Separating Sulfur from Fuel Gas Desulfurization Gypsum with an Oxalic Acid Solution

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ABSTRACT: The separation of sulfur from the wet limestone fuel gas desulfurization (FGD) gypsum using oxalic acid solution was studied. Optimal separation conditions and a separation mechanism of sulfur were investigated. The obtained results indicate that the sulfur in FGD gypsum can be separated efficiently by oxalic acid solution. When separating under the optimal experimental conditions of 0.3 mol/L oxalic acid solution, 30 °C, and a 5/150 g/mL solid to liquid ratio for 8 min, the separation rate reached 97.0 wt %. Besides, the Avrami equation is more suitable for the kinetic analysis of the sulfur separation reaction than the unreacted shrinking core model. When the reaction temperature is less than or equal to 20 °C, the mechanism of the sulfur separation process is chemical-reaction-controlled; otherwise, it is diffusion-controlled. The activation energy E_a of the sulfur separation reaction is 34.84 kJ/mol. During the separation process, the pH of the solution gradually decreased due to the conversion of oxalic acid to sulfuric acid, so the liquid obtained after the sulfur separation of FGD gypsum can be recycled as industrial sulfuric acid. Nearly 1 mol of sulfuric acid can be obtained for every mole of oxalic acid consumption.

1. INTRODUCTION

Sulfur dioxide (SO_2) is a harmful gas that can cause acid rain, and it is mainly from the combustion of coal and petroleum.\(^1\sim3\) In the current fuel gas purification system, the limestone gypsum wet desulfurization technique is widely used as an efficient and stable method for removing SO_2 from coal-fired fuel gas.\(^4\) The main byproduct of wet limestone fuel gas desulfurization, fuel gas desulfurization (FGD) gypsum, has drawn increasing attention due to its increasing annual production. It is reported that the annual production of FGD gypsum in China has been up to 70 million tons.\(^5\) Therein, the great amount of FGD gypsum has brought about a series of severe problems, such as the waste of land resources, water pollution, dust pollution, and heavy-metal pollution.\(^6\sim8\) Therefore, how to deal with FGD gypsum to reduce environmental pollution has been widely studied by researchers.

Wet desulfurization technology consists of irreplaceable flue gas desulfurization methods at present because of their economy and availability. Therefore, the disposition of desulfurized gypsum depends on the utilization of FGD gypsum. Caillahua et al.\(^9\sim11\) studied the feasibility of using FGD gypsum as a cement retarder instead of natural gypsum. The addition of FGD gypsum can increase the setting time without affecting the compressive strength. Xu\(^12\) found that FGD gypsum could be applied to eco-friendly calcium sulfoaluminate cement manufacturing due to the high purity of calcium sulfate dehydrate. Another application is gypsum production with FGD gypsum such as for fire-resistant panels.\(^13,14\) Actually, a lot of research has focused on utilizing FGD gypsum blocks as building materials.\(^15\) When the building materials are prepared, FGD gypsum needs to be calcined into hemihydrate gypsum with good setting properties,\(^16\) which causes high production costs. Notably, considerable efforts have been devoted to preparing calcium sulfate whiskers using FGD gypsum,\(^17\sim19\) but just a small amount of FGD gypsum has been used for high-quality utilization. At present, a large amount of FGD gypsum is still used under ineffective utilization conditions,\(^20\) and the amount of FGD gypsum increases with the continuous restrictions of coal-fired flue gas emission standards. Therefore, it is urgent to develop a new utilization method for FGD gypsum.

