

Ca removal and Mg recovery from flue gas desulfurization (FGD) wastewater by selective precipitation

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ABSTRACT

Selective removal of Ca and recovery of Mg by precipitation from flue gas desulfurization (FGD) wastewater has been investigated. Thermodynamic analysis of four possible additives, Na_2CO_3 , $\text{Na}_2\text{C}_2\text{O}_4$, NaF and Na_2SO_4 , indicated that both carbonate and oxalate could potentially provide effective separation of Ca via precipitation from Mg in FGD wastewater. However, it was found experimentally that the carbonate system was not as effective as oxalate in this regard. The oxalate system performed considerably better, with Ca removal efficiency of 96% being obtained, with little Mg inclusion at pH 6.0 when the dosage was $\times 1.4$ the stoichiometric requirement. On this basis, the subsequent recovery process for Mg was carried out using NaOH with two-step precipitation. The product was confirmed to be $\text{Mg}(\text{OH})_2$ (using X-ray diffraction and thermo gravimetric analysis) with elemental analysis suggesting a purity of 99.3 wt.%.

Key words | Ca removal, FGD wastewater, Mg recovery, precipitation, thermodynamics

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INTRODUCTION

Wet scrubber technologies (Huang *et al.* 2013) are widely applied in thermal power plants for flue gas desulfurization (FGD). In particular, the limestone-gypsum method accounts for 85% of FGD processes in the USA (Gude 2015) due to its technological maturity and stability. However, to ensure the on-going quality of the gypsum and to prevent corrosion from chloride (Tatani *et al.* 2004), some of the FGD wastewater should be discharged periodically with addition of fresh water to maintain the chloride concentration at less than $20,000 \text{ mg L}^{-1}$ (Ma *et al.* 2016).

The discharged FGD wastewater has complex composition containing heavy metals, and high concentrations of suspended solids and total dissolved solids (TDS) (Enoch *et al.* 1994), the concentrations of which vary with coal source and discharge cycle (Huang *et al.* 2013). The aim of the traditional FGD treatment technology focuses on reaching the emission standard. As this process is not effective for removing salinity, the direct discharge of FGD wastewater can cause a serious threat to aqueous environments and may lead to salinization of soil. Recently, with the adoption of new stricter emission standards, especially the zero emission requirement (i.e. that no liquid may be discharged to the environment) implemented in China, traditional

treatment and discharge of FGD wastewater does not meet the increased environmental protection requirements. At present, this requirement can be satisfied using evaporation treatment through flue gas (Deng *et al.* 2014) and membrane technology coupled with evaporation crystallization technology. As the second of these two approaches provides effective recovery of crystalline salt and reuse of desalted water, generating significant economic value, it has become the focus of continuing development.

Unfortunately, membrane fouling caused by the elevated water hardness, mainly due to Ca and Mg, affects the efficiency of the FGD wastewater treatment. Hence, process steps are required to remove Ca and Mg from the FGD, enabling normal operation of the membrane system. However, it is desirable to remove the Mg separately from the Ca. Mg and its compounds are used in many applications such as insulation, agriculture, construction and other industries (Luo *et al.* 2015). High purity MgO is used in food and pharmaceuticals and $\text{Mg}(\text{OH})_2$ is a major component in the manufacture of fire retarding reagents (Hull *et al.* 2011). Furthermore, it is also involved in the alkaline peroxide bleaching process as an alkali source (Han *et al.* 2015).

Several approaches have been reported for Ca and Mg removal or recovery, mainly concentrating upon solvent extraction and chemical precipitation (Virolainen *et al.* 2016). Xiao *et al.* applied an aqueous two phase system (ATPS) to selectively remove Ca from a sulfate solution containing Mg and Ni using 1N2N as the cationic extractant (Santos *et al.* 2015). Ca removal of up to 80% was obtained with 90% of the Mg remaining in solution. Bukowsky *et al.* used D2EHPA (di-2-ethylhexyl phosphoric acid) to extract Mg from lithium chloride solution with 99% of the Mg recovered (Bukowsky *et al.* 1992). However, the solvent extraction process is relatively complicated and the organic extractant causes secondary pollution, thus reducing its suitability as a treatment for FGD wastewater.

Selective chemical precipitation offers significant advantages including easy operation, low cost and no secondary pollution. Alamdari *et al.* studied the recycling of Mg from a bittern solution using sodium hydroxide, and obtained good crystallization of magnesium hydrate on the addition of magnesium hydrate seeds (Alamdari *et al.* 2008). Other reagents such as sulfate (Naseri *et al.* 2015), fluorinon (Misra 1999), carbonate (Pervov 2015; Lin *et al.* 2016) and oxalate (Hamzaoui *et al.* 2003; East *et al.* 2014) have already been demonstrated to have the ability to precipitate Ca or Mg. However, systematic comparisons of the wide range of additives with their corresponding thermodynamic models in FGD wastewater treatment have not been found in the literature. This comparison could provide sound data for strategic decisions regarding implementation.

The aim of this research was to selectively remove Ca and recover Mg from FGD wastewater. Being able to do this effectively would not only decrease the risk of membrane fouling, which leads to reduced membrane flux, but also provide potential economic benefit through the recovery of Mg(OH)₂. To obtain high quality magnesium hydrate without calcium contamination, calcium should be

separated first. In view of this, four possible reagents (Na₂CO₃, Na₂C₂O₄, NaF and Na₂SO₄) were considered due to their capacity to combine with Ca to produce solid precipitation. Thermodynamic diagrams were derived using the systems of Mg²⁺ – Ca²⁺ – B^{x-} (representing CO₃²⁻, C₂O₄²⁻, SO₄²⁻ and F⁻ in the respective thermodynamic system) – H₂O to screen these additives and provide theoretical process parameters for maximum removal of Ca, and recovery of Mg, from FGD wastewater. The two most favorable candidates for Ca precipitation were then examined experimentally, and sodium hydroxide solution was applied to recover Mg as Mg(OH)₂.

