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EXECUTIVE SUMMARY

Carbon dioxide capture and storage (CCS) is a promising process for removing carbon dioxide (CO₂) from industrial sources such as coal fired power stations and thereby limiting the effects of global climate change. The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) is involved in research and development of technologies for carbon dioxide capture and geological storage of CO₂. The CO2CRC solvent absorption capture group has been researching the use of potassium carbonate (K₂CO₃) solvent for CO₂ capture under both pre- and post- combustion capture conditions for a number of years. More recently the CO2CRC has been developing a novel precipitating K₂CO₃ solvent absorption process, known as UNO MK 3, which is designed to capture 90% of carbon dioxide emissions from large scale emission sources such as power stations. The UNO MK 3 process uses higher concentrations of K₂CO₃ and precipitates potassium bicarbonate (KHCO₃) which allows lower solvent circulation rates and hence lower energy usage and smaller regeneration equipment sizes when compared to the non-precipitating system. Some of the key benefits of this process, compared to traditional amine based capture processes, include lower regeneration energy, lower overall cost, low volatility and environmental impact, low toxicity and the ability to incorporate multi-impurity capture of CO₂, SOₓ and NOₓ and production of valuable by-products.

Funding from ANLEC R&D has enabled a pilot plant to be built at The University of Melbourne for testing this precipitating K₂CO₃ process. The pilot plant has been designed to capture 4 - 10 kg/hr of CO₂ from an air/CO₂ feed gas rate of 30 – 55 kg/hr and equipment was chosen specifically for handling a bicarbonate slurry process. Operational data has been collected over a range of operating conditions including L/G ratios from 2 – 6, solvent concentrations from 20 to 45 wt% K₂CO₃ with and without a rate promoter and different absorber packing materials. Plant data has been used to validate thermodynamic models developed using Aspen Plus® simulations.

Although there was some precipitation observed around joints and fittings, no major operational issues were encountered with equipment such as pumps or heat exchangers while operating with a precipitating solvent system. Increasing the K₂CO₃ solvent concentration, operating with a higher CO₂ feed gas concentration and the addition of a rate promoter were all found to be important for increasing the CO₂ recovery results and optimising the regeneration energy of the process.

Aspen Plus® simulations have been developed to model the performance of the UNO MK 3 process. The simulations were validated with data from the pilot plant for K₂CO₃ concentrations up to 45 wt%. Both rate-based and equilibrium models were used with regressed physical property data in the e-NRTL model. The predicted values showed good agreement with the experimental results for CO₂ in the gas phase, rich solvent loading and temperature difference in the absorber.

This study was completed to confirm the thermodynamics and equilibrium conditions of the K₂CO₃ UNO MK 3 process and assess the equipment options for operating with a slurry process. Limitations to the equipment meant that efficient operation was not achieved and therefore we must rely on predictions of the Aspen Plus® model to determine the optimum operational conditions.
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1. INTRODUCTION

Carbon capture and storage (CCS) of carbon dioxide (CO$_2$) has the potential to significantly reduce the greenhouse gas emissions from power stations that are fired by fossil fuels including coal and natural gas. In particular, CCS will be essential for continued power generation from coal where the CO$_2$ emission intensity (kg CO$_2$/kWh) is relatively high. A major challenge facing the large scale deployment of CCS is the cost and in particular the cost of capture. One of the founding objectives of the CO2CRC has been to find ways of reducing the cost of capture. It was from this objective, that the original concept for the UNO MK 3 process was conceived.

The UNO MK 3 process is a precipitating potassium carbonate (K$_2$CO$_3$) solvent process for post-combustion capture of CO$_2$ emissions, which is expected to have a cost of capture of less than $50/tonne, which is less than half that of leading amine-based process. In addition to the low cost, the UNO MK 3 process has the added benefit of a significantly lower environmental impact than amine-based solvents [1] along with the unique nature of delivering fertiliser products from the process.

Over the last decade, the original concept of the UNO MK 3 process has been developed through an extensive experimental work program [2-7] and pilot plant demonstrations in both pre-combustion and post-combustion capture [8-12]. Through additional process development and simulation the original process was further developed which led to the construction and operation of two further pilot plants, one at the University of Melbourne (described in this report and substantially funded by ANLEC R&D) and another at Hazelwood Power Station (substantially funded by BCIA) [13, 14]. The pilot plant built at The University of Melbourne is the focus of this report and has been built to demonstrate the UNO MK 3 process in order to provide confidence in modelling, promoter requirements and an ability to operate a precipitating system.

This report provides a description of the pilot plant built and operated with substantial funding from ANLEC R&D at The University of Melbourne including operational procedures and selection and performance of equipment items chosen specifically for a precipitating solvent system. The analytical methods developed for measuring the performance of the pilot plant using a promoted precipitating K$_2$CO$_3$ based solvent have been described. Pilot plant performance results including CO$_2$ absorption and regeneration performance over a range of operating conditions have been presented. A process for dealing with flue gas impurities including SO$_x$ and NO$_x$ has been developed. Finally performance data collected from the pilot plant has been used to further develop and validate Aspen Plus® simulations.
1.1. PREVIOUS WORK / MILESTONES ACHIEVED

All milestones relevant to this ANLEC R&D project have been completed as described in Table 1.

Table 1: Update on the status of milestones relevant to this ANLEC R&D project

<table>
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<th>Date</th>
<th>Milestone description</th>
<th>Status and comments</th>
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<td>11/11/2010</td>
<td>Signing of contract &amp; Agreement of detailed plan</td>
<td>Complete</td>
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<tr>
<td>2</td>
<td></td>
<td>Adequate Human Resources</td>
<td>Complete</td>
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<tr>
<td>3</td>
<td>30/06/2011</td>
<td>Redeployment of test facilities is well organized and test program developed</td>
<td>Redeployment of equipment is complete</td>
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<tr>
<td>4a</td>
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<td>1&lt;sup&gt;st&lt;/sup&gt; Half yearly report. Evidence of progress made on Aspen simulation</td>
<td>Report complete</td>
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<tr>
<td>4b</td>
<td></td>
<td>Evidence that equipment is redeployed and test program &amp; data collection are in progress</td>
<td>Redeployment complete and test program progressing well</td>
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<tr>
<td>5a</td>
<td>30/12/2011</td>
<td>2&lt;sup&gt;nd&lt;/sup&gt; Half Yearly Report for publication to an ANLEC R&amp;D audience on Aspen simulation for handling 3-phase system and progress on data analysis</td>
<td>Report complete</td>
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<td>Delivery of a technical report that includes:</td>
<td>Report prepared and submitted as below:</td>
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<td></td>
<td>4c</td>
<td>(4c) Evidence that test program and data collection are in progress</td>
<td>Test program progressing well with data collection</td>
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<td></td>
<td>5b</td>
<td>(5b) Evidence that data analyses are performed to verify the simulation results for the key parameters</td>
<td>Simulations are continuously updated as data is collected from the test rig</td>
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<td></td>
<td>5c</td>
<td>(5c) Evidence that data analyses are performed with publication to an ANLEC audience having particular emphasis on impurities and by-product handling</td>
<td>Experiments for 2 different by-product removal processes have been completed</td>
</tr>
<tr>
<td>5d</td>
<td>30/12/2013</td>
<td>Delivery of a Final Technical Report acceptable to ANLEC R&amp;D that addresses Project Objectives in cl 1.3 of Schedule 1 and includes the following: Evidence that data analyses are performed with particular emphasis on overall validation of simulation results with experimental work</td>
<td>This report is the final technical report. Project objectives have been addressed and the report has been prepared according to ANLEC R&amp;D requirements.</td>
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1.2. UNO MK 3 (POTASSIUM CARBONATE) PROCESS
DESCRIPTION

The UNO MK 3 process is a precipitating potassium carbonate ($\text{K}_2\text{CO}_3$) process developed by the CO2CRC. The reaction of $\text{CO}_2$ with $\text{K}_2\text{CO}_3$ to form potassium bicarbonate ($\text{KHCO}_3$) occurs through the following overall reaction:

$$\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{KHCO}_3$$ (1)

Potassium carbonate has a number of advantages over traditional amine based solvents. Potassium carbonate is less volatile, non-toxic and less corrosive which reduces the overall environmental impact of this process. Potassium carbonate can also capture $\text{SO}_x$ and $\text{NO}_x$ which reduces or eliminates the need for dedicated $\text{SO}_x$ and $\text{NO}_x$ removal equipment and can produce valuable fertilizer products. The main challenge associated with this potassium carbonate based process is the slow rate of reaction resulting in the need for large and therefore expensive equipment. 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, a $\text{KHCO}_3$ precipitate is formed during absorption and subsequent cooling. The precipitate is then separated from the liquid phase for selective regeneration of the $\text{KHCO}_3$ species. In this way, less water is passed to the regeneration stage and thus drives down the energy requirements from over 3 GJ/tonne $\text{CO}_2$ for a liquid system to less than 2.5 GJ/tonne $\text{CO}_2$ for a precipitating system.

![Figure 1: UNO MK 3 Process Flow Diagram](image-url)
Another feature of the UNO MK 3 process is the ability to tolerate flue gas impurities such as SO\textsubscript{x} and NO\textsubscript{x}, which will react with the K\textsubscript{2}CO\textsubscript{3} solvent to form the valuable fertiliser by-products, potassium sulfate (K\textsubscript{2}SO\textsubscript{4}) and potassium nitrate (KNO\textsubscript{3}) according to the following reactions.

\[
\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{K}_2\text{CO}_3 \rightarrow \text{K}_2\text{SO}_4 + 2\text{KHCO}_3
\]

\[
2\text{NO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{K}_2\text{CO}_3 \rightarrow 2\text{KHCO}_3 + 2\text{KNO}_3
\]

In order to design and implement efficient and cost effective CO\textsubscript{2} capture facilities using precipitating solvent systems the following key areas need to be addressed:

1. The development and/or validation of appropriate solvent handling equipment for bicarbonate slurries
   - Design and construction of plant for precipitating solvents
   - Conduct trials to examine fluid handling/equipment issues
   - Investigate process variables that reduce cost of capture

2. The ability to simulate the precipitating solvent system’s performance using Aspen Plus\textsuperscript{®} software
   - Validate physical properties
   - Incorporate VLSE
   - Incorporate rate promoters
   - Demonstrate promoted carbonate system
   - Demonstrate ability of simulation to match and predict the promoted K\textsubscript{2}CO\textsubscript{3} system

To test the performance of solvent handling equipment and develop models that can predict the capture of CO\textsubscript{2} with a precipitating K\textsubscript{2}CO\textsubscript{3} solvent, a pilot plant has been designed and built at The University of Melbourne. This report details the pilot plant equipment chosen for operating a precipitating solvent absorption process and the experimental data obtained from operating this pilot plant over a range of operating conditions with varying K\textsubscript{2}CO\textsubscript{3} solvent concentrations including a rate promoter. This data has been used to develop and validate the thermodynamic models developed with Aspen Plus\textsuperscript{®} simulation software for predicting the performance of the pilot plant.
2. RESULTS & DISCUSSION

A laboratory scale pilot plant, designed to capture 4 - 10 kg/hr of CO\(_2\) from an air/CO\(_2\) feed gas rate of 30 – 55 kg/hr, has been built in the Department of Chemical and Biomolecular Engineering at The University of Melbourne. The plant has been designed to test the hydraulics of a precipitating potassium carbonate solvent system and use this data to validate Aspen Plus® simulations. A description of the pilot plant along with performance data collected over a range of operating conditions and corresponding Aspen Plus® simulations have been provided in the following sections.

