Final Report for Brown Coal Innovation Australia (BCIA)

CO2CRC UNO MK 3 Capture Project

[CO2CRC's Solvent-Based Carbon Capture Technology in Brown Coal Fired Power Plants (CSCCT-BCFPP) –

Capture Demonstration for Cost Reduction]

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Executive Summary

This report summarises the outcomes of the CO2CRC UNO MK 3 capture pilot plant project (July 2011 – June 2014), mostly funded by Brown Coal Innovation Australia (BCIA), located at the GDF SUEZ Australian Energy's Hazelwood power station. UNO MK 3 is a precipitating potassium carbonate based solvent technology that has been developed since 2003 through liquid potassium carbonate based trials at the University of Melbourne and at the Hazelwood power station. The UNO MK 3 solvent promises numerous benefits over amine-based solvents. The carbonate/bicarbonate reaction has a fundamentally low regeneration energy requirement. It is oxygen tolerant, less volatile, non-toxic and less corrosive which reduces the overall environmental impact of the process. Potassium carbonate can also capture sulphurous oxides (SO_x) and nitrous oxides (NO_x) which reduces or eliminates the need for dedicated SO_x and NO_x removal equipment and can produce valuable fertilizer by-products. Solvent costs and equipment costs are also expected to be lower than amine-based solvents.

The UNO MK 3 process has a higher concentration compared to traditional liquid based potassium carbonate processes, such as those seen in gas separation processes often under the Benfield^{TM} trade name. The benefit of moving to higher concentrations is to lower solvent regeneration requirements and therefore lower energy penalties.

The weakness of potassium carbonate solvents is their slower reaction kinetics compared to amine solvents resulting in lower rates of CO_2 capture when used in flue gas with low partial pressure of CO_2, as found in post-combustion capture. However, the absorption rate of CO_2 can be increased by adding rate promoters to the solvent, having enhanced absorbers and ensuring optimised operating conditions and process design. Further consideration also needs to be made for the added complexity of precipitation of the solvent, which requires solids tolerant absorbers and associated equipment.

The current project equipment was the result of modification of a solvent pilot plant used in CO2CRC pre-combustion trials for CO_2 separation from a gasifier using UNO MK 2; a potassium carbonate based solvent system without precipitation. Modifications included increasing the absorber height, moving from random to structured packing, increasing the plant automation and control, adding solids tolerant pumps and heat exchangers and solids separation equipment. The project also trialled two additional absorption technologies; the WES absorber, the results of which were reported in a separately funded BCIA project and the FTL/Osprey TurboScrubber®.

The objectives of the project were to trial and demonstrate the UNO MK 3 process using real flue gas. Specifically it included trialling UNO MK 3 with and without a promoter blend, solid separation and handling, and, impurities removal using ion exchange bed. It also included validating simulation models, assessing heat and process integration, and updating economic estimates.

Campaign 1 with non-precipitating solvent was used to stabilise operations, to provide a benchmark for simulation models and to compare against previous trials. Despite experiencing difficulties in accurately confirming the effects of operational parameters on the absorption rate, it was observed that lowering gas rates and increasing solvent temperature appeared to improve the absorption rate. As expected, the 30 wt% un-promoted solvent absorbed between 4 and 17 % of the incoming CO_2 with 5.8 m of packing.

Campaign 2 was used to trial the pilot plant with a precipitating solvent, to provide a base for modelling and to compare the impact of the promoter in subsequent campaigns. Intermittent operation

of the plant, as opposed to 24/7 continuous operation, caused delays from start-up to stabilisation and reduced the time available each day for trials. Flooding in the absorber also rendered stable operation difficult. The CO_2 capture rate was low, but in line with expected results and also with results from Campaign 1. The precipitates were suitably characterised, which provides a good reference point for designing future plants.

Campaign 3 used the P1 solvent blend which contained a rate promoter. The CO_2 capture rate varied from 10 to 50 % under a range of conditions, with decreasing superficial gas velocities having the biggest positive influence and increasing solvent rates also having a positive effect. The issue of premature absorber flooding continued to be a constraint and occurred more frequently and over a wider range of conditions than in Campaign 2. The use of an antifoam added in batches to the solvent resulted in longer run-lengths before flooding was observed, but did not alleviate the issue altogether. The promoted solvent improved the absorption rate by 2 to 2.8 times the un-promoted solvent. There was no observable deterioration in the capture rate as a function of time over the 44 days of operation in this campaign.

Sodium glycinate, a generic commercial amino acid solvent was used in Campaign 4 to provide a comparison to a solvent with rapid reaction rate. The short campaign operated only at high gas rates (180 kg/hr) and the average absorption rate was 43 % with a strong dependency of the absorption rate on the liquid rate. The sodium glycinate had no flooding issues over the short operating time (9 days); more time would be required to test the long term effects of operation on the foaming and flooding tendency of this solvent.

In Campaign 5 the structured packing in the absorber was replaced with FTL/Osprey's TurboScrubber® fluidised bed packing. Two packing configurations (PC-A and PC-B) were established and new packing types (PT-1 and PT-2) were employed in the tests. The packing proved to be very solids tolerant and could operate without any observable impact caused from foaming. It has a wide gas and liquid velocity operating range and optimal performance is generally achieved at higher gas rates. This can result in smaller diameter absorber columns relative to packed bed systems. Due to equipment constraints this feature was not fully explored or exploited in the current trials. The total pressure drop was in line with FTL/Osprey's predictions. It was higher than the structured packing, but still lower than 10 kPa, which is generally considered maximum for post-combustion capture. Different packing types with variable size, shape and density are available and other packing types are under development that will help to increase efficiency per unit height and lower the pressure drop. The absorption rate varied considerably depending on the gas rate and the solvent rate, concentration and loading. The rate varied between 1.5 and 14 % with an average of 5 %. These rates are comparable to, or better than, the structured packing per unit height for PT1 and PT2 based on unexpanded bed heights and similar gas and liquid rates. As observed in the trials, new proprietary shapes have apparent interfacial areas per volume that are potentially significantly above the structured packing used in the trials. Furthermore different density, size and shape versions of PT-2 and other 'PT-3' packing types are under development/consideration where additional area and lower pressure drop are anticipated. Additionally increases in the capture rate are likely with internal recycles to increase the turbulence, hold-up and interfacial area.

The mean particle diameter of solids obtained from the absorber from two trials under two different set of conditions were found to be 161 and 229 μm. Downstream of the rich solvent cooler a single test provided a mean particle diameter of 78 μm. As expected, the mean particle size was smaller downstream of the cooler compared to the absorber due to rapid cooling in the cooler. The structured packing, as expected, flooded under conditions where solids were likely to occur. It was not possible to isolate whether the flooding was caused by an excessive level of solids, by foaming or a combination of the two. The rich solvent pump and lean-rich heat exchanger operated well under the solids load.