METHODOLOGY

Chemicals

All chemicals applied in this research (MgCl₂·6H₂O, NaCl, CaCl₂, Na₂SO₄, Na₂CO₃, NaOH, Na₂C₂O₄, NaF and HCl) were purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China, and were of analytical grade with purity between 96 and 99%. A typical FGD wastewater containing Ca²⁺ 0.80 g L⁻¹ (0.02 mol L⁻¹), Mg²⁺ 4.80 g L⁻¹ (0.20 mol L⁻¹), Cl⁻ 11.12 g L⁻¹, Na⁺ 0.50 g L⁻¹, SO₄²⁻ 7.04 g L⁻¹ was prepared by stirring the required amounts of the specific chemicals in distilled water.

Thermodynamics

In the systems of Ca²⁺ – Mg²⁺ – B^{x-} – H₂O, the species in solution are numerous and are affected by pH, with variation in pH being possible at full scale implementation. The thermodynamic data (Dean 1985) for the major relevant equilibrium reactions in solution at 25 °C are tabulated in Table 1. On the basis of the equilibrium

Table 1 | Equilibrium reactions and constants of Ca²⁺ – Mg²⁺ – B^{x-} – H₂O systems at 25 °C

Reactions	Equilibrium constants (-log K)	Reactions	Equilibrium constants (-log K)
H ₂ O → H ⁺ + OH ⁻	(1) 14	CaF _{2(s)} → Ca ²⁺ + 2F ⁻	(9) 9.82
Mg(OH) _{2(s)} → Mg ²⁺ + 2(OH) ⁻	(2) 11.29	CaSO _{4(s)} → Ca ²⁺ + SO ₄ ²⁻	(10) 4.15
MgC ₂ O _{4(s)} → Mg ²⁺ + C ₂ O ₄ ²⁻	(3) 4.07	H ₂ C ₂ O → H ⁺ + HC ₂ O ₄ ⁻	(11) 1.27
MgCO _{3(s)} → Mg ²⁺ + CO ₃ ²⁻	(4) 5.17	HC ₂ O ₄ ⁻ → H ⁺ + C ₂ O ₄ ²⁻	(12) 4.27
Ca(OH) _{2(s)} → Ca ²⁺ + 2(OH) ⁻	(5) 5.34	H ₂ CO ₃ → H ⁺ + HCO ₃ ⁻	(13) 6.38
CaC ₂ O _{4(s)} → Ca ²⁺ + C ₂ O ₄ ²⁻	(6) 8.64	HCO ₃ ⁻ → H ⁺ + CO ₃ ²⁻	(14) 10.33
CaCO _{3(s)} → Ca ⁺ + CO ₃ ²⁻	(7) 8.31	HF → H ⁺ + F ⁻	(15) 3.16
MgF _{2(s)} → Mg ²⁺ + 2F ⁻	(8) 10.13	HSO ₄ ⁻ → H ⁺ + SO ₄ ²⁻	(16) 2

data from Table 1, thermodynamic analysis was carried out. The concentration of any species can be deduced according to the mathematical relationships from each other.

Ca removal verification and Mg recovery experiments

Two litres of synthetic FGD wastewater stirred at 180 rpm was used for each trial. To ensure the reliability of the experimental data, all the experiments were carried out at least three times and the results averaged.

Stage 1 – Ca removal

In this stage, the calcium precipitation reagents carbonate and oxalate were selected and were investigated to demonstrate and evaluate the removal of Ca and the degree of exclusion of Mg from the precipitate with variation of dosage and pH. The range of pH values (Thermo Orion, 230A+) were referred to thermodynamic results and adjusted by addition of 5 mol L⁻¹ NaOH solution. The

dosages were calculated, with the range of $\times 1$ to $\times 1.5$ the stoichiometric requirement for complete Ca precipitation. After precipitation equilibration, the suspension was vacuum filtered using a 0.45 μm membrane and the filtrate was reserved for Ca and Mg analysis.

Stage 2 – Mg recovery

On consideration of the poor settling and poor filterability (Henrist *et al.* 2003) of magnesium hydrate at high TDS, centrifugal separation (5,000 rpm, Cence, H1850) was conducted for separation of the solid. In this stage, fractional precipitation was investigated to improve the utilization efficiency of the precipitation reagent, NaOH. To this end, part of the sodium hydroxide solution was added to the filtrate then centrifuged after reaction equilibration. This process was repeated until exhaustion of the NaOH based on the residual Mg content in the FGD wastewater. The recovered precipitates were then mixed and washed several times using distilled water.

