Removal of sulfate from wet FGD wastewater by co-precipitation with calcium hydroxide and sodium aluminate

Jicheng Yu, Jia Lu and Yong Kang

ABSTRACT

Chemical precipitation method was adopted to remove sulfate from wet flue gas desulfurization (FGD) wastewater and mixtures of Ca(OH)₂ (CH) and NaAlO₂ (SA) were used as precipitants. The mechanisms of sulfate removal were explored according to the experimental and simulated results. These showed that three kinds of precipitations, which were gypsum, ettringite and co-precipitation onto aluminum hydroxides, were formed when sulfate in water reacted with CH and SA. The optimum operation condition for removing sulfate was that the molar ratio of CH/SA was 2, the initial pH value 5, the precipitant dosage 15 g/L, the reaction time 20 min, and the reaction temperature 55°C. The sulfate was reduced from 4,881 mg/L to 784 mg/L under the optimized condition. In addition, the heavy metals and fluoride were also mostly removed. The post treatments of the supernatant illustrated that removal of sulfate from wet FGD wastewater by co-precipitation with CH and SA was a better choice.

Key words | chemical precipitation, sulfate removal, wet FGD wastewater

INTRODUCTION

The wet flue gas desulfurization (FGD) technologies have extensive applications in coal-fired power plants for controlling SO₂ emissions (Cordóba 2015). As a common wet FGD technology, SO₂ in the flue gas reacts with alkaline slurry (lime or limestone) in an absorber, and is converted into sulfate. Then the calcium sulfate slurry is converted into gypsum in an oxidation reactor (Srivastava & Jozewicz 2001; Higgins et al. 2009). To prevent accumulation of chloride ions and keep high efficiency of desulfurization, the waste FGD slurry is discharged and the wet FGD wastewater, which is abundant in dissolved calcium, sulfate, sulfite, suspended solids and other trace pollutants, is formed. The high concentration of sulfate in FGD wastewater will lead to many problems, such as promotion of corrosion and scaling in pipes, structures and equipment, deterioration of the soil and effects on agricultural irrigation and water resources (Silva et al. 2010; Silva & Rubio 2011). Therefore, removal of sulfate from wet FGD wastewater is necessary.

Removal of sulfate is a rather complex problem due to the high solubility and stability of sulfate salts in aqueous solution. Various methods have been discussed on treating high concentrations of sulfate in wastewater. The biological degradation method is widely utilized in sulfate removal (Biswas et al. 2010; Hao et al. 2014). The costs are low and is easy to operate. Besides, the heavy metals can be removed by co-precipitated with sulfon. But this takes a long residence time and needs large reaction equipment, and the process is suited to low or moderate sulfate loadings (Silva et al. 2012). Membrane separation is widely used in desalination and water recycling, which takes a short time and shows high efficiency (Elghaffar & Tieama 2017). However, it has to face an obvious challenge of scale formation on the membrane surface, especially in treating the aqueous solution, which is rich in sulfate, silicate and calcium (Lee et al. 2011). Adsorption and ion exchange are of high efficiency, and the costs are lower than membrane separation. But the two methods require frequent bed regeneration, and they also have to overcome scale formation on sorbents (Moret & Rubio 2003; Silva et al. 2012). Compared with the above methods, the chemical precipitation method can be a better method although it has a few disadvantages. The main disadvantage of the chemical precipitation method is the production of large quantities of sludges, which are difficult to handle.

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There are reports on various chemical precipitation methods for sulfate removal in virtue of formation of gypsum, barium sulfate, lead sulfate or ettringite precipitations \((Ca_6Al_2(SO_4)_3(OH)_{12}\cdot26H_2O)\). Compared with barium or lead sulfate, the removal efficiency of sulfate by forming gypsum is not high, because the formation of gypsum depends on the composition and ionic strength of the aqueous solution \((Bader 2007; Tait et al. 2009)\). However, gypsum precipitation is still utilized frequently for its low costs and safety. Barium sulfate and lead sulfate precipitation ensure very low residual sulfate, but they are usually expensive and any residual barium and lead ions in aqueous solution are of greater concern than any sulfate. Ettringite precipitation occurs when the dissolved \(Ca^{2+}\) and \(Al^{3+}\) react with sulfate in an alkaline condition. Because of this special condition, sulfate can be also removed by gypsum precipitation and co-precipitated with aluminum hydroxides \((Silva et al. 2010)\). Thus it obtains high efficiency when integrating gypsum with ettringite precipitation. It can be considered as a promising method for removing sulfate from wet FGD wastewater.