The upstream once through direct contact cooler (DCC) was so efficient in removing the SO_x and NO_x that the sulphate and nitrate level in the solvent did not build up sufficiently during the trials to require the ion-exchange removal process to be operated. The level of SO_x and NO_x removal in the DCC was greater than expected as the water to gas ratio was much larger than the design due to the large scale solvent plant not operating during the trials. In lieu of operating the pilot plant ion exchange column, more laboratory tests were conducted on different ion exchange resins at varying concentrations of sulphates, nitrates and carbonates. Dowex 1 resin is capable of providing the required sulphate and nitrate removal rates, however a resin was identified for nitrates that is less affected by carbonates than Dowex 1. This suggests it may be possible to find a better resin for sulphates and the system can be further improved.

Aspen Plus® models were tested for the pure potassium carbonate for Campaigns 1 and 2. For Campaign 1, the rate based models generally agree with the experimental results within the experimental uncertainty. As rate based models cannot currently be used with precipitating solvents an equilibrium model was used for Campaign 2. Thermodynamic models for the P1 solvent were generated with good correlation for physical properties and vapour-liquid-solid equilibrium especially with loadings less than 0.4. Improvements have been made to a theoretical rate limited model based on the Dankwerts enhancement factor which has shown good correlation between pilot plant results across Campaigns 1 to 3.

Large scale designs of the UNO MK 3 process retrofitted to a 500 MW brown coal fired power station were completed. These indicate that the UNO MK 3 process should significantly cut the cost of CO_2 avoided and the levelised cost of electricity (LCOE) compared to conventional amine processes at large scale. A range of process improvements offer additional reductions in the costs. Changes to the process designs or assumptions that may lead to a doubling of the absorber packing height or an increase in the regeneration duty from the estimated 2.5 GJ/t to 2.8 GJ/t, each resulted in an increase of approximately 5 % in the cost of CO_2 avoided.

Options for auxiliary units have been assessed to enable the existing power station output to be maintained. An auxiliary coal fired power boiler, a parallel gas turbine (GT) and a hot windbox repowering using a gas turbine were assessed in detail. The coal fired auxiliary requires minimal intervention with the existing power plant. The parallel GT requires some modifications to the LP turbine of the main plant unless an oversized GT is installed and the total power output of the power station is increased. The hot windbox GT requires at least the same amount of modifications as would be required for the base CO_2 capture plant without the auxiliary. The emissions intensities (kg/MWh) are very different for each option and in part this leads to different abatement costs for the three cases. The LCOE is highly dependent on the natural gas price and the price on carbon. A range of prices have been estimated based on natural gas prices between $4 /GJ and $12 /GJ and carbon prices of between $0 and $200 per tonne of CO_2. The coal-fired auxiliary unit has the lowest LCOE when there is no carbon price. The hot windbox is the preferred option for low natural gas prices, provided there is at least a moderate price on carbon (>$20 /t). As natural gas prices increase the coal fired auxiliary boiler progressively becomes more attractive provided the carbon price remains below $50 /t.

The UNO MK 3 process may increase the cooling duty of the total power station by 60 %. The options of using air cooling heat exchangers for the power station or the capture plant or both have been assessed. The water requirements will reduce from the current levels even if only the capture plant uses air cooling rather than water cooling. The preliminary economic assessment suggests that the LCOE impact of moving to air cooling will be between $1 /MWh and $2 /MWh whilst reducing the annual water use from a wet cooled power station with capture by 10 to 17 GL.

The pilot plant provided an invaluable source of information for developing the UNO MK 3 process, including the performance of the rate promoters, the solids characterisation, the impurities removal processes and various pieces of absorber and downstream equipment. Laboratory experiments and laboratory scale pilot plant data were able to be validated and models to predict the performance of the system were tested and improved. Further research is recommended to develop the UNO MK 3 process including:

- Validation of the predicted solubility of the P1 solvent;
- More incorporation of promoter chemistry into the theoretical models and/or develop methods to incorporate the impact of precipitation in the rate based Aspen Plus® models;
- Trialling of more active rate promoters at the pilot plant scale;
- Identification of the mechanism for absorber flooding and development of a method to avoid it becoming an operational constraint;
- Increasing the height of the packing and/or modifying the equipment and/or process design to test the process with 90 % capture rate;
- Running the plant continuously to assess the effect of long-term operation on performance.

Publications

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1 Introduction

The United Nations International Panel for Climate Change (IPCC) indicates that to provide at least 50 % chance of the global average temperature rising no more than 2 °C since 1861-1880 requires the cumulative CO_2 emissions from all anthropogenic sources to be less than 4,440 $GtCO_2$ (IPCC 2013). To ensure the temperature rise is limited to less than 2 °C by 2050 requires annual CO_2 emissions to reduce by more than 50 % in 2050 compared to the emissions in 2011. The International Energy Agency (IEA) suggests that a portfolio of options is required for the least cost scenario to achieve the required reductions in emissions (IEA 2014). In the 2DS scenario, they suggest that up to 14 % of the required reductions can be achieved using Carbon Capture and Storage (CCS) from the energy, fuel transformation and industrial sectors.

Victoria has over 6000 MW of installed pulverised coal fired power stations accounting for more than 70 % of the installed electricity generation capacity and over 500 years of accessible brown coal reserves available for continued electricity generation (DPI 2008). Therefore it is critical to ensure options exist to maintain the viability of the existing fleet of power stations and the vast reserves of brown coal within a carbon constrained environment.

CCS has the potential to significantly reduce greenhouse gas emissions from thermal power stations fired by fossil fuels. However, significant reductions in the cost of CCS need to be achieved to facilitate large-scale implementation. With the cost of capturing CO_2 from the emission source often representing 60 % to 80 % of the total cost of CCS, there has been considerable research on reducing this cost through improving capture processes.

Solvent absorption of CO_2 from power station flue gases is arguably the most advanced of the capture technologies, which also include gas separation membranes, gas adsorbents and oxyfuel combustion. Amine-based solvents are often considered the favoured solvent technology for post-combustion capture because of the high rate of reaction that is beneficial for gases with low partial pressure of CO_2. However, potassium carbonate based solvents, as investigated in this project promise numerous benefits over amines in regard to lower regeneration energy, lower overall costs, lower volatility and environmental impacts and the option of multi-impurity capture with linkages to the fertiliser industry.

1.1 Project drivers

Since 2003, the CO2CRC has harnessed the efforts of leading researchers from Australian and international Universities and research institutes, government organisations and top international companies to drive down CO_2 capture costs. The focus has been on: a) solvent absorption, b) membrane, c) adsorption, and d) cryogenic separation for a range of applications in post-combustion and pre-combustion. The first three technologies have been tested in pilot plants under real power plant conditions (both post and pre-combustion in two separately funded projects funded by the Victorian State Government through their Energy Technology Innovation Strategies (ETIS) program with extension funding from BCIA). This has established an enviable base on which we have grown a leading edge separation research capability with practical engineering experience. Current funding, provided substantially by Brown Coal Innovation Australia (BCIA), has allowed us to further develop the solvent technology.