2.1. LABORATORY BASED PILOT PLANT TRIALS

2.1.1. PILOT PLANT DESCRIPTION AND OPERATIONAL PROCEDURES

A process flow diagram of the pilot plant has been provided in Figure 2.

![Figure 2: Process Flow Diagram of Laboratory Scale Pilot Plant](image)

The plant consists of two main equipment items: an absorber column and a regeneration column, operating in counter-current mode. Feed gas containing 10 to 25 vol% CO\(_2\) and remainder compressed filtered air is fed to the packed absorption column via Bronkhorst EL-FLOW mass flow controllers and a heated water bath. In a typical experimental run the total gas flow rate is 30 kg/hr and the gas mixture is at 50 °C. A gas saturator can also be used to obtain a feed gas with 80 – 95 % relative humidity. The temperature and humidity of the feed gas is measured via a humidity probe located near the gas entry to the absorber. The absorber column is made of borosilicate glass and has a diameter of 100 mm and a total...
height of 4.25 m with PTFE gaskets. The absorber has 3 packed bed sections, each 0.8 m in height. The packed bed sections are filled with stainless steel (304SS) pall rings with a diameter of 10 mm. Structured packing was also obtained for the absorber (Sulzer Mellapak M250.X SS316). The rich solvent tank at the base of the absorber is used for storage and contains a heating element for use during column start-up procedures. Unlike traditional amine plants, a water wash section was not included in the design as potassium carbonate and the rate promoters used in the UNO MK 3 process are non-volatile. The rich solvent leaving the absorber is sent to the regeneration column via a rich solvent tank, rich solvent pump and the lean-rich exchanger. The lean-rich exchanger is a spiral heat exchanger which heats the rich solvent stream via the lean solvent from the reboiler. The gas leaving the top of the absorber passes through a glass condenser to remove any moisture in the gas before flowing through a rotameter and Horiba VA-3000 gas analyser to determine CO$_2$ concentration.

The regenerator consists of a borosilicate glass column with a diameter of 0.1 m and a stainless steel reboiler tank attached directly to the base of the regenerator column. The total height of the column is 4.6 m, inclusive of the reboiler tank, and the glass column contains 3 packed bed sections each 1 m in height filled with the same Pall rings as in the absorber. The reboiler is heated by an electrical two-stage element bundle (made of Incoloy 800) which can provide a heating duty of 12, 18 or 30 kW. The temperature of the solvent in the reboiler tank can be controlled up to 150 °C. Gas leaving the top of the regenerator is fed to an overhead condenser followed by a separator/reflux drum. Condensed water is either returned to the regeneration column or sent to drain in order to maintain the water balance of the system. CO$_2$ gas is sent to the exhaust via a back pressure control valve which could control the pressure of the regenerator up to 100 kPag, once a pressure vessel rated reboiler was installed (100 kPag at 160 °C are the pressure/temperature ratings of the bellow connecting the glass column and the reboiler). Prior to installation of the pressure vessel rated reboiler tank the pressure of the regenerator was limited to 50 kPag. The lean solvent from the reboiler is fed back to the top of the absorber via the spiral heat exchanger, lean solvent pump and lean solvent cooler. Refer to Figure 3 for some photos of the pilot plant.

![Figure 3: General photos of the pilot plant](image-url)
Absorber overhead CO₂ gas concentration readings were taken every 5-15 minutes and solvent samples were taken every 30 minutes at the absorber inlet and outlet via sample valves. Numerous temperature (Pt100 resistance temperature detectors) and pressure (GE PTX1400 pressure transducers) indicators are located throughout the plant and recorded every 10 seconds into an Excel file using LabView software. The CO₂ loading of the un-promoted K₂CO₃ solvent samples was determined via acid titration (refer to section 2.1.3). The CO₂ loading of the promoted K₂CO₃ solvent samples was determined via the Chittick method and ICP (refer to section 2.1.3).

2.1.2. EQUIPMENT SELECTION & PERFORMANCE

In order to design and implement a large scale precipitating carbonate solvent system for CO₂ capture it is important to consider the design and assess the ongoing performance of individual equipment items for handling bicarbonate slurries. The design characteristics and performance for the heat exchangers, pumps, flowmeters and general piping used in this pilot plant are described below.

**Spiral heat exchanger**

The spiral heat exchanger was chosen as the lean/rich cross flow heat exchanger due to its ability to tolerate suspended solids without clogging. The spiral heat exchanger was sized by Alfa Laval using the maximum flow rate information provided. The model supplied was Alfa Laval ALSHE LTL 4S with a heat transfer area of 3.56 m². The plate material is 2.0 mm 316 SS and the gasket material is nitrile bonded fibre and DN50 flanges. Refer to Figure 4 for photos and flow diagram of the spiral heat exchanger.

![Figure 4: Spiral heat exchanger including lean solvent entry and schematic flow diagram](image-url)
The lean solvent from the reboiler enters the spiral and is cooled before being suctioned into the LS Pump. Upon startup of the pilot plant, it is important to establish a good flow of lean solvent through the spiral heat exchanger. Often, if the spiral has not been adequately flushed with hot water, or there has been no flow for > 5 days, the cooler piping around the spiral will begin to grow bicarbonate crystals internally, leading to a slow startup. This can be prevented by draining all low points around the spiral and returning the drained solvent to one of the tanks. No operational problems were encountered during normal operation with this heat exchanger.

**Plate heat exchangers**

Both the overheads condenser on the regeneration column and the lean solvent cooler are plate heat exchangers from Alfa Laval (refer to Figure 5). Both heat exchangers were sized for the maximum projected cooling duties of 14 kW and 5 kW respectively. Although there were no ongoing issues such as clogging when operating these heat exchangers with a precipitating solvent process, on one occasion a gasket between the plates did fail resulting in solvent loss from the plant and the need to replace that particular gasket. The gasket was made from EPDM (ethylene propylene diene monomer (M-class) rubber) which is compatible with potassium carbonate so it is unclear what caused this once only failure.

![Image](image)

**Figure 5: Plate heat exchangers (a) overheads condenser, (b) lean solvent cooler and (c) schematic of plate and frame heat exchanger**

**Helical rotor pumps**

Helical rotor pumps are used to pump both the lean and rich solvent (refer to Figure 6). The speed of each pump is controlled by a VFD (variable frequency drive) unit. Both pumps have managed to pump solvent at concentrations ranging from 0 - 45 wt% K\textsubscript{2}CO\textsubscript{3}. However, there were differences in the performance of the pumps, even though they are both the same model (CSF MAE 25/1, single stage 0.55 kW/700 rpm/std 3 phase motor, BSP, fan-cooled, hard-face seals, hardened rotor). The RS Pump generally delivered a higher flow rate of solvent for the same VFD setting than the LS Pump. However, the RS Pump required a higher initial torque on startup compared to the LS Pump, most likely due to higher concentrations of solids in this line following shut-down periods.
Both pumps developed crystals around the main connections with time, despite an extensive commissioning and leak-testing period with water. The lean solvent pump in particular showed crystallisation at the suction and outlets points to the pump as shown in Figure 7.

![Figure 6: Helical rotor pump used for pumping lean and rich solvent](image)

**Figure 7: Crystallisation around lean solvent pump**

**Solvent flow meters**

The solvent flow rate is measured using magnetic flow meters (Magmeters) which have been calibrated with solvent concentrations ranging from 0 to 45 wt% $K_2CO_3$ (refer to Figure 8). Calibration results show that there is no significant difference in flow rate readings (in L/min) with solvent concentration however the Magmeter calibration for tap water was slightly different to that of $K_2CO_3$. This difference is due to the difference in density between water and aqueous $K_2CO_3$. No operational problems were encountered while operating with a slurry solvent system.
Column packing

Both the absorber and regenerator columns contained 3 packed bed sections each filled with random packing (stainless steel 304SS pall rings with a diameter of 10 mm) as shown in Figure 9. Trials were also completed with structured packing in the absorber (Sulzer Mellapak) however these trials were limited due to the low gas rates obtained with the existing gas line sizes. Further experiments with larger gas lines are recommended. There were no other operational issues encountered when using these packing materials.

Figure 8: Solvent flow rate (Magmeter) calibration curve for varying solvent concentrations

Figure 9: Random and structured packings: (a) and (b) pall rings; (c) Sulzer Mellapak
Solvent pipelines and other instrumentation

Solvent precipitation in piping surrounding the spiral heat exchanger, lean solvent cooler and solvent pumps has been described in previous sections. Precipitation was also found in instrumentation on the gas inlet line to the absorber. Originally during start-up and shutdown, the solvent circulated between the absorber and regenerator columns without any gas. This allowed some solvent to pass into the gas inlet distributor and down into the gas line. Solvent precipitation was observed at the inlet port to the humidity meter, inside the manual drain valve (which is the low point of this gas line) and in the piping downstream of the air mass flow controller, MFC1.

