

# Regeneration of sulfate-rich postcombustion capture amines through reactive crystallisation

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## Abstract

Flue gas desulfurisation is a prerequisite for successful CO<sub>2</sub> capture in coal-fired power stations utilising aqueous amine absorbents. For nations like Australia, where there is nonexistence of mandatory flue gas desulfurisation, this increases the cost for power plants retrofitting CO<sub>2</sub> capture. The CSIRO's CS-Cap process, a potentially low cost method for combined CO<sub>2</sub> and SO<sub>2</sub> capture, provides an alternate sulfur management solution to such plants. The CS-Cap process, however, results in high sulfur-loaded amines that require continuous regeneration to retain cost benefits. Reactive crystallisation by KOH addition is shown to be successful in removing the bulk of the sulfate from aqueous amines without any additional heating or cooling requirements. Increasing initial sulfate loading by amine recycling initially improves sulfate removal efficiency, up to the postsaturation level where the systems ionic strength determines further sulfate solubility. Oxidative amine degradation had no significant effect on the precipitation efficiency or purity of K<sub>2</sub>SO<sub>4</sub> crystals apart from their slight discoloration. The behaviour of the residual potassium in these 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, CS-cap process, flue gas desulfurisation, MEA, precipitation

## 1 | INTRODUCTION

Combined capture of SO<sub>2</sub> and CO<sub>2</sub> offers capital and energy benefits and is considered a next generation postcombustion capture (PCC) process.<sup>1</sup> Companies like Shell Cansolv, Union Carbide and Babcock & Wilcox provide processes that combine the capture of SO<sub>2</sub> and CO<sub>2</sub>. The integration is either infrastructural, through heat integration or using single or dual absorbent loops to capture the acid gases from various

emission sources.<sup>2–4</sup> Saskpower's Boundary Dam plant incorporates the Shell Cansolv process in the first commercial scale PCC unit applied to a coal-fired power station. At Boundary Dam, the CO<sub>2</sub> and SO<sub>2</sub> are captured in separate loops using different amines, and the captured SO<sub>2</sub> can be used to produce H<sub>2</sub>SO<sub>4</sub>.<sup>5</sup>

The CSIRO's CS-Cap process is a similar combined capture process that utilises the chemical nature of basic amines being highly selective for SO<sub>2</sub> absorption over CO<sub>2</sub>.<sup>6</sup> Here, the absorption of CO<sub>2</sub> and SO<sub>2</sub> 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.

The upstream removal of acidic gases like  $\text{SO}_2$  and  $\text{NO}_x$  is essential as they degrade the performance of amine-based PCC. Here the CS-Cap process eliminates the requirement for a separate FGD pretreatment unit by combining the removal of  $\text{SO}_2$  and  $\text{CO}_2$  into a single absorber column. The upper section of the column captures the  $\text{CO}_2$ , whereas the lower section captures  $\text{SO}_2$ . The flue gas is effectively 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  $\text{CO}_2$  rich absorbent from the upper section of the column. This absorbent is recycled in the lower part of the column to capture  $\text{SO}_2$ . The S loaded absorbent is sent for reclamation (i.e., the removal of absorbed  $\text{SO}_2/\text{SO}_4$ ) so that it can be re-used. 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.<sup>6–8</sup>

More than 97% of the  $\text{CO}_2$  rich amine exiting from the top section of the absorber column is sent to the stripper for thermal removal of the  $\text{CO}_2$ . 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. Although the  $\text{CO}_2$  stripping is a standard regeneration process, optimal  $\text{SO}_2$  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  $\text{O}_2$  concentration in the flue gases (typically 5–8 vol.%), the absorbed  $\text{SO}_2$  is converted into heat stable  $\text{SO}_4^{2-}$  salts