Usually, the calcium in FGD gypsum has a high utilization value, such as when it is used as a flux in metallurgical processes.\(^21,22\) Therefore, considering FGD gypsum for metallurgical utilization can greatly improve the overall utilization of FGD gypsum. However, sulfur is harmful in most metallurgical processes because it can reduce the strength of the steel.\(^23\) If the sulfur in FGD gypsum can be separated, then the future looks bright for the use of remaining solid
material. On the basis of eqs 1 and 2, Kang$^{24,25}$ successfully removed fluoride and silicate from wastewater by using FGD gypsum. The sulfur in FGD gypsum can be separated into wastewater in the form of SO$_4^{2-}$. Because the solubility of CaF$_2$ and CaSiO$_3$ is lower than that of FGD gypsum, the sulfate in calcium sulfate can be replaced by fluoride and silicate.

$$\text{CaSO}_4 + 2\text{F}^- \rightarrow \text{CaF}_2 \downarrow + \text{SO}_4^{2-}$$ (1)

$$\text{CaSO}_4 + \text{SiO}_3^{2-} \rightarrow \text{CaSiO}_3 \downarrow + \text{SO}_4^{2-}$$ (2)

Similar to calcium fluoride and calcium silicate, the solubility of calcium oxalate is also much lower than that of FGD gypsum, and the solubility constants ($K_{sp}$s) of calcium sulfate and calcium oxalate at 25 °C are shown in eqs 3 and 4.

$$\text{CaSO}_4(s) \rightarrow \text{Ca}^{2+} + \text{SO}_4^{2-} \quad K_{sp1} = 9.1 \times 10^{-6}, \text{25°C}$$ (3)

$$\text{Ca}_2\text{C}_2\text{O}_4(s) \rightarrow 2\text{Ca}^{2+} + 2\text{C}_2\text{O}_4^{2-} \quad K_{sp2} = 4.0 \times 10^{-8}, \text{25°C}$$ (4)

Therefore, in the water solution, the oxalate can replace the sulfate in calcium sulfate to achieve sulfur separation in FGD gypsum. Compared with fluoride and silicate, oxalate is a better choice because it does not cause secondary contamination. In addition, the generated calcium oxalate can be decomposed into CaCO$_3$ in the temperature range of 400–500 °C,$^{26}$ and it can then be recycled in the metallurgical process.

Oxalic acid is a common water-soluble organic acid, and its ionization processes in water at 25 °C are shown as eqs 5 and 6. While the oxalic acid solution can provide oxalate, the hydrogen ions therein can be combined with sulfate to form sulfuric acid. Then the liquid obtained after the separation is sulfuric acid, which perhaps can be recycled as an industrial acid while the solid material without sulfur can be utilized as a metallurgical additive.

$$\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{H}^+ + \text{HC}_2\text{O}_4^- \quad K_{a1} = 5.9 \times 10^{-2}, \text{25°C}$$ (5)

$$\text{HC}_2\text{O}_4^- \rightarrow \text{H}^+ + \text{C}_2\text{O}_4^{2-} \quad K_{a2} = 6.4 \times 10^{-7}, \text{25°C}$$ (6)

Although it is theoretically feasible to use oxalic acid to separate sulfur from FGD gypsum, few studies have been carried out on the separation process. Therefore, it is necessary to conduct an experimental study on the sulfur separation of FGD gypsum with oxalic acid solution. And the kinetic mechanism should be analyzed to clarify the main influencing factors and control step in the sulfur separation process.

In this study, a novel approach toward separating sulfur from FGD gypsum with oxalic acid solution was studied by a series of experiments. The effects of acid concentration, temperature, and the solid to liquid ratio (S/L) on the separation rate were investigated to optimize the separation conditions. The separation kinetics was examined in order to clarify the control process of the reaction. The activation energy ($E_a$) of the reaction was determined according to the Avrami equation.

2. RESULTS AND DISCUSSION

2.1. Optimization of the Separation Conditions. 2.1.1. Effect of Stirring Speed. The effect of the stirring speed is complicated because it is usually attributed to the shape and size of the reactor and magnetic rotor. Therefore, the aim of this study was to determine an appropriate stirring speed to eliminate the effect of the stirring speed on the sulfur separation rate. The preliminary experimental research indicated that when the stirring speed was less than 300 rpm some FGD gypsum would be deposited on the bottom of the reactor and greatly reduced the sulfur separation rate. Therefore, the effect of the stirring speed on the sulfur separation of FGD gypsum was investigated at stirring speeds of 300 to 600 rpm under the conditions of 0.3 mol/L oxalic acid, 20 °C, and S/L = 5/150 g/mL. The results shown in Figure 1 indicate that the increase in the stirring speed had a positive effect on the sulfur separation rate, but the effect gradually decreased as the stirring speed increased. When the stirring speed reached 500 rpm, further increasing the stirring speed had almost no effect on the sulfur separation rate. Therefore, a stirring speed of 500 rpm was chosen in the following experiments to ensure that the external diffusion was completely eliminated.