This work focused on removal of sulfate from wet FGD wastewater by chemical precipitation method, in which calcium hydroxide (CH) and sodium aluminate (SA) were used as precipitants. The co-precipitation mechanism is discussed. The batch experiments were carried out and the post treatment of the effluent and the precipitate sludge were investigated. And the comparisons between the precipitants in this study and other reported precipitants were also made.

**Experimental procedures**

Some indexes of the raw wet FGD wastewater were determined. The initial pH value was 4.35 and the concentration of sulfate, calcium, aluminum, and suspended solid were 4,811, 1,420, 4.2 and 15,105 mg/L, respectively. Sulfate solution was prepared in experiments for studying the sulfate removal mechanism. 7395.83 mg sodium sulfate was dissolved in 1.0 L deionized water \((5,000 \text{ mg/L SO}_4^{2-})\) and the pH value was adjusted to 5.0 by adding 0.2 M HNO_3 solution. The precipitant was a mixture of CH and SA, in which the molar ratio of CH to SA was kept at 2 \((CH/SA-2)\). The precipitant powder was added in sulfate solution directly, following with stirring for 2 hours at 200 rpm. Then the treated sulfate solution was filtered with 0.45 um membrane filter and the filtrate was analyzed for its sulfate content and pH value.

For the batch experiments with raw wet FGD wastewater, the operation procedures were as the above but the experiment conditions varied. The molar ratio of CH/SA, the precipitant dosage, the initial pH value of the wastewater, the reaction time and the reaction temperature were investigated as the experimental factors. The initial pH value of the wastewater was adjusted with 0.2 M HNO_3 or NaOH solution and the temperature was controlled by water bath. In the end, the evaluation experiments under the optimum conditions obtained from batch experiments were carried out.

In the post-treatment experiment, sodium bicarbonate was also added directly for removing the residual calcium and aluminum in the filtrate which was collected from the above evaluation experiment.

**Mechanism exploration of sulfate co-precipitation**

The principles of sulfate co-precipitations with CH and SA were shown as the following Equations (1)–(4).

\[
\begin{align*}
Ca^{2+} + SO_4^{2-} + 2H_2O & \rightarrow CaSO_4 \cdot 2H_2O(s) \\
6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_4^- + 4OH^- & \rightarrow Ca_6Al_2(SO_4)_3 \cdot (OH)_{12}(s) \\
SO_4^{2-} + Al(OH)_{2+} & \rightarrow Al(OH)SO_4(s) \\
SO_4^{2-} + 4Al^{3+} + 10OH^- & \rightarrow Al_4(HO)_{10}SO_4(s)
\end{align*}
\]
The possibility of produced components in the solution reaction system could be represented with the saturation indices (SI) calculated by Visual MINTEQ 3.1. (Gustafsson 2006). SI was defined as the log ratio of the ion activity product (K_{IAP}) observed in solution to the solubility product (K_{s}), as shown in Equation (5) (Song et al. 2002).

\[
SI = \lg \frac{K_{IAP}}{K_{s}}
\]  

(5)

The calculated results of SI did not prove the presence or absence of one component in the solution system, but provided an indication of the tendency for a reaction occurring and showed the potential for equilibrium with a particular mineral phase. A positive SI value indicated a supersaturated condition, which meant that the precipitation of the respective mineral phase was thermodynamically possible; a SI of zero indicated the equilibrium of the solid mineral phase with its ionic components; and a negative SI value indicated an unsaturated condition, which meant the phase dissolved in solution to its ionic components (Liu et al. 2015).

