‘targeting’ and ‘design’ stages, taking the research conducted on each capture technology and developing the flowsheets and operating conditions to maximise the net power generation from power stations with CCS. The addition of CCS to a power station has the potential to reduce the efficiency of a power station by 30 – 40% (IPCC (2005)). The aims of the process and heat integration studies is to reduce the energy penalty by ensuring that waste heat in the process is minimised and to optimise the capture process and power station operating variables to achieve reductions in the energy penalty and cost of electricity.

The heat and process integration studies for each of the capture technologies trialled in the H3 project, scaled up to a full scale capture from a 500MW brown coal-fired power station is provided in section 6.2 of this report, which are then used to generate cost estimates for the technologies in Section 7. A number of additional process and heat integration studies have been completed during the ETIS project which are summarised below;

Steam Cycle: The impact of adding solvent based CCS to three different power stations; a subcritical low (A) and high (B) efficiency brown coal power station and a subcritical black coal fired power station (C) without heat integration (CO2CRC symposium, 2009) has been examined in detail. Results show that energy penalties range from 39% for the inefficient brown coal fired power station to 24% for the black coal fired power station.

Heat Integration: The impact of various levels of heat integration; None, full and “moderate” (refer to the results in Figure 6.1) have been examined. Full integration results provide the target for the minimum energy penalty when the CCS is added, which may require significant capital infrastructure. Economic design will generally lie between the case with no and full integration. Moderate integration is, for the purposes of our studies, where changes are only made to the low pressure heaters and deaerator of the steam cycle and in the flue gas, downstream of the existing economisers.

Coal Pre- drying: It has been shown that small improvements can be obtained when coal pre-drying is added in conjunction with CCS in brown coal-fired power stations (Refer to Figure 6.1).

Combustion Air-preheat: Our studies suggest the importance of the level of combustion air-preheat in the power station may be reduced with the addition of CCS. (Fourth International Conference on Clean Coal Technologies, 2009). For the brown coal-fired power stations, there appears to be little benefit to increasing the air-preheat temperature above the temperature of the solvent reboiler. This may be important in the design of new-coal fired power stations as it could help to reduce costs for air-preheat.

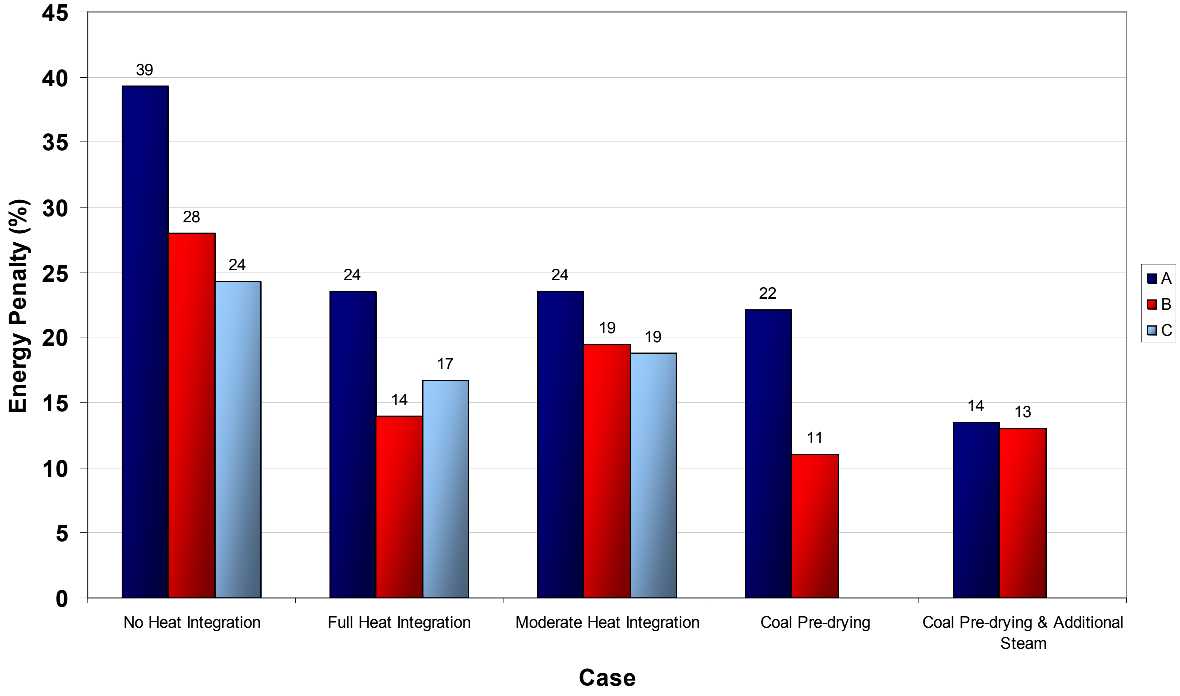

Figure 6.1 – Energy penalty due to the addition of a solvent based (3 GJ/tCO$_2$ at 120°C / 1.8bara regeneration) for a subcritical low (A) and high (B) efficiency brown coal power station and a subcritical black coal fired power station (C) with various levels of heat integration.

Heat exchanger minimum approach temperature (ΔT_{min}): The impact of targeting parameters has been examined. Targets provided in Figure 6.1 are generated using a ΔT_{min} of 3°C, which may be applicable for streams in the steam cycle but will generally be low for gas-gas heat exchangers. Studies on the energy targets for various ΔT_{min} have been performed (Journal of Cleaner Production, Harkin et al. (2010)). With ΔT_{min} of 20°C the energy penalty of the process is still better than the process without any heat integration by 12%. Having different ΔT_{min} for different processes is likely to leads to the best energy versus capital trade-off and has been used in the ETIS economics.

Multi-objective optimisation to maximise power production: Multi-objective optimisation(MOO) has been developed allowing the selection of operating variables in both the capture process and the power station itself to ibe modified for mproved outcomes Studies have been completed using MOO for a power station using potassium carbonate solvent CO_2 separation (23rd International Conference on Efficiency, Cost, Optimisation, Simulation and Environmental impact of energy systems, (2010)). The study showed the importance of heat integration to maximise the net power from the power station but also showed that the optimal solutions to maximise the net power generation may be different to the solutions to minimise the reboiler duty.

Multi-objective optimisation with economics: The MOO tools can also be used in conjunction with capital cost estimating tools to study the impact of trade-offs between capital costs and operating costs. (CO2CRC symposium, 2010). The results reproduced here in Figure 6.2 show that the solutions obtained when minimising the ΔCOE are all lower than for the solutions when trying to maximise the net power generation.

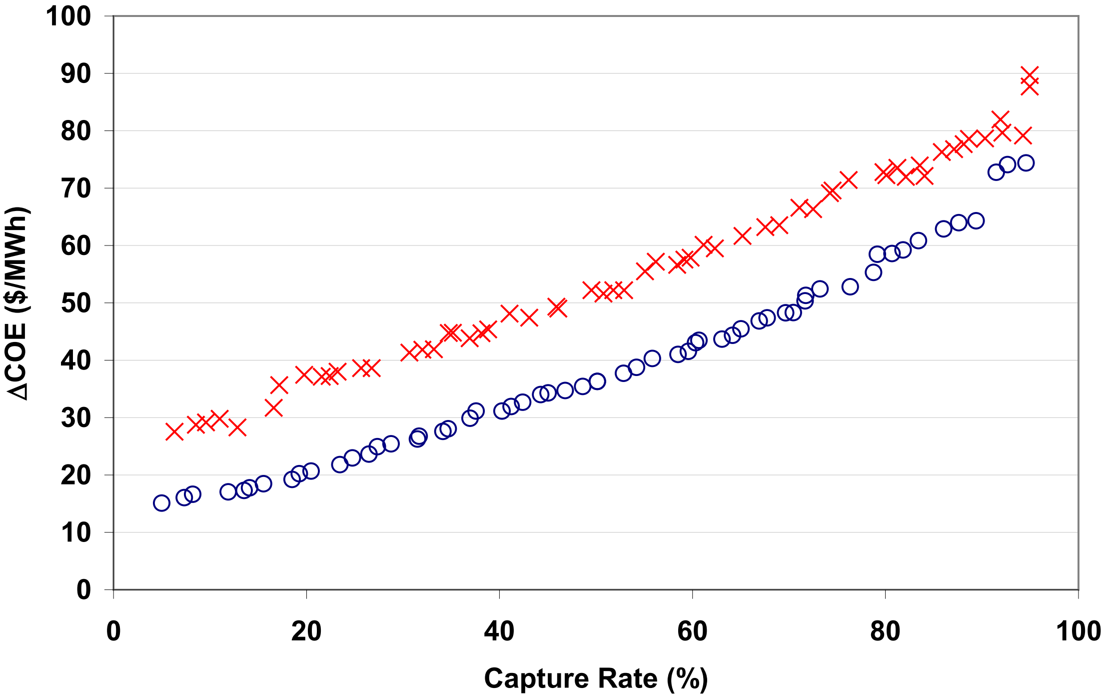

Figure 6.2 – ΔCOE for various CO_2 capture rates for the potassium carbonate process optimised to maximise the net power (×) and to minimise the ΔCOE(○).

6.2 H3 Capture project heat and process integration

The heat and process integration studies for the CO2CRC H3 Capture Project involved the prediction of the CO_2 capture processes on a full scale (500MW) pulverised brown coal power station. The most promising options that came from the research conducted in the H3 capture project for the three technologies; solvent, membrane and adsorption have been developed to a full scale capture plant. The heat and process integration studies using pinch analysis helps to identify the maximum amount of power that can be generated from the system, however the optimal design will not always be at the maximum generation as there are trade-offs between the capital cost to build the heat exchanger network to maximise the power generation. Also the design that maximises the power generation may reduce the operability of the process.

The heat and process integration studies are also used as the basis for the economics studies conducted on the following six capture technologies;

- Solvents: MEA, Generic 3 GJ/tCO_2 Solvent, and UNO Mk. 3
- Membranes: PRISM and Polaris^{TM}
- Adsorption: VSA using 13X

For each CO_2 capture technology the basis provided in Table 6.1 was used for the process. An Aspen Plus® model of the power plant without CO_2 capture has been developed using design and operational data obtained from the Loy Yang B power station. It includes the coal pulverising and drying, the boiler, the steam generation and the steam turbine.

Table 6.1 – Basis for the CO_2 capture technologies

Basis	Nominal Figure	Composition	mole % (wet basis)
Nominal power generation	500 MW	N_2	62.0
CO_2 Recovery Rate	90 wt%	O_2	3.9
Nominal (Actual) CO_2 rate	12,000 (12,192) tpd	CO_2	11.0
CO_2 pressure	100 Bara	H_2O	22.5
CO_2 purity	95 mol% (min.)	Ar	0.6
Flue gas flow rate	3,238,000 kg/h 2,758,000 Sm^3/h 4,364,000 Am^3/hr	NO_x	151 ppmv (dry basis)
Pressure	2.0 kPag	CO	13.9 ppmv (dry basis)
Temperature	192 ºC	SO_2	211 ppmv (dry basis)
		SO_3	0.5 ppmv (dry basis)

In this report, the maximum power generation targets, ie. those with full heat integration, are derived for a number of the capture technologies. Nonetheless potential designs are also considered for those capture technologies that take into account the trade-off between the additional capital costs and the improvements in power generation and also the limitations due to having to retrofit the new equipment, these designs are referred to as using "moderate" heat integration. For the Generic 3 GJ/t solvent, the UNO Mk. 3 solvent, the Polaris^{TM} membrane and the VSA system, the following three cases will be provided;

- Case 1 - CCS added to power station without any heat integration
- Case 2 - CCS added with maximum heat integration
- Case 3 - CCS added with moderate heat integration

The economics provided in section 7 is based on the moderately heat integrated case for all the capture technologies except MEA solvent systems and PRISM membranes, where the economics were considered without heat integration.

To determine heat integration options for the power station with CCS or to show the potential for improvements in heat recovery of the base plant, minimum temperature driving forces for each stream need to be specified. These can later be adjusted to modify operating and capital cost trade-offs. Minimum temperature differences (ΔT_{min}) used through this report are provided in Table 6.2. The ΔT_{min}'s shown in Table 6.2 are for when two of the same streams provide heat exchange, therefore each side of the heat exchange requires a ΔT_{min} half of that shown in Table 6.2. For example when the flue gas is used to generate steam the overall ΔT_{min} will be 30°C. The results for the heat and process integration studies for the H3 capture project are provided in Table 6.3.

