

Combined low-cost pre-treatment of flue gas and capture of CO₂ from brown coal-fired power stations using a novel integrated process concept

Closing the sulfur loop: coCAPco₂

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Public summary

Australia currently has vast coal reserves and a historical high reliance on coal to provide electricity. This results in significant emissions of carbon dioxide from coal-fired power stations through the generation of that electricity. Technologies such as carbon capture and storage offer the potential to continue utilising these valuable coal resources whilst significantly reducing the CO₂ emissions associated with power production. A significant challenge however is the current high cost of installing CO₂ capture facilities in Australia. Part of this high cost is the need to install pre-cleaning technologies, such as flue gas desulfurisation units, to coal-fired power stations before conventional carbon capture technologies can be applied. To lower the cost of applying carbon capture technologies in Australia, the CSIRO have developed a process which combines these pre-cleaning and CO₂ removal steps into a single process, known as the CS-Cap process. This project, coCAPco2, has progressed the CS-Cap technology from an initial concept, through laboratory and early proof-of-concept evaluation at pilot-scale. The project was sponsored by Australian Carbon Innovation Ltd, and is a collaboration between CSIRO, Federation University, AGL Loy Yang, and Energy Australia. The results achieved through the project have confirmed the potential to apply the CS-Cap process to Australian coal-fired power stations. The data obtained in the project has allowed an initial costing to be completed for the process, suggesting that the CS-Cap process should indeed lower the cost of CO₂ capture from Australian coal-fired power plant compared to current conventional technologies.

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Executive summary

This report is to cover the final reporting requirement of the project entitled: “Combined low-cost pre-treatment of flue gas and capture of CO₂ from brown coal-fired power stations using a novel integrated process concept; closing the Sulphur loop. coCAPco2.” This project is carried out by the CSIRO, Federation University, and AGL Loy Yang, whilst co-funded by Australian Carbon Innovation (formerly Brown Coal Innovation Australia, BCIA) and Energy Australia.

The overall aim of the project was to progress a CSIRO process concept for low-cost CO₂ capture from coal flue gases from concept through to a process ready for pilot-scale evaluation. The unique part of the CS-Cap process is the use of CO₂ loaded aqueous amine to capture flue gas SO₂ in a step preceding CO₂ capture. This will generate an amine absorbent rich in absorbed SO₂ that will require regeneration for the process to be continuous. Progressing this technology required: information on the properties of the SO₂ loaded absorbent generated, identifying a suitable technology for regenerating the absorbent, experimentally determining the effectiveness of the selected technology for recovering amine from the sulfur loaded absorbent, and finally a high level cost comparison to determine any economic benefit when applying the CS-Cap process to an Australian brown coal power station.

Initial proof-of-concept operation was undertaken using a CO₂ loaded amine absorbent to capture SO₂ from a coal flue gas at the Loy Yang CO₂ capture pilot plant. This confirmed the ability of the CO₂ loaded aqueous amine absorbents to rapidly capture 95-100% of the flue gas SO₂. The absorbent collected from the pilot plant confirmed that the absorbed SO₂ is rapidly converted to sulfate in solution, with only a minor part remaining as sulfite. The pilot plant generated absorbent provided real process solutions that were then used to evaluate potential reclamation technologies. A literature review identified several potential technologies that could be used to regenerate the sulfate loaded absorbent. Critical assessment of these technologies, including their potential for scale-up and incorporation into the CS-Cap process, identified two for additional experimental evaluation: thermal reclamation and reactive crystallisation.

Laboratory scale evaluation confirmed the ability of both processes to regenerate the sulfate loaded amine absorbent. The experimental work provided data on the chemical requirements and effectiveness of both processes, under a range of operating conditions. This information was then used to validate a process simulation of both technologies. This simulation was then used to size and cost the equipment required if the CS-Cap process was applied to a full-scale power plant. This cost information was combined with literature data on the cost of applying CO₂ capture to Australian coal-fired power plant. It is important to note that the CS-Cap simulations used were based on the process developed in the laboratory, and an economic optimisation of the process design has not been completed at this point. The high-level economic analysis showed the un-optimised CS-Cap process to be lower capital cost when compared to conventional flue gas desulfurisation (FGD), but higher operating cost as a result of the higher cost chemicals used, and higher make-up absorbent (monoethanolamine, MEA) requirements. The flue gas SO₂ concentration had a strong effect on the operational cost, and hence the overall cost, of the CS-Cap process. The high level cost assessment showed cost benefit when the CS-Cap process was used instead of conventional CO₂ capture (30

wt% MEA) combined with FGD and selective catalytic reduction (SCR). However, no cost benefit was observed when a brown coal power plant was instead combined with minimal FGD and SCR. This requires further evaluation to determine what 'minimal FGD/SCR' constitutes, its applicability to Australian power plant, and if it is still economic compared to an optimised CS-Cap case. In addition, the minimal FGD/SCR case made use of a caustic scrubber, which typically uses NaOH to capture the flue gas SO₂. The production of NaOH can be carbon intensive, so a recommendation is to also complete a life-cycle analysis of both the minimal FGD/SCR and CS-Cap cases to ensure an overall reduction in CO₂ emissions is achieved.

One of the aims of this project was to approach a CO₂ avoided cost of \$40-50/tCO₂ avoided. This is a very ambitious target. The US DOE has a target CO₂ avoided cost of nearer \$60/tCO₂, whilst emerging CO₂ capture technologies are anticipated to achieve CO₂ avoided costs in the range \$65-100/tCO₂ avoided. Currently, for the CS-Cap process incorporating reactive crystallisation, CO₂ avoided costs are around \$114-116 AUD/tCO₂ avoided. This is lower than current conventional technologies when applied to a coal-fired power plant in Australia, but still double the target identified at the start of this project. Note that cost reductions, such as using advanced absorbents and process modifications, can be used to lower the cost of the CO₂ capture plant. Such cost reductions would also be applicable to the CS-Cap process and would be anticipated to lower the cost of CO₂ avoided further.

This project has progressed the CSIRO CS-Cap process from an initial concept, through to a full-scale design incorporating all aspects of the full-scale process. The high level economic comparison suggests that the CS-Cap process has the potential for cost savings when applied to Australian coal-fired power stations. The next step in the development of this technology is to design a crystallisation unit that can be evaluated at pilot-scale. It is suggested that this crystallisation unit be evaluated separately initially, and then incorporated into one of the CSIRO pilot plants for evaluation of the complete process at pilot-scale. Pilot-scale evaluation will provide useful information on the practical operating results of the process, and provide updated information for a more detailed economic comparison.

1 Introduction

This report is to provide the final results of the coCAPco2 project. The overall aim of this project was to progress the development of a CSIRO patented process concept for the low-cost removal of CO₂ and SO₂ from coal combustion flue gases (Meuleman et al. 2012). Typically, when applying conventional CO₂ capture technologies to coal-fired power plant in Australia, a large and expensive flue gas pre-treatment step is also required. This is because flue gas desulfurisation technologies are not currently employed at coal-fired power plant in Australia, but would be required before conventional CO₂ capture technologies can be installed. This is because despite being present at much lower concentrations in the flue gas, the SO₂ will react much more strongly with the aqueous amine absorbents typically used for CO₂ capture. The SO₂ will bind with the amine, reducing its ability to capture CO₂. Combining the SO₂ and CO₂ removal steps into a single process unit removes the need for the upstream flue gas pre-treatment steps, potentially saving hundreds of millions of dollars per CO₂ capture plant. This combined capture concept, the CS-Cap process, is outlined in Figure 1.

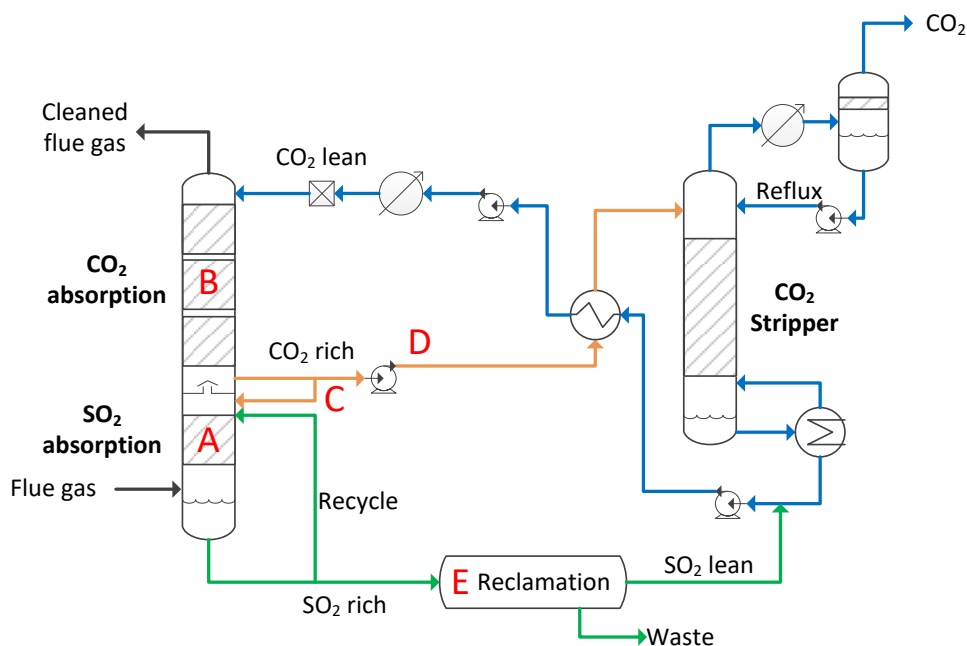


Figure 1 Process flow diagram of CS-Cap concept for SO₂ and CO₂ removal from coal combustion flue gases

A: SO₂ is removed from the flue gas at the base of the column; **B:** CO₂ is removed from the flue gas in upper stages of the column; **C:** a slip stream of the CO₂ loaded absorbent is used in the base of the column for SO₂ removal resulting in a small absorbent volume highly concentrated in sulfur; **D:** the remainder of the SO₂ free CO₂ loaded absorbent can be regenerated via a standard stripping column; **E:** the SO₂ loaded absorbent will require separate regeneration

At the start of the project the CS-Cap process had not been experimentally demonstrated. In addition, the method for removing the absorbed sulfur from the aqueous amine absorbents (step E in Figure 1) was not defined. This step is required for the CS-Cap process to be able to operate continuously. This project aimed to address these issues, progressing the technology through to readiness for pilot-scale demonstration.

To progress the development status of the process from a conceptual idea, to a process suitable for pilot-scale demonstration, the following questions required addressing:

- Can CO₂ loaded amine absorbent effectively capture SO₂ from flue gas?
- What technologies can be used to remove the absorbed S from solution?
- What is the practical effectiveness of the selected reclamation technology for removing sulfate from aqueous amine solutions?
- Is the final process anticipated to be lower cost compared to conventional CO₂ capture technologies combined with flue gas desulfurisation?

The following report outlines the achievements completed in addressing these questions.

2 Can we use CO₂ loaded amine solution to capture SO₂ from coal flue gas?

The first challenge tackled as part of this project was to verify that CO₂ loaded amine solutions can be used to capture SO₂ from coal combustion flue gases. This was achieved through operation of CSIRO's CO₂ capture pilot plant located at AGL Loy Yang's brown coal-fired power station in Victoria. To achieve this the pilot plant pre-treatment column was re-purposed. Previously this column was operated with a caustic solution (see Figure 2). This solution removed all trace acid gases from the inlet flue gas upstream of the CO₂ capture section of the plant. During this proof-of-concept demonstration, CO₂ loaded amine absorbent left over from previous operation of the pilot plant was used in the pre-treatment column for SO₂ removal. This operation not only demonstrated the ability of the CO₂ loaded absorbent to remove SO₂ from the flue gas, but also provided necessary process information including: what level of sulfur loading was achieved in the absorbent; what form the absorbed S takes in solution; and the practical operating ranges of the process. Further information on this section of the report can be found in the Milestone 5 report.

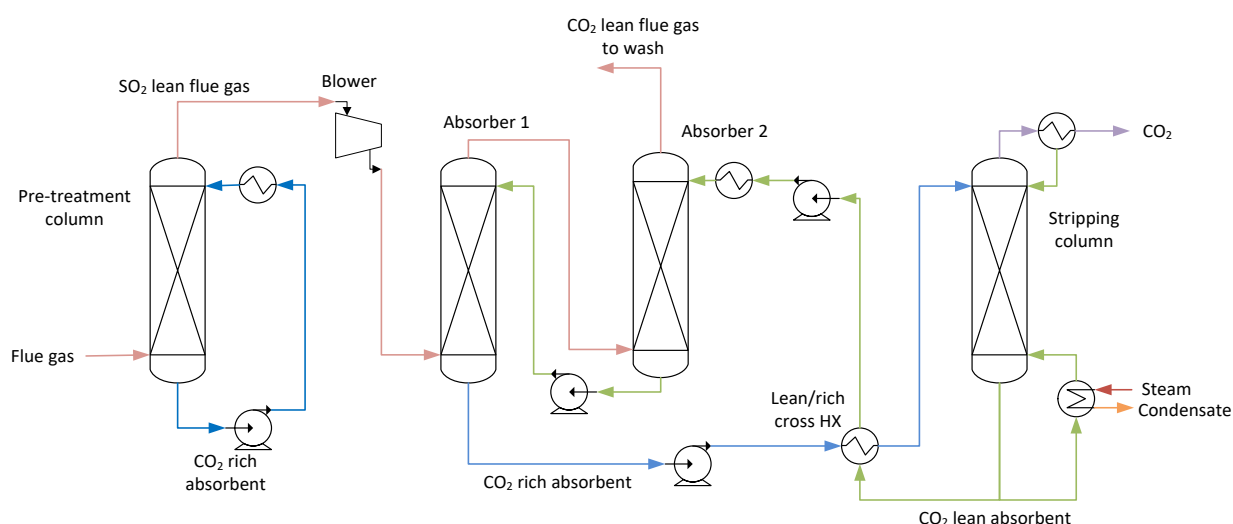


Figure 2 Line diagram of CSIRO's CO₂ capture pilot plant at AGL Loy Yang

2.1 Proof-of-concept pilot scale operation

For this proof-of-concept evaluation, CO₂ rich amine absorbents were recirculated in the pre-treatment column as a batch process, i.e. with no removal of spent amine, and no addition of fresh amine. This meant that the absorbent became fully loaded with absorbed SO₂, and provided an understanding on the maximum operating conditions for the process. Operation was continued until the absorbent was fully loaded with absorbed SO₂, as evidenced by the sharp drop in pH of the absorbent and break-through of SO₂ into the gas stream exiting the column.

Initial operation of the pilot plant was completed with low concentration amine absorbents (~0.6 wt% monoethanolamine, MEA). This allowed operational changes, such as pH of the recirculating

absorbent and saturation of the solution, to be observed within 1-2 days operation. Measurements taken from the pre-treatment column when operating with dilute (~0.6 wt%) MEA are provided in Figure 3. The SO₂ concentration in the inlet flue gas was in the range 100-140 ppm. This dropped to 0 ppm at the exit to the pre-treatment column for the majority of the operation. As SO₂ is absorbed into the absorbent, an initial decrease in pH is observed. This is followed by a buffering region, where only a small change in pH is observed as further absorption of SO₂ takes place. Once the solution is saturated, the pH drops rapidly, and break-through of SO₂ into the gas stream leaving the pre-treatment column is observed. At that point, the experiment was stopped, and the absorbent removed for use in subsequent regeneration experiments. These results highlight the ability of CO₂ loaded MEA to fully and rapidly absorb SO₂ from a flue gas stream. Progress of absorbent loading can be monitored through observing the pH of the absorbent in the column.

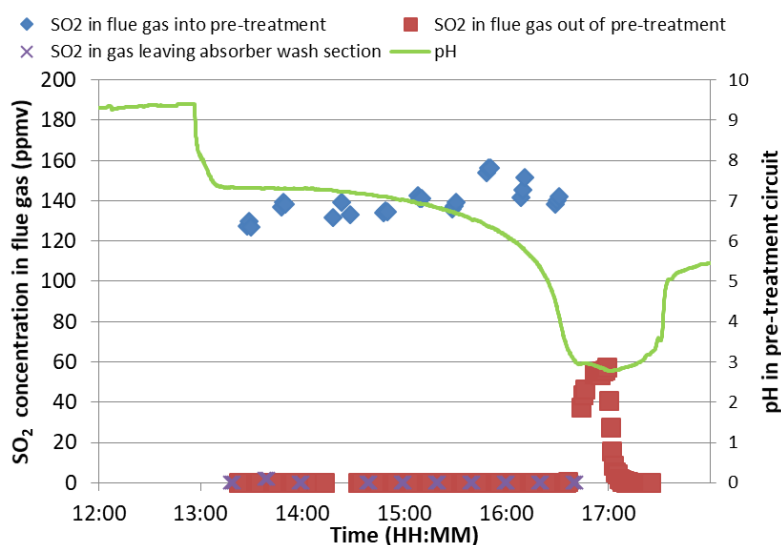


Figure 3 Flue gas SO₂ concentration and pH of amine absorbent in pre-treatment column of CSIRO's Loy Yang CO₂ capture pilot plant when operating with dilute (~0.6 wt%) MEA

This was followed by longer operation of the pilot plant with higher concentration absorbents used in the SO₂ capture loop to generate sufficient quantity of SO₂ loaded absorbent for use in the subsequent laboratory experimental campaign. The first absorbent utilised was a MEA/AMP blend (5.8 wt% MEA, 6.7 wt% AMP). This was used for SO₂ capture for 88 hours before becoming fully saturated. This absorbent maintained a buffering region at a pH 8 – 8.5 throughout most of the operation. When fully loaded, the pH dropped to 3.6, and breakthrough of SO₂ into the flue gas leaving the pre-treatment column was again observed. The second absorbent, ~ 18wt% MEA, was used in the pre-treatment column for 200 h before becoming fully saturated. The buffering region this time was in the range 8.5 – 9, and the pH dropped to 4.3 upon saturation. This operation generated approximately 100-130 L of each SO₂ loaded absorbent. These are currently stored in the CSIRO Clayton facility (see Figure 4). The SO₂ loaded MEA sample was provided to Federation University for use in the subsequent laboratory experimental campaigns.



Figure 4 Photo of liquid absorbent solutions in storage at CSIRO's Clayton facilities

2.2 Corrosion measurements

Due to the unique nature of the loaded absorbent generated in the CS-Cap process, there is no information currently available on expected corrosion rates applicable to the process. Knowledge of corrosion rates under CS-Cap conditions will aid in material selection, and de-risking the overall process when it is considered for scale-up.

The CS-Cap process can lead to a lower pH in the absorber solution than typically seen in CO₂ capture plant. Work completed at the Loy Yang pilot plant has shown that pH levels can drop to as low as 4-5 (Meuleman 2014) before break-through of flue gas SO₂ is observed, and that most of the absorbed SO₂ is oxidised to sulfate (SO₄²⁻).

Chemical plant are generally constructed from cheaper carbon steels to minimise cost, with more expensive higher grade steels used in equipment where significant corrosion is known to occur. There will be a trade-off between the operating pH of the CS-Cap process, and the construction costs based on metal requirements. To better understand this correlation, information is required on expected corrosion rates under conditions relevant to the CS-Cap process. As a result, the corrosion rate of carbon steel caused by a blended amine solution (monoethanolamine, MEA, and 2-Aminomethylpropanol, AMP) of varying pH was evaluated during this project. The corrosion rate was evaluated via electrochemical methods on both pilot plant and laboratory prepared test solutions. In the laboratory prepared samples, amine solutions of the same concentration as those used in the pilot plant were prepared. These were saturated with CO₂ and sulfate, via H₂SO₄ addition, to match the pH levels measured in the pilot plant samples. Comparison of the pilot plant samples versus laboratory prepared samples allowed the effect on corrosion rates of other flue gas constituents present in the pilot plant samples to be observed. Figure 5 provides an overview of the results achieved from this work. Decreasing the pH from 8 to 2 resulted in a ~100 fold increase in corrosion rate for the pilot plant sample, and ~50 fold increase in corrosion rate for laboratory prepared samples. The increased corrosion rate in the pilot plant samples compared to laboratory prepared

solutions at very low pH values (i.e. high sulfate concentration) suggests that other impurities present in the pilot plant samples may also affect corrosion rates.

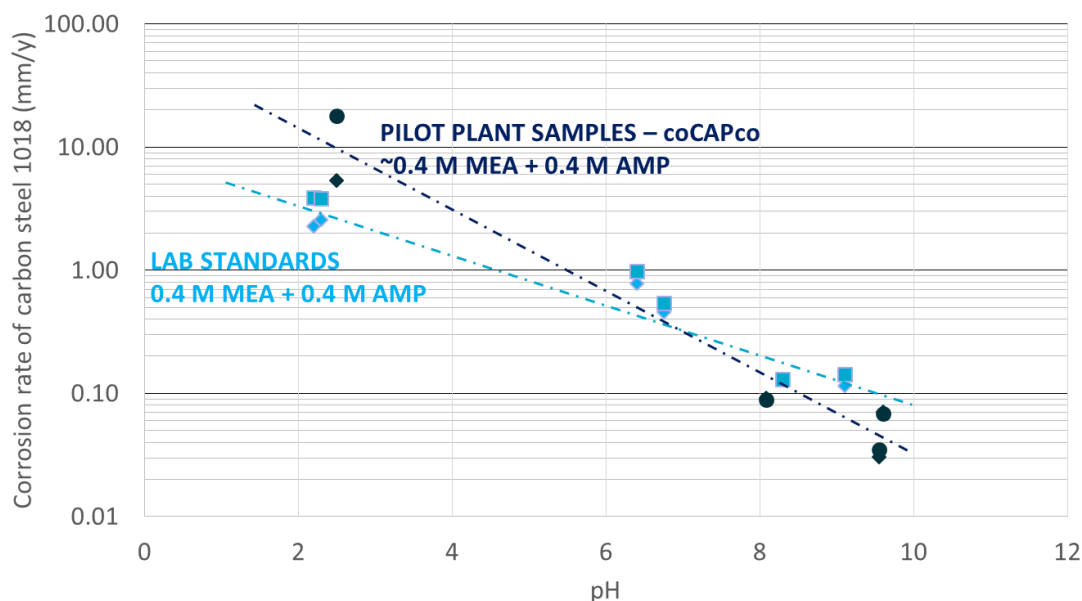


Figure 5 Log corrosion rates of carbon steel in pilot plant and laboratory prepared MEA/AMP blended samples with varying pH. For laboratory samples, pH was achieved by H₂SO₄ addition

It should be noted that the corrosion rates provided in Figure 5 were from early pilot plant samples that were comparatively dilute compared to typical CO₂ capture absorbents. For comparison, 30 wt% MEA at pH 8 has typical corrosion rates in the range 0.5 – 0.7 mm/yr.

2.3 Conclusions

Operation of the pilot plant with CO₂ loaded amine solution in the pre-treatment column has shown the ability of CO₂ loaded amine solution to remove SO₂ from combustion flue gas. The pH of the solution was seen to enter a buffering region, with a final sharp drop in pH observed once the solution became fully saturated with SO₂. Thus the pH of the absorbent solution is a potential method for monitoring and controlling the SO₂ absorption process. Maintaining CS-Cap operation in the buffering pH range should also ensure minimal slippage of flue gas SO₂ into the CO₂ capture plant.

Corrosion of carbon steel in CS-Cap samples was noted to increase dramatically at low pH values. This highlights that operation of the CS-Cap process should be maintained within the buffering region (~ pH 7 – 9 as observed at the pilot plant) to minimise corrosion. At pH in the buffering region, corrosion rates of carbon steel were measured to be 0.1 – 0.5 mm/yr for dilute amine absorbents. This would be expected to increase for the more concentrated absorbents typically used. The trend of increasing corrosion rates at lower pH shows that operation at higher pH in the SO₂ absorption column (i.e. lower sulfate loading) is desirable to minimise corrosion.

3 What technologies can be used to remove the absorbed S from solution?

One of the advantages of the CS-Cap process is that flue gas can enter the amine absorption loop with minimal pre-treatment. However this means that the level of acid gases present in the flue gas will be much higher than from power stations that employ de-SO_x and de-NO_x technologies. As a result, the formation of heat stable salts (HSS) in the amine absorbents will likely be much higher under CS-Cap conditions. Removal of impurities from amine-based absorbents is currently practiced in acid-gas removal plants to avoid operational problems such as corrosion, increased absorbent viscosity, foaming, fouling, absorbent loss, and increased energy requirements. Guidelines for the maximum allowable level of contaminants in amine absorbents vary. In general for natural gas processing applications it is recommended to maintain HSS levels below 5000 ppm to maintain trouble free operation of the amine plant (Cummings et al. 2007).

There are a number of technologies and techniques commercially available for amine purification, removing a range of impurities including HSS, metals, ionic and non-ionic impurities. Techniques include solvent purging/feeding, solvent replacement, mechanical and activated carbon filtration, and neutralisation of organic/inorganic acids. A commonly used absorbent reclamation method is thermal reclamation. Due to the unique nature of the CS-Cap loaded absorbent (small volume concentrated in absorbed SO₂), alternative lower cost regeneration options might be more appropriate, including: precipitation, membranes, ion exchange, and electrodialysis. To understand which technologies will work best with the unique absorbent generated during the CS-Cap process requires an understanding of the absorbent properties, and a review of the pros and cons of the various reclamation technologies when applied to high HSS absorbents.

3.1 Properties of the pilot plant SO₂ loaded absorbent

The main item to determine was the level and form of sulfur present in the absorbent used during the pilot-scale operation. This is important as the CASPER process, which uses precipitation of K₂SO₄ to remove sulfate from an amino acid solution, found the oxidation of sulfite to sulfate to be a rate limiting step¹. An approximate mass balance completed at the pilot plant during the operation suggested that the majority of the sulfur was most likely present as sulfate in the amine absorbents evaluated. This was confirmed by ion chromatography analysis of the absorbent samples collected. The MEA absorbent used at the pilot plant was found to have 110 g/kg (± 10g/kg) sulfate and 2-3 g/kg sulphite (R² >0.99; relative standard deviation <6%). The lower concentration of sulfite compared to sulfate confirms that most of the absorbed SO₂ was converted into sulfate.

¹ The CASPER process is a combined capture process developed by TNO. It uses an amino-acid absorbent to capture CO₂ and SO₂ from combustion flue gases. Removal of absorbed SO₂ is achieved by cooling the solution and precipitating K₂SO₄. This process was evaluated at the Loy Yang CO₂ capture pilot plant as part of the coCAPco project.

Analysis of organic and inorganic anions, metals and cations showed these were at a much lower concentration than the sulfate in solution. They typically showed lower levels in the CS-Cap absorbent compared to other pilot MEA samples. This is most likely due to the lower operating time achieved on the CS-Cap absorbent. See Milestone 7 report and Garg et al. 2019a for additional information.

The proof-of-concept operation of the pilot plant was completed as a batch operation (i.e. no amine was removed from the process, and no fresh amine was added during operation). This led to the absorbent becoming fully saturated with absorbed SO₂. It is unlikely that such a process would be followed in the real process. Instead, operation in the buffering region, ensuring no break-through of SO₂ to the CO₂ capture section of the plant, would most likely be followed. The absorbent generated here though provides a good example of the likely higher operating limit of the process. This analysis confirms that for the CS-Cap process to be continuous, the reclamation technology chosen will need to be able to efficiently remove ~10 wt% sulfate from aqueous amine solutions.

3.2 Summary of literature review on technologies suitable for removal of high sulfate concentrations from amine absorbents

A number of processes are currently available for reclaiming amine absorbents exposed to flue gas streams. The benefits and application of these technologies have been summarised by a number of researchers (Kohl and Nielsen 1997, Cummings et al. 2007, Wang et al. 2015, ElMoudir et al. 2012, Dumeé et al. 2012). A summary of the technologies applicable to the removal of HSS from amine absorbents is provided in Table 1.

From the information provided on the various technologies it is apparent that no technology is an ideal fit for the CS-Cap process. Instead it is likely that a hybrid process will be required. For example, whilst electrodialysis and precipitation are both suited to the high concentration of salts likely to be present in the CS-Cap absorbent, both are suited to lean amine streams. Thus both techniques may require an upstream CO₂ removal step for maximum efficiency. Distillation (thermal reclamation) could also be applicable, with the potential for some energy saving via heat integration with the CO₂ stripping column. The high concentration of salts suggest ion exchange is less applicable to the CS-Cap process. However, should low levels of residual salt be required, ion exchange could be implemented as the final purification step in a hybrid process. At the Cansolv CO₂ capture plant (Boundary Dam power station, Saskatchewan) thermal reclamation is used for the removal of the bulk of the amine contaminants. This is followed by downstream filtration and ion exchange for final purification. For further information on this section, refer to Milestone Report 6 and Garg et al. 2018.

Table 1 Comparison of reclamation methods for removal of HSS and degradation products from amine absorbents (Kohl and Nielsen 1997, Wang et al. 2015)

Method	Ion exchange	Distillation/Thermal reclamation	Electrodialysis	Precipitation/Reactive crystallisation
Applicability	Removal of ionised impurities	Removal of solids and non-volatile species	Removal of ionised impurities	Removal of ionised impurities

Operating principle	Ions captured by ion exchange resin	Vaporisation of volatile species (water amine) from salts and degradation products	Ions moved by electricity from amine to waste solution	Reaction of aqueous anions with added chemical to form insoluble salt
Limitations	Cannot remove non-ionic species. Moderate cost. Resin fouling and thermal degradation, expensive at larger plant sizes anticipated for PCC	Energy intensive, most amines need vacuum, high cost	Cannot remove non-ionic species, membrane selection and durability. Moderate energy demand, large amount of waste. Dissolved metals can poison membranes.	Cannot remove non-ionic species, will only remove specific ionic species. Less commonly practiced, possibility for contamination of precipitate product and recycle of salt, high chemical use
Forté	Best option for low concentration salts. Low energy demand, low product salt concentrations achievable	High concentration salts and degradation products	Amine concentration remains the same. Best for moderate to high salt concentrations. Efficient for charged species, low chemical consumption	High salt concentrations. Possibility for generation of saleable by-product
Waste products	Dilute aqueous stream containing removed ions, excess regeneration chemicals and rinse water	Reclaimer bottoms concentrated stream containing salts, non-volatile organics and some amine. Normally hazardous waste	Aqueous brine containing removed ions	Solid salt if end use not available
Volume of wastes	High to moderate (40-50% of inventory)	Low (5-15% of inventory)	Moderate	Could be high if end use not available
Amine recovery	High (95-99%)	Moderate (85-95%)	High (98%)	Still to be quantified. Likely to be moderate to high
Amine feed requirements	Lean, cool, hydrocarbon and particulate free	HSS neutralised	Lean, cool, hydrocarbon and particulate free, HSS neutralised	Lean amine. Depending on precipitant used, cooling step may be required
Special requirements	Regeneration chemicals as low as 1mol/mol	Flue gas or high temperature heat source, chemicals 1 mol/mol	DC power, chemicals 1 mol/mol	Method for removing salt from solution and potentially purifying salt if saleable product generated
Commercial technologies and/or providers	MPR services Inc. (HSSX), Eco-Tec inc. (Amipur CCS), DOW (DOWEX)	CCR Technologies, Chem Group	DOW (UCARSEP), ElectroSep	

3.3 Conclusions

Based on the assessment of the CS-Cap absorbent properties, and the understanding of the challenges associated with the various different reclamation technologies, it was decided that reactive crystallisation was an interesting process to explore for regenerating the CS-Cap absorbent. In addition, the most widely applied reclamation method currently used industrially is thermal reclamation. We were interested to understand how the CS-Cap absorbent would affect the operational requirements of this well-known technology. As such, the next stage of the project

explored the experimental evaluation of these two technologies when applied to reclaiming the CS-Cap absorbent.

4 What is the practical effectiveness of the selected reclamation technology for removing sulfate from aqueous amine absorbents?

The literature review was instrumental in identifying the most optimal technologies to evaluate for incorporation into the CS-Cap process. The next stage was to complete laboratory scale experiments to determine the effectiveness of reactive crystallisation and thermal reclamation for regenerating the sulfate loaded CS-Cap absorbent. Some of the key findings are provided below. Further information can be found in Milestone Reports 5, 7 – 10, and also the journal articles prepared as part of this project (see Appendices A-C).

4.1 Reactive crystallisation

The reactive crystallisation process regenerates the sulfate loaded absorbent by forming a sulfate-salt crystal that precipitates out of solution. The sulfate-salt formed has the potential to be sold commercially. A number of inorganic alkali compounds can be added as a precipitant including potassium hydroxide (KOH), which has been studied previously (Xu 2008) and was identified as a favourable precipitant due to the formation of potassium sulfate (K_2SO_4) that could potentially be sold for use in industry, or as a fertiliser.

4.1.1 Sulfate solubility

One of the first aspects considered was the solubility of potassium sulfate (K_2SO_4) in aqueous amine solutions. Experimental trials determined that K_2SO_4 solubility increases with higher temperature, reduced amine concentration and greater CO_2 concentration, due to the increased ionic concentrations of protonated MEA and carbamate (Figure 6), which was consistent with previous literature (Xu 2008). At higher CO_2 loadings, the salt-in effect by CO_2 increases the ionic concentrations of protonated amine and carbamate, resulting in higher ionic strength and consequently higher sulfate solubility (Misiak et al. 2013).

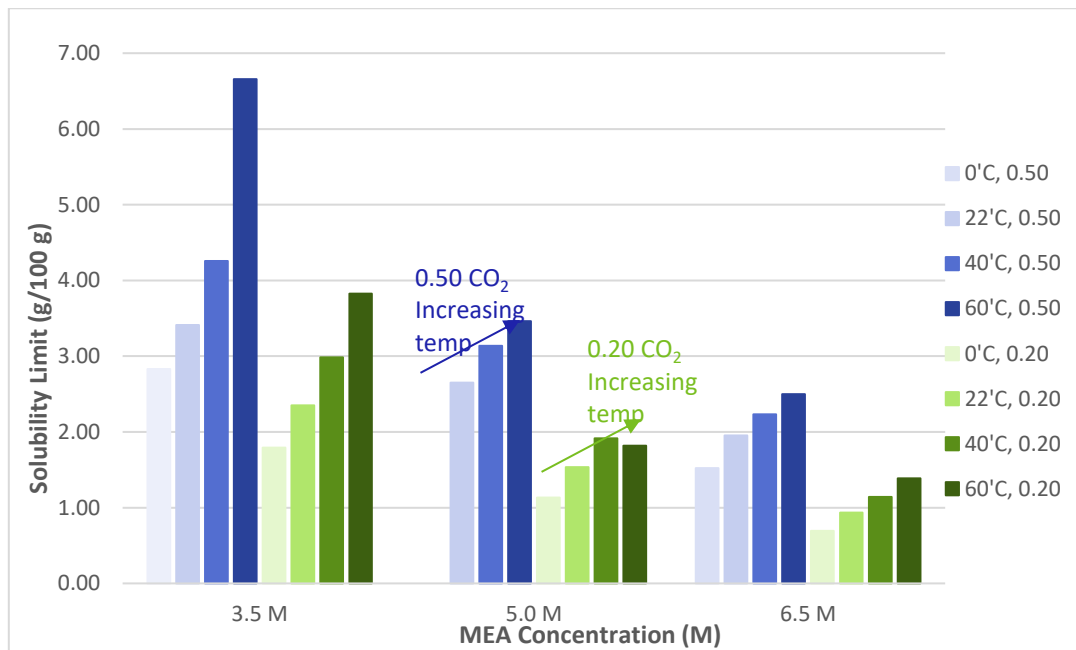


Figure 6 Solubility limit of potassium sulfate in CO₂ loaded MEA solutions at various temperatures

These results show that amine regeneration via crystallisation (i.e. low sulfate solubility) is better suited to the conditions of low temperature, high amine concentration and low CO₂ loading.

4.1.2 Sulfate removal

Laboratory precipitation experiments were completed to determine the effectiveness of reactive crystallisation for removing sulfate from aqueous amine solutions. KOH was added to the samples and K₂SO₄ was formed as the precipitate product. This was completed for both synthetic laboratory prepared samples, pilot plant samples, and synthetically degraded samples. Figure 7 outlines the effect if varying KOH addition on the removal of sulfate from the amine solutions.

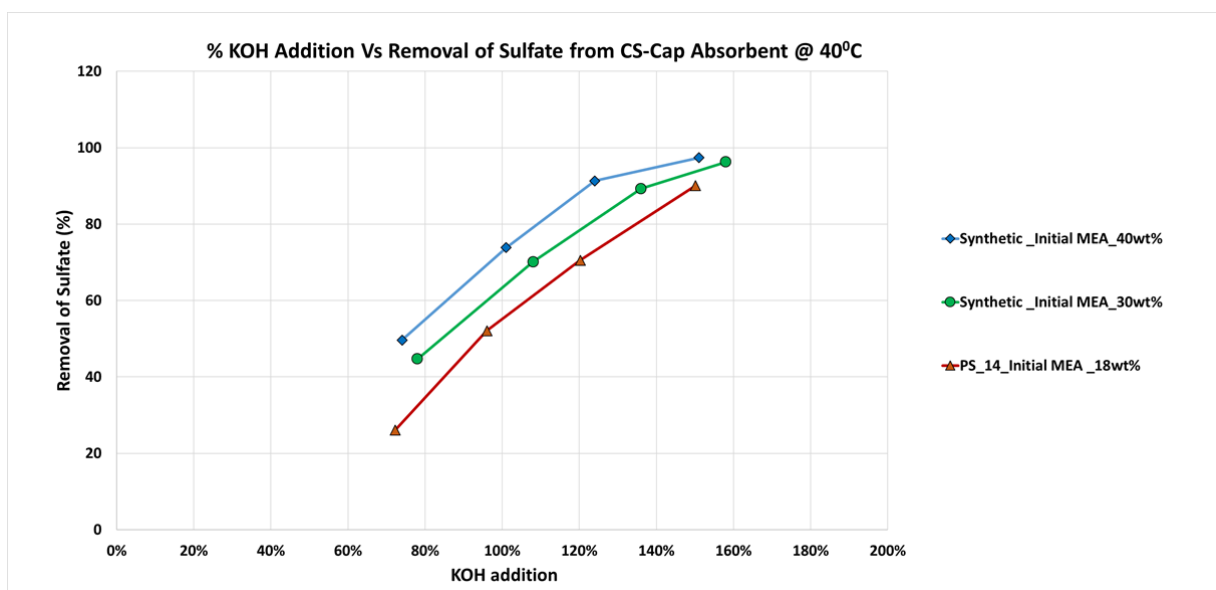


Figure 7 Effectiveness of reactive precipitation for removing sulfate from the CS-Cap absorbent at 40 °C

As can be seen in Figure 7, nearly complete removal of the sulfate from solution can be achieved when KOH is added 60% in excess of that stoichiometrically required to react with the sulfate

present in the solution. Whilst complete removal may be advantageous, this will increase reactant costs, and leave significant residual unreacted KOH in solution. Instead, optimal operation will likely involve partial removal of the sulfate in solution. The absorbent recycled from the reactive crystallisation process will be below the sulfate saturation limit and still able to absorb further SO₂ from the flue gas. This is analogous to the operation of the CO₂ capture circuit. In the CO₂ capture plant, full removal of the absorbed CO₂ is not achieved. Instead, optimal operation typically involves reducing the CO₂ concentration to a lean loading of ~0.2 molCO₂/molMEA (for a 30wt% MEA solution). Partial removal of the sulfate will also minimise the KOH addition requirements and minimise the amount of unreacted K⁺ remaining in the recirculated absorbent.