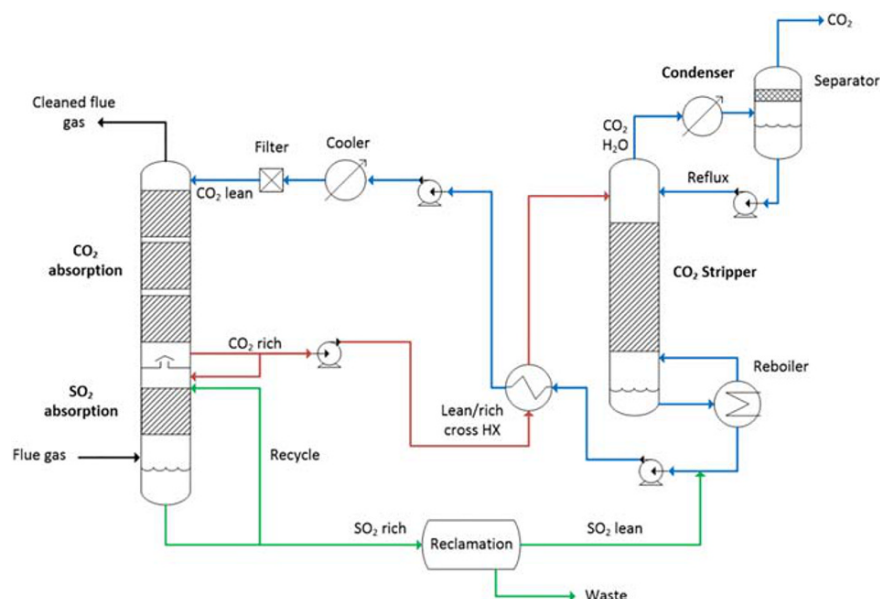
that cannot be reversibly converted back to  $\text{SO}_2$  via the conditions used for standard  $\text{CO}_2$  stripping.

### 1.1 | CS-Cap's sulfur-rich pilot plant absorbent

In a standard FGD unit, the sulfur gases typically react with limestone slurry producing gypsum, which does not require any regeneration process. In contrast, the CS-Cap technology utilises a small portion of the  $\text{CO}_2$  rich amine to capture  $\text{SO}_2$  and rapidly producing unsaleable sulfur-rich amine waste from valuable PCC amines. Hence, effective low cost amine regeneration is necessary. The properties of 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. The heat stable salt concentration in a PCC unit in a coal-fired power plant is usually <5,000 ppm,<sup>4</sup> whereas in CS-Cap process, the HSS concentration is 11–12 wt%.

As a proof of concept, CSIRO's pilot plant at AGL's Loy Yang power station in Victoria, Australia, demonstrated  $\text{SO}_2$  capture using  $\text{CO}_2$  loaded amines. The successful trial showed the full and rapid absorption of  $\text{SO}_2$  into the  $\text{CO}_2$  rich aqueous monoethanolamine (MEA), when exposed to raw plant flue gases directly after electrostatic precipitation (ESP), that is, with no prewash step. This  $\text{SO}_4^{2-}$  rich MEA is referred to as "pilot plant sample (PS\_14)."

The pilot plant sample serves as a model to investigate various regeneration techniques enabling practicable desulfurisation. These techniques were identified through



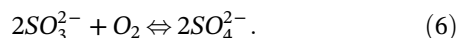
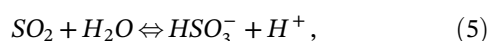
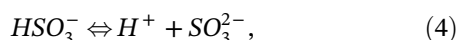
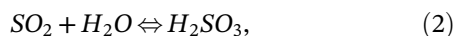
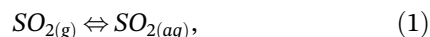
**FIGURE 1** Process flow diagram of the CS-Cap process<sup>7</sup>

an earlier literature review.<sup>9</sup> Xu and Rochelle<sup>10</sup> identified crystallisation as one of the techniques to reduce the cost of PCC. Sulfate-rich amine absorbents were tested with KOH as the precipitating agent. The solubility behaviour of potassium sulfate ( $K_2SO_4$ ) was studied by varying temperature,  $CO_2$  loading and amine concentration. The CASPER ( $CO_2$ -capture And Sulphur Precipitation for Enhanced Removal) process investigated low temperature precipitation of  $K_2SO_4$  from an amino acid salt solution. The Siemens Post-Cap  $CO_2$  capture process used an amino acid absorbent and precipitation to remove sulfate as potassium sulfate. They found that crystallisation rates decreased in degraded samples compared with fresh laboratory prepared samples, highlighting the need to evaluate new technologies under realistic conditions. The previous work on crystallisation in a PCC process is discussed in more detail in our previous publication.<sup>9</sup>

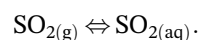
For completeness, the key reaction chemistry is outlined below.

### 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 flue gas  $SO_2$  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.<sup>11,12</sup>



### 1.1.2 | Amine reactions

Figure 1 reveals the  $CO_2$  loaded absorbent regenerates through thermal stripping by exposing 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 expected to be present.