Table 6.2 – ΔT_{min} used for the heat integration analysis

Stream	ΔT_{min} (°C)
Gas streams (flue gas, air-preheat etc)	50
Steam cycle	10
Condensing / Reboiling	10
Liquid streams	10

6.2.1 MEA

The MEA case is used as the base CO_2 capture technology and is being evaluated with no heat integration. The MEA details and economics are provided in section 7.

6.2.2 Generic 3 GJ/t Solvent

The H3 solvent pilot plant operating with potassium carbonate was only able to capture between 20% and 25% of the inlet CO_2. The rate of CO_2 capture was limited by the slow reaction kinetics of the conversion of carbon dioxide and hydroxide to bicarbonate. If a conventional promoter, which is both thermally sensitive and produces heat stable salts, is used, the benefits of the potassium carbonate system are less compelling. While the search for such promoters for potassium carbonate is underway it was decided to represent this form of solvent as a generic 3GJ/t that still requires full gas treatment. This provides a broader range of technologies for review and discussion.

Where the generic solvent system is added to the power station and heat is required for solvent regeneration the steam is extracted from the steam turbine at the appropriate extraction point and the condensate is returned to the steam cycle at the point in the BFW (Boiler Feed Water) heating circuit closest to the condensate temperature. As the extraction steam will return downstream of some of the LP heaters, the BFW flow rate in the LP heaters will be reduced and therefore the amount of steam required for the LP heating will also be reduced. These reductions have been taken into account in this case.

Table 6.3 – Results for the heat and power integration studies for the H3 capture project

		Base Case	Generic Solvent Case 1	Generic Solvent Case 2	Generic Solvent Case 3	UNO Mk 3 Case 1	UNO Mk 3 Case 2	UNO Mk 3 Case 3	Membrane Case 1	Membrane Case 2	Membrane Case 3
Main Steam Production	kg/s	433	433	472	433	433.2	470.8	433.2	433.2	473.6	433.2
Steam Extraction Rates											
HP (351°C)	kg/s	45.808	45.81	45.33	45.81	45.808	38.11	45.808	45.81	44.84	45.81
IP1 (429°C)	kg/s	20.08	20.08	29.53	20.08	20.08	24.6	20.08	20.08	30.4	20.08
IP2 (318°C)	kg/s	15.44	15.44	8.62	15.44	15.44	13.4	14.14	15.44	14.3	15.4
LP1 (247°C)	kg/s	13.9	12.9	4.62	0	161.5	174.7	144	13.9	9.04	0
LP2 (179°C)	kg/s	25.8	214.5	220.0	183	14	1.62	0	25.8	7.1	0
LP3 (79°C)	kg/s	15.09	5.8	0	0	8.3	-12.54	0	15.09	-1	0
Gross Electricity Produced	MW	520	440	497	463	444	505.6	462	520	584	542
Base Plant Auxiliary Power	MW	20	20	21	20	20	20	20	20	20	20
New Auxiliary Power	MW	-	10.6	10.2	10.2	3.9	3.9	3.9	124	124	124
CO_2 Compression Power	MW	-	60	60	60	48	48	48	58	58	58
Net Electrical Power	MW	500	349	406	373	372	434	390	318	382	340
Net Cycle HHV Efficiency	%	28.6	20.0	23.3	21.3	21.3	24.8	22.3	18.2	21.9	19.5
Reduction in HHV Efficiency	% pts	-	8.6	5.4	7.3	7.3	3.8	6.3	10.4	6.7	9.2
Energy Penalty	%	-	30.1	18.7	25.4	25.7	13.2	22.3	36.4	23.6	32.0
CO_2 Emissions	t/MWh	1.12	0.16	0.14	0.15	0.15	0.13	0.14	0.18	0.15	0.17
Total Cooling Water Duty	MW	653	1226	1223	1271	1269	1191	1248	1212	1149	1189
Cooling water usage	ML/yr	10.6	19.8	19.8	20.55	20.5	19.3	20.2	19.6	18.6	19.2
Cooling water usage	t/MWh	2.41	6.38	5.49	6.21	6.3	5.1	5.9	6.9	5.5	6.3

Table 6.3 (cont'd) – Results for the heat and power integration studies for the H3 capture project

		Base Case	Adsorption Recovery 90% Purity 93% Case 1	Adsorption Recovery 90% Purity 93% Case 2	Adsorption Recovery 90% Purity 93% Case 3	Adsorption Recovery 86% Purity 95% Case 1	Adsorption Recovery 86% Purity 95% Case 2	Adsorption Recovery 86% Purity 95% Case 3
Main Steam Production	kg/s	433	433.2	472.8	433.2	433.2	472.8	433.2
Steam Extraction Rates								
HP (351°C)	kg/s	45.808	45.81	44.83	45.81	45.81	44.8	45.81
IP1 (429°C)	kg/s	20.08	20.08	30.68	20.08	20.08	30.74	20.08
IP2 (318°C)	kg/s	15.44	15.44	13.84	15.4	15.44	14.06	15.4
LP1 (247°C)	kg/s	13.9	13.9	8.94	0	13.9	9.3	0
LP2 (179°C)	kg/s	25.8	25.8	15.9	0	25.8	16.52	0
LP3 (79°C)	kg/s	15.09	15.09	5.84	0	15.09	6.63	0
Gross Electricity Produced	MW	520	520	574	542	520	577	542
Base Plant Auxiliary Power	MW	20	20	20	20	20	20	20
New Auxiliary Power	MW	-	79	79	79	80	80	80
CO_2 Compression Power	MW	-	62	62	62	58	58	58
Net Electrical Power	MW	500	359	417	381	362	419	384
Net Cycle HHV Efficiency	%	28.6	20.5	23.9	21.8	20.7	24.0	22.0
Reduction in HHV Efficiency	% pts	-	8.1	4.7	6.8	7.9	4.6	6.6
Energy Penalty	%	-	28.2	16.6	23.8	27.6	16.2	23.2
CO_2 Emissions	t/MWh	1.12	0.16	0.13	0.15	0.22	0.19	0.20
Total Cooling Water Duty	MW	653	1259	1184	1236	1255	1181	1232
Cooling water usage	ML/yr	10.6	20.4	19.2	20.0	20.3	19.1	19.9
Cooling water usage	t/MWh	2.41	6.5	5.2	6.0	6.4	5.2	5.9

The Generic solvent process without heat integration reduces the net power station output to 349MW, a reduction of 151MW (30.1%). Of those losses, 53 % is due to the change in heat load caused by the regenerator reboiler and 40 % by the CO_2 compressor with the residual caused by new auxiliary power demands.

The full heat integration case of the generic 3 GJ/t solvent shows the maximum net power generation possible with the given steam cycle and the CO_2 capture process. It provides a target, where the ultimate design is likely to be between the case without heat integration and this case. The results show that with thorough heat integration the net power increases to 406 MW, an increase of 56 MW above the case with no heat integration, reducing the energy penalty to 19%. To achieve the maximum net power the main steam flow needs to be increased by approximately 10%. It is likely that additional area would be required for the additional steam generation, for the air preheat and cross heating between the BFW circuit and the solvent absorption and CO_2 compression equipment. Meeting these targets would be easier with a pulverised coal power plant especially designed for CCS but will be more difficult for retrofitting of existing power stations. Retrofitted power stations will have energy penalties between those suggested by the case without heat integration and that with full integration.

For the retrofit case in this report it is assumed that no changes will be made to the existing boiler or steam circuit downstream of the deaerator. However, that leaves the heat available in the flue gas, the lean solvent cooler, regenerator condenser and the compressor intercoolers to be used for the rich solvent heating, the regenerator reboiler and for the boiler feedwater heating. There are a number of ways in which the hot and cold streams can be matched to maximise the heat integration. One arrangement is for the flue gas to provide a proportion (15%) of the energy for regeneration, and the boiler feed water is heated up using the heat in the regenerator condenser, the compressor intercoolers and the superheat in the LP steam. The LP steam after being desuperheated is used for the remaining regeneration reboiler duty. The benefit of recovering the heat in the flue gas, the regenerator condenser, and the CO_2 compressors is a reduction in the amount of steam required for the solvent regeneration and the BFW heating which means the net power is increased by 23 MW from the case with no heat integration. There is very little reduction in the total amount of cooling water used as the steam that is not used for process heating carries on through the steam turbine and condenses in the steam turbine condenser. Therefore, any reductions in cooling requirements obtained through process heating result in an increase in cooling duty in the turbine condenser. However, although the total cooling duty does not change significantly, the cooling water requirements on a net power perspective are reduced.

6.2.3 UNO Mk.3

UNO Mk. 3 uses a high concentration potassium carbonate solution allowing precipitation of bicarbonate in the process equipment. The higher concentration solution and the precipitation of bicarbonate ensure that the CO_2 removal rate is increased. Precipitation of bicarbonate will occur in the absorber, the rich solution will have a fraction of solids in the bottoms stream which are dissolved in the rich solvent heater prior to the stripper, so that the stripper will operate as a conventional stripper.

The UNO Mk. 3 process without heat integration reduces the net power station output to 372 MW, a reduction of 128 MW (25.7%); 59 % of those losses are caused by the change in heat load from the solvent regeneration, 38 % from the CO_2 compressor and the residual from new auxiliary loads. The addition of UNO Mk.3 also has a large impact on the cooling water usage of the power station with the cooling water duty increasing by 94% in total and 161% per megawatt-hour of net power produced.

The full integration of the UNO Mk.3 process enables the heat in the regenerator condenser, the flue gas cooler and the compressor intercoolers to provide heat to the streams that require it, including the regenerator reboiler, the air-preheat, and the BFW circuit. The fully integrated case reduces the energy penalty from 25.7% to 13.2%, increasing the net power from 372 MW up to 434 MW with a 6.5% reduction in the required cooling duty. To achieve the targets given in the fully heat integrated design, the steam flow rate through the HP and IP sections of the steam turbine will be increased by 10% whilst the steam flow rate in the LP section of the turbine will be 60% of the design flow. In addition, the temperature driving force in the convection section of the boiler and the air-heater will be reduced, the air-preheat may also require heating from other sources including the compressor intercoolers or extraction steam. Therefore, to meet these targets will require major modifications to the power station.

These targets will provide outputs that are likely to be achieved in a new-build plant rather than a retrofit. Whereas the case with moderate heat integration is likely to give realistic designs for a retrofit. The parameters for the UNO Mk. 3 moderate heat integration case is the same as for the generic 3GJ/t solvent process design. There is assumed to be no changes to the BFW circuit downstream of the deaerator, and no changes to the air-preheat or flue gas upstream and including the air-preheat.

A design for the moderately integrated case involves performing a proportion (~12 %) of the solvent reboiling with flue gas and heating the BFW upstream of the deaerator with heat from the regenerator condenser, the flue gas and to de-superheating the LP steam extracted for the remaining solvent regeneration duty. This design reduces the energy penalty from 25.7% to 22.3% and produces an additional 18 MW of electricity.

6.2.4 PRISM Membrane

The PRISM membrane used in the H3 trials is not thought to be the most optimum membrane for post-combustion separation and more promising membranes will be trialled in the future (refer to section 5.1.2.6). However large scale designs using the PRISM membrane have been postulated in section 5.1.2.6. One strategy was to use a single membrane with no recycle to recover the required 90% of CO_2. This strategy enabled the CO_2 to be concentrated from 13 mol% in the feed to 34 mol% in the permeate stream, using a vacuum pressure of 22 kPa_{abs}. However with a single stage it is not possible to get to the required purity of 95% CO_2 even with a recycle stream on the permeate. A second strategy was developed in section 5.1.2.6 that uses three PRISM membranes in series, this arrangement allowed the product purity to be increased to 95%, but due to the low stage cuts the recovery is less than 1% of the feed CO_2. The second strategy has been used in the economic evaluation of the PRISM membrane, but given the low recovery rate, no heat integration has been postulated. However, a number of three stage designs with recycle have been developed and there are a number of variables that can be optimised in this process including the permeate pressure, the stage cut of each stage, the recycle of permeate or retentate from each stage and the return location of each recycle stream. Using a minimum pressure in permeate stream of 22 kPa_{abs} it was not possible to obtain both the purity and recovery specifications in a three stage design. However three designs are provided in Table 6.4 to provide indicative performance of the membrane in three stage designs including recycle. The power presented in Table 6.4 is the total internal compression requirements to get the product gas back to atmospheric pressure and so it does not include CO_2 compression to transport pressures (100 bar). The PRISM membranes cannot meet the required product purity and recovery specifications and when it approaches the required specifications the power requirements are much greater than the other technologies. Therefore, it is clear that the PRISM membrane will not be competitive with the other capture technologies reviewed in this report for post–combustion capture. However, it cannot be discounted that the use of membranes with higher perm-selectivity’s than the PRISM membrane may provide designs that are competitive on a stand-alone basis or possibly as a hybrid technology.