2.1.2. Effect of Oxalic Acid Concentration. The effect of oxalic acid concentration (0.2–0.6 mol/L) on the sulfur separation of FGD gypsum was investigated under conditions of 20 °C, S/L = 5/150 g/mL, and 500 rpm. The reaction time of each sample increased by 2 min, and the sulfur separation results are shown in Figure 2. It is obvious that the separation rate was affected by the concentration of oxalic acid solution. The separation rate increased significantly with the reaction time within the initial 8 min and achieved stability after 8 min. Comparing the separation rates after 4 min, it can be seen that when the oxalic acid concentration was lower than 0.4 mol/L
the separation rate increased with the oxalic acid concentration because the increase in the oxalate ion concentration in the solution accelerated the reaction rate. But when the oxalic acid concentration was greater than 0.4 mol/L, the separation rate decreased with the oxalic acid concentration, for which an excessively high acid concentration inhibited the diffusion rate of ions in the solution. The H+ ionized by the sulfuric acid produced by the reaction inhibited the ionization of oxalic acid, thereby further reducing the reaction rate. A similar rule can be observed in other studies.27–30 When the reaction time was longer than 8 min, the separation rate of all samples except the sample in 0.3 mol/L oxalic acid solution changed slightly. In addition, the separation rates of 0.3 and 0.4 mol/L samples were 95.81 and 95.88 wt %, respectively. Considering their similar separation rates and the economy of this separation technology, 0.3 mol/L was chosen as the optimal oxalic acid concentration for the following experiments to achieve a higher separation rate and a lower acid consumption.

2.1.3. Effect of Reaction Temperature. Since the reaction temperature has a great effect on the chemical reaction, experiments were performed under the following conditions: 20–40 °C, 0.3 mol/L oxalic acid, S/L = 5/150 g/mL, and 500 rpm. As shown in Figure 3, the sulfur separation reaction could obviously be promoted by increasing the reaction temperature, especially during the reaction time range of 0–6 min. In the initial stage of the reaction, the separation rate was significantly affected by the temperature, but the effect gradually decreased with the increase in the reaction time. When the reaction time increased to 8 min, the separation rates under different temperatures except 20 °C were improved to 97 wt %. It is commonly known that a high reaction temperature determines the increase in energy consumption. And the sulfur separation equilibrium can be observed at 8 min at a temperature of 30 °C. Therefore, 0.3 mol/L oxalic acid, 30 °C, and 8 min were determined as the optimal conditions for the following experiments.

2.1.4. Effect of the Solid to Liquid Ratio. The effect of the solid to liquid ratio (S/L) on the separation rate of FGD gypsum was investigated in this article. During the experiment, the volume of oxalic acid solution for each experiment was kept at 150 mL, and the amount of the FGD gypsum sample was varied in the range of 3–13 g under optimum conditions of 0.3 mol/L oxalic acid, 30 °C, 500 rpm, and 8 min of reaction time. As Figure 4 shows, the separation rate decreased with the increase in S/L from S/150 to 13/150 g/mL. In the previous experimental research, it was found that the separation rate increased very slowly after the separation rate reached 97 wt %. Considering the treatment capacity and separation rate, 5/150 g/mL was selected as the optimal solid to liquid ratio.