Initially a humidity and temperature meter from ECEfast (Center 310 RH) was used for measuring temperature and humidity of the saturated gas entering the absorber. After several runs, the humidity reading did not register and then the temperature reading did not register due to solvent contact with the probe. This meter was replaced by a more robust probe and separate data logger from Testo Pty Ltd. This probe has a 12 mm diameter protective PTFE cap and operational procedures were developed to ensure solvent does not contact the humidity probe. The manual drain valve at the low point of the gas inlet pipe to the absorber was installed to drain any water in the line from the saturator bath. However it has been observed that the drain valve fills slowly upon solvent circulation in the rig. The precipitate at the bottom of the valve was analysed and results indicated the presence of CO$_3^{2-}$ ions which confirmed that the precipitate was due to bicarbonate crystals. Mass Flow Controller 1 (MFC1) was serviced due to its sudden inability to reach setpoint during startup. Some white precipitate was found in the gas line downstream of the mass flow controller and was suspected to be bicarbonate crystals. A Swagelok poppet check valve (SS-CHS6-1/3) was replaced on the gas line but this did not prevent back flow of the solvent. In order to prevent the backflow of solvent, air was allowed to flow through the gas inlet pipeline during startup. The port for the humidity probe was kept open during this time so that air did not flow up the absorber column, but exited through this port.

A check valve on the rich solvent line was also found to be blocked on one occasion due to bicarbonate precipitation after operation with 45 wt% K$_2$CO$_3$. Although this precipitation caused some minor delays in start-up of the plant (generally after an extended period of shut-down) there were no major ongoing equipment issues associated with solvent precipitation.

Tap water lines were hard plumbed to the rig due to the necessity for flushing during startup and shutdown. Pipelines containing highly concentrated solvent were also heat traced. In addition to the heat tracing, the rich solvent and lean solvent lines were flushed with hot tap water for approximately 1 to 2 minutes before shutdown. On start-up of the pilot plant, it is sometimes necessary to spike the lean solvent line upstream of the LS Pump with hot water to obtain good solvent flow rates.
2.1.3. ANALYTICAL METHODS & SOLVENT PERFORMANCE

A range of analytical methods were developed for determining the performance of the pilot plant including solvent loading and gas phase concentrations as well as investigating other issues such as solvent speciation and corrosion.

**Solvent loading**

Solvent loading is an important parameter to understand when operating a solvent absorption pilot plant and is defined for this work as follows:

\[
\text{Solvent loading} = \frac{\text{CO}_2 \text{ absorbed}}{\text{CO}_2 \text{ loading}}
\]  

where \([\text{CO}_2]_{\text{absorbed}}\) is the concentration of \(\text{CO}_2\) absorbed in the solvent and \([\text{K}]\) is solvent concentration of \(\text{K}_2\text{CO}_3\) with no \(\text{CO}_2\) loading. Solvent loading was measured using an auto-titrator for un-promoted \(\text{K}_2\text{CO}_3\) samples and via the Chittick apparatus and ICP for promoted \(\text{K}_2\text{CO}_3\) samples described as follows.

**Auto-titrator (for un-promoted solvent samples)**

Titration was used to determine solvent loading in un-promoted \(\text{K}_2\text{CO}_3\) solvent samples by measuring the amount of carbonate (\(\text{CO}_3^{2-}\)) and bicarbonate (\(\text{HCO}_3^-\)) ions in a sample. The carbonate solvent is a buffer solution as the carbonate and bicarbonate ions are in equilibrium. Titration was completed with a Metrohm 905 Titrando auto-titrator with 0.4 M \(\text{H}_2\text{SO}_4\). 2 mL of the sample was pipetted into a beaker using an Eppendorf 5000 pipette, and diluted using 60 mL of RO water. This sample was then titrated to determine the two end points at pKa’s of 10.33 and 6.37, corresponding to the concentrations of \(\text{CO}_3^{2-}\) and \(\text{HCO}_3^-\) ions respectively. The total uptake capacity of the solvent can be obtained as follows:

\[
= [\text{HCO}_3^- + 2[\text{CO}_3^{2-}]]
\]

Therefore for un-promoted solvent samples solvent loading is defined as:

\[
\text{Solvent loading} = \frac{[\text{HCO}_3^-]}{[\text{K}^+] + \frac{[\text{HCO}_3^-]}{\text{HCO}_3^- + 2[\text{CO}_3^{2-}]} }
\]

**Chittick apparatus and ICP (for promoted solvent samples)**

The addition of an amine promoter to the system results in \(\text{CO}_2\) absorption via carbamation and the hydrolysis of the carbamate species [2]. The carbamate obtained in this study was assumed to be relatively stable and solvent loading for promoted samples was defined as follows:

\[
\text{Solvent loading} = \frac{\text{HCO}_3^- + [\text{P}] \text{COO}^-}{[\text{K}^+]} 
\]


Note that the total uptake capacity of the promoted system differs from the un-promoted system because the addition of promoter can change the amount of $K^+$ present in solution and the pH of the solution, which will again have an impact on the bicarbonate/carbonate equilibrium.

Therefore the Chittick apparatus (refer to Figure 10) was used to measure the volume of total $CO_2$ evolved from a known volume of solvent. 2 mL of solvent was titrated using 2 M HCl using methyl orange as indicator. When the colour changes from transparent to pink, the end point pH of 3.7 has been reached. At this pH, all of the $CO_2$ existing in the solvent has been released. The evolved $CO_2$ displaces the acid and can therefore be quantified.

![Figure 10: Schematic of Chittick apparatus](image)

Inductively Coupled Plasma Spectrometry, or ICP, using a Varian ICP-720 was used to determine the total $K$ concentration [$K^+$] in the solvent samples when using a promoter. This result was then used to normalise the Chittick results in order to compare the total $CO_2$ between rich and lean solvent samples whilst accounting for dilution of solvent. Samples being analysed for $K$ concentration must be diluted 1000 times in order to be measured via ICP. Solvent loading for promoted $K_2CO_3$ samples can then be determined via:

$$\text{Solvent loading} = \frac{\text{evolved } CO_2}{[K^+]} \quad (8)$$

**Promoter concentration**

The concentration of promoter in the solvent samples was determined via an Agilent 1200 series High Performance Liquid Chromatography (HPLC) unit.
**Solvent speciation**

Both $^1$H-NMR and $^{13}$C-NMR spectroscopy were used to analyse the samples to identify the speciation of compounds in the solvent. $^1$H-NMR was used to determine relative amounts of carbamite and any other active species in the solvent. $^{13}$C-NMR determined the carbonate/bicarbonate ratio.

**Gas phase analysis**

CO$_2$ concentration on the gas outlet of the absorber was measured using a Horiba VA-3000 Multi-component gas analyser via a non-dispersive infrared (NDIR) module. CO$_2$ removal efficiency (or recovery) was then calculated using the following equation:

\[
\text{CO}_2 \text{ removal efficiency (\%) = } \frac{\text{Flow rate of CO}_2 \text{ removed from the absorber}}{\text{Flow rate of CO}_2 \text{ in feed gas}} \times 100
\]  

(9)

**Corrosion**

The first air-water experiments were performed in the pilot plant during February 2012. There was no visible change in colour or quality of the water during these experiments. K$_2$CO$_3$ was first added to the pilot plant in April 2012 and the solvent was initially at a concentration of 20 wt% K$_2$CO$_3$. The solvent concentration was increased to 30 wt% K$_2$CO$_3$ in June 2012 and then 40 wt% K$_2$CO$_3$ in August 2012. At the end of September 2012, the solvent in the tank showed a slight greenish colour. The observed colour of the solvent intensified after the addition of promoter in October 2012. It is possible that the promoter contributed to colour changes to the solvent. It is known that certain promoters can form complexes with metals in solution such as copper [15]. It has also been found that 304SS and Incaloy are likely to corrode in the presence of K$_2$CO$_3$ solvent. Although there were no major performance issues seen with the change in colour, preventative measures, such as removal of any brass fittings in the plant, were completed to minimise any corrosion problems.

At the end of 2012 the plant was shut down for maintenance. During this time various sections of the pilot plant were examined for corrosion including the reboiler element. The reboiler element showed only very minor corrosion as shown in Figure 11. During another plant shutdown in September 2013 for installation of a new pressure vessel rated reboiler, the plant was again examined for corrosion and no significant changes were observed.

Recent laboratory scale testing has shown that 316SS will not corrode in the presence of K$_2$CO$_3$ under a range of operating conditions and is recommended for future materials of construction.
Solvent quality/colour change

As the colour of the solvent was observed to change with time (refer to Figure 12) full elemental analysis of the solvent samples over time was performed using ICP. Due to limited availability of element standards the current results provide only a qualitative elemental analysis. Results of the lean solvent samples at steady state in comparison to tap water are given in Figure 13. K levels have been removed from this figure as they were 3 orders of magnitude larger than the trace elements. Results show significant levels of Si, Na and Ni in the lean solvent. The Na and Si are most likely due to solvent leaching of the borosilicate glass of the absorber and regenerator columns. This analysis does not consider organics or metal complexes that could cause colour changes and further investigation is required to quantitatively determine the amounts of each element in the samples. As the colour change did not affect the overall performance of the solvent, no further work has been completed at this stage to determine the cause of the colour change.
Figure 13: ICP analysis of solvent samples over time compared to tap water
2.1.4. HYDRODYNAMIC PLANT PERFORMANCE

The hydrodynamic performance of the pilot plant was studied over a range of operating conditions as described in the following sections.

**Pressure drop**

Gas and liquid flow rates were chosen to satisfy a range of L/G ratios and to maximize the pressure drop through the column. Packed columns are usually designed to be operated at the highest economical pressure drop to ensure good gas and solvent distribution. The theoretical pressure drop across the Pall ring packing used in both the absorber and regenerator, was calculated using the generalized pressure drop correlation (GPDC)[16], assuming negligible effect on pressure drop from the packing support plates. This assumption is justified by the choice of packing support plates with similar open area to that of the packing. Experimental and predicted pressure drop per meter of packing for a range of gas flow rates at a constant liquid rate using water can be found in Figure 14. At low gas flow rates the correlation tends to under-predict the experimental data and this trend is reversed at higher gas flow rates. The variability in these predictions could be due to limitations of this correlation for non-industrial size packing. It has been found that the pressure drop in a packed column will vary with column diameter if the diameter of the column is less than 0.9 m [17]. In columns of diameter less than 0.22 m, the effect of diameter on pressure drop has been observed to intensify [18], leading to larger errors in pressure drop prediction using the GPDC charts. To ensure the column operates below flooding conditions and to provide adequate gas to liquid contact in the absorber at different L/G ratios the flow rate of gas was maintained at 1.06 kg/m$^2$s. The flow rate of liquid was also maintained above the minimum wetting rate.