Table 6.4 – Selected results for a three stage design using PRISM membranes

Case	Stage 1 RC	Stage 2 RC	Stage 3 RC	Purity (%)	Recovery (%)	Power (MW)
1	None	Ret. to stage 1	Ret. to stage 2	90	70	220
2	None	Per. to stage 2	Per. to stage 3	79	92	220
3	None	Per. to stage 2	Per. to stage 3	53	90	137

6.2.5 POLARIS Membrane

As discussed in section 5.1.2.6 the POLARIS membrane shows promise in the separation of CO_2 from post-combustion flue gases. Therefore this membrane has been used as the basis for the process and integration studies and the economic evaluation. There are many designs suggested in the paper (Merkel et al. (2010)) that details the POLARIS membrane. A simple two stage membrane is able to meet the required purity and recovery specifications and is used in this report as shown in Figure 6.3.

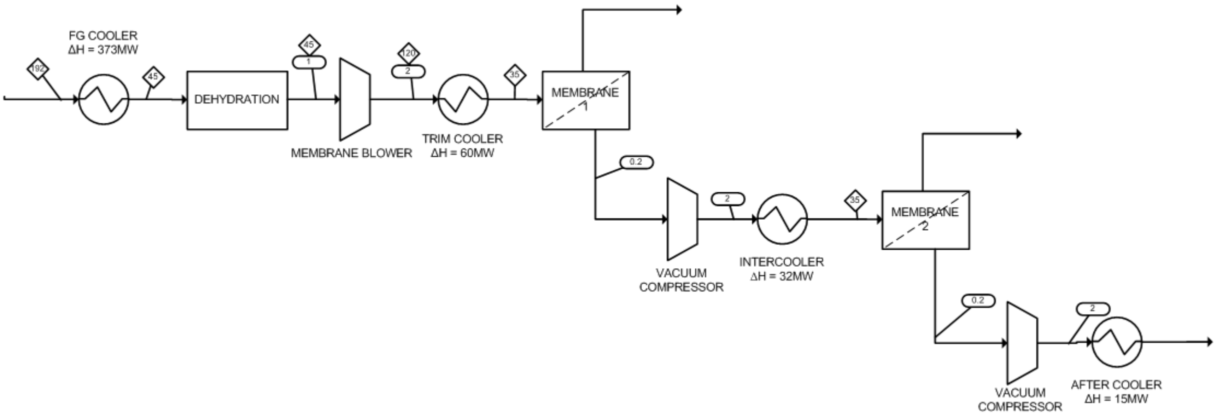

Figure 6.3 – POLARIS two stage membrane CO_2 capture design

The POLARIS membrane design has a total of 124 MW of electrical power requirements, comprising 57 MW of feed Gas Compression, 33 MW of 1st stage recompression, 15 MW of second stage recompression and 19MW for dehydration. The membrane designs require little in the way of process heating and therefore there is no extraction steam demand for the membrane system for process heating, however due to flue gas needing to be cooled to 35°C and the compression systems there is significant amount of low grade heat that can be used in the BFW circuit.

Unlike the solvent systems the membrane system losses are entirely electrical and therefore the changes to the system do not require any modifications to the steam turbine. As there is a significant increase in the waste heat available due to the flue gas cooling and the compressor intercooling with full heat integration the plant is capable of generating significant quantities of additional steam that could be used to produce additional power that will recoup some of the losses that are incurred from the addition of the membrane capture plant. However, as discussed in previous sections, this will require large investment in heat exchange area, the LP turbine may also require modifications as the steam rate is increased significantly and the steam turbine condenser may also require additional area to maintain the desired vacuum pressure. Also, as the gross power produced from the turbine is greater than the current maximum power production, changes are very likely to be required for the electricity generation side of the steam turbine. Increasing the electrical capacity of the power station is likely to incur high costs, alternatively many of the drives for the compressors could be steam driven rather than electrical driven, which will be discussed in section 6.2.7.

The moderately integrated case is a 22 MW improvement over the unintegrated case and is 42 MW from the fully integrated case. In this case, as per the solvent cases the main steam rate is kept constant at 433 kg/s and the steam cycle is not altered downstream of the deaerator. With the additional low temperature heat available in the flue gas cooling and various compression steps, the low pressure BFW heaters can be replaced with heat from the flue gas and/or the compressor intercoolers.

6.2.6 Adsorption

An adsorption system has been designed in section 5.1.3.5 that uses a standard 13X adsorbent. Using this adsorbent and the design conditions provided both the purity and recovery specifications could not be met. With 90% recovery of CO_2 the purity is 93% compared to a target of 95%. For a purity of 95%, the recovery is 86% compared to a target of 90%. The results are close to the required targets and with small improvements in capacity/selectivity and or process design the targets should be able to be met.

Refer to Figure 6.4.

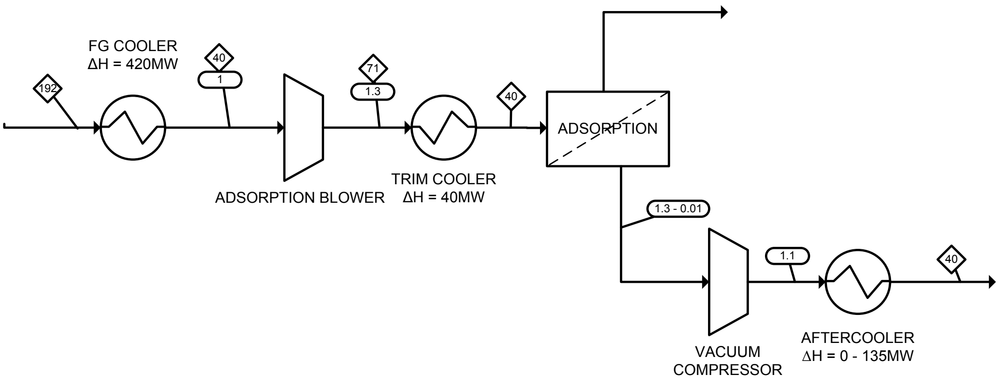

Figure 6.4 – Adsorption process for CO_2 capture design

The adsorption system has a total of 79 MW for the 90% recovery case and 80 MW for the 86% recovery case, comprising 24 MW for the feed gas blower and approximately 56 MW for the vacuum compression. As there are two designs, one that meets the recovery specification and one that meets the purity specification and each design has a case with no, full and moderate heat integration, there will be six adsorption cases (Table 6.3).

The results between the high recovery and the high purity are similar in the net power produced from the power station. The net power is 2-3 MW higher for the high purity case but the CO_2 emissions are higher due to less CO_2 being recovered. The benefit of heat integration is similar to the membrane case with close to 60 MW of additional power generated in the fully integrated case compared to the case with no heat integration. The moderately integrated case is also about 23 MW improvement on the cases without integration which is comparable to the membrane technology. The design of the moderately integrated case is comparable to the design for the membrane case with the low pressure

BFW heating replaced with heating from the CO_2 compressors and the flue gas; as described in the membrane section the additional electricity production may hit the limit of the installed capacity and the use of steam drives may be used an alternative as described in the following section.

6.2.7 The use of steam drives

In the case of membrane and adsorption CO_2 capture systems the energy required for the separation is in the form of work rather than heat. The work is required in the blowers, compressors and vacuum compressors required to create the driving force for separation. In this report it has been assumed that the work is provided by electrical drives. However when the heat from the process is recovered into the steam cycle the integration leads to gross electrical production greater than the current generator capacity. To avoid making changes to the generator side of the power station it is possible to use steam drives for the work in the compressors. However, the efficiency of steam drives are unlikely to be as high as the main steam turbine and therefore the targets provided in Table 6.3 may be optimistic for the membrane and adsorption processes. The trade-offs between increasing the generation capacity and the use of steam driven motors is an area for further development.

6.3 Conclusion

The energy penalty for the various capture technologies are provided in Figure 6.5. The energy penalty for the UNO Mk. 3 system is the lowest when compared to the other technologies with comparable level of heat integration. The solvent systems in general have lower energy penalties than the membrane and adsorption cases, however it must be pointed out that the optimisation of the membrane and adsorbent systems are not as far advanced as the solvent systems. There are significant improvements that can be gained by both moderate and full heat integration of the CO_2 capture technology and the power stations. The economic integration will be a trade-off between capital and operating costs and will be very site specific when retrofits are considered as each power station will have various levels of design margins in the existing equipment and available plot space for new equipment. For new build power stations the targets provided by the full integrated cases are likely to be achievable and further improvements are still possible if the steam cycle, air-preheat and coal drying are designed with the impact of the addition of the capture technology to the power station. The impact of pre-drying and air pre-heat is not provided in this report, but is available in Harkin et al. (2010) and Harkin et al. (2009) that show that further reductions in the energy penalty are possible.

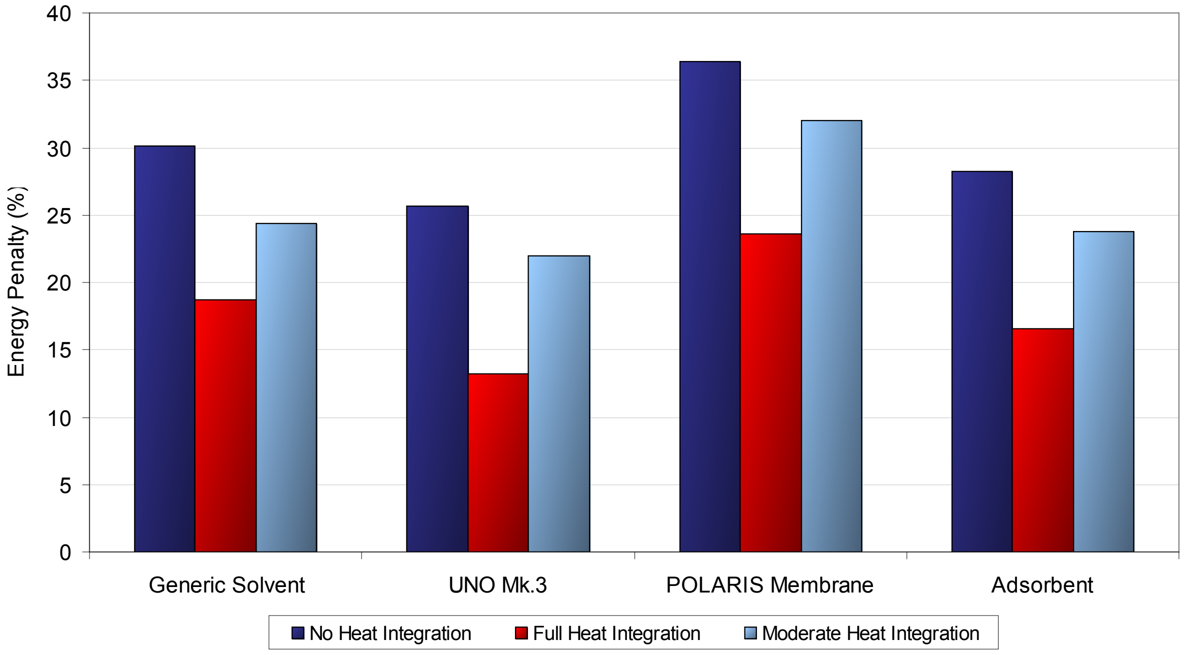

Figure 6.5 – Energy penalty for the options reviewed in section 6.

The energy penalty for these systems are all greater than 25% when no heat integration is included, whereas even with only moderate heat integration most of the capture technologies have an energy penalty less than 25%. In a 500 MW plant, heat integration can provide between 17 and 64 MW of additional power.

The cooling duty for the power stations with CCS is increased dramatically by the addition of each of the capture technologies, increasing the cooling duty by between 75 and 105% from the existing power station. Heat integration can help to reduce the cooling duty but not significantly as usually any reduction in the cooling duty of the process is offset by increases in the steam through the turbine which increases the duty of the steam turbine condenser. However the impact of heat integration on the cooling duty per megawatt of net power is significant due to the increase in the power output. Note that although the cooling duty increases by 75 to 105% and that throughout this report the cooling duty has been represented by cooling water, there is substantial potential for the cooling to be done with dry cooling. The economic trade-offs associated with dry versus wet cooling, especially in Victoria where water is a valuable resource, is worth investigation. The cooling duty for each technology without heat integration is within 5% of each other.