### Analytical methods

Sulfate concentrations were measured by the barium chromate spectrophotometry method. The calcium ion concentrations were measured by the EDTA titrimetric method. The chloride ion, suspended solids and total dissolved salts (TDS) were measured according to Standard Methods for the Examination of Water and Wastewater (World Environment Federation & American Public Health Association 2005). The pH value determination was performed with a pHS-3C determiner. Analysis of Cu^{2+}, Fe^{2+}, Ni^{2+}, Cr^{2+}, Al^{3+} and F⁻ were conducted using the Multi-parameter Photometer (HI83200, HANNA Instruments, Italy).

The components and the morphology of the solid residues were analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), respectively. The XRD measurements were carried out by a D8-Focus X-ray diffraction meter with Cu-Kα radiation (\(\lambda = 1.54056 \) Å) at 40 kV and 200 mA. The scan rate of 5°/min was applied to record the XRD patterns in the range of 12° – 65° at a step of 0.02°. FTIR studies were analyzed by Bruker TENSOR 27, and its spectra were recorded in the transmittance mode in the 400–4,000 cm⁻¹ region, with a minimum of 32 scans at a 4 cm⁻¹ resolution. SEM investigations were performed with a HITACHI S-4800.

### RESULTS AND DISCUSSION

#### Mechanisms of sulfate removal

Study on mechanisms of sulfate removal in sulfate solution was conducted with CH/SA-2, and the SI values of possible precipitants were simulated by Visual MINTEQ 3.1. The samples of the precipitation solids were analyzed by XRD and FTIR.

The results shown in Table 1 indicated that the removal efficiency increased obviously when the dosage of CH/SA-2 was less than 15 g/L, and increased slightly when it was over 15 g/L. The variation trend of the sulfate removal efficiency corresponded to that of the SI values calculated by Visual MINTEQ 3.1. And according to the results shown in Table 1, the fate of the sulfate reacting with CH/SA-2 was to form three kinds of possible precipitations, which were gypsum, ettringite and co-precipitation onto aluminum hydroxides. A high pH condition was produced when CH/SA-2 were added in sulfate solution, and dissolved Cu^{2+}, Al^{3+} and SO₄^{2⁻} ions reacted. Calcium sulfate was formed when Ca^{2+} reacted with SO₄^{2⁻}, and it had three principal forms, including gypsum (CaSO₄·2H₂O), hemihydrate (CaSO₄·1/2H₂O) and anhydrite (CaSO₄), among which gypsum was the main form when the reaction temperature was below 90 °C (Bader 2007). The SI values of gypsum in Table 1 ranged from −0.325 to 0.876, and its solubility would not be affected severely in pure sulfate solution. Ettringite was one of the dominant products of Ca^{2+}, Al^{3+}, and SO₄^{2⁻} ions in water solution. SI values of ettringite in Table 1 increased with the raise of CH/SA-2’s dosage, and it illustrated that ettringite was a stable mineral in water solution. The sulfate ion could co-precipitate with aluminum hydroxides, and it was also investigated in (Xu et al. 2004; He et al. 2008; Goldberg 2010). Al₄(OH)₁₀SO₄ and AlOHSO₄ were also produced at lower pH value, though they were dissolved in strong alkalinity aqueous solution (Ajwa & Tabatabai 1995).

The XRD and FTIR analysis of the precipitation solids are displayed in Figure 1. As shown in Figure 1(a), gypsum, ettringite and aluminum hydroxides formed in the solution reaction system. CH was found in the solid residuals when the precipitant dosage was 15 g/L. As shown in Figure 1(b), the peaks at 605, 1,125, 1,651 and 3,553 cm⁻¹ in the FTIR curves corresponded to Al–O–H bending vibration, SO₄^{2⁻} v3 vibrations, v₂ H₂O and free OH stretching, respectively. The peaks at 1,435 cm⁻¹ might correspond to NO₃⁻ due to the adjustment of the initial pH value. The XRD and FTIR analysis of solid residuals also proved the fate of sulfate removal.
Effect factors of sulfate removal from wet FGD wastewater

Effect of the molar ratio of CH/SA

The molar ratio of CH/SA was important for sulfate removal by the chemical precipitation method. In this section, optimization of the molar ratio of CH/SA was carried out for removing sulfate, and the results are shown in Figure 2.