2.2. Separation Mechanism. 2.2.1. Unreacted Shrinking Core Model. In order to clarify the relationship between the sulfur separation mechanism and the reaction parameters, kinetic conditions of the sulfur separation process were analyzed. On the basis of eq 6, the sulfur separation reaction can be regarded as a solid—liquid reaction, and the reaction product is calcium oxalate with lower solubility. Therefore, the unreacted shrinking core model was considered, and the sulfur separation process could be refined to the following steps: (1) mass transfer of $\text{C}_2\text{O}_4^{2-}$ through a liquid film to a residue—film interface, (2) $\text{C}_2\text{O}_4^{2-}$ diffusion from the residue—film interface through the residue layer to the reaction interface, (3) chemical reaction on the surface between the oxalic acid and FGD gypsum, (4) product $\text{SO}_4^{2-}$ diffusion through the residue layer, and (5) product $\text{SO}_4^{2-}$ transfer through the liquid film to the solution.33

The sulfur separation process is controlled by a chemical reaction or mass transfer, and the following equations can be used to describe the reaction kinetics of different control processes:28 eq 7 is for liquid film diffusion control, eq 8 is for chemical reaction control, and eq 9 is for ash diffusion control.

\[ X = kt \]  
\[ 1 - (1 - X)^{1/3} = kt \]  
\[ 1 - 3(1 - X)^{2/3} + 2(1 - X) = kt \]

$X$ is the separation rate, $k$ is the apparent rate constant (min$^{-1}$), and $t$ is the reaction time (min). In this study, the unreacted shrinking core model was tested at various temperatures, and the correlation coefficients are shown in Table 1. It indicates that the unreacted shrinking core models were not fit for the sulfur separation process. The columnar shape of the FGD gypsum crystal was not applicable to the basic unreacted shrinking core model, which requires particles with a spherical or nearly spherical shape.38

Considering that the solid particles involved in the solid–liquid or gas–solid reaction process were not all spherical, Levenspiel et al.34 proposed a variety of unreacted shrinking core models for solid particles of different shapes, such as plat plate particles and cylindrical particles. Since the crystal shape of FGD gypsum was columnar, the unreacted shrinking core model...
model applicable to the cylindrical particles was investigated. The following equations can be used to describe the reaction kinetics of different control processes: eq 10 is for chemical reaction control, and eq 11 is for ash diffusion control. The liquid film diffusion control equation is still eq 7.

\[
1 - (1 - X)^{1/2} = kt \\
X + (1 - X) \ln(1 - X) = kt
\]

(10)  
(11)

The correlation coefficients of the unreacted shrinking core model for cylindrical particles are shown in Table 2. The results indicate that the revised unreacted shrinking core model was still not fit for the sulfur separation process. This is because although the reaction between desulfurized gypsum and oxalic acid is a solid–liquid reaction, the nucleation and growth process of calcium oxalate on the surface of FGD gypsum crystals cannot be completely analyzed by the unreacted shrinking core models.

**2.2.2. Avrami Equation.** The Avrami kinetic equation\(^\text{35}\) shown as eq 12 was also used to describe the sulfur separation mechanisms, and the natural logarithm of eq 12 was calculated to obtain eq 13. This equation is usually used to describe the crystallization kinetics of crystals in solution and is well verified.\(^\text{36}\) In eq 12, \(X\) is the volume fraction of the material that is crystallized, \(k\) is the crystallization rate constant, \(t\) is the crystallization time (min), and \(n\) is a parameter that represents the nature of the crystallization (dimensions).\(^\text{37,38}\)

\[
-\ln(1 - X) = kt^n \tag{12}
\]

\[
\ln(-\ln(1 - X)) = ln k + ln t \tag{13}
\]

The sulfur separation reaction of FGD gypsum can be regarded as the dissolution process of CaSO\(_4\cdot\)2H\(_2\)O crystals and the crystallization process of CaC\(_2\)O\(_4\)·H\(_2\)O crystals. Therefore, when the \(X\) is considered to be the separation rate, the Avrami equation can be applied to the sulfur separation reaction process.\(^\text{36}\) But in this case, the corresponding \(k\) is the separation reaction constant, \(t\) is the separation time (min), and \(n\) is a parameter that represents the nature of the separation process. When \(n\) is higher than 0.5, the mechanism is controlled by a chemical reaction. Otherwise, it is controlled by diffusion.\(^\text{36}\)

On the basis of eq 13, the plot of ln(−ln(1 − \(X\))) vs ln \(t\) at the same temperature is a straight line, and \(n\) and ln \(k\) represent the slope and intercept of the line, respectively. All results show good linear relationships at all temperatures as shown in Figure 5 and Table 3. Correlation coefficients \(R^2\) are all greater than 0.97, which are much higher than the correlation coefficients of the unreacted shrinking core models. This proves that the Avrami equation is more suitable for the kinetic analysis of the sulfur separation reaction of FGD gypsum than the unreacted shrinking core model.