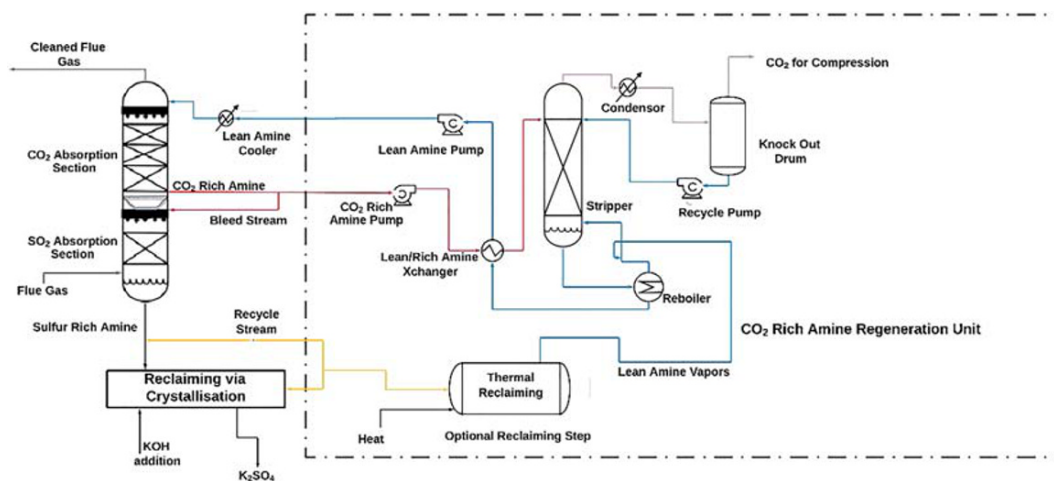
### 1.1.3 | pH

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  $SO_2$ ,<sup>7</sup> as no amine make-up was added to the column. Instead, the absorbent recirculated until it became fully saturated. It is 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

Due to their high sulfate loading, reactive crystallisation is a promising regeneration technique (Figure 2) for CS-Cap absorbents. This paper experimentally evaluates reactive crystallisation by chemical super saturation of sulfate loaded MEA with KOH. Alkali sulfate salts precipitate as soon as sufficient alkali hydroxide (KOH) is added. The by-product ( $K_2SO_4$ ) 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.

Due to recycling of the sulfur-rich absorbent (Figure 2), it not only gets richer in sulfate but in other degradation products as well. Alkali addition will primarily remove sulfate from the amine absorbent resulting in other soluble degradation products accumulating over time. Hence, an additional reclaiming process might be required after a certain time period.



**FIGURE 2** CS-Cap process sulfur loop regeneration scheme utilising reactive crystallisation

The results from other researchers<sup>10</sup> and our previous work<sup>7</sup> 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 CO<sub>2</sub> loading.<sup>10</sup> Most of this research was conducted on amines prepared synthetically in the laboratory. Their CSIRO pilot plant MEA had only limited exposure to real flue gases (200 h). Laboratory research into crystallisation behaviour needs to include more degradation products and contaminants that may reflect real process conditions. The initial precipitation results by Pearson et al.<sup>7</sup> revealed a reduction in sulfate removal efficiency for pilot plant sample (PS\_14) (200-h operation) compared with 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<sup>7</sup> focussed on determining whether reactive crystallisation is effective in desulfurising loaded amines, at various temperatures, amine concentrations and initial sulfate loadings. Here, crystallisation experiments are conducted on pilot plant sample (PS\_14), PS\_14 dosed with degradation compounds and MEA with tailored levels of sulfate and amine. The aim's 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

## 2 | EXPERIMENTAL

Previous work<sup>7,10</sup> 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. Here, the mass balance method is only used to investigate the yield and quality of crystals produced under one set of conditions. Most data are collected from a more efficient continuous laboratory precipitation experiment. The continuous method differs from 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 (PS\_14)

The origin of the sulfur-loaded aqueous amine absorbent is detailed in previous work.<sup>7</sup> The SO<sub>2</sub> loading continued in the pilot plant until the MEA became saturated.