Even though the some of the samples were generated at the pilot plant (PS_14), the short operational time led to low levels of degradation products being present in the solution. As such, a set of samples was spiked with additional degradation products. A severely oxidised MEA solution (prepared in an autoclave with additional organic acids) was added to pilot plant sample to raise its 0.1 wt% organic anions concentration to 1 wt%. Precipitation experiments showed negligible difference in the removal of sulfate between spiked and un-spiked samples.

4.1.3 Crystal purity and size

One of the advantages of the crystallisation process is the potential for selling the solid K₂SO₄ produced. To understand potential challenges facing this, the purity of the crystals formed was evaluated by x-ray diffraction (XRD). A master sizer and light microscopy were used to provide information on the size and shape of the crystals formed.

The XRD analysis confirmed that the K₂SO₄ crystals, from both the PS-14 pilot plant sample and PS-14 sample spiked with additional degradation products, were 99% pure. Light microscopy analysis showed that the crystals formed into 50-100 μm flocs. Figure 8 shows a light microscopy image of the K₂SO₄ crystals produced.

It should be noted that the impact of K₂SO₄ purity on handling and saleability of this product as a potential fertiliser are not yet known and requires further investigation.

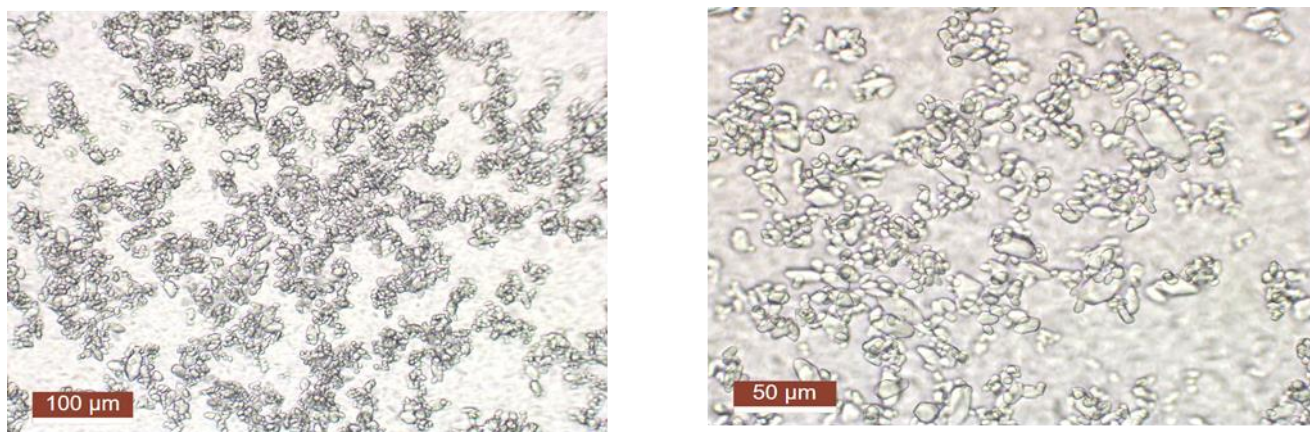


Figure 8 Light microscope images at two magnifications of K₂SO₄ crystals produced during reactive crystallisation experiments

4.2 Thermal reclamation

The most commonly used technique for reclaiming spent amine absorbent solutions industrially is thermal reclamation. Caustic (NaOH) is added to the amine absorbent to 'free' the amine bound in the HSS. The caustic treated solution is then heated to boil off and recover the amine. The sludge remaining contains degradation products and some residual amine, and is a hazardous waste requiring disposal.

Experiments were completed as part of this project to determine the effect of the high sulfate loading of the CS-Cap absorbent on the operating characteristics of a thermal reclamation process.

4.2.1 Effect of operating conditions

A number of operating conditions were varied during the thermal reclamation experiments including: temperature, pressure, MEA concentration, initial sulfate loading, and NaOH addition. Amine recovery was found to improve with operation at higher temperatures, and under vacuum conditions (Figure 9), as expected. Overall amine recoveries via thermal reclamation however were often lower than anticipated.

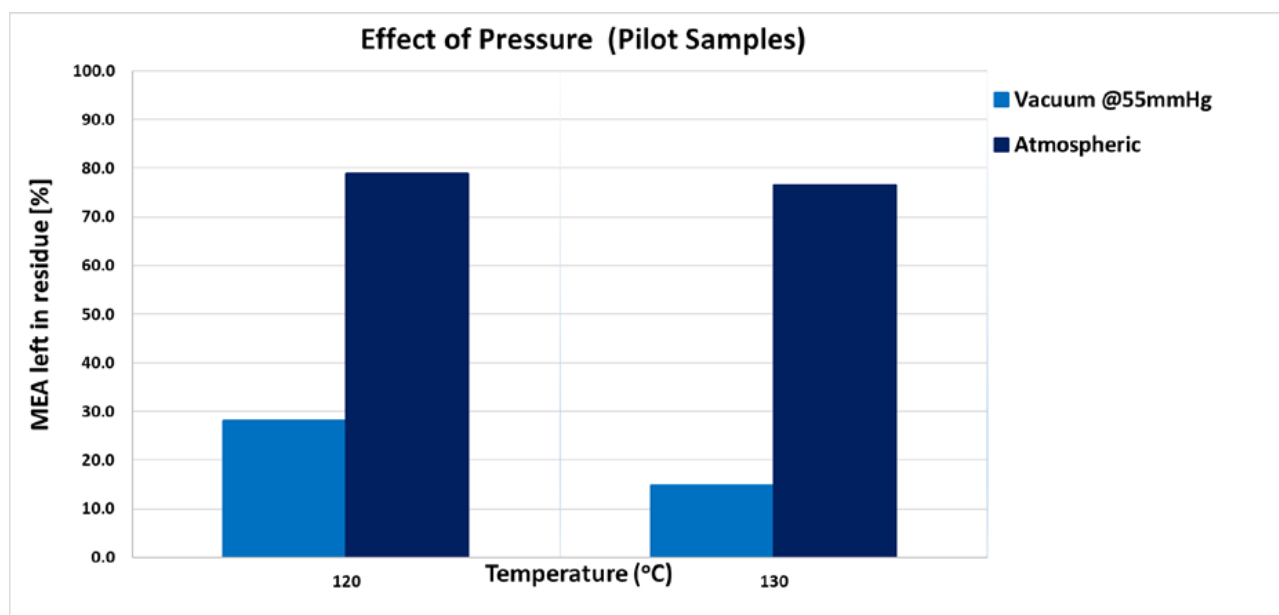


Figure 9 Effect of pressure on amine recovery for pilot plant samples via thermal reclamation

4.2.2 Effect of pH

Interestingly, the pH of the solution after caustic addition was found to play an important role in the recovery of amine via thermal reclamation. Due to the high sulfate concentration, the initial pH in the pilot plant absorbent was quite low, near 4-5. It was expected that the bound amine would be released as soon as the pH of the absorbent is raised beyond the pKa of monoethanolamine (9.5). However, the high sulfate concentrations impacted the caustic required to release the bound amine. Even after maintaining favourable temperature and pressure conditions, amine recovery remained poor at pH 10. When the pH was raised to 11 or 12, amine recovery increased. Typically, for thermal reclamation, 1 mol caustic is added per mol HSS that requires neutralisation. This is because most

of the organic acid degradation products that form have a single negative charge. For the CS-Cap process however the sulfate salt in solution dominates. Sulfate has a double negative charge, and thus requires twice as much caustic addition to neutralise the HSS and recover the amine.

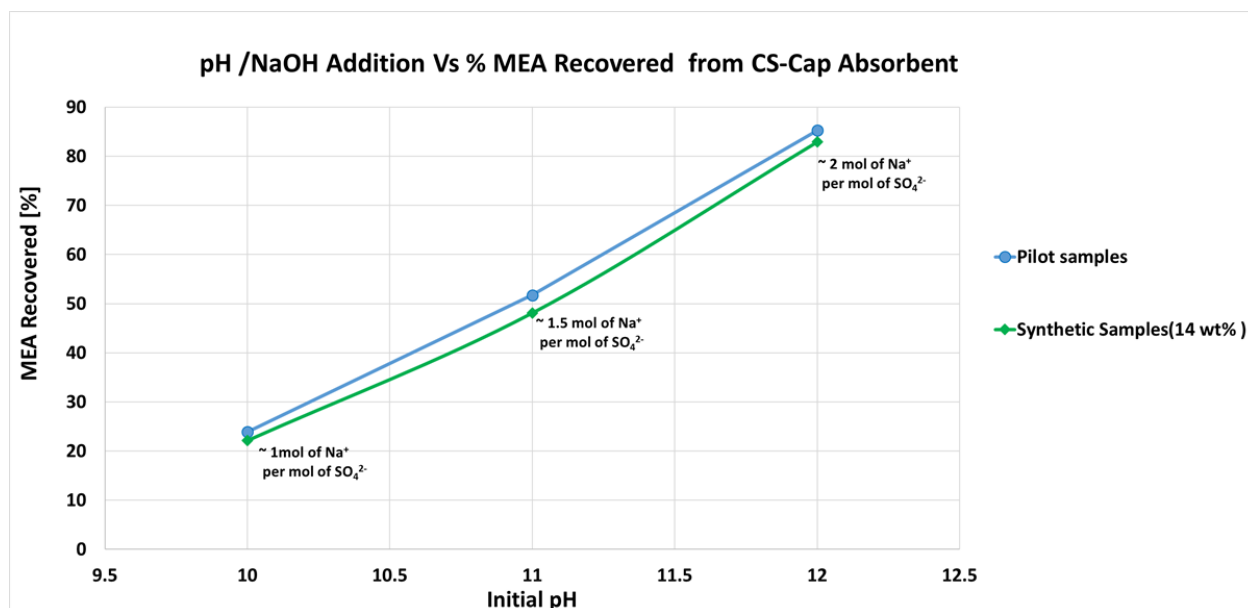


Figure 10 Effect of absorbent pH after NaOH dosing on amine recovery via thermal reclamation

4.3 Conclusions

The reactive crystallisation and thermal reclamation experiments showed that both techniques are able to remove the bulk of the high concentration sulfate salts from aqueous amine absorbents. In reactive crystallisation, it is the sulfate that is removed from solution. In thermal reclamation, regenerated MEA is boiled off from the solution, leaving behind the sulfate and other salt wastes. Both processes will likely have high chemical requirements, and hence potentially higher variable operating costs, compared to the conventional FGD processes. Thus an economic analysis is required to understand whether the capital cost saving achieved when using the CS-Cap process is out-weighed by the higher operating costs of the reclamation technologies.

5 Is the process anticipated to be lower cost than conventional CO₂ capture technologies combined with FGD?

The final stage of this project was to assess the likely economics of the CS-Cap process with the chosen methods for removing sulfate from the aqueous amine solutions. To achieve this, simulations of the CS-Cap process were prepared using ProTreat and Aspen Plus simulation software. These provided information on the equipment sizes expected for a full scale process, and the mass and energy balance of the process. This information is required for a cost analysis to be completed. Aspen Plus data banks were used to provide information on the cost of the reclamation technologies. This was combined with literature information relating to the cost of CO₂ capture facilities applied in Australian coal-fired power plant. Further information is provided below, and in Garg et al. 2019c (see also Appendix C).

5.1 Simulation of CS-Cap process absorption section

A simulation of the overall CS-Cap process was completed in ProTreat. As ProTreat does not contain modules allowing the simulation of the reclamation processes, these were estimated in the simulation using a black-box approach, as outlined in Figure 11. For the reactive crystallisation process, this black-box removed K₂SO₄ from the absorbent solution at a rate comparable to that observed in the laboratory experiments. This allowed an overall mass balance of the SO₂ and CO₂ capture facility to be obtained. This provided information on the column sizes, and in particular, the packed height and liquid flow rate required in the SO₂ capture section. Further detail can be found in Milestone Report 11 and Cousins et al. 2018, Cousins et al. 2019.

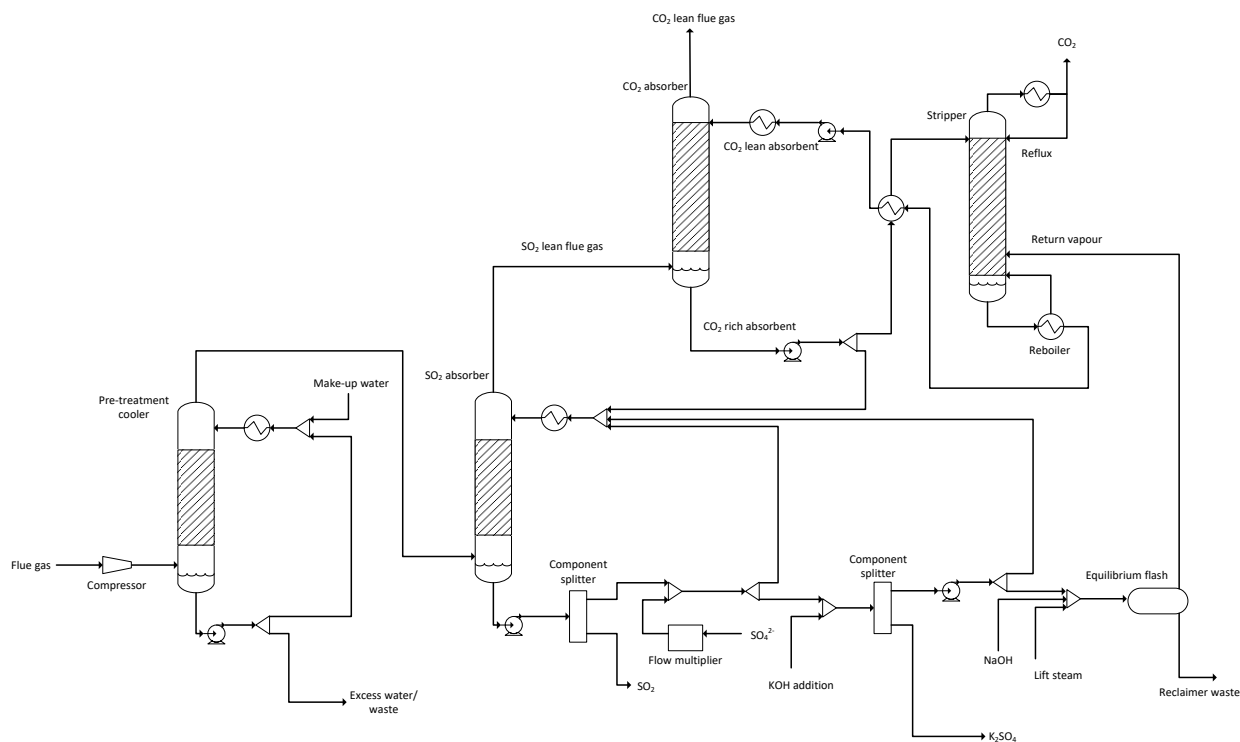
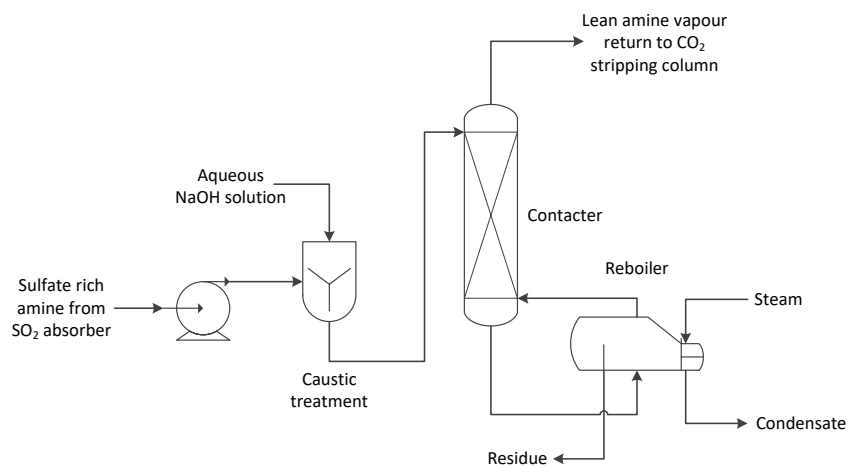


Figure 11 Flow diagram of the CS-Cap process simulated using the ProTreat simulation software

The simulation results showed that only a small packed section (4m) was required to capture the SO₂ in the flue gas, as absorption into the CO₂ loaded amine absorbent was rapid. The mass balance determined from the ProTreat simulations was then applied to an Aspen Plus simulation of thermal reclamation and reactive crystallisation.

5.2 Simulation of reclamation technologies

Simulations of the two reclamation technologies chosen, thermal reclamation and reactive crystallisation, were prepared in Aspen Plus. These models were verified against laboratory experimental data (see Appendix B for further information). This allowed these technologies to be sized, and their costs added to literature information on the cost of CO₂ capture facilities in Australia. The flow diagrams of the two reclamation technologies simulated are provided in Figure 12.



(a)

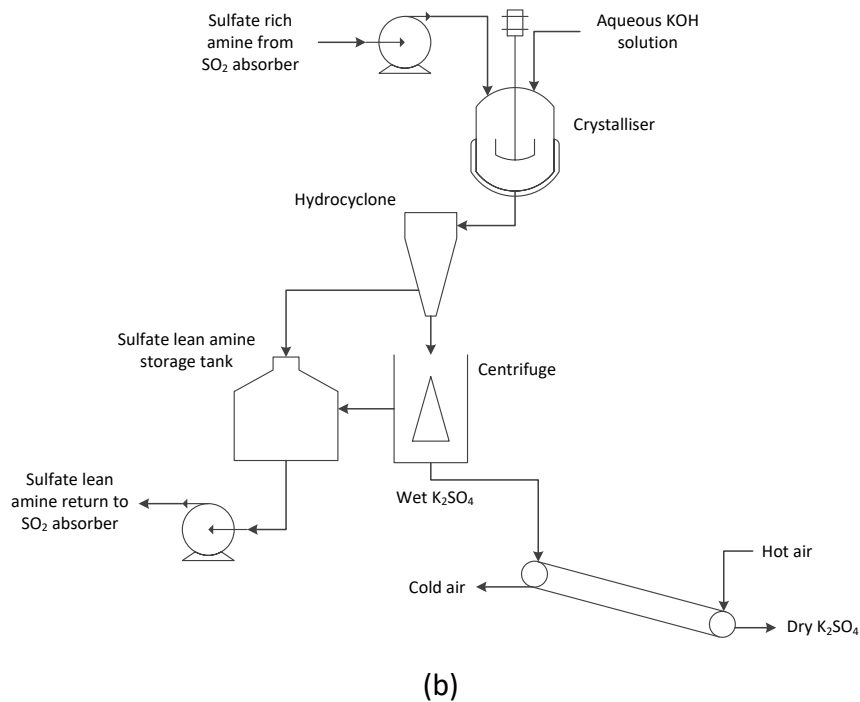


Figure 12 Flow diagrams of (a) thermal reclamation and (b) reactive crystallisation processes simulated in Aspen Plus simulation software

5.3 Economic evaluation and comparison to conventional technologies

According to a study undertaken by the CO2CRC, adding CCS to a coal-fired power station doubles the total plant cost (TPC) compared to that of a plant built without CCS, be it a brown or black Australian coal-fired plant. The total plant cost includes the equipment, materials, direct labour, engineering, erection costs and contingencies. The variable operating and maintenance costs are expected to rise by around 3-4 times if CCS is integrated with a new power plant in Australia. This increases the levelised cost of electricity (LCOE) by approximately 100% compared to the case where no CCS is applied. The cost increase mentioned above includes FGD unit installations which are a pre-requisite for any amine based PCC technology to be deployed in Australia (Australian Power Generation Technology report, 2015).

5.3.1 Cost of reclamation technologies

The Aspen Plus simulation software was used to return the equipment purchase cost for the two reclamation technologies evaluated. The remaining direct and indirect plant costs are based on a percentage of the equipment price (Ulrich and Vasudevan, 2004). The total direct, indirect, working capital and fixed capital investment provided the total capital cost of the reclamation technologies. The Aspen simulation models were also used to provide the operating expenditure of the processes. It is important to note that the Aspen simulations were based on the process and results achieved in the laboratory-scale experiments. These showed MEA losses above those typically reported in CO₂ capture designs. This requires further investigation to determine whether the current CS-Cap

process design can be optimised to minimise costs further. The operating costs at this stage do not include the potential sale of the K_2SO_4 produced from the reactive crystallisation process, and do not include waste disposal costs of the residue from thermal reclamation. Thermal reclamation operating costs included low pressure steam (4.8 bar), pumping, and a 50 wt% NaOH solution (385 USD/tonne, \$15/t shipping). For crystallisation, costs include cooling water, electricity (hydro cyclones, centrifuges, dryers, pumps), compressed air heating (direct contact electrical heaters) and a 48 wt% KOH solution (530 USD/tonne, \$15/t shipping). A MEA price of 1.8 USD/kg was also used. The price of steam, cooling water and electricity have been taken from Hosseini et al. (2016). All capital and operating and maintenance (O&M) costs are expressed in June 2015 Australian dollars. A currency exchange rate of 0.71 USD = 1 AUD was used.

The cost information determined for the two reclamation technologies was combined with literature cost information for CO₂ capture technologies applied in Australia. PCC cost information was sourced from The Australian Power Generation Technology report (2015) and the Retrofitting CCS to Coal: Enhancing Australia's Energy Security report (2017). Both the thermal reclamation and reactive crystallisation processes are found to be less capitolly intensive compared to flue gas desulfurisation (FGD) (i.e. lower Finance costs). The use of higher cost chemicals for the removal of sulfate from the amine solutions, and higher MEA make-up requirements, however increases the operating (O&M) costs compared conventional CO₂ capture processes with FGD. Reactive crystallisation was found to perform economically better than thermal reclamation due to lower make-up MEA requirements for this technology. As the crystallisation process is only removing the sulfate salts, thermal reclamation may still be required periodically with this process to remove other degradation products from the amine absorbent. This is not considered here². Approximately 5-6% of the thermal reclaimer operating cost relates to the steam used to boil the MEA solution. There is potential for heat integration with the CO₂ capture stripping column, recovering much of this added heat, and hence lowering the overall operating cost. As mentioned previously, the CS-Cap process simulated here does not yet consider such optimisations.

It should be noted that this is a high level cost comparison. There are a number of assumptions that have gone into these calculations that require verification before more accurate cost numbers can be provided. The more accurate cost numbers should rely on data from pilot-scale evaluation, and include a complete bottom up design of the entire CO₂ capture process for a specific power plant. Further detail on the economic assessment completed as part of this study can be found in Garg et al. 2019c (Appendix C).

5.3.2 Cost of applying the CS-Cap process to Australian coal-fired power plant

The CS-Cap process using 30 wt% MEA combined with both reactive crystallisation and thermal reclamation were compared to cost data for retrofitted brown and black coal-fired power stations based in Australia. The 5 scenarios considered are as follows:

² In most PCC cost studies, thermal reclamation requirements are typically not included. In order to be consistent with other cost studies, the cost of the periodic thermal reclamation required to remove amine degradation products generated in the CO₂ capture plant are not included in this cost analysis.

Scenario 1: Retrofitted power plant with standard FGD, selective catalytic reduction (SCR) and PCC units

The design for the base case is taken from the two reference reports: Retrofitting CCS to coal (2017) and the Australian Power Generation Technology report (2015). Power station capacity was assumed at 85%. A site in the Latrobe Valley, Victoria, was selected for the brown coal plant, and a New South Wales location was selected for the black coal power plant. CO₂ transportation pipelines and storage site costs were not included, however, a \$15/tonne CO₂ cost was added to the levelised cost of electricity (LCOE) for transportation and storage.

Scenario 2: Retrofitted power plant with FGD, SCR and PCC units combined with an improved CO₂ capture absorbent

This scenario has a similar design basis as scenario 1, but uses an improved solvent for CO₂ absorption. The improved solvent requires less steam for absorbent regeneration in the CO₂ capture section, raising the net MW_e output of the power plant.

Scenario 3: Retrofitted power plant with minimal FGD combined with a standard PCC unit

The scenario is similar to scenario 1, but does not include the cost of a deep FGD and SCR. Victorian brown coals are known for their low sulfur content, and hence it is believed that minimal FGD and SCR is sufficient, reducing the costs of the overall CO₂ capture process. This includes a direct contact cooler along with alkali treatment for SO₂ removal, and low NO_x burner installation instead of SCR.

Scenario 4: CS-Cap case with thermal reclamation

This scenario includes PCC retrofit in a base plant with no FGD or SCR. The FGD is replaced by the CS-Cap process combined with thermal reclamation. The SCR is not included as a result of the very low NO₂ concentrations in the total NO_x typically emitted (~99% NO, balance NO₂ and N₂O) in Victorian coal-fired flue gases. NO does not react with amines and hence passes through without affecting the CO₂ capture system.

Scenario 5: CS-Cap case with reactive crystallisation

This scenario includes PCC retrofit in a base plant with no FGD or SCR. The FGD is replaced by the CS-Cap process combined with reactive crystallisation. As outlined above, SCR costs are also not included.

The initial simulation of the CS-Cap process was completed for a 900 MW gross output black coal fired power station. This power station had a flue gas SO₂ concentration of 700 ppm. This simulation was also repeated for a gas composition more closely resembling that from a typical brown coal fired power station, with a flue gas SO₂ concentration of 200 ppm. The results of these simulations were scaled to allow them to be combined with cost information for CO₂ capture plant as outlined in the two reference reports mentioned in scenario 1 above. The cost of the FGD and SCR units is subtracted from the total plant cost for scenario 1 to provide the cost of the power plant with PCC only. This is then added to the thermal reclamation or reactive crystallisation costs to provide the total plant and O&M costs for scenarios 4 and 5.

The levelised cost of electricity (LCOE) is then calculated as outlined in section 17.2.5 of the Australian Power Generation Technology Report (2015). Table 2 provides the LCOE calculated for

the different scenarios for a black coal-fired power plant. Note that the flue gas SO₂ concentration in the baseline reports (see scenario 1 description) is not provided. A flue gas SO₂ concentration of 700 ppm has been assumed here when calculating the costs for scenarios 4 and 5. Table 3 provides the LCOE calculated for the different scenarios for a brown coal power plant with a flue gas SO₂ concentration of 200 ppm.

Table 2 LCOE for 450 MW_{gross} Australian black coal power plant

Scenario	1	2	4	5
	Base case (with FGD and SCR)	Base case (with FGD, SCR and improved absorbent)	CS-Cap case with thermal reclamation	CS-Cap case with reactive crystallisation
Finance charges	55	52	31	31
Fixed O&M	10	9	6	6
Variable costs	11	11	36	32
Fuel cost	41	41	41	41
Transportation and storage	16	16	16	16
Average LCOE (\$/MWh)	133	129	130	126
CO ₂ emissions (tCO ₂ /MWh)	0.13	0.11	0.13	0.13
Cost of CO ₂ avoided (\$/tCO ₂ avoided)	125	117	121	116

Table 3 LCOE for 2100 MW_{gross} Australian brown coal power plant

Scenario	1	2	3	4	5
	Base case (with FGD and SCR)	Base case (with FGD, SCR and improved absorbent)	Base case (with minimal FGD and SCR)	CS-Cap case with thermal reclamation	CS-Cap case with reactive crystallisation
Finance charges	63	60	50	35.2	35.4
Fixed O&M	9	9	8	5.9	6.5
Variable costs	14	14	12	58	43
Fuel cost	38	34	34	34	34
Transportation and storage	28	25	25	25	25
Average LCOE (\$/MWh)	152	142	129	158	144
CO ₂ emissions (tCO ₂ /MWh)	0.24	0.18	0.17	0.24	0.24
Cost of CO ₂ avoided (\$/tCO ₂ avoided)	120	104	86	126	112

From Tables 2 it can be seen that the CS-Cap process is anticipated to be lower cost than conventional CO₂ capture combined with FGD and SCR. From Table 3 the CS-Cap process with reactive crystallisation is showing a cost advantage for retrofit to brown coal power plant. It is unclear whether there is cost advantage if a minimal FGD and SCR process is applied to the base power plant. As mentioned previously, the CS-Cap process evaluated at this stage is based on the laboratory results achieved, and has not yet been optimised. It should also be noted that the cost estimate applied here is high level, and that all costs reported are within the expected accuracy of the results. A more detailed and higher accuracy cost analysis is recommended in future work. One of the challenges with the CS-Cap process is that operating costs increase relative to a FGD process. This is due to the use of higher cost chemicals (NaOH, KOH) for the removal of the sulfur from the flue gas stream, compared to the comparatively cheap lime typically used for FGD. You would anticipate a similar challenge for the minimal SCR/FGD case that utilises a caustic scrubber. This however does not appear to be the case as outlined in Table 3, with the operating costs of the minimal case lowering compared to the standard FGD case. It is not at this stage apparent why this is the case. In addition, the production of NaOH (i.e. used in the caustic scrubber in the minimal FGD case) is known to be carbon intensive. It is recommended to complete a life-cycle assessment of the minimal FGD/SCR and CS-Cap cases to ensure an overall reduction in CO₂ emissions is achieved.

One of the aims of this project was to approach a CO₂ avoided cost of \$40-50/tCO₂ avoided. This is a very ambitious target. The US DOE has a target CO₂ avoided cost of \$40 USD/tCO₂ avoided (roughly \$60 AUD/tCO₂ avoided). Current and emerging CO₂ capture technologies are anticipated to achieve CO₂ avoided costs in the range €40-60/tCO₂ avoided (IEAGHG 2019) when applied to a coal-fired power plant based in Europe (approximately \$65-100 AUD/tCO₂ avoided). Currently, for the CS-Cap process incorporating reactive crystallisation, CO₂ avoided costs are around \$114-116 AUD/tCO₂ avoided. This is lower than current conventional technologies when applied to a coal-fired power plant in Australia, but still double the target identified at the start of this project. Note that cost reductions, such as using advanced absorbents and process modifications, can be used to lower the cost of the CO₂ capture plant. Such cost reductions would also be applicable to the CS-Cap process, and would be anticipated to lower the cost of CO₂ avoided further.

5.3.3 Potential for cost recovery through sale of K₂SO₄ generated through reactive crystallisation

One of the benefits of choosing reactive crystallisation as a reclamation technology for the CS-Cap process was the potential for selling the K₂SO₄ produced. Any mined and manufactured salt that contains potassium in a water-soluble form is known as potash. This includes sulfate of potash (K₂SO₄). Most of the potash used commercially is mined from marine deposits and is often found deep in the earth. These ores are typically rich in potassium chloride (KCl) and sodium chloride (NaCl), which are usually obtained by shaft-mining methods (TechNavio 2015). Sulphate of potash, or SOP or arcanite, is another important constituent of potash. This form of potash is often used as a water-soluble source of potassium as well as sulfur. It is typically prepared by reacting KCl with H₂SO₄, as in the Leblanc process, with HCl produced as an important by-product.

Potash is widely used globally. About 92% of the overall potash produced is consumed by the fertilizer industry and the remaining 8% is used in other industrial uses such as plastics, pharmaceuticals, and soaps. There are three main product types of potash: Muriate of potash (KCl

– 80% market share), potassium nitrate (9% of market share), and sulfate of potash (K_2SO_4 – 7% of market share) (TechNavio 2015). About 60% of the global demand for potash is contributed by Asia. Demand from countries such as China, India, Indonesia, Malaysia, and Vietnam, which together harbor about 40% of the world's population, plays a major role in the global potash trade. These countries remain the net importers of potash, with the majority of production coming from Canada and the US (TechNavio 2015).

KCl is typically the most cost effective form of potash, hence, it is the most widely used in the production of fertilizers. K_2SO_4 is most commonly used to produce fertiliser for crops that are sensitive to the chlorine in KCl based fertilisers (e.g. avocado, pineapple, tobacco). It is also used as an alternative blast media, and for soils that face a deficiency of sulfur content.

Australia does not have potassium chloride deposits, and thus depends solely on imports of potash from other countries (Euromonitor International 2017). 5 – 6 million tonnes of fertiliser is sold in Australia each year (Richardson 2016). Approximately half of this is manufactured locally, with the remainder being imported. Potash fertilisers (potassium nitrate, muriate of potash and sulphate of potash) account for only about 6% of the local market. Impact Fertilizers Australia Pty Ltd is an Australia-based subsidiary of Ameropa Holding AG. The company is engaged in the manufacture of fertilizers such as phosphates, potash, sulphates, urea and sulphur. Its production facilities are concentrated in Tasmania, but the company also has plants in New South Wales, Victoria, Queensland and South Australia (Euromonitor International 2017, Impact 2019).

Italy is the top country for potassium sulphate production in the world. As of 2017, potassium sulphate production in Italy was 49,400 tonnes, accounting for 33.6 % of the world's potassium sulfate production. The top 5 countries (the others are Russian Federation, Republic of Korea, Indonesia, and Greece) account for 100 % of K_2SO_4 production. The world's total potassium sulfate production was estimated at 146,900 tonnes in 2017 (Knoema 2019).

If there is no market for the K_2SO_4 produced, then it will add a disposal cost to the CS-Cap CO_2 capture process that will need to be accounted for. K_2SO_4 is a non-hazardous substance, but run-off into drainage systems should be avoided. If disposal is chosen, then it would be worth investigating other precipitants in addition to KOH that are potentially cheaper.

Production of K_2SO_4 from one Australian power station could be in the range 30,000 to 90,000 tonne per annum (200 – 700ppm flue gas SO_2). This is a significant fraction of the current world production of potassium sulfate from one power station. This suggests that K_2SO_4 production would likely swamp current market requirements. Global production of potash however (predominately KCl) was nearer 60 million tonnes in 2017 (NRCAN 2019). This is largely due to the lower cost of KCl which can simply be mined. It is possible that should K_2SO_4 be cheaper than KCl, its market share for fertiliser production could increase. In 2017 global potash prices were approximately \$200 US per tonne. Some potash producers, such as BHP, are increasing their investment in potash production. They anticipate a growing but geographically constrained food market as a result of growing population, and consequently long-term growth in the fertiliser market. A low-cost supplier of potash could potentially have a competitive advantage in the growing market (Burnside, 2017).

Currently there is no market in Australia for K_2SO_4 in the quantities that would be generated if the CS-Cap process was used to remove all of the sulfur from coal-combustion flue gases. There is the potential for long-term growth in the global potash market, with a growing market share possible

for K_2SO_4 should CS-Cap derived potash prove to be a low-cost source. A recommendation for future work is to also consider other precipitation products and other markets.

6 Challenges that require addressing for pilot-scale evaluation

This project has identified two reclamation technologies that can be incorporated into the CS-Cap process. The flow diagram and equipment required for implementation of a full-scale plant has been identified. This will allow development of a process suitable for pilot-scale evaluation. There are still however some challenges that require addressing before pilot-scale evaluation is recommended.

6.1 Removal of flue gas condensate and particulate

In the standard process, the pre-treatment column at the CSIRO pilot plants is used to cool the incoming flue gas, lowering its water content and removing particulate. During operation the process has a regular blow down to remove particulate from the system. This would not be possible if amine is used in the pre-treatment column for SO₂ capture (i.e. the CS-Cap process) as blow down is typically pumped to the power station ash pit. This would also significantly increase amine waste/loss from the process. This is why the pilot-scale work completed at the beginning of this project was completed as a batch process. For integrated pilot-scale evaluation of the full CS-Cap process, a solution will need to be found to avoid the requirement of blowing down the pre-treatment column if it is to be used for SO₂ capture using an amine.

The simulations completed for the CS-Cap process in this project were done with no gain or loss of water from the SO₂ absorber. This required an upstream cooler to lower the flue gas water content, particularly for the brown coal case. If this is done in practice, this water will dissolve some of the flue gas acid gases, and be quite acidic. Waste water from the process would thus require treatment before disposal/discharge. If the particulate could be effectively removed from the flue gas upstream of the pilot plant, then it is possible that the SO₂ absorber could also be used to cool the incoming flue gas. This however will result in water condensation into the SO₂ absorption loop, which will require removal. An alternative is to have an upstream direct contact cooler to remove particulate and knock out flue gas water. This however will require treatment and disposal of the acidic waste water generated. This will also lead to lower pH conditions in the DCC cooler, and likely higher corrosion rates than designed for. If an upstream cooler/knock-out vessel is selected as the best alternative, this may require the design of a new vessel adapted for low pH conditions (e.g. with plastic packing material). Any solution to the pre-treatment requirements of the CS-Cap process should be completed in consultation with the pilot plant host site to ensure the solution meets their requirements/obligations.

6.2 Method for crystallisation and filtration

A pilot-scale crystallisation unit needs to be designed or purchased. This should be possible as pilot-scale crystallisers applied to CO₂ capture sorbents have been evaluated by Siemens, and also as part

of CASPER process³. In the current CS-Cap configuration, hydrocyclones and centrifuges are used for particle separation. It is unknown if these scale effectively for pilot-scale adaption. When evaluating precipitation as part of the CASPER process, filters were used for particle separation, but this required off-stream evaluation. It is unlikely that the method for drying the crystals will be implemented at pilot-scale. Thus the CS-Cap process may require some adaption to allow effective evaluation at pilot-scale.

³ The CASPER process is a combined capture process developed by TNO. It uses an amino-acid absorbent to capture CO₂ and SO₂ from combustion flue gases. Removal of absorbed SO₂ is achieved by cooling the solution and precipitating K₂SO₄. This process was evaluated at the Loy Yang CO₂ capture pilot plant as part of the coCAPco project.

7 Conclusions and recommendations for future work

Previously, the high capital cost associated with FGD when applied to Australian power plant was found to be prohibitive, and a major challenge facing the use of CCS in the country. The CS-Cap process uses the fast kinetics of SO₂ with amine absorbents to achieve the SO₂ capture step in a small column segment. This lowers the capital cost of the pre-treatment requirements for CO₂ capture, however at the start of this project a suitable method for removing the absorbed SO₂ from the aqueous amine absorbents still needed to be determined. Early pilot plant operation showed the ability of CO₂ loaded amine absorbents to rapidly remove SO₂ from coal combustion flue gases, and generated a SO₂ loaded absorbent useful for subsequent analysis of potential reclamation methods. Analysis of the absorbent showed that the majority of the absorbed SO₂ is converted to sulfate, with SO₄²⁻ concentrations ~ 11 wt% determined. A literature review highlighted reactive crystallisation and thermal reclamation as reclamation technologies likely to be able to cope with the high sulfate loading of the CS-Cap absorbent. Laboratory scale evaluation then proved the ability of these two techniques to regenerate and free the aqueous amine bound with the sulfate in a heat stable salt. Reactive crystallisation experiments completed at 40 °C showed nearly complete removal of sulfate from solution if the precipitant (KOH) was added in excess (60%) of that stoichiometrically required to react with the sulfate present in solution. Spiking pilot plant samples with additional degradation products showed no adverse effect on the technique, with similar sulfate removal levels achieved. XRD analysis of the generated crystals showed them to be 99% pure, however some discoloration from the amine absorbents was noticed. Regeneration of the amine absorbent was found to improve under vacuum conditions when regenerating the absorbent using thermal reclamation. Higher caustic additions than typically used were found to be required to achieve MEA recoveries above 80%. This is due to the double negative charge of the sulfate ion, leading to pH above 12 required for high (> 80%) MEA recoveries.