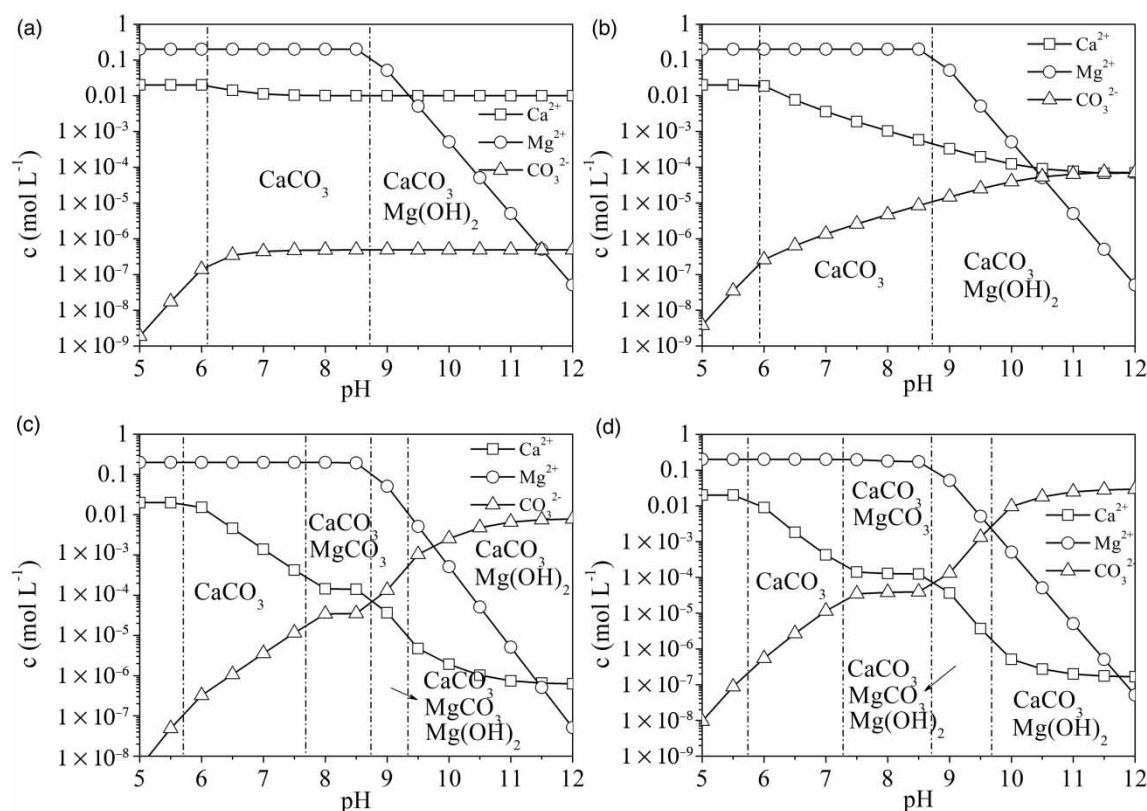


Figure 1 | Effect of pH on speciation in the simulated FGD wastewater system containing 0.20 mol L⁻¹ Mg²⁺ – 0.02 mol L⁻¹ Ca²⁺ – CO₃²⁻ – H₂O as a function of initial carbonate concentrations at 25 °C: (a) 0.01 mol L⁻¹, (b) 0.02 mol L⁻¹, (c) 0.028 mol L⁻¹ and (d) 0.05 mol L⁻¹.

Characterization of precipitate and analysis method

X-ray diffraction (XRD) (PANalytical, X'Pert Pro) with Cu K α radiation at the scan rate of 1° 2 θ min⁻¹ was used to identify the crystalline precipitates. Thermo gravimetric analysis (TGA) and differential thermal analysis (TG/DTA 6300) were carried out at the heating rate of 15 °C in N₂ to characterize the thermostability and compositions of the Mg-containing precipitates. The cation composition was measured using an atomic absorption spectroscope (PinAAcle, 900F) equipped with Ca and Mg hollow-cathode lamps.

RESULTS AND DISCUSSION

Thermodynamic analysis of Mg²⁺ – Ca²⁺ – CO₃²⁻ – H₂O

Figure 1 shows the effect of pH on precipitation from the Mg²⁺ – Ca²⁺ – CO₃²⁻ – H₂O system with different initial carbonate concentrations in the simulated FGD wastewater containing 0.2 mol L⁻¹ Mg²⁺ and 0.02 mol L⁻¹ Ca²⁺. Figure 1(a) indicates that $\times 0.5$ of the stoichiometric dosage

could remove half of the Ca²⁺ with Mg²⁺ still remaining in the solution at pH 7.0–8.5. According to Figure 1(b), Ca²⁺ removal is close to 100% at pH values smaller than that required for the formation of Mg(OH)₂ at the stoichiometric dosage. On increase in the carbonate concentration, the composition of the solid phase becomes more complicated. MgCO₃ (in both Figure 1(c) and 1(d)) is predicted to precipitate on dosages at $\times 1.4$ to $\times 2.5$. It can also be seen from Figure 1(c) and 1(d) during the co-precipitation of MgCO₃ and CaCO₃, both Mg²⁺ and Ca²⁺ removal efficiency remain stable. Upon the formation of Mg(OH)₂ and on increasing pH, the solution concentrations of Ca²⁺ and Mg²⁺ decrease rapidly. On further increase of pH, MgCO₃ is no longer predicted to precipitate and CaCO₃ and Mg(OH)₂ are the precipitating phases.

Thermodynamic analysis of Mg²⁺ – Ca²⁺ – C₂O₄²⁻ – H₂O

Figure 2 shows the effect of pH on the Mg²⁺ – Ca²⁺ – C₂O₄²⁻ – H₂O system with different initial oxalate concentrations in the simulated FGD wastewater containing 0.20 mol L⁻¹ Mg²⁺ and 0.02 mol L⁻¹ Ca²⁺.