#### 2.1.2 | Synthetic samples

Synthetic amine samples were prepared in the laboratory with varying amine concentrations. Aqueous 5 M

(~30 wt%) and 6.5 M (~40 wt%) MEA concentrations were prepared using neat MEA (purity 98%) from Sigma Aldrich diluted with Milli-Q water. The CO<sub>2</sub> was loaded by bubbling CO<sub>2</sub> through the aqueous MEA using a Dreschel bottle with a sintered frit. The CO<sub>2</sub> was presaturated with water to minimise the effect of evaporation from the gas flow.

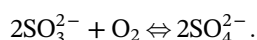
CO<sub>2</sub> loading is expressed as

$$\text{CO}_2 \text{ Loading } (\alpha) = \frac{\text{moles of CO}_2}{\text{moles of MEA}}.$$

Aqueous MEA CO<sub>2</sub> loading of 0.5 was confirmed gravimetrically. After the addition of CO<sub>2</sub>, the SO<sub>4</sub> was loaded using H<sub>2</sub>SO<sub>4</sub> (ACI Labscan, 94% purity). On the addition of H<sub>2</sub>SO<sub>4</sub>, as expected, some of the absorbed CO<sub>2</sub> was spontaneously released. The mass decrease of the total solution was assumed to be entirely due to CO<sub>2</sub> loss. CO<sub>2</sub> loading and amine concentrations were then recalculated based on the new weight. Here, the process of CO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> loading is a lab scale representation of the CS-Cap process, where the CO<sub>2</sub> rich solution absorbs flue gas SO<sub>2</sub>. Typically, very little CO<sub>2</sub> will remain in the CS-Cap's small stream (sulfur-rich amine stream in Figure 2) while it absorbs SO<sub>2</sub>. This was evident through the lab experiments, which calculated a new loading of 0.21 mol (CO<sub>2</sub>)/mol (MEA) for 5-M MEA solutions upon addition of H<sub>2</sub>SO<sub>4</sub> to the CO<sub>2</sub> loaded solution.

## 2.2 | Sulfite/sulfate analysis

Sulfate was determined using a Metrohm 930 compact IC Flex chromatograph fitted with a 20-μl loop, with Metrosep A Supp 16 anion column –250/2.0. The mobile phase was 0.75-mM sodium carbonate (BDH Chemicals, >99% purity) and 0.75-mM sodium hydroxide (Chem-Supply, >98% purity), and the flow rate was 0.2 ml/min. Similarly, where sulfite analysis was required, the anion eluent (Na<sub>2</sub>CO<sub>3</sub> + 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).<sup>11,13</sup> One per cent to 5% formaldehyde (Chem-Supply, 37% purity) 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-μl loop, with Metrosep A Supp 16 anion column –250/2.0. The mobile phase 0.75-mM sodium carbonate (BDH Chemicals, >99% purity) and 0.75-mM sodium hydroxide (Chem-Supply, >98% purity), and the flow rate was 0.5 ml/min; 600 μl of 5 N NaOH (Chem-Supply, >98% purity) was added to 500–550 mg of each sample and stored in the dark overnight to hydrolyse amides. 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 anions

The IC procedure used was similar to that used for sulfate analysis. The multielement standards (high purity standards, Sigma Aldrich, i.e., multielement IC std. 2-solution A) were used for instrument calibration.

## 2.5 | Metals and cations

ICP-MS analysis was conducted on the PS<sub>14</sub> samples. Preweighed absorbent samples were acidified with 1:1 HNO<sub>3</sub> (70% analytical grade, ACI Labscan and deionised water, Milli-Q Academic, Millipore) and diluted to 100.0 ml with 1% HNO<sub>3</sub>. Prior to analysis, samples were diluted a further 2:5 (v:v) in 1% HNO<sub>3</sub>. Standards were prepared from a mixed metals and cations standard (Sigma Aldrich multielement standard solution 5 for ICP) in 10% HNO<sub>3</sub>. 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 | X-ray diffraction analysis