![Figure 14: Comparison of experimental and theoretical pressure drop using the generalised pressure drop correlation [16] for the absorber with stainless steel pall rings (diameter = 10 mm) and air/water system. Liquid flow rate was kept constant at 4 kg/m$^2$s.](image-url)
Operation of a solvent absorption column under foaming conditions is not desirable as efficiency of the column is reduced and the column is likely to flood. Flooding occurs at high gas flow rates resulting in excessive entrainment of solvent which is also not desirable. Increasing the pressure drop across the packed bed will also lead to flooding. As packed columns are usually designed to be operated at the highest economical pressure drop to ensure good gas and solvent distribution, pressure drop is an important parameter to understand when operating a pilot plant. Therefore pressure drop was measured throughout the testing period to understand what causes an increase in pressure drop which can reduce efficiency and potentially lead to flooding conditions.

Figure 15 shows experimental pressure drop for a range of solvent concentrations with varying L/G ratio at a liquid rate of 1.1 – 1.7 L/min. It can be seen that as L/G increased (or gas rate decreased) the pressure drop per meter of packed bed also decreased. There was no significant change in pressure drop with increasing K$_2$CO$_3$ concentration, however higher pressure drop was observed when operating with promoter P1, especially when using 45 wt% K$_2$CO$_3$. This could be due to the presence of solids at these higher concentrations or due to a change in interfacial tension of the solvent after extensive operation of the plant with a rate promoter (further discussion is in the promoted solvent results section). When operating with 45 wt% K$_2$CO$_3$ and 10 wt% promoter P1 the column was also found to flood at lower operating rates, as would be expected with higher pressure drop. In order to prevent undesirable flooding conditions antifoam has been added to the solvent to successfully prevent these problems.

Figure 15: Pressure drop per meter of packing for a range of solvent concentrations and varying L/G ratio (Liquid rate: 1.1 - 1.7 L/min)
**Liquid holdup**

Liquid holdup is defined as the liquid retained in the packed bed including liquid on the surface of the packing and liquid trapped in the space between the packing. It is important to understand the liquid holdup because it has a direct influence on liquid phase mass transfer performance. The liquid holdup (m$^3$/m$^3$) in the absorber column as a function of solvent flow rate, for different K$_2$CO$_3$ concentrations is presented in Figure 16. The holdup was measured by collecting the volume of liquid that drained from the packing after simultaneously stopping solvent and gas flows. Prior experiments confirmed that the liquid holdup remained constant at constant liquid flow rate and varying gas flow rate, confirming that the column was operating below the loading point. Operation of the packed column below the loading point is important in liquid holdup measurements to prevent accumulation of liquid in the packing with varying gas flow rate. Figure 16 shows that the holdup increased linearly with L/G ratio at a constant gas rate of 30 kg/hr (or 1.1 kg/m$^2$s). The figure shows very little change in holdup when increasing solvent concentration from 20 wt% to 40 wt% K$_2$CO$_3$ (including when 10 wt% promoter was added). However there was a noticeable increase in holdup for 45 wt% K$_2$CO$_3$ with 10 wt% promoter. This could again be due to the presence of solids at these higher concentrations or change in surface tension of the solvent after extensive operation of the plant with a rate promoter (further discussion is in the promoted solvent results section).

![Figure 16: Liquid holdup as a function of L/G for various K$_2$CO$_3$ solvent concentrations at a gas rate of 30 kg/hr (or 1.1 kg/m$^2$s)](image)
2.1.5. **CO₂ ABSORPTION PERFORMANCE**

**Operational trends**

Solvent samples were collected every 30 minutes and CO₂ loading was determined for both lean and rich solvent samples using techniques described in section 2.1.3. Figure 17 shows a typical trend for lean and rich solvent loadings using un-promoted 30 wt % K₂CO₃. It can be seen that steady state conditions were achieved after approximately 1 hour of operation with CO₂ gas. Temperature and pressure were logged continuously throughout the plant via Labview software using temperature and pressure transmitters. Typical experimental trends for absorber and regenerator pressure and temperature using 40 wt% K₂CO₃ with 10 wt% promoter P1 are shown in Figure 18 and Figure 19.

![Figure 17: Typical solvent loading results over time for un-promoted 30 wt% K₂CO₃](image-url)
Figure 18: Typical absorber and regenerator pressure profiles over time for 40 wt% $\text{K}_2\text{CO}_3$ with 10 wt% promoter P1

Figure 19: Typical absorber and regenerator temperature profiles over time for 40 wt% $\text{K}_2\text{CO}_3$ with 10 wt% promoter P1
CO₂ recovery or CO₂ removal efficiency was calculated based on the inlet and outlet absorber CO₂ gas concentrations (as defined by equation (9)). A typical set of experimental data, including inlet and outlet CO₂ concentration and corresponding CO₂ recovery, has been shown in Figure 20 and Figure 21 for 40 wt% K₂CO₃ with 10 wt% promoter P1 at an L/G ratio of 4.

Figure 20: Typical experimental data, including CO₂ inlet and outlet concentration, for 40 wt% K₂CO₃ with 10 wt% promoter P1 at L/G ratio of 4 with a gas flow rate of 30 kg/hr

Figure 21: Typical experimental CO₂ recovery results for 40 wt% K₂CO₃ with 10 wt% promoter P1 at L/G ratio of 4 with a gas flow rate of 30 kg/hr
**CO₂ recovery results**

A summary of operating conditions and CO₂ recovery results for a range of absorption experiments is provided in Table 2 along with Figure 22 and Figure 23. From Figure 22 it can be seen that the addition of rate promoter P1 increased the CO₂ recovery by up to 6 times when compared to similar results without a rate promoter. From Figure 23 it can be seen that CO₂ recovery increased as the CO₂ feed gas concentration increased. Higher recoveries were also obtained when operating at higher L/G ratios as shown in Figure 23 and in Table 2.

**Table 2: Summary of operating conditions and CO₂ recovery results for a range of absorption experiments**

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<th>Experiment Number</th>
<th>K₂CO₃ concentration, wt%</th>
<th>Promoter P1 concentration, wt%</th>
<th>Liquid rate, kg/hr</th>
<th>Gas rate, kg/hr</th>
<th>L/G</th>
<th>CO₂ inlet concentration, vol%</th>
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Figure 22: CO₂ recovery results for K₂CO₃ concentrations between 30 and 40 wt% K₂CO₃ with and without rate promoter P1. The closed points are for a feed gas concentration of 10 vol% CO₂ and the open points are for 25 vol% CO₂.

Figure 23: CO₂ recovery results for 36 wt% K₂CO₃ and 8 wt% P1 for a range of CO₂ inlet concentrations at L/G ratios of 3 and 4

The data collected using un-promoted K₂CO₃ showed low CO₂ recovery results due to a slow CO₂ absorption rate which would lead to excessively large absorption equipment in a full-scale plant. To overcome this the organic rate promoter P1 was added to the solvent as it has been shown to increase the CO₂ absorption rate in K₂CO₃ solutions. However the downside of using a promoter is that it increases the energy usage in the regenerator. Addition of this rate promoter increased the CO₂ recovery from around 5-10 % up to 30%. Recovery rates were also limited by the height of the packed column which was constrained due to its location within an enclosed laboratory. Aspen Plus® simulations have shown that
for the same pilot plant under similar operating conditions 30 wt% MEA would have a CO$_2$ recovery of approximately 55%. The majority of the results presented here were limited by the reboiler pressure (and therefore regeneration temperature) due to pressure vessel regulations which prevented full regeneration of the promoted solvent. Although a new pressure vessel reboiler has since been installed limited time was available to fully investigate the effect of regeneration temperature on recovery. The new reboiler was operated for a limited time at 80 – 90 kPag, however the solvent regeneration temperature was not able to go higher than 124 °C which was most likely due to dilution of the solvent because of difficulties in maintaining the water balance.

The addition of rate promoter P1 also initially resulted in an increase in the surface tension of the solvent, as shown in Figure 24. However over time the surface tension started to decrease which was most likely the cause of increased foaming of the solvent (as shown by increased foam volume resting time in Figure 25) as well as higher pressure drop and increased holdup at lower operating conditions, as discussed in section 2.1.4. Antifoam has since been shown to successfully prevent operational issues associated with solvent foaming.

![Figure 24: Change in surface tension of solvent samples with time](image-url)
Crystallization studies

Crystallization studies of the growth rate and morphology of potassium bicarbonate crystals grown under the UNO MK 3 process conditions will be important for the design of the slurry process. The growth and nucleation rates of potassium bicarbonate crystals will control the shape and size distribution of crystals and will influence the operability of the slurry absorber and ancillary equipment. Preliminary experiments were completed to study the bicarbonate crystal size distribution in the promoted solvent system using a Malvern Mastersizer 2000. As can be seen in Figure 26 and Figure 27 the median particle size of the crystals in a rich solvent sample was between 150µm and 200 µm.

Figure 25: Foam test results after addition of rate promoter

Figure 26: Differential volume percent vs particle diameter size distribution for a rich solvent sample using 40 wt% K₂CO₃ and 10 wt% promoter P1.
Figure 27: Cumulative volume percent vs particle diameter size distribution for a rich solvent sample using 40 wt% \( \text{K}_2\text{CO}_3 \) and 10 wt% promoter P1.

Bench scale experiments were also completed to determine the distribution of promoter P1 between the solid and liquid phase of the precipitating solvent samples. Results showed that more than 99% of promoter P1 remained in the liquid phase (< 1% solids), which minimized the amount of promoter sent to the regenerator and therefore helped to reduce the regeneration energy requirements of the process.

2.1.6. SOLVENT REGENERATION PERFORMANCE

The bulk of the energy required for the promoted and un-promoted system is the heat energy input (\( \Delta H_{\text{reboiler}} \)) required for regeneration. This is not simply the energy required to reverse the chemical \( \text{CO}_2 \) absorption process but also includes the sensible heat (\( \Delta H_{\text{sensible}} \)) required to heat the solvent, the latent heat of steam evaporation (\( \Delta H_{\text{latent}} \)) and the heat losses of the regenerator (\( \Delta H_{\text{losses}} \)) as shown in equation (10):

\[
\Delta H_{\text{reboiler}} = \Delta H_{\text{reaction}} + \Delta H_{\text{sensible}} + \Delta H_{\text{latent}} + \Delta H_{\text{losses}}
\]  

(10)

For \( \text{CO}_2 \) capture from a power station, this heat energy is taken from the power station’s steam cycle and is therefore a parasitic load on the power station. This results in less available energy for dispatch to the electricity grid and hence lost revenue for the power station, which is a significant component of the overall cost of \( \text{CO}_2 \) capture. It is therefore important to know the heat required for the reboiler per tonne of separated \( \text{CO}_2 \) (GJ/t \( \text{CO}_2 \)).