Innovations from our core program and our plant based experience have led to concepts for the development of a new solvent process based on potassium carbonate with anticipated benefits over existing solvent processes as described previously. 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 and improving the packing in the absorber and regenerator columns. The initial CO2CRC concept for a liquid based potassium carbonate system for CO_2 capture was patented under the name of UNO MK 1 (Hooper et al. 2006).

Up until recently, no system had exploited the ability of bicarbonate, formed by the reaction of carbon dioxide with carbonate, to exceed its solubility limit. When the bicarbonate exceeds the solubility limit and precipitates from solution, the partial pressure of the CO_2 in the liquid reduces and allows more CO_2 to be absorbed from the flue gas. Traditional potassium carbonate systems, including UNO MK 1, operating as liquid systems can only be viably employed when the pressure driving force for CO_2 is high, which is not the case for post-combustion capture. Using a precipitating system not only improves the driving force for CO_2 removal, it also significantly reduces the flow rate of solvent required and the reboiler energy usage compared with amine-based solvent processes. Research conducted at the CO2CRC through our core program has confirmed the thermodynamic benefits of a precipitating system. In addition, extensive process modelling has indicated that the energy requirements for the carbonate based capture system can be reduced from 3.5 GJ/tonne of CO_2 captured for a traditional amine based system to around 2.4 GJ/tonne of CO_2 captured for a precipitate based system. The CO2CRC concept for a precipitating based potassium carbonate system was patented under the name of UNO MK 3 (Hooper et al. 2011).

Another considerable challenge to traditional solvent systems is the presence of oxygen and impurities such as SO_x and NO_x in the flue gas, which cause degradation of the solvent resulting in the subsequent requirements for pre-treatment or solvent rectification and solvent make-up. The CO2CRC's UNO MK 3 process incorporates impurity removal in an effective manner. As such the additional equipment required is minimised and marketable by-products are produced.

For this project, our aim was to validate our thermodynamic laboratory work and further improve our simulation models developed from the Australian National Low Emissions Coal Research and Development (ANLEC R&D) funded lab-scale precipitating column trials using simplified feed gas. The research used a precipitating potassium carbonate pilot plant under real flue gas conditions. This is an important step forward for large-scale implementation of our solvent technology. Field testing was designed to build confidence in plant operation and to improve the full-scale design and costing of our solvent process at commercial scale. It also improved our current knowledge of equipment design for slurry systems and our impurities removal process at the pilot scale.

A particular challenge of potassium carbonate systems is the slow kinetics which for post-combustion capture requires enhancement by the addition of a promoter and/or equipment to improve the mass transfer in the absorber to compete with faster chemical solvents. In order to enhance the process recovery with UNO MK 3 technology, trials were undertaken using a novel packing (TurboScrubber®) and also using unconventional absorber/internals designed and manufactured by Westec Environmental Solutions, LLC (WES Absorber^{TM} Technology). The latter trials were completed under a separately funded BCIA project and are not reported here.

As part of this project, our younger engineers, PhD students and Postdoctorial Fellows gained invaluable design and operating experience. In addition, design, construction, installation, commissioning and operation of the pilot plant provided opportunities for the development of local skills and expertise for solvent-based CO_2 capture equipment.

1.2 Project scope

The project involved the operation of a pilot plant designed for the UNO MK 3 solvent system located at the GDF-SUEZ Australian Energy brown coal fired power station at Hazelwood. Plant data was used to aid in and improve the modelling, large scale design and economic assessment of the system. The project scope included:

1. Design, modification and relocation of the UNO pilot plant used in the ETIS pre-combustion solvent plant to Hazelwood Power Station for demonstration of the CO2CRC's UNO MK 3 process.
    a. Complete detailed design of pilot plant modifications;
    b. Order and construct/modify new equipment;
    c. Install and commission pilot plant at Hazelwood.
2. Run pilot plant, collect operating data and analyse results.
    a. Undertake detailed planning of plant operation schedules and personnel requirements;
    b. Operate plant and collect operating data;
    c. Collect operating data over a range of conditions in order to assess optimal performance of the precipitating solvent system;
    d. Test novel packing;
    e. Analyse results including validating simulation models.
3. Use GDF SUEZ flue gas in the pilot plant to test, validate and improve the thermodynamic model of the solid-liquid-vapour equilibrium system of potassium carbonate/bicarbonate from the experimental work completed in the lab (funded by ANLEC R&D).
    a. Based on the results of the experimental column work (funded by ANLEC R&D), identify further trials in the pilot plant;
    b. Update thermodynamic model with experimental and pilot plant data;
    c. Incorporate updated thermodynamic model into APSEN Plus^{TM} in collaboration with Aspentech.
4. Develop simulation models from thermodynamic modelling and pilot plant data for the design and costing of a large scale plant.
    a. Determine large-scale simulation inputs from pilot plant data;
    b. Complete simulation and sensitivity studies where necessary;
    c. Complete detailed costing of equipment based upon simulation results.
5. Optimise equipment design for slurry handling systems.
    a. Undertaken performance monitoring during operation;
    b. Develop a model for particle size distribution of the bicarbonate system for large-scale removal system design;
    c. Identify equipment operability issues and potential solutions;
    d. Incorporate solutions into pilot plant where feasible;
    e. Develop recommendations for equipment design.
6. Optimise equipment design for impurities removal systems.
    a. Complete detailed design of impurities removal systems for incorporation in pilot plant;
    b. Undertake performance monitoring during operation;
    c. Identify equipment operability issues and potential solutions;
    d. Incorporate solutions into pilot plant where feasible.
7. Examine cost effective heat integration methodologies including the impact of auxiliary heating, air cooling and alternate stripper designs.

8. Develop front-end engineering design of larger-scale precipitating solvent system for a fast-track PCC project.
9. Obtain data on solvents over a range of operating conditions.
10. Perform economic assessment.
11. Facilitate WES Absorber^{TM} Technology tests (under separate BCIA project not reported here).

2 Overview of the project

2.1 UNO MK 3 process description

The UNO MK 3 process is a precipitating potassium carbonate (K_2CO_3) process developed by the CO2CRC. The reaction of CO_2 with K_2CO_3 to form potassium bicarbonate ($KHCO_3$) occurs through the following overall reaction.

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2KHCO_3 \quad [1]$$

Potassium carbonate has a number of advantages over traditional amine based solvents. It is oxygen tolerant, less volatile, non-toxic and less corrosive which reduces the overall environmental impact of this process. Potassium carbonate can also capture SO_x and NO_x which reduces or eliminates the need for dedicated SO_x and NO_x removal equipment and can produce valuable fertilizer products. Solvent costs and equipment costs are also expected to be lower than amine based solvents.

The main challenge associated with the potassium carbonate based process is the slow rate of reaction resulting in the need for large and therefore expensive equipment when used for post-combustion capture of CO_2 where the partial pressure of CO_2 is low. In order to improve reaction rates, promoters can be added to the system.