X-ray diffraction (XRD) analyses were carried out for PS<sub>14</sub> precipitates on a Panalytical X'Pert Pro powder diffractometer, equipped with an incident beam BBHD CoKα monochromator and an X'Celerator linear detector, operated at 40 kV and 25 mA and scanned over 5–80° 2θ with a step size of 0.017° 2θ at a rate of 0.08° 2θ 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 100 g of CO<sub>2</sub> loaded (initially 0.50 mol CO<sub>2</sub>/mol MEA) aqueous MEA solution (either 5.0 M or 6.5 M) was weighed into a beaker. The solution was loaded with SO<sub>4</sub><sup>2-</sup> (115 g/1,000 g) by adding H<sub>2</sub>SO<sub>4</sub> (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 SO<sub>4</sub><sup>2-</sup> present in the solution. The solution was then heated to the desired temperature and stirred for 1 h. After 1 h, 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 stirred and heated to the next target temperature and held for 1 h before taking another liquid sample and so on. The samples withdrawn at each temperature were analysed via IC for SO<sub>4</sub><sup>2-</sup> concentration giving a direct measure of residual SO<sub>4</sub><sup>2-</sup> and an indirect measure of sulfate crystal recovery. KOH addition varied between 80% to 160% of stoichiometric requirements for 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 110 g/kg ± 10 g/kg and 2–3 g/kg ( $R^2 > 0.99$ ; relative standard deviation <6%). The lower concentration of sulfite compared with sulfate confirms that most of the absorbed SO<sub>2</sub> was converted into SO<sub>4</sub><sup>2-</sup>. PS\_14 organic anion measurements are provided in Table S1. Niederaussem pilot plant data are included there for comparison. Table S1 reveals, by its lower formate, oxalate and acetate levels in PS\_14, the lower MEA degradation level in the CS-Cap pilot campaign, in accord with its 200 operational hours compared with Niederaussem's 5,000 h.

Inorganic multianions (metals and cations) are listed in Tables S2 and S3, for PS\_14 and aged MEA from the same pilot plant. Despite its lower operational hours, the PS\_14 absorbent sample reports higher levels of chloride (0.435 vs. 0.167 g/kg) and some metals (i.e., Cu, Mn and Ni) than the 700 h sample generated at the same pilot plant. This is likely a result of the lack of caustic wash pretreatment used in the CS-Cap campaign. This will have removed other acid gases (including HCl) and fly ash from the flue gas before it entered the CO<sub>2</sub> capture plant.

### 3.2 | Effectiveness of reactive crystallisation in removal of sulfate

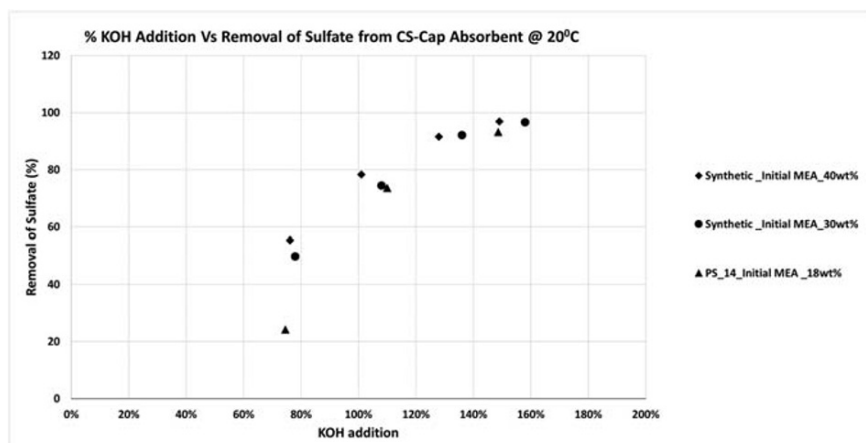
Unlike the pilot plant campaign, a conceptual CS-Cap plant would not allow sulfate saturation of its amine leading to SO<sub>2</sub> breakthrough in real plant operation. There will always be varying SO<sub>4</sub><sup>2-</sup> concentrations entering the regeneration unit due to recycling the absorbent and changes in flue gas SO<sub>2</sub> 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. Here, synthetic 5 M and 6.5 M solutions loaded with CO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup> are compared 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 controlling the residual sulfate concentration of the MEA returning to the capture loop.