As can be seen from Figure 2, with the increase in the molar ratio of CH/SA, the sulfate removal efficiency enlarged first and then diminished. There existed a maximum value of the efficiency affected by the molar ratio

Table 1 | The results of demonstration experiments and SI of some possible components estimated by visual MINTEQ 3.1

<table>
<thead>
<tr>
<th>Items</th>
<th>Dosage of CH/SA-2 (g/L)</th>
<th>0.5</th>
<th>2</th>
<th>5</th>
<th>7.5</th>
<th>10</th>
<th>12.5</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>10.27</td>
<td>11.04</td>
<td>11.89</td>
<td>12.15</td>
<td>12.36</td>
<td>12.54</td>
<td>12.61</td>
<td>12.63</td>
<td>12.62</td>
</tr>
<tr>
<td>Residual sulfate (mg/L)</td>
<td></td>
<td>4,102</td>
<td>3,918</td>
<td>3,665</td>
<td>3,325</td>
<td>2,671</td>
<td>2,330</td>
<td>2,024</td>
<td>1,922</td>
<td>1,935</td>
</tr>
<tr>
<td>Removal efficiency (%)</td>
<td></td>
<td>17.96</td>
<td>21.64</td>
<td>26.7</td>
<td>33.5</td>
<td>46.58</td>
<td>53.4</td>
<td>59.52</td>
<td>61.56</td>
<td>61.30</td>
</tr>
</tbody>
</table>

**SI calculated by MINTEQ 3.1**

- **Al(OH)$_3$ (am)**
  - 0.841 – 1.009 – 1.466 – 1.556 – 1.646 – 1.733 – 1.727 – 1.624 – 1.446
- **Al(OH)$_3$ (Soil)**
  - 1.669 1.501 1.044 0.954 0.864 0.777 0.783 0.886 1.064
- **Al$_2$O$_3$(s)**
  - 0.268 – 0.068 – 0.982 – 1.161 – 1.341 – 1.514 – 1.5 – 1.294 – 0.936
- **Al$_4$(OH)$_{10}$SO$_4$(s)**
- **AlOHSO$_4$(s)**
- **Anhydrite**
  - 0.575 – 0.004 0.303 0.4 0.45 0.48 0.509 0.56 0.633
- **Boehmille**
  - 1.382 1.214 0.757 0.667 0.577 0.49 0.497 0.6 0.779
- **Diasporo**
  - 5.087 2.919 2.462 2.372 2.282 2.195 2.202 2.305 2.484
- **Ettringite**
- **Gibbsite**
  - 2.219 2.051 1.594 1.504 1.414 1.327 1.333 1.436 1.614
- **Gypsum**
  - 0.325 0.245 0.552 0.647 0.697 0.727 0.755 0.805 0.876
- **Lime**
- **Portlandite**
  - 5.36 – 3.18 – 1.036 – 0.328 0.209 0.645 0.857 1.029 1.229

**Figure 1** | XRD (a) and FTIR (b) analysis of solid residuals at different dosages of CH/SA-2 (sulfate solution with sulfate concentration of 5,000 mg/L, an initial pH of 5, reaction time of 2 h and temperature of 20 °C).
of CH/SA. When the molar ratio of CH/SA was below 2, the efficiency increased with an increase in the molar ratio of CH/SA. The reason was closely relevant to the increasing content of the CH in CH/SA. Compared with SA, the same amount of CH could remove more sulfate according to Equations (1), (3) and (4). When the molar ratio of CH/SA was 0, the sulfate could only be removed by SA and co-precipitate with aluminum hydroxides. As the molar ratio of CH/SA increased, in addition to the co-precipitation with aluminum hydroxides, more gypsum and ettringite precipitations were formed. Thus, more sulfate could be removed during the process. So the sulfate removal efficiency would increase with the increase in the molar ratio of CH/SA. However, when the molar ratio of CH/SA was over 2, the removal efficiency decreased with the increase of the molar ratio. The reasons for this could be explained as follows: (1) as the molar ratio increased, the proportion of SA gradually decreased. As a result, the content of dissolved $\text{Ca}^{2+}$ in the water solution decreased, which would result in reduced ettringite and co-precipitation with aluminum hydroxides; (2) when precipitants were added in the water solution, a high pH condition was produced due to the increasing proportion of CA. The high pH value was detrimental to the production of ettringite and co-precipitation with aluminum hydroxides. Besides, the precipitations would dissolve in a strong alkalinity aqueous solution as well.