The experimental data acquired through the project was then used to validate Aspen Plus models of the reactive crystallisation and thermal reclamation processes. These models were then used to size the equipment required to capture CO₂ from a full-scale power plant (900 MW gross). The Aspen Plus economic tool was used to provide the purchase cost of the equipment required. This was converted to Australian dollars, and combined with literature information on the cost of CO₂ capture power plant in Australia. The CS-Cap simulation evaluated was based on results achieved in the laboratory, and has not at this stage been optimised for minimal cost. A comparison of the un-optimised CS-Cap process against conventional CO₂ capture processes (30 wt% MEA) that used FGD and SCR as the upstream pre-treatment steps was completed. The analysis showed that the CS-Cap process is lower capital cost compared to FGD, but has a higher operational cost. The cost of the CS-Cap process is affected by the flue gas SO₂ concentration. The un-optimised CS-Cap process (reactive crystallisation) was determined to be ~5% lower LCOE than a conventional plant incorporating FGD and SCR for a black coal power station assuming 700ppm SO₂ in the flue gas (note: SCR not included in CS-Cap case). For a brown coal power plant with 200ppm flue gas SO₂, the CS-Cap process was found to be ~5% lower LCOE. However, it was higher than the standard plant with minimal FGD and

SCR. CO₂ avoided costs were found to be in the range \$114-116/tCO₂ avoided for the CS-Cap process with reactive crystallisation.

The economic evaluation did not consider waste disposal costs from the CS-Cap process, nor the potential sale of the K₂SO₄ produced. Market analysis suggests that there is currently no market in Australia for the K₂SO₄. However, if the K₂SO₄ could be sold at a cheaper rate than conventional mined sources of imported potash, there is potential for a growing market share. This however, requires further evaluation.

Future work

This evaluation has identified reactive crystallisation as a suitable technology to be combined with the CS-Cap process for the low cost combined removal of CO₂ and SO₂ from flue gas streams. This cost analysis was completed on the basis of models validated against bench-scale batch experiments. A first recommendation for future work would be to design, build and operate continuous crystallisation and solids separation units of suitable size for incorporation into one of CSIRO's CO₂ capture pilot plants. This crystallisation unit should be operated in a stand-alone fashion to begin with to confirm the operating characteristics as identified here (i.e. the amount of precipitate formed and ability to be removed from solution). It will also provide information on the potential for incorporating a crystallisation unit into one of CSIRO's CO₂ capture pilot plants.

Assuming promising results from the above analysis, the pilot-scale crystalliser can be incorporated into one of CSIRO's CO₂ capture pilot plants. This will however require liaising with the host site, and determining a suitable method for upstream removal of flue gas condensate and precipitate prior to the SO₂ absorber. Pilot-scale evaluation will provide essential information on the practical operating experience of the process under real flue gas conditions, and more relevant information to update the techno-economic assessment.

The economic analysis has highlighted that the un-optimised CS-Cap process may not be cost-competitive with alternative minimal FGD/SCR options for Australian power plant. This requires further evaluation. As part of that evaluation, the potential for sale of the K₂SO₄ produced, and evaluation of other potentially saleable precipitates, should also be evaluated. In addition, a life-cycle assessment should be completed for both technologies to ensure overall reductions in CO₂ emissions are achieved.

8 Project dissemination and publications

Information on this project has been disseminated to project partners through 6-monthly milestone reports and project review meetings. Information has been distributed to a wider audience through conference attendance, and publishing articles in magazines and peer-reviewed journal articles. An overview of publications prepared from this work is provided in Table 4. All published articles have been sent separately to BCIA, and included in previous Milestone Reports. Some of the more recently prepared articles are currently under-going review by CSIRO or the scientific journal. Where an article is not yet published, a copy of the submitted paper is included in the appendices, as outlined in Table 4.

Table 4 Publications and presentations prepared as part of this project

DESCRIPTION	REFERENCE
Oral Presentations	
International Conference on Coal Science and Technology	Presented by Ashleigh Cousins, Melbourne, September 2015
GHGT-13	Presented by Paul Feron, Switzerland, November 2016
Confirmation of Candidature	Presented by Bharti Garg, Federation University, November 2016
Workshop: Low Emission Energy Technologies for the Indian Scenario	Presented by Ashleigh Cousins, India, April 2017
2 nd Australia-Japan Symposium on Carbon Resource Utilisation	Presented by Bharti Garg, Brisbane, April 2018
Distillation and Absorption	Presented by Paul Feron, Florence, September 2018
GHGT-14	Presented by Bharti Garg, Melbourne, October 2018
Asia Development Bank	Requested presentation given by Bharti Garg, Philippines, June 2019
Poster presentations	
1 st Australia-Japan Symposium on Carbon Resource Utilisation	Poster presented by Bharti Garg, Melbourne, November 2016
2 nd Australia-Japan Symposium on Carbon Resource Utilisation	Poster presented by Ashleigh Cousins, Brisbane, April 2018
Journal articles	
GHGT-13 conference paper	Pearson, P., Moscatelli, J., Garg, B., Cousins, A., Meuleman, E., Puxty, G., Verheyen, V., Feron, P.H.M., 2017, An update on the development of the CSIRO's CS-Cap combined CO ₂ and SO ₂ capture process, <i>Energy Procedia</i> 114, 1721 – 1728
PhD Literature review	Garg, B., Verheyen, T.V., Pearson, P., Feron, P., Cousins, C., 2018, A technology review for regeneration of sulfur rich amine systems, <i>International Journal of Greenhouse Gas Control</i> 75, 243 – 253
Distillation and Absorption conference paper	Cousins, A., Puxty, G., Pearson, P., Weiland, R., Garg, B., Verheyen, V., Feron, P., 2018, Simulation of an SO ₂ tolerant amine based post-combustion CO ₂ capture process, <i>Chemical Engineering Transactions</i> 69, 817 – 822
GHGT-14 conference paper	Garg, B., Pearson, P., Cousins, A., Verheyen, V.T., Puxty, G., Feron, P., 2019, Experimental evaluation of methods for reclaiming sulfur loaded amine absorbents

PhD Experimental results	Garg, B., Pearson, P., Cousins, A., Mcknight, S., Verheyen, V., 2019a, Regeneration of sulfur-rich absorbent through reactive crystallisation in CS-Cap's integrated approach to capture CO ₂ and SO ₂ from flue gases, submitted See Appendix A, Submitted to International Journal of Greenhouse Gas Control. Under review.
PhD Simulation results	Garg, B., Cousins, A., Pearson, P., Larkins, J.-A., Verheyen, V.T., Feron, P.H.M., 2019b, Aspen Plus simulation model for amine reclamation in combined CO ₂ and SO ₂ capture: Validation of model See Appendix B. To be submitted
PhD Economic analysis results	Garg, B., Haque, N., Cousins, A., Pearson, P., Verheyen, T.V., Feron, P.H.M., 2019c, Techno-economic evaluation of amine reclamation technologies and combined capture CS-Cap process for Australian coal-fired power stations See Appendix C. To be submitted
CSIRO simulation paper	Cousins, A., Pearson, P., Puxty, G., Jiang, K., Garg, B., Zhai, R., Ott, P., Verheyen, V., Feron, P.H.M., 2019, Simulating combined SO ₂ and CO ₂ capture from combustion flue gas streams See Appendix D. To be submitted
Conference papers	
International Conference on Coal Science and Technology	Cousins, A., Beyad, Y., Puxty, G., Meuleman, E., Pearson, P., Jansen, J., Huang, S., Cottrell, A., Conway, W., Castelow, P., Feron, P., 2015, Low cost combined capture of SO ₂ and CO ₂ for Australian brown coal-fired power stations, Proceedings ICCS&T, 27 Sept – 01 Oct 2015, Melbourne, Australia, Paper No. 3127270
Other	
Confirmation of candidature report	Submitted by Bharti Garg as fulfilment of 1 st year PhD obligations
Carbon Capture Journal	Cousins, A., Pearson, P., Puxty, G., Huang, S., Feron, P., Garg, B., Verheyen, V., 2018, CS-Cap: Development of an SO ₂ tolerant post combustion CO ₂ capture process, July/August edition, 2 – 3

In addition to the above, Ms Bharti Garg was also able to attend the IEAGHG CCS Summer School during the course of this project (see Milestone 6 Report for trip report). She was also invited to attend and present at the Asia Development Bank Clean Energy Forum held in the Philippines in June 2019.

Appendix A : Regeneration of sulfur-rich absorbent through reactive crystallisation in CS-Cap's integrated approach to capture CO₂ and SO₂ from flue gases

Publication submitted to International Journal of Greenhouse Gas Control – Under review

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Abstract

Flue gas desulfurisation (FGD) is a pre-requisite for successful CO₂ capture in coal-fired power stations utilising aqueous amine absorbents. For nations like Australia, where there is no FGD, this increases the cost for power plants retrofitting CO₂ capture. The CSIRO's CS-Cap process, a potentially low-cost method for combined CO₂ and SO₂ capture, provides an alternate sulfur management solution to such power stations. The CS-Cap process however results in sulfur-loaded amines that require continuous regeneration to retain cost benefits. Reactive crystallisation via adding KOH to sulfur rich aqueous amines is shown to be successful in removing the bulk of the sulfate from aqueous amines without any additional heating or cooling requirements. Amine degradation had no significant effect on the precipitation efficiency or purity of K₂SO₄ crystals despite their slight discoloration. The presence of residual potassium in regenerated aqueous amines needs further investigation as it could lead to unwanted precipitation inside the absorber column and other parts of the process.

Keywords: Combined Capture, Flue Gas Desulfurisation, MEA, Precipitation, CS-Cap Process

1. Introduction

Combined capture of SO₂ and CO₂ offers capital and energy benefits and is considered a next generation post-combustion capture (PCC) process (Misiak et al. 2013). Companies like Shell Cansolv, Union Carbide, and Babcock & Wilcox, provide processes that combine the capture of SO₂ and CO₂. The integration is either infrastructural, through heat integration, or using single or dual absorbent loops to capture the acid gases from various emission sources (Shaw, 2008; McDonald & Moorman, 2012). The CSIRO's CS-Cap process is a similar combined capture process which utilises the chemical nature of amines being highly selective for SO₂ absorption over CO₂ (Puxty et al., 2014). Here, the absorption of CO₂ and SO₂ is carried out in different sections of a single absorber column using a single amine absorbent. A schematic of the process is shown in Figure-1.

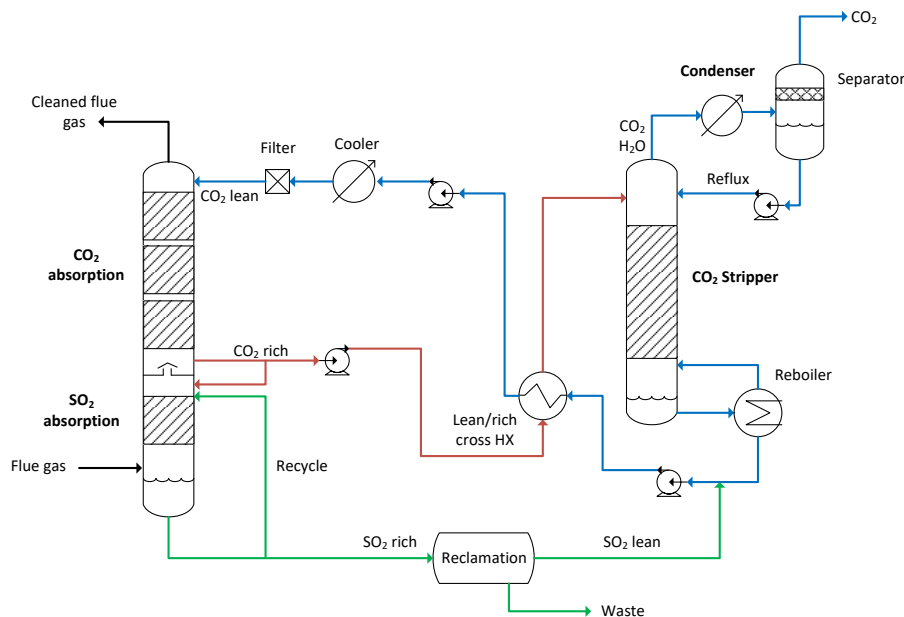


Figure 1: Process flow diagram of the CS-Cap process (Pearson et al., 2017a)

The upstream removal of acidic gases like SO_2 and NO_x is essential as they degrade the performance of amine-based PCC. Here the CS-Cap process diminishes the requirement for a separate pre-treatment unit by combining the removal of SO_2 and CO_2 into a single absorber column. The upper section of the column captures the CO_2 while the lower section captures SO_2 . This makes the flue gas sulfur free before it enters the upper section of the column. The unique feature of this process is that it utilises a very small portion of the CO_2 rich absorbent from the upper section of the column. This absorbent is recycled in the lower part of the column to capture SO_2 . The S loaded absorbent is sent for reclamation (i.e. the removal of absorbed SO_2) so that it can be re-used in the process. Here we will focus on absorbent regeneration, as our previous publications provide information on the overall conceptual utility of the CS-Cap process for Australian coal fired power plants (Beyad et al., 2014; Puxty et al., 2014; Pearson et al., 2017a).

More than 97% of the CO_2 rich amine exiting from the top section of the absorber column is sent to the stripper for thermal removal of the CO_2 . The small portion (0.1-3% of total absorbent in recirculation) recycled in the lower portion of the absorber column generates amines rich in sulfur. While the CO_2 stripping is a standard regeneration process, optimal SO_2 removal requires experimental evaluation of potential regeneration methods. Due to the recycling of absorbent in the lower portion of the absorber column, and the high O_2 concentration in the flue gasses (typically 5-8 vol.%) the absorbed SO_2 is converted into heat stable SO_4^{2-} salts which cannot be reversibly converted back to SO_2 via the conditions used for standard CO_2 stripping.

1.1. CS-Cap's sulfur rich pilot plant absorbent

In a standard FGD unit, the sulfur is captured by limestone slurry, which produces gypsum and as a result, does not require any regeneration process. However, the CS-Cap technology utilises a small portion of the CO_2 rich amine to capture SO_2 and produces unsaleable SO_2 rich amine waste from the valuable PCC amines. Hence, effective low cost amine regeneration is necessary. These sulfur loaded CS-Cap absorbents require further investigation as their heat stable salt loading is much higher than operating limits set for typical PCC amines.

As a proof of concept, CSIRO's pilot plant at AGL's Loy Yang power station in Victoria, Australia was used to demonstrate SO_2 capture using CO_2 loaded amine absorbents. The successful trial showed the full and rapid absorption of SO_2 into the CO_2 rich absorbent, modelled with aqueous monoethanolamine (MEA), when

exposed to raw plant flue gases directly after electrostatic precipitation (ESP) i.e. with no prewash step. This SO_4^{2-} rich MEA generated in the pilot campaign is referred to as “pilot plant sample (PS_14)” throughout this paper.

The pilot plant sample serves as a model to investigate various regeneration techniques enabling practicable desulfurization. These techniques were identified through an earlier literature review (Garg et al., 2018). For completeness, the key reaction chemistry is outlined below:

1.1.1. Reactions of Sulfur

SO_2 converts into various forms of sulfite /bisulfite and sulfate dependent on the prevailing reaction conditions. The absorption of SO_2 into the pilot plant absorbent generally takes place as per the following standard reactions:



Recycling of the S loaded amines in the CS-Cap process effectively increases the residence time in the absorber column. The presence of oxygen in the flue gas irreversibly converts sulfite to sulfate (6) in this column. Sulfite is not a stable form of SO_2 in the absorbent. The continuous incoming concentration of SO_2 in flue gas forms more sulfite and pushes the overall oxidation reactions to the right (6). Pilot-scale evaluation has shown that the majority of SO_2 absorbed from the flue gas is converted to the more stable sulfate (Thompson et al. 2014; Reynolds et al. 2012).

1.1.2. Amine reactions

Fig. 1 reveals the CO_2 loaded absorbent is regenerated through thermal stripping which exposes it to high temperatures. This results in the generation of organic anions that produce heat stable salts with MEA. Hence, the CO_2 rich absorbent recycling in the SO_2 removal loop will contain organic anions. When choosing a regeneration technique for the S rich absorbent, it is important to gauge the amount of organic anions present, as this will affect the performance of particular regeneration techniques. Due to the pilot plant sample’s exposure to brown coal derived flue gas and metal surfaces, metals, inorganic cations and anions are also expected to be present.

1.1.3. pH

During pilot plant operation, the ingress of SO_2 into the CO_2 rich MEA, dropped its pH from 9-10 to near 4-5. This sharp drop in the pH was a result of the pilot plant sample becoming saturated with absorbed SO_2 (Pearson et al., 2017a), as no amine make-up was added to the column. Instead, the absorbent recirculated until it became fully saturated. It’s unlikely this process would be used in an operating plant, but here it assisted in determining the boundaries of the process.

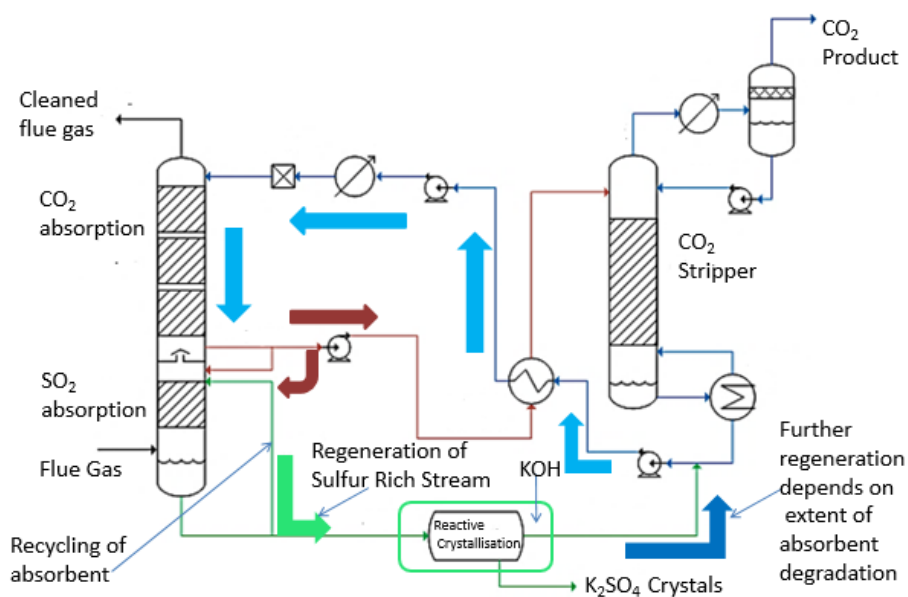
1.2. Optimising the Reactive crystallisation method for the CS-Cap process conditions

This paper experimentally evaluates reactive crystallisation (Figure 2) to regenerate the sulfate rich CS-Cap absorbent. Reactive crystallisation involves solid product formation resulting from reactions between components present in two feed streams that change the chemical state or charge of their ionic species. It simultaneously involves reactive mass transfer, nucleation, growth, agglomeration and breakage of solid precipitates or crystals formed. The driving force for reactive crystallisation is chemical super saturation. Reactive crystallisation is a promising regeneration technique due to the high sulfate loading in the CS-Cap absorbent. Alkali sulfate salts precipitate as soon as sufficient alkali hydroxide is added. The by-product generated from the crystallisation technique (Figure 2) may have commercial potential, making the technique efficient as well as low cost. However, the economics require further evaluation based on the type of alkali or base used and the downstream operations required to separate the crystal product.

The results from other researchers (Xu & Rochelle, 2009) and our previous work (Pearson et al., 2017a) have already shown that crystallisation will remove sulfate from sulfur-rich aqueous amines. The key parameters affecting sulfate solubility identified in these previous studies are amine concentration, temperature and the CO₂ loading. Most of this research was conducted on amines prepared synthetically in the laboratory. Their CSIRO pilot plant sample had only limited exposure to real flue gases (200 hr); hence, laboratory research into crystallisation behaviour needs to model absorbents that in real process will be significantly more degraded. The initial precipitation results by Pearson et al. revealed a reduction in sulfate removal efficiency for pilot plant samples (200 h operation) compared to synthetic samples. This is possibly due to increased ionic strength as a result of impurities in the absorbent, the presence of HSS, and metal ions. Research is needed to confirm if higher absorbent degradation under real PCC conditions will likely increase the solubility of sulfate in the amine, and negatively affect precipitate purity.

Initial precipitation trials (Pearson et al., 2017a) focussed on determining whether reactive crystallisation is effective in desulfurizing loaded amines, at various temperatures, amine concentrations and initial sulfate loadings. Here crystallisation experiments, are conducted on pilot plant MEA, pilot plant dosed with degradation compounds, and MEA with tailored levels of sulfate and amine . The aims being to achieve an:

- Improved understanding of crystallisation process performance under more realistic plant conditions
- To investigate the effect of amine degradation on the effectiveness of reactive crystallisation to remove its sulfate burden



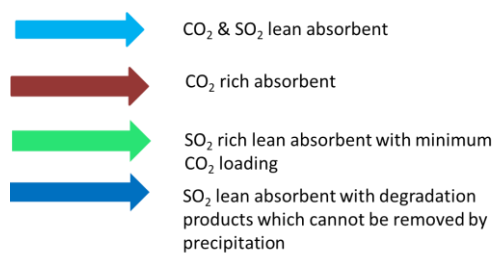


Figure 2: CS-Cap Process Sulfur loop Regeneration Scheme utilising reactive crystallisation

2. Experimental

Previous work (Pearson et al., 2017; Xu & Rochelle, 2009) used filtration for the physical separation of solid and liquid after precipitation and to determine the amount of precipitated sulfate removed after the addition of potassium hydroxide (KOH) to the absorbent. Although effective, this mass balance method involves considerable time, energy and material consumption. The mass balance method is used here to investigate the yield and quality of crystals produced under one particular set of conditions. However, most data is collected from a more efficient continuous laboratory precipitation experiment. The continuous method differs to the mass balance method as the precipitate and liquid are not physically separated at each temperature. This reduces the time required to conduct the precipitation trials and relies on direct Ion Chromatographic (IC) measurements of the residual soluble sulfate loadings instead of theoretically calculating the soluble sulfate by difference from the total and crystal yield.

2.1. Sample Sets

2.1.1. Pilot Plant Samples (PS₁₄)

Sulfur loaded aqueous amine absorbent was produced at CSIRO's PCC pilot plant located at AGL's Loy Yang power station, Victoria, Australia. The removal of SO₂ from the flue gas was carried out by recirculating CO₂ loaded aqueous amine (~18wt% aqueous monoethanolamine) in the flue gas pre-treatment column, replacing the caustic wash otherwise used for removing SO₂ from flue gases (Pearson et al., 2017a). The SO₂ loading continued until the MEA became saturated. This S loaded pilot plant absorbent sample (PS₁₄) was used to evaluate the reactive crystallisation technique.

2.1.2. Synthetic Samples

Synthetic amine samples were prepared in the laboratory with varying amine concentrations. Aqueous 5M (~30wt%) and 6.5M (~40wt%) MEA concentrations were prepared using neat MEA (purity 98%) from Sigma Aldrich diluted with Milli-Q water. The CO₂ was loaded by bubbling CO₂ through the aqueous MEA using a Dreschel bottle with a sintered frit. The CO₂ was pre-saturated with water to minimise the effect of evaporation from the gas flow.

CO₂ loading is expressed as:

$$CO_2 \text{ loading } (\alpha) = \frac{\text{moles } CO_2}{\text{moles MEA}} \quad (7)$$

Aqueous MEA CO₂ loading of 0.5 was confirmed gravimetrically. After the addition of CO₂, the SO₄²⁻ was loaded using H₂SO₄ (ACI labscan, 94% purity). On the addition of H₂SO₄, as expected, some of the absorbed CO₂ was spontaneously released. The mass decrease of the total solution was assumed to be entirely due to CO₂ loss. Based on the new weight of the solution, CO₂ loading and amine concentrations were recalculated. Here the process of CO₂ and SO₄²⁻ loading is a lab scale representation of the CS-Cap process, where the CO₂ rich solution is used to absorb SO₂. There will be typically very little CO₂ left in the CS-Cap's small stream (green stream in Fig. 2) while it absorbs SO₂. This was evident through the lab experiments, which calculated a new loading of 0.21 mol (CO₂)/mol (MEA) for 5M MEA solutions upon addition of H₂SO₄ to the CO₂ loaded solution.

2.2. Sulfite/Sulfate analysis

Sulfate was determined using a Metrohm 930 compact IC Flex chromatograph fitted with a 20 μ L loop, with Metrosep A Supp 16 anion column -250/2.0. The mobile phase was 0.75mM sodium carbonate (BDH Chemicals, >99% purity) and 0.75mM sodium hydroxide (chem-supply >98% purity) and the flow rate was 0.2 mL/min. Similarly, where sulfite analysis was required the anion eluent (Na₂CO₃ + NaOH) was dosed with 5% acetone (ACI Labscan >99%, HPLC grade) which resulted in clear separation of the sulfite and sulfate peaks (Metrohm application IC notes no S-155). (Thompson et al. 2014; Lin et al. 2014). 1 - 5% formaldehyde (Chemsupply, purity 37%) was used as a sulfite stabiliser. All analyses of the samples and standards were completed within a period of 14 days.

2.3. Organic Anions

Samples were analysed using a Metrohm 930 compact IC Flex chromatograph fitted with a 5 μ L loop, with Metrosep A Supp 16 anion column -250/2.0. The mobile phase 0.75mM sodium carbonate (BDH Chemicals, >99% purity) and 0.75mM sodium hydroxide (chem-supply >98% purity) and the flow rate was 0.5 mL/min. 600 μ L of 5N NaOH (chem-supply >98% purity) was added to 500-550 mg of each sample and stored in the dark overnight to hydrolyse amides as described by (Sexton and Rochelle 2011). Prior to analysis, hydrolysed samples were diluted to 25.00 mL in mobile phase. Initial eluent (i.e. reagent grade water, 18.2 mOhm) was run for 25 min. then 100% (Sodium carbonate/hydroxide) eluent to the end of the runtime.

2.4. Inorganic Anion

The IC procedure used was similar to that used for sulfate analysis. The multi element standards (High purity standards, Sigma Aldrich multi-element IC std 2 solution A) were used as check for the calibration of the instrument.

2.5. Metals and Cations

ICP_MS analysis was conducted on the PS_14 samples. Pre-weighed absorbent samples were acidified with 1:1 HNO₃ (70% Analytical grade, ACI Labscan and deionised water, MilliQ Academic, Millipore) and diluted to 100.0 mL with 1% HNO₃. Prior to analysis, samples were diluted a further 2:5 (v:v) in 1% HNO₃. Standards were prepared from a mixed metals and cations standard (Sigma Aldrich multi-element standard solution 5 for ICP) in 10% HNO₃. Metals and cations were measured using Agilent 7900 ICPMS.

2.6. pH

pH was estimated using pH paper (Aldrich chemistry, 0-14) and measured by SmartChem-Lab pH analyser.

2.7. XRD Analysis

XRD analyses were carried out for PS_14 precipitates on a Panalytical X'Pert Pro powder diffractometer, equipped with an incident beam BBHD CoK α monochromator and an X'Celerator linear detector, operated at 40kV and 25mA and scanned over 5-80 $^{\circ}$ 2 θ with a step size of 0.017 $^{\circ}$ 2 θ at a rate of 0.08 $^{\circ}$ 2 θ per second. Panalytical High Score software was used for phase identification by search-match of the ICDD PDF4 2018 data-file.

2.8. Continuous crystallisation method

Approximately 100g of CO₂ loaded (initially 0.50 mol CO₂/mol MEA) aqueous MEA solution (initially 5.0M, 6.5M) was weighed into a beaker. The solution was loaded with SO₄²⁻ (115 g/1000g) by adding H₂SO₄ (94% purity). Initial sulfate loadings were determined by IC. Solid KOH pellets (Biolab PRONALYS assay 85% (Purity) Analytical Reagent Grade) were added in excess of the theoretical requirement to precipitate all of the SO₄²⁻ present in the solution. The solution was then heated to the desired temperature and stirred for one hour. After one hour, a liquid sample was collected by turning off the stirrer and holding the solution at

the same temperature until a clear visible separation of solid and liquid occurred. A small liquid sample (< 1% of the total solution) was taken out and diluted immediately for IC analysis. The remaining mixture was then heated to the next desired temperature, with stirring, and held for one hour before taking another liquid sample and so on. The samples withdrawn at each temperature were analysed via IC for SO_4^{2-} concentration giving a direct measure of residual SO_4^{2-} and an indirect measure of sulfate crystal recovery. KOH addition varied between 80% to 160% of stoichiometric requirements for reaction with the sulfate present. The effect of temperature and KOH addition are evaluated here for different amine concentrations

3. Results and Discussion

3.1. Characterisation of pilot plant sample

The sulfate and sulfite concentrations in the pilot plant absorbent (PS_14) were determined as 110g/kg +/- 10g/kg and 2-3 g/kg ($R_2 > 0.99$; relative standard deviation <6%). The lower concentration of sulfite compared to sulfate confirms that most of the absorbed SO_2 was converted into SO_4^{2-} . PS_14 organic anion measurements are provided in Table 1. Niederaussem pilot plant data are included for comparison.

Table 1: Organic anions

Component	PCC Pilot Plant at Loy Yang, Victoria Australia (PS 14)	PCC pilot plant at Niederaussem, Germany (Moser et al. 2011)
Glycolate	0.025%(w/w)	Not reported
Formate	0.052%(w/w)	0.2% (w/w)
Acetate	0.022%(w/w)	1.8% (w/w)
Oxalate	<0.01% (w/w)	<0.1% (w/w)

The above results are in accord with the lower degradation level of PS_14 in CS-Cap pilot campaign, due to its 200 operational hrs compared to Niederaussem's 5000 hrs. The right column indicates the degradation of MEA after 5000 hrs of operation under long-term test at the post-combustion capture pilot plant in Niederaussem.

Inorganic multi-anions (metals and cations) are listed in Tables 2 and 3; for PS_14 and aged MEA from the same pilot plant.

Table 2: Inorganic multi-anions

Component	PCC Pilot Plant at Loy Yang, Victoria Australia (200 hrs CS-Cap operation) PS_14	PCC Pilot Plant at Loy Yang, Victoria Australia (700 hrs operation) (Reynolds et al. 2015)
Fluoride	< LDL of 0.1 ppm	Not reported
Chloride	Average 0.435 g/kg (range 0.395 – 0.512 g/kg)	0.1017 – 0.167 g/kg
Bromide	< LDL of 0.1 ppm	Not reported
Nitrate	Average 0.016 g/kg (range 0.015 – 0.016 g/kg)	0.60–1.51 g/kg
Phosphate	Not detected	< 4
Nitrite	< LDL of 0.1 ppm	0.107–0.108 g/kg

LDL: Lower detection limit

Table 2: Metals and cations

	PCC Pilot Plant at Loy Yang, Victoria Australia (200 hrs CS-Cap operation) PS_14	PCC Pilot Plant at Loy Yang, Victoria Australia (700 hrs operation) (Reynolds et al. 2015)
Cations (mg/kg)		
Ca	4.3	9.8 – 36.5
K	1.1	4.5 – 10.2

Mg	1.7	2.4 – 6.2
Na	31.4	17.5 – 62
Metals (mg/kg)		
Cr	2.34	1.8 – 4.20
Cu	5.0	2.23 – 3.54
Fe	45.2	14.1 – 199
Mn	7.5	0.48 – 2.12
Mo	0.2	0.21 – 0.49
Ni	44.4	2.2 – 4.6
V	0.04	0.32 – 0.44
Zn	0.3	5.7 – 11.5

Despite its lower operational hours, the PS_14 absorbent sample reports higher levels of chloride and some metals than the 700h sample generated at the same pilot plant. This is likely a result of the lack of pre-treatment used in the CS-Cap campaign. For the 700h campaign a caustic wash pre-treatment was used. This will have removed other acid gases (including HCl) and fly ash from the flue gas before it entered the CO₂ capture plant.

3.2. Effectiveness of Reactive Crystallisation in Removal of Sulfate

Unlike the pilot plant campaign, a conceptual CS-Cap plant would not allow sulfate saturation of its amine leading to SO₂ breakthrough in real plant operation. There will always be varying SO₄²⁻ concentrations entering the regeneration unit due to recycling the absorbent, and changes in flue gas SO₂ concentration. Based on this understanding the continuous precipitation method was used to perform reactive crystallisation experiments at conditions near to actual plant operating conditions. It is important to investigate the effectiveness of precipitation at various initial sulfate concentrations, temperatures, and KOH additions. Synthetic 5M and 6.5 M solutions loaded with CO₂ and SO₄²⁻ are compared here with the pilot plant sample's behaviour during precipitation. One must also determine experimentally for a given initial sulfate loading and temperature, how much sulfate can be removed if the addition of KOH is varied. This assists in optimising the KOH requirements, as well as deciding the residual sulfate to remain in solution and returned to the capture loop.

3.2.1. Effect of varied KOH Addition

Figures 3 & 4 show the effectiveness of precipitation to remove sulfate from synthetic and pilot CS-Cap MEA absorbents at 20°C and 40°C. More than 90% of sulfate removal is possible through this technique with excess KOH driving higher yields. The pilot plant sample shows a similar trend to the synthetic 30 wt.% and 40 wt.% MEA samples.

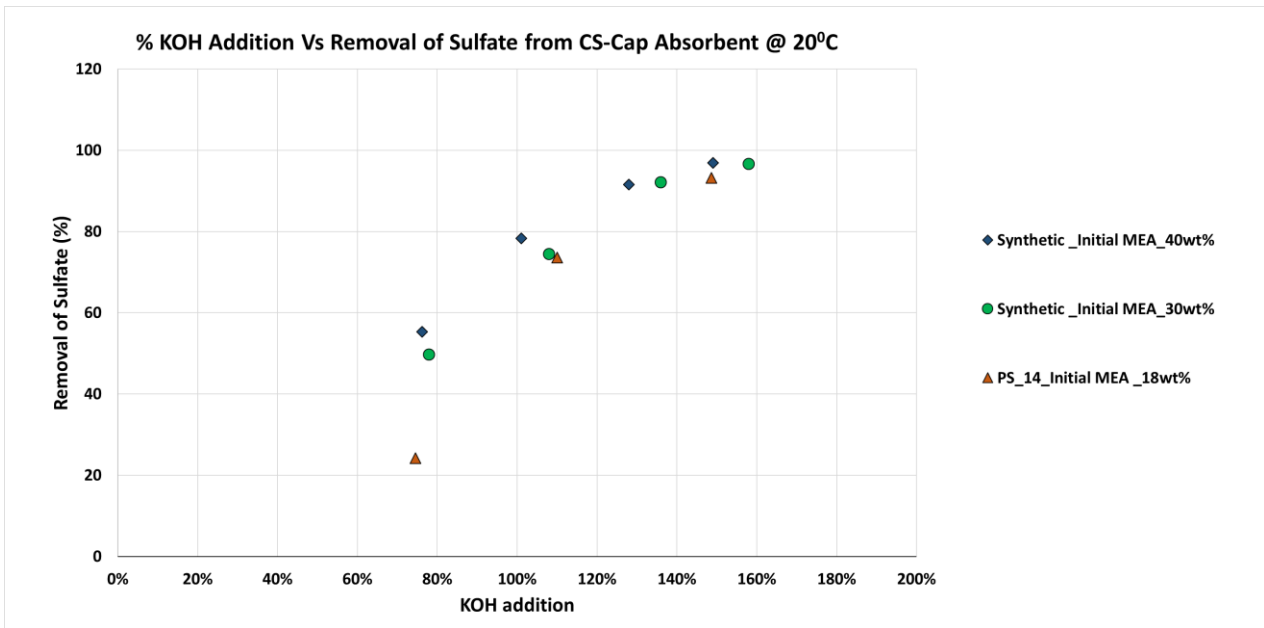


Figure 3: Effectiveness of Reactive Precipitation in Removal of Sulfate from the CS-Cap Absorbent at 20°C

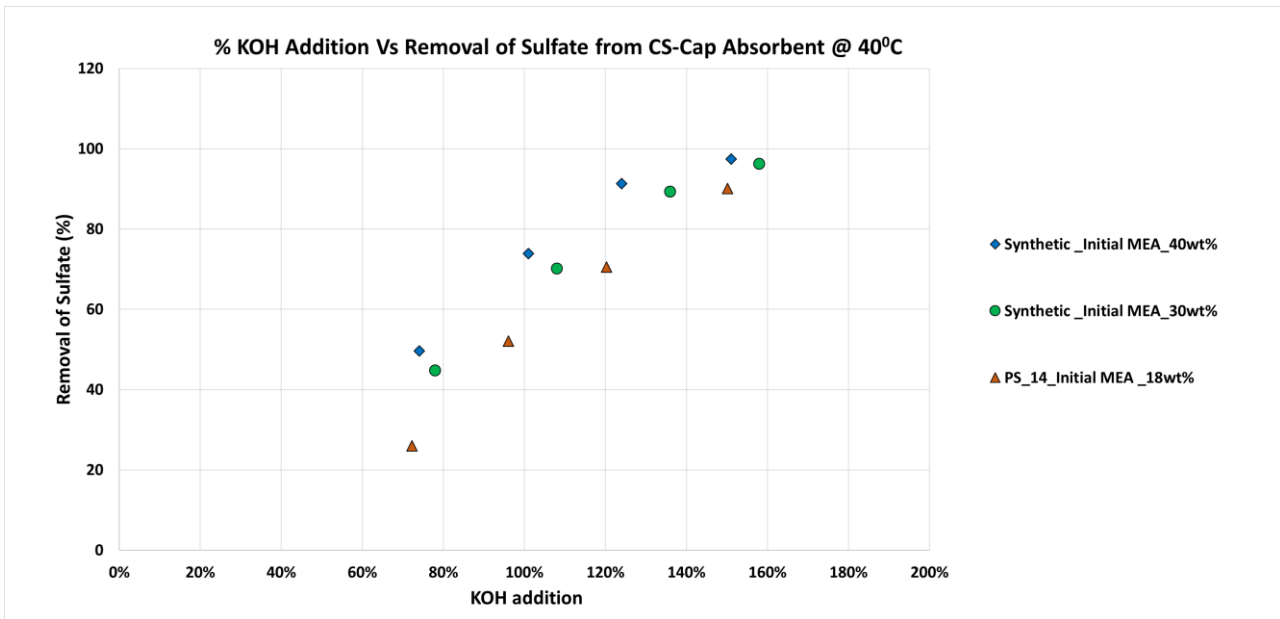


Figure 4: Effectiveness of Reactive Precipitation in Removal of Sulfate from the CS-Cap Absorbent at 40°C

The more energy efficient 40°C crystalliser temperature has only a minor negative impact on sulfate removal.