#### 3.2.1 | Effect of KOH addition

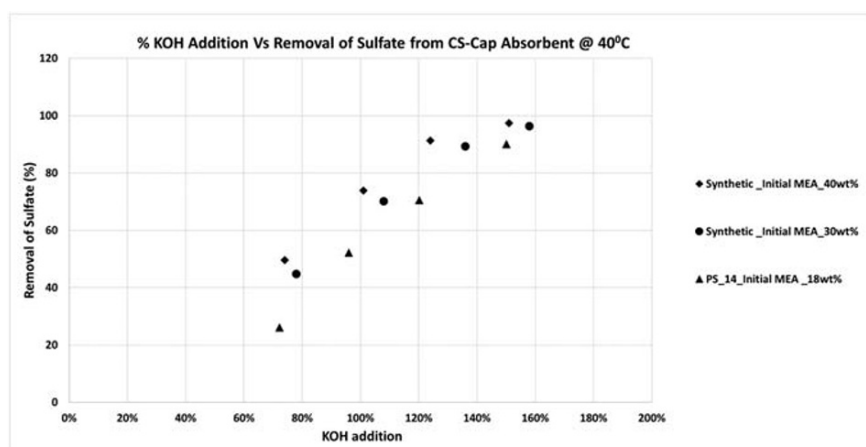
Figures 3 and 4 reveal that precipitation is effective in removing sulfate from synthetic and pilot CS-Cap MEA absorbents at 20°C and 40°C. More than 90% of sulfate removal is possible through this technique with excess KOH driving higher yields. The pilot plant sample follows a similar trend to the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

The increased solubility resulting from the more energy efficient 40°C crystalliser temperature has only a minor negative impact on sulfate removal. A typical reduction (Figures 3 and 4) from 75–79% to 70–75% is observed at 100–120% KOH addition.

**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



### 3.2.2 | Effect of MEA concentration

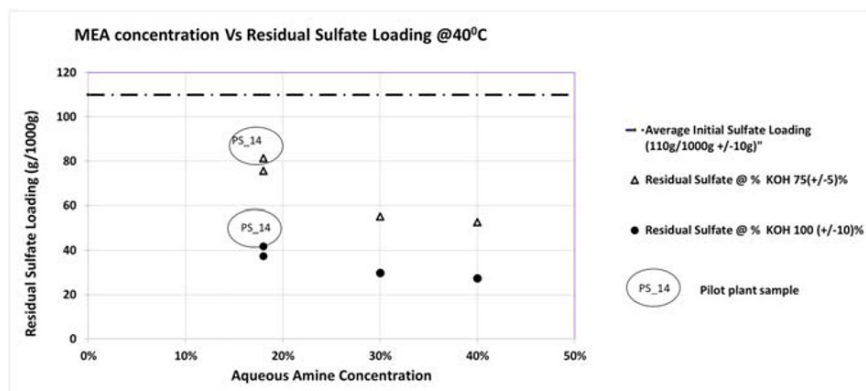
Experiments were conducted to investigate the impact of varying MEA concentrations at a particular temperature, initial sulfate loading and KOH addition. Figure 5 reveals that the residual sulfate (in solution) after harvesting the crystalline  $K_2SO_4$  was highest in the pilot plant sample (PS\_14). Synthetic samples at the same PS\_14 amine concentration produced comparable values. In contrast, the higher concentration synthetic amines (30 and 40 wt%)

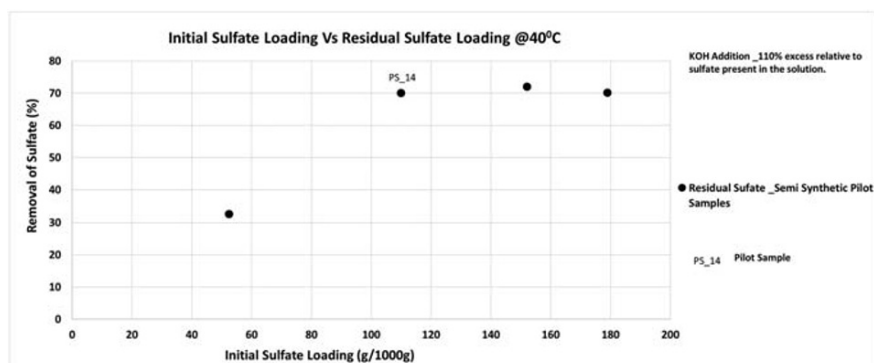
produced significantly lower residual sulfate concentrations as the sulfate solubility decreases on increased amine concentrations.