The UNO MK 3 process contains the absorption and regeneration stages of a standard solvent absorption process as shown in Figure 1. However, unlike a standard liquid-based solvent system the concentration of potassium carbonate is increased so that a $KHCO_3$ precipitate is formed during absorption and subsequent cooling. The precipitate is then separated from the liquid phase for selective regeneration of the $KHCO_3$ species. The higher concentration of solvent allows for greater CO_2 absorption capacity reducing the solvent circulation rates. In addition, the precipitation enables further reduction in the overall solvent circulation rates reducing the amount of water passed to the regeneration stage thus driving down the solvent regeneration requirements from over 3 GJ/tonne CO_2 for a liquid system to less than 2.5 GJ/tonne CO_2 for a precipitating system.

Another feature of the UNO MK 3 process is the ability to tolerate flue gas impurities such as SO_x and NO_x, which will react with the K_2CO_3 solvent to form the valuable fertiliser by-products, potassium sulphate (K_2SO_4) and potassium nitrate (KNO_3) according to the following reactions.

$$SO_2 + H_2O + \tfrac{1}{2}O_2 + 2K_2CO_3 \rightarrow K_2SO_4 + 2KHCO_3 \quad [2]$$

$$2NO_2 + H_2O + \tfrac{1}{2}O_2 + 2K_2CO_3 \rightarrow 2KHCO_3 + 2KNO_3 \quad [3]$$

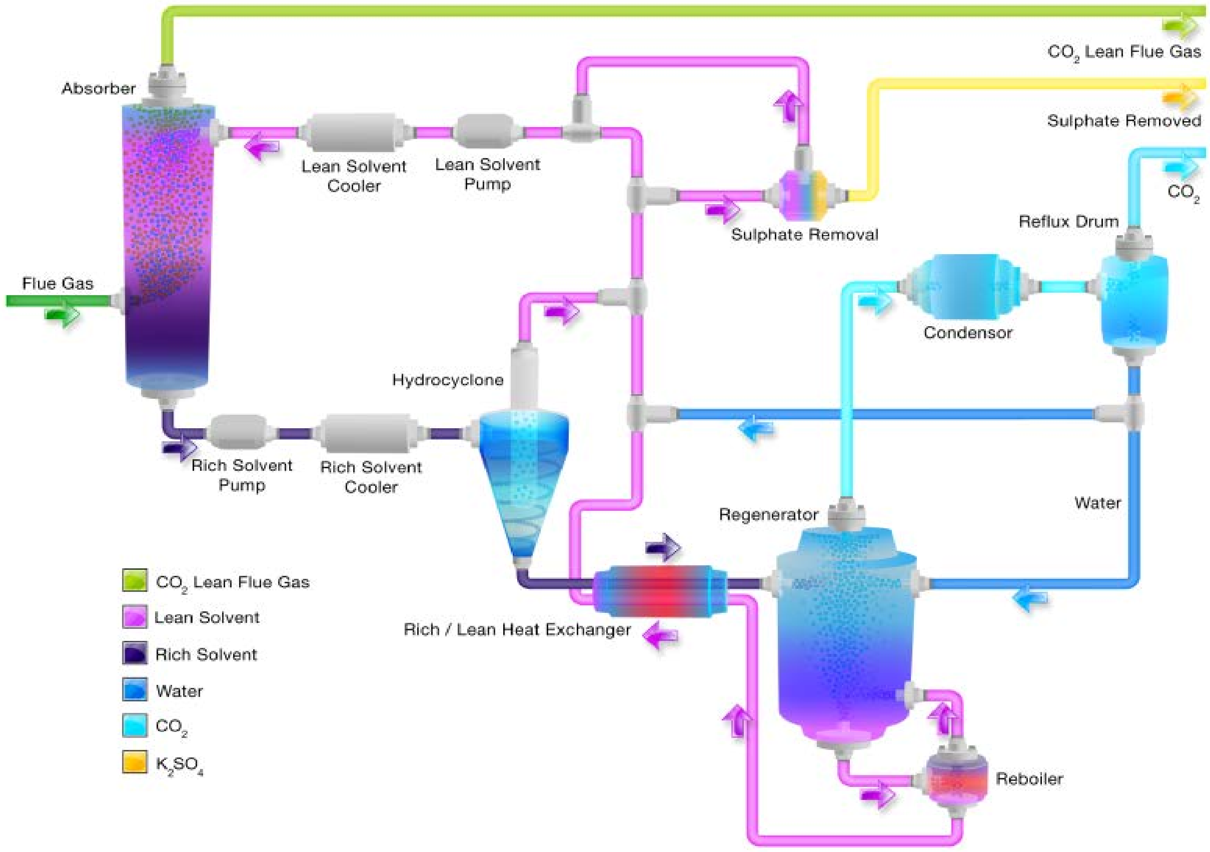

Figure 1: UNO MK 3 process flow diagram.

2.2 Pilot plant details and construction

2.2.1 Pilot plant description

The ETIS pre-combustion solvent pilot plant was modified into the UNO MK 3 Hazelwood pilot plant (UPP) and located adjacent to the existing large solvent based GDF SUEZ owned Carbon dioxide Capture Plant (CCP) at Hazelwood. The CCP is fed by approximately 1 % of the flue gas from Unit 8; a 220 MWe subcritical coal fired boiler. The flue gas is extracted downstream of the Unit 8 induced draft fan and is therefore also downstream of the plant's electrostatic precipitator. The flue gas diverted from the Unit 8 stack is sent directly into the bottom of the CCP's direct contact cooler (DCC) where it is contacted counter-currently with a spray of cooling water intended to reduce the flue gas temperature from ~240 °C to 40 – 50 °C. The once-through cooling water flowrate is controlled by a temperature controller to maintain the gas outlet temperature of the flue gas, with a minimum flowrate set to maintain the minimum the flowrate of the cooling water through the outlet pumps. The gas inlet to the UPP is extracted from the outlet of the DCC upstream of the CCP's flue gas blower; this enables the UPP pilot plant to operate with only the DCC of the CCP. The design gas conditions are provided in Table 1.

Table 1: Hazelwood and UNO MK 3 carbon capture plants flue gas design basis.

Item	Unit	CCP	UPP
Flue Gas Flowrate	(kg/hr)	6400	200
Temperature	(°C)	240	40
Pressure	(kPag)	2	< 2
Gas Composition			
CO_2	mol %	13	15.3
N_2	mol %	62	72.4
O_2	mol %	3.5	4.1
H_2O	mol %	20.5	7.4
Ar	mol %	0.8	0.8
NO_x	ppm (vol) (dry basis)	151	< 150
SO_x	ppm (vol) (dry basis)	212	5

The UPP described herein and shown in the process flow diagram (PFD) (Figure 2) was designed specifically for development and testing of the UNO MK 3 solvent, but can also be used with a variety of solvents. The aim of the capture plant was to separate CO_2 from the power station flue gas by absorption with a potassium carbonate based solvent (UNO), either in a conventional absorption tower, or a new type of absorber (the WES^{TM} absorber).