3.2.2. Effect of varied MEA concentration

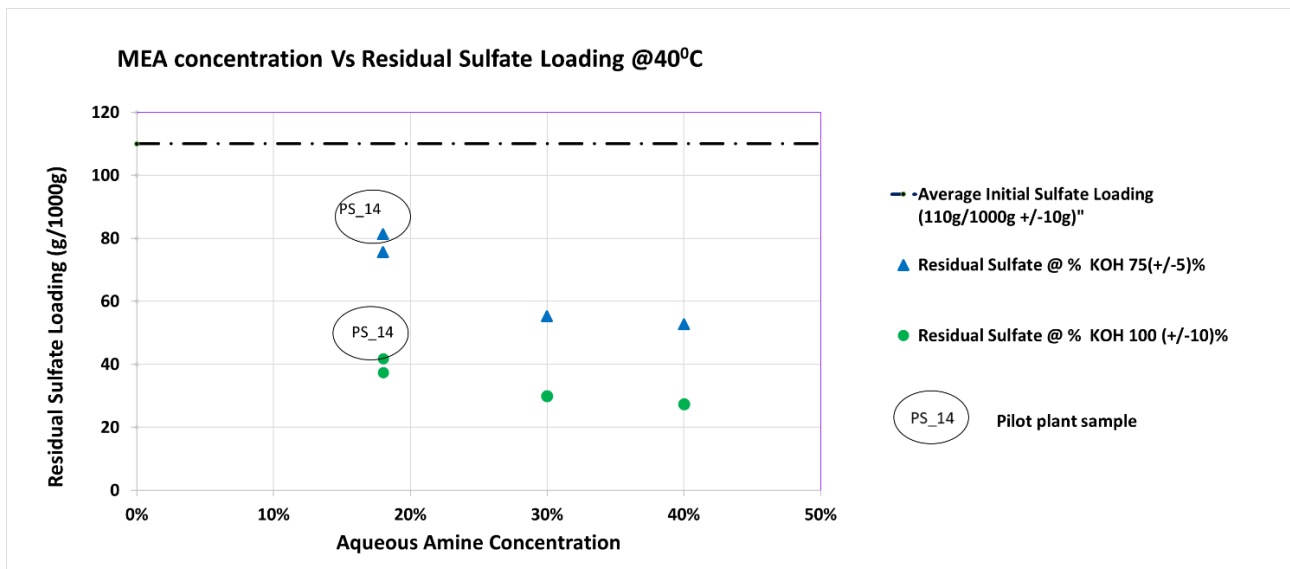


Figure 5: Effect of MEA concentration on Reactive Precipitation in Removal of Sulfate from the CS-Cap Absorbent at 40°C

Experiments were conducted with an intent to understand the impact of varying MEA concentrations at a particular temperature, initial sulfate loading and % of KOH addition. As shown in Figure 5, the residual sulfate left in solution was highest in the pilot plant sample (PS_14). Synthetic samples at the same concentration as PS_14 produced slightly lower residual sulfates, but the difference is quite small and within experimental error. In comparison, the higher concentration synthetic amines (30 and 40 wt.%) produced significantly lower residual sulfate concentrations as the sulfate solubility decreases on increased amine concentrations.

3.2.3. Effect of varied Initial sulfate loadings

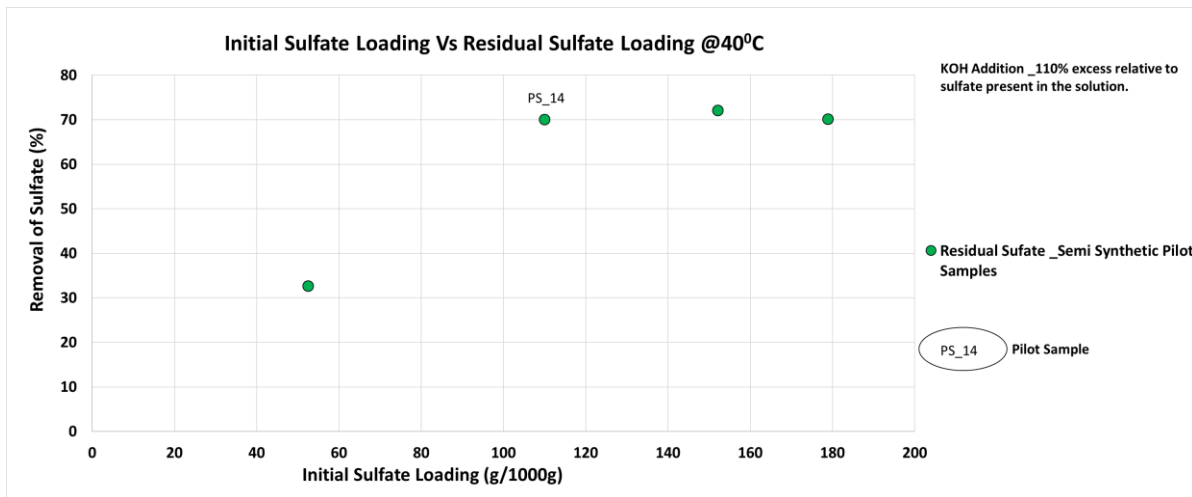


Figure 6: Effect of Initial Sulfate Loading on Reactive Precipitation in Removal of Sulfate from the Pilot Plant Absorbent (PS_14) at 40°C, 110% KOH

Figure 6 reveals the effect of increasing the initial sulfate loading of PS_14 at 40°C under constant 110% KOH excess (based on sulfate present) .It has a positive impact on the % of crystalline sulfate formed during reactive precipitation. The measured values were 32% sulfate removed at 5.2 %w/w initial sulfate loading and almost constant 70% sulfate removal at 11, 15 and 18 % w/w. Our data is consistent with that of (Xu, 2008) who investigated the impact of conductivity on sulfate concentration in similar MEA systems). Xu found that conductivity increases up to saturation and then increases, decreases or remains constant depending on the ionic composition and strength of the solution. Conductivity heavily depends on the ionic

strength, which then determines sulfate solubility. The data is important from a PCC process engineering design perspective in that it confirms for a given MEA loading and $\text{KOH}/\text{SO}_4^{2-}$, it is not possible to withdraw more sulfate (by allowing higher sulfate accumulation) than that present at saturation. Further sulfate withdrawal relies on increasing either the MEA concentration and/or KOH loading.

3.3. Investigation of K_2SO_4 obtained out of Reactive Precipitation

One of the attractions of precipitation as a reclamation technology is the potential to sell the K_2SO_4 produced for use in fertiliser or glass manufacture. To provide further information on the quality of the PS_14 precipitates; they were evaluated by x-ray diffraction (XRD), light microscopy and laser particle sizer. The particle size data suggested precipitates ranged between 10 – 150 μm . This is a large size distribution range, suggesting these precipitates form flocs. As a result, the precipitates were also evaluated using light microscopy (images in Figure 7).

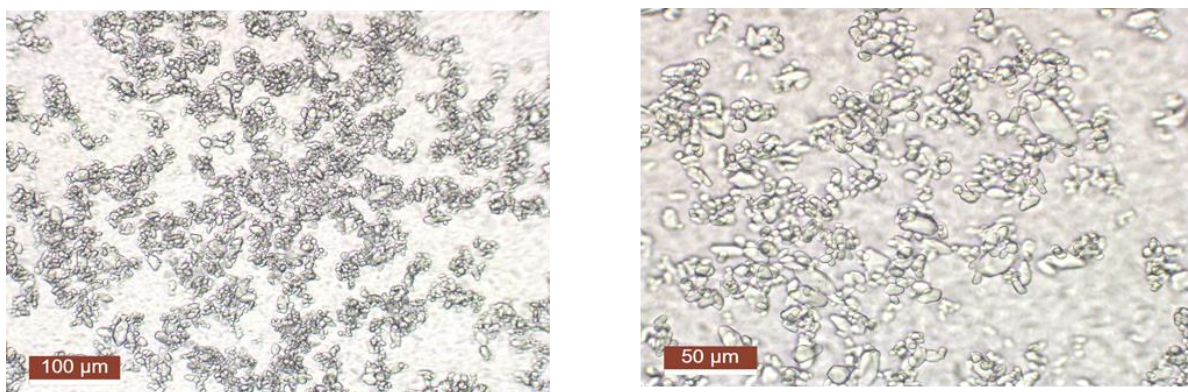


Figure 7: Light microscope images at two magnifications of K_2SO_4 crystals produced during precipitation experiments

K_2SO_4 crystals can have orthorhombic or hexagonal symmetry depending on preparation conditions. Figure 7 reveals pictures of the crystals suggesting they have formed 50 – 110 μm flocs. This was confirmed by XRD data (Supplementary Information Fig. S1) revealing a spectrum of highly pure synthetic arcanite (orthorhombic polymorph of potassium sulfate) crystals less than 40 μm in length. Figure S1 presents an XRD spectrum of the K_2SO_4 precipitate generated from a PS_14 solution at 40 °C. The only crystalline phase identified is orthorhombic K_2SO_4 , confirming the structure observed in the microscopy images, with all peaks on the XRD trace accounted for by this phase.

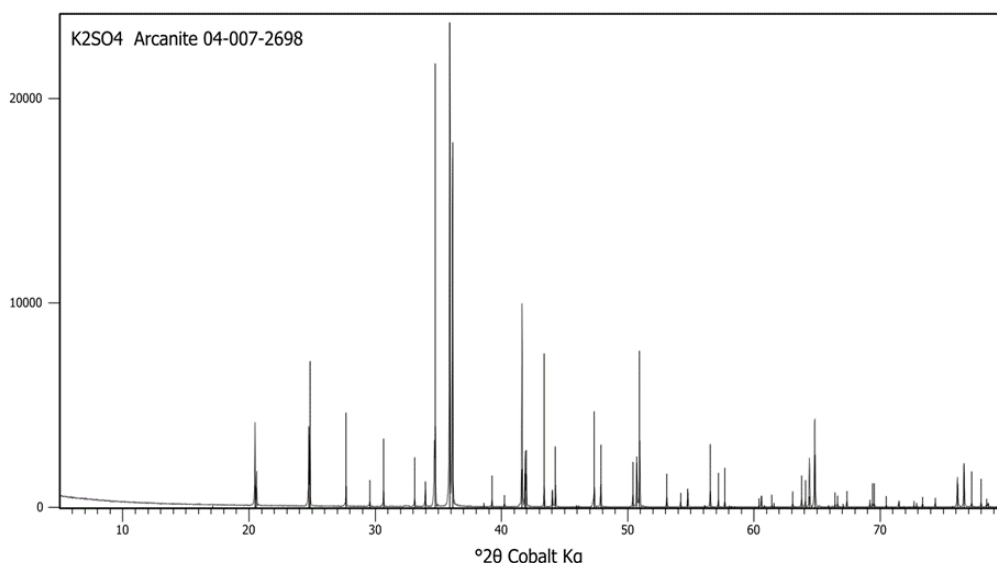


Figure S1: XRD trace of K_2SO_4 precipitate generated from precipitation experiment completed with PS_14 at 40 °C. Log I scale

XRD analysis confirms this precipitate is highly crystalline and pure ~99%, however, it cannot identify impurities < 1% of the total mass including any amorphous phases present.

3.4. Rate experiments

In order to size a crystalliser to generate the K_2SO_4 product as part of a continuous process, information is required on the rate with which the crystals form. This information will also be required for process optimisation and economic evaluation. Precipitation experiments were performed with solution samples removed periodically over one hour after the KOH was added. These solutions were analysed for sulfate, allowing its removal rate via precipitation to be determined. Results are provided in Table 5 for pilot plant samples and Table 6 for lab prepared 6.5 M (~40wt% MEA) synthetic samples.

Table 5: Rate of K_2SO_4 precipitation reaction for pilot plant sample (PS_14)

Temperature 40°C, Reaction time 1 hr, KOH addition ~105% excess to that of sulfate

Minutes from start of experiment	Sample number	Residual Sulfate Loading (g/1000g)
0	Initial sulfate loading	104.3
14	1	37.76
27	2	38.91
39	3	39.19
51	4	37.68
62	5	35.45

Table 5: Rate of K_2SO_4 precipitation reaction for 6.5M synthetic samples (~40wt% MEA)

Temperature 20°C, Reaction time 1 hr, KOH addition ~160% excess to that of sulfate

Minutes from start of experiment	Sample number	Residual Sulfate Loading (g/1000g)
0	Initial sulfate loading	96.5
7	1	4.25
13	2	3.52
18	3	3.19
24	4	3.16
35	5	2.92
45	6	2.89
59	7	2.75

Tables 5 and 6 reveal that the precipitation reaction is rapid, with the majority of sulfate removal occurring within five to fifteen minutes. This fast reaction rate was observed for both laboratory and pilot plant samples. A fast reaction rate suggests smaller sized equipment for the crystallisation process.

3.5. Effect of Degradation on Appearance and Purity of K_2SO_4 Crystals

Our previous publication (Garg et al., 2018) showed no impact of higher level of degradation products on the level of sulfate removal from pilot plant samples. As described in section 3.1, PS_14 did not have particularly high levels of salts or degradation products, so it was dosed with extra degradation products. A severely oxidised MEA solution (prepared in autoclave with additional organic acids - formate, acetate and oxalate) was added to PS_14 to raise its 0.1 wt% organic anions concentration to 1wt%. There was negligible difference in the removal of sulfate between the two samples as shown in Figure 8. Further, there was no discernible difference in the colour (supplementary information Figure S2) of crystals obtained from the initial pilot plant samples and extra-degraded pilot plant samples. The colour of crystals

generated from degraded 5M and 6.5 MEA solutions, however, is darker as an effect of their higher degraded amine concentration.

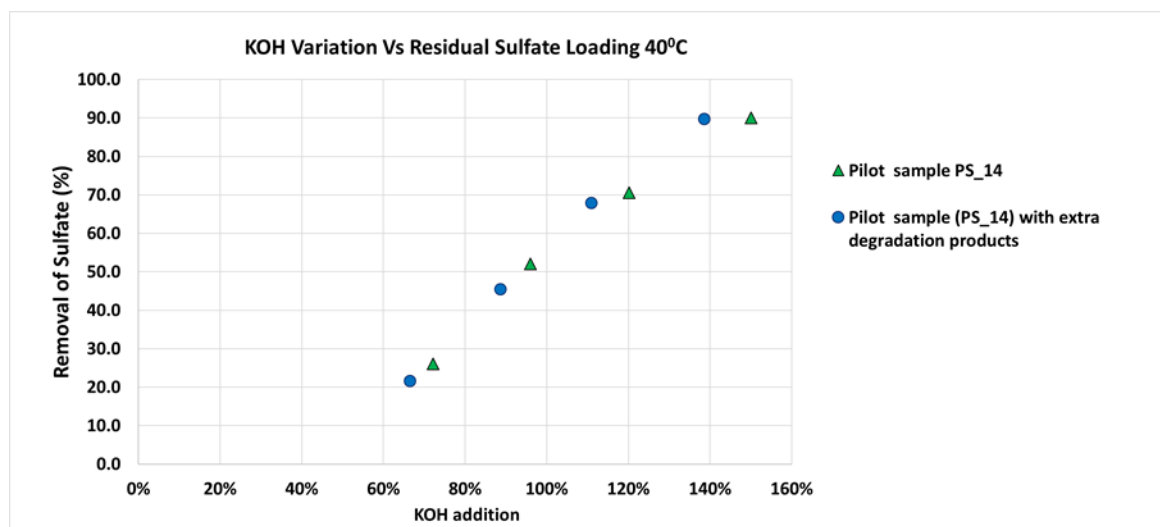
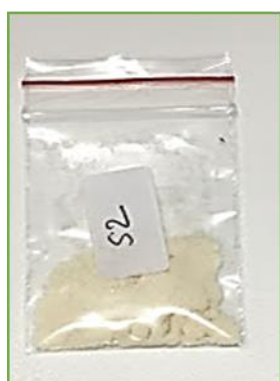
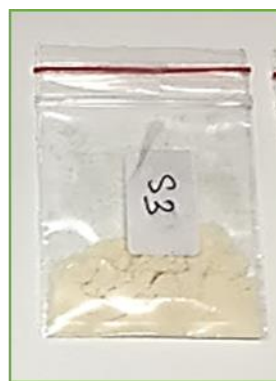


Fig 8: Effect of degradation products on precipitation of sulfate from PS_14



(a)



(b)

Figure S2: Images of precipitates, (a) (S2) PS_14, (b) (S3) PS_14 spiked with extra degradation products

Though the colour of precipitates could be an issue for saleability, the XRD analysis determined that the purity of the precipitates was not affected by either the colouring or higher level of degradation products in the initial amine absorbent.

4. Conclusions

Reactive crystallisation is demonstrated as an effective technology for removing the high sulfur content, as sulfate, from aqueous amines. These experimental data will help in optimising the economic evaluation of the process. As described in section 1, there is high level of sulfate absorbed by the absorbent as a result of recycling in the lower portion of the absorber column in the CS-Cap process. Increasing initial sulfate loading improves the removal efficiency of the sulfate, up to a certain extent. Hence recycling the absorbent would be beneficial for the CS-Cap process up to the extent after which the recovery of sulfate gets constant or falls off.

An important consideration when selecting a reclamation technology to be employed with the CS-Cap process includes whether the technology should be batch or continuous. The high sulfate achieved is advantageous for crystallisation to be operated batch wise as depicted from Figure 6, the quick reaction time offers the capability of the process to be operated in continuous operation. Further research into

these factors is warranted given reactive crystallisation not only offers the ease of operation but could also potential for energy savings. This can be predicted as the bulk sulfate removal can be achieved with reduced heating or cooling requirements for crystallisation compared to a similar scale thermal reclamation process, where the temperature of the absorbent needs to be raised from 40 to 110 or 120 °C to boil off amine. However the experiments completed here are at laboratory scale, with comparatively small amounts of absorbent KOH addition. On a large scale, the heat of reaction will likely be significant, and an additional cooling duty may be required. This cooling duty is still expected to be smaller than a comparative process utilising thermal reclamation.

The lower energy requirement and short reaction time (< 15 minutes) for almost 90% sulfate removal in a single step at both at 20 °C and 40 °C makes reactive crystallisation an attractive process. Additionally, it produces a high purity K_2SO_4 precipitate which could be potentially saleable. The experimental results showed no significant effect of amine degradation on the purity of the crystals for pilot plant samples which is key in terms of saleability. However, the colour of the crystals could be an issue in the real plant conditions operating at higher amine concentrations. This could be solved by giving a final wash to crystals with saturated K_2SO_4 solution.

The crystallisation process enables more than 90% sulfate removal from MEA by adding 130% KOH relative to the amount required to react with the total amount of sulfate present, it simultaneously produces higher amount of crystals by lowering the crystallisation temperature from 40 °C to 20 °C. Though the variation of amount of crystals generated at both the temperatures lies within the experimental error but will be a useful information for the simulating the crystallisation process. Hence the experimental data generated will help in optimising the economic evaluation of the process.

One limitation of the process is that the mother liquor separated during filtration will still contain non-ionic degradation products which could not be removed through precipitation. Hence there might be a requirement of additional reclaiming of the absorbent on a batch basis.

5. Future Work

The effect of additional degradation on pilot plant samples was evaluated here. The results showed no significant effect of degradation on the precipitation of the crystals using relatively low amine pilot plant samples with added degradation products. However, in a real plant amine concentrations will be much higher, around 30-40wt%. The effect of degradation products on sulfate precipitation and crystal purity generated from higher concentration amines still requires evaluation.

Future work requires computer simulation of the precipitation process i.e. feeding system, crystallisation, and filtration and drying. The data provided here can be used to validate the simulation, which can then be used to optimise the process and evaluate cost. This will allow comparison to a standard process using standard reclamation technologies available commercially like thermal reclamation, ion exchange etc. A simulation model in Aspen Plus using current experimental work will be developed to optimise the crystallisation process, the results of which shall be a part of our future publication.

It is also important to understand the impact of the continued presence of potassium in the absorbent to assess whether excess potassium could cause any issues to the overall system. Excess potassium in the absorbent could lead to unwanted crystallisation. It is very important to control the potassium concentration in the recirculating absorbent at all times. The online or continuous measurement of sulfate concentrations is necessary for control of the CS-Cap process so that KOH dosing can be tailored to the incoming sulfate concentrations. Understanding the impact of K will be useful in designing a better chemical dosing system and overall process operation.

Acknowledgements

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Appendix B : Aspen Plus simulation model for amine reclamation in combined CO₂ and SO₂ capture: Validation of model

Publication has undergone CSIRO review. To be submitted to journal

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Abstract:

Sulfur dioxide affects the performance of CO₂ absorption in post combustion CO₂ capture (PCC) using aqueous amines. This causes an additional cost for its removal in PCC facilities in Australian coal fired power plants. CSIRO's patented CS-Cap process aims to reduce the capital cost of PCC installations by combining SO₂ and CO₂ capture. However, the combined capture process generates a distinctive sulfate rich aqueous amine stream, which requires continuous regeneration. Reclamation techniques including thermal reclamation and reactive crystallisation were previously investigated experimentally to understand the benefits and drawbacks of each technology for removing sulfate from aqueous amines. The parameters of those experiments are used to validate equilibrium-based models in Aspen Plus for Thermal Reclamation and Reactive Crystallisation. The model's predictions are evaluated against experimental results achieved with pilot and synthetic samples at various operating conditions. The models replicate experimental results reasonably well for synthetic amine samples with a high variation (up to 25%) in only a few cases, however the variation is higher for pilot samples. This builds confidence in using Aspen Plus models for future cost estimations under certain conditions. Further, an attempt has been made to identify the parameters that could cause the higher variation between the simulation and experimental results.

Keywords: Aspen Plus; Combined Capture; Crystallisation; MEA Recovery; Sulfate Removal; Thermal Reclamation

1. Introduction

Figure 1 shows the pre-treatment requirements for retrofitting PCC units in Australia. There would be a large need of capital investments for flue gas pre-treatment in association with full-scale deployment of PCC units in Australian coal fired power plants. The CSIRO's CS-Cap process aims to capture CO₂ and SO₂ through a single amine absorbent system eliminating the large capital investments required for pre-

treatment units in Australia (Puxty et al. 2014). As shown in Figure 2, the process removes the requirement of these units by combining the CO₂ and SO₂ capture using a single amine absorbent in a single absorption column. A very small volume of the CO₂ rich stream (CO₂ rich, red stream in Fig. 2) is sufficient to capture the incoming SO₂, thereby generating a stream rich in sulfur (SO₂ rich, green stream in Fig. 2) (Beyad et al. 2014).

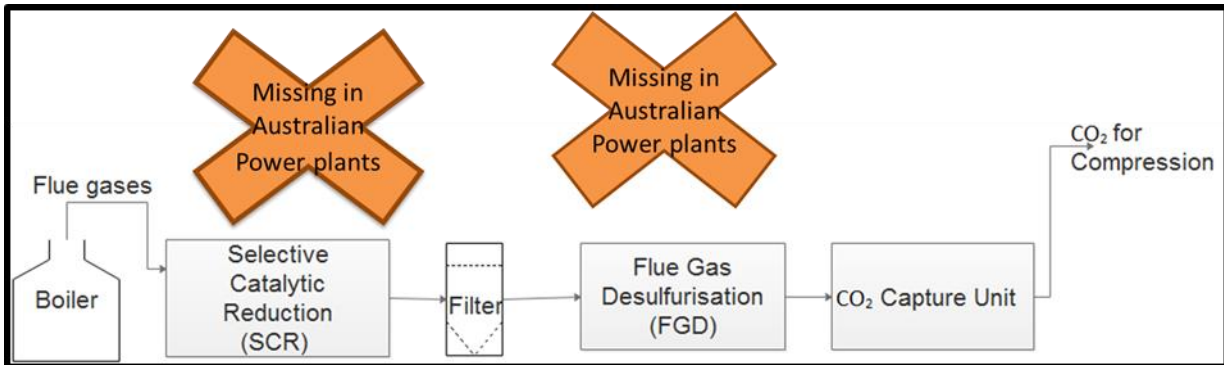


Figure 1: Scenario for PCC retrofit installations in Australia

The CS-Cap absorbent utilises CO₂ rich amine coming from the upper section of the absorber column and recycles it to the lower portion of the column to absorb SO₂ from the incoming flue gases as shown in Fig.2. The selectivity of amines to absorb stronger against weaker acids allows the absorption of SO₂ over CO₂ (Puxty et al. 2014). The absorption of SO₂ results in the release of CO₂ making the absorbent lean in CO₂. Commercial application of the process requires validation of the process at pilot scale. Hence CSIRO's pilot plant campaign held in 2014 at AGL's Loy Yang power station aimed to capture SO₂ and CO₂ using a single amine (monoethanolamine) and was successful in absorbing incoming SO₂ from the flue gas using a CO₂ rich absorbent (Puxty et al. 2014). Due to the continuous recycling of the CO₂ rich stream in the lower portion of the absorber column, and presence of water and O₂ in the system, the absorbed SO₂ will convert to sulfate, SO₄²⁻. This was confirmed by analysing the absorbent samples generated in the pilot campaign (Garg et al. 2018a). Sulfate forms a heat stable salt with protonated amine making the amine unavailable for CO₂ capture, thereby increasing the requirement of makeup amine in the overall amine loop.

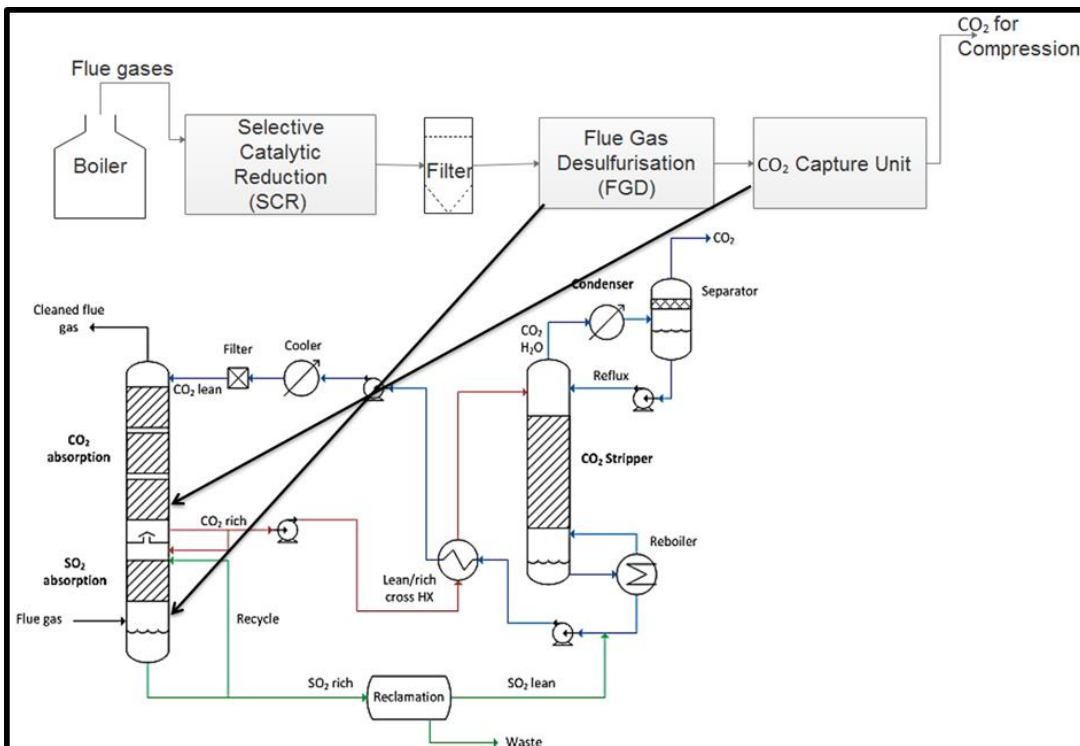


Figure 2: CS-Cap process capturing CO₂ and SO₂ in a single absorber column

The protonated amine forms a strong ionic bond with sulfate, does not reversibly convert back to free amine on application of heat, and are hence named heat stable salts. A similar gradual degradation phenomena occurs in natural gas processing where amines are used to capture H₂S and CO₂ from well gas (Cummings et al. 2007). While the kind of HSS and their amount differ to that generated in the CS-Cap process, we can learn from the experience in the natural gas industry. The formation of heat stable salts creates problems in amine plants like corrosion, foaming and plugging in columns, and fouling in heat exchangers. To deal with such problems, either fresh amine is added to the system, or amine cleaning is required. Amine replacement is an expensive option and environmentally unsafe. Instead, operations like thermal reclaiming, ion exchange or electro dialysis are used in practice to remove the heat stable salts from the spent amine absorbent (CCR Technologies, 2013).

In our previous publication (Garg et al. 2018a), the reclamation technologies mentioned above were reviewed for their applicability to the CS-Cap process. We concluded that experimental evaluation was required to verify the genuine benefits and drawbacks of the most promising technologies: Thermal Reclamation and Reactive Crystallisation.

Thermal Reclamation is one of the most established technologies in the natural gas treating industry. It offers the benefit of removing all kinds of degradation products including ionic, non-ionic, and solid contaminants. However drawbacks include high amine losses and high energy consumption (Wang et al. 2015). There have been several advancements in thermal reclamation technology over the past few decades, including changing operation from atmospheric to vacuum pressure, and changing from batch to continuous mode. Several kinds of reclaimers are used in the gas treating and carbon capture industry to cater for the different needs of the process operation. However, for the CS-Cap process, the thermal reclaimer will need to operate continuously due to the high level of SO₂ removal required from the flue gas. Bench scale experiments were conducted to evaluate thermal reclamation as a regeneration technology for reclaiming sulfur rich aqueous amines (Garg et al. 2018 b). Experimental evaluation was necessary to understand the system behaviour as the heat stable salt content, which is primarily sulfate in CS-Cap case, is high compared to the standard stream sent for reclamation in the natural gas industry (Pearson et al. 2017). Usually the concentration of heat stable salts in amine absorbents is maintained below 2 wt% to avoid operational problems (Burns & Gregory, 1995). However, the concentration of heat stable salts of sulfate in the pilot sample generated (PS_14) through the pilot campaign was almost 11-12% by weight as analysed by ion chromatography(IC).

In addition to Thermal Reclamation, Reactive Crystallisation has also been experimentally evaluated as an option to regenerate the sulfur rich CS-Cap stream. This involves adding sufficient potassium hydroxide, KOH, to react with the SO₄²⁻ ions present in the solution to form crystalline potassium sulfate, K₂SO₄. This process offers comparatively lower energy requirements than thermal reclamation with the potential of selling the K₂SO₄. It is relatively a new technique for PCC, and is unable to remove the non-ionic degradation products. However, as the CS-Cap absorbent is rich in ionic impurities, the crystallisation technology was selected for experimental analysis.

The objectives of this paper are to:

- Develop CS-Cap absorbent regeneration simulations using Aspen Plus based on theoretical physico-chemical reaction chemistry for both thermal reclamation and reactive crystallisation.
- Validate these models against laboratory experimental data

These models enable more detailed evaluation of the CS-Cap process's commercial potential via optimisation and economics studies. These reclamation simulations provide an important desktop tool for

evaluating different operating cases, conducting "what if" analyses, and performing sensitivity and optimization studies.

2. Experimental

2.1. Materials

The pilot sample referred to throughout this paper as PS_14 was generated at CSIRO's PCC pilot plant, located at AGL's Loy Yang power station in Victoria Australia, in 2014. The 200 h campaign has been described in our previous publication (Pearson et al. 2017). The campaign used ~ 18 wt% monoethanolamine, MEA, (initial concentration before CO₂ & SO₂ absorption) loaded with CO₂ to absorb SO₂ from incoming flue gas. The CO₂ loaded absorbent was re-circulated in the pre-treatment column until there was breakthrough of SO₂ to the flue gas exiting the column (Pearson et al. 2017).

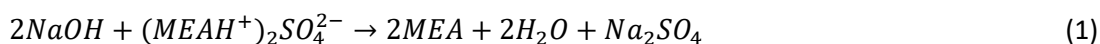
The concentration of sulfate in PS_14 after absorption of SO₂ was 110 g/1000 g (+/-10 g) (Garg et al. 2018a), and the concentration of MEA after CO₂ & SO₂ absorption dropped to 14 wt% as analysed by ion chromatography (Garg et al. 2018b). The concentration of other ionic and non-ionic contaminants present in PS_14 as a result of thermal and oxidative degradation was relatively low (< 1 wt%) due to the relatively short operating time for this campaign (200 h) (Garg et al. 2019).

Synthetic MEA solutions were also prepared using neat monoethanolamine (purity 98%, from Sigma Aldrich) diluted with Milli-Q water to the desired concentration (2.5 M, 5.0 M or 6.5 M). CO₂ loading was achieved by bubbling CO₂ through the solution until the desired weight change was achieved. Sulfate loading was completed after CO₂ bubbling by adding H₂SO₄ (ACI labscan, 94% purity).

2.2. Thermal Reclamation

The procedure for regenerating the pilot plant CS-Cap absorbent (PS_14) through thermal reclaiming, was as follows:

Neutralisation of PS_14 by adding NaOH as per the following reaction 1:



The pH of the pilot plant sample PS_14 was 4.5-5. The pH was raised beyond the pKa of MEA (9.5) during the neutralisation step to an initial pH of 10, 11 or 12 to investigate the MEA recoveries at different pH conditions which could help in optimising the caustic addition. The effect of various parameters including pH, temperature, pressure, initial sulfate loading, and higher amine concentrations were investigated on PS_14 and 5M synthetic samples (~30wt%). A more detailed procedure is described in (Garg et al. 2019)

After neutralisation, the absorbent was added to a reclaimer and the amine was boiled off from the solution while the less volatile contaminants stayed behind in the reclaimer vessel. For experiments under vacuum, a rotary evaporator fitted with a hot oil bath for temperature control, and a recirculating chiller and pump for condensing emitted vapours was used as shown in Appendix Fig. 1(a). For atmospheric experiments, a three-neck flask was placed in a hot oil bath. Thermometers were used to measure the temperature of vapour and liquid. An air cooled condenser and a receiver were used to condense and collect emitted vapours, as shown in Appendix Fig 1(b). Table 1 provides a brief overview of some of the thermal reclamation experimental conditions investigated for various MEA concentration and initial sulfate loadings.

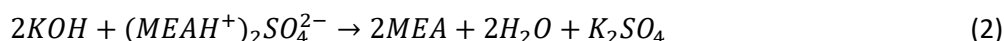
Table 1: Thermal reclamation experiments conducted at laboratory scale

Solution		PS_14	PS_14	PS_14	PS_14	PS_14	PS_14	2.5M	2.5M	2.5M	5M	5M	5M	5M	5M	2.5M	2.5M
Mass of loaded solution (with SO4)	g	101.48	100.65	100.58	100.11	100.37	100.40	100.62	100.59	100.33	105.22	99.79	105.49	110.42	119.25	104.94	111.99
Temp (Residue)	C	130	120	130	120	130	130	130	130	130	130	130	110	110	130	180	180
Pressure	torr	760.0	760.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	760.0	760.0
MEA Concentration after Sulfate loading	wt%	14%	14%	14%	14%	14%	13%	15%	15%	15%	29%	26%	27%	24%	20%	13%	13%
SO4 Concentration	wt%	11%	11%	11%	11%	11%	11%	12%	12%	12%	5%	11%	4%	10%	14%	5%	10%
Solid NaOH added	g	9.82	9.87	8.98	8.01	4.38	5.47	4.49	6.36	9.57	0.00	0.00	0.00	0.00	0.00	0.00	4.22
CO2 Concentration	wt%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pH in Simulation		12.0	12.0	10.8	10.1	9.4	9.6	9.4	9.6	11.0	9.9	9.8	9.9	9.7	9.1	9.5	9.4
pH measured in Laboratory		12.0	12.0	12.0	11.0	10.0	11.0	10.0	11.0	12.0	11.0	11.0	11.0	11.0	10.0	10.0	10.0
Difference in pH		0.0	0.0	1.2	0.9	0.6	1.4	0.6	1.4	1.0	1.1	1.2	1.1	1.3	0.9	0.5	0.6
Variation in pH	%	0.0	0.0	-9.9	-8.4	-5.6	-13.1	-5.7	-12.4	-8.7	-10.2	-11.0	-10.1	-11.9	-8.7	-4.7	-5.9

2.3. Reactive Crystallisation

The procedure mentioned below outlines the method followed to regenerate PS_14 through reactive crystallisation.

KOH was added to sulfate rich absorbent PS_14 as per the following reaction 2:



The above reaction involved removing sulfate from PS_14 in the form of K₂SO₄ crystals. The solubility of sulfate in aqueous amine solutions at various temperatures was experimentally investigated in our previous work (Pearson et al. 2017). This allowed us to identify the conditions that could result in the formation of K₂SO₄ crystals. The experiments conducted in the laboratory added excess KOH relative to the amount required to precipitate the total sulfate present in the PS_14 solution. In addition to the pilot sample, experiments were conducted on synthetically prepared 5M (~30wt%) and 6.5M (~40 wt%) MEA solutions loaded with CO₂ and SO₄²⁻ (by addition of H₂SO₄). Experiments were conducted at 20°C and 40°C, maintaining experimental conditions similar to those anticipated in a real operating plant. The crystallisation experiments used a continuously stirred beaker, fitted with a thermometer. A water bath was used to maintain temperature as shown in Appendix Fig. 2(a). The sulfate loaded absorbent solution was maintained at the desired temperature for an hour after the addition of solid KOH. The crystals were separated from the MEA solution via vacuum filtration as shown in Fig 2(b) and dried in an oven at 50°C for 24 hours. Various factors influence the removal of sulfate and the formation of K₂SO₄ crystals from the sulfate rich CS-Cap absorbent including temperature, amine concentration, initial sulfate loading, and % excess KOH addition. The experimental evaluation of these parameters is detailed in our previous publication (Garg et al. 2019).