### 3.2.3 | Effect of initial sulfate loadings

Figure 6 reveals a plateau in sulfate removal efficacy with increasing initial sulfate loading. The measured values were 32% sulfate removed at 5.2% w/w initial sulfate

**FIGURE 5** Effect of MEA concentration on reactive precipitation in removal of sulfate from the CS-Cap absorbent at 40°C





**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

loading and almost constant 70% sulfate removal at 11, 15 and 18% w/w initial sulfate loadings. Our data are consistent with that of Xu<sup>14</sup> who investigated the impact of conductivity on sulfate concentration in similar MEA systems. Xu found<sup>14</sup> that conductivity increases up to saturation, and then its behaviour is dependent on the ionic composition and strength of the solution. Conductivity heavily depends on the ionic strength, which then determines sulfate solubility. These data are important from a PCC process engineering design perspective in that they confirm 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. As a large amount of KOH is used in the CS-Cap process to get a satisfactory sulfate separation, an initial techno economic study has been conducted.<sup>15</sup> This study supported the feasibility of using KOH in such quantity and confirms crystallisation's potential role in lowering the cost of  $\text{CO}_2$  capture in plants processing low sulfur flue gases.

### 3.3 | Investigation of $\text{K}_2\text{SO}_4$ obtained out of reactive precipitation

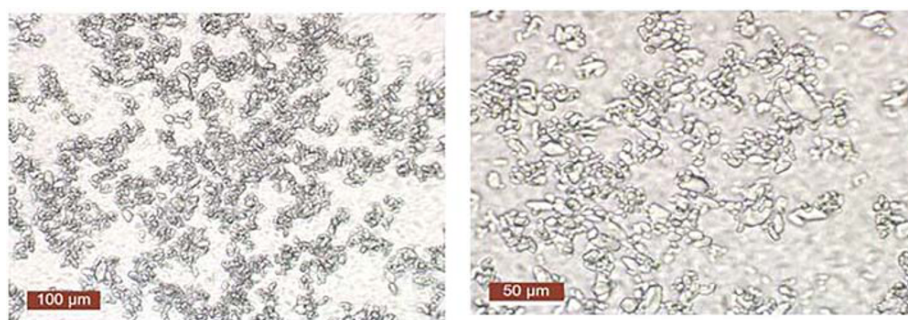
One of the attractions of precipitation as a reclamation technology is the potential to sell the  $\text{K}_2\text{SO}_4$  produced for use in fertiliser or glass manufacture. To provide further

information on the quality of the PS\_14 precipitates; they were evaluated by XRD, light microscopy and laser particle sizer. The particle size data suggested that precipitates ranged between 10 and 150  $\mu\text{m}$ . This is a large size distribution range, suggesting that these precipitates form flocs. As a result, the precipitates were also evaluated using light microscopy (images in Figure 7).

$\text{K}_2\text{SO}_4$  crystals can have orthorhombic or hexagonal symmetry depending on preparation conditions. Figure 7 reveals pictures of the crystals suggesting that they have formed 50–110  $\mu\text{m}$  flocs. This was confirmed by XRD data (Figure S1) revealing a spectrum consistent with highly pure synthetic arcanite (orthorhombic polymorph of potassium sulfate) crystals less than 40  $\mu\text{m}$  in length. Figure S1 presents an XRD spectrum of the  $\text{K}_2\text{SO}_4$  precipitate generated from a PS\_14 solution at 40°C. The only crystalline phase identified is orthorhombic  $\text{K}_2\text{SO}_4$ , confirming the structure observed in the microscopy images. XRD analysis confirms that 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 | Crystallisation rate experiments

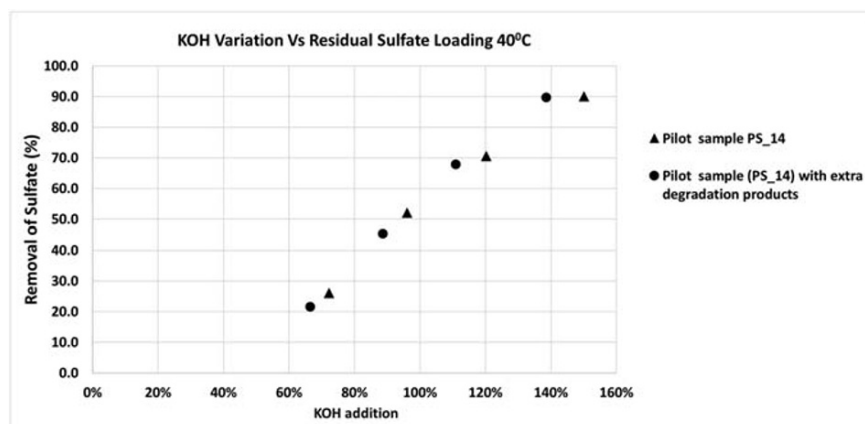
In order to size a crystalliser to generate the  $\text{K}_2\text{SO}_4$  product as part of a continuous process, information is required on the rate with which the crystals form. This