The compressor models are based on the DATUM Dresser Rand estimation tool which is an in-line compressor. Efficiency improvements can be obtained using integrally geared compressors or compressor simplicity can be improved using supersonic compressors which when the heat of compression is returned to the steam cycle show improved net power generation, refer to Harkin et al. (2010).

The moderately integrated cases designed throughout this report invariably utilise some of the flue gas for BFW heating and a combination of condenser or heat of compression for the rest of the BFW heating. The fully integrated cases invariably increased the amount of steam generated from 433 kg/s to approximately 472 kg/s, in order to achieve this increase the temperature driving forces in the boiler convection section will be reduced. Boilers are often designed with a margin of additional heat exchange so that it may be possible to generate the additional steam. The steam turbine may also have some margin to handle the additional steam and usually the first limit that is reached is the generator side of the steam turbine. With solvent systems the requirement of LP steam will reduce the load on the turbine and therefore if the generator load shed from the LP turbine can be transferred to the HP turbine the potential for realised energy penalties between the moderately integrated case and the fully integrated case are possible. Maximum steam test would provide valuable insight into the amount of improvements that could be attained for little modifications.

From the heat and process integration studies it appears that currently the solvent systems have a lower energy penalty to the membrane and adsorption systems. The UNO Mk.3 system shows promise as a low energy option with the energy penalty ranging from 13.2% to 25.7% depending on the level of heat integration and the system could still undergo further optimisation in many variables including the regeneration pressure. The adsorption system energy penalty is between 16.6% and 28.2% depending on the level of integration, which although higher than the solvent systems could easily be lowered with small improvements in adsorption capacity and selectivity. Adsorbents with improved CO_2 capacity are already available so the potential to have lower energy penalties is a real possibility. The membrane system has the highest energy penalty of the systems reviewed at between 23.6% and 36.4%. However the membrane system has the potential for significant improvements in either the membrane permeability or selectivity but also in the process design. Further optimisation of the design of the membrane plant could lead to large savings, as suggested by the work on the PRISM membrane, which although the membrane characteristics were not ideal for CO_2 capture for post-combustion, improvements in its performance can be obtained by optimisation of the process flowsheet structure and the operating conditions.

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7. Economic Evaluation

7.1 Introduction

This section presents a scoping-level assessment of the economics of capturing CO_2 from the flue gas of a post-combustion process. The study assesses the economics based on the experimental results of the pilot plant trials carried out at the Hazelwood H3 Capture Project.

The following cases were evaluated for CO_2 capture –

1. Amine solvent (Case 1)
2. Generic 3 GJ/t promoted solvent (Case 2)
3. Precipitating potassium carbonate slurry (UNO Mk3) (Case 3)
4. Gas separation membrane using Air Product PRISM commercial membrane (Case 4)
5. Gas separation membrane using new POLARIS membrane (Case 5)
6. Vacuum swing adsorption (Case 6)

7.1.1 Processing assumptions

The process data (including equipment size and energy consumption) are based on simulations (as described in Sections 4, 5 and 6) of capture for a full-scale pulverised brown coal power plant with a gross output of 520 MW.

For the baseline economics (Case 1), CO_2 is assumed to be captured using a commercially available chemical solvent absorption technology, a mono-ethanol-amine (MEA) solvent. MEA is chosen because it is used widely in industry for CO_2 recovery from natural gas. Cases 2 to 6 evaluate the economics for the technologies investigated by CO2CRC at the H3 Post-combustion Pilot Plant. Ancillary pre-treatment facilities such as NO_x and SO_x removal are included in the cost estimates except for Cases 3 and 6 where the capture technology is considered to be tolerant to the NO_x and SO_x levels in the flue gas. An estimate for the increased cooling water duty in the form of a new cooling tower is also included.

7.1.2 Economic assumptions

The cost estimates are generated using the CO2CRC techno-economic model developed by UNSW. Based on the process model outputs, the techno-economic model estimates the equipment, operating and the total costs of CO_2 capture. Capture costs include costs for compression of CO_2 to 100 bar ready for transport. Costs for transport and storage are excluded unless otherwise indicated. Normal scoping level process engineering economic assumptions are used (Peters, Timmerhaus and West 2003).

The capital cost for the capture plant includes all major process equipment items, plus a general facilities cost. For the capture plants, equipment items include the absorber, stripper, membrane modules, membrane housing, heat exchangers, solvent handling facilities, compressors and pumps as appropriate to each capture technology. The general facilities cost includes ancillary equipment such as storage tanks, spare pumps, valves and the control system. The capital cost for the capture process is spread over 2 years with a breakdown of 40 and 60 percent in years 1 and 2 respectively.

The operating cost for the capture plant includes fixed general maintenance costs comprising labour, non-income government taxes and general insurance cost. The variable operating costs include costs for cooling water and materials (solvent, adsorbent, membrane) replacement. For the solvent absorption system, the latter incorporate costs for waste (precipitate) disposal. The annual operating cost and amount of CO_2 avoided is assumed to remain constant over the project life. Post operational (decommissioning) costs for the capture plant such as disassembly and site remediation are assumed to be offset by the salvage value of the equipment. Therefore, the decommissioning cost is assumed to be zero. A project life of 25 years is used, along with a capture plant capacity factor of 85% and a 7% real discount rate.

The cost year of the analysis is 2010. All results are presented in Australian (A$) dollars. Equipment costs are obtained from vendors and publications. For items available from the US market, the procurement cost of the item is estimated using a factor that takes into account the exchange rate for purchased equipment, freight and local labour costs. An exchange rate of 1 Australian dollar to 85 US cents is used. The costs are estimated on a pre-tax basis, thus factors such as income tax, R&D tax concessions and carbon price / tax are neglected.

7.1.3 CO_2 avoided and LCOE

The net reduction in CO_2 emissions as a result of CCS is referred to as the amount of CO_2 avoided. The amount of CO_2 avoided is different from the amount of CO_2 captured. The amount of CO_2 avoided takes into account the amount of CO_2 that is not captured from the emission source as well as a factor for CO_2 emitted due to energy used by the capture process itself, i.e.,

$$\begin{aligned} CO_2 \text{ avoided} = \quad & CO_2 \text{ emitted to atmosphere before capture} - \\ & CO_2 \text{ emitted to atmosphere after capture} - \\ & CO_2 \text{ factor from energy consumption for capture} \end{aligned}$$

The cost of CO_2 avoided is calculated using standard CO2CRC methodology viz. a discounted cash flow analysis that takes into account the total project costs (capital and operating) and the net CO_2 avoided –

$$\text{Cost of CO}_2\text{avoided} = \frac{\sum_{i=1}^{n} \frac{K_i + O_i}{(1+d)^i}}{\sum_{i=1}^{n} \frac{(CO_2 \text{ avoided})_i}{(1+d)^i}} \qquad (1)$$

where K_i and O_i are the real capital and operating costs ($ million) in i^{th} year, d is the discount rate (% pa), n is the total project life and CO_2 avoided is the annual amount of CO_2 avoided in million tonnes. The levelised cost of electricity (LCOE) is calculated using a similar method. The capital cost of the existing brown coal power plant without capture is assumed to be $1,340/kW (NETT 2006). More details of the methodology can be found in Ho et al. (2008a, 2008b).

7.2 Capture cases

7.2.1 Solvent capture

Case 1 evaluates the cost of capturing the CO_2 from the flue gas using MEA solvent. The cost of the solvent is taken to be A$1.5 /kg. The analysis does not include heat integration.

Case 2 evaluates the cost of capturing CO_2 using a generic promoted solvent with low regeneration energy requirements (3 GJ / t). The cost of the solvent is taken to be A$2/kg. The analysis uses a moderate level of heat integration as outlined in Section 6.

Case 3 evaluates the cost of capturing CO_2 using potassium carbonate solvent/slurry system. The cost of the solvent is taken to be A$2/kg. The analysis uses a moderate level of heat integration.

Table 7.1 summarises the results for the solvent systems evaluated as Cases 1, 2 and 3.

Table 7.1 Estimate of capture and electricity cost for solvent capture of flue gas

Parameter	MEA (Case 1)	Generic (Case 2)	UNO Mk3 (Case 3)
CO_2 capture rate (%)	90	90	90
CO_2 purity in product (%)	>95	>95	>95
CO_2 captured (MMtpa)	3.78	3.78	3.78
CO_2 avoided (MMtpa)	1.94	2.72	2.86
Energy penalty (MJ_e / kg CO_2 captured)	1.56	0.90	0.78
Capital cost for capture plant (A$million)	810	880	620
Operating cost for capture plant (A$million / yr)	70	70	62
CO_2 avoided cost (A$ / t CO_2 avoided)	108	70	53
$LCOE_{\text{with capture}}$ (A$ / MWh) (no carbon price)	142	111	94

7.2.2 Membrane capture

Case 4 evaluates the cost of capturing CO_2 using the Air Products PRISM membrane in a series configuration as described in Section 5. The cost of the membrane is taken to be A$60/m^2 with a life expectancy of 3 years. The analysis uses a moderate level of heat integration.

Because the capture rate for Case 4 is very low (<1%), Case 5 evaluates the cost of capturing CO_2 using the POLARIS membrane (Merkel et al. 2010) with a permeance of 1000 GPU and CO_2/N_2 selectivity of 50. For this case, the CO2CRC techno-economic model is used to estimate the system performance. The configuration used is a simplified 2-stage cascade process as shown in Figure 7.1. The cost of the membrane is taken to be A$60/m^2 with a life expectancy of 3 years. The analysis uses a moderate level of heat integration.

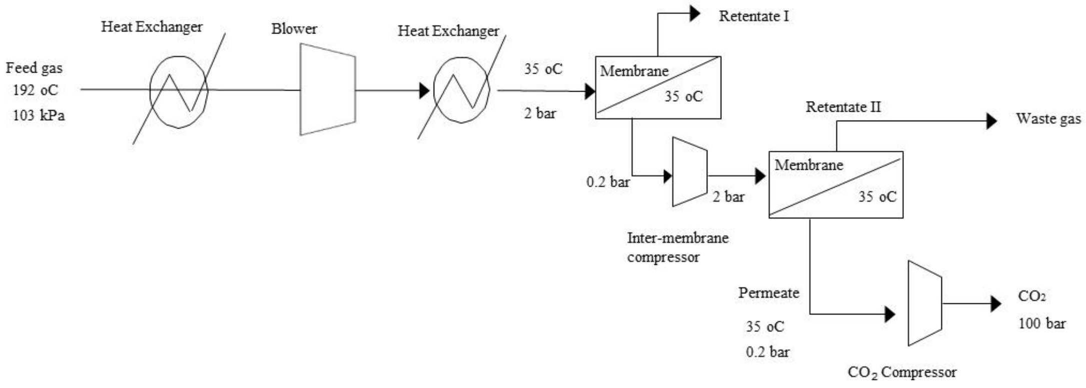

Figure 7.1 Schematic of two-stage cascade membrane system with vacuum permeate

Table 7.2 summarises the results for the membrane systems evaluated as Cases 4 and 5.

Table 7.2 Estimate of capture and electricity cost for membrane capture of flue gas

Parameter	PRISM Membrane (Case 4)	POLARIS Membrane (Case 5)
CO_2 capture rate (%)	< 1	90
CO_2 purity in product (%)	>95	>95
CO_2 captured (MMtpa)	<0.04	3.78
CO_2 avoided (MMtpa)	<0.001	2.44
Energy penalty (MJ_e / kg CO_2 captured)	70	1.13
Capital cost for capture plant (A$million)	>3700	795
Operating cost for capture plant (A$million / yr)	240	70
CO_2 avoided cost (A$ / t CO_2 avoided)	>1000	78
$LCOE_{\text{with capture}}$ (A$ / MWh) (no carbon price)	>1000	117

7.2.3 Adsorption capture

Case 6 evaluates the cost of capturing CO_2 zeolite 13X in a vacuum swing adsorption system. The cost of the adsorbent is taken to be A$6/kg with a life expectancy of 5 years. The analysis uses a moderate level of heat integration. Table 7.3 summarises the results.