Some of the experimental conditions investigated during reactive crystallisation are listed in Table 2 below:

Table 2: Reactive Crystallisation experiments conducted at laboratory

Case		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Solution		PS_14	PS_14	PS_14	PS_14	PS_14	3M	5M	5M	5M	5M	5M	5M	5M	5M	5M	6.5M	6.5M	6.5M	6.5	6.5	6.5	6.5
Mass of loaded solution (with SO4 + CO2)	g	104.13	104.48	100.43	100.19	110.63	109.15	100.57	100.44	87.386	109.25	106.02	119.59	120.7	75.81	109.25	100.112	100.32	100.44	89.36	114.25	127.64	95.08
Temp	C	4	41	20	40	22	39	20	20	40	39	40	40	40	23	21	20	20	40	20	40	41	40
MEA Concentration	wt%	14.1%	14.1%	14.1%	14.1%	14.1%	14.9%	24.0%	24.0%	24.0%	26.0%	26.0%	24.0%	24.0%	24.0%	26.0%	31.0%	31.0%	31.0%	34.0%	33.0%	31.0%	31.0%
SO4 Concentration	wt%	10.9%	10.9%	10.9%	10.9%	10.9%	11.5%	9.3%	9.3%	9.3%	5.4%	5.4%	11.5%	11.5%	11.5%	5.4%	10.4%	10.4%	10.4%	5.4%	5.3%	11.0%	11.0%
CO2 Concentration	wt%	0.00%	0.00%	0.00%	0.00%	0.00%	0.90%	4.00%	4.00%	4.00%	7.37%	7.37%	4.24%	4.24%	4.24%	7.37%	6.20%	6.20%	6.20%	9.38%	9.69%	6.20%	6.20%
% excess KOH addition relative to sulfate present in solution	%	109	109	148	150	100	87	160	160	160	59	110	110	83	95	68	148	148	150	76	109	110	89

3. Model development and validation

Aspen Plus is a leading software package used for chemical process simulation, optimisation, sizing and design. These simulators can model most chemical processes and are an important tool in predicting the system's behaviour at various operating conditions. Hence using these simulators saves a lot of time and expenditure by applying process modifications to the model without the need for large scale testing.

Thermal reclamation and reactive crystallisation models were built using this process simulator so that the effect of varying process parameters could be evaluated. The sulfate rich CS-Cap absorbent is a unique stream compared to the routine post combustion CO₂ capture spent absorbent streams and there is little data available in the literature for reclaiming amine from such absorbents using thermal reclamation or crystallisation. Hence, it was important to select an appropriate process simulator to model the CS-Cap absorbent stream.

3.1. Property package and components

The CS-Cap process uses an aqueous amine solution to capture CO₂ and SO₂. This is represented as an electrolyte system as the absorbed CO₂ and SO₂ ionize in water. Due to ions and molecules present, there

are ionic reactions, ion–molecule interactions, and molecular interactions involved in physical and chemical interactions. Further most of the molecular species involved in the pilot plant sample or synthetic samples have partial dissociation or will be completely dissociated into ions in the liquid solvent, and some of the molecular species will be precipitating as salts, system reactions occur very fast and could be considered to be at chemical equilibrium. Hence, for this system an electrolyte non-random two-liquid model (elecNRTL) in Aspen Plus was used as the basic property method. The non-random two-liquid model utilizes the activity coefficients of a component and its mole fraction in the liquid phase in order to generate the phase equilibria data. The Redlich-Kwong model was used for any vapour-liquid equilibrium between water and carbon dioxide and their Henry constants were retrieved from the Aspen Plus data bank.

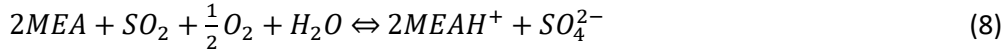
The major components selected to define the CS-Cap sulfate rich absorbent stream (PS_14 obtained from pilot campaign & synthetic samples) in the simulation model were H₂O, monoethanolamine (MEA), protonated MEA (MEA^{H+}), sulfate (SO₄²⁻), CO₂, HCO₃⁻, CO₃²⁻, and MEACOO⁻. During the pilot campaign the MEA absorbent was fully saturated with SO₄²⁻. This was observed via the sharp drop in pH of the solution and break-through of SO₂ to the flue gas leaving the column, and confirmed through IC analysis of the liquid absorbent. Hence it was assumed that no absorbed CO₂ is left in the pilot plant sample. However, for the synthetic samples, CO₂ was added and additionally defined in the system, as the synthetic samples have a higher amine concentration. When adding a similar amount of SO₄²⁻ to the higher concentration amine samples (5M and 6.5M), it is assumed that the absorbed CO₂ would not be fully released upon the addition of sulfuric acid due to the initial higher pH of the MEA itself. The above assumptions were confirmed by completing total organic carbon and inorganic carbon analysis for both the PS_14 and synthetic samples. The results confirmed there was no CO₂ present in the pilot plant samples, whereas the synthetic samples did have some CO₂ present. The pH of the pilot samples was between 4.5-5, whereas the pH of the 5M and 6.5 M synthetic samples was between 8-9 after the addition of a similar amount of SO₄²⁻ as that of PS_14.

All model components were defined as conventional in the simulation apart from NaOH and KOH, which were defined as solid components. The simulation was simplified by not considering the other minor components known to be present in the pilot plant samples (e.g. degradation products). The CO₂ loaded MEA solution generated in the top section of the CS-Cap absorber shall reach a loading of 0.5 molCO₂/molMEA. On absorption of SO₂, the CO₂ loading should decrease to around 0.2 molCO₂/molMEA depending on the amount of SO₂ absorbed. As mentioned before, CO₂ was not considered present in the pilot plant absorbent but was considered in the synthetic samples for reactive crystallisation. The CO₂ concentration in the synthetic samples ranged between 4-9 wt% depending on the sulfate loading of the solution. In the thermal reclamation experiments, CO₂ was not added to the synthetic samples, as it was believed that at the higher reclaiming temperatures the CO₂ would simply boil off and not add to protonating MEA due to the preferential reactivity of MEA with SO₂ over CO₂. However due to the lower operating temperature in reactive crystallisation, the CO₂ will stay in various ionic forms in the sulfate loaded CS-Cap absorbent, affecting the solubility of sulfate in the solution.

3.2. Reaction Chemistry of the Process

The major chemical reactions taking place in the CS-Cap process in the lower section (SO₂ absorption section) of the absorber column are as follows (Garg et al. 2018).





The main chemical equilibrium reactions taking place in a MEA + CO₂ + H₂O system, additional to reaction 7, in the upper section of the absorber column (CO₂ absorption section) are described below:



The above reactions will take place in the CS-Cap absorber for CO₂ and SO₂ absorption and will generate the spent CS-Cap absorbent. The CS-Cap absorber has been simulated in Pro-Treat simulation software in our previous work (Cousins et al. 2018).

3.2.1. Reactions used in the Models

For both the reactive crystallisation and thermal reclamation simulations, the feed stream was a slipstream of the spent absorbent leaving the SO₂ absorption column (green stream Fig. 2). Due to the presence of O₂ in the flue gas, and the recirculation of absorbent in the SO₂ absorption column, the absorbed SO₂ was converted to sulfate.

Reactions 7, 9, 10, 11, & 12 were fed as equilibrium reactions in both the models.

As both the regeneration technologies required the addition of alkali to release the amine from the protonated amine, the following equations were also added in the chemistry of the model.

3.2.2. Additional Reactions: Thermal Reclamation

Dissociation Reactions:



3.2.3. Additional Reactions: Reactive Crystallisation

Dissociation Reactions:



Salt formation:



3.2.4. Equilibrium data

The above equations were respectively used in the models and the mole fractions of each component in the liquid and vapour phase were calculated by solving the above equations. The equilibrium constants were calculated using following equilibrium equation:

$$\ln K_j = A_j + \frac{B_j}{T} + C_j \ln T + D_j T \quad (18)$$

The equilibrium constant data used in equation 18 are provided in Table 3 (Sampath et al. 2012):

Table 3: Equilibrium constants data

Parameter	Reaction 7	Reaction 9	Reaction 10	Reaction 11	Reaction 12
A _j	-3.038	-0.52	231.46	216.05	132.89
B _j	-7008.3	-2545.53	-12092.1	-12431.7	-13445.9
C _j	0	0	-36.78	-35.48	-22.47
D _j	-0.00313	0	0	0	0

3.3. Simulation Models: Process Flow Scheme

3.3.1. Thermal Reclamation

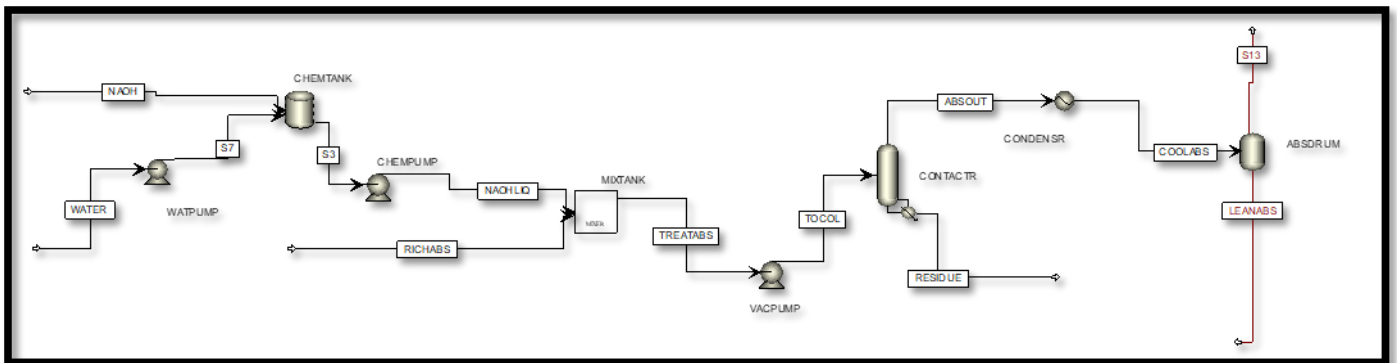


Figure 3: Process Flow Scheme for Thermal Reclamation

Figure 3 provides a flow diagram of the thermal reclamation process as simulated in Aspen Plus. The sulfate rich absorbent is treated with NaOH solution (50 wt%) before entering the reclaimer. The NaOH addition neutralises the solution, releasing the amine from its protonated form. The recovery of amine in thermal reclamation depends on the amount of caustic addition /pH of the solution as well as the operating pressure and temperature. In the Aspen Plus simulation a traditional reclaimer has been modelled which has a packed column and a steam-heated reboiler. To simplify the simulation and allow comparison to the laboratory experimental results, an equilibrium Radfrac column was used as the contactor.

3.3.2. Reactive Crystallisation

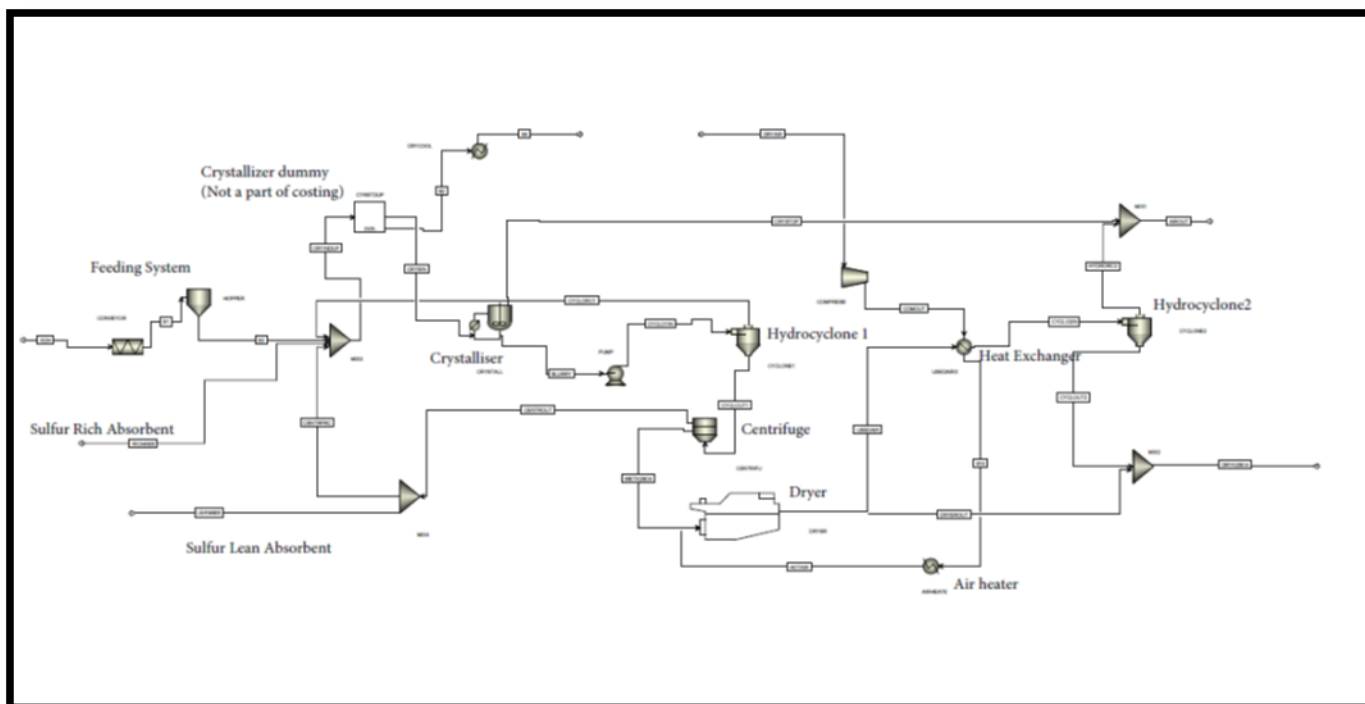


Figure 4: Process Flow Scheme for Reactive Crystallisation

Figure 4 provides a process flow diagram of the reactive crystallisation model developed in Aspen Plus. This includes all the equipment that would be required to implement the technology at commercial scale. The process steps represented are the same as those employed in the laboratory experiments including: solid KOH addition, crystallisation, filtration and drying of the crystals.

The sulfate rich absorbent stream was defined as MIXCIPSD in the model, which represents conventional components and inert solids with a particle size distribution. The formation of K_2SO_4 crystals was added in the crystalliser simulation and the saturation calculation method was selected for the chemistry.

4. Model Performance Validation

To determine the accuracy of the simulation, it was tested for the experimental conditions. Physical property data obtained in simulation were compared against the experimental data gathered for the PS_14 and synthetic samples. The regeneration of the sulfur rich amine via thermal reclamation or crystallisation was then simulated in the respective models and key simulation results were compared to the respective values obtained in the experiments.

4.1. Thermal Reclamation

Data from the experiments completed with PS_14 and 5M synthetic samples was used to validate the thermal reclaimer simulation. A number of operating conditions were varied including: temperature, pressure, MEA concentration, initial sulfate loading, and NaOH addition. This provided a range of data points against which the simulation could be compared. The laboratory experiments were completed as a batch process. The mass added in the laboratory experiments was converted to a mass flow rate when used in the simulation.

In the experimental work, the effect of temperature, pressure, pH, and initial sulfate loading were investigated. Amine recovery was found to be higher under vacuum than at atmospheric conditions and increased with an increase in temperature as expected. Interestingly, the initial pH of the solution after caustic addition was found to play an important role in the recovery of amine. Due to the high sulfate concentration, the initial pH in the absorbent was quite low, near 4-5. It was expected that the bound amine would be released as soon as the pH of the absorbent is raised beyond the pKa of

monoethanolamine (9.5). However, the high sulfate concentrations impacted the caustic required to release the bound amine. Even after maintaining favourable temperature and pressure conditions, amine recovery remained poor at pH 10. When the pH was raised to 11 or 12, amine recovery increased. A test experiment was also done by adding an equivalent amount of hydrochloric acid (HCl) instead of H₂SO₄ in 5M MEA solution and maintained the solution at 10 pH. This was done to understand whether the sulfate ion or the pH was the cause of the low MEA recovery. The results showed more than 90% of the MEA stayed in the residue. It proved that poor amine recovery was associated with the amount of heat stable salt in the solution. The higher amount of HSS will drop the pH and will require more caustic to break all the ionic bonds. Hence, pH/amount of caustic addition played a significant role in the experimental recovery of amine via thermal reclamation. Increasing the initial sulfate loading also had an impact on amine recovery at similar operating conditions. Our previous publication (Garg et al. 2018b) provides detailed information on the results. Results of the laboratory experiments, and the corresponding simulation results, are provided below in Table 4.

Table 4: Simulation Versus Laboratory Results for Thermal Reclamation

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
		Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 8	Case 9	Case 10	Case 11	Case 13	Case 14	Case 15	Case 16	Case 17	Case 18
Solution		PS_14	PS_14	PS_14	PS_14	PS_14	PS_14	2.5M	2.5M	2.5M	5M	5M	5M	5M	5M	2.5M	2.5M
Mass of loaded solution (with SO4)	g	101.48	100.65	100.58	100.11	100.37	100.40	100.62	100.59	100.33	105.22	99.79	105.49	110.42	119.25	104.94	111.99
Temp (Residue)	C	130	120	130	120	130	130	130	130	130	130	130	110	110	130	180	180
Pressure	torr	760.0	760.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	760.0	760.0
MEA Concentration after Sulfate loading	wt%	14%	14%	14%	14%	14%	13%	15%	15%	15%	29%	26%	27%	24%	20%	13%	13%
SO4 Concentration	wt%	11%	11%	11%	11%	11%	11%	12%	12%	12%	5%	11%	4%	10%	14%	5%	10%
Solid NaOH added	g	9.82	9.87	8.98	8.01	4.38	5.47	4.49	6.36	9.57	0.00	0.00	0.00	0.00	0.00	0.00	4.22
CO2 Concentration	wt%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
pH in Simulation		12.0	12.0	10.8	10.1	9.4	9.6	9.4	9.6	11.0	9.9	9.8	9.9	9.7	9.1	9.5	9.4
pH measured in Laboratory		12.0	12.0	12.0	11.0	10.0	11.0	10.0	11.0	12.0	11.0	11.0	11.0	11.0	10.0	10.0	10.0
Difference in pH		0.0	0.0	1.2	0.9	0.6	1.4	0.6	1.4	1.0	1.1	1.2	1.1	1.3	0.9	0.5	0.6
Variation in pH	%	0.0	0.0	-9.9	-8.4	-5.6	-13.1	-5.7	-12.4	-8.7	-10.2	-11.0	-10.1	-11.9	-8.7	-4.7	-5.9
MEA left in Residue in Simulation	%	94.3%	94.5%	9.6%	24.1%	58.9%	41.4%	61.1%	41.8%	9.0%	23.7%	34.9%	24.2%	62.8%	93.9%	58.3%	75.1%
MEA left in Residue in Laboratory	%	98.6%	98.5%	14.7%	28.0%	76.1%	48.3%	77.8%	51.9%	17.1%	25.3%	36.2%	29.3%	62.9%	82.3%	67.1%	76.7%
Variation		4.34%	4.11%	34.70%	14.16%	22.59%	14.24%	21.55%	19.38%	47.18%	6.38%	3.39%	17.55%	0.09%	-14.07%	13.14%	2.08%
MEA left in Residue in Simulation	g	13.50	13.42	1.37	3.40	8.32	5.35	9.19	6.29	1.35	7.10	9.10	6.90	16.71	22.71	8.16	11.30
MEA left in Residue in Laboratory	g	14.13	13.83	1.95	3.31	8.94	5.99	10.77	7.14	2.32	7.08	9.14	8.01	15.24	20.27	8.64	11.54
Variation		4.43%	2.98%	29.80%	-2.52%	6.92%	10.70%	14.75%	11.97%	41.66%	-0.30%	0.48%	13.83%	-9.69%	-12.03%	5.55%	2.03%

As shown in Table 4, the variation in % of MEA left in the residue between the simulation and experimental results ranges from 0.09-23%, excluding cases 3 and 9 which have the largest variation. Overall, the simulation shows higher MEA recovery (less MEA left in residue) compared to the laboratory results. The variation in experimental and simulation results was found to be less than 15% for atmospheric conditions compared to vacuum conditions.

However, when compared with absolute mass in grams of MEA left in the residue the variation is less than 20% (excluding the case 3 and 9 again due to their higher variation). The potential cause of the higher variation for cases 3 and 9 is discussed in section 5.1.1. A comparison plot between the laboratory and simulation results for the mass of MEA remaining in the residue is provided in Figure 5. Dashed lines in the plots represents the variation (+/-) 20%.

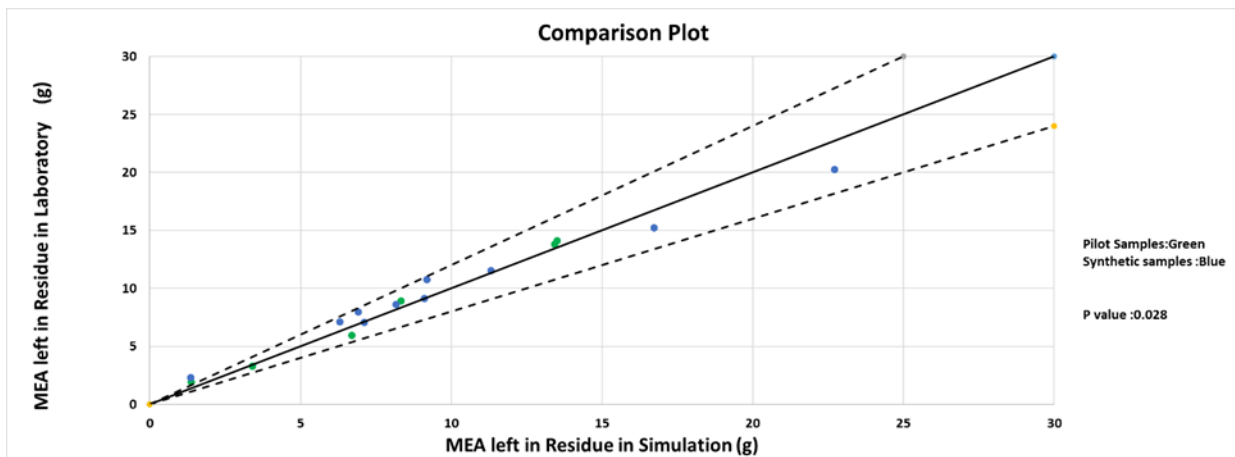


Figure 5: Comparison Plot for MEA left in Residue in (g) in Simulation and Laboratory Experiments

Although there was around (+/-) 20% variation between the experimental and simulated results for the amount of MEA remaining in the residue, the behaviour of the simulated system was quite similar to trends observed in the experimental results. Various parameters affecting the thermal reclamation of MEA were plotted against the amine recovery for both experimental and simulated data to provide further insight into the accuracy of the model.

Figure 6 shows the impact of varying the initial sulfate loading in the pilot (PS_14) and 5M synthetic samples. The laboratory experiments showed a higher fraction of amine remaining in the residue as initial sulfate loading was increased. Whilst the values were slightly lower, a similar trend was observed for the simulated results. The % variation in the experimental and simulation results was <15% for synthetic samples and up to 30% for pilot samples. However the absolute difference in MEA left in the residue in simulation and experimental results was 0.46 & 0.59g of MEA per 14g of MEA solution at data point 1 & 2 in Figure 6, hence has been considered insignificant.

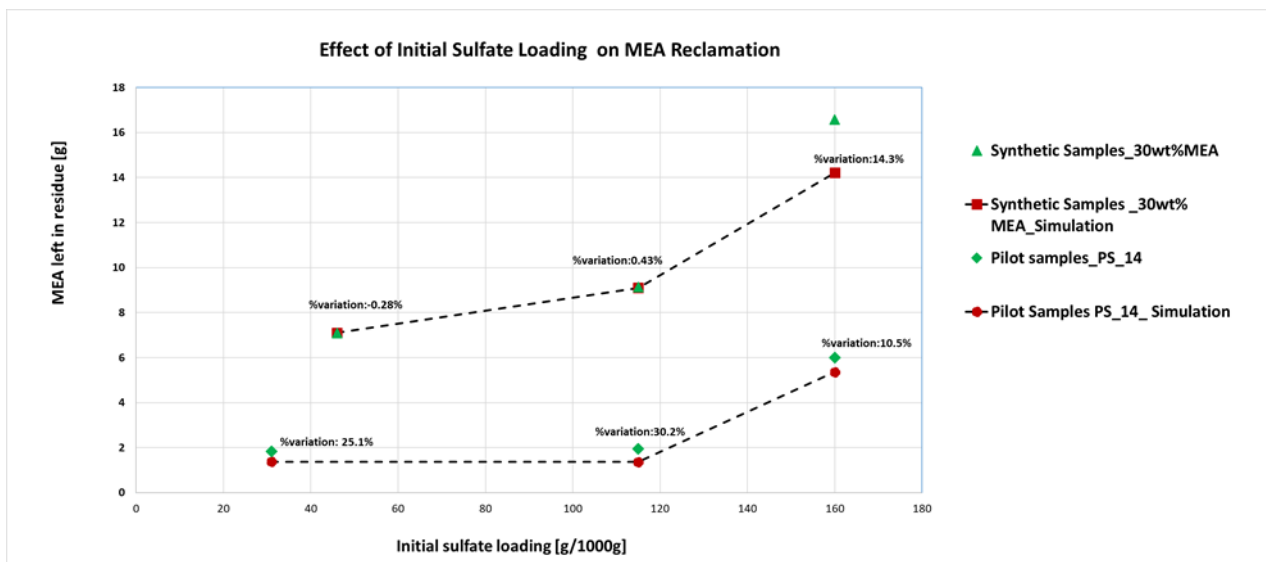


Figure 6: Simulation and laboratory results showing the effect of initial sulfate loading on MEA reclamation

Figure 7 shows the impact of pH on the recovery of amine in thermal reclaiming for both the experimental and simulated results. Caustic addition was completed prior to boiling the aqueous sulfate loaded MEA solution. The pH referred to here is the initial pH after adding caustic solution. In the laboratory experiments amine recovery was found to be poor unless the initial pH was maintained above 10. i.e. upon higher caustic addition leading to pH 11 or 12 increased the recovery of amine. A similar trend was observed for the simulation results, however, a similar amount of NaOH addition resulted in 9.5 pH

compared to an experimental pH of 10. The pH measured in the experiments was consistently 0.5-1.4 pH units higher than predicted by the simulation. This could be the result of the fact that the pH measurement was completed without a high objective level of precision (pH paper used) as opposed to instrument measurement. The variation in pH is shown in Table 4 above. Usually 1 mol of NaOH is used against 1 mol of heat stable salt as a standard practice in the gas treating industry (Wang et al. 2014). However, in the CS-Cap absorbent, as the major HSS is sulfate which required 2 moles of Na against 1 mol of sulfate, therefore the MEA recovery was poor in cases where an equimolar amount of NaOH was added. Further, from the simulation results, it was seen that there is an almost 10% decrease in the MEA left in the residue for the pilot samples when moving from a pH of 9.5 – 9.7 (0.13-0.18 mol NaOH per 0.11 mol of sulfate), (point 2 & 3 in Figure 7), whereas per experimental results, there was only a 3-4% decrease in the MEA left in the residue for a similar NaOH addition (pH was 11 in both experiments as measured by pH paper). The MEA left in the residue decreased to 15% at 12 pH in the experiments, and a corresponding 10% at 10.8 pH in the simulation. Hence, similar to the theoretical consumption, experimentally it was found that maintaining a minimum pH of 12 (2 moles of NaOH per mole of sulfate) is favourable for achieving MEA left in residue < 15%. However, simulation results showed a similar amount of MEA left in the residue at a pH of 10.5. Hence higher MEA recoveries were attained by adding twice the moles of caustic to that of the sulfate present in the spent absorbent. The variation between the experimental and simulated results for each data point are shown in Figure 7.

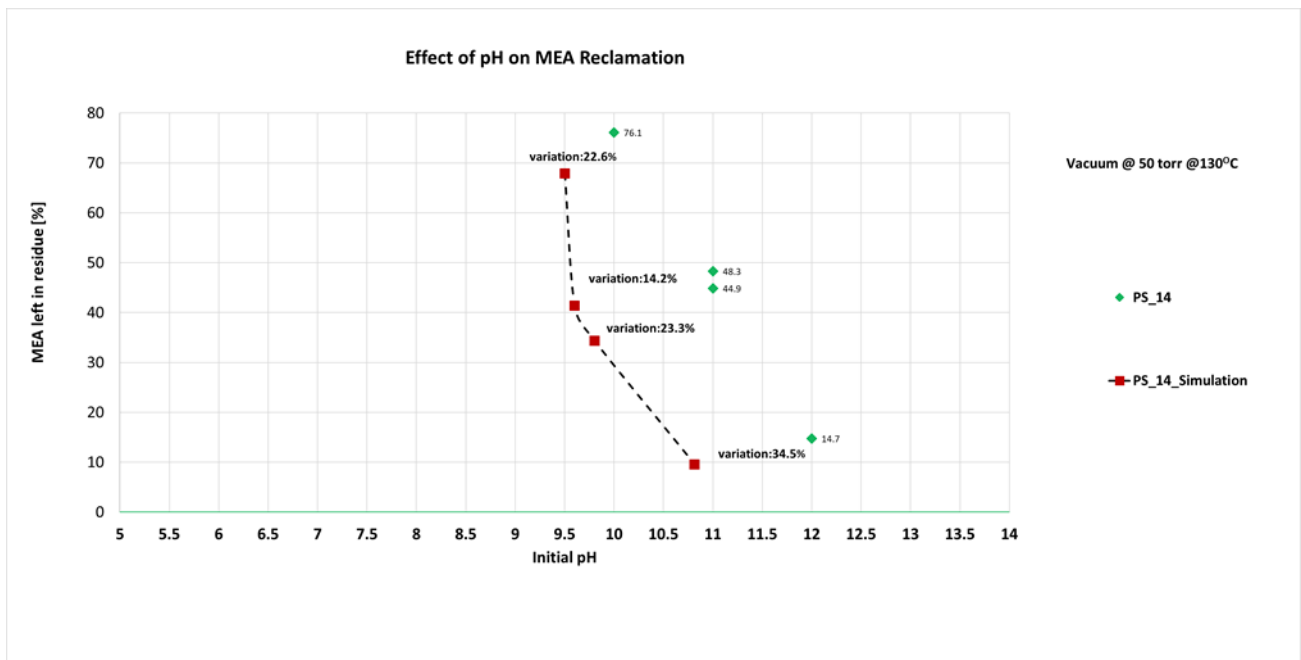


Figure 7: Simulation and laboratory Results showing the effect of pH on MEA reclamation

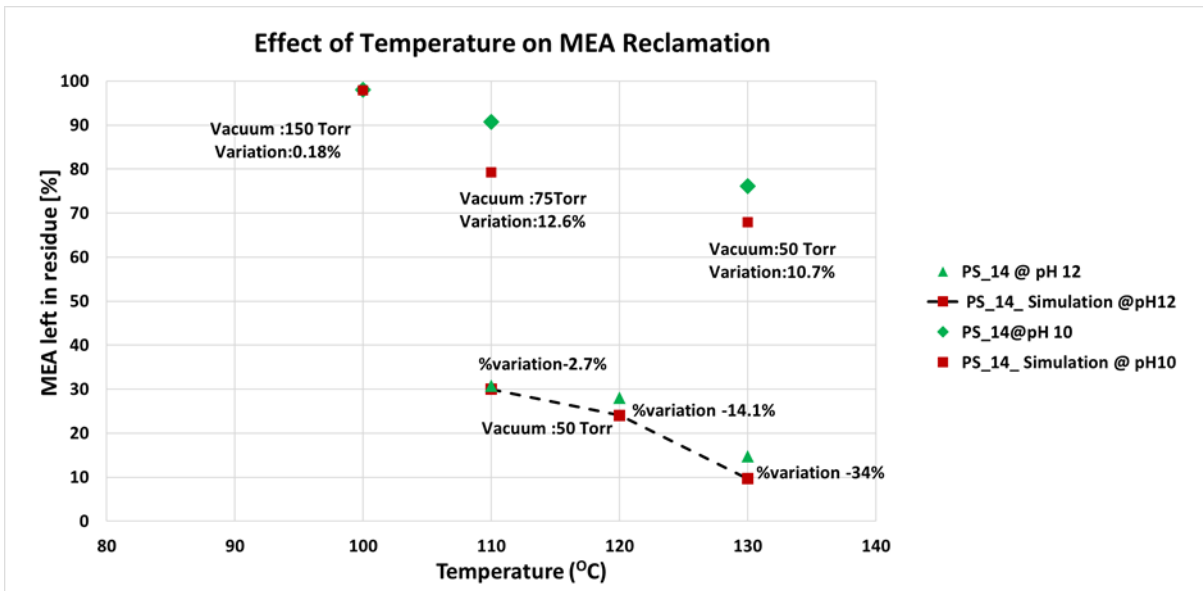


Figure 8: Simulation and laboratory Results showing the effect of temperature on MEA reclamation

The effect of increased temperature on the amine recovery achieved (or lower amine left in residue) was also investigated experimentally. The % of MEA remaining in the residue decreased when the temperature was increased beyond 110°C under 50 torr vacuum conditions. Theoretically, near to 100% recovery of the MEA was expected at these conditions after the addition of sufficient caustic (achieving an experimental pH 12). However MEA recoveries of only 85-87% were observed for the pilot samples experimentally. The lower recovery could be due to the higher wt% of sulfate present in the solution compared to typical solutions sent for reclamation in CO₂ capture. Similar trends were predicted by the simulation as shown in Figure 8, but the simulation predicted higher MEA recoveries of 90% (% MEA left in residue ~10%) for the pilot samples against an experimental recovery of 85% (% MEA left in residue ~15%) under similar conditions (50 torr at 130°C, point number 3 at pH 12) leading to a higher variation between the simulation and experimental results of up to ~34%.

There are three more experimental results shown in Figure 8 to authenticate the validity of the simulation results. The three experimental conditions for PS_14 tested at corresponding temperature and respective vacuum mentioned in the Figure 8 at a pH of 10. The variation in the simulation and experimental results for all the three conditions is less than 13% which validates the model to be used at varying operating conditions.

4.2. Reactive Crystallisation

Reactive crystallisation solutions consisted of aqueous MEA loaded with SO₄²⁻ and CO₂. Data from experiments conducted on PS_14 (Pilot Samples), 5M, and 6.5M synthetic samples was fed into the reactive crystallisation model to evaluate the performance against various operating conditions including: temperature, MEA concentration, initial sulfate loading, and % KOH addition. A comparison between 22 experimental and simulated results is provided in Table 5.

Table 5: Simulation Versus Laboratory Results for Reactive Crystallisation

Case	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
Solution	PS_14	PS_14	PS_14	PS_14	PS_14	3M	5M	5M	5M	5M	5M	5M	5M	5M	5M	6.5M	6.5M	6.5M	6.5	6.5	6.5	6.5
Mass of loaded solution (with SO ₄ + CO ₂)	g	104.13	104.48	100.43	100.19	110.63	100.57	100.44	87.386	109.25	106.02	119.59	120.7	75.81	109.25	100.112	100.32	100.44	89.36	114.25	127.64	95.08
Temp	°C	4	41	20	40	22	20	20	40	39	40	40	40	23	21	20	20	40	20	40	41	40
MEA Concentration	wt%	14.1%	14.1%	14.1%	14.1%	14.1%	24.0%	24.0%	24.0%	26.0%	26.0%	24.0%	24.0%	24.0%	26.0%	31.0%	31.0%	31.0%	34.0%	33.0%	31.0%	31.0%
SO ₄ Concentration	wt%	10.9%	10.9%	10.9%	10.9%	10.9%	9.3%	9.3%	9.3%	5.4%	5.4%	11.5%	11.5%	11.5%	5.4%	10.4%	10.4%	10.4%	5.4%	5.3%	11.0%	11.0%
CO ₂ Concentration	wt%	0.00%	0.00%	0.00%	0.00%	0.00%	4.00%	4.00%	4.00%	7.37%	7.37%	4.24%	4.24%	4.24%	7.37%	6.20%	6.20%	6.20%	9.38%	9.69%	6.20%	6.20%
% excess KOH addition relative to sulfate present in solution	%	109	109	148	150	100	160	160	160	59	110	110	83	95	68	148	148	150	76	109	110	89
% SO ₄ Removal Simulation	%	96%	84%	99%	98%	86%	100%	100%	99%	28%	28%	86%	59%	78%	6%	99%	99%	98%	23%	46%	91%	73%
% SO ₄ Removal Laboratory	%	84%	67%	94%	90%	74%	95%	97%	96%	46%	46%	77%	55%	69%	2%	97%	97%	97%	31%	61%	87%	68%
Variation	%	-14.43%	-25.48%	-5.33%	-8.62%	-15.89%	-4.68%	-3.18%	-2.77%	38.27%	38.66%	-11.80%	-6.41%	-13.93%	-281.02%	-2.39%	-2.38%	-0.88%	24.50%	25.19%	-4.34%	-7.63%
KZ5O4 Generation Simulation	g	19.83	17.45	19.69	19.41	18.81	18.30	18.28	15.78	0.00	2.98	20.86	14.33	11.99	0.74	19.13	19.17	19.01	2.02	5.05	22.87	13.71
KZ5O4 Generation Laboratory	g	14.00	10.34	16.68	16.76	12.37	17.19	18.59	15.49	0.18	4.78	19.27	13.92	10.87	2.27	19.23	19.23	18.70	3.00	6.45	23.04	13.40
Variation	%	-41.6%	-68.7%	-18.0%	-15.8%	-52.1%	-6.5%	1.7%	-1.9%	100.0%	37.8%	-8.2%	-3.0%	-10.3%	67.5%	0.5%	0.3%	-1.6%	32.5%	21.7%	0.7%	-2.4%

The variation in the results between the experimental and simulated cases for sulfate removal in PS_14, 5M and 6.5 M samples ranged from 0.5~ 25 %, however higher variations were observed in cases with lower initial sulfate concentrations (Case 10, 11, 15, 19, 20). In addition, the generation of K_2SO_4 crystals was significantly lower in the actual experiments than predicted by the model for the pilot plant samples. This was not the case with 5M and 6.5 M cases, where the variation in the generation of crystals ranged from 0.3-10% (excluding cases with low sulfate loadings: 10, 11, 15, 19, 20).

Figures 9 and 10 provide comparison plots between the experimental and simulated results for the percentage of sulfate removed from solution, and the generation of K_2SO_4 crystals, respectively. Dashed lines in the plots represents the variation (+/-) 20%.