The flue gas from the DCC enters the UPP blower, B-001 which compresses the gas from 2 kPag to a nominal pressure of 10 kPag to overcome the pressure drop in equipment piping, the absorber and the pressure in the discharge line for the flue gas. The gas rate is controlled by a manual butterfly valve FCV-009 and/or a manual butterfly valve that recirculates the gas back to the suction inlet of the blower. It then enters the absorber V-001 where it ascends through two sections of Sulzer Mellapak 350X structured packing to be brought into contact with the lean solvent solution (lean in CO_2). As the gas rises through the column, the CO_2 concentration in the gas is progressively reduced as the CO_2 passes into the solvent. The lean flue gas (lean in CO_2) exits the top of the absorber and is piped into the CCP CO_2 discharge line to the Unit 8 power station chimney upstream of the induced draft fan. The pilot plant was designed to capture 18 to 33 % of the CO_2 at the low and high liquid rates at design gas rates using UNO MK 3 in the conventional column.

The gas exiting V-002 contains CO_2 removed from the solvent. It passes through the overheads condenser H-003, a plate type heat exchanger, to condense as much of the associated water vapour as possible. The fluid then passes through the reflux accumulator V-003 to separate the vapour and liquid streams. The water stream is then pumped back to the top of the regenerator V-002 via the reflux pump P-002. The process is operable under conditions where water accumulates in the solvent, is lost from the solvent or the water balance is neutral. If water accumulates in the solvent it can be drained under level control LCV-003 from the reflux accumulator to a dilute solvent IBC. If water is lost from the solvent, make-up water is added intermittently to maintain the solvent concentration.

The product gas stream that exits the top of the reflux accumulator is water saturated CO_2 at approximately 50 kPag and 50 °C. This stream is returned along with the lean gas to the power station chimney via the CO_2 discharge line.

UNO MK 3 solvent precipitates easily as it cools and can potentially cause blockages in pipes and other equipment. Therefore, when the plant was not in use, the solvent was stored in the reboiler and the electric heater was used to maintain a minimum temperature to avoid precipitation. Three IBC's were maintained on-site for make-up solvent, reflux water/dilute solvent and for waste water.

The UPP was controlled by a stand-alone unit control panel (UCP) controlled by an Allen Bradley CompactLogix Programmable Logic Controller (PLC). Interfacing with the PLC was via an Allen Bradley Human Machine Interface (HMI) located in the existing CCP hut. The plant instrument data was recorded to an onsite laptop that captured data for most instruments on the plant every five seconds.

2.2.2 Pilot plant modifications

The following lists the major equipment changes made in converting the pilot plant for post-combustion capture using UNO MK 3.

- New Feed gas blower (B-001);
- Replaced feed gas (FIT-001), lean gas (FIT-002) and CO_2 (FIT-006) flowmeters;
- Doubled the absorber (V-001) height and replaced random packing with structured packing;
- New Rich solvent slurry pump (P-003);
- New Rich solvent cooler (H-005);
- New Variable Speed Drive on the lean solvent pump (P-001);
- New hydrocyclone (DS-001) and manual globe valves for flow control, pressure and flow indicators;
- Replaced the lean/rich plate heat exchanger (H-002);
- Increased the pilot plant instrumentation and automation;
  - New pressure control on the regenerator overheads (PCV-003);
  - New level control (LCV-003) and reflux flow control (FCV-003) on the reflux system;
  - New temperature control on the lean solvent cooler (TCV-007), overhead condenser (TCV-011) and rich solvent cooler (TCV-006);
  - New DP meters across the two packed sections of the absorber (PDIT-001/2);
  - New Rich solvent Coriolis mass flowmeter (FIT-003);
  - Various temperature indicators;
- New cooling water booster pump (P-004);
- New solvent filter (F-001) and reclaimer (F-002);
- New programmable logic controller (PLC), HMI and motor control centre (MCC);
- New heat tracing on the rich solvent equipment and piping;
- New skid for the absorber and the WES absorber;
- All civil, piping, electrics, instrumentation and software to integrate the plant with the power station.

2.2.3 Absorber packing

The 16 mm super mini rings used in the absorber during the pre-combustion trials would have operated above the flood point during the post-combustion capture trials. Therefore selection of replacement packing for the UPP considered the following:

- Specific area of the packing;
- Effective area of the packing;
- Flooding point;
- Pressure drop;
- Liquid hold-up;
- Propensity for fouling;
- Ability to model the packing in Aspen Plus®.