The value of \(n\) in Table 3 is usually used to determine the controlled step of the reaction process. The value of \(n\) obviously decreased with the increasing temperature during the sulfur separation process. When the reaction temperature was 20 °C, the value of \(n\) was 0.523, which was higher than 0.5. But when the reaction temperature was higher than 20 °C, the value of \(n\) was less than 0.5 and gradually decreased. It indicates that when the reaction temperature was less than or equal to 20 °C, the sulfur separation process was controlled by chemical reaction; otherwise, it was controlled by diffusion.\(^\text{36}\)

**2.2.3. Determination of Activation Energy.** The activation energy is a significant parameter for kinetic analysis, and it can be calculated by the separation reaction constant \(k\). For the sulfur separation system, the separation reaction constant \(k\) can be expressed as eq 14

\[
k = Ae^{-E_a/RT} \tag{14}
\]

where \(A\) (1/min) is the pre-exponential factor, \(E_a\) (J/mol) is the apparent activation energy, \(R\) (J/mol·K) is the universal gas constant, and \(T\) (K) is the reaction temperature. In order to obtain \(E_a\) by using the values of \(k\), eq 14 was converted to eq 15:

\[
\ln k = -\frac{E_a}{RT} + \ln A \tag{15}
\]
Equation 15 shows that the plot of \( \ln k \) vs \( 1/T \) is a straight line with a slope of \(-E_a/R\) when the oxalic acid concentration and \( S/L \) are constant. On the basis of the values of \( \ln k \) shown in Table 3, when the oxalic acid concentration was 0.3 mol/L and \( S/L \) was 5/150 g/mL, a straight line with a correlation coefficient (\( R^2 \)) of 0.989 was obtained as shown in Figure 6. The calculated activation energy, \( E_a \), was 34.84 kJ/mol.

In general, the activation energy can also reflect the control step of the chemical reaction. The apparent activation energy of diffusion control is \(-20\) kJ/mol, and that of a chemical process is \(-40\) kJ/mol. The activation energy of sulfur separation was 34.84 kJ/mol, which means that the sulfur separation process was not simply controlled by a surface chemical reaction or diffusion. Under different reaction conditions, the control step of the reaction would also change accordingly.

2.3. Characterization of the Precipitates and Solutions after Sulfur Separation of FGD Gypsum.

2.3.1. Characterization of the Precipitates. In order to study the change in the precipitate composition after sulfur separation, X-ray diffraction (XRD) and X-ray fluorescence (XRF) were used to characterize the precipitates, which were obtained under the optimum conditions (0.3 mol/L oxalic acid, 30 °C, \( S/L = 5/150 \) g/mL, and 500 rpm) at different intervals. As shown in Table 4, the sulfur content in the precipitate decreased with the increase in reaction time. On the contrary, the calcium content gradually increased with the increase in reaction time. The XRD patterns of the precipitates are presented in Figure 7. The phase identification clearly indicates that the main components of the precipitates were \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) and \( \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \). The peak strength of \( \text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \) increased with the decrease in \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) content. The XRF and XRD results prove that while oxalic acid can separate sulfur from FGD gypsum, it can also increase the yield of calcium in the precipitate.