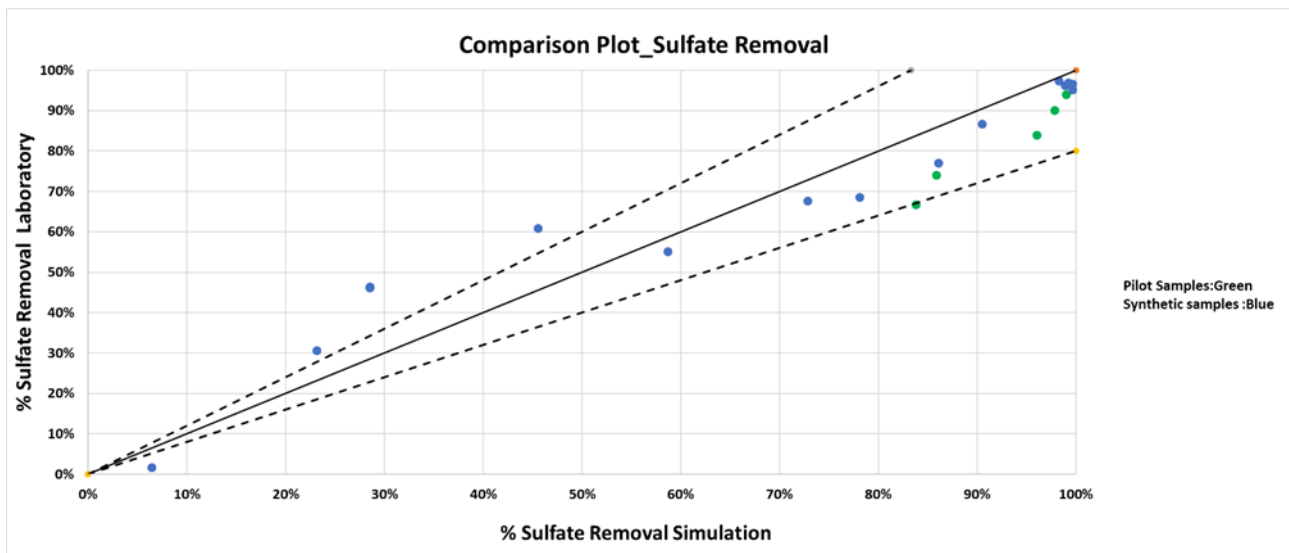


Figure 9: Comparison Plot for % of Sulfate Removal in Simulation and Laboratory Experiments

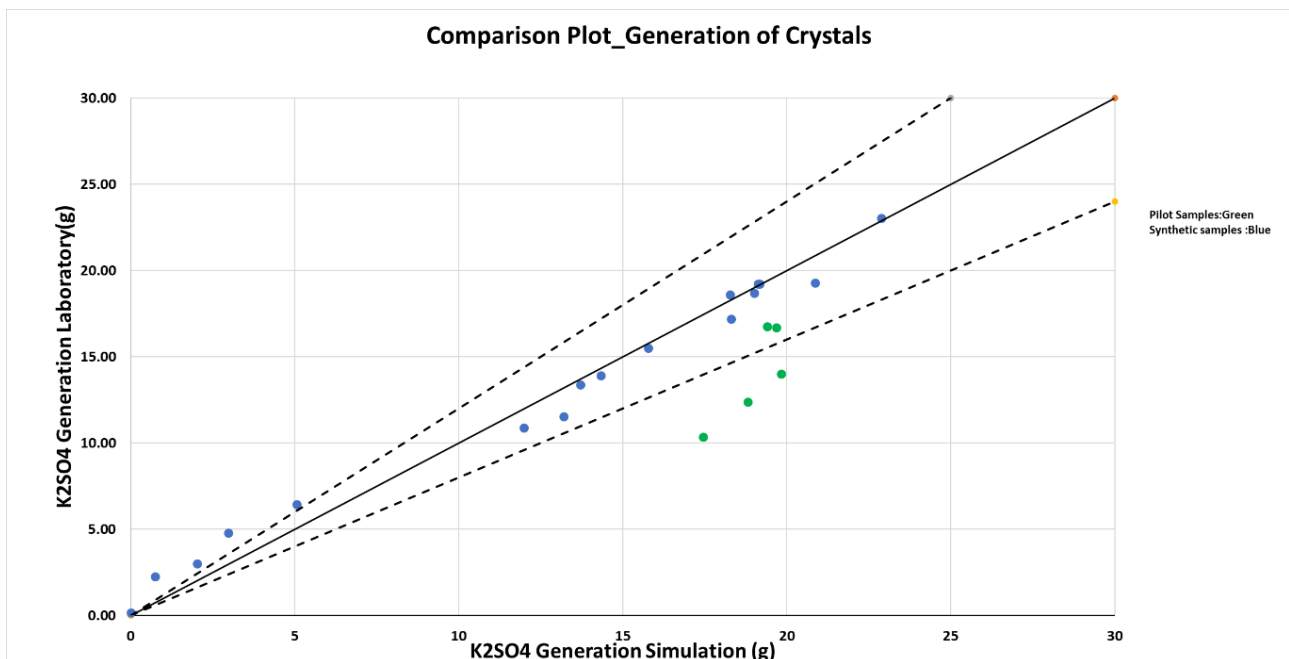


Figure 10: Comparison Plot for K_2SO_4 generation in (g) in Simulation and Laboratory Experiments

Simulation results were compared to experimental results at various process operating conditions including: % excess of KOH addition relative to amount of sulfate present in the solution, amine concentration, initial sulfate loading, and temperature.

Excess KOH addition led to higher sulfate removal as shown in our previous publication (Pearson et al. 2017). Figure 11 shows a similar behaviour exhibited by both the simulation and experimental results when excess KOH was added at one particular condition (40°C, 30wt% MEA, initial sulfate loading 100g/1000g). The variation is less than 15% resulting in a good match between the experimental and simulated results.

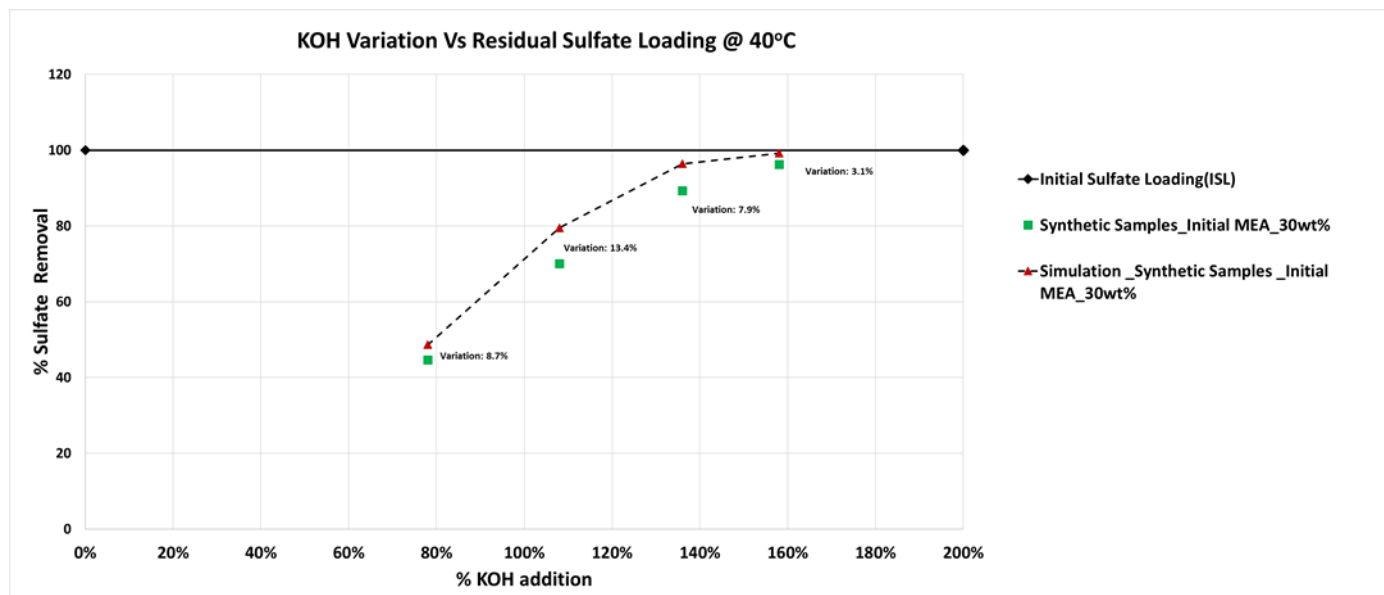


Figure 11: Simulation and laboratory results showing the effect of % excess KOH addition relative to amount of sulfate present in the solution on the percentage of sulfate removal

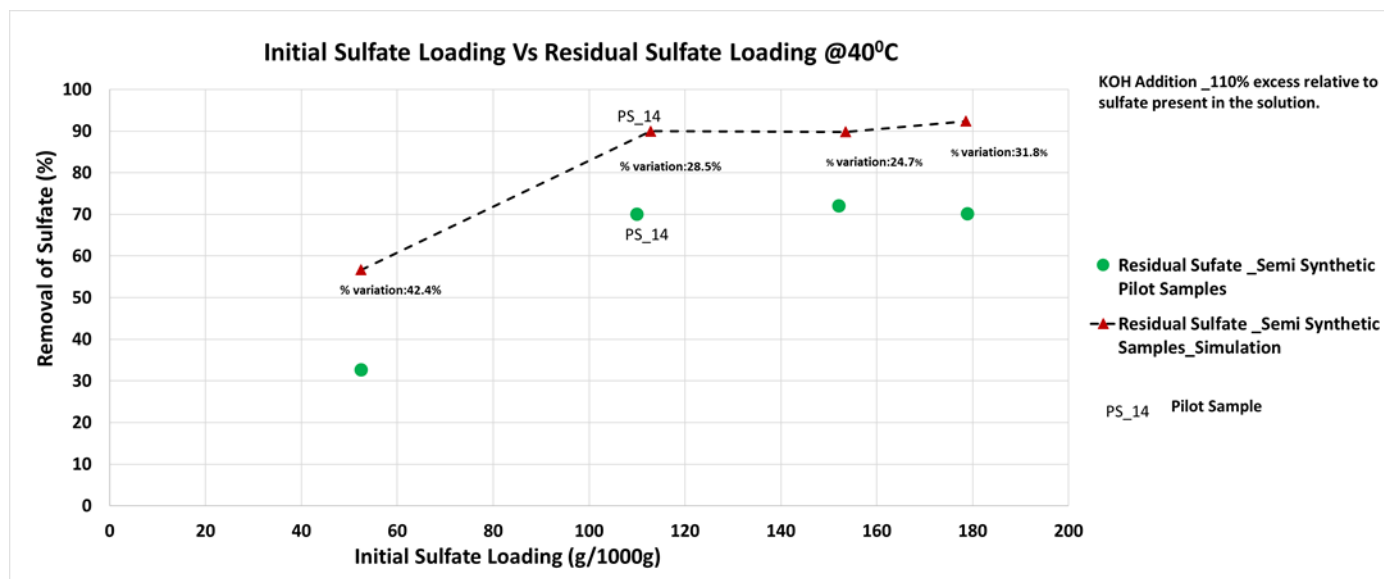


Figure 12: Simulation and laboratory results showing the effect of initial sulfate loading on the percentage of sulfate removal

In Figure 12, it can be seen that increasing the initial sulfate loading increases the amount of sulfate withdrawn from the solution. The pilot sample was dosed with either 14 wt% MEA or additional sulfate (H_2SO_4) to vary its initial sulfate concentration. This allowed the effect of varying initial sulfate concentration on its removal from the solution via crystallisation. The trend followed by the simulation was similar to that up until the initial sulfate loading of 150g/1000g. Above this point, the simulation showed a slight further removal of sulfate whereas the experiments showed no further removal. However, the slight increase lies in the experimental error range.

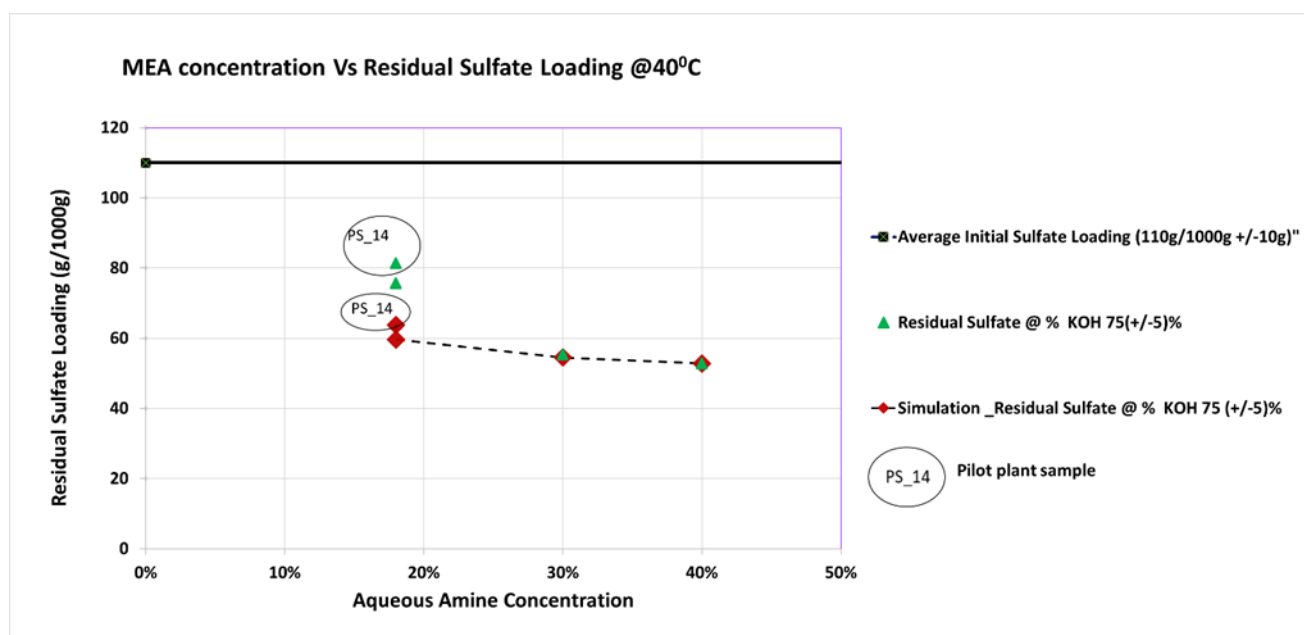


Figure 13: Simulation and laboratory results showing the effect MEA concentration on sulfate removal

A higher amine concentration had a positive effect on the removal of sulfate from solution, as identified in our previous publication (Pearson et al., 2017). A similar effect was also observed in the simulation results where ~75% of KOH, against the sulfate present in the solution, was added to PS_14, 2.5M, 5M, 6.5M samples operating at 40°C. As shown in Figure 13, a good match was observed between the simulation and the synthetic sample results with an overall variation less than ~22%.

5. Findings and Discussion

5.1. Thermal Reclamation

Though there is a reasonable agreement in Figure 5 between the data predicted from the model to the data obtained in the actual experiments, it is still important to recognise the possible sources of error. This will allow any anticipated uncertainty to be taken into account in future simulation work and understand the effect on cost analysis. Below are some of the possible explanations for the variation between the simulation and experimental results.

5.1.1. pH measurement and amount of caustic dosage

Our previous experimental results showed a considerable effect of pH on reclaiming amine from sulfate rich CS-Cap absorbent (Garg et al. 2018b).

pH measured in the laboratory was found to be 0.4-1.5 pH higher than obtained for most of the simulated cases despite the same amounts of NaOH, MEA, CO₂ and sulfate being added to the solutions (see Table 4). A possible reason for this variation could be the use of a lower precision pH measurement done by pH paper. It is also possible that a slightly higher or lower amount of amine or sulfate were present in the actual experiments than were analysed by IC.

For the pilot plant samples at vacuum conditions, variation between the simulation and experimental results in the experimental pH range 10 – 11 (corresponding pH range in simulation 9.4-10.1) stays < 22% as shown in Table 4. However the variation is higher, around 30-50%, at an experimental pH of 12 (corresponding pH range in simulation 10.8-12) for both pilot and synthetic samples at vacuum conditions as seen in Table 4, and Figures 6, 7 and 8. This is not the case for experiments completed under atmospheric conditions (cases 1, 2, 15 and 16 in Table 4), where the variation is less than 15% for any pH range.

From the above results, a high variation (30-50%) between the simulation and experimental results is observed under vacuum conditions when the moles of NaOH supplied is twice or more the number of moles of sulfate present in the solution. In the simulation, the MEA recovery is higher and reaches more than 90% (or MEA left in residue <10%) when the moles of NaOH added are double or more the moles sulfate present in solution (refer to Figures 7 or 8). A similar behaviour is observed for both the pilot plant and synthetic samples. However, the MEA recoveries are 25-30% (MEA left in residue 70-75%) when 1 mol of NaOH is supplied per mol sulfate, and 50-60 % when 1.5mol of NaOH is supplied per mol sulfate. In both the cases the variation in simulation and experimental results stays <22% as stated above.

From the above analysis, it can be shown that the variation in amine recovery between the simulation and experimental results increases as the addition of NaOH per mol sulfate increases. It can be explained that the simulation is releasing an ideal amount of bound amine as soon as the theoretically required moles of caustic are provided (i.e. 2 moles NaOH per mole sulfate). However, in actual experiments the pilot plant sample is not able to release enough bound amine despite the addition of a theoretically sufficient amount of the NaOH. This implies that the simulation is not able to fully account for the molecular interactions of the various species, which may be present in the pilot plant sample. This can be supported by the fact that the variations were less than 20% for the 5M synthetic samples.

5.1.2. Composition of pilot samples defined in the simulation

The pH of the pilot sample was measured in the laboratory between 4-5. When the pilot sample composition was entered in the simulation, the only components defined were SO_4^{2-} , MEA, MEA^+ and water. The pH of the simulation stream was 4.8 after adding these components. All other ionic and non-ionic impurities were not added as they were below 1wt%. Hence, a possible cause of the variation between the simulation and experimental pH and corresponding MEA recoveries could be the composition of the pilot sample as defined in the simulation. The presence of other chemical species in the aqueous pilot sample that are not defined in simulation could also interact and affect the experimental results.

5.1.3. Temperature measurements

In the atmospheric reclamation experiments, the temperature of the vapour and liquid in the still were measured using thermometers inserted in the 3-neck flask. However, for the vacuum reclamation experiments the temperature of the bath was measured instead of the actual liquid/residue temperature. This could have added to the higher variation between the simulation and experimental results at vacuum conditions compared to the atmospheric conditions. A variation of 7-8°C was observed for the similar results compared for experimental and simulation work.

5.2. Reactive Crystallisation

The comparison plots in Figures 9 and 10 reveal a typically positive deviation between the simulation and experimental results. The % variation in sulfate removal in simulation and experiments for pilot samples or synthetic 5M samples was higher when the initial sulfate loading in the samples was lower (~ 5wt%) (case 10, 11, 15, 19, and 20). However, for cases with higher initial sulfate loadings, the simulation and experimental results varied between 0.8-25% as shown in Table 5.

The variation between simulation and experimental results for crystal formation was between 14-69% for pilot plant samples. The synthetic samples had higher variation between the simulation and experimental results for only those cases with a lower initial sulfate loading (~5wt%) (case 10, 11, 15, 19, and 20). Apart from those cases, the variation was between 0.5-22% as shown in Table 5.

The following paragraphs provide some discussion on the possible reasons for the high variation between some of the experimental and simulation results:

5.2.1. Product formation at lower initial sulfate loadings

It is an already established fact that higher initial sulfate loadings will drive the crystal formation reaction towards saturation as indicated in Figure 12. However, for lower initial sulphate concentrations, the simulation generated no crystals or relatively fewer crystals compared to the actual experiments. This indicates that the dependency of crystal formation on solubility data and saturation is even more critical at lower initial sulfate concentrations. Even though the amount of crystal formation was low, crystals were still generated and were higher in amount in the actual experiments than simulation results (case 10, 11, 15, 19 and 20). In the simulated crystalliser, the saturation calculation method chosen was the chemistry of the salt rather than solubility data. The variation in the amount of crystal product was less at higher initial sulfate loadings because the solution was highly loaded with sulfate. The crystal product was formed due to the reaction pushed towards right hand side because of continuous supply of KOH and sulfate ions. At the lower initial sulfate loadings the solution was not as loaded and hence the system behaved in equilibrium. The equilibrium constants for K_2SO_4 salt formation were not defined in the simulation and hence the simulation did not make any crystals in a continuous process in steady state because of unsaturated solution in terms of sulfate ions.

5.2.2. Parameters affecting crystallisation

During crystallisation, there are many factors that can affect particle size formation and distribution including agitator tip rotation speed, nucleation sites, overall nucleation rate, solubility, and ionic concentrations. The default Aspen Plus values were used in the simulation for these factors. This may have affected the amount and generation of crystals.

5.2.3. Total inorganic and organic carbon

The CO_2 loading in the synthetic samples was calculated based on the weight gain when absorbing CO_2 , and the weight loss after the addition of sulfate to the samples. The CO_2 concentration impacts the pH and ionic activity of the solution. The CO_2 concentration assumed in simulation may have impacted the ionic activity and corresponding crystal formation resulting in variation between the experimental and simulation results. This potential source of variation was minimised for pilot samples where CO_2 concentration was analysed by total organic and inorganic carbon content. These measurements confirmed there was no CO_2 present in the pilot plant samples.

5.2.4. Composition of Pilot samples defined in the simulation

Similar to thermal reclamation, the composition defined in the simulation for the pilot plant samples could be a possible cause of the higher variation seen for these samples compared to the synthetic samples. The higher variation observed in Figure 12, even at higher initial sulfate loadings, is due to the fact that all samples analysed were either pilot samples or modified pilot samples.

6. Conclusions

Simulations were built in Aspen Plus to replicate the reclamation of sulfate loaded absorbent samples by both thermal reclamation and reactive crystallisation. Simulation results were compared to experimental data to validate the models. Both the thermal reclamation and reactive crystallisation simulations were able to adequately replicate experimental results, with most cases resulting in variation between 15%-25%. The simulations were also able to predict system behaviour accurately, following similar trends as observed with the experimental data when operational conditions were altered. This builds confidence in the simulation results, suggesting they can be used in the future for feasibility studies and cost estimations. However, the model can only be used with higher confidence for a certain set of conditions and should be improved further in order to operate the full range of CS-Cap's process operation.

While modelling thermal reclamation applied to the CS-Cap process in Aspen Plus, the simulation was able to adequately replicate the experimental results. However, more precise pH measurements should be acquired for the experimental work due to their importance in determining amine recovery and the required NaOH addition. Currently it can be inferred that the model is predicting higher MEA recoveries (less MEA left in residue) when the simulated treated amine solution pH range is 10.8-12 (corresponding twice or more NaOH moles supplied per mole sulfate). However, the model predicts closer MEA recoveries to experimental results at pH range of 9.4-10.1 (corresponding to 1 or 1.5 moles NaOH supplied per mole sulfate) when operated under vacuum conditions. This can be useful information for calculating the optimised consumption of NaOH during costing. It can also be inferred that MEA recoveries stay less than 70% when 1 or 1.5 moles of NaOH per mol of sulfate is supplied, observed for both experimental and simulation results. Hence it can be concluded that to achieve higher MEA recoveries of ~ 85%, the NaOH addition has to be optimised somewhere between 1.5- 2 mol per mol of sulfate. This is an effect of the double negative charge of the kind of heat stable salts present in CS-Cap absorbent. The simulation is able to account for this effect and satisfactorily replicates the system behaviour.

Further, when similar amounts of reactants were added, the pH as predicted by the simulation was consistently 1 to 1.5 pH less than the experimentally determined pH. However, it is important to highlight that an error of 10-12% is in most cases acceptable for a predictive feasibility study. Hence, it can be concluded that the accuracy of the model in predicting pH is acceptable particularly, for synthetic samples. In addition, it is expected that the accuracy can be increased for pilot plant samples if the composition of minor components is included.

The model showed less variation between experimental and simulation results for atmospheric conditions compared to vacuum conditions. However both experimental and simulation results showed poor MEA recoveries at atmospheric conditions for both pilot samples, 2.5 M and 5M synthetic samples, suggesting that atmospheric conditions are not suitable for the regeneration of the sulfate loaded CS- Cap sulfate absorbent via thermal reclamation.

In simulation Case 1 and 2 in Table 4, where despite the experimental pH being raised to a pH of ~12, most of the MEA remained in the residue. In these cases atmospheric boiling at 120°C and 130°C was unable to recover the MEA as the boiling point of MEA is 170°C at atmospheric conditions. The simulation predicted similar results. When the temperature was raised to 180 °C (case 15, 16), there was around 25-40% amine recovered in both the simulation and actual experiments. This highlights the ability of the simulation to predict the effect temperature on amine recovery via thermal reclamation.

With the crystallisation model developed in Aspen Plus, the synthetic samples can be run with higher confidence due to less variation (<15%) as shown in Table 5.. The model predicts better for pilot plant absorbent samples with higher initial sulfate loadings. It should be noted that in the CS-Cap process recycling of the absorbent stream will be used to improve the process by increasing the sulfate concentration in the absorbent. Hence, it is expected that the CS-Cap process will run at higher sulfate loadings for which the current Aspen Plus simulation is showing a lower variation to the experimental results. Hence, the model can be used with higher confidence for cases with a higher initial sulfate loading.

The results provided here builds the confidence in using the simulation models for future preliminary cost estimation studies. The simulation showed lower variations to experimental data when applied to operating conditions closer to those expected in the CS-Cap process.

7. Future Work

Any simulation model should be able to predict the data for wide operating range, hence to make the current simulation model operate for a wider range, more experiments on pilot or synthetic samples with low initial sulfate loadings should be conducted to generate accurate solubility data which should then be

used in defining the crystalliser operation even more accurately. The CO₂ loading in the samples should also be analysed by instruments compared to weight method to gain higher confidence in the composition added and the corresponding results in the simulation.

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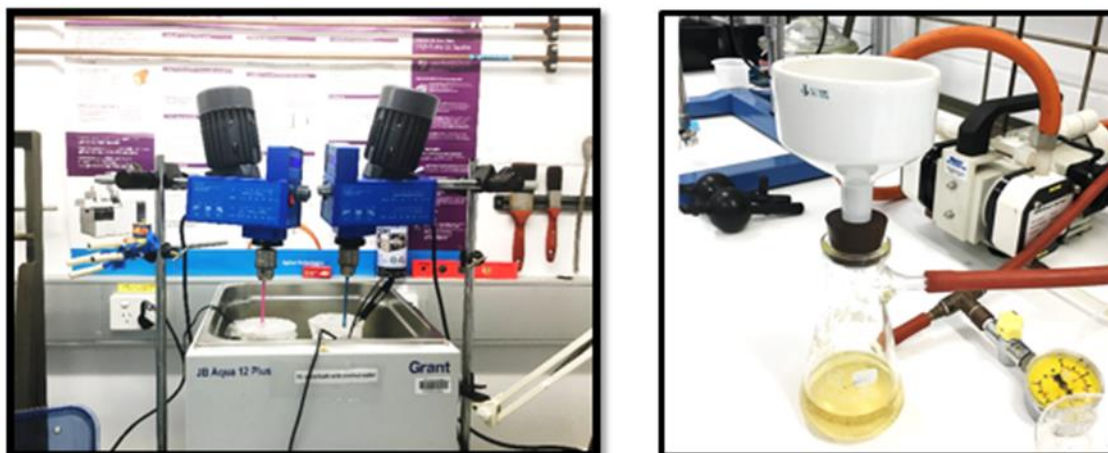
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<https://doi.org/10.1016/j.jes.2014.06.037>

Appendix

Fig.1: Apparatus for (a) vacuum, and (b) atmospheric distillation experiments



Fig 2: a) Apparatus for reactive crystallisation, and b) Apparatus for vacuum filtration



Appendix C : Techno-Economic Evaluation of Amine Reclamation Technologies and Combined Capture CS-Cap Process for Australian Coal-Fired Power Stations

Publication currently undergoing CSIRO review. To be submitted to journal

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Abstract

This paper presents the cost estimate for amine reclamation techniques investigated for CSIRO's CS-Cap process to remove the high sulfate content (~ 15-17wt %) from amine absorbent used for combined capture of CO₂ and SO₂ from Australian power plant flue gases. Regeneration via reactive crystallisation was found to be economically more attractive than thermal reclamation. Despite the generation of such a high content of heat stable salt of sulfate, the CS-Cap process offers potential cost savings to deploy post-combustion CO₂ capture (PCC) in coal-fired power stations in Australia. The process provides a low-cost alternative to installing standard post-combustion CO₂ capture along with flue gas desulfurisation units for Australian coal-fired power plants. The cost estimate suggests a reduction of 38%-44% in total plant cost by utilising the CS-Cap process instead of a standard PCC + (FGD) configuration. The levelised cost of electricity (LCOE) estimation reveals that retrofitting the CS-Cap process is economical for both black and brown coal fired power plants if reactive crystalliser is utilised. The incoming sulfur levels in flue gases have a significant impact on the operating costs of the reclaimers which reduces to almost 50% on reduction of sulfur levels from 700 ppm to 200ppm. The overall cost of the CS-Cap process is governed by the operating costs of the reclaimer utilised for sulfur rich amine regeneration.

Keywords: Thermal Reclamation, Reactive Crystallisation, Total Plant Cost, Aspen Plus Economic Analyser, Cost Estimation

Introduction

Australia's electricity generation depends heavily on local black and brown coal and the availability of abundant cheap coal has underpinned the nation's prosperity over the past 50 years. Many believe that

coal is going to continue to be significant contributor to Australia's power sector in the coming few decades through the existing power plants and its abundant reserves. However, coal-based electricity generation faces significant emission constraints due to climate change mitigation. Further, the advancements in renewables also add on to the pressure on the future of Australia's fossil fuel derived energy. Electricity generation will, however, not be solely dependent on any one technology to provide energy security. A strategic approach with a combination of existing and emerging low emission technologies will lead to a smooth and sustainable transition in Australia's power generation. As per the Australian government's Energy White Paper (Engineers Australia, 2017), coal can be expected to continue supplying energy provided it reduces emissions at low cost. Carbon capture and storage (CCS) applied to power stations reduce the emissions significantly but will result in high-cost electricity. Hence, the deployment of CCS not only needs to be fast-paced but also needs low-cost technologies applied to the capture process in order to make the technology commercially successful. This paper updates on development in CSIRO's CS-Cap process and estimates the cost of the process along with cost estimation of its regeneration technologies involved.

1.1. CSIRO's CS-Cap Process

Chemical absorption using aqueous amines is technologically an advanced process for post-combustion CO₂ capture (PCC) and has been widely accepted in the gas processing industry. The technology has been scaled up in coal and natural gas facilities and is currently the leading technology for capturing CO₂ from power plants (IEAGHG, 2019). The CO₂ capture efficiencies are generally in the range from 85-90% but can be increased approaching 100%. However, this level increases the cost and energy consumption of the process. Furthermore, the pre-treatment of flue gases including removal of SO₂ is an essential requirement for PCC's efficient performance as SO₂ preferentially reacts with amines to form degradation products thus increasing amine make-up requirements (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017).

Flue gas desulfurisation (FGD), particularly the wet limestone process, is used for the removal of SO₂ in countries like USA, Japan, Germany, China, and many other Asian countries (Jamil et al. 2013). Application of PCC technologies requires prior installation of FGD units to reduce SO₂ levels to < 10ppm. Existing FGD units may not reduce SO₂ levels to such low levels and plants might require additional scrubbers or deep FGD's (Puxty et al. 2014). However, countries like Australia do not have FGD units due to their low sulfur coal (Puyvelde, 2009) and hence require additional investment on top of PCC facility cost (Rubin et al. 2015).

Offering an alternative to the installation of high-cost FGD + PCC facilities to capture SO₂ and CO₂ from Australian coal-fired power plants, CSIRO has developed a combined capture process which is capable of simultaneously capturing SO₂ and CO₂ in a single absorber column using a single aqueous amine solution (Beyad et al. 2014). The process has the potential to save millions of dollars due to a reduction in capital cost by avoiding the need for a separate FGD unit (Puxty et al. 2014). The process has been demonstrated in CSIRO's PCC pilot plant at AGL's Loy Yang brown coal-fired power station in Victoria, Australia in 2014. The proof of concept operation simultaneously captured SO₂ and CO₂ from the power plant flue gases at CSIRO's pilot facility. Details of the pilot campaign are provided in our previous publication (Pearson et al. 2017). The process has been patented by CSIRO and is named the CS-Cap process. A flow diagram of the CS-Cap process is provided in Figure 1.

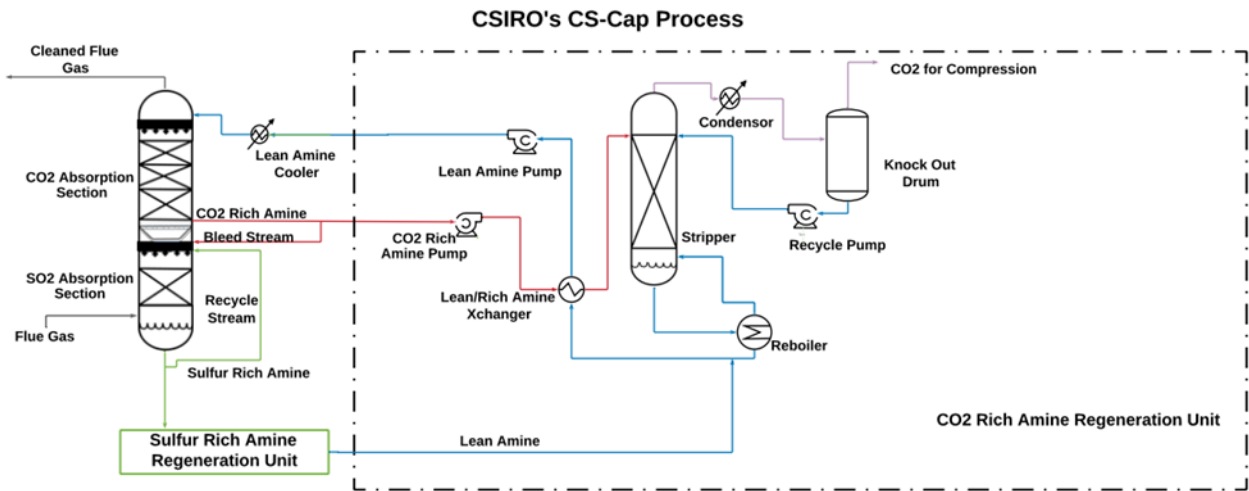


Figure 1: Process flow diagram of CSIRO's CS-Cap process (Puxty et al. 2014)- Recreated

In Figure 1, the absorber is capturing CO₂ and SO₂ in upper and lower sections of the absorber column respectively. The selectivity of amines to absorb stronger acids allows the absorption of SO₂ in the bleed stream despite the presence of CO₂ in that stream. Only a small percentage of the total volumetric flowrate (~0.01-3%) (Beyad et al. 2014) of the CO₂ rich stream (red stream) is required to capture the incoming SO₂ in the flue gas. The principal concept of the process is to eliminate the requirement for FGD, which is a pre-requisite for PCC installations in Australia. This is expected to bring large cost savings when applying PCC to facilities that do not currently employ FGD. The CO₂ rich amine from the top section of the absorber column is regenerated in a standard stripping process where CO₂ is stripped from the amine by the application of heat using steam. However, it is not possible to regenerate the SO₂ rich amine formed in the lower section of the absorber by this process. This is because the absorbed SO₂ forms a heat stable salt of sulfate with the amine recirculating in the lower portion of the absorber column. (Pearson et al. 2017). Heat stable salts are ionic in nature and do not convert back to SO₂ on the application of heat. Hence a part of the recycle stream exiting from the bottom section of the absorber column is sent to a separate regeneration section, the sulfur-rich amine regeneration unit as shown in Figure 1.

The composition of the sulfate rich stream sent for regeneration is quite distinct compared to a standard regeneration stream due to higher weight % of HSS (approximately 11-12% compared to 2wt%)(Garg et al. 2018b). The regeneration of the amine from the heat stable salt could be possible not only through conventional established techniques like thermal reclamation (ElMoudir et al. 2012) but also through non-conventional regeneration techniques utilised in the chemical process industry. Techniques like electrodialysis, ion exchange, nanofiltration, and crystallisation are capable of breaking the ionic bond between the sulfate and the protonated amine(Garg et al. 2018).

1.2. Investigating the cost-effectiveness of the CS-Cap process

Adding CCS to a coal-fired power plant doubles the total plant cost (TPC) compared to that of a plant built without CCS, be it a brown or black Australian coal-fired plant (Australian Power Generation Technology Report, 2015). The total plant cost includes the equipment, material, direct labour, engineering, erection costs along with other contingencies. The variable operating and maintenance cost is expected to rise even higher around 3-4 times if CCS is integrated with a new power plant in Australia. This increases the levelised cost of electricity (LCOE) by approximately 100% compared to the case where no CCS is applied to a pulverised supercritical or ultra-supercritical power plant (Australian Power Generation Technology Report, 2015). The cost increase mentioned above includes FGD unit installations which are a pre-requisite for any amine based PCC technology to be deployed in Australia.

The huge increase in the capital, operating and maintenance costs of a new power plant build with CCS results in increased electricity prices along with decreased plant efficiencies. These pose a serious barrier to CCS commercialisation in Australia. The CSIRO's CS-Cap technology aims to lower the capital cost of amine-based PCC by eliminating the capital cost requirements of a separate FGD unit. CSIRO's successful pilot campaign proved the possibility of the combined capture concept and its potential as a cost-effective technology with commercial applicability. However, the regeneration of the CO₂ and SO₂ rich amine still needs to be investigated for its cost-effectiveness compared to a standard FGD+PCC system.

As shown in Figure 1, amine regeneration is chiefly required for two streams in the CS-Cap process, the CO₂ rich amine stream (red stream) and the SO₂ rich amine stream (green stream). Regeneration of the CO₂ rich stream is carried out in a standard stripper using steam as shown in Fig 1. This part of CS-Cap process (CO₂ rich amine stream regeneration) may not offer huge savings as it is a standard stripping method applied to release CO₂ from the rich amine. However, regeneration of the sulfur rich stream has scope for cost reduction due to its unique nature (highly concentrated with sulfate) making it applicable to non-standard reclamation techniques (Garg et al. 2018).

To investigate the effectiveness of the regeneration technologies and their cost benefits, if any, the thermal reclamation and crystallisation techniques were experimentally evaluated at the laboratory scale using the sulfur rich absorbent generated during the CSIRO's 2014 pilot campaign. Further, the experimental conditions and parameters were used to build a simulation model in Aspen plus to evaluate the cost of the regeneration technologies which could be integrated into the overall cost of the CS-Cap technology.

The current paper includes a cost estimation of the thermal reclamation and crystallisation techniques using an Aspen Plus simulation that has been validated against experimental results (Garg et al. 2019). The cost of these regeneration techniques has been integrated individually with the unit operations shown in Figure 1 to evaluate the overall cost of the CS-Cap process. Further, the cost of CS-Cap process has been compared to:

- A retrofitted power plant with FGD + PCC unit,
- A retrofitted power plant with FGD + PCC unit+ improved solvent,
- a retrofitted power plant with minimal FGD+PCC unit

2. Cost Evaluation Methodology: CS-Cap Regeneration Techniques

2.1. Process description and model development

Figure 2 represents the CS-Cap process with two options for sulfur rich amine regeneration. Options 1 and 2 show the thermal reclamation and reactive crystallisation unit respectively. Each of the two options will be separately integrated with the combined absorption section (SO₂ and CO₂) and CO₂ regeneration section to determine the overall cost of the CS-Cap process.