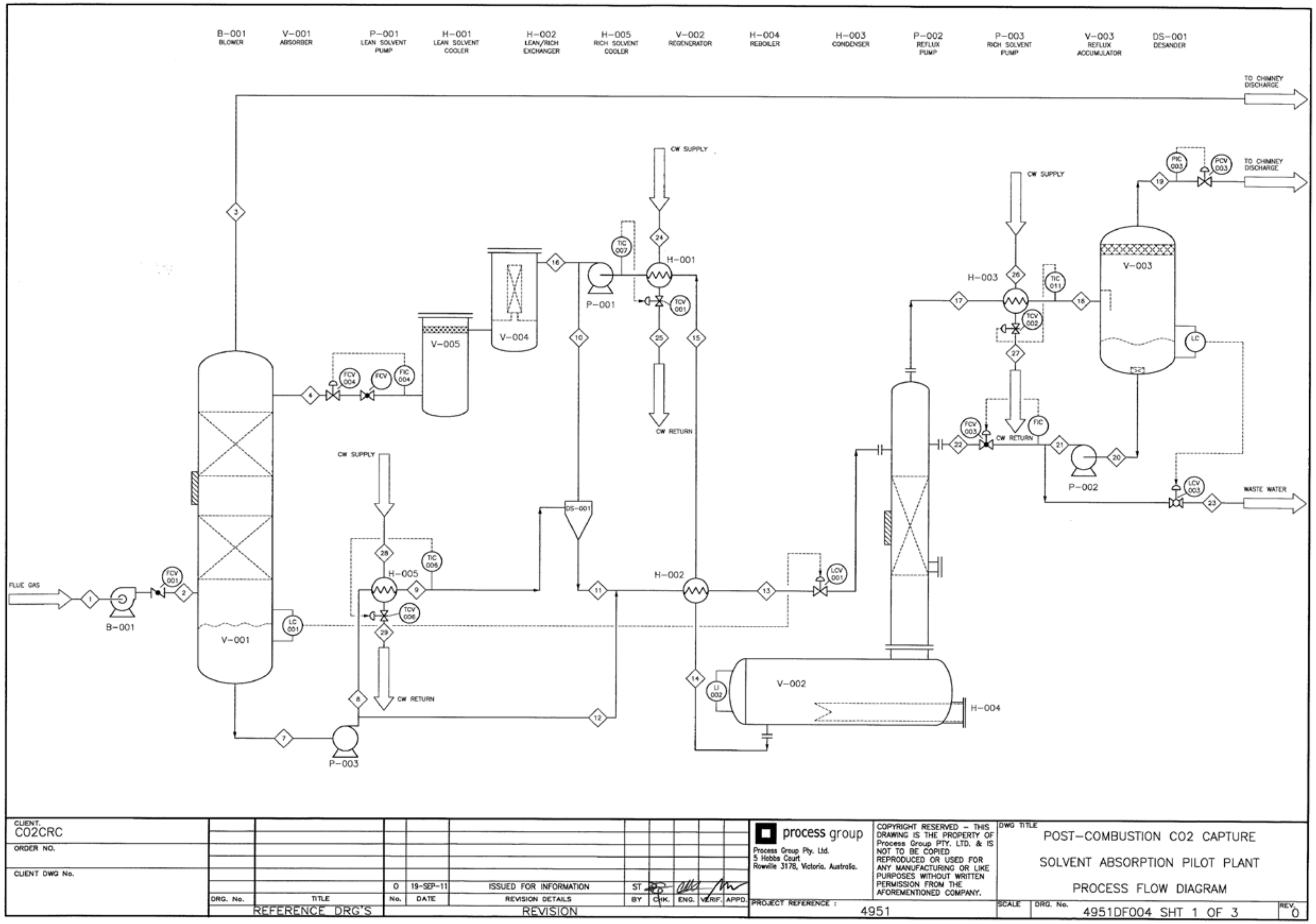

Figure 2: UPP process flow diagram (not including WES absorber).

The ideal packing has a high specific area and also a high wetted area at the liquid rates used in the pilot plant. The high area ensures that the absorption of CO_2 from the gas to the liquid is as high as possible.

The flood point relates to the operating window of the packing. As the gas and to a lesser extent the liquid rates increase, the amount of liquid that is held up in the packing increases until the amount of liquid exiting the column is less than that entering it. The plant must run below the flood point; running around 80 % of the flood point is generally a good design point.

The pressure drop has a small impact on the pilot plant. Lower pressure drops are advantageous in larger scale designs as the amount of energy required for the flue gas blowers increases with pressure drop. However for the pilot plant this was not as much of a concern as long as the total pressure drop (including piping, valves, distributors) was less than approximately the 5 to 10 kPa that the blower can provide.

The liquid hold-up was an important consideration as it influences the solvent residence time. As the residence time increases, sufficient time is provided for the rate limiting step of conversion of CO_2 in the liquid to bicarbonate to proceed.

The propensity to fouling was also an important consideration as we anticipated precipitation of the bicarbonate occurring in the column. Typical bicarbonate crystals in the lab are between 2 – 5 mm. However if the crystals are trapped in the column they may grow larger in size.

There is a trade-off between these parameters. As the specific area increases usually the liquid hold-up and the pressure drop will increase. Also the gaps in the packing will reduce as specific area increases, which will increase the propensity for fouling and blockages to occur.

Two cases were considered in the design; the gas flow rate was designed at 186 kg/hr with liquid-to-gas ratio (L/G) of 2 (low flow) and 6 (high flow). The hydraulic performance was estimated using SULCOL, a proprietary Sulzer sizing program (Table 2). Packing type M350X was selected as it maintained the desired minimum absorption performance below the flood point, provided low pressure drop and greater gap sizes than the lab based crystal size predictions of the potassium carbonate process.

Table 2: Hydraulic performance of alternative packing types for use in the UPP absorber.

Items	Units	M250X	M350X	M500X	M750Y	IR15
Absorber – High Flow						
Gap size	mm	9 – 10	6 - 8	4 - 5	-	-
Capacity	%	54	59	71	94	80
ΔP	kPa	0.45	0.64	1.05	5.4	3.0
Surface Area	m^2/m^3	250	350	500	750	291
Effective Area	m^2/m^3	~230	-	-	-	-
Hold-up	%	9.1	11.6	16	22	15
Absorber – Low Flow						
Capacity	%	42	46	53	72	58
ΔP	kPa	0.40	0.54	0.8	2.4	2.3
Effective Area	m^2/m^3	~190	-	-	-	-
Hold-up	%	5.8	7.5	10	12.7	7.9

2.2.4 Pilot plant construction

As much as practical, the pilot plant modifications were completed in the Process Group factory in Rowville, Victoria. The pilot plant was then transported and installed at the Hazelwood site. Photos in Figure 3 show various stages from the start of modifications to installation. The plant was delivered to site in two skids – the regeneration column skid and the absorber skid. This two-skid arrangement was developed when the detailed designs of the absorbers were completed. An outdoor Motor Control Centre (MCC) cabinet and a HMI screen were other new requirements identified during the final detailed design stages. Other items that were installed and prepared at site included solvent container bunding, a safety shower, fencing with a gate and signage, emergency shut-down button, tagging for all valves and instruments and locks for maintenance isolation. Analytical tools and space were also established within the GDF SUEZ site laboratory at Hazelwood.

Figure 3A: Pre-combustion UNO rig before modifications.

Figure 3B: Rig under construction at Rowville.

Figure 3C: Civil construction at site.

Figure 3D: Rig installation at site.

Figure 3E: Installed rig at site.

Figure 3: Pilot plant construction photos

2.3 Pilot plant campaigns

The pilot plant was operated for a total of five campaigns; 1. Un-promoted liquid K_2CO_3 campaign, 2. Un-promoted precipitating K_2CO_3 campaign, 3. Promoted UNO MK 3 precipitating campaign 4. Commercial solvent campaign. 5. TurboScrubber® campaign using UNO MK 3 solvent.

Each of the first four campaigns involved tests in both the conventional absorber and the WES™ absorber. Data from the latter absorber are not reported here. The primary solvent tested was potassium carbonate in either precipitating or non-precipitating mode and with or without a promoter. Campaign 4 used a commercial solvent for benchmarking purposes.

The specific objectives of each campaign were as follows and the outcome status for each objective is also provided in Table 3.

Table 3: Pilot plant detailed campaign objectives.