As illustrated in Figure 2, the results showed that the maximum sulfate removal was achieved at the molar ratio of 2. Hence, this molar ratio of CH/SA was selected for treatment of wet FGD wastewater in the subsequent studies.

**Effect of initial pH value**

The influence of the initial pH value of the wastewater on sulfate removal is illustrated in Figure 3. The initial pH values of 1 and 5 appeared to be ideal for sulfate removal by SA and CH/SA-2, respectively. And CH obtained good performances when the initial pH values were higher than 4. The maximal removal efficiencies of CH/SA-2, CH and SA were 79.5%, 72.5% and 35.0%, respectively.

When CH was added at a low pH value condition, dissolved $\text{Ca}^{2+}$ ions were produced and gypsum precipitations were formed with sulfate in the wastewater, but the solubility of CH decreased with the increase in pH value. When the initial pH value was less than 4, the sulfate removal efficiency increased positively with the increase in initial pH value, which might result from the increase in dissolved $\text{Ca}^{2+}$. However, the removal efficiency maintained little fluctuation when the initial pH value was above 4. This might be due to the equilibrium of dissolved $\text{Ca}^{2+}$ and undissolved CH at high pH points, which affected the formation of gypsum. This also showed the buffer function of CH in a high pH value condition (Gitari et al. 2008). SA dissolved easily in water, and its aqueous solution was alkaline. The appropriate initial pH value for sulfate removal by SA was at 1.0 and the sulfate removal efficiency decreased with the increase in initial pH value. The reason was that a high pH value was not fitted for co-precipitation with aluminum hydroxides according to the SI values in Table 1. Ettringite might also be produced because dissolved $\text{Ca}^{2+}$ existed in the wastewater, but its content in the reaction was limited since it had to compete for $\text{Ca}^{2+}$ ions.
with hydroxyl and sulfate. When the initial pH value was below 5, the sulfate removal efficiency by CH increased with the increase in the initial pH value, and was about 20.2–52.2% higher than that by SA. Although the sulfate removal efficiency by SA decreased as the initial pH value increased, the increasing rate of sulfate removal efficiency by CH was close to the decreasing rate by SA. What’s more, in addition to gypsum and co-precipitation with aluminum hydroxides, more ettringite precipitation was formed when the dissolved Ca$^{2+}$ from CH and Al$^{3+}$ from SA reacted with sulfate in the alkaline condition. As a result, the efficiency of sulfate removal by CH/SA-2 increased when the initial pH value was below 5. So the efficiency decrease by SA could not change the increasing efficiency of sulfate removal by CH/SA-2 when the initial pH value was below 5.

When the initial pH value of the wastewater was over 5, the sulfate removal efficiency decreased slightly and drew near to that of CH. This could be explained by the ettringite precipitation and co-precipitation with aluminum hydroxides being reduced in a high alkalinity situation (Wang et al. 2016).

**Effect of the precipitant dosage**

In Figure 4, the sulfate removal efficiency obtained with different dosages of CH/SA-2, CH and SA is presented. The maximum efficiency of sulfate removal was 71.4% and 82.6% when the dosage of CH and CH/SA-2 was 10 g/L and 15 g/L, respectively, but was only 32.8% for the addition of 5 g/L SA.

When the dosage of CH/SA-2 was 15 g/L, the maximum sulfate efficiency was obtained. Observed on the varying tendency of removal efficiency below 15 g/L, this could be divided into two sections, one being 0.5 to 7.5 g/L and the other being 7.5 to 15 g/L. The rising rate of the first section was apparently bigger than that of the second section. In the first section, the removal efficiency increased in both individual treatments with CH and SA, namely that all the gypsum precipitation, ettringite and co-precipitation with aluminum hydroxides worked on removing sulfate; in the second section, the co-precipitation onto aluminum hydroxides might be affected by the high pH condition, resulting in the decrease of the rising rate of sulfate removal efficiency. When the dosage was over 15 g/L, the removal efficiency decreased as the precipitations, except for gypsum, dissolved in the high pH condition. The sulfate removal efficiency reached a stable level when the dosage of CH was over 7.5 g/L. This could be explained by the following two reasons, one being that the solubility of CH was limited, another being that the gypsum was slightly soluble and the greater ionic strength of the aqueous solution made the gypsum dissolve. The maximum removal efficiency was obtained when the dosage of SA was 5 g/L. When the dosage was below 5 g/L, the productivities of boehmite, gibbsite and ettringite increased with the increase in dosage. However, with the continual increase in dosage, the high pH value condition reduced the production of boehmite and gibbsite, and the ettringite might also dissolve.