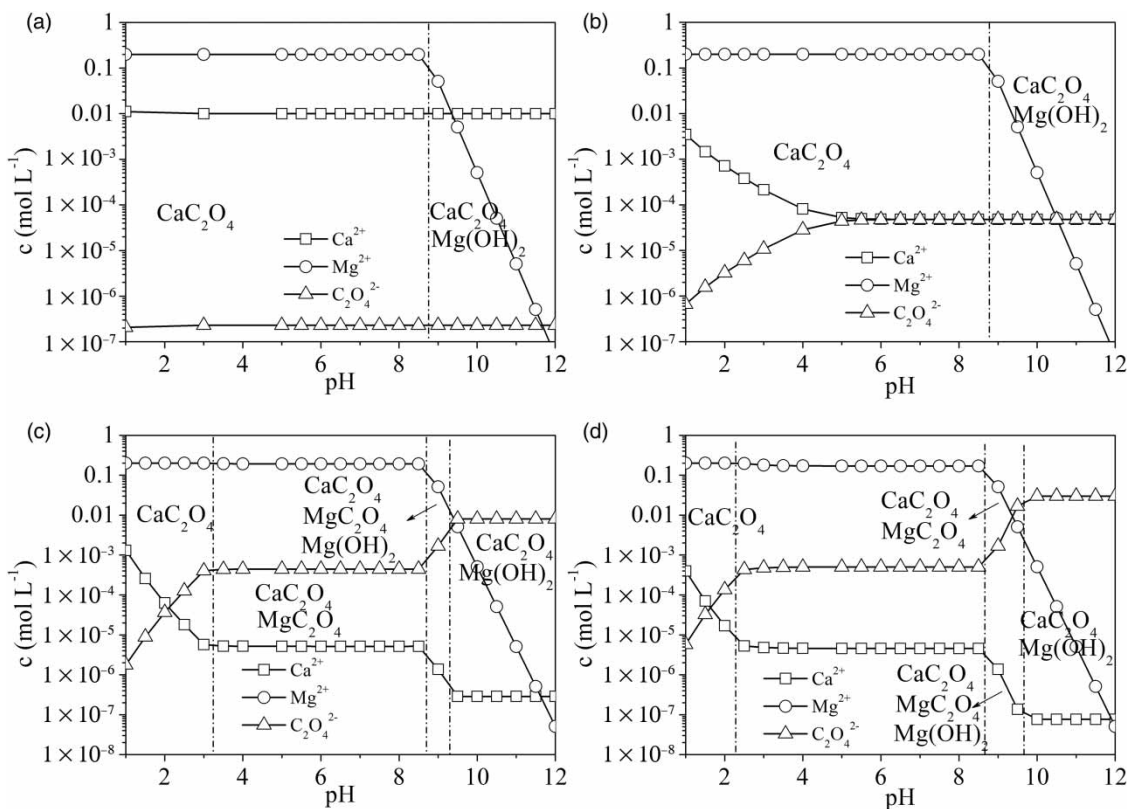


Figure 2 | Effect of pH on speciation in the simulated FGD wastewater system containing 0.20 mol L⁻¹ Mg²⁺ – 0.02 mol L⁻¹ Ca²⁺ – C₂O₄²⁻ – H₂O as a function of initial oxalate concentrations at 25 °C: (a) 0.01 mol L⁻¹, (b) 0.02 mol L⁻¹, (c) 0.028 mol L⁻¹ and (d) 0.05 mol L⁻¹.

CaC_2O_4 is predicted to precipitate under acidic conditions. On increasing the oxalate dosage, simultaneous precipitation of CaC_2O_4 and MgC_2O_4 is predicted and the Mg^{2+} and Ca^{2+} concentrations hold steady prior to obtaining a pH sufficiently alkaline for $\text{Mg}(\text{OH})_2$ precipitation (Figure 2(c) and 2(d)). Similar to the MgCO_3 precipitated trend from the carbonate system, MgC_2O_4 precipitation is predicted to gradually decline as the degree of precipitation of $\text{Mg}(\text{OH})_2$ increases. Figure 2(b) indicates that almost 100% of the aqueous Ca^{2+} can be removed on addition of the stoichiometrically required concentration of oxalate in the pH range of 5–8. Across this pH range, the precipitation of CaC_2O_4 is highly differentiated from the precipitation of $\text{Mg}(\text{OH})_2$, exhibiting high performance in the separation of Ca^{2+} from the Mg^{2+} that remains in the aqueous system.

Thermodynamic analysis of $\text{Mg}^{2+} - \text{Ca}^{2+} - \text{SO}_4^{2-} - \text{H}_2\text{O}$

The sulfate system speciation versus pH is given in Figure 3. It is found that the Ca^{2+} removal is not complete and is independent, in part, of pH. When the dosage is the

stoichiometric dosage required for CaSO_4 precipitation, only 60% Ca removal is predicted (Figure 3(b)). Even when the dosage is elevated to $\times 2.5$, the result is still unsatisfactory, with $>10\%$ Ca^{2+} left in the solution (Figure 3(d)). This suggests that it would be unwise to use sulfate as the Ca precipitation reagent. Similarly, the high concentration of sulfate retained in the FGD solution is also of concern.

Thermodynamic analysis of $\text{Mg}^{2+} - \text{Ca}^{2+} - \text{F}^- - \text{H}_2\text{O}$

In contrast to the thermodynamic simulation results depicted above, the $\text{Mg}^{2+} - \text{Ca}^{2+} - \text{F}^- - \text{H}_2\text{O}$ system shows a reversed precipitation process. The precipitation trend regarding CaF_2 , MgF_2 and $\text{Mg}(\text{OH})_2$ is clearly shown in Figure 4. MgF_2 is predicted to form at lower pH. As pH is increased, CaF_2 begins to precipitate with the co-precipitation of $\text{Mg}(\text{OH})_2$ and MgF_2 under alkaline conditions, leading to the unsuccessful separation of Ca and Mg. This suggests that F^- addition would not be effective for FGD wastewater treatment.