**FIGURE 7** Light microscope images at two magnifications of  $\text{K}_2\text{SO}_4$  crystals produced during precipitation experiments



**FIGURE 8** Effect of degradation products on precipitation of sulfate from PS<sub>14</sub>



information will also be required for process optimisation and economic evaluation. Precipitation experiments were performed with solution samples removed periodically over 1 h 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 S4 for pilot plant samples and Table S5 for lab prepared 6.5 M (~40 wt% MEA) synthetic samples. These tables reveal that precipitation reaction is rapid, with the majority of sulfate removal occurring within 5 to 15 min. This fast reaction rate is observed for both laboratory and pilot plant samples. A fast reaction rate suggests smaller sized equipment for the crystallisation process.

An important consideration when selecting a CS-Cap process reclamation technology is whether the technology should be batch or continuous. The high sulfate achieved is advantageous for batch wise crystallisation; however, the quick reaction time aligns with continuous operation. Further research into these options is warranted, given that reactive crystallisation offers not only an ease of operation but also potential energy savings. These savings result from bulk crystalline sulfate removal requiring less heating or cooling compared with a similar scale thermal process (at 110–120°C). In commercial crystallisation, the heat of the KOH addition 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.

### 3.5 | Effect of degradation on appearance and purity of K<sub>2</sub>SO<sub>4</sub> crystals

Our previous publication<sup>16</sup> found that higher amine degradation product concentrations had no impact on sulfate removal from pilot plant samples. As described in Section 3.1, PS<sub>14</sub> does not contain 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<sub>14</sub> to raise its 0.1 wt% organic anions concentration to 1 wt%. 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 (Figures S2 and S3) of crystals obtained from the initial and extra-degraded pilot plant samples. The colour of crystals generated from degraded 5 M and 6.5 MEA solutions, however, is darker as an effect of their higher degraded amine concentration. 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 the higher level of degradation products in the initial amine absorbent.

## 4 | CONCLUSIONS

Increasing initial sulfate loading by amine recycling improves sulfate removal efficiency, up to the postsaturation level where the systems ionic strength determines further sulfate solubility. Recycling the absorbent is only beneficial for the CS-Cap process up to the level where sulfate recovery stabilises.

The lower energy requirement and short reaction time (<15 min) 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 K<sub>2</sub>SO<sub>4</sub> precipitate, which is potentially saleable. Amine degradation has no significant effect on the purity of the crystals; however, their colour could be an issue in commercial plants requiring a final saturated K<sub>2</sub>SO<sub>4</sub> wash to whiten the product. One limitation of the process is that the mother liquor separated during filtration will still contain nonionic degradation products that could not be removed through precipitation. Hence, there

might be a requirement of additional reclaiming of the absorbent on a batch basis.

Overall, reactive crystallisation has been demonstrated as a prospective technology for removing the high sulfur content, as sulfate, from aqueous amines.

## 5 | FUTURE WORK

The pilot and lab MEA systems investigated here are limited in scope. Commercial scale plant amine concentrations will be higher, around 30–40 wt%, and likely contain other impurities built up under long-term operation. The effect of degradation products on sulfate precipitation and crystal purity generated from higher concentration amines and highly degraded amines requires further evaluation. The impact of recycle rate and residence time on crystal size also needs an investigation.

A computer simulation of the precipitation process, that is, feeding system, crystallisation, and filtration and drying, to enable further process optimisation is required. Such a model would evaluate costs for options including batch versus continuous operation. The data provided here assisted with the generation of a preliminary Aspen Plus simulation and its validation (publication underway). Material and energy balances generated through such a model can aid in monitoring the concentration of potassium at all times during amine recirculation.

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 apparatus/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 is tailored to the incoming sulfate concentrations. A steady state Aspen Plus simulation model as mentioned above provides basic information on potassium concentration. However, a dynamic state model is required to better understand the parameters controlling potassium concentration as solvent is recycled. Understanding the impact of K will also be useful in designing a better chemical dosing system and overall process operation.

Though the reaction time experiments revealed that most of the sulfate present in the solution reacts with potassium within the first few minutes, they do not provide information on rate of the reaction. Future work should also focus on determining the rate kinetics for the amine regeneration reaction to assist in

reactor/crystalliser design. The measurements of particle size distribution and magma density would help determine such kinetics.

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## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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