**Effect of reaction time**

In Figure 5, the effect of the reaction time on sulfate removal from wastewater with CH/SA-2 and its two components is presented. It was observed that the different reaction rates

![Figure 4](https://example.com/figure4.png)  **Figure 4** Effect of CH, CH/SA-2 and SA dosage on sulfate removal at the initial pH of 5, reaction time of 2 h and temperature of 20°C.

![Figure 5](https://example.com/figure5.png)  **Figure 5** Effect of reaction time on sulfate removal at CH, CH/SA-2 and SA dosage of 15 g/L, the initial pH of 5 and temperature of 20°C.
were obtained with different precipitants. When the reaction times were 20, 40 and 5 minutes, CH/SA-2, CH and SA achieved the maximal sulfate removal efficiency, respectively. The maximal sulfate removal efficiencies were 82.4%, 73.3% and 16.3%, respectively, and then all of them reached a stable level.

The removal efficiency of CH/SA-2 reached a stable level within 20 minutes, and its rate fell between those of CH and SA. It comprehensively showed the characteristics of CH and SA. SA was soluble in aqueous solution and the co-precipitation onto aluminum hydroxides was a fast process, while the dissolution rate of CH was slower, especially in an alkali solution. Thus the reaction rate (i.e. the sequence of reaction speed) was SA > CH/SA-2 > CH. The removal efficiency of CH reached a stable level after 40 min. As shown in Figure 5, the reaction rate of CH from 0 to 10 minutes was higher than that from 10 to 40 minutes. The reason was that CH dissolved in the mildly acidic wastewater quickly, and then dissolved slowly because of the increase in pH value; as a result, the rate of gypsum formation reduced and the removal rate reduced.

**Effect of reaction temperature**

As observed in Figure 6, both SA and CH/SA-2 obtained a maximum removal efficiency at 55 °C, and CH had a stable removal efficiency except when the temperature was 10 °C. The maximal removal efficiencies of CH/SA-2, CH and SA were 80.8%, 71.4% and 24.6%, respectively.

As shown in Figure 6, CH and CH/SA-2 had the lowest removal efficiency at 10 °C, which increased with the increase in temperature, though they showed different variation tendencies. The reason was that the probability of ion collision and precipitation formation would increase with the increase in temperature. However, the removal efficiencies obtained by SA and CH/SA-2 reduced when the temperature was above 55 °C. This is because the co-precipitation with aluminum hydroxides would melt in a high temperature condition, and the solubility of ettringite increased with the rise in temperature (Perkins & Palmer 1999). The removal efficiency obtained by CH maintained a stable level when the temperature was above 25 °C. Even though the solubility of gypsum increased with the temperature, the dissolved Ca\(^{2+}\) in aqueous solution was sufficient for the precipitation of gypsum, and could not affect the sulfate removal efficiency.

**Comprehensive results of sulfate removal from the wet FGD wastewater**

According to the above discussions, sulfate removal by co-precipitation with CH/SA-2 was an appropriate method, and the optimum operation conditions were the initial pH value of 5.0, precipitant dosage of 15 g/L, reaction time of 20 minutes and reaction temperature of 55 °C. Under the optimum operation conditions, the evaluation experiment for sulfate and heavy metals removal from the wet FGD wastewater and the post treatment experiments for removal of Ca\(^{2+}\) and Al\(^{3+}\) that remained in the filtrate were carried out. In the end, a comparison of sulfate removal with the chemical precipitation method was made.