Un-promoted \( \text{K}_2\text{CO}_3 \) regenerator results

Preliminary analysis of the regeneration performance for un-promoted \( \text{K}_2\text{CO}_3 \) solvent over a range of solvent concentrations has been investigated. In general the energy use was higher than desired, however with increasing solvent concentration the energy usage decreased. This fits well with the theoretical knowledge that as solvent concentration increases the \( \text{CO}_2 \) partial pressure increases which encourages the desorption of \( \text{CO}_2 \) in the regenerator. In
addition, the increased solvent concentration reduces the relative amount of water boil-off. 
Experimental results also showed a reduction in energy use as loading increased which fits 
with the theoretical understanding that as loading increases so does partial pressure of CO₂ 
and regeneration requires less energy.

**Promoted K₂CO₃ regenerator results**

Analysis of the experimental regeneration energy consumption for 40 wt% K₂CO₃ with 
10 wt% promoter P1 showed that energy consumption decreased as CO₂ feed gas 
concentration increased. Figure 28 shows that by increasing the CO₂ loading in the rich 
solvent and decreasing the CO₂ loading in the lean solvent (ie. increasing the working 
capacity of the solvent) the regeneration energy usage can be reduced to potentially less 
than 2.5 GJ/t CO₂. The lean and rich loadings in this pilot plant ranged from approximately 
0.2 to 0.5 respectively which is in agreement with the energy usage predicted in Figure 28. 
Further experiments are required to optimise the operating conditions required to achieve 
these solvent loadings.

![Figure 28: Projected reduction in energy usage for 40 wt% K₂CO₃ with 10 wt% 
promoter P1 by increasing the working capacity of the solvent (and comparison with 
experimental data – environmental heat losses not accounted for)](image-url)
2.1.7. IMPURITIES & BI-PRODUCT HANDLING

Potassium sulfate (K$_2$SO$_4$) and potassium nitrate (KNO$_3$) are formed from the reaction of K$_2$CO$_3$ with sulfur oxides and nitrous oxides (SO$_x$ and NO$_x$) in the flue gas (refer to section 1.2 for reactions). This multi-impurity capture capability leads to cost reductions due to the avoidance of flue gas pre-treatment facilities [19]. Over time these sulfate and nitrate compounds will build up in the liquid phase until the concentration reaches the saturation point and precipitation will occur. The K$_2$SO$_4$ and KNO$_3$ can be removed by either crystallization or ion exchange processes. These by-products can then be sold to the fertilizer industry [20].

**Crystallisation for removal of K$_2$SO$_4$ and KNO$_3$**

Crystallisation requires cooling the lean solvent to a temperature below the saturation temperature of K$_2$SO$_4$ and KNO$_3$ but higher than that for KHCO$_3$. This will enable the KHCO$_3$ to stay in solution while the K$_2$SO$_4$ and KNO$_3$ will precipitate and then be removed via a solid-liquid separation process step such as a hydrocyclone.

Crystallisation experiments for a range of K$_2$CO$_3$ concentrations were completed in the laboratory using a crystallization rig [21]. Refer to Figure 29 for a sample image of bicarbonate crystals. The solid-liquid equilibrium (SLE) of potassium carbonate containing sulfate and nitrate formed by the reaction of SO$_x$ and NO$_x$ gases with the solvent was investigated using the Electrolyte-NRTL model and the Pitzer Ion-interaction model. The parameters to describe the potassium carbonate-bicarbonate-water system were obtained from the literature. The potassium sulfate-water and potassium nitrate-water parameters were regressed using data from the literature while mixing parameters were used to fit ternary solubility data.

![Figure 29: Bicarbonate crystal image](image)

From the vapour-liquid equilibrium (VLE) and solid-liquid equilibrium (SLE) models it was determined that a precipitating slurry can be formed when the absorber operates below 60 °C and contains K$_2$CO$_3$ in overall concentrations higher than 40 wt%. SO$_x$ and NO$_x$ co-capture in a standard potassium carbonate solvent was analyzed using the SLE model. It was determined that potassium sulfate could be removed by crystallization after three days of operation. In contrast, due to the low reactivity of NO$_x$ and the high solubility limit of nitrate,
it was found that continuous operation for over three years would be required before nitrate could be removed by crystallization.

A crystallization study for potassium sulfate grown in 30 wt% K$_2$CO$_3$ solution was completed in the laboratory. A mixed suspension mixed product removal (MSMPR) crystallizer was used to experimentally determine nucleation and growth rates. It was found that the growth rate was similar to that of potassium sulfate grown in aqueous solution, although minimal supersaturation dependence was observed. However a noticeable change occurred to the crystal morphology with mostly octahedral crystals being formed across the entire size range beyond 50 microns. Due to the high nucleation rate, the median crystal width was 400 microns while the coefficient of variation was 52 %. Further work will be required to better understand the crystallization behaviour.

Solubility data of K$_2$SO$_4$ in water and K$_2$SO$_4$ in an aqueous solution of K$_2$CO$_3$ have been collected from literature and used in Aspen Plus® to predict the behaviour of the UNO MK 3 system (refer to Figure 30). The simulation was conducted using a 45 wt% K$_2$CO$_3$ solution as a reference case. In this instance, a temperature of 55 °C was chosen as the reference temperature to replicate industrial operating conditions. The presence of CO$_2$ in the K$_2$CO$_3$ solution promotes the formation of KHCO$_3$ as follows:

$$
\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{KHCO}_3
$$

The formation of KHCO$_3$ is consistent with the observed drop in K$^+$ concentration. As a result, the equilibrium dissociation is shifted to the product side and sulfate solubility decreases:

$$
\text{K}_2\text{SO}_4 \rightarrow 2\text{K}^+ + \text{SO}_4^{2-}
$$

At loadings lower than 0.21, only K$_2$SO$_4$ is present in the solid form. However, when the loading is above 0.21, solid KHCO$_3$ starts to form in the system and dominates the precipitation reaction. From Figure 30, it can be seen that the formation of KHCO$_3$ solid depletes the amount of available K$^+$ ions in the solution significantly and hence the solubility of sulfate increases.

The model also predicts a positive relationship between sulfate solubility and temperature (refer to Figure 31). Operating at higher temperature may provide the system with higher tolerance towards sulfate ions along with better kinetics. However, it is important to take into account the trade-off between these benefits and the vapour-liquid-equilibrium behaviour.
Figure 30: Solid saturation curve for K$_2$SO$_4$ and KHCO$_3$ at 55 °C

Figure 31: Effect of temperature on solid saturation curve
Ion exchange for removal of K$_2$SO$_4$ and KNO$_3$

Ion exchange is a method that can be used for removal of K$_2$SO$_4$ and KNO$_3$. In this case, no crystallisation is required and it is important that K$_2$SO$_4$ and KNO$_3$ remain in solution. The SO$_4^{2-}$ and NO$_3^-$ ions are exchanged with OH$^-$ ions embedded in a resin contained in a fixed bed within a vessel. The resin is then regenerated offline with a potassium hydroxide (KOH) wash to remove the SO$_4^{2-}$ and NO$_3^-$ ions.

A laboratory based study tested the selectivity of a number of resins for sulfate and nitrate removal. The resins, in the hydroxide form, react with sulfate and nitrate as shown in reactions (13) and (14). Note that R refers to the resin functional group (quaternary amine) and the overstrike signifies that the component is in the solid phase.

(13)

(14)

Laboratory based resin selectivity tests were initially completed using Dowex 1. As shown in Figure 32 K$_2$SO$_4$ removal is possible in the absence of K$_2$CO$_3$ however the amount of K$_2$SO$_4$ removed is significantly reduced in the presence of 4 wt% K$_2$CO$_3$ due to the selective uptake of K$_2$CO$_3$. This will result in reduced sulfate removal efficiency as well as other operational issues such as the loss of K$_2$CO$_3$ from the main solvent circuit and the regenerated resin will result in a K$_2$SO$_4$ product that is contaminated with K$_2$CO$_3$.

![Figure 32: K$_2$SO$_4$ uptake in Dowex 1 resin in the presence of 4 wt% K$_2$CO$_3$](image)

In order to reduce the amount of K$_2$CO$_3$ present in the ion exchange process, various changes to the flowsheet have been made such that the feed stream to the ion exchange unit will contain a lower concentration of K$_2$CO$_3$. Three different ion exchange resins, Dowex 1, Amberlite IRA 410 and Amberlite PWA 5, were tested for sulfate and nitrate removal both in the absence of K$_2$CO$_3$ and in the presence of 1 wt% K$_2$CO$_3$. Further details on the properties of each resin can be found in Table 3. Selectivity results for each resin are shown
in Figure 33, Figure 34 and Figure 35 for Dowex 1, Amberlite IRA 410 and Amberlite PWA 5 respectively. From these results it can be seen that sulfate and nitrate selectivity did increase with lower K$_2$CO$_3$ concentrations. However for Dowex 1 and Amberlite IRA 410 the resin uptake for nitrate and sulfate still decreased by about 40 % in the presence of 1 wt% K$_2$CO$_3$. In contrast, as shown in Figure 35 Amberlite PWA 5, which was chosen for its high nitrate selectivity, did not show any significant reduction in nitrate selectivity in the presence of K$_2$CO$_3$. This is a promising result and further testing will need to be completed to find a resin with high selectivity for sulfate.