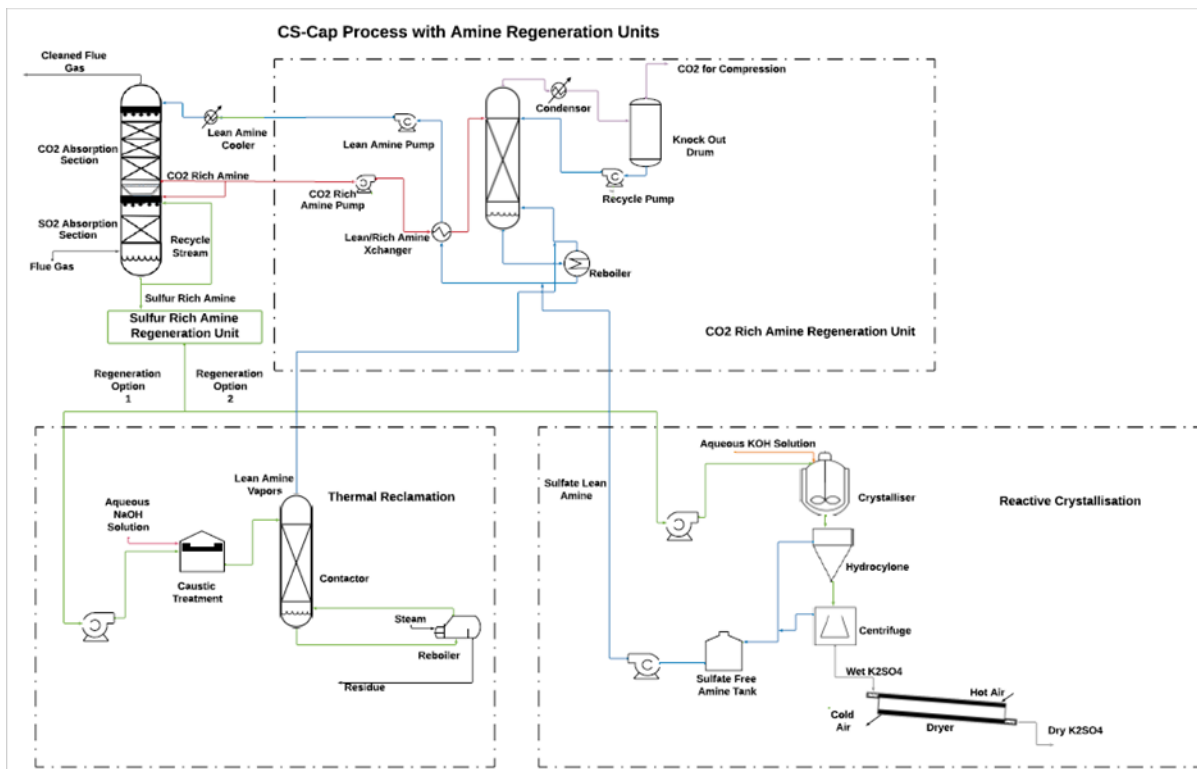


Figure 2: CS-Cap process showing reclamation of sulfur rich amine through thermal reclaiming or crystallisation

2.1.1. Scenario A: Thermal reclamation for regeneration of sulfur rich amine stream

Thermal reclamation is the most widely applied technique used in the gas processing industry to remove heat stable salts and other degradation products from the spent amine solutions (Sexton et al. 2014). The sulfur rich amine stream sent for regeneration out of the CS-Cap process is almost similar in magnitude (0.1-3% volume) as the volume removed for reclamation from a standard gas sweetening process (1-3%)(Wang et al. 2014). The amount of heat stable salts in the CS-Cap sulfur rich stream is 3-4 times or even higher than that of a standard process however the magnitude is similar which implies that the CS-Cap contaminated stream is much more concentrated and should require less or similar energy to boil off and recover the amine. This makes the thermal reclaiming technique worth comparing against the other non-conventional techniques mentioned in section 1.1.

The sulfur rich stream generated in the bottom of the absorber column is sent through regeneration option 1 to a thermal reclamation unit as shown in Figure 2. The absorbed SO_2 gets converted into sulfate which bonds with the protonated amine, forming a heat stable salt. A similar process takes place in natural gas processing where similar kinds of heat stable salts are formed due to H_2S instead of SO_2 . These heat stable salts lower the pH of the CS solution however, the addition of a base (NaOH) raises back the pH and releases the protonated amine which upon further boiling separates aqueous amine from the salts or residue. A similar method was applied to the CS-Cap SO_2 rich amine obtained from CSIRO's pilot campaign and conditions were investigated at which the amine boiled off. It was expected that spent amine will boil off at atmospheric conditions after the caustic treatment. However, due to the high amount of heat stable salt in the solution, there was a limited recovery of MEA at atmospheric conditions. This may be due to the increase in the boiling point of the solution sent for reclaiming as an effect of a large amount of heat stable salts present and base added for neutralisation (Wang et al. 2014). Hence vacuum conditions of 50 mmHg vacuum and 110°C - 130°C were investigated to obtain higher amine recoveries. Further, the amount of caustic addition was calculated based on the moles of heat stable salt present or the pH of the final solution. The laboratory experiments were conducted for a pilot plant sample which was $\sim 3\text{M}$ MEA initially

(~14wt% amine after absorption) and synthetic sample of 5M MEA initially but ~ 25wt% after loading it with CO₂ and SO₄²⁻.

The details of the laboratory set up used for the thermal reclaiming experiments are available in our previous publication (Garg et al. 2018). However, for the costing purpose, the Aspen Plus simulation model was built and validated using the laboratory experimental conditions. The lab scale model was then scaled up for a large scale facility and equipment as shown in the thermal reclamation section in Figure 2. This included the addition of a packed contactor with a reboiler, mixing tank, and pump to the model to evaluate the capital cost of the full-scale technique. The amine vapours exiting the thermal reclaiming were added directly to the stripper section of the CO₂ rich stream regeneration.

2.1.2. Scenario B: Reactive crystallisation for regeneration of sulfur rich amine stream

Crystallisation from a solution occurs typically as a result of cooling or evaporation but also by reaction of one of the solute with the other present in a saturated solution. Though crystallisation is not a common technique applied in the gas processing or carbon capture, it is applicable to the CS-Cap process due to the high concentration and the ionic nature of the heat stable salts in CS-Cap's sulfur rich stream. The addition of sufficient KOH to the sulfate rich amine absorbent releases protonated amine as free amine and the SO₄²⁻ reacts with K⁺ to form K₂SO₄ crystals. K₂SO₄ can be potentially sold as fertilizer which brought the interest in investigating this technique. The effectiveness of the technique was evaluated at a laboratory scale, as mentioned in our previous publication (Garg et al. 2018). The technique was evaluated at conditions close to the anticipated absorber operating conditions so as to avoid any excessive cooling or heating load on the process. The main aim was to draw more sulfate out of the system at optimised experimental conditions. Further, the lab data was used to validate an Aspen Plus model which was scaled up to allow costing of the technique at full scale. Though a simple reaction beaker, vacuum filtration, and oven drying was utilised for the laboratory scale tests, at full scale the technique requires a crystalliser, hydro cyclones, centrifuge, and a dryer. Figure 2 represents the flow scheme of the reactive crystallisation (Regeneration option 2) process and its integration into the CS-Cap Process.

2.2. Assumptions and Economic Inputs to Cost Estimation - Regeneration Techniques

2.2.1. Flowrates of Sulfur Rich Amine Stream

CSIRO has completed an in-house simulation in ProTreat™ of the SO₂ and CO₂ absorbers from the CS-Cap process applied to a 900 MW (gross output) coal-fired power station (Cousins et al. 2019). The net power output from the power station after the addition of 90% CO₂ capture using a 30 wt% Monoethanolamine (MEA) absorbent was 666 MW. The results of that simulation have been used to provide the flowrate and composition of the sulfur rich stream to be sent for reclamation in the CS-Cap process. The ProTreat simulations were completed for both brown and black coal-fired power stations. Australian Black coal is considered to have high sulfur content of 700ppm against brown coal with a sulfur content of 200 ppm.

There is a total of three trains for the full-scale system (900MW), out of which the flowrate from one train is used for the simulation in Aspen Plus and forms the basis of the cost estimation. From the total flow rate of CO₂ rich amine, 0.1% of the stream is used as a bleed stream to capture SO₂ in the lower portion of the absorber. 98% of the SO₂ rich stream coming from the bottom section of the absorber column has been recycled and only remaining 2% of the sulfur rich stream generated is sent for the reclamation.

2.2.2. Composition of Sulfur Rich Amine Stream for Regeneration

A 30 wt% MEA solution was used to absorb the SO₂ and CO₂ in the simulation. Formate was included as a representative degradation product apart from sulfate. The total amine present after absorption was divided into protonated and free amine to match the final pH of the absorbent as obtained in the

laboratory experiments. Below is the flow rate and composition of the stream used in Aspen Plus for both the regeneration techniques evaluated.

Table 1: Table 1: Composition and flow rates used for Aspen Plus Simulation Regeneration model for one PCC train (900MW)

Component	Thermal Reclamation		Reactive Crystallisation	
	700 ppm Sulfur Mass Fraction	200 ppm Sulfur Mass Fraction	700 ppm Sulfur Mass Fraction	200 ppm Sulfur Mass Fraction
Water	0.62	0.5	0.57	0.48
MEA	0.07	0.2	0.06	0.18
CO ₂	0.03	0.08	0.02	0.08
MEAH ⁺	0.1	0.1	0.1	0.11
SO ₄ ²⁻	0.17	0.095	0.16	0.09
K ⁺	0	0	0.07	0.04
HCOO ⁻	0.01	0.02	0.01	0.02
Sulfur Rich Amine Flowrate(tonne/hr)	29.1	14.4	30.5	14.6
Temperature (°C)	40.4	37.3	40.4	37.3

2.2.3. Capital Cost

The capital cost was divided into direct plant costs, indirect costs and working capital. Only the equipment purchase cost (EPC) has been taken from Aspen Plus. The remaining expenses are based on a percentage of the equipment price (Ulrich & Vasudevan, 2004), as outlined in Table's 2,4,6 and 8 for thermal reclamation and crystallisation respectively.

2.2.4. Operating Cost

The operating costs include the raw material and utilities costs as variable components. The labour charge, maintenance and repairs, taxes, and insurance were included under fixed operating charges. Labour is considered for operation and maintenance for regeneration units but not for administration. A rate of \$73 AUD per hour is considered with 1800 hrs yearly for each working person. Fixed capital depreciation and interest on capital is also included under operating costs. No waste disposal cost, co-product or by-product credit was considered.

2.2.5. Utilities and Chemical Requirements

For thermal reclamation, low pressure (LP) steam was used in the reboiler section. It is anticipated that LP steam will be available at around 4.8 bar (Australian Power Generation Technology Report, 2015). An electrical load was considered for pumping. NaOH solution is required for the caustic treatment. For the Australian case, it was assumed that NaOH solution (50wt %) shall be imported. An MEA price of 1.8 US \$/kg and a NaOH solution price of 385 US \$/tonne were used. The chemical prices have been taken from <https://www.alibaba.com>. A conversion rate of 1 AUD = 0.71 USD was used. The price of steam, cooling water and electricity have been referred from (Hosseini et al. 2016).

For crystallisation, cooling water is required to operate the crystalliser at a constant temperature. Apart from this, there is an electrical load to run the hydro cyclones, centrifuges, dryers, and pumps. Compressed air heating was done using direct contact electrical heaters. The KOH solution assumed to be imported in a similar manner as the NaOH solution. A KOH solution (48wt %) price of 530 US\$/tonne was used.

All capital and O&M costs are expressed in June 2015 Australian dollars similar to those considered in the reference reports. A currency exchange rate of 1AUD= 0.71 USD is used.

3. Cost Comparison: CS-Cap Process with conventional PCC technologies retrofitted to an Australian coal-fired power plant

This section of the paper is aimed at estimating the overall cost of the CS-Cap process and then comparing it with a conventional PCC + FGD configuration. As Australian coal-fired power plants do not have FGD units installed, the cost estimation of CO₂ capture must include the cost of FGD installation, whether it is for a new build or retrofitted power plant. Since the CS-Cap process is capable of capturing CO₂ and SO₂ and is intended for application in Australia, its cost has been compared with the costs calculated in case studies previously completed for Australian coal-fired power plants utilising PCC + FGD. Reports prepared by Gamma Energy Technology and CO2CRC (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017) and (Australian Power Generation Technology Report, 2015) are used extensively for comparison to the CS-Cap process.

3.1. Assumptions and Economic Inputs to Cost Estimation

3.1.1. Basis of the reference reports for cost comparison

(Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017) is used as one of the reference reports for the CS-Cap process cost comparison in this section. The report covers black and brown coal-fired power plants retrofitted with PCC using an amine-based PCC technology. The PCC facility in that study report includes 2 absorber trains, 1 regenerator per absorber train, 1 compression train per regenerator and 8 reboilers per regenerator (16 reboilers in total). 90% of CO₂ capture is considered and the plant runs for 24 X 7. The PCC plant retrofit obtains steam for solvent regeneration via the crossover between intermediate pressure (IP) and low-pressure (LP) systems in the existing plant. A backpressure steam turbine is introduced to step down the steam to the correct conditions for solvent stripping in the reboiler. The heat from the hot condensate returning from the reboiler is used via heat exchangers to supplement feedwater heating. The base case PCC coal retrofit case is a fully integrated MEA solvent facility. For the retrofit case, the existing pulverised coal base plant without capture is a fully paid-off asset, in good condition with a suitably long life (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017). The retrofit case assumes wet cooling and there are no upgrades considered to the base plant.

The other reference report used for the cost comparison is the (Australian Power Generation Technology Report, 2015). This report details the cost and performance of black and brown coal supercritical and ultra-supercritical coal-fired power plants with and without CCS. The study also details about retrofitting black coal-fired with PCC unit which results in the lesser levelised cost of electricity (LCOE) compared to the new build pulverised black coal power plant with dry cooling. The cost of FGD installation and the cost of retrofitting PCC without FGD in an existing Australian black coal-fired power plant is provided in the report. This information has been utilised here for comparing the CS-Cap case with other reference cases utilising a standard CO₂ capture process.

3.2. Scenarios comparing the CS-Cap process with conventional PCC + FGD installations

Scenario 1: Base plant retrofitted with PCC, FGD + SCR (Selective Catalytic Reduction)

The design basis for the base case (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017) is referred from (Australian Power Generation Technology Report, 2015) which consists of a pulverised coal case with 85% capacity factor. Key equipment included in the base power plant are pulverised coal boilers, combustion turbine generators, steam turbine generator, circulating water pumps and drivers, cooling systems, condensers, air separation units, and main transformers.

For the PCC retrofit, the site chosen in the study was a generic greenfield site in the Latrobe Valley in Victoria, Australia for the brown coal case and an Australian (New South Wales) location for the black coal case at an elevation of 110 m. No nearby rail line or road was considered in the study for fuel delivery as the sites were assumed to be at mine mouth. Dry cooling and ash handling systems were considered due to a shortage of supply for cooling water in some parts of Australia. The CO₂ transportation pipeline and storage sites were not included in the capital cost estimates, however, a \$15/tonne CO₂ cost was added to the levelised cost of electricity (LCOE) for transportation and storage.

The total plant cost (TPC) includes the cost of equipment (complete with initial chemical and catalyst loadings), materials, labour (direct and indirect), engineering and construction management, and contingencies (process and project). However, the owner's costs were excluded from TPC estimates.

Operation and maintenance (O&M) costs have fixed and variable components. The fixed component includes operating labour, maintenance material and labour, administrative and support labour. The variable component includes consumables, waste disposal, co-product or by-product credit, and fuel costs. For the purposes of the O&M cost analysis, the value of these waste streams was assumed to be zero.

The project and process contingency, other exclusions in the cost estimate, maintenance, material, and other cost details can be found in chapter 15 of (Australian Power Generation Technology Report, 2015).

The new PCC plant in the base case scenario 1 included the cost of FGD and SCR as these units are missing in the Australian coal-fired power plants.

Scenario 2: Base Case (with FGD & SCR and Improved Solvent)

This scenario has a similar design basis as scenario 1 but uses an improved solvent for CO₂ absorption. The improved solvent was assumed to require less steam to regenerate and hence will raise the net MWe output of the power plant. This case was considered in the report based on the confidence gained from learning by doing and reducing capital requirements resulting from the performance of advanced solvents in several CCS projects worldwide.

Scenario 3: Base Case (with minimal FGD & SCR)

The scenario is similar to scenario 1 but does not include the cost of a deep FGD & SCR. This scenario was for Australia, particularly Victorian brown coal with low sulfur content. It is believed that the use of minimal FGD and SCR would significantly reduce the capital requirements resulting in a decreased LCOE. Minimal FGD and SCR may include a direct contact cooler along with alkali treatment for SO₂ removal (Retrofitting An Australian Brown Coal Power Station With Post-Combustion Capture, 2018) and low NO_x burners installation instead of SCR. This reduces the cost of adding PCC by approximately 45% for the black coal-fired power plant (Australian Power Generation Technology Report, 2015). Hence a similar assumption has been considered for a brown coal case. The retrofit report, however, does not provide the cost for scenario 3 for black coal hence this case has not been considered for black coal case here.

Scenario 4: CS-Cap Case with Thermal Reclamation

This scenario will include PCC retrofit in a base plant with no FGD and SCR. The FGD is replaced by the CS-Cap process combined with thermal reclamation as discussed in section 2.1.1. The SCR is not included as a result of the very low NO₂ concentrations in the total NO_x typically emitted (~99% NO, balance NO₂ and N₂O) in Victorian coal-fired flue gases. NO does not react with amines and hence passes through without affecting the CO₂ capture system.

Scenario 5: CS-Cap Case with Reactive Crystallisation

This scenario will include PCC retrofit in a base plant with no FGD and SCR. The FGD is replaced by the CS-Cap process combined with reactive crystallisation as discussed in section 2.1.2. SCR costs will be not be included for the Victorian coal case.

3.3. Calculation Basis for Total Plant Costs of Scenario 1-5

The TPC in A\$/kW for scenarios 1-3 with wet cooling as applicable for black and brown coal has been taken from (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017).

Any type of cost involved for PCC deployment in Australia has two components: CO₂ capture cost (PCC cost) and FGD cost for SO₂ capture. The cost breakup of the TPC for PCC Retrofit + FGD/SCR with dry cooling for the black coal case is provided in (Australian Power Generation Technology Report, 2015). The TPC of PCC equipment retrofit + FGD/SCR for a wet cooling case is available in the report (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017) but no breakup is available for the individual cost of PCC retrofit and FGD/SCR for wet case.

Hence to evaluate the PCC retrofit TPC in scenarios 4 & 5, the ratio of FGD/SCR cost requirements to the total TPC utilising dry cooling for a black coal power plant has been used to calculate the individual PCC equipment retrofit cost. An air-cooled condensing plant design can reduce plant gross output by as much as 1% compared to wet cooling but because of the limited data the cost for wet cooling case, similar cost ratio of 44-45% for FGD/SCR (dry cooling) is considered for the TPC breakup for wet case. The cost obtained for FGD/SCR is then subtracted from the combined TPC of PCC retrofit + FGD/SCR of scenario 1. The cost of the regeneration technique is then added to the modified TPC taken from scenario 1. This replaces the cost of FGD/SCR with the cost of the CS-Cap process

3.4. Calculation Basis for fixed and variable O&M costs for Scenarios 4 & 5

The total fixed and variable costs in A\$/kW-yr and A\$/MWh for scenarios 1-3 have been taken from the report (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017). For the breakup of individual fixed costs for PCC retrofit and FGD/SCR, a similar factor of 44-45% as identified in the (Australian Power Generation Technology Report, 2015) has been used. This is based on the cost estimation methodology which assumes that the fixed part of the operating cost is taken as a percentage of the capital cost. Since the capital cost was reduced by 45% while excluding FGD, fixed operating cost has been reduced by the same percentage. The fixed O&M cost of regeneration techniques then has been added to the fixed O&M cost of the PCC retrofit obtained from the report.

In the Australian Power Generation Technology report, 2015, FGD/SCR was found to provide 20% of the variable O&M costs. This factor was applied to the variable O&M costs obtained from the (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017). This allowed FGD/SCR proportion of the variable O&M costs to be replaced by those calculated for the CS-Cap process.

3.5. Calculation Basis for Levelised Cost of Electricity & Cost of CO₂ avoided

The LCOE of technology is defined as the average cost of producing electricity from any technology over its entire life. Levelised cost of electricity is calculated by converting the capital and O&M costs of a plant into a cost per MWh. This helps in comparing different technologies based on their operation and sizes. The cost of electricity consists of four components: the capital costs, the O&M costs, fuel costs & CO₂ transportation and sequestration. When the cost is calculated independently then a cost basis can be different, however, when comparing different size units, they must all have the same cost unit basis when combined to calculate the cost of electricity (typically \$/MWh).

The criteria used to convert all costs including the capital, O&M costs into \$/MWh has been followed that described in section 17.2.5 of (Australian Power Generation Technology Report, 2015).

Further, the cost of CO₂ avoided has been calculated using the following equation 1:

$$\text{Avoided cost} = \frac{\{LCOE_{\text{with removal}} - LCOE_{\text{reference}}\}}{CO_2\text{emissions}_{\text{reference}} - CO_2\text{emissions}_{\text{with removal}}} \quad (1)$$

4. Results and Discussion

4.1. Cost estimation results of Scenario A and Scenario B described in Section 2.

As the incoming sulfur content in the flue gases affect the capital and operating cost of the reclaimers, Scenario A and B have been evaluated for both high and low sulfur content.

Scenario A

Table 2 and 3 detail the Capital Expenditure and Operating Cost of Thermal Reclamation when applied to the CS-Cap process for 700 ppm sulfur content in the incoming flue gas.

Table 2: Capital Cost of Thermal Reclaimer for one train of 900 MW gross power station (700 ppm Sulfur)

<u>Direct Plant Costs</u>	Basis (DEC = EPC + Freight)	\$M ex GST	ASSUMPTIONS
Equipment Purchase	EPC	0.92	From APEA (AUD)
Freight	% of (EPC)	0.09	10%
DEC		1.01	
Installation	% of (DEC)	0.46	45%
Instrumentation	% of (DEC)	0.25	25%
Minor piping	% of (EPC)	0.15	16%
Structural	% of (EPC)	0.14	15%
Electrical	% of (DEC)	0.25	25%
Buildings	% of (EPC)	0.23	25%
Yard Improvements	% of (EPC)	0.14	15%
Service Facilities	% of (EPC)	0.37	40%
HSE Functions	% of (EPC)	0.09	10%
		3.09	
<u>Total Indirect Costs</u>			
Land			
Engineering Supervision	% of (DEC)	0.51	50%
Legal Expenses	% of (DEC)	0.04	4%
Construction Expenses	% of (DEC)	0.41	40%
Subtotal so far		4.05	
<u>Working Capital</u>			
Working Capital		0.20	5%

<u>Fixed Capital Investment</u>		4.25	
Total Capital (ex GST)		4.25	

The equipment cost has been taken from Aspen Plus Economic Analyser (APEA) in USD and converted into AUD at an exchange rate of 1AUD= 0.71USD

Table 3: Operating Cost of Thermal Reclaimer for one train of 900 MW gross power station (700 ppm Sulfur)

<u>Operating Costs Summary</u>				
-	Item	Total cost (\$M)	Consumption t/yr	Price per unit(AUD)
Raw Materials	MEA	13.79	5441	2.5 \$/kg
	NaOH	52.328	96500	542\$/t
			-	
Utilities	Electricity	0.0001	514 MWh/yr	0.1\$/MWh
	Steam	4.41	127475MWh/yr	34.57 A\$ / MWh
	Cooling water	0.00	0	2.5 A\$ / cubic meter
	Air	0.00	0	Free
	Item		Assumptions	Price per unit
Total fixed charges	Labour	0.39	2 people for operation 1 for maintenance	\$73/hr
	Maintenance and repairs	0.21	5% of total capital cost	NA
	Operating supplies	0.04	1% of total capital cost	NA
	Taxes (property)	0.08	2% of total capital cost	NA
	Insurance	0.04	1% of total capital cost	NA
Depreciation & Capital	Fixed Capital Depreciation	0.21	5% of total capital cost	NA
	Interest on capital	0.21	5% of total capital cost	NA
Total Product Cost		71.73		

The fresh MEA requirement is calculated based on the simulation result for the worst case of 5M MEA with 16-17 wt% sulfate in the recycled stream sent for regeneration. Based on experimental and modelling results, the worst case MEA losses determined are 15-16 wt%. The amine required to compensate this loss has been added to the chemical requirements. Table 4 and 5 detail the Capital Expenditure and Operating Cost of Thermal Reclamation when applied to the CS-Cap process for 200 ppm sulfur content in the incoming flue gas

Table 4: Capital Cost of Thermal Reclaimer for one train of 900 MW gross power station (200 ppm Sulfur)

<u>Direct Plant Costs</u>	Basis (DEC = EPC + Freight)	\$M ex GST	ASSUMPTIONS
Equipment Purchase	EPC	0.49	From APEA (AUD)
Freight	% of (EPC)	0.05	10%
DEC		0.54	
Installation	% of (DEC)	0.24	45%
Instrumentation	% of (DEC)	0.14	25%
Minor piping	% of (EPC)	0.08	16%
Structural	% of (EPC)	0.07	15%
Electrical	% of (DEC)	0.14	25%
Buildings	% of (EPC)	0.12	25%
Yard Improvements	% of (EPC)	0.07	15%
Service Facilities	% of (EPC)	0.20	40%
HSE Functions	% of (EPC)	0.05	10%
		1.65	
<u>Total Indirect Costs</u>			
Land			
Engineering Supervision	% of (DEC)	0.27	50%
Legal Expenses	% of (DEC)	0.02	4%
Construction Expenses	% of (DEC)	0.22	40%
Subtotal so far		2.15	
<u>Working Capital</u>			
Working Capital		0.11	5%
<u>Fixed Capital Investment</u>		2.26	
Total Capital (ex GST)		2.26	

Table 5: Operating Cost of Thermal Reclaimer for one train of 900 MW gross power station (200 ppm Sulfur)

Operating Costs Summary				
-	Item	Total cost (\$M)	Consumption t/yr	Price per unit(AUD)
Raw Materials	MEA	12.17	4801	2.5 \$/kg
	NaOH	20.188	37230	542\$/t
			-	
Utilities	Electricity	0.000048	477 MWh/yr	0.1\$/MWh
	Steam	4.41	127475MWh/yr	34.57 A\$ / MWh
	Cooling water	0.00	0	2.5 A\$ / cubic meter
	Air	0.00	0	Free
	Item		Assumptions	Price per unit
Total fixed charges	Labour	0.39	2 people for operation 1 for maintenance	\$73/hr
	Maintenance and repairs	0.11	5% of total capital cost	NA
	Operating supplies	0.02	1% of total capital cost	NA
	Taxes (property)	0.05	2% of total capital cost	NA
	Insurance	0.02	1% of total capital cost	NA
Depreciation & Capital	Fixed Capital Depreciation	0.11	5% of total capital cost	NA
	Interest on capital	0.11	5% of total capital cost	NA
Total Product Cost		37.59		

Scenario B: Table 6 and 7 detail the Capital Expenditure and Operating Cost of Reactive Crystallisation when applied to the CS-Cap process for 700 ppm sulfur content in the incoming flue gas.

Table 6: Capital Cost of Reactive Crystalliser for one train of 900 MW gross power station (700 ppm Sulfur)

<u>CAPITAL EXPENDITURE</u>			
<u>Direct Plant Costs</u>	Basis (DEC = EPC + Freight)	\$M ex GST	ASSUMPTIONS
Equipment Purchase	EPC	1.57	From APEA (AUD)
Freight	% of (EPC)	0.16	10%
DEC		1.73	
Installation	% of (DEC)	0.78	45%
Instrumentation	% of (DEC)	0.43	25%
Minor piping	% of (EPC)	0.25	16%
Structural	% of (EPC)	0.24	15%
Electrical	% of (DEC)	0.43	25%
Buildings	% of (EPC)	0.39	25%
Yard Improvements	% of (EPC)	0.24	15%
Service Facilities	% of (EPC)	0.63	40%
HSE Functions	% of (EPC)	0.16	10%
		5.28	
<u>Total Indirect Costs</u>			
Land			
Engineering Supervision	% of (DEC)	0.87	50%
Legal Expenses	% of (DEC)	0.07	4%
Construction Expenses	% of (DEC)	0.69	40%
Subtotal so far		6.91	
<u>Working Capital</u>			
Working Capital		0.35	5%

<i>Fixed Capital Investment</i>		7.26	
Total Capital (ex GST)		7.26	

Table 7: Operating Cost of Reactive Crystalliser for one train of 900 MW gross power station (700 ppm Sulfur)

<u>Operating Costs Summary</u>				
<u>Variable cost</u>	Item	Total cost (\$M/yr)	Amount used	Price per unit (AUD)
Raw Materials	MEA	9.20	3628 t/yr	\$2.5/kg
	KOH	48.024	64333 t/yr	\$ 530/t
			-	
Utilities	Electricity	0.00	1816 MWh/yr	0.1\$/MWh
	Steam	0.00	0	34.57 A\$ / MWh
	Cooling water	0.76	303683 m3/yr	2.5 A\$ / cubic meter
	Air	0.00		Free
Total Variable O& M		57.98		
	Item	M\$/year	Assumptions	Price per unit
Total fixed charges	Labour	0.53	3 for operation 1 for maintenance	\$ 73/hr
	Maintenance and repairs	0.36	5% of total capital cost	NA
	Operating supplies	0.07	1% of total capital cost	NA
	Taxes (property)	0.15	2% of total capital cost	NA
	Insurance	0.07	1% of total capital cost	NA
Depreciation & Capital	Fixed Capital Depreciation	0.36	5% of total capital cost	NA

	Interest on capital	0.36	5% of total capital cost	NA
Fixed O& M		1.18		
Total Product Cost		59.89		

The fresh MEA requirement has been calculated based on the MEA losses occurring during the separation of the mother liquor from the crystals during filtration. Further, there are some losses during drying as well. As per the simulation, the MEA losses are insignificant but in actual experimental results, the total loss of mother liquor is around 8-10% resulting in ~ 1-2% of MEA loss depending upon the concentration of MEA in the spent absorbent sent for regeneration. At large scale, the industrial filters, centrifuges are unlikely to achieve 100% separation of crystals from the mother liquor. Hence the actual loss of MEA as determined in experimental work has been used as a worst-case scenario for the MEA makeup requirements here.

Table 8 and 9 detail the Capital Expenditure and Operating Cost of Reactive Crystallisation when applied to the CS-Cap process, for 200 ppm sulfur content in the incoming flue gas.

Table 8: Table 8: Capital Cost of Reactive Crystalliser for one train of 900 MW gross power station (200 ppm Sulfur)

<u>CAPITAL EXPENDITURE</u>			
<u>Direct Plant Costs</u>	Basis (DEC = EPC + Freight)	\$M ex GST	ASSUMPTIONS
Equipment Purchase	EPC	1.53	From APEA (AUD)
Freight	% of (EPC)	0.15	10%
DEC		1.68	
Installation	% of (DEC)	0.76	45%
Instrumentation	% of (DEC)	0.42	25%
Minor piping	% of (EPC)	0.24	16%
Structural	% of (EPC)	0.23	15%
Electrical	% of (DEC)	0.42	25%
Buildings	% of (EPC)	0.38	25%
Yard Improvements	% of (EPC)	0.23	15%
Service Facilities	% of (EPC)	0.61	40%
HSE Functions	% of (EPC)	0.15	10%
		5.13	
<u>Total Indirect Costs</u>			
Land			
Engineering Supervision	% of (DEC)	0.84	50%
Legal Expenses	% of (DEC)	0.07	4%

Construction Expenses	% of (DEC)	0.67	40%
Subtotal so far		6.71	
<u>Working Capital</u>			
Working Capital		0.34	5%
<u>Fixed Capital Investment</u>		7.05	
Total Capital (ex GST)		7.05	

Table 9: Operating Cost of Reactive Crystalliser for one train of 900 MW gross power station (200 ppm Sulfur)

<u>Operating Costs Summary</u>				
<u>Variable cost</u>	Item	Total cost (\$M/yr)	Amount used	Price per unit (AUD)
Raw Materials	MEA	8.02	3163 t/yr	\$2.5/kg
	KOH	16.01	21444 t/yr	\$ 530/t
			-	
Utilities	Electricity	0.00012	1191 MWh/yr	0.1\$/MWh
	Steam	0.00	0	34.57 A\$ / MWh
	Cooling water	0.29	117430 m3/yr	2.5 A\$ / cubic meter
	Air	0.00		Free
Total Variable		<u>24.32</u>		
O& M				
	Item	M\$/year	Assumptions	Price per unit
Total fixed charges	Labour	0.53	3 for operation 1 for maintenance	\$ 73/hr
	Maintenance and repairs	0.35	5% of total capital cost	NA
	Operating supplies	0.07	1% of total capital cost	NA
	Taxes (property)	0.14	2% of total capital cost	NA
	Insurance	0.07	1% of total capital cost	NA

Depreciation & Capital	Fixed Capital Depreciation	0.35	5% of total capital cost	NA
	Interest on capital	0.35	5% of total capital cost	NA
Fixed O& M		1.16		
Total Product Cost		26.19		

Comparing the cost of the regeneration techniques outlined in Tables 2-9 for Scenarios A and B, it can be seen that crystallisation is a cheaper technique compared to thermal reclamation for the CS-Cap process for any levels of sulfur in the flue gas. The crystallization capital requirements are nearly double those of thermal reclamation due to the multiple process operations involved. However, due to comparatively lower MEA losses, crystallisation is a cost-effective technique compared to thermal reclamation.

It is noted, however, that thermal reclamation is capable of removing all kinds of impurities which will not be a case with reactive crystallisation. The latter will not remove the non-ionic degradation products. Due to the slower build-up of degradation products other than sulfate, thermal reclaiming may still be required in addition to the crystallisation process. It might not be a continuously running reclaimer, but would be needed periodically to remove the non-ionic impurities. The current research focussed only on the removal of sulfate and hence the comparison is done based on the efficiencies of the process to remove only sulfate from the spent absorbent.

4.2. Cost comparison results of Scenario 1-5 described in Section 3 (Black Coal Case).

For retrofitting PCC to existing Australian coal-fired power plant, the total plant cost for CO₂ capture will include the TPC of PCC + FGD/SCR as there are no FGD/SCR currently installed in Australia. This is applicable for Scenario 1- 3 of section 3. However, for Scenario 4 and 5, the TPC will include the TPC of PCC retrofit + TPC of Reclaimer (either Thermal Reclaimer or Reactive Crystalliser).

4.2.1. PCC Retrofit Cost & FGD/SCR Cost Capital Cost

The cost of the regeneration techniques outlined in Scenario A and B and calculated in section 4.1 is for one train of the PCC system installed at a 900 MW gross power station. The net output of the plant is 662 MWe for a black coal case.

Further for Scenarios 4 and 5, the basic PCC equipment retrofit cost for the CS-Cap case should be slightly higher than scenarios 1-3 as the CS-Cap absorber column has to be larger than a standard CO₂ absorber column as a result of the additional SO₂ absorption section. An additional packing height of 4 meters was required for the SO₂ absorption section. The CO₂ capture section is otherwise not altered by the addition of the CS-Cap process. The only slight differences will be an increased flue gas flow rate through the blower (depending on its location) and cooling duty applied to the direct contact cooler. The water balance in the SO₂ capture loop can be maintained by operating column close to 40°C. It is believed that the above changes will not make add a significant cost to the CS-Cap retrofit evaluated for scenarios 4 and 5 and compared to scenarios 1, 2, & 3, and thus have not been included in this cost analysis. Only the additional costs of the thermal reclamation or crystallisation process have been considered.

The TPC, operating and maintenance costs as outlined in Tables 2, 3, 6, and 7 have been calculated for a 900 MW gross power plant. However, the costs provided in (Australian Power Generation Technology Report, 2015) for the black coal cases are calculated based on 450 MW gross power plant with a net output of 331 MW with PCC. Hence all the costs mentioned in Tables 2, 3, 6, and 7 are converted to a similar basis for a 450MW power plant as shown in Table 10 in order to provide a similar basis for all scenarios to be

compared. A power law equation (equation 2) commonly used to scale plant and equipment costs with changes in throughput or capacity has been used to adjust the costs (Haque & Somerville, 2013).

$$New\ plant\ cost = \left(\frac{new\ capacity}{base\ capacity} \right)^{0.65} \quad (2)$$

Table 11 provides the Total Plant Cost for scenarios 1-5 as described in section 3 for the black coal case. Scenario 3, PCC with minimal FGD/SCR for black coal case, has not been considered in the reference report and hence is not included in the comparison below.

Table 10: Total plant and O&M costs adjusted for reclamation techniques applied to a 450 MW (331MW net) black coal power plant (700 ppm Sulfur content)

Cost deduced to 450 MW(331MW net) for a Black Coal Case			
Capital Cost		Thermal Reclamation	Reactive Crystallisation
One Train TPC for 662 MW sent out	A\$	4247562.9	7256037.0
TPC for 3 trains		12742688.8	21768110.9
Factor of cost reduction from 662 MW to 331 MW		0.6	0.6
TPC for 3 train for 331 MW sent out	A\$	8120664.7	13872388.6
TPC	A\$/kW	24.5	41.9
Operating Costs			
Fixed			
Fixed Cost for one train	A\$	776480.7	1178643.3
Fixed Cost for three trains		2329442.0	3535930.0
Fixed Cost for three trains	A\$/kW-yr	3.5	5.3
Factor of cost reduction from 662 MW to 331 MW		0.6	0.6
Fixed Cost for 3 train for 331 MW sent out	AS/kW-yr	2.2	3.4

Variable			
Cost for one train	A\$/MWh	14.3	12.1
Cost for three trains		42.9	36.4
Factor of cost reduction from 662 MW to 331 MW		0.6	0.6
Cost for 3 train for 331 MW sent out	A\$/MWh	27.4	23.2

Table 11: Total Plant Costs for retrofitting PCC in a 450 MW (331MW net) Black Coal power plant

	Scenario 1	Scenario 2	Scenario 4	Scenario 5
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
PCC equipment retrofit cost (\$/kWe)	2,283	2,118	2,283	2,283
FGD + SCR retrofit cost (\$/kWe)	1,817	1,742	24.5	41.9
Total plant cost (A\$/kW sent out)	4,100	3,860	2,307	2,325
Total plant cost (A\$bn)	1.85	1.37	1.04	1.05

From the above scenario comparison, it is found that the capital cost of retrofitting the CS-Cap process using a thermal reclaimer or crystalliser in an existing plant would be the cheapest option for an Australian black coal-fired plant. As mentioned previously, the crystalliser will not remove all potential impurities and hence may need a periodic application of a thermal reclamation process which may slightly raise the cost of scenario 5. On the other hand, the Scenario 4 does not need any additional batch thermal reclaimer as the continuous thermal reclaimer of the CS-Cap process will be able to remove the degradation products other than sulfate. The total plant cost reduction from scenario 1 to scenario 4 is around 43%. It is to be noted that the scenarios 4 and 5 do not include any SCR installations as the NO_x component of the flue gas from Australian coal power plants is mostly NO, which will not affect the CO₂ absorption process. The FGD/SCR retrofit cost reductions are considerable when comparing Scenario 1 to Scenarios 4 and 5.