The filtration performance experiments for the sludge in the evaluation experiment were carried out with an experimental filter-press setup. The results are listed in Table 2, and the XRD and FTIR analyses of the filter cake are shown in Figure 7. The residual sulfate in the filtrate was below 1,000 mg/L, and it could be reused in the wet FGD system. The residual heavy metals and fluoride were also at low levels after treatment, the reason for which might be not only precipitation of hydroxide or calcium fluoride, but also adsorption of ettringite or aluminum hydroxides (Zhang & Reardon 2005; Chrysochoou & Dermatas 2006; Hamamoto et al. 2015). The treated wastewater achieved a faster average filtration rate, and a higher filter cake moisture content for the existence of aluminum hydroxide. As illustrated in Figure 7(a), ettringite and aluminum hydroxides were formed and the content of gypsum increased after treatment. As shown in Figure 7(b), the FTIR peaks at 980, 1,132 and 3,549 cm\(^{-1}\) corresponded to sulfite vibration, SO\(_4^{2-}\), \(\nu_3\) vibrations, \(\nu_2\) H\(_2\)O and free OH stretching, respectively. The peaks at 1,429 might correspond to
The image in Figure 7(c) shows the different amorphous solid residuals before and after treatment.

The post treatment experiments were carried out for removing the residual Ca$^{2+}$ and Al$^{3+}$ in the supernatant; as a result, the optimum dosage of NaHCO$_3$ was 1.5 g/L after the series of experiments and the final pH value, TDS, Ca$^{2+}$, Al$^{3+}$ were reduced to 8.05, 11,758 mg/L, 72 mg/L and 0.415 mg/L, respectively. The filter cake was abundant in sulfur, aluminum and calcium, and its components were similar to elements of calcium sulfur aluminate cement pastes as described in Martín-Sedeño et al. 2010 and García-Maté et al. 2012. This solid sludge could be used as an additive in cement or converted to cement; it could also be used as the main material for producing fire resistant wallboard (Ko 2002), or mixed with fly ash and used as land filler in mined-out areas.

A comparison with the previously reported precipitants for sulfate removal was made and the results are listed in Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameters</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supernatant</td>
<td>pH value (mg/L)</td>
<td>4.32</td>
<td>12.56</td>
</tr>
<tr>
<td></td>
<td>Fluoride (mg/L)</td>
<td>35.2</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>Chloride (mg/L)</td>
<td>5,942</td>
<td>5,451</td>
</tr>
<tr>
<td></td>
<td>Sulfate (mg/L)</td>
<td>4,811</td>
<td>784</td>
</tr>
<tr>
<td></td>
<td>TDS (mg/L)</td>
<td>17,416</td>
<td>11,443</td>
</tr>
<tr>
<td></td>
<td>Zinc (mg/L)</td>
<td>3.72</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>Copper (mg/L)</td>
<td>4.04</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>Aluminum (mg/L)</td>
<td>4.2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Calcium (mg/L)</td>
<td>1,420</td>
<td>1,023</td>
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<tr>
<td></td>
<td>Nickel (mg/L)</td>
<td>0.394</td>
<td>Not detected</td>
</tr>
<tr>
<td></td>
<td>Chrome-VI (mg/L)</td>
<td>0.545</td>
<td>0.059</td>
</tr>
<tr>
<td>Sludge</td>
<td>Average filtration rate (m/s)</td>
<td>0.0117</td>
<td>0.0194</td>
</tr>
<tr>
<td></td>
<td>Filter cake moisture content (%)</td>
<td>42.65</td>
<td>65.69</td>
</tr>
</tbody>
</table>

Figure 7 | XRD (a), FTIR (b), SEM of the filtration cake before (c) and after (d) treatment under the optimum co-precipitation conditions.
It was concluded that CH/SA-2 was better than many other precipitants for sulfate removal. Moreover, it was a safe treatment without introducing any chloride ions or heavy metals, although the final content of chloride ions in the treated water was not very different.