Table 3: Properties of the resins tested for nitrate and sulfate removal

<table>
<thead>
<tr>
<th>Resin Trade name</th>
<th>Dowex™ 1</th>
<th>Amberlite IRA410</th>
<th>Amberlite PWA5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Type 1 strongly basic anion exchange</td>
<td>Type 2 strongly basic anion exchange resin</td>
<td>Strongly basic anion exchange resin</td>
</tr>
<tr>
<td>Matrix</td>
<td>Styrene-DVB, gel</td>
<td>Styrene-DVB, gel</td>
<td>Cross linked copolymer</td>
</tr>
<tr>
<td>Ionic form *</td>
<td>Cl$^-$</td>
<td>Cl$^-$</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>Total exchange capacity (eq/L)</td>
<td>1.4</td>
<td>≥ 1.25</td>
<td>≥ 1</td>
</tr>
<tr>
<td>Moisture holding capacity (%)</td>
<td>43-48</td>
<td>45-51</td>
<td>52-58</td>
</tr>
<tr>
<td>Service flowrate (PV/hr)</td>
<td>15-20</td>
<td>5-40</td>
<td>5-40</td>
</tr>
<tr>
<td>Maximum operating temperature (°C)</td>
<td>100</td>
<td>35</td>
<td>75</td>
</tr>
</tbody>
</table>

* Ionic form of resins was converted to OH$^-$ prior to first use
Figure 33: Dowex 1 resin selectivity results for sulfate and nitrate in the absence of $K_2CO_3$ and with 1 wt% $K_2CO_3$

Figure 34: Amberlite IRA 410 resin selectivity results for sulfate and nitrate in the absence of $K_2CO_3$ and with 1 wt% $K_2CO_3$
Figure 35: Amberlite PWA 5 resin selectivity results for sulfate and nitrate in the absence of K$_2$CO$_3$ and with 1 wt% K$_2$CO$_3$
2.2. ASPEN PLUS® SIMULATIONS

Aspen Plus® simulations have been developed to predict the performance of the pilot plant using both un-promoted and promoted K$_2$CO$_3$ over a range of operating conditions. Aspen Plus® is a chemical process modelling program with specialised functions for different reaction types and includes a large database of physical properties. Modelling of the UNO MK 3 process with Aspen Plus® initially involved development of a thermodynamic model, which describes the fundamental chemistry and physical properties of the solvent. This thermodynamic model was then used with a process model developed for the plant (absorber and regenerator) to enable prediction of the overall plant performance.

2.2.1. THERMODYNAMIC & PHYSICAL PROPERTY MODELLING

**VLSE Model**

Experimental data measured by the CO2CRC via laboratory studies and literature surveys have resulted in the development of a vapour liquid solid equilibrium thermodynamic model that is valid over a temperature range suitable for the absorption systems under investigation. The VLSE model for the potassium carbonate, potassium bicarbonate, carbon dioxide system is based on the Electrolyte NRTL activity co-efficient model (E-NRTL).

Key characteristics of the model prediction compared to experimental data collected in-house and from literature [22] are presented from Figure 36 to Figure 38. Figure 36 plots the vapour liquid equilibria determined in-house and that presented by Korbutova [22] against that predicted by the new VLSE model at 50 and 70 °C. As shown, a reasonable fit over the temperature range was obtained. The vapour liquid equilibria over a 50 wt% slurry at 50 and 60 °C is presented in Figure 37. This shows that the simulation results fits the experimental data within an acceptable margin of error over the temperature conditions that the absorption processes occur. Figure 38 shows the proportion of solids formed determined experimentally against that predicted by the new model at 50 and 60 °C. Similarly a reasonable fit is obtained.
Figure 36: The partial pressure of CO\(_2\) above a 30 wt% K\(_2\)CO\(_3\) solution at 50 and 70 °C.

Figure 37: The partial pressure of CO\(_2\) above a 50 wt% K\(_2\)CO\(_3\) slurry at 50 and 60 °C
Physical Property Model

Physical property data including pH, density and viscosity for the K$_2$CO$_3$/KHCO$_3$ system has been measured in the laboratory. The measurement of pH is important as it indicates the concentration of OH$^-$ ions in solution. Initial comparison of experimental data to Knuutila’s data [23] showed 0.5 - 1.0 pH scale higher pH values for the CO2CRC data at 40 – 70 °C. While the Figure shows that this set of data matched the predicted values for pH using the default e-NRTL model in Aspen Plus® at 40 °C, comparison of the measured values to Aspen® predictions at 60 – 70 °C did not show a match. The measurement of pH was repeated at 40 °C with a new buffer solution that had been temperature-calibrated. Figure 12 shows that the new set of data matched both Knuutila’s data and the predictions from Aspen Plus® using the Cullinane parameters within a smaller margin of error.
Figure 39: Comparison of pH measurements at 40 °C with literature and Aspen® predictions

Literature data for the density of K$_2$CO$_3$ solutions as a function of concentration and temperature were available from 25 – 70 °C. The CO2CRC data, measured at 40 - 70°C, were compared to the literature [8-9] and to an equation developed by Cullinane [10].

Figure 40: Comparison of measured density at 40 °C with literature and predictive correlation
Figure 40 and Figure 41 show that the CO2CRC experimental data is marginally lower than that in the literature and of the prediction, at 40 - 70°C, although still within experimental error. Cullinane’s predictive model for the density of K$_2$CO$_3$ aqueous solutions as a function of temperature is given by equation (15). As this predictive model fits the data well at 70 °C despite having been developed at temperatures below 50 °C [10], it is recommended that its use be limited to temperatures between 25 – 70 °C.

\[
\rho = 1.130 + 0.0537 [K^+] - 1.204 \times 10^{-3} [K^+]^2 - 0.442 \times 10^{-3} T
\]  

where \( \rho = \) density in g.cm$^{-3}$  
\([K^+] = \) concentration in molal  
\( T = \) temperature in Kelvin

The CO2CRC viscosity data agrees well with the literature data at 40 – 70 °C. However, the default Aspen® prediction at 50 °C, shown in the Figure below, only matches the data for 20 wt% K$_2$CO$_3$. Other measured viscosity data obtained by the CO2CRC for loaded K$_2$CO$_3$ solutions also show complete deviation from Aspen® predictions. It is not clear, at this stage, whether the error in Aspen® viscosity prediction will affect the overall simulation significantly, but this discrepancy will be investigated.
2.2.2. ABSORBER ASPEN PLUS® SIMULATIONS

Un-promoted $\text{K}_2\text{CO}_3$ absorber model

A non-equilibrium rate-based model for $\text{CO}_2$ absorption into aqueous $\text{K}_2\text{CO}_3$ was developed using Aspen Plus® RateSep™ to interpret the results obtained from the pilot plant. The absorber model incorporated the VLSE model, rate constants and physical property correlations developed by the University of Melbourne. Heat and mass transfer and physical properties of the solvent were calculated using the absorber model. Due to the exothermic nature of $\text{CO}_2$ absorption, the column temperature changed significantly along its length. Importantly, this change in temperature impacted the thermodynamics, reaction kinetics and physical properties of the solvent. The rate-based distillation module of Aspen Plus® (RadFrac) uses proven models for estimating gas and liquid film mass and heat transfer coefficients and interfacial areas that reliably account for these temperature changes. The RadFrac model assumes equilibrium stages but it is possible to use Murphree efficiencies to match plant data. RateSep extends Radfrac to allow the simulation of rate-based, non-equilibrium separation processes by accounting for the inter-phase mass and heat transfer processes. In order to simulate a precipitating solvent system the prediction of potassium bicarbonate solid is required. In Aspen Plus® liquid-solid reactions are treated as equilibrium reactions with the solids phase a single salt. Therefore RateSep cannot be used when salt precipitation is to be predicted so Murphree efficiencies in the equilibrium model are required. Table 4 describes the characteristics of the packed column used in the absorption simulation. The composition, flow rate and conditions of aqueous $\text{K}_2\text{CO}_3$ and inlet gas were supplied from the experimental data produced by the pilot plant trials. A schematic representation of the simulation design is presented in Figure 43.

Figure 42: Comparison of measured viscosity at 50 °C with literature and Aspen® prediction
Table 4: Characteristics of the packed column used in simulations

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column diameter (m)</td>
<td>0.1</td>
</tr>
<tr>
<td>Column Height (m)</td>
<td>4.25</td>
</tr>
<tr>
<td>Number of segments</td>
<td>26</td>
</tr>
<tr>
<td>1 (Equilibrium)</td>
<td>0.2</td>
</tr>
<tr>
<td>2-5 (Rate-based)</td>
<td>0.8</td>
</tr>
<tr>
<td>6-9 (Equilibrium)</td>
<td>0.7</td>
</tr>
<tr>
<td>10-17 (Rate-based)</td>
<td>0.8</td>
</tr>
<tr>
<td>18-21 (Equilibrium)</td>
<td>0.7</td>
</tr>
<tr>
<td>22-25 (Rate-based)</td>
<td>0.8</td>
</tr>
<tr>
<td>26 (Equilibrium)</td>
<td>0.2</td>
</tr>
<tr>
<td>Bottom Liquid holdup</td>
<td>0.25</td>
</tr>
<tr>
<td>Type of packing</td>
<td>Pall rings 304SS (10mm)</td>
</tr>
<tr>
<td>Surface area (m²/m³)</td>
<td>483</td>
</tr>
<tr>
<td>Void fraction (ε)</td>
<td>0.93</td>
</tr>
<tr>
<td>Stichlmair constants</td>
<td></td>
</tr>
<tr>
<td>C₁</td>
<td>3.125539</td>
</tr>
<tr>
<td>C₂</td>
<td>13.5957</td>
</tr>
<tr>
<td>C₃</td>
<td>1.88108</td>
</tr>
</tbody>
</table>

Figure 43: Process flow diagram of Rate-based absorber
The Aspen® Rate-Based distillation model RadFrac can model reactions occurring in the film. Since the reaction rates in the film are calculated, enhancement factors for film reactions are not needed. For kinetic reactions, the reaction rates are evaluated at a point in the film. The reaction condition factor (1 for the gas-liquid interface, 0 for the edge of the film next to the bulk) determines the point where the reaction takes place and the holdup in the film region is used to compute the reaction rates. The correlations developed by Onda et al. [24] were used for predicting liquid and gas side mass transfer coefficients and interfacial area. The heat transfer coefficients for the liquid and vapour were estimated using the Chilton-Colburn analogy between heat and mass transfer.