Table 7.3 Estimate of capture and electricity cost for adsorption capture of flue gas

Parameter	VSA (Case 6)
CO_2 capture rate (%)	86
CO_2 purity in product (%)	95
CO_2 captured (MMtpa)	3.62
CO_2 avoided (MMtpa)	2.64
Energy penalty (MJ_e / kg CO_2 captured)	0.86
Capital cost for capture plant (A$million)	658
Operating cost for capture plant (A$million / yr)	51
CO_2 avoided cost (A$ / t CO_2 avoided)	55
$LCOE_{\text{with capture}}$ (A$ / MWh) (no carbon price)	93

7.3 Comparative Studies

7.3.1 Sensitivity analysis

In this study, the estimate of the cost for capturing CO_2 from the flue gas of the full-scale 520 MW power plant using the baseline MEA solvent without heat integration is over $100/t CO_2 avoided. The cost of capture using the alternate technologies ranges from $53/t to $78/t. However, there is uncertainty and variability in the parameters used to estimate the costs. Figure 7.2 shows results for a sensitivity analysis for the following key parameters:

- Discount rate (halving and doubling of the baseline value);
- Energy penalty (increased from the baseline estimate by 20%);
- Capital and operating costs (varied from the baseline estimate by 20%); and
- Electricity price (increased by 20%).

The figure shows the ratio of the upper and lower cost estimates of the alternate post-combustion capture technologies (Case 2, 3, 5 and 6) relative to MEA without heat integration (figure 7.2A) and with heat integration (figure 7.2B). Because of the low capture rate, data for Case 4 is omitted from the figure. For all the technologies, the ratio is below 0.8 compared to MEA solvent both with and without heat integration. In some cases, a ratio as low as 0.5 may be achieved. The results indicate that all of the alternate technologies are cheaper post-combustion capture options than using MEA solvent.

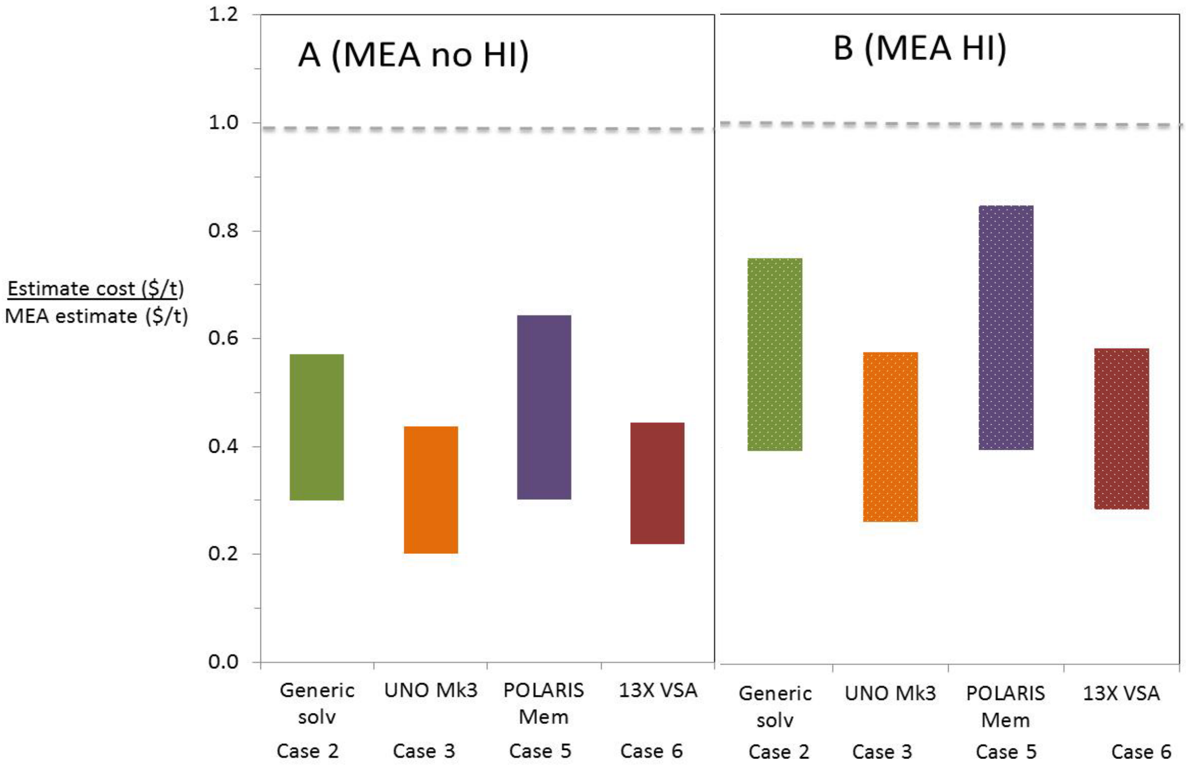

Figure 7.2 Ratio of upper and lower estimates for cost of alternative technologies compared to MEA solvent without (A) and with (B) heat integration

7.3.2 Comparison of levelised cost of electricity generation

7.3.2.1 The effect of capture

At a zero carbon price, the levelised cost of electricity generation ($LCOE_{gen}$) for the full-scale 520 MW power plant with capture ranges from just above A$90 per MWh for the UNO Mk3 solvent (Case 3) and VSA process (Case 6) to almost A$120 per MWh for gas separation membrane technology (Case 5). The LCOE for MEA solvent (with no heat integration) is above $140/MWh. Figure 7.3 shows the effect of carbon price on $LCOE_{gen}$ with capture for the different technologies.

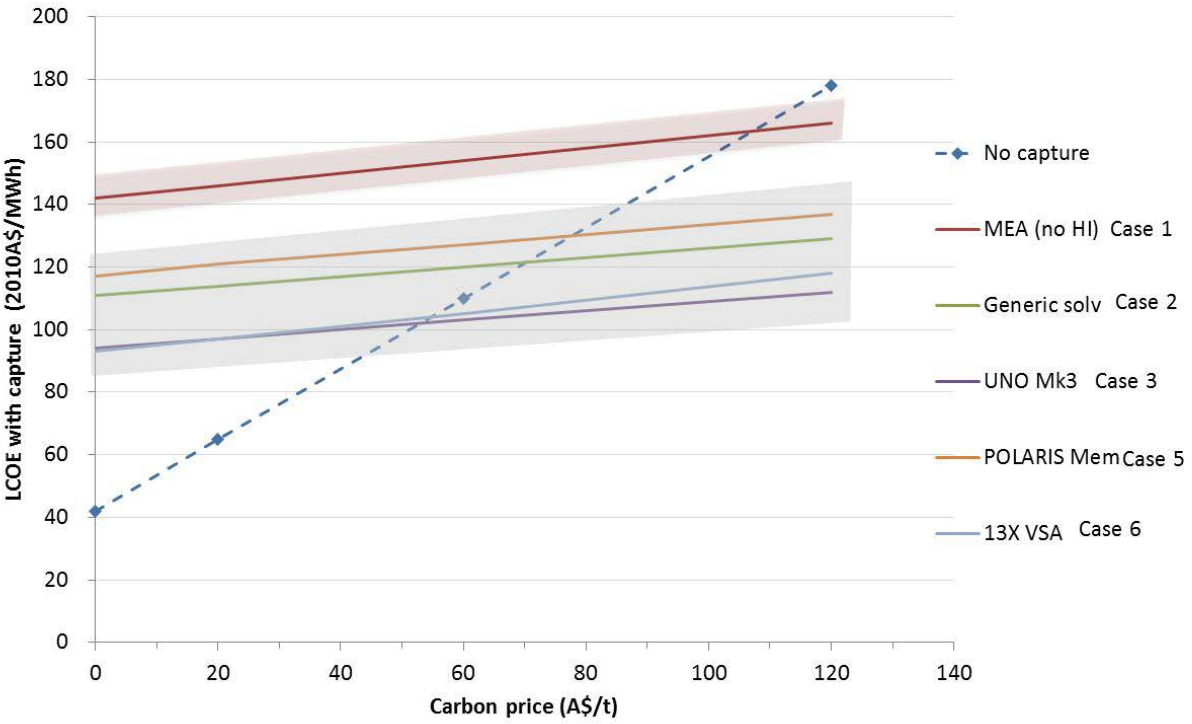

Figure 7.3 Changes in $LCOE_{gen}$ for the full-scale 520 MW power plant with and without capture with increasing carbon price

7.3.2.2 The additional effect of transport and storage

The above results for the $LCOE_{gen}$ only show the costs of CO_2 capture. However in deploying CCS, the transport and storage of CO_2 will also affect the LCOE. Capture typically represents 60% to 80% of the total CCS cost (Fimbres-Weihs and Wiley 2010). Based on this assumption, the estimated LCOE for the full-scale 550 MW power plant with CCS assuming that costs for transport and storage range from A$20 to A$30 per tonne CO_2 avoided (Neal et al. 2006) is of the order of A$110 to A$140 per MWh. When no carbon price is included in the analysis, the increase in the LCOE with CCS compared to the LCOE for a power plant without CCS is A$70 to A$120 per MWh. Figure 7.4 shows the estimated LCOE with CCS and for increasing carbon price.

The costs of CCS projects are very case specific. This analysis does not consider the condition of the sinks or the effect of source, pipeline and storage networks. Therefore the LCOE estimates presented in this study are indicative only. Having said this it is recognised that in the case of Latrobe Valley the proximity to Gippsland offshore storage potential will offer comparatively low transport and storage opportunities.

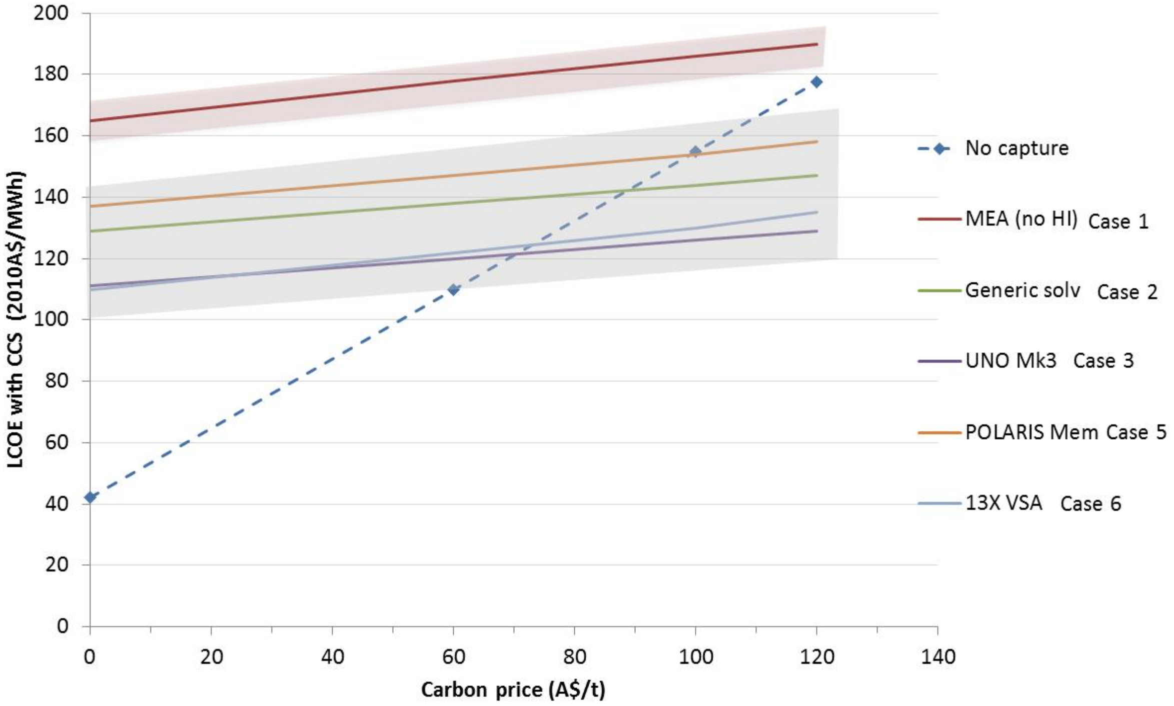

Figure 7.4 Cost of electricity generation (LCOE) with CCS (A$ / MWh) with increasing carbon price

7.4 Other Outcomes (communications, collaborations, skill development, etc)

The economic analyses have involved collaboration with CSIRO to compare our economic methodology and with Process Group to obtain comparative capital cost estimates for Case 3. The economic assessment for that case was presented at the Tenth International Greenhouse Gas Conference (GHT-10) in a joint paper between Process Group and the CO2CRC.

The economic assessment carried out for this project has enabled further development of the CO2CRC techno-economic model. The professional skills of 2 research fellows have been developed in the economics of post-combustion capture.