Campaign/Objective	Status
1. UNO (Un-promoted 30 wt% K_2CO_3)	
• Iron out pilot plant operation with conventional liquid based solvent;	Completed
• Determine absorber hydraulic operating window;	Determined
• Provide cross reference point to ETIS performance.	Provided
2. UNO MK 3 (Higher concentration 40-50 wt% K_2CO_3)	
• Operate UNO process in precipitating mode, identify and resolve issues with regards to solids handling;	Operated and addressed issues
• Confirm VLSE and calorimetry of models developed from lab data;	Complete / Further work required
• Validate absorption and simulation models for UNO MK 3 – especially the reaction condition factor and liquid hold-up correlations;	Addressed and validated
• Validate physical properties and determine impact of impurity build up on physical properties;	Validated physical properties
• Understand impact of impurity build up on absorption and desorption performance;	Addressed
• Test the ion-exchange process for sulphate and nitrate removal;	On-site testing was not possible due to absence of sulphates/nitrates
• Test the performance of the hydrocyclone (de-sander) in the UNO process.	Tested
3. Promoted UNO MK 3 (Higher concentration 40-50 wt% K_2CO_3 with various promoters)	
• Confirm VLSE and calorimetry of models developed from lab data for UNO MK 3 with promotion;	Complete / Further work required
• Validate absorption and simulation models for UNO MK 3 with promotion	Complete / Further work required
• Benchmark lab rate promotion results with pilot plant (i.e. determine whether the rate data obtained from the wetted wall columns results in the anticipated improvement in the pilot plant);	Addressed
• Validate physical properties and determine impact of impurity build up on physical properties of UNO MK 3 with promotion;	Validated physical properties

• Determine the impact of impurities on the degradation of promoters and the absorption performance;	Impurities build up was negligible
• Test the ion-exchange process for sulphate and nitrate removal in the presence of promoters;	Not possible due to absence of sulphates/nitrates, but tests conducted in laboratory
• Determine the impact on the system energy requirements from the addition of the promoter.	Complete / Further work required
4. *Commercial Solvent – 30 - 40 wt% Sodium Glycinate	
• Benchmark performance with a commercial solvent with fast CO_2 reaction rates.	Completed
5. *TurboScrubber® UNO MK 3	
• Evaluate the effect of packing type on pilot plant absorption rate;	Evaluated
• Operate UNO MK 3 under highly loaded and precipitating process conditions.	Operated successfully

* Work additional to original project proposal.

2.4 Large scale design and economics

Data from the pilot plant design and operation phases in concert with data from the laboratory and simulation have been used to estimate the performance of a full scale UNO MK 3 process. The large scale design is based on retrofitting a 500 MW brown coal fired subcritical power station typical of those found in the Latrobe Valley. Simulations, material and energy balances, equipment sizing and costing were completed for numerous cases including by-product production, variations on the absorber design, heat integration designs, advanced compression, inclusion of integration of alternative products, options for partial capture, for auxiliary heating and for alternative cooling utilities. The details of these options are provided in Sections 5 and 6 with economic assessment of the various cases, in particular the cost of abatement and the levelised cost of electricity (LCOE), presented in Section 7.

The Sections from 3 to 7 are detailed in the Appendix (Commercial in Confidence)

3 Pilot plant activities

4 Simulation

5 Large-scale designs

6 UNO MK 3 economics

7 Heat Integration

8 Next steps for UNO MK 3

8.1 Status of the technology

The pilot plant provided an invaluable source of information for developing the UNO MK 3 process, including the performance of the rate promoters, the solids characterisation, the impurities removal processes and various pieces of absorber and downstream equipment. Laboratory experiments and laboratory scale pilot plant data were able to be validated and models to predict the performance of the system were tested and improved. Large-scale design and techno-economic assessment for the UNO MK 3 technology were also completed. The CO2CRC developed heat integration and steam cycle optimisation algorithm for existing or modified steam cycles for a given CO_2 capture plant and a power station was used to evaluate the integration of the UNO MK 3 system into a coal fired power station. Additionally it was used to review options for the use of auxiliary heating and power (Section 1), air cooling compared to cooling water (Section 1) and alternative regenerator designs including multi-pressure stripping columns (Section 1).

8.2 Further research areas and recommendations

Despite the research completed for the UNO MK 3 process, there are still R&D areas worthy of investigation as scale up progresses. Further work is recommended including:

- Validation of the predicted solubility of the promoted solvent;
- Incorporation of promoter chemistry into the theoretical models and/or the impact of precipitation incorporated into the rate based Aspen Plus® models;
- Trialling in a pilot plant with more active rate promoters that have been identified from laboratory scale experiments;
- Identification of the mechanism for absorber flooding and developing a method to avoid it becoming an operational constraint;
- Increasing the height of the packing and/or modifying the equipment and/or process design to test the process with 90 % capture rate;
- Running the plant continuously to assess long-term running effects on performance.

9 Training objectives of the project

Since 2003, the UNO MK 3 technology has gone through a number of research development phases beginning with fundamental research, bench scale testing and laboratory pilot plant testing before progressing to this phase of field based pilot plant testing. As a result, many people from a diverse range of backgrounds, skills and qualifications have been involved in the project and have had the opportunity to develop new and advanced skills in solvent-based capture for CO_2. Many of them have also been involved in the current project. Participants have included plant operators, research assistants, technicians, engineers, postgraduate research students, post-doctoral fellows, academics, patent lawyers, contractors, construction companies and managers. From a training perspective, this project has specifically involved 2 plant operators, 2 research assistants, 2 postgraduate research students, 4 post-doctoral fellows and 2 engineers.

All these people have had the opportunity to learn valuable skills in plant operation, data and sample collection, sample and data analyses, research and operation management, and report writing. This project has provided a unique opportunity of learning by doing in running a chemical plant inside a coal fired power plant, an experience that is still rare around the world. In terms of capability development, there is no doubt that this experience will place these individuals at the forefront of the future workforce that will be essential for large scale capture plant implementation of CCS.

This is an invaluable outcome of the project that would not have been possible without the support of BCIA, GDF SUEZ and the CO2CRC industry and government partners.

10 Project management

10.1 Management structure

The participant organisations in the UNO MK 3 project were CO2CRC, GDF SUEZ Australian Energy Hazelwood, The University of Melbourne, the University of New South Wales (UNSW Australia) and Monash University. Equipment maintenance work was performed by contractors based at Hazelwood Power Plant. Figure 4 shows the project's field management structure.

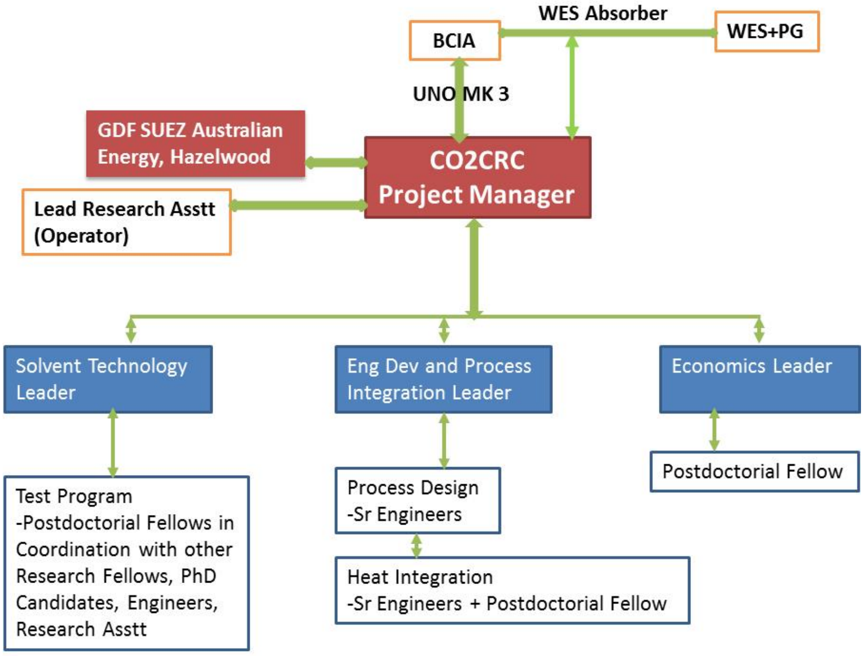

Figure 4: Project field management structure.