The above capital cost comparison in Table 11 definitely favours utilising the CS-Cap process for Australian black coal-fired power plants. However, it is important to calculate the Levelised Cost of Electricity that includes the Operating & Maintenance costs in addition to the fuel and CO₂ transportation & sequestration costs. This would help in identifying whether the electricity produced would be cheaper against standard techniques if the CS-Cap process is utilised in Australian black coal-fired power plants.

4.2.2. Levelised Cost of Electricity (LCOE) & CO₂ avoided cost for Scenarios 1-5 of Section 3

Table 12 shows the capture costs for retrofitting PCC to a black coal power plant for all scenarios (1-5). The data for scenarios 1 and 2 is taken from the reference report (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017). The various cost data for Scenarios 4 and 5 have been calculated based on the methodology described in section 3.2, 3.3, 3.4 and data calculated in Table 10.

Table 12: PCC Retrofitting costs in a 450 MW (331 MW net) Black Coal power plant

	Scenario 1	Scenario 2	Scenario 4	Scenario 5
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
TPC (A\$/kW sent out)	4,100	3,860	2,307	2,325
Fixed O&M (A\$/kW-year)	75	70	44	45
Variable (A\$/MWh)	11	11	36	32

The costs in Table 12 have been used to calculate the LCOE for Black Coal Case as shown in Table 13.

Table 13: LCOE for retrofitting PCC to Black Coal-fired Power Station (450MW)

	Scenario 1	Scenario 2	Scenario 4	Scenario 4
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
Finance Charges	55	52	31	31
Fixed O& M	10	9	6	6
Variable Cost	11	11	36	32
Fuel Cost	41	41	41	41
Cost of T& S	16	16	16	16
Cost of Carbon	0	0	0	0
Average LCOE(\$/MWh)	133	129	130	126
CO ₂ emitted (mil t/year)	0.32	0.3	0.32	0.32
MWnet	331	356	331	331
CO ₂ emissions (tonnes/MWh)	0.13	0.11	0.13	0.13
CO ₂ avoided (\$/tonnes)	125	117	121	116

The LCOE without CCS has been used as 39\$/MWh with CO₂ emissions of 2.95 mil tonne/year for a 450MW power plant. Table 13 reveals that the cost of electricity would be cheapest by retrofitting the CS-Cap process utilising a reactive crystalliser to 500 MW (331 MW net) black coal power plant.

4.3. Cost comparison results for Scenarios 1-5 of Section 3 (Brown Coal Case)

4.3.1. PCC Retrofit Cost and FGD/SCR Cost

The scenarios 1-2 of this paper, compared in the report (Retrofitting CCS To Coal : Enhancing Australia’s Energy Security Results And Discussions, 2017) are based on a supercritical 2100 MW brown coal power plant with a net output of 1283 MW when retrofitted with PCC. Hence for all the LCOE cost comparison, the costs of regeneration techniques were converted to the larger plant size.

Further, the capital and operating costs for the thermal reclaimer and reactive crystalliser calculated in Tables 4, 5, 8 and 9 in section 4.1. The flow rates for the brown coal case of similar capacity power plant are anticipated to be similar to that of the black coal case. However, power plant efficiency would reduce. A net capacity of 550 MW is assumed here for a 900MW gross output brown coal power plant for scenarios 4 and 5.

Table 15 provides the Total Plant Cost for scenarios 1-5 as described in section 3 for the brown coal case.

Table 14: Total plant and O&M costs adjusted for reclamation techniques applied to a 2100 MW (1283MW net) brown coal power plant (200 ppm Sulfur content)

Cost deduced to 2100 MW (1283MW net) for a Brown Coal Case			
Capital Cost		Thermal Reclamation	Reactive Crystallisation
One Train TPC for 550 MW sent out	A\$	2262684.0	7047683.1
TPC for 3 trains		6788052.1	21143049.3
Factor of cost increase from 550 MW to 1283 MW		1.7	1.7
TPC for 3 train for 1283 MW sent out	A\$	11772176.0	36667322.8
TPC	A\$/kW	9.2	28.6
Operating Costs			
Fixed			
Fixed Cost for one train	A\$	597841.6	1159891.5
Fixed Cost for three trains		1793524.7	3479674.4
Fixed Cost for three trains	A\$/kW-yr	3.3	6.3
Factor of cost increase from 550 MW to 1283 MW		1.7	1.7
Fixed Cost for 3 train for 1283 MW sent out	AS/kW-yr	5.7	11.0

Variable			
Cost for one train	A\$/MWh	9.0	6.1
Cost for three trains		26.9	18.3
Factor of cost increase from 550 MW to 1283 MW		1.7	1.7
Cost for 3 train for 1283 MW sent out	A\$/MWh	46.7	31.8

Table 15: Total Plant Costs for retrofitting PCC in a 2100 MW (1283 MW net) Brown Coal power plant

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	Base Case (with minimal FGD & SCR), Single Boiler Retrofit	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
PCC equipment retrofit cost (\$/kWe)	2,728	2,579	2,728	2,728	2,728
FGD + SCR retrofit cost (\$/kWe)	2,172	2,121	1172	9.2	28.6
Total plant cost (A\$/kW sent out)	4,900	4,700	3,900	2,738	2,757
Total plant cost (A\$bn)	10.29	9.87	1.48	5.75	5.79

The above capital cost comparison in Table 15 again favours utilising the CS-Cap process for Australian for brown coal-fired power plants. However the Levelised Cost of Electricity is calculated further to identify whether the electricity produced would be cheaper against standard techniques if the CS-Cap process is utilised in Australian brown coal-fired power plants.

4.3.2. Levelised Cost of Electricity (LCOE) & CO₂ avoided cost for Scenarios 1-5 of Section 3

Table 16 shows the capture costs for retrofitting PCC to the Brown coal case for the scenarios 1-5. The data for scenarios 1, 2 and 3 is taken from the reference report (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017).

The costs in Table 16 have been used to calculate the LCOE for the Brown Coal Case as shown in Table 17.

Table 16: PCC Retrofitting costs in a 2100 MW (1283 MW) Brown Coal power plant

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	Base Case (with minimal FGD & SCR)	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
TPC (A\$/kW sent out)	4,900	4,700	3,900	2,738	2,757
Fixed O&M (A\$/kW-year)	70	65	60	45	50
Variable (A\$/MWh)	14	14	12	58	43

Table 17: LCOE for retrofitting PCC to Brown Coal-fired Power Station (2100MW)

	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
	Base Case (with FGD & SCR)	Base Case (with FGD & SCR and Improved Solvent)	Base Case (with minimal FGD & SCR)	CS-Cap Case with Thermal Reclaimer	CS-Cap Case with Reactive Crystalliser
Finance Charges	63	60	50	35.19	35.43
Fixed O& M	9	9	8	5.9	6.5
Variable Cost	14	14	12	58	43
Fuel Cost	38	34	31	34	34
Cost of T& S	28	25	23	25	25
Cost of Carbon	0	0	0	0	0
Average LCOE(\$/MWh)	152	142	124	158	144
CO ₂ emitted (mil t/year)	2.34	0.47	0.47	2.34	2.34
Mwe	1,283	343	380	1283	1283
CO ₂ emissions (tonnes/MWh)	0.24	0.18	0.17	0.24	0.24
CO ₂ avoided (\$/tonnes)	120	104	86	126	112

The LCOE without CCS has been used as 29\$/MWh with CO₂ emissions of 19.88 mil tonne/year for a 2100 MW power plant.

From Table 17, comparing scenario 1, 4 and 5, the CS-Cap is the cheapest option if utilised with a crystalliser in a brown coal fired power plant. However the cost of retrofitting FGD+PCC lowers further if only single boiler is retrofitted as shown in scenario 2& 3. However comparison of CS-Cap cases scenario 4&5 against scenario 2 & 3 is not a true comparison as CS-Cap cases have not been evaluated here for single boiler retrofit which will further bring down the cost of CS-Cap scenario 4 & 5. Further, the case of minimal FGD/SCR case with single boiler retrofit (scenario 3) results in the lowest LCOE the brown coal case as mentioned in the report. However, it is to be noted that the optimistic approach of applying minimal FGD/SCR as reported in (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017) is not based on any bench or pilot scale study, but has been considered as a very likely the cheapest option for Australian coal power plant. On the other hand, the current costing study for the CS-Cap case is based on the results of the pilot and bench-scale testing. Apart from this, no cost benefit of selling by-product has been included in the costing study. It might be possible to further improve the economics of the CS-Cap technology by selling K₂SO₄ generated as a by-product out of the process.

5. Conclusions and Future Work

Either of the technologies evaluated experimentally can regenerate sulfate rich absorbent produced by the CS-Cap process. Where the thermal reclaimer brings the capital savings of nearly 41% for a 900 MW power plant, it increases the operating cost by almost 30% compared to that for a reactive crystalliser. Overall comparison in terms of LCOE, reveals, the CS-Cap process with the reactive crystalliser is the cheaper option among the two options to regenerate the sulfate rich CS-Cap absorbent due to the lower amine make-up requirements of the process.

The total plant cost when the CS-Cap process is retrofitted to an existing power plant offers a reduction in capital investment of almost 38-44% for both the regeneration techniques. The capital savings, however, cannot be the only governing criteria when deciding whether to utilise the CS-Cap process at a commercial scale in Australian coal-fired power plants. Therefore the levelised costs of electricity were calculated for various cases. The levelised cost of electricity was cheapest for a black coal power plant utilising the CS-Cap with a reactive crystalliser for both new build (450 MW) and retrofitting to an existing power plant (450MW). It can be concluded that the CS-Cap process will offer potential savings to Australian black coal-fired power plants.

For the Brown coal case, the LCOE was lowest for the CS-Cap process utilising a crystalliser compared to a standard PCC retrofit process with FGD for a 2100 MW power plant. Literature already reports an LCOE of 110A\$/MWh for a 380 MW (net output) by utilising an advanced solvent and minimal FGD/ SCR for a single boiler PCC retrofit. However, this LCOE figure reported is not based on any experimental work as reported in (Retrofitting CCS To Coal : Enhancing Australia's Energy Security Results And Discussions, 2017). As such comparing a PCC retrofit with minimal FGD/SCR (scenario 3) with the CS-Cap process retrofit is not considered ideal for comparison. Hence the PCC retrofit utilising standard a FGD/SCR process for a full power plant retrofit (scenario1) was compared with the CS-Cap case (utilising reactive crystalliser). In this comparison scenario, the CS-Cap process (with crystalliser) was found to be cheapest. Further if the CS-Cap process will be applied to single boiler retrofit, it will further bring down the cost. Hence it can also be concluded that utilising the CS-Cap process in brown coal-fired power plants can offer potential savings to small sized power plants or when retrofitting only a portion part of the large-sized power plants. The cost estimation, however, must be based on real plant information for smaller sized power plants. Lack of available data for brown coal power plants in current research has led to many assumptions being taken from information available for black coal power plant costs.

Another conclusion can be made based on current research which reveals that the CS-Cap process costs are majorly governed by the operating costs rather than capital costs due to continuous and relatively higher chemical requirements including MEA makeup and alkali (KOH or NaOH) addition. The capital and operating costs shown in Tables 2-9 for thermal or crystalliser reclaimer reveals the impact of sulfur content on the operating cost of the regeneration which increases to nearly 50% if sulfur levels go up from 200 to 700 ppm in the flue gases. These costs increase the variable operating cost of CS-Cap process upto 3-4 times against standard PCC+FGD retrofit case as shown in Table 12 and 16, offering less margin in lowering the cost of electricity which otherwise would have been offered higher by the process as a result of almost 43% reductions in capital cost. The decrease in the capital cost of CS-Cap process is offset by the increased operating cost of the reclaimer. However the process still resulted to be cheapest among all the similar standard PCC+FGD retrofit options as shown in Table 13 and 17.

Future work should be focussed on further bringing down the operating costs by conducting experiments at pilot scale which can improve the performance of the regeneration process and lower the amine makeup requirements. Due to the continuous mode of operation of the process, the losses of ~15% MEA for thermal reclamation and ~8-9 % for reactive crystallisation add a significant operating cost to the process. Hence, an effort to reduce these costs is required to make the process cost-effective in terms of operation.

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Appendix D : Simulating combined SO₂ and CO₂ capture from combustion flue gas streams

Publication has undergone review. To be submitted to Industrial and Engineering Chemistry Research journal

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Abstract

A challenge when using aqueous amine absorbents for capturing CO₂ from coal-fired power station flue gases is the requirement to pre-treat the flue gas prior to the CO₂ capture step. A potentially lower cost alternative is to combine the capture of both the CO₂ and SO₂ from the flue gas into a single process, removing the requirement for the desulfurisation pre-treatment step. The CSIRO's CS-Cap process uses a single aqueous amine absorbent to capture both of these acid gases from flue gas streams. This paper covers the initial simulation of this process applied to both brown and black coal flue gases. Removal of absorbed SO₂ is achieved via reactive crystallisation. This is simulated here using a 'black box' process, resulting in a K₂SO₄ product. Different operating conditions have been evaluated that increase the sulfate concentration of the absorbent in the SO₂ capture section of the process, expected to increase the efficiency of the reactive crystallisation step. This paper provides information on the absorption of SO₂ into the amine solution, and heat and mass balances for the wider process. This information will be required for further detailed simulation of the reactive crystallisation step, and economic evaluation of the CS-Cap process.

Introduction

The most technologically advanced method for capturing CO₂ from combustion flue gases is to use aqueous solutions of amines and amine blends. This technology is currently being employed at two commercial-scale CO₂ capture plant: The Shell-Cansolv process at SaskPower's Boundary Dam Power Station, and Mitsubishi Heavy Industry's KM-CDR process at the NRG-owned WA Parish Power station. One of the challenges when using amine based absorbents for CO₂ capture is the requirement to treat the flue gas prior to the CO₂ capture plant. This includes cooling the flue gas, removing particulate, and removing other acid gas components present in the flue gas, such as SO₂. This is because SO₂ will bind more strongly with the absorbents than CO₂, and is not released under the conditions used to strip CO₂ from the rich absorbent solution. This leads to a build-up of sulfate salts in the absorbent, reducing its ability to capture CO₂.

In most countries, flue gas desulfurisation (FGD) is employed on power stations to lower the SO₂ content in the flue gas. However, the inlet requirements for amine-based CO₂ capture plant are likely to be more stringent than current emissions regulations. This means that either an additional spray bank will need to be added to existing FGD units, or a polishing step (e.g. caustic scrubber) will be required. Another option is to develop a process that removes both SO₂ and CO₂ from the flue gas stream as a combined capture process.

Combined capture processes have the potential to be cheaper overall than a conventional amine based process with FGD. Examples include amino acid processes (such as Siemen’s PostCap), ammonia and potassium carbonate (which remove SO₂ as ammonium and potassium sulfate), and also some amine based processes (e.g. Shell Cansolv). The CSIRO have been developing an amine-based combined capture process, CS-Cap. This concept uses a single amine solution to capture both the SO₂ and CO₂ from the flue gas stream, as outlined in Figure 1. The CS-Cap process essentially consists of separate SO₂ and CO₂ capture loops. The CO₂ capture loop follows the standard liquid absorbent-based CO₂ capture process. In the SO₂ capture section, a slip stream of the CO₂ rich absorbent is recirculated to capture the SO₂ from the flue gas upstream of the CO₂ capture circuit. This generates an amine absorbent rich in sulfate. This high level of sulfate builds up more quickly than conventional degradation products, and requires removal for the process to be continuous. Possible methods for removing this sulfate from solution have been reviewed as part of an ongoing research project (Garg et al. 2018, Pearson et al. 2017), with identified technologies evaluated in the laboratory. One such technology of interest is reactive crystallisation. Ongoing work has focused on simulating the CS-Cap process to allow an economic comparison to be made between the CS-Cap process and a standard liquid-absorbent based CO₂ capture process incorporating FGD. This paper covers the results of that simulation work. The results of the economic analysis will be provided in a future paper.

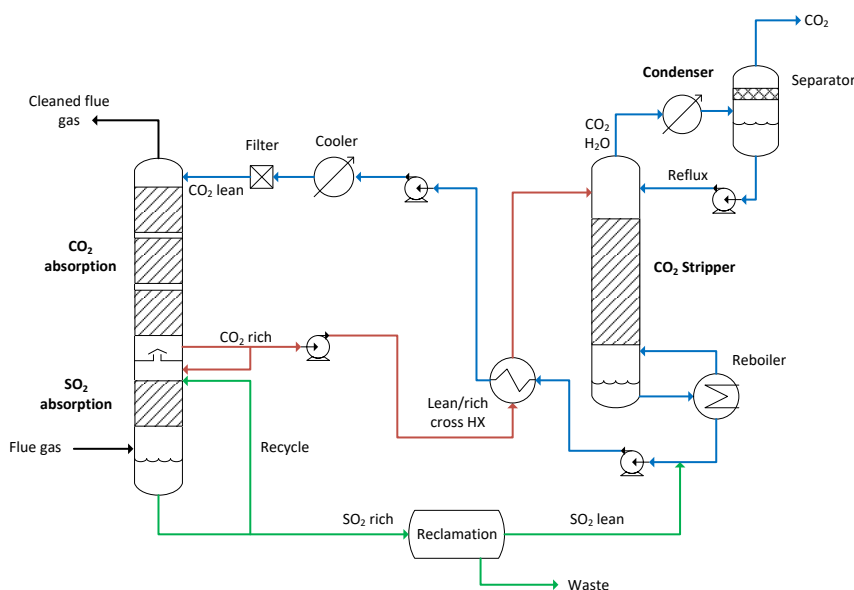


Figure 1 Flow diagram of the CS-Cap process (Pearson et al. 2017)

Methods

The ProTreat simulation software has been shown to effectively replicate amine based CO₂ capture processes evaluated at pilot scale (Cousins et al. 2012, Brown et al. 2017). The ProTreat simulation software was used here to simulate both a standard CO₂ capture plant in addition to the combined capture concept. These simulations were completed for both a brown and black coal-fired power stations. The flue gas compositions evaluated are provided in Table 1.

Table 1 Flue gas compositions used in the simulations

Unit		Case				
		Base Case USPC Black coal with FGD	USPC black coal with CS-Cap, 200ppm SO ₂ in flue gas	USPC black coal with CS-Cap, 700ppm SO ₂ in flue gas	Brown coal flue gas with CS-Cap, 200ppm SO ₂ in flue gas	Brown coal flue gas with CS-Cap, 700ppm SO ₂ in flue gas
Temperature	°C	56.9	90.83	90.83	170	170
Pressure	kPa-a	108	110	110	110	110
Flow rate	kg/s	275.6	271.23	271.23	271.23	271.23
Concentration						
H ₂ O	mol%	12.1	9.49	9.49	20	20
CO ₂	mol%	13.4	13.75	13.75	10	10

SO ₂	mol%	0	0.02	0.07	0.02	0.07
N ₂	mol%	70.4	72.48	72.43	63.96	63.91
NO, Ar	mol%	0.8	0.87	0.87	0.02	0.02
O ₂	mol%	3.3	3.39	3.39	6	6

For the base case simulation, the flue gas was sourced downstream of the FGD unit. This simulation matched that used in a recently completed IEAGHG study (IEAGHG 2019). For the cases with SO₂, the flue gas was sourced upstream of the FGD unit used in the IEAGHG study. For the brown coal cases, the flue gas composition is a rough average of that measured at the CO₂ capture pilot plant located at the AGL Loy Yang Power Station (Artanto et al. 2012).

The CO₂ capture facility was simulated with 30 wt% monoethanolamine (MEA), including 2 wt% formate as indicative of a typical heat stable salt (HSS). The production of formate was taken into account, with the thermal reclamation vessel sized to remove the HSS at the rate at which it forms, thus achieving a constant steady state level of 2 wt% formate in the absorbent. In a previous IEAGHG study (2012) the average degradation rate of MEA was determined to be 0.46 kg/tCO₂. This rate was used here as the formation rate of formate in the absorbent, assuming 1 mol MEA degrades to form 1 mol formate. For all simulations, 90% capture of the inlet CO₂ was achieved.

Standard process CO₂ capture process

The standard CO₂ capture process consists of a pre-treatment cooler, CO₂ absorber, and CO₂ stripping column. To simplify the simulation, a wash stage was not simulated downstream of the CO₂ capture stage. In practice, this stage is used to capture water and amine carried over in the exiting flue gas, maintaining the water balance of the process and limiting the amount of absorbent make-up required. Here, the simulation control-block was used to add water and amine back into the simulation lost in the gas stream exiting the absorber, maintaining steady state conditions.

A slip stream of lean absorbent is removed from the CO₂ capture section and sent to a thermal reclaimer. Thermal reclamation is often a batch process. To simulate this step here as a continuous process in the steady state model, an equilibrium flash vessel is used. Na⁺ (to replicate NaOH) is added to the absorbent stream as a 10 wt% solution. Steam (150 °C, 450 kPa-a) is then added until the MEA remaining in the waste stream is 5% of that in the inlet. The hot vapour stream exiting the reclaimer is returned to the stripping column.

A line diagram of the standard CO₂ capture process, including thermal reclamation, is provided in Figure 2.

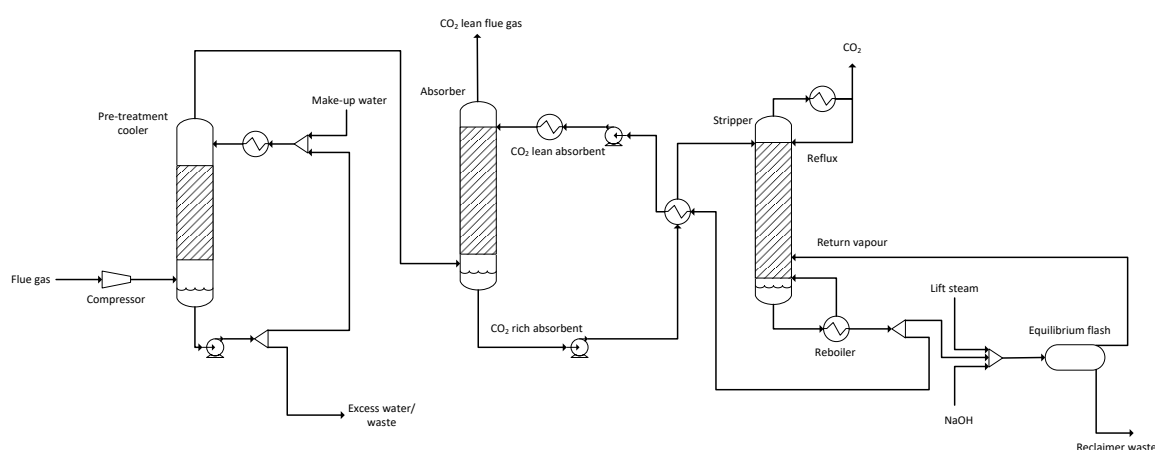


Figure 2 Flow diagram of standard liquid-absorbent based CO₂ capture process simulated. Flue gas sourced downstream of the FGD unit

CS-Cap process

The first step of the process incorporates a pre-treatment cooler to reduce the flue gas temperature, and condense excess water present in the flue gas stream. The cooled flue gas then enters the SO₂ capture step

where the CO₂ rich absorbent from the CO₂ capture stage is used to remove the SO₂ from the flue gas. In the simulation, the SO₂ and CO₂ capture steps have been simulated as separate columns. These may be combined into a single column in the real process. Pilot-scale evaluation has shown that the majority of absorbed SO₂ is quickly converted to sulfate (Pearson et al. 2017, Renoys et al. 2012). To replicate this in the simulation, a component splitter (1 in Figure 3) is used to remove 95% of the SO₂ from the recirculating absorbent. An inlet stream with a flow multiplier is then used to add an equimolar amount of sulfate back into the absorbent solution. SO₂ lean flue gas then enters the CO₂ capture section, where sulfur free amine absorbent is used to capture CO₂ from the flue gas. A stripping column is used to remove the CO₂ from the solution and regenerate the absorbent.

A portion of the recirculating sulfate-rich absorbent is separated from the SO₂ capture loop and enters the crystallisation step. Here, K⁺ (to replicate KOH) is added in 10% excess of that required to react with the sulfate present in solution. A 'black box' approach was then used to simulate the reactive crystallisation step. Experimental results achieved in the laboratory were used to determine the level of sulfate removal that could be achieved in this stage (Garg et al. 2019). A component splitter (2 in Figure 3) was then used to remove K₂SO₄ in the required quantity. The absorbent remaining after the crystallisation step is then split, with a portion of the sulfate-reduced stream being recirculated to the SO₂ capture loop. The remainder of the sulfate-reduced absorbent is then sent to a thermal reclamation step. The thermal reclamation step is the same as that described above for the standard process. However, experimental work completed in the laboratory evaluating thermal reclamation has shown that pH above 10 was required for recovery of MEA from sulfate rich solutions (Garg et al. 2018b). For simulations of the CS-Cap process, which result in high sulfate loaded absorbents, sufficient Na⁺ was added to increase the pH of the stream entering the reclaimers to 11

A line diagram of the CS-Cap process is provided in Figure 3.

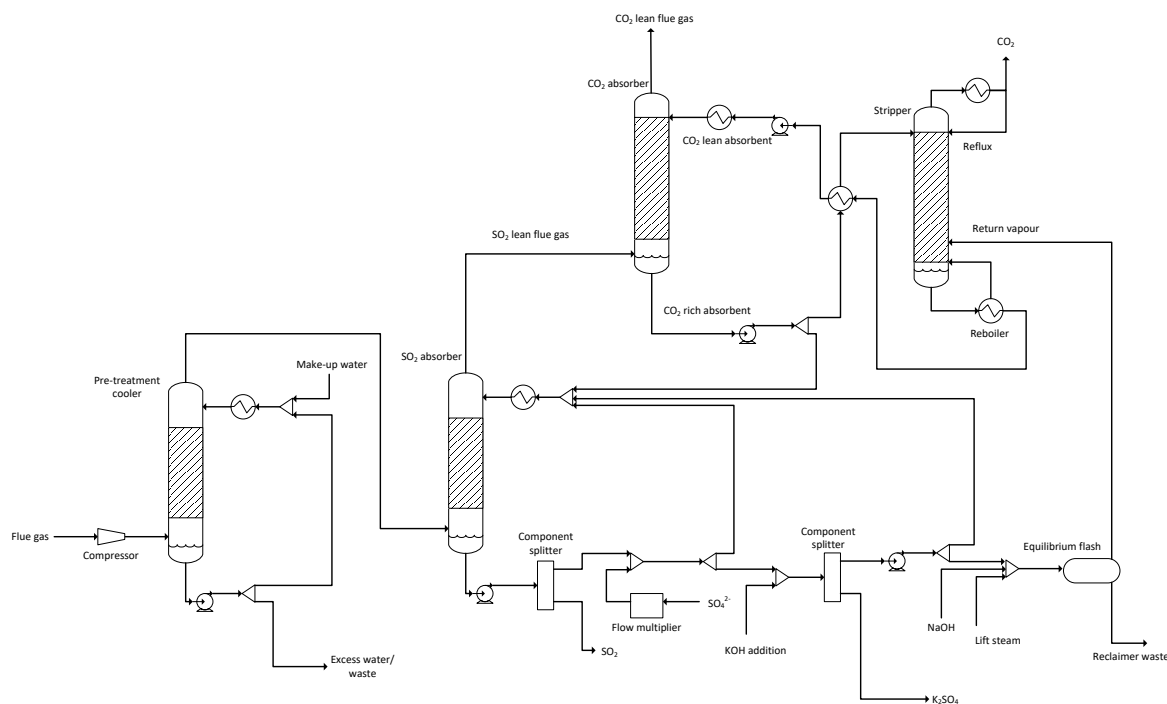


Figure 2 Flow diagram of the CS-Cap process

Initial simulations of the CS-Cap process have already been completed incorporating the SO₂ capture loop of the process only. This provided insight into the operating conditions of this novel section of the process (Cousins et al. 2018). These simulations were recently upgraded to include the full process, as outlined in Figure 3. The results of these full simulations are provided in this paper.

Results

Proof-of-concept of the CS-Cap process was completed at the Loy Yang CO₂ capture pilot plant, using a CO₂ rich MEA absorbent in the pre-treatment column for SO₂ removal. This was completed as a batch process. Initially all SO₂ was removed from the incoming flue gas. The pH of the recirculating absorbent decreased to a pH ~ 7 to 8, where it entered a buffering region. Once the absorbent was saturated with sulfur, the pH of the solution was noted to drop rapidly, and break-through of SO₂ into the flue gas leaving the column was observed (Pearson et al. 2017). The pilot-scale operation used ~2.5 mol/L MEA in the pre-treatment column to capture SO₂ from the flue gas. The batch operation resulted in saturation of the MEA solution with absorbed sulfur. This was determined by ion chromatography to be predominately sulfate (Garg et al. 2018b, Garg et al. 2019), with a concentration of approximately 10 wt% sulfate (or loading of 0.4 mol sulfate/mol MEA). Assuming the same loading is possible for higher concentrations of amine, suggests that for 30 wt% MEA (5 mol/L) a sulfate concentration up to 20 wt% should be possible.

Increasing the proportion of recycling absorbent up to 98% was possible for the simulations completed here. This led to an increase in sulfate concentration up to 15 wt% in the recirculating absorbent stream, for the simulation cases with high SO₂ concentration flue gas streams. This sulfate concentration was below the upper limit predicted from the pilot-scale operation. The pH of the recirculating absorbent was in the range 7.7 – 8. It is anticipated that increasing the recirculating absorbent flow rate (i.e. minimising the slip stream taken off for crystallisation) increases the concentration of sulfate in the solution, increasing the efficiency of the downstream separation step. Before the process is operated in reality, consideration will also have to be given towards the allowable corrosion rates of the process. Increasing sulfate loaded lowers the solution pH, increasing corrosion rates.

Laboratory scale experiments of reactive crystallisation with sulfate loaded 30 wt% MEA solutions has shown the removal of sulfate, as K₂SO₄, to increase with increasing amount of precipitant addition (in this case KOH). Where KOH is added 10% in excess of that stoichiometrically required to react with the sulfate present in solution, between 70-75% of the sulfate is removed from solution at 20-40 °C (Garg et al. 2018b, Garg et al. 2019). These laboratory experiments were completed in a structured environment as a batch process. Thus the removal of sulfate from solution might not be as efficient when the process is run continuously in a real plant. To be conservative, a lower fractional removal of 40% of the sulfate as K₂SO₄ has been assumed for all cases simulated here.

Simulation results

To observe the impact of increasing the recycle rate of absorbent in the SO₂ capture loop (increasing sulfate concentration), simulations were completed for two different recycle rates for the brown coal case with 700 ppm SO₂ in the inlet flue gas (90 and 98% of absorbent recycled). The results of these two simulations are provided in Table 2. The properties of the DCC, CO₂ absorber and stripper were found to be unaffected by the change in operating conditions of the SO₂ loop. Increasing the recirculating absorbent flow rate increased the concentration of sulfate in the absorbent solution, and also requires a larger SO₂ absorption column. Hence the improved efficiency of the crystallisation step comes at a slightly increased capital cost.

Further simulations were completed with 98% of the absorbent recycled in the SO₂ capture loop. These results, for both black and brown flue gases, are provided in Table 3.

Table 2 Effect of sorbent recirculation rate in SO₂ absorption section

	Unit	Case	
		Brown coal flue gas with CS-Cap, 700ppm SO ₂ in flue gas Low sorbent recirculation rate	Brown coal flue gas with CS-Cap, 700ppm SO ₂ in flue gas High sorbent recirculation rate
Fraction sorbent recirculated		90%	98%
SO ₂ column L/G ratio	kg/kg	0.7	1.7
pH of recirculating absorbent		7.9	7.7
SO ₂ column diameter (80% flooding capacity)		7.9	8.4

Sulfate concentration in recirculating absorbent	wt%	8.8	15.4
Waste stream from thermal reclaimer	kg/s	0.27	0.34
Sulfate in reclaimer waste	kg/s	0.06	0.12
NaOH addition required to thermal reclaimer	kg/s	0.3	0.1

Table 3 Properties of standard CO₂ capture plant and plant employing CS-Cap process for both brown and black coal flue gases

	Unit	Case				
		Base Case USPC Black coal with FGD	USPC black coal with CS-Cap, 200ppm SO ₂ in flue gas	USPC black coal with CS-Cap, 700ppm SO ₂ in flue gas	Brown coal flue gas with CS-Cap, 200ppm SO ₂ in flue gas	Brown coal flue gas with CS-Cap, 700ppm SO ₂ in flue gas
DCC diameter	m	10.9	9.9	9.8	10.3	10.3
DCC L/G	kg/kg	2.7	2.2	2.2	2.6	2.6
SO ₂ ABS diameter	m	N/A	8.6	8.7	8.1	8.4
SO ₂ ABS L/G	kg/kg	N/A	1.0	1.5	0.8	1.7
CO ₂ ABS diameter	m	11.0	11.0	11.0	10.6	10.6
CO ₂ ABS L/G	kg/kg	2.5	2.5	2.5	2.7	2.7
STR diameter	m	6.3	6.3	6.3	5.7	5.7
Reboiler duty	kW	160.6	145.5	138	120.7	111.8
Total thermal energy	kW	170.4	168.2	167	136.9	136.1
Total thermal energy	MJ/kgCO ₂	3.4	3.3	3.3	3.5	3.5
Absorbent flow to crystallisation	kg/s	N/A	5.2	8.2	4.1	8.5
Sulfate concentration	wt%	N/A	6.4	14.6	8.9	15.4
Absorbent flow to thermal reclamation	kg/s	0.81	1.1	1.5	0.7	1.3
pH absorbent SO ₂ loop		N/A	7.9	7.7	7.9	7.7
pH into thermal reclamation		11	11	11	11	11
Waste stream	g/s	108.0	256.1	402.3	192.8	340.5
Waste stream H ₂ O	g/s	33.5	69.7	84.6	49.6	69.1
Waste stream CO ₂	g/s	16.7	33.8	12.4	20.9	7.0
Waste stream MEA	g/s	12.8	12.7	13.2	9.9	9.9
Waste stream SO ₄ ²⁻	g/s	0.0	40.6	132.4	36.7	118.7
Waste stream formate	g/s	17.0	17.1	17.2	13.1	13.3
Waste stream Na ⁺	g/s	28.0	43.0	18.0	27.3	9.5
Waste stream K ⁺	g/s	0.0	39.2	124.4	35.4	113.0
NaOH addition	kg/s	0.28	0.43	0.18	0.27	0.09
KOH addition	kg/s	N/A	0.3	1.0	0.3	1.1
K ₂ SO ₄ produced	kg/s	N/A	5.1	18.0	5.5	19.7

The higher moisture content of the brown coal flue gas is the main difference between the brown and black coal cases. This moisture was removed in the DCC to avoid dilution of the downstream SO₂ absorption loop. This resulted in a larger DCC requirement for the brown coal case, and a smaller downstream flue gas flow rate then entering the SO₂ and CO₂ absorption columns. As the flue gas SO₂ concentration increased, the concentration of sulfate in the absorbent in the SO₂ capture loop also increased. It is likely that this will affect the efficiency of the crystallisation step, but that was not investigated as part of the simulations completed here.

The higher absorbent recirculation rates leads to a small effect on the SO₂ absorber column size. Despite the increase in sulfate concentration, the pH in the recirculating absorbent remained within the buffering region observed during the pilot plant operation. At the pilot plant, breakthrough of SO₂ into the flue gas exiting the SO₂ absorption section was not observed until the absorbent was fully saturated with sulfate, and a sharp drop in pH was observed. Whilst in the buffering region, all SO₂ was removed from the flue gas. This is

observed in the simulations here with SO₂ in the flue gas exiting the SO₂ absorption section being below 0.1 ppm in all cases.

The flow rate entering the thermal reclaimer was sized such that it removed the formate anticipated to be formed during the CO₂ capture process. As the concentration of sulfate in the solution increased, a higher mass flow of absorbent was sent to the reclaimer for both the brown and black coal cases. This then required a higher energy input to the reclaimer to meet the criteria of only 5% of the inlet MEA in the waste stream. In the simulations completed here, this higher energy input is recovered by recycling the reclaimer vapour stream to the stripping column, resulting in the overall thermal energy requirement being roughly similar for the 200 and 700ppm flue gas cases. Such thermal efficiency might not be completely effective in a real process.

As the concentration of sulfate in the absorbent increased, the K⁺ addition necessarily also increased. Some of the excess, unreacted K⁺ then passed to the thermal reclamation circuit, resulting in a lower amount of Na addition to achieve pH 11 in the absorbent sent for reclamation. However, as KOH is typically a higher cost commodity than NaOH, the reduced NaOH usage resulting from KOH addition may not be favourable. An economic assessment is required to determine if the increased operating costs of the CS-Cap process outweigh the reduced capital costs achieved by the process. This economic comparison is to be the focus of a subsequent paper.

Finally, it should be noted that as only 95% conversion of SO₂ to sulfate was assumed, this left some residual SO₂ entering the thermal reclaimer in the simulation. This SO₂ was released with the vapour stream, entering the CO₂ stripping column. Thus, despite the flue gas being SO₂ free, SO₂ can still enter the CO₂ capture loop if any unreacted SO₂ remains in the absorbent sent to the reclaimer.

Conclusions

Combined capture of CO₂ and SO₂ from flue gases is being explored as a potentially lower cost method for reducing gaseous emissions from coal-fired power plant. This could be advantageous in countries such as Australia, that don't currently employ flue gas desulfurisation (FGD) at coal-fired power stations. Removing the requirement for FGD could impart significant capital savings for the overall capture process.

The CS-Cap process combines the removal of CO₂ and SO₂ from flue gas streams. This process however results in the generation of an amine absorbent rich in sulfate that requires regeneration to allow for a continuously operating process. A possible method for recovering the sulfate from amine absorbents is to use reactive crystallisation. Simulation of the CS-Cap process has been explored in this paper to provide information that will allow an economic comparison to be made to a standard CO₂ capture process combined with flue gas desulfurisation in the future. Results show that increasing the recirculation rate of absorbent in the SO₂ capture loop will increase the concentration of sulfate in the absorbent, anticipated to improve the efficiency of any downstream removal step. The overall energy requirement of the CO₂ capture process does not appear to be significantly affected by the addition of the SO₂ capture stage. There will however be an increase in the operating costs as KOH addition is required to remove the sulfate from the aqueous amine absorbents.

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Glossary

AMP	Amino Methyl Propanol
FGD	Flue gas desulfurisation
HSS	Heat stable salts
MEA	Monoethanolamine
O&M	Operating and maintenance
PCC	Post combustion capture
SCR	Selective catalytic reduction
TPC	Total plant cost

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