The following kinetics for the rate-controlled reactions were supplied to RadFrac:

\[
\text{kinetic factor} = k T^n e^{-\frac{E}{R T}} \quad \text{if } T_0 \text{ is not specified} \tag{16}
\]

\[
\text{kinetic factor} = k \left( \frac{T}{T_0} \right)^n e^{-\frac{E}{R \left( \frac{1}{T} - \frac{1}{T_0} \right)}} \quad \text{if } T_0 \text{ is specified} \tag{17}
\]

\[
\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-
\tag{18}
\]

\[
\text{HCO}_3^- \rightarrow \text{CO}_2 + \text{OH}^-
\tag{19}
\]

The equilibrium controlled chemical reactions were as follows:

\[
\ln K_{eq} = A + \frac{B}{T} + C \ln T + D T, \ T \text{ in (K)}
\tag{20}
\]

\[
\text{CO}_2 + 2\text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}_3\text{O}^+
\tag{21}
\]

\[
\text{HCO}_3^- + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{CO}_3^{2-}
\tag{22}
\]

\[
2 \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-
\tag{23}
\]

In addition to liquid and vapor phase reactions, salt precipitation reactions were also included. These reactions are liquid/solid phase equilibrium reactions, where the solid phase consists of a single salt. The included reactions were:

\[
\text{KHCO}_3 \leftrightarrow \text{K}^+ + \text{HCO}_3^{2-}
\tag{24}
\]

\[
\text{K}_2\text{CO}_3 \leftrightarrow 2\text{K}^+ + \text{CO}_3^{2-}
\tag{25}
\]

The Henry’s Law constant was obtained from literature[23, 25, 26]. The reaction rate constants (k) and equilibrium constants (K) for reactions used in this work are listed in Table 5. The constants for reactions (24) and (25) were regressed in this work using a large VLSE data available in the literature. Transport properties such as density, viscosity, surface tension, thermal conductivity and diffusivity were estimated by the built-in correlations in Aspen Plus® with the regressed parameters. All the properties were predicted within ±5%. The difference in the estimation of physical properties in default Aspen Plus® rate-based model and the model developed in this work are provided in Table 6. The Chilton-Colburn averaging parameter was set to a default value of 0.0001 to calculate average diffusivity and average mass transfer coefficient.
### Table 5: Coefficients for power law kinetic expression and equilibrium constants expression

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>Reaction</th>
<th>Basis</th>
<th>Coefficients</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Kinetic</td>
<td>Molarity</td>
<td>4.32E13</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Kinetic</td>
<td>Molarity</td>
<td>4.50E-06</td>
<td>14.3043</td>
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</table>

**Equilibrium constant coefficients**

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Coefficients</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Equilibrium</td>
<td>mole-fraction</td>
<td>231.47</td>
<td>-12092.10</td>
<td>-36.78</td>
<td>0.00</td>
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<tr>
<td>11</td>
<td>Equilibrium</td>
<td>mole-fraction</td>
<td>216.05</td>
<td>-12431.70</td>
<td>-35.48</td>
<td>0.00</td>
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<tr>
<td>12</td>
<td>Equilibrium</td>
<td>mole-fraction</td>
<td>132.90</td>
<td>-13445.90</td>
<td>-22.48</td>
<td>0.00</td>
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<tr>
<td>13</td>
<td>Salt</td>
<td>mole-fraction</td>
<td>-451.81</td>
<td>9855.01</td>
<td>78.72</td>
<td>-0.12</td>
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<tr>
<td>14</td>
<td>Salt</td>
<td>mole-fraction</td>
<td>-77.95</td>
<td>-1908.16</td>
<td>17.88</td>
<td>-0.08</td>
</tr>
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</table>

### Table 6: Physical properties estimated using Rate-based model

<table>
<thead>
<tr>
<th>Properties</th>
<th>Process Conditions</th>
<th>Default</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Densities (kg/m³)</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>0-50 wt%</td>
<td>333.15</td>
<td>0.44</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>323.15</td>
<td>0.47</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>0.49</td>
<td>0.17</td>
</tr>
<tr>
<td>Viscosities (cP)</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>0-50 wt%</td>
<td>333.15</td>
<td>13.99</td>
<td>5.26</td>
</tr>
<tr>
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<td>5.03</td>
</tr>
<tr>
<td></td>
<td>313.15</td>
<td>15.85</td>
<td>6.19</td>
</tr>
<tr>
<td>Diffusivities (cm².s⁻¹×10⁵)</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>0-4 mol/L</td>
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<td>295.66</td>
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<td>363.15</td>
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<td>7.28</td>
</tr>
<tr>
<td></td>
<td>373.15</td>
<td>218.86</td>
<td>6.58</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>5-25 wt%</td>
<td>333.15</td>
<td>3.09</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>3.17</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>373.15</td>
<td>3.27</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>393.15</td>
<td>3.36</td>
<td>0.29</td>
</tr>
<tr>
<td>Surface tension</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>0-50 wt%</td>
<td>293.15</td>
<td>14.48</td>
<td>2.84</td>
</tr>
<tr>
<td>Heat Capacity</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>0-50 wt%</td>
<td>313.15</td>
<td>11.27</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>333.15</td>
<td>11.87</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>353.15</td>
<td>12.49</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>393.15</td>
<td>14.19</td>
<td>2.83</td>
</tr>
<tr>
<td>Vapour Pressure</td>
<td>K₂CO₃</td>
<td>T (K)</td>
<td>%AAD</td>
</tr>
<tr>
<td>20 wt%</td>
<td>343.15-403.15</td>
<td>25.69</td>
<td>23.33</td>
</tr>
<tr>
<td>30 wt%</td>
<td>343.15-403.15</td>
<td>11.77</td>
<td>13.90</td>
</tr>
<tr>
<td>40 wt%</td>
<td>343.15-403.15</td>
<td>30.28</td>
<td>22.28</td>
</tr>
</tbody>
</table>
Reaction condition factors of 0 (slow reaction), 0.5 (very fast reaction) and 1 (instantaneous reaction) were tested to find the reaction point in the bulk. It was found that for un-promoted aqueous K$_2$CO$_3$, the reaction condition factor of 0 (slow reaction) represents the properties of the solvent well by comparing the concentration and temperature profiles with the pilot-plant data. To represent this condition and the option for the reaction handling the solids, an equilibrium model was also developed. Aspen Plus® uses residence time to calculate the holdup for rate-controlled reactions in equilibrium calculations. So, the residence times were calculated using the liquid and gas flow rates as follows:

$$\text{Residence time} = \frac{\text{Flow rate}}{\text{Flow rate} + \text{Holdup}}$$  \hspace{1cm} (26)

The experimentally measured holdup and the simulated holdup in both equilibrium and rate based models are given in Table 7. In order to match the equilibrium model to the experimental data, the Murphree efficiency ($\text{Eff}$) of CO$_2$ was adjusted. Murphree efficiency is given as:

$$\text{Eff} = \frac{\text{Actual transfer rate}}{\text{Ideal transfer rate}}$$  \hspace{1cm} (27)

where, $x_j$ is the liquid mole fraction of CO$_2$ in the j$^{th}$ stage; $y_j$ is the vapor mole fraction of CO$_2$ in the j$^{th}$ stage; $K_j$ is the equilibrium K value for CO$_2$ at stage j. The equilibrium model was matched with the experimental data and rate-based model to find the operating of the absorber column used in this work.

**Table 7: Experimental and predicted holdup per stage used in rate-based and equilibrium models**

<table>
<thead>
<tr>
<th>wt%</th>
<th>L/G</th>
<th>Holdup (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Experiment</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>1.39</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>1.71</td>
</tr>
<tr>
<td>30</td>
<td>4</td>
<td>1.39</td>
</tr>
<tr>
<td>40</td>
<td>4</td>
<td>1.38</td>
</tr>
</tbody>
</table>

A comparison of the simulation results from the absorber simulation model and pilot plant experimental data for un-promoted K$_2$CO$_3$ is presented in Figure 44 to Figure 49. The operating conditions that these experiments were conducted at are provided in Table 8. As described in section 2.2.2, both rate-based and conventional equilibrium models were used to model the performance of the absorber. Absorber holdup was predicted using the rate based model to within ± 5.5 % as shown in Figure 44. CO$_2$ exit gas concentration was predicted using both the rate based and equilibrium models to within ± 2.8 % and ± 7.5 % respectively as shown in Figure 45. Lean solvent loading was predicted using the rate based model to within ± 2.0 % as shown in Figure 46. Rich solvent loading was predicted using both the rate based and equilibrium models to within ± 7.0 % and ± 7.8 % respectively as shown.
in Figure 47. Lean solvent temperature was predicted using both the rate based and equilibrium models to within ± 1.0 % and ± 4.6 % respectively as shown in Figure 48. Absorber bottom temperature was predicted using both the rate based and equilibrium models to within ± 16.0 % and ± 5.6 % respectively as shown in Figure 49. It can therefore be concluded that both the rate-based model and the equilibrium model can predict the pilot plant data using un-promoted K₂CO₃ very well.

Table 8: Experimental operating conditions for un-promoted K₂CO₃ Aspen® modelling for the absorber

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Gas flow rate (kg/hr)</th>
<th>Solvent flow rate (kg/hr)</th>
<th>Gas composition (vol %)</th>
<th>K₂CO₃ concentration (wt %)</th>
<th>Gas inlet temperature (°C)</th>
<th>Solvent inlet temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>120</td>
<td>10</td>
<td>28.3</td>
<td>34.9</td>
<td>54.7</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>27.7</td>
<td>31.0</td>
<td>55.2</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>24.5</td>
<td>34.1</td>
<td>54.8</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>29.2</td>
<td>26.3</td>
<td>54.9</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>32.0</td>
<td>23.0</td>
<td>54.5</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>24.5</td>
<td>30.0</td>
<td>56.6</td>
</tr>
<tr>
<td>7</td>
<td>30</td>
<td>120</td>
<td>25</td>
<td>28.3</td>
<td>50.4</td>
<td>51.9</td>
</tr>
<tr>
<td>8</td>
<td>30</td>
<td>120</td>
<td>10</td>
<td>29.5</td>
<td>50.6</td>
<td>57.0</td>
</tr>
</tbody>
</table>

Figure 44: Comparison between pilot plant experimental data and Aspen® rate based model predictions for absorber holdup using un-promoted K₂CO₃
Figure 45: Comparison between pilot plant experimental data and Aspen® model predictions (both rate-based and equilibrium) for composition of CO₂ in exit gas of absorber using un-promoted K₂CO₃.