7.5 Conclusions

Post-combustion capture of CO_2 from the flue gas of a 520 MW pulverized brown coal power plant has been estimated to cost of the order of A$55 to over A$100 per tonne CO_2 avoided. The results show that the cost of capturing CO_2 using new post-combustion technologies such as potassium carbonate solvent, gas separation membranes and VSA is significantly lower than for MEA solvent. This report is a preliminary analysis based on limited process and cost data. Simplified rules of thumb and equations have been used to model the capture technologies. Detailed process simulations and process optimisation have not been used. As such, the results of this report are only indicative. While some effects of a carbon price have been included, the effect of tax has been neglected.

7.6 Comparative Results with CSIRO-LYP Stream

In 2009, the CO2CRC and CSIRO undertook a scoping level assessment to compare the economic methodology of both research institutions. The outputs from the comparative benchmark study between CSIRO and CO2CRC show that the methodology from both research groups is similar. There are minor differences in the outputs, primarily the capital and operating costs estimates for the power plant. This would arise from the different unit costs assumed by each institution. However, the differences are less than 10%.

Appendix 2 summarizes the results of this study.

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8. Commercialisation of Post-Combustion CO_2 Capture Technologies for Latrobe Valley Brown Coal Fired Power Plants

The application of any new technology to an existing process requires evaluation across a range of technical and commercial parameters. This section seeks to address a number of these factors reflecting the transition of the key findings from this study to a range of CO_2 capture technologies of varying technological maturity, as low emission retrofit and new build for Latrobe Valley brown coal fired power plants.

8.1 Technical Maturity

The fact that this project compares three separate technologies (solvents, membranes, and adsorbents) in parallel in a comprehensive technical and economic evaluation for brown coal fired power plant retrofit, is unique to the world of CCS. This approach examines current and next generation technologies thus allowing both first-generation and second-generation options to be considered.

The characteristics of post combustion capture (low pressure and low CO_2 concentration) mean that the scale up issues are most pressing in this situation. Furthermore while all the technologies have been applied industrially in other industries and hence have some industrial experience, they have not been applied widely in the post combustion environment. Consequently these technologies are at a lower maturity than application in pre-combustion capture situations. Added due diligence is required in commercialisation and scale up in these cases.

8.1.1 Solvent – Generic 3 GJ/t CO_2

This case is representative of any of a range of alternative available solvents having 'state-of-the-art' energy usage of approximately 3 GJ/t CO_2. These include already available amine solvents from Mitsubishi Heavy Industries (MHI), Fluor and Cansolv as well as emerging solvents from BASF and RITE. While our trials show that un-promoted K_2CO_3 liquid systems are uneconomic, the promoted solvent (such as with piperazine) is expected to be capable of state-of-the-art energy usage. All these solvents can be represented but the case which is developed in this report as a moderately heat integrated design and compared to unintegrated MEA as a base case. For all these solvents, flue gas desulphurisation (FGD) and nitrogen removal (deNOx) facilities are considered necessary to reduce solvent and promoter losses.

It is considered that these solvents are capable of deployment at large scale (millions of tonnes per annum) now, though possibly not with the level of guarantees required for commercial operation. Consequently several providers are progressing 'hundreds of thousands of tonnes per annum' commercial demonstrations prior to full scale deployment. Given these considerations, solvent absorption capture technology is considered to be highly developed and from a capture perspective could be applied at full scale in the medium term (5-10 years).

8.1.2 Solvent– UNO Mk3 precipitating K_2CO_3

This process is a development in CO2CRC's solvent-based K_2CO_3 research. It offers considerable reductions in energy usage, better mass transfer characteristics compared to the liquid K_2CO_3 system and with robust promoters under development offers the potential to be applied without the addition of FGD and deNOx facilities. This project has clearly demonstrated that the removal of sulphur and nitrogen is adequately managed in K_2CO_3 systems. Precipitation caused some problems during the trials and this was exacerbated by the fact that much of the equipment, having been designed for a different solvent, was not adequately designed to cope with this situation. A purpose built unit should overcome this issue.

The potassium carbonate process is under review and further refinements are being progressed within the CO2CRC research program. The technology relies on well known solvent systems. The main challenges are in the area of equipment design and selection. Being a PCC technology, issues of scale are relevant and could add additional delays to implementation. Nevertheless it is considered as a medium term (3-10 year) prospect for large scale demonstration with learning expected to come from other PCC applications under development worldwide such as chilled ammonia, which also utilises a slurry based system. Leveraging this knowledge base should speed development.

8.1.3 Membrane - post combustion

Membranes are already used commercially in natural gas CO_2 separation and for hydrogen separation in syngas processing but not for bulk CO_2 removal in post-combustion capture. Some further development and review of the processes and materials issues for this application will be required. A number of overseas organisations have recently outlined novel concepts using membranes and documented pilot projects. The development pathway is expected follow development pathways in other membrane applications such as desalination. It is expected that such systems could be applied from a technical perspective in the medium term (3-10 years) at a significantly larger scale. One benefit of membrane technology is that it is highly scalable with additional modules capable of being added as required. Close scrutiny of the larger scale pilots are recommended as this technology develops.

8.1.4 Adsorbent - post combustion

Adsorbents for post combustion capture either use temperature or pressure swing (or more correctly as vacuum swing - VSA) adsorption. This study uses VSA which is being used increasingly for air separation. Once again the equipment issues for scale up are the most important. CO2CRC's research is progressively identifying equipment from various industries that can be used in large scale PCC applications with VSA. Some further development and review of the processes and materials issues for this application are required but the findings from this project show promise for full-scale application. The processes analysed in this report suggest that an economically viable process can be developed and consequently it is expected the technology could be technically applied in the medium term (5-15 years) as a large scale demonstration.

8.2 Large Scale Designs

The laboratory, plant, and simulation data have allowed credible large scale designs to be developed for all technologies. The heat and process integration methodologies developed in this project enabled flowsheets to be designed that target the key cost reduction areas for carbon capture. The designs presented have not been optimised, particularly in the case of membranes and adsorbents (due to time constraints) but are considered to represent feasible and conservative flowsheets. Process integration between power plant and capture facilities is often viewed with concern as it may lead to complexity and problems in control. It is considered that the proposed integration opportunities identified do not introduce undue complexity and should not compromise large scale designs.

While credible conservative designs have been provided in this report it is recommended that further optimisation of the technologies, particularly membranes and adsorbents, be completed. These should be re-evaluated in the light of both their performance and large scale implementation opportunities.

The cases evaluated in this study have been retrofits to existing power plant based on one of the inherent strengths of PCC, namely the ability to be seamlessly integrated into the current power plant steam cycle. Furthermore the comprehensive evaluation and development of heat integration methodologies for the brown coal fired power plants has identified a range of benefits to the use of retrofit to all Australian power plants.

The designs are equally applicable to new builds and indeed other fossils fuels, including black coals and natural gas, so the findings are widely relevant. The question of which option might prove the best for any given site does become the subject of very site specific factors which are outside the scope of this report. It is noteworthy that the CO2CRC believes recent large capital cost increases leading to the high cost of new build assets with capture suggest that retrofits to existing assets could deliver lower cost LCOE’s than equivalent new builds. This hypothesis has been discussed with EPRI, who recently performed the work on comparative power costs for Australia, and this will be the subject of further separate work on the subject. It is fair to say that the outcomes of this retrofit study show the LCOE’s to be distinctly at the low end of the range of the EPRI new build PCC numbers for what are good and understandable reasons.

It should be noted that a key determinant for any CCS project, let alone demonstration projects, is the access to viable storage. The Latrobe Valley offers the best storage locations for Australian power plants and should not be ignored in the evaluation of options for CO2 emission reduction.

8.3 Technical and Commercial Viability

8.3.1 Technical Viability

Given the technical maturity of several of the capture separation methods and the integrated flowsheets discussed above it is considered that the solvent routes are technically implementable at large and even commercial scale. Several of the other emerging technologies, including the precipitating carbonate systems, adsorbents and membranes offer considerable promise to provide lower costs in the medium term, albeit at large demonstration scale. The technical challenges of each of these routes can be articulated and used to define targeted development programs. In the case of the precipitating carbonate systems it is conceivable that those systems are close enough to the structure of conventional solvent systems they could be retrofitted into any large scale demonstration units eliminating concern of technology obsolescence.

All technologies can be designed at varying recoveries to deliver transitional abatement, particularly those which offer high degrees of scalability such as membranes. Capital costs for the range of cases presented in this report are $620-880 million (see Section 7.2) with annual operating costs ranging from $50-70 million. Net efficiency drops for capture configurations range from ~ 6% (28.6% HHV to 22.3% HHV) for the better technologies (which are the medium term alternatives) to 9.2% for the less developed designs.

Water usage for all capture cases increases and this could create problems for PCC unless addressed. Further work is planned to evaluate air cooling for the additional capture plant loads thus limiting overall site water usage.

The overall performance of the technologies is best examined through the impact on LCOE which is discussed in the next section.

8.3.2 Commercial Viability

The true commercial viability of a technology can only be evaluated with a knowledge of the policy and regulatory environment in which it operates. In the current situation it is only possible to comment on the likely impact of commercially relevant performance estimates. The most relevant parameters considered here are the cost of capture and the levelised cost of electricity (LCOE).

Figure 7.3 and Table 7.7 show the capture costs for the range of large scale designs. Cases 2 - 6 are a direct comparison against the base case of MEA scrubbing. Each of these cases has a physical capture rate of 90%. The capture cost for all integrated technologies show a marked reduction from the base case 1. Cases 3 (UNO Mk 3) and 6 (adsorption) are roughly equivalent and show the best capture cost reduction of ~50% from the base case 1, whereas cases 2 (generic 3GJ/t solvent) and case 5 (membrane) produce 35% and 28% cost reductions respectively.

Figure 7.10 demonstrates the LCOE with varying carbon price values and the inclusion of relevant economic scale transportation and storage costs for a Latrobe Valley/Gippsland source/sink match. The graph shows bands of LCOE which incorporate a range of uncertainties in the analysis. It indicates that, due to the low base cost of the electricity from the current assets, below $70/t carbon price, paying that price would still result in lower LCOE than any of the cases reviewed. Above this carbon price, implementation of CO_2 capture results in lower LCOE. Should the base price for existing power be lower (due to different decisions on the residual asset value factored into the calculation) the cross over point would increase.

The studies show that different low emissions technology retrofit configurations can provide a range of LCOE outcomes. These LCOEs are at the low end of a range of studies for future new build Australian low emission power costs recently completed by EPRI for the Federal Government. [*Australian Electricity Generation Technology Costs – Reference Case 2010.* EPRI, Palo Alto, CA and Commonwealth of Australia: November 2009]. (http://www.ret.gov.au/energy/Documents/facts-stats-pubs/AEGTC%202010.pdf) This reinforces the view that retrofit should be considered when examining low emissions outcomes from Australian power plants, and particularly brown coal plants given their location adjacent to attractive storage sites in the Gippsland Basin.

It is important to note that the outcomes of this study are largely indicative and based on well thought out but un-optimised designs. Further studies and detailed review with proponents may result in revision to the current findings. Any preferred approach will have to be fully designed to determine the final project cost estimate.

8.4 Project Issues

A number of project issues must be reviewed when assessing the commercialisation of capture technologies. Issues such as safety, operability, disposal of solvents and overall risk management are but a few needing considerations.

Each of the capture technologies rely on standard chemical industry processing techniques however these are not necessarily common practice for existing power producers. The experience of the commercial solvent Puratreat^{TM} in the Hazelwood Carbon Capture Plant has shown that such plants can run reliably with minimal attention once fully commissioned. Nevertheless there is a need for inclusion of substantial training and development on any project involving new capture technology.

As all the technologies were operated as either adds-on or , in the case of the solvent trails, in plant not specifically designed for that solvent, they all experienced some degree of ‘compromise’. This resulted in operating problems which would be expected to be engineered out of any full scale design. Examples of this are (1) the need for fully traced equipment to avoid precipitation occurring in unwanted places in equipment and (2) solvent depletion (due to impurities) and hence performance losses being avoided through the addition of impurity removal and replacement systems. Trials such as these allow problem areas to be identified and engineering designs to be modified accordingly. One issue that should be considered in more depth for such CCS projects is the issue of equipment redundancy and decisions on the required plant availability targets.

There are no undue safety or operability concerns for any of the proposed techniques influencing commercial implementation although the issue of environmental emissions from amines is still to be clarified.