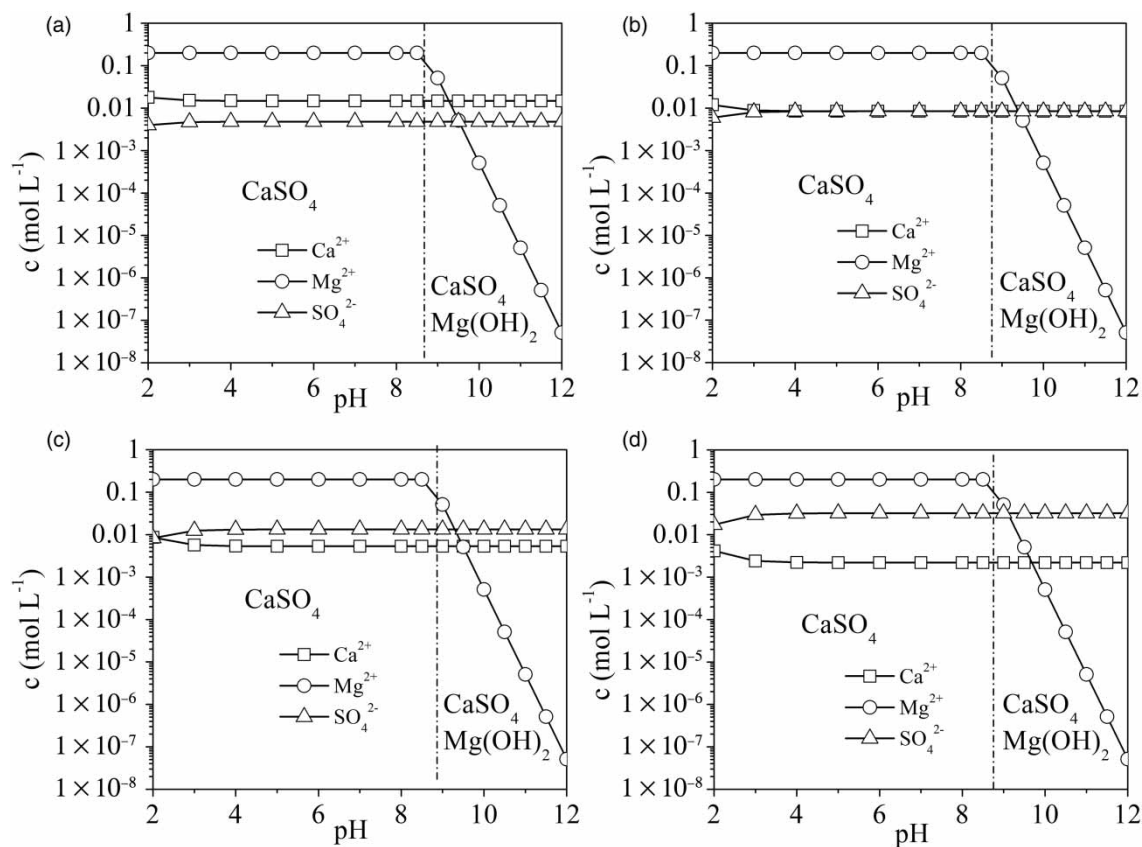


Figure 3 | Effect of pH on speciation in the simulated FGD wastewater system containing $0.20 \text{ mol L}^{-1} \text{Mg}^{2+} - 0.02 \text{ mol L}^{-1} \text{Ca}^{2+} - \text{SO}_4^{2-} - \text{H}_2\text{O}$ as a function of initial sulfate concentrations at 25°C : (a) 0.01 mol L^{-1} , (b) 0.02 mol L^{-1} , (c) 0.028 mol L^{-1} and (d) 0.05 mol L^{-1} .