Figure 46: Comparison between pilot plant experimental data and Aspen® rate based model predictions for lean solvent loading using un-promoted K₂CO₃.
Figure 47: Comparison between pilot plant experimental data and Aspen® model predictions (both rate-based and equilibrium) for rich solvent loading using un-promoted \( \text{K}_2\text{CO}_3 \)

Figure 48: Comparison between pilot plant experimental data and Aspen® model predictions (both rate-based and equilibrium) for lean solvent temperature using un-promoted \( \text{K}_2\text{CO}_3 \)
Figure 49: Comparison between pilot plant experimental data and Aspen® model predictions (both rate-based and equilibrium) for absorber bottom temperature using un-promoted $K_2CO_3$. 
**Promoted K\textsubscript{2}CO\textsubscript{3} absorber model**

In order to model the performance of the absorber using solvents with rate promoters, the existing Aspen Plus\textsuperscript{®} RateSep model was extended to include the effects of the promoter. The addition of promoter P1 improved the rate of absorption of CO\textsubscript{2} into the solvent by providing an alternate pathway for the formation of HCO\textsubscript{3}\textsuperscript{−} ions via an intermediate species, I, as shown in reactions (28) and (29).

\[
\text{CO}_2 + \text{P1} \rightleftharpoons \text{I} \tag{28}
\]

\[
\text{I} \rightleftharpoons \text{P1+HCO}_3^- \tag{29}
\]

Reaction (28) was modelled as a rate controlled reaction with both forward and reverse reactions, whilst reaction (29) was modelled as an equilibrium reaction. As well as adding chemical reactions to the system, addition of the rate promoter also affected the physical properties of the solvent which needs to be accounted for. These effects can be accounted for by adding additional parameters to the physical properties models in the existing Aspen Plus\textsuperscript{®} model. Experimental and literature data for the density and viscosity of promoter P1 both in water and in potassium carbonate solutions were used to regress values for these parameters.

The addition of a rate promoter to the solvent is expected to change the reaction condition factor required to model the absorber behaviour, as it changes the speed of the reaction. For the promoted solvent, it was found that a reaction condition factor of 0.96 (almost instantaneous) was required to match the experimental data as compared to the reaction condition factor of 0 used for the unpromoted solvent. In addition, a transport condition factor (analogous to the reaction condition factor used to calculate the mass transfer coefficients) for mass transfer of 0.04 (slow) was required.

**Table 9: Experimental operating conditions for promoted K\textsubscript{2}CO\textsubscript{3} Aspen\textsuperscript{®} modelling for the absorber**

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Flow Rates</th>
<th>Gas composition</th>
<th>Solvent Concentrations</th>
<th>Inlet Temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gas (kg/hr)</td>
<td>Solvent (kg/hr)</td>
<td>CO\textsubscript{2} vol %</td>
<td>K\textsubscript{2}CO\textsubscript{3} (wt %)</td>
</tr>
<tr>
<td>1</td>
<td>30</td>
<td>90</td>
<td>10</td>
<td>36.4</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>120</td>
<td>10</td>
<td>41.0</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>120</td>
<td>10</td>
<td>41.0</td>
</tr>
</tbody>
</table>

A comparison of the simulation results from the absorber simulation model and pilot plant experimental data for promoted K\textsubscript{2}CO\textsubscript{3} is presented in Figure 50 to Figure 54. The operating conditions that these experiments were conducted at are provided in Table 9. Absorber holdup was defined for the system based on experimental measurements taken from the column. Total CO\textsubscript{2} removal was predicted to within ±15.0 % as shown in Figure 50, whilst gas and liquid temperatures leaving the absorbed were predicted to within ±34.8 % and
± 3.5 % respectively, as shown in Figure 51 and Figure 52. CO₂ exist gas concentration was predicted to within ± 11.6 % as shown in Figure 53, whilst rich solvent loading was predicted to within ± 8.4 % as shown in Figure 54.

**Figure 50:** Comparison between pilot plant experimental data and Aspen® model predictions for absorber recovery using promoted K₂CO₃.

**Figure 51:** Comparison between pilot plant experimental data and Aspen® model predictions for absorber outlet gas temperature using promoted K₂CO₃.
Figure 52: Comparison between pilot plant experimental data and Aspen® model predictions for absorber rich solvent temperature using promoted K$_2$CO$_3$.

Figure 53: Comparison between pilot plant experimental data and Aspen® model predictions for absorber outlet gas composition using promoted K$_2$CO$_3$. 
Figure 54: Comparison between pilot plant experimental data and Aspen® model predictions for absorber rich solvent loading using promoted K$_2$CO$_3$. 
2.2.3. REGENERATOR ASPEN PLUS® SIMULATIONS

Un-promoted K₂CO₃ regenerator model

An Aspen Plus® process model of the regenerator was developed based on the thermodynamic model developed for the absorber with modifications to the reaction rates which better suit the operating conditions in the regenerator [31]. The model was updated to use Astarita’s reaction rate equation [32] which covers temperatures from 80 to 130 °C and K₂CO₃ concentrations from 15 to 45 wt% which are relevant to regeneration operating conditions used in the current pilot plant. The pilot plants’ heat losses and operational factors were thoroughly considered so that the energy use of the plants could be accurately apportioned.

ASPEN’s Radfrac block was used as the stripper column and a separate heater was used as the reboiler (refer to schematic in Figure 55). Radfrac requires the use of either an equilibrium model or a rate-based model. A rate-based model is more accurate because it allows the reaction rate to be included in the calculation. However this model cannot handle solids which is not a problem with the majority of data collected with the un-promoted system because solids were generally not observed in the regenerator. If the streams are not at equilibrium this is allowed for by adjusting efficiencies. Another important factor in the performance of the column is the type of packing used. The packing determines the contact area between the liquid and the gas and determines the open area available for the two flows. The packing used in this plant was 10 mm x 10 mm Pall Rings.

![Figure 55: Aspen Plus® schematic of the regenerator](image)

The VLSE and physical properties component of the chemical model that was developed for the absorber model was used for the regenerator. The reaction rates were calculated over the temperature range 80°C to 150°C which covers the temperature range of the regenerator. Once the run-specific reaction rate constant equation was input to the model, the process of matching the model to the experimental data was as follows:

1. Constrain the system by specifying the following parameters to equal the experimental values:
   a. the RS temperature, composition and volume flowrate
   b. the column pressure at the top and bottom
   c. the column temperature at the top
d. the reboiler pressure (equal to the pressure at the bottom of the column)
e. the temperature and flowrate of the reflux

2. Manually vary the temperature in the reboiler until the loading of the lean solvent out matches the experimental data.

Aspen Plus® outputs the heat input of the reboiler and the amount of CO₂ out of the column, which allows the energy usage in GJ/t of CO₂ to be calculated. The heat input to the reboiler is the heat required for regeneration and should be less than the experimental energy use because of heat losses. The experimental energy use is made up of the energy required for regeneration and any heat losses.

The experimental energy use (kW) for all experimental runs using un-promoted K₂CO₃ solvent was 12 kW. This should be equal to the energy required for regeneration plus the heat losses. If the modelled energy use (kW) is used as the energy required for regeneration, and it is subtracted from the total 12kW, the heat loss is the quantity remaining. Figure 56 shows how the 12 kW is divided between the regeneration energy and the heat loss.

![Figure 56: Modelled heat input and heat loss contributions to the total experimental reboiler power](image)

The calculated heat loss varied considerably between each experiment. In particular, for Run 2 the simulated energy use was above 12 kW so the heat loss was calculated to be negative. This is obviously not possible because the temperature inside the regenerator is ~120 °C. The real heat losses were expected to be quite consistent, because the difference between the inside temperature and the room temperature was estimated to only vary from 87-91 °C and the overall heat transfer coefficient should be constant. 15 runs were modelled and it is reasonable to except that the average heat loss calculated is close to the actual heat loss. The average heat loss, neglecting Run 2 which is clearly an outlier, was 6.2 kW. Assuming this is consistent for all runs the regeneration energy use was actually 5.8 kW for all runs.

Further work will be required to develop an Aspen Plus® simulation that can predict the regeneration performance of the promoted K₂CO₃ system. This will require new vapour-liquid equilibrium data to be measured for the promoted solvent system as the current VLE data is limited to temperatures below 60 °C due to equipment limitations in measuring solvent speciation at temperatures greater than 60 °C.
3. CONCLUSIONS

A pilot plant for carbon dioxide capture from an air-CO$_2$ mixture was built and tested with potassium carbonate solvent. Experiments were conducted with solvent concentrations ranging from 20 to 45 wt% K$_2$CO$_3$ and L/G ratios ranging from 2 - 6. Experiments examining the effects of rate promoter on the CO$_2$ removal rate were also completed. The hydraulic performance of the pilot plant was monitored over time. It was found that the measured air-water pressure drop for the Pall ring packing followed the trend predicted by the generalized pressure drop correlation. The operating holdup did not vary significantly with gas water content, but did vary slightly with solvent concentration. Although there was some precipitation observed around joints and fittings, no major operational issues were encountered with the pumps or heat exchangers while operating with a precipitating solvent system. Increasing the K$_2$CO$_3$ solvent concentration, operating with a higher CO$_2$ feed gas concentration and the addition of a rate promoter were all found to be important for increasing the CO$_2$ recovery results and optimising the regeneration energy of the process.

Aspen Plus$^\text{®}$ simulations were developed to model the performance of K$_2$CO$_3$ solvent in the pilot plant. The simulations were validated with data from the plant for 0 - 45 wt% K$_2$CO$_3$ solvent. Both rate-based and equilibrium models were used to model the absorber with regressed physical property data in the e-NRTL model. The data showed good agreement with the experimental results. A rate-based model for the regenerator was developed using Astarita’s reaction rate equation. Experimental data was used to simulate the energy use (GJ/tCO$_2$) of the reboiler. The simulated energy use was included in an assessment of the experimental energy uses. This provided additional understanding of the pilot plant operation. As optimal operating conditions were not achieved when operating this pilot plant with precipitating potassium carbonate solvent the simulations will be very important for optimising the performance of the UNO MK 3 process. Operational data from the pilot plant at Hazelwood Power Station will also be used to validate this model.

Processes for the removal of potassium sulfate and potassium nitrate by-products were also investigated. The use of crystallization or ion exchange processes show promise for removal of these products from the rich solvent stream.

4. RECOMMENDATIONS

Further work is recommended in the following areas:

- Further experiments on regeneration of the loaded solvent to increase the working capacity of the solvent
- Development of Aspen Plus$^\text{®}$ simulations for the promoted solvent in the regenerator
- Testing of equipment such as a hydrocyclone to increase solids sent to regenerator
- Further experiments with alternative rate promoters
- Further experiments with alternative packing materials
- Further development of ion exchange and crystallisation processes for impurity and by-product removal
5. REFERENCES


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