From a project management and risk assessment perspective the introduction of capture facilities is a large capital expenditure project and will require the same strict protocols and processes used for similar projects. Capture facilities are subject to a known regulatory regime for process plant and hence should not create undue project risk in that respect.

8.5 Recommendations

The CO2CRC H3 Capture Project has provided a solid base for reviewing the incorporation of carbon capture and storage to the existing Latrobe Valley power plants. The fundamental R&D performed at the Hazelwood site has been converted into large scale designs and the techno-economic performance of a range of options evaluated.

As a result of this work it is recommended that:

- Further engagement between CO2CRC and International Power be pursued to formalize the project findings in terms of potential designs and commercialisation issues for the range of capture technologies;
- Optimisation of the process designs be carried out, in particular for the membrane and adsorption technologies. This will provide greater confidence in the comparisons and subsequent selections of technologies for more detailed study;
- Continue to run targeted tests on membranes and adsorbents at the Hazelwood site to gather additional information under the CO2CRC program;
- Targeted R&D resulting from the evaluation of different separation technologies be initiated and potential future pilot facilities be identified as required. In particular work on UNO Mk3, membranes and adsorbents should be investigated;
- The learning developed from the pilot facilities in this project be incorporated in any future development facility;
- Transport and storage be included in future economic analyses;
- Local vendor quotes be obtained for capital and operating expenses as more detailed designs are developed; and
- Ongoing communication of the project findings be provided to local and international stakeholders to demonstrate the potential for low emissions power as retrofits to existing plants. In particular communicate the opportunities of formal heat integration studies for CCS projects.

9. Conclusions

The key objective of the CO2CRC H3 Capture Project was to reduce the technical risk and cost of post combustion capture for Victorian coal-fired stations. For each of the three capture technologies (namely, solvent absorption, membrane and adsorption), the more specific objectives were to:

- Identify and quantify the impact of realistic post combustion gas contaminants (SO_x, $NO_{x,}$ fly ash) and water on the performance of each technology;
- Identify and quantify the impact of post combustion gas temperature and concentration variations on the performance of the capture medium and process;
- Optimise process operating parameters;
- Develop engineering solutions at a scale so that confidence can be established for full scale plant design and assessment;
- Assess the post combustion capture process and energy integration options; and
- Review the technical and economic viability of the commercial use of post combustion capture for Victorian brown-coal power stations.

Having completed the research program the CO2CRC has successfully delivered a multi-party, multi-technology carbon capture demonstration project in the post combustion area unique to the CCS world. It has enabled local skill development and gaining of confidence in construction, commissioning and operation of capture plants for a real PCC plant.

The project has gathered valuable information to facilitate technology development for three post combustion techniques (solvent absorption, membranes and adsorption) resulting in substantial reduction in technical risk and cost for all three technologies. Furthermore the large scale designs indicate a range of options for carbon dioxide capture. Various technology cases are evaluated and result in a better understanding of the range of carbon capture costs and LCOE’s.

Specific achievements are summarized below in the context of each group involved.

9.1 Solvents

In the solvent absorption area, the Hazelwood Carbon Capture plant has successfully demonstrated the feasibility of solvent capture at a considerable scale and provided an insight into the issues for larger scale demonstrations.

Research and trialing on the UNO liquid K_2CO_3 system has led to the development of the significantly lower energy alternative process, UNO Mk3, utilising precipitating carbonate technology.

Large scale design evaluations have successfully demonstrated the CO2CRC UNO Mk 3 process to be a highly competitive post combustion technology through both the energy reduction of the precipitating system and it's inherent sulphur and nitrogen removal capability - obviating the need for supplemental or new gas treatment facilities such as FGD and deNOx. Additional potential benefits such as deep energy reduction (approaching 2 GJ/t) and by-products credits have yet to be incorporated into the economics and these will further deliver cost reductions.

9.2 Membranes

Despite limited run time, the trials provided valuable information about performance with real flue gas. The evidence of selectivity drop offs over time and the effects of competitive sorption provided valuable insight. There was little evidence of ash build up in the current plant configuration.

Considerable work was done on the impact of impurities (including water) on membranes which will be valuable in larger scale designs. Results have enabled identification of suitable membrane materials and process designs that can attain the degree of CO_2 recovery and purity required for effective storage. Further reviews of the membrane design are required.

Additional opportunities for trials using the Hazelwood rig are being considered.

9.3 Adsorbents

The VSA trials using Zeolite 13X proved to be very stable and ran with minimal intervention once commissioned. The trials provided valuable insight into the impacts of water and other impurities.

Water management protocols were readily established and it has been demonstrated that no expensive pre-treatment steps will be necessary for VSA operation with the CO2CRC designed process.

Additional runs are planned to gather more data with the objective to construct a case for further larger scale test work.

The adsorbent system offered the equal lowest cost alternative for retrofit with UNO Mk3 and as such warrants further analysis of the cycles, materials alternatives and importantly the capital equipment required. Further enhanced designs are expected to lead to even better outcomes.

9.4 Heat and Process Integration

The analysis of optimal energy penalty targets for Australian power plants is a major outcome for this project. It stresses the benefits that can be achieved through greater understanding of the energy flows available for comprehensive heat integration of capture plant into power cycles. This can enhance the opportunity for retrofit PCC to Australian power plants. In particular the brown coal power plants have the opportunity of innovative pre-drying as potential add-ons to capture plant. Moderate levels of pre-drying have been shown to offer efficiency benefits when combined with carbon capture however at this stage it is not clear whether further levels of drying will lead to additional benefits.

A multi-objective optimisation tool for CO_2 capture from power stations has been developed by the CO2CRC as part of the CO2CRC's ETIS post and pre-combustion projects. The tools enable the creation of highly integrated designs that minimisze energy usage and reduce costs.

Based on a 500MW brown coal fired plant a baseline analysis was completed to show that it is thermodynamically possible for considerable additional power to be produced from Latrobe Valley power plants (up to 42 MW) through better matching of power cycles to the available heat. However an increase in power is not physically possible with the current design; due to limitations on the existing generator equipment and to a lesser extent limitations of the existing steam turbine and heat exchangers. More detailed analysis of specific retrofit options may open up other alternative approaches and modifications that could utilise this latent opportunity. This would need closer study but it emphasizes the worth of the tools developed and also highlights that considerable amounts of post combustion capture can be done with minimal impact on the Net Power from a given plant. This may offer interesting project opportunities in the transition to full capture.

Four post combustion capture processes (two solvents, one membrane and one adsorbent) were evaluated as a retrofit to a 500MW brown power plant at three levels of heat integration. While each option has positive attributes, the energy penalty is the lowest for the UNO Mk3 solvent case (22%) followed closely by the generic solvent process (25%) and the adsorption process (23%). These energy penalties could be further reduced both by an optimisation procedure targeting process parameters and though more aggressive, but still manageable, heat integration strategies. Work on more novel energy penalty reduction strategies such as the use of supersonic compressors for CO_2 has been reported in journal and conference articles.

9.5 Economics

Using simplified methods, the cost to capture CO_2 from the post-combustion stream from a 500 MW brown coal fired power plant are of the order of A$52 to over A$108 per tonne CO_2 avoided. The maximum cost of capture for the heat integrated cases is however A$70 per tonne CO_2 avoided. The levelised cost of electricity with capture (allowing for appropriate transportation and storage in Gippsland) for a retrofitted power plant range from A$110 to A$165 per MWh. The sensitivity results show that cost estimates are strongly affected by the discount rate and energy penalty estimates. Observations are made about uncertainty and a range of carbon prices and their impact on LCOE for all capture and non capture cases.

9.6 Intellectual Property

Intellectual property has been developed/tested in the following areas:

- Knowledge in designing and operating plant & process for removing CO_2 from gas streams using;
    - Solvents
    - Gas-liquid membrane contactors
    - Gas separation membranes
    - CO_2 adsorption systems and adsorbents
- Large scale designs for these systems
- Heat & Process Integration methodologies for reduced parasitic load

9.7 Communications, Publications, Awards, Collaborations and Skills Development

One of the key features of the ETIS project was to communicate the results widely. The project has been active in this area as outlined below.

- The project has been visited by more than fifty groups from Australia and overseas, raising the profile of CO_2 capture researchers and industry collaborators.
- At least 53 publications including 27 refereed journal articles, a book chapter, media releases, news/web articles, interviews and public lectures have been produced related to this project. They have enhanced public and scientific knowledge and awareness of CO_2 capture.
- More than 20 researchers and higher degree research students have been involved in the project. Their involvement with the industrial partners has assisted in developing high calibre R&D skills for the Brown Coal industry in Victoria. The capabilities of our researchers has been formally acknowledged by the awarding of a Fulbright scholarship to one of our postdoctoral fellows, Dr Colin Scholes in 2009, which provided the opportunity to collaborate with one of the leading international gas separation membrane researchers at The University of Texas at Austin, USA.

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The contribution by Les Hunt who, on behalf of Loy Yang Power, has helped in reporting progress to the ETIS/BCIA funding bodies, is also recognised.

11. Appendices

- Appendix 1: "Large Scale Integrated Projects with Post-combustion Capture" extracted from Global CCS Institute we page
- Appendix 2: CO2CRC/CSIRO Benchmarking Study on economic models comparison

Appendix 1 - Large Scale Integrated Projects (Post-combustion)