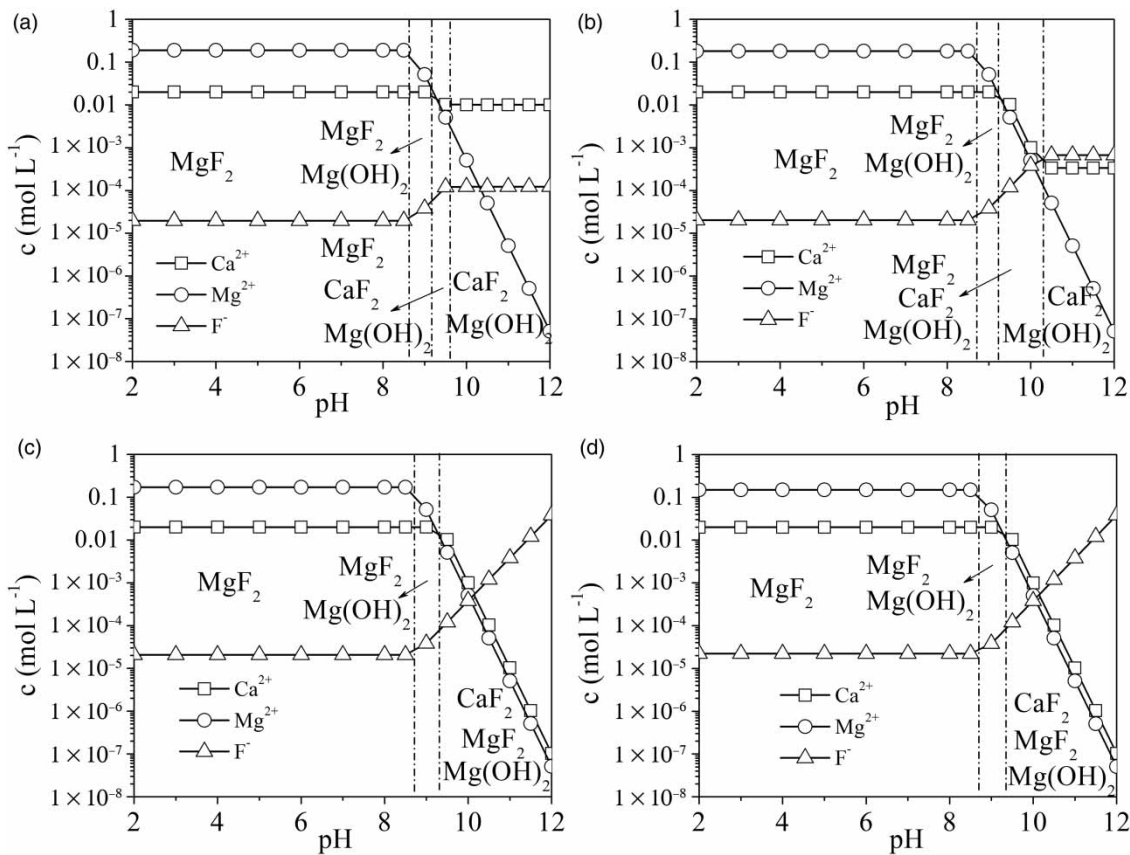


Figure 4 | Effect of pH on speciation in the simulated FGD wastewater system containing $0.20 \text{ mol L}^{-1} \text{ Mg}^{2+} - 0.02 \text{ mol L}^{-1} \text{ Ca}^{2+} - \text{F}^{-} - \text{H}_2\text{O}$ as a function of initial fluorine concentrations at 25°C : (a) 0.02 mol L^{-1} , (b) 0.04 mol L^{-1} , (c) 0.056 mol L^{-1} and (d) 0.10 mol L^{-1} .

Ca removal verification and Mg recovery

According to the thermodynamic analysis, it seems either carbonate or oxalate are the two additives most likely to be effective in precipitating Ca, while leaving Mg in solution. Figure 5(a) summarizes the experimentally derived Ca and

Mg removal efficiencies as a function of precipitation reagent (carbonate and oxalate) over selected pH ranges.

The pH range of 7.5 – 8.5 on addition of carbonate ($\times 1.4$ is the stoichiometric dosage required for CaCO_3 precipitation) is predicted to result in the reasonable precipitation of Ca^{2+} without significant loss of Mg^{2+} (Figure 1(c)).

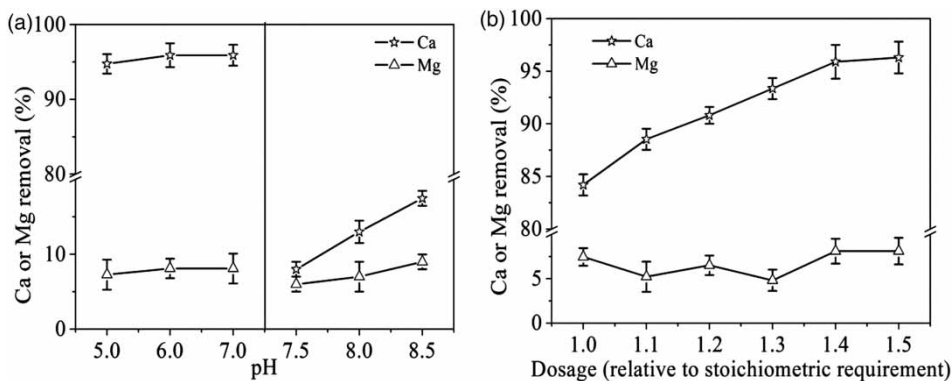


Figure 5 | Ca^{2+} or Mg^{2+} removal as a function of (a) pH using carbonate (right) and oxalate (left) at $\times 1.4$ the theoretical dosage required for Ca^{2+} precipitation, (b) varying dosages (relative to that required for stoichiometric precipitation of CaC_2O_4) of oxalate at pH 6.0 from simulated FGD wastewater at $22\text{--}25^\circ\text{C}$.

However, the separation of Ca and Mg was not found in practice to be obtainable. At pH 8.5, only 17.5% of the Ca^{2+} was precipitated, accompanied by 9.0% of the Mg^{2+} (Figure 5(a)). Most of the Ca^{2+} remained in the solution, significantly more than the theoretical value shown in Figure 1(c). The Ca^{2+} removal efficiency was considerably lower than that of the treatment of Red Sea water and RO brine reported by Sorour *et al.* (2016), which could be attributed to the lower pH used in our work and the strong competition between Mg^{2+} and Ca^{2+} , which was induced by the 2–3 times higher Mg^{2+} concentration than that of the Red Sea or RO brine. Additionally, the high Mg loss in Red Sea water (24.8%) and RO brine (22.8%) indicated the separation of Ca and Mg was unsatisfactory and was less competitive for Mg recovery, contrasted with oxalate as the Ca precipitation reagent (discussed below). Similarly, it could also explain the experimental phenomenon in real FGD wastewater treatment (Yeboah *et al.* 2015), which Ca^{2+} concentration was much larger than Mg^{2+} with the molar ratio of Ca^{2+} to Mg^{2+} reaching 6, significantly greater than 0.1 in this work, implying the interference of Mg^{2+} for CaCO_3 precipitation could be neglected even at higher pH value. Conclusively, compared to the simulation results, this smaller Ca^{2+} removal efficiency may be due to the decrease in dissociation constant for carbonic acid in systems containing high TDS, resulting in a reduced carbonate ion concentration across the pH range examined experimentally.

For oxalate addition, the pH range of 5.0–7.0 was chosen with oxalate addition of 0.028 mol L^{-1} . In contrast, nearly 100% of the Ca^{2+} was removed with little Mg^{2+} loss using oxalate as the precipitation reagent, and Ca^{2+} removal efficiency remained stable (Figure 5(a)), consistent with the thermodynamic analysis (Figure 2(c)).