Table 3 | Comparison of treatment results by various reported precipitants

<table>
<thead>
<tr>
<th>Precipitants</th>
<th>Dosage (g/L)</th>
<th>Initial sulfate (mg/L)</th>
<th>Final sulfate (mg/L)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>25</td>
<td>588.0</td>
<td>87.4</td>
<td>Silva et al. (2012)</td>
</tr>
<tr>
<td>Limestone/lime</td>
<td>–</td>
<td>3,000</td>
<td>1,090</td>
<td>Geldenhuys et al. (2005)</td>
</tr>
<tr>
<td>FA (fly ash)</td>
<td>500</td>
<td>4,603</td>
<td>1334.9</td>
<td>Madzivire et al. (2011)</td>
</tr>
<tr>
<td>CaCl₂, 75%</td>
<td>80</td>
<td>296</td>
<td>29.6</td>
<td>Kabdasli et al. (1999)</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>5.71</td>
<td>7,410</td>
<td>5,040</td>
<td>Kabdasli et al. (1999)</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>23.14</td>
<td>6,870</td>
<td>5,750</td>
<td>Kabdasli et al. (1999)</td>
</tr>
<tr>
<td>BaCl₂·2H₂O</td>
<td>80</td>
<td>263</td>
<td>101.5</td>
<td>Benatti et al. (2009)</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>15.65</td>
<td>6,870</td>
<td>480</td>
<td>Kabdasli et al. (1999)</td>
</tr>
<tr>
<td>Pb(NO₃)₂</td>
<td>26.05</td>
<td>6,870</td>
<td>&lt;10</td>
<td>Kabdasli et al. (1999)</td>
</tr>
<tr>
<td>PAC (polyaluminum chloride)</td>
<td>PAC/SO₄²⁻ = 10 (molar)</td>
<td>1,800</td>
<td>306</td>
<td>Silva et al. (2010)</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>AlCl₃/SO₄²⁻ = 7 (molar)</td>
<td>1,800</td>
<td>&lt;250</td>
<td>Silva et al. (2010)</td>
</tr>
<tr>
<td>FA and mine drainage</td>
<td>Liquid/solid = 2</td>
<td>20,870</td>
<td>1,970</td>
<td>Madzivire et al. (2011)</td>
</tr>
<tr>
<td>FA and Al(OH)₃</td>
<td>500 + 0.784</td>
<td>4,800</td>
<td>23</td>
<td>Madzivire et al. (2010)</td>
</tr>
</tbody>
</table>

Table 3. It was concluded that CH/SA-2 was better than many other precipitants for sulfate removal. Moreover, it was a safe treatment without introducing any chloride ions or heavy metals, although the final content of chloride ions in the treated water was not very different.

CONCLUSIONS

This work studied sulfate removal from wet FGD wastewater by co-precipitation with CH and SA. The mechanism of sulfate removal was that sulfate reacting with CH and SA could generate three kinds of possible precipitations, which were gypsum, ettringite and co-precipitation onto aluminum hydroxides. The optimum operation condition for sulfate removal from wet FGD wastewater was that the molar ratio of CH/SA was 2, the initial pH value 5, the precipitant dosage 15 g/L, the reaction time 20 min and the reaction temperature 55 °C, respectively. Under this operational condition, the sulfate was reduced from 4,881 mg/L to 784 mg/L, and its removal efficiency was 83.9%. The heavy metals and fluoride were also mostly removed and the sludge was more easily filtrated. The gypsum, ettringite and aluminum hydroxides’ precipitation were found according to the analysis results of residual solids by XRD, FTIR and SEM. The residual Ca²⁺ and Al³⁺ in the filtrate could be removed by the addition of NaHCO₃. Overall, it was found that CH/SA-2 was an appropriate precipitant for removal of sulfate in wet FGD wastewater.

REFERENCES


Elghaffar, M. A. A. & Tieama, H. A. 2017 A review of membranes classifications, configurations, surface modifications, characteristics and its applications in water purification. Chemical and Biomolecular Engineering 2 (2), 57–82.


Goldberg, S. 2010 Competitive adsorption of molybdenum in the presence of phosphorus or sulfur on gibbsite. Soil Science 175 (3), 105–110.


Ko, S.-C. 2002 Aluminosilicate and calcium sulfate; alkali metal salt activator; blast furnace slag, clay, marl, fly ash, and cement kiln dust mixture. Google Patents.


World Environment Federation & American Public Health Association 2005 Standard Methods for the Examination of Water and Wastewater. American Public Health Association (APHA), Washington, DC, USA.