Monday, 20 June 2011

Project Name	Description	Volume CO_2	Operation Date	Facility Details	Capture Type	Storage Type
AEP Mountaineer 235-MWe CO2 Capture and Storage Project	AEP's Mountaineer coal-fired power station was retrofitted with Alstom's patented chilled ammonia carbon capture technology. This project has been operational at pilot scale since September 2009 and full-scale operation is expected by 2015. Location: USA	1.5 Mtpa	2015	235 MWe slipstream from 1300 MW net coal-fired power plant	Post-Combustion capture	Deep Saline Formations
Belchatow CCS	Alstom and PGE EBSA are partnering to build an 858 MW lignite-fired power plant with CCS. Around 1.8 million tonnes per annum of carbon dioxide will be captured and stored in deep saline formations. POLAND	1.8 Mtpa	2015	260 MW equivalent on 858 MW lignite-fired power plant	Post-Combustion capture	Deep Saline Formations
Bow City Power Plant CO2 Capture	The Bow City Power Project is a proposed super critical 1,000 MW coal-fired power plant incorporating post combustion carbon capture and storage. Around 1 million tonnes per annum of carbon dioxide will be captured at the plant. CANADA	1 Mtpa	2016	1000 MW coal-fired power plant	Post-Combustion capture	Enhanced Oil Recovery
Coolimba Power Project	Aviva Corporation Ltd proposes the construction of a "CCS-ready", coal-fired base-load power station using circulating fluidized bed (CFB) technology. Suitable storage sites are being sought. AUSTRALIA	2 Mtpa	2015	2x200 MW or 3x150 MW coal-fired CFB power plant	Post-Combustion capture	Depleted Oil and Gas Reservoirs
Entergy Nelson 6 CCS Project	This project developed by Tenaska and Entergy will capture up to 4 million tonnes per annum of carbon dioxide from an existing coal-fired power station when operating at full scale. The carbon dioxide will be used for enhanced oil recovery. USA	4 Mtpa	2015	585 MW coal-fired power plant	Post-Combustion capture	Enhanced Oil Recovery
Korea-CCS1	This project proposes to capture up to 1.5 million tonnes per annum of carbon dioxide from an integrated Circulating Fluidized Bed Combustion (CFBC) power plant. The carbon dioxide captured at the plant would be stored in deep saline formations. KOREA	1.5 Mtpa	2017	300 MW coal-fired power plant	Post-Combustion capture	Deep Saline Formations
Lianyungang IGCC with CCS Project	This project will construct a 1200 MW IGCC capturing up to 1 million tonnes per annum of carbon dioxide. Substitute natural gas (SNG) and chemicals will be co-produced at this plant. CHINA	1 Mtpa	2015	1200 MW IGCC and 2x1300 MW ultra supercritical PC plants coproduction power/chemical	Pre-Combustion and Post-Combustion	Deep Saline Formations
Longannet Clean Coal Power Station	This project led by Scottish Power will retrofit two 600 MW turbines with amine-based carbon capture units. Up to 2 million tonnes per annum of carbon dioxide will be transported by pipeline to depleted gas fields in the Central North Sea for storage. UK	2 Mtpa	2014	2x600 MW units at a 2400 MW coal-fired power plant with co-firing capability	Post-Combustion capture	Depleted Oil and Gas Reservoirs
Mongstad Full-Scale CCS	StatoilHydro and the Norwegian government entered into an implementation agreement to develop carbon capture solutions at the Mongstad natural gas energy plant, with a view to capture and store up to 1 million tonnes per annum of carbon dioxide. NORWAY	1 Mtpa	2020	Natural gas-fired power plant (280 MW electric, 350 MW heat)	Post-Combustion capture	Deep Saline Formations
Peel Energy CCS Project (formerly Hunterston Power Station)	Ayrshire Power is developing a new multi-fuel power station fitted with CCS infrastructure at Hunterston, Scotland. The project intends to capture around 2 million tonnes per annum of carbon dioxide when operating at full scale. UK	2 Mtpa	2017	2x926 MW multi-fuel (coal/biomass)-fired power plant	Post-Combustion capture	Depleted Oil and Gas Reservoirs
Peterhead Plant	Around 1 million tonnes per annum of carbon dioxide will be captured at GCTT Peterhead, the largest power station in Scotland. The carbon dioxide captured at the plant will be used for enhanced oil recovery at the Miller Field in the North Sea. UK	1 Mtpa	By 2020	400MW gas-fired power plant	Post-Combustion capture	Deep Saline Formations and EOR
Porto Tolle	This project will capture around 1 million tonnes per annum of carbon dioxide from 660 MW coal power station units using post-combustion capture technology. The carbon dioxide will be injected into a deep saline aquifer in the northern Adriatic Sea. ITALY	1 Mtpa	2015	3x660 MW ultra supercritical PC power unit	Post-Combustion capture	Deep Saline Formations
Romanian CCS Demo Project (Getica)	This project will capture around 1.5 million tonnes per annum of carbon dioxide from a lignite-fired power plant. The carbon dioxide captured at the plant will be stored in offshore deep saline formations. ROMANIA	1.5 Mtpa	2015	330 MW lignite-fired power plant	Post-Combustion capture	Deep Saline Formations
Rotterdam Afvang en Opslag Demo (ROAD)	Electrabel and E.ON are developing this project in partnership with the Rotterdam Climate Initiative (RCI). A 250 MW capture plant is being built at E.ON's Maasvlakte power plant and operation is expected to start in 2015. NETHERLANDS	1.1 Mtpa	2015	250 MW on 1070 MW coal and biomass-fired power plant	Post-Combustion capture	Depleted Oil and Gas Reservoirs
RWE Eemshaven	RWE and Gasunie aim to capture and store around 1.2 million tonnes per annum of carbon dioxide in this project, which is scheduled to become operational in 2015. NETHERLANDS	1.2 Mtpa	2015	780 MW net coal-fired power plant (biomass in future)	Post-Combustion capture	Depleted Oil and Gas Reservoirs
SaskPower Boundary Dam 3 CCS Project	SaskPower proposes to rebuild a coal-fired power generator with carbon capture technology near Estevan, in the Saskatchewan province. When fully operational in 2015, this project will capture around 1 million tonnes per annum of carbon dioxide. CANADA	1 Mtpa	2013	115 MWe coal-fired power plant	Post-Combustion capture	Enhanced Oil Recovery
Taweelah Asia Power Company / Emirates Aluminium CCS Project	This project proposes to capture up to 3.4 million tonnes per annum of carbon dioxide from two natural gas-fired power plants by 2017. The project is being developed as part of the Abu Dhabi CCS Network (Masdar). UAE	3.4 Mtpa	2017	Amine-based natural gas-fired power plant	Post-Combustion capture	Enhanced Oil Recovery
Tenaska Trailblazer Energy Center	Tenaska, Inc. is developing a site near Sweetwater, Texas, upon which to construct a supercritical pulverized coal-fueled electric generating plant designed to capture up to 85-90 per cent of the carbon dioxide that would otherwise enter the atmosphere. USA	5.75 Mtpa	2016	600 MW net supercritical PC power plant	Post-Combustion capture	Enhanced Oil Recovery
The Collie South West Geosequestration Hub Project	This project proposes to develop a transport and storage hub collecting carbon dioxide captured from various facilities in Western Australia. The project aims to store between 2.5 and 7.5 million tonnes per annum of carbon dioxide in saline formations. AUSTRALIA	2.5 Mtpa	2015	Various CO2 capture facilities	Pre-Combustion and Post-Combustion	Deep Saline Formations
The Compostilla Project	This project uses oxyfuel and fluidised bed technology on a 30 MW pilot plant which will scale up to 300 MW. It has received funding from the European Energy Programme for Recovery (EEPR). SPAIN	1.1 Mtpa	2015	300 Mwe (Phase 2) coal-fired oxyfuel combustion power plant	Oxyfuel Combustion capture	Deep Saline Formations
TransAlta Project Pioneer	This project will capture 1 million tonnes per annum of carbon dioxide from one of TransAlta's three local coal-fired power plants, using Alstom's chilled-ammonia process. The carbon dioxide will be used for enhanced oil recovery or sequestered locally. CANADA	1 Mtpa	2015	450 MW gross coal-fired power plant	Post-Combustion capture	EOR or Geological
ULCOS Florange	The Ultra-Low-CO2-Steel (ULCOS) consortium proposes to build a prototype blast furnace that will be able to efficiently capture around 500,000 tonnes per annum of carbon dioxide from a steel plant. The CO2 will be stored in a deep saline formation. FRANCE	0.5 Mtpa	2015	Steel plant	Post-Combustion capture	Deep Saline Formations
Vattenfall Jänschwalde	Vattenfall's Jänschwalde project will capture 1.7 million tonnes per annum of carbon dioxide using oxyfuel and post-combustion capture at a 3000 MW lignite-fired power plant. Storage options in the area are under investigation. GERMANY	1.7 Mtpa	2015	300 MW equivalent (250 MW oxyfuel and 50 MW PCC) on a 3000 MW lignite-fired power plant	Oxyfuel Combustion and Post-Combustion	Deep Saline Formations
Victorian CarbonNet Project	The Victorian Government is developing this carbon transport and storage hub project in the state of Victoria. The project aims to collect between 3 and 5 million tonnes per annum of carbon dioxide from various capture facilities. AUSTRALIA	3.3 Mtpa	2018	Various CO2 capture facilities	Pre-Combustion and Post-Combustion	Deep Saline Formations

Appendix 2: CO2CRC/CSIRO Benchmarking Study

The following section lists the processing and economic assumptions and outputs from the CO2CRC/CSIRO benchmarking study.

Processing and economic assumptions

Table 1 Coal properties

Parameter	Value
HHV (MJ/kg)	10
LHV (MJ/kg)	8
Moisture content (%)	62
Ash content (%)	1

Table2 Economic assumptions

Parameter	Value
Thermal efficiency of power plant (% HHV)	29
Fuel (coal) cost (A$ / GJ HHV)	0.5
Project life (years)	30
Construction period (years)	3
Plant Capacity Factor (%)	85
Discount rate (% real)	10
Unit cost for solvent (A$ / kg)	1.8

All energy for the capture plant in this study is parasitically obtained from the original power plant. That is, the net energy sent out to the grid after capture will be less than 500 MW.

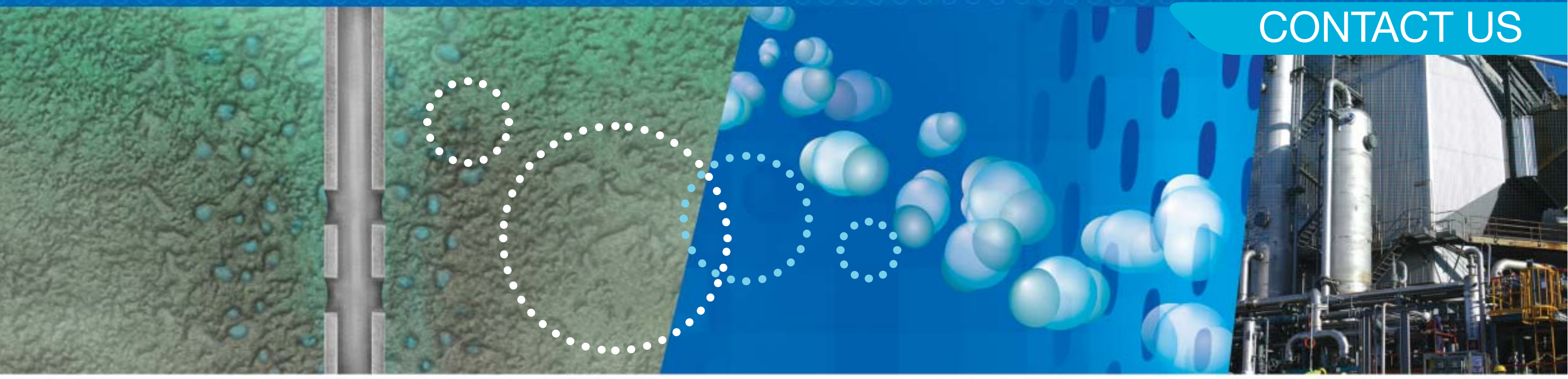
Table 3 Processing assumptions

Parameter	Value
Power plant (brown coal)	
Coal type	Brown (lignite)
Net power sent out before capture (MW_e)	500
Gross Output (MW_e)	540
CO_2 emission intensity before capture (t / MWh)	1.2
Capture plant	
Capture technology	Solvent absorption
Type of solvent used	MEA (30% weight)
Operating pressure of the absorption system (bar)	1.2
Operating temperature of the absorption system (Kelvin)	313 K
Operating pressure of the stripper (bar)	1.5
Operating temperature of the reboiler (Kelvin)	396 K
Kg of solvent loss per tonne of CO_2 captured	1.6
Lean Solvent Inlet Temperature (°C)	40
Lean solvent loading (moles of CO_2 / moles of Solvent)	0.21
Rich solvent loading (moles of CO_2 / moles of Solvent)	0.45
Pretreatment facilities if any	
Is SOxpretreated – FGD (Y/N)	Y
Is NOxpretreated – SCR (Y/N)	N
Is there direct contact cooler (Y/N)	N
Flue gas characteristics into absorption separation process	
Flue gas flowrate (m^3 / s or kg / s)	890 m^3 / s or 860 kg / s
Flue gas inlet pressure (bar)	1
Flue gas temperature (Kelvin)	366K before FGD
Flue gas compositions (% molar or volumetric)	
CO_2	12
N_2	60
O_2	3
H_2O	25
SOx	~200 ppm
CO_2 mass balance	
Overall recovery rate of CO_2 from the feed gas stream (%)	90
Percentage of CO_2 in the product stream (leaving CO_2 compressor) (%)	> 97
Pressure of the CO_2 product stream leaving the stripper (bar)	1.2
Pressure of CO_2 stream leaving CO_2 compressor (bar) / temperature (°C)	100 / 40

Output comparison

Table 4 Economic output from CSIRO and CO2CRC economic models

Parameter	CSIRO value	CO2CRC value
Energy penalty		
HHV reduction [%]	28.9% HHV reduced to 17.1% HHV	29% HHV reduced to 16% HHV
Net MW_e reduction	46% (0.46*500 = 230 MW_e)	230
Net MW_e sent out after capture	288.8	270
CO_2 mass balance		
CO_2 emission intensity before capture (t / MWh)	1.2	1.2
CO_2 emission intensity after capture (t / MWh)	0.176	0.22
□CO_2 emission intensity (t / MWh)	1.024	0.98
Amount CO_2 captured (MMtonnes / yr)	3.8	3.987
Amount CO_2 avoided (MMtonnes / yr)	2.1	1.932
Capital costs		
CAPEX (A$ million) - capture plant only	700	680
CAPEX (A$ million) - power and capture plants	2,100	2,250
Operating costs		
OPEX (A$ / MWh) - capture plant only	40	36
OPEX (A$ / MWh)- (capture and power plant operating costs). Includes amortisation for capture	83	72
OPEX (A$ / MWh) - Total (power and capture plants) Fully amortised (both new plant and capture train)	64	65
$ / tonne CO_2 avoided		
Cost of CO_2 avoided (A$ / t), Fully amortised power plant, new capture plant	75	78
Cost of CO_2 avoided (A$ / t)	136	113
Cost of Electricity		
Cost of electricity generation (A$ / MWh) before capture	60	42
Variable operating cost for fuel (A$ / MWh)	10	7
LCOE (A$ / MWh) generation after capture (new plant + capture)	191.5	153
□ COE [A$ / MWh]	131.5	111
LCOE (A$ / MWh) generation after capture (for capture only). Fully amortised power plant (neglects capital and operating costs of power plant)	83	80



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