Figure 5(b) presents the percentage of Ca^{2+} and Mg^{2+} precipitation as function of oxalate dosage (shown as the amounts relative to the stoichiometric requirement for CaC_2O_4 formation) at pH 6.0. On increasing the dosage from $\times 1$ to $\times 1.4$, the Ca^{2+} removal efficiency improved from 84% to 96%. When the dosage was greater than $\times 1.4$, the removal efficiency plateaued. The relatively small Ca^{2+} removal efficiency of 84% at the stoichiometric oxalate dosage may be attributed to the reduced activity of Ca^{2+} due to ion pairing (Safari *et al.* 2014) in the high salinity synthetic FGD wastewater solution, resulting in increased solubility of Ca^{2+} . The variation in dosage had little effect on Mg^{2+} removal efficiency, the value for which fluctuated by 5%. This Mg loss was more than likely produced by the physical incorporation into the precipitate rather than co-precipitation, because the precipitation of magnesium oxalate

formed so slowly that the crystallization was largely similar to coagulation of a colloid (Hallm 1928).

After Ca^{2+} precipitation due to the addition of oxalate, Mg recovery was examined. Fractional precipitation was found to improve the Mg recovery, with almost 100% recovery from a two-step process as compared to 95% from one precipitation step (Figure 6).

Characterization of the precipitate

To evaluate the crystalline phase composition of the precipitate, the product was analyzed using XRD (Figure 7(a)). The nine diffraction peaks observed all conformed to those of JPCDS Card No. 44-1482, suggesting that magnesium hydroxide was the only resulting crystalline phase. TGA-DTA data is presented in Figure 7(b). The start of weight loss commenced at 302°C , accompanied by an endothermic process agreeing well with the decomposition of magnesium hydrate into magnesium oxide. The final weight loss of 30.7%, close to the theoretical value of 30.9% for pure magnesium hydrate, indicates, as for XRD analysis, the formation of high purity $\text{Mg}(\text{OH})_2$. Atomic absorption spectroscopy analysis of the precipitate dissolved in HCl solution suggested the purity of the precipitate is in the order of 99.3 wt.%.

CONCLUSIONS

FGD wastewater contains significant amounts of magnesium, which presents a significant loss of value if disposed of as a solid waste resulting from the hardness

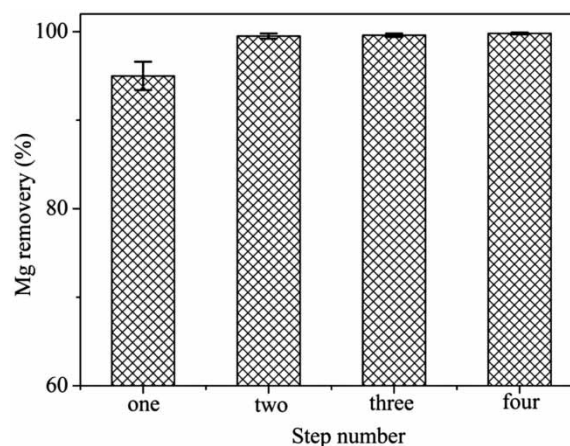


Figure 6 | Effect of fractional precipitation on Mg recovery from synthetic FGD wastewater (after treatment by $\times 1.4$ stoichiometric dosage of oxalate for CaC_2O_4 precipitation at pH 6.0) using sodium hydroxide solution at $22\text{--}25^\circ\text{C}$.

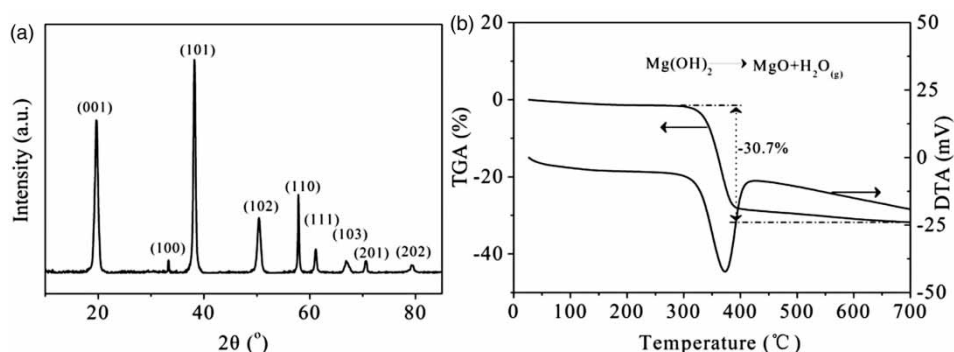


Figure 7 | (a) XRD pattern of the precipitate, magnesium hydroxide, recovered by two-step precipitation using sodium hydroxide at the scan rate of $1^\circ 2\theta \text{ min}^{-1}$; (b) TG-DTA trace of the solid product over a temperature range of 25–720 °C in an N_2 environment.

removal wastewater treatment process. In order to recover the magnesium from FGD wastewater, with exclusion of calcium, selective precipitation methods were examined. Four possible reagents were examined using theoretical thermodynamic analyses for the precipitation of calcium. The simulation results suggested that both carbonate and oxalate had the potential to remove Ca, separately to Mg, i.e. leaving Mg in solution. However, the experimental results indicated that only the oxalate system conformed to the thermodynamic analysis, with the calcium removal efficiency reaching 96% at the optimum conditions of pH 6.0 and dosage $\times 1.4$ the stoichiometric requirement. Subsequent fractional precipitation indicated that two-step precipitation could efficiently recover the Mg with efficiency close to 100%. The purity of the two-step precipitation process was determined to be high purity (99.3 wt.%) $\text{Mg}(\text{OH})_2$ without Ca impurities.