GDF SUEZ managed the operational aspects within the power plant in coordination with CO2CRC. The University of Melbourne was responsible for the UNO MK 3 technology while CO2CRC and Monash University were responsible for the heat and process integration. UNSW was responsible for the economic evaluation. CO2CRC engaged three local engineering companies for the design, construction, commissioning and maintenance of the rig.

10.2 Management strategies

A range of strategies was adopted to manage the project, ensure its safe operation and achieve outcomes as defined by the project objectives and aims and under the available timelines. These have included strategies for:

1. Quality and effectiveness of the test campaigns against R&D development needs;
2. Progress of the test campaigns against R&D objectives and timelines;
3. Strict implementation of the CO2CRC HSE policy;
4. Efficient resource utilisation; and,
5. Operating risk mitigation.

11 Conclusions

The UNO MK 3 capture plant trials at the GDF SUEZ Australian Energy, Hazelwood power station was the first trial of the CO2CRC's precipitating based UNO MK 3 process at a power station. The modifications applied to the original pilot plant increased control which made it more functional for testing solvent processes using real flue gas.

The trials built confidence in modelling and operating the pilot plant with rate promoters and precipitating solvent. The un-promoted campaigns resulted in low rates of absorption but were in line with predictions and in line with results from previous trials. The highly concentrated trials created some difficulties with absorber flooding and intermittent operation lead to blockages at start-up. There were generally minimal issues with blockages once the system was stabilised, except in the structured packing which was not expected to be solids tolerant at high solid fractions. Precipitating systems require more attention to be paid to the piping design and layout than a non-precipitating system would. The plant was able to provide invaluable data on the particle size distribution obtained from the process to enable more robust future equipment design.

The P1 solvent increased the absorption rate by 2 to 2.8 times the un-promoted solvent. The CO_2 capture rate varied from 10 to 50 % under a range of conditions. There was no observable deterioration in the capture rate as a function of time over the 44 days of operation in this campaign. The foaming tendency of the solvent appeared to be the cause of premature absorber flooding. Other promoters have shown less foaming tendency in the lab and may provide a method of overcoming this issue. Likewise the addition of an antifoam reduced the foaming tendency, but identification of a more suitable antifoam, or a continuous addition method thereof, may be required.

Sodium glycinate, a generic commercial amino acid solvent, was run in the system and it achieved an average absorption rate of 43 % at high gas rates.

Two alternative absorption systems were also trialled with the P1 solvent and progress on identifying the best absorber system for the UNO MK 3 process was made.

The sulphate and nitrate removal process on the pilot plant was not operated due to a lack of build-up in the solvent. However progress was made in the optimum design of a large-scale impurities removal system and identifying improved resins.

Aspen Plus® and theoretical rate limited absorber models have been developed for P1 with some success. The Aspen Plus® models have good thermodynamic and physical property predictions for the P1 solvent, especially at lower loadings. The theoretical rate limited absorber model provided a rapid tool leading to a good estimate of the performance of the system under a wide range of conditions.

Large-scale designs of the UNO MK 3 process retrofitted to a 500 MW brown coal fired power station have been completed and promise to significantly cut the cost of CO_2 avoided and the LCOE compared to conventional amine processes. A range of process improvements to the UNO MK 3 process provided additional reductions in the costs with the LCOE reducing from over \$150 /MWh for an MEA solvent to under \$100 /MWh for the best UNO MK 3 system. Changes to the process designs or assumptions that may lead to a doubling of the absorber packing height or an increase in the regeneration duty from the estimated 2.5 GJ/t to 2.8 GJ/t each result in an increase of approximately \$3 per tonne CO_2 avoided.

Options for auxiliary units have been assessed to enable the existing power station output to be maintained. An auxiliary coal fired power boiler, a parallel gas turbine (GT) and a hot windbox repowering using a gas turbine were assessed in detail. The coal fired auxiliary requires minimal intervention with the existing power plant, the parallel GT requires some modifications to the LP turbine of the main plant unless an oversized GT is installed and the total power output of the power station is increased, whilst the hot windbox GT requires at least the same amount of modifications as would be required for the base CO_2 capture plant without the auxiliary. The emissions intensities (kg/MWh) are very different for each option: 147 (Base), 488 (Coal fired auxiliary), 288 (Parallel GT) and 111 (Hot windbox GT). In part this leads to different abatement costs for the three cases, which vary between $38 and $49 per tonne of CO_2 avoided with the hot windbox option the lowest whilst gas prices are lower than $4 /GJ. The LCOE is highly dependent on the natural gas price and the price on carbon. As natural gas prices increase the coal fired auxiliary boiler progressively becomes more attractive provided the carbon price remains below $50 /t.

Air cooling the capture plant and/or the power station can reduce the annual water usage on the power station with CO_2 capture by 10 to 17 GL with an increase in the LCOE of between $1 /MWh and $2 /MWh.

The pilot plant trials have provided invaluable information for developing the UNO MK 3 process, including the performance of the rate promoters, the solids characterisation, the impurities removal processes and various pieces of absorber and downstream equipment. Further laboratory and pilot plant activities are required to continue to develop the process. Ongoing research to develop the UNO MK 3 process is required particularly in solubility prediction, better rate promoters, promoter chemistry, smooth operation, higher capture rate using taller columns and long term runs.

12 Acknowledgements

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13 Nomenclature and Abbreviations

Abbreviation	
ACC	Air-cooled condenser
CCP	Hazelwood large scale carbon capture plant
CCS	Carbon capture and storage
DCC	Direct contact cooler
DICE	Direct injection carbon engine
DP	Differential pressure
GT	Gas turbine
HMI	Human machine interface
HPLC	High performance liquid chromatography
HRSG	Heat recovery steam generator
ICP	Inductively coupled plasma optical emissions spectrometer
IEA	International Energy Agency
IPCC	International Panel for Climate Change
ITD	Initial temperature difference
LCOE	Levelised cost of electricity
L/G	Liquid to gas ratio (Total Lean Solvent (kg) / Total Feed Gas (kg))
LS	Lean solvent
MCC	Motor control centre
NGCC	Natural gas combined cycle
NO_x	Nitrous oxides
PFD	Process flow diagram
PLC	Programmable logic controller
RS	Rich solvent
RCF	Reaction condition factor
SO_x	Sulphur oxides
UCP	Unit control panel
UPP	UNO MK 3 pilot plant

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