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REFERENCES

- Alamdari, A., Rahimpour, M. R. & Esfandiari, N. 2008 Kinetics of magnesium hydroxide precipitation from sea bittern. *Chemical Engineering and Processing: Process Intensification* **47**, 215–221.
- Bukowsky, H., Uhlemann, E., Gloe, K. & Mühl, P. 1992 The separation of calcium and magnesium from lithium chloride by liquid-liquid extraction with di(2-ethylhexyl) phosphoric acid. *Hydrometallurgy* **28**, 323–329.
- Dean, J. A. 1985 *Lange's Handbook of Chemistry*. McGraw-Hill, New York.
- Deng, J. J., Pan, L. M., Chen, D. Q. & Kang, M. Q. 2014 Numerical simulation and field test study of desulfurization wastewater evaporation treatment through flue gas. *Water Science and Technology* **270**, 1285–1291.
- East, C. P., Fellows, C. M. & Doherty, W. O. 2014 Modeling the co-precipitation of silica and calcium oxalate in sugar solutions. *Journal of Food Engineering* **121**, 166–73.
- Enoch, G. D., Broeke, W. & Spiering, F. W. 1994 Removal of heavy metals and suspended solids from wastewater from wet lime (stone)–gypson flue gas desulphurization plants by means of hydrophobic and hydrophilic crossflow microfiltration membranes. *Journal of Membrane Science* **87**, 191–198.
- Gude, V. G. 2015 Energy and water autarky of wastewater treatment and power generation systems. *Renewable and Sustainable Energy Reviews* **45**, 52–68.
- Hallm, W. T. 1928 The oxalate method for separating calcium and magnesium. *Journal of the American Chemical Society* **50**, 2704–2707.
- Hamzaoui, A. H., M'Nif, A., Hammi, H. & Rokbani, R. 2003 Contribution to the lithium recovery from brine. *Desalination* **158**, 221–224.
- Han, S., Liu, W., Wu, S., Long, Z. & Hou, Q. 2015 Investigation on the application of industrial grade MgO in the alkaline peroxide bleaching of poplar CTMP. *Journal of Industrial and Engineering Chemistry* **21**, 121–125.
- Henrist, C., Mathieu, J. P., Vogels, C., Rulmont, A. & Cloots, R. 2003 Morphological study of magnesium hydroxide nanoparticles precipitated in dilute aqueous solution. *Journal of Crystal Growth* **249**, 321–330.
- Huang, Y. H., Peddi, P. K., Tang, C., Zeng, H. & Teng, X. 2013 Hybrid zero-valent iron process for removing heavy metals and nitrate from flue-gas-desulfurization wastewater. *Separation and Purification Technology* **118**, 690–698.
- Hull, T. R., Witkowski, A. & Hollingbery, L. 2011 Fire retardant action of mineral fillers. *Polymer Degradation and Stability* **96**, 1462–1469.

- Lin, Q. Q., Gu, G. H., Wang, H. & Wang, C. Q. 2016 Separation of manganese from calcium and magnesium in sulfate solutions via carbonate precipitation. *Transactions of Nonferrous Metals Society of China* **26**, 1118–1125.
- Luo, Z., Yang, J., Ma, H. W., Liu, M. T. & Ma, X. 2015 Recovery of magnesium and potassium from biotite by sulfuric acid leaching and alkali precipitation with ammonia. *Hydrometallurgy* **157**, 188–193.
- Ma, S. C., Chai, J., Chen, G. D., Yu, W. J. & Zhu, S. J. 2016 Research on desulfurization wastewater evaporation: present and future perspectives. *Renewable and Sustainable Energy Reviews* **58**, 1143–1151.
- Misra, D. N. 1999 Interaction of citric or hydrochloric acid with calcium fluorapatite: precipitation of calcium fluoride. *Journal of Colloid and Interface Science* **220**, 387–391.
- Naseri, S., Moghadasi, J. & Jamialahmadi, M. 2015 Effect of temperature and calcium ion concentration on permeability reduction due to composite barium and calcium sulfate precipitation in porous media. *Journal of Natural Gas Science and Engineering* **22**, 299–312.
- Pervov, A. G. 2015 Precipitation of calcium carbonate in reverse osmosis retentate flow by means of seeded techniques—A tool to increase recovery. *Desalination* **368**, 140–151.
- Safari, H., Shokrollahi, A. & Moslemizadeh, A. 2014 Predicting the solubility of SrSO_4 in Na–Ca–Mg–Sr–Cl– SO_4 – H_2O system at elevated temperatures and pressures. *Fluid Phase Equilibria* **374**, 86–101.
- Santos, L. H., Carvalho, P. L. G., Rodrigues, G. D. & Mansur, M. B. 2015 Selective removal of calcium from sulfate solutions containing magnesium and nickel using aqueous two phase systems (ATPS). *Hydrometallurgy* **156**, 259–263.
- Sorour, M. H., Hani, H. A. & Shaalan, H. F. 2016 Separation of calcium and magnesium using dual precipitation/chelation scheme from saline solutions. *Desalination and Water Treatment* **57**, 22818–22823.
- Tatani, A., Imai, T. & Fujima, Y. 2004 Effect of Mn^{2+} on sulfite oxidation in limestone scrubbing. *Energy & Fuels* **18**, 54–62.
- Virolainen, S., Fallah, F. M., Miettinen, V., Laitinen, A. & Sainio, T. 2016 Removal of calcium and magnesium from lithium brine concentrate via continuous counter-current solvent extraction. *Hydrometallurgy* **162**, 9–15.
- Yeboah, N. N., Ellison, K. M. & Minkara, R. 2015 Treatment and Disposal Alternatives for Flue Gas Desulfurization Wastewater. World of Coal Ash (WOCA) Conference. Nashville, USA.

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