2.3.2. Determination of the Conversion Ratio of Oxalic Acid to Sulfuric Acid. In order to study the sulfuric acid concentration in the liquid after the sulfur separation of FGD gypsum, an ion chromatography test was used to determine the concentration of sulfate radicals in the liquid under the conditions of 0.2–0.5 mol/L oxalic acid concentration and 30 °C for 10 min. The solid to liquid ratio was 9/150 g/mL to ensure that FGD gypsum was present in excess and that oxalic acid could be completely converted to sulfuric acid. The relationship between the sulfuric acid concentration after sulfur separation and the initial oxalic acid concentration was also studied, and the results are shown in Table 5. After the sulfur separation of FGD gypsum, the concentration of sulfuric acid in the solution was proportional to the initial concentration of the oxalic acid solution, and the ratio was nearly 1. This means that 1 mol of sulfuric acid could be obtained for every mole of oxalic acid consumed after the sulfur separation of FGD gypsum. Therefore, the sulfur in FGD gypsum can be separated and utilized as an industrial sulfuric acid for recycling.

2.3.3. pH Analyses of the Solutions. The change in the pH trend of the solution during the separation process is shown in Figure 8, and the changes in the trends in the pH and sulfur separation rate were completely opposite. The solution pH decreased as the separation rate increased. This is mainly due to the fact that oxalic acid is a weak electrolyte, the secondary ionization is weak, and it is incompletely ionized in water. Sulfuric acid is a strong electrolyte that can be almost completely ionized in water as \( \text{H}^+ \) and \( \text{SO}_4^{2-} \). With the
conversion of oxalic acid to sulfuric acid, the H⁺ concentration in the solution gradually increased, which resulted in the pH decreasing. This is consistent with the results shown in Table 5.

3. CONCLUSIONS

This study further proved the feasibility of separating sulfur from FGD gypsum by a series of experiments. The optimal experimental conditions and separation mechanism of separating sulfur from FGD gypsum were investigated. On the basis of the experimental results, the optimal separation conditions could be confirmed, and the separation rate reached 97 wt % with 5/150 g/mL for the solid to liquid ratio and 0.3 mol/L oxalic acid at 30 °C for 8 min.

Compared with the unreacted shrinking core model, the Avrami equation was more suitable for the kinetic analysis of the reaction between FGD gypsum and oxalic acid solution. Kinetic analysis results indicate that the mechanism of the sulfur separation process was a chemical reaction controlled at 20 °C; otherwise, it was diffusion-controlled. The activation energy Ea of the sulfur separation reaction was 34.84 kJ/mol. XRD and ion chromatography were employed to detect the components of the solution and precipitate after the sulfur separation. The main component of the precipitate was calcium oxalate, which could be used as a flux in metallurgical processes. On the basis of the sulfur separation reaction by oxalic acid, 1 mol of sulfuric acid could be obtained for every mole of oxalic acid consumed, which could be recycled as industrial sulfuric acid. By this new method, the utilization rate of FGD gypsum could be greatly improved, and the secondary environmental pollution problem caused by FGD gypsum would be effectively resolved.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. FGD gypsum was obtained from a coal-combustion power plant equipped with a wet limestone FGD scrubber in Chongqing, China. It was dried to a constant weight at 40 °C to eliminate the effect of free water on the experiment, and then it was crushed into particles with a diameter of 0.074 mm for use. Oxalic acid (H₂C₂O₄·2H₂O, analytical reagent) and deionized (DI) water were used to prepare the oxalic acid solution. The elemental composition, mineralogical composition, and morphology of FGD gypsum are shown in Table 6 and Figures 9 and 10, respectively. As shown in Table 6, Ca, S, and O were the main components of FGD gypsum, and the sulfur content was 16.02 wt %. Phase analysis results show that the main component of FGD gypsum was CaSO₄·2H₂O. The crystal morphology of FGD gypsum was short columnar, as shown in Figure 10.

4.2. Sulfur-Separating Experiment. The flow sheet of the sulfur separation process is shown in Figure 11. First, different concentrations of oxalic acid solutions were prepared. Then the oxalic acid solution was placed in a glass reactor (glass reactor, diameter 105 mm, and height 145 mm) with magnetic stirring at 500 rpm. The constant-temperature water bath was used to keep the sulfur separation process at a specified temperature. After the temperature of oxalic acid solution was stable, FGD gypsum powder was added to the reactor and kept stirring. The reaction between FGD gypsum and oxalic acid is shown as eq 16:

\[
\text{CaSO}_4 + \text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CaC}_2\text{O}_4 \downarrow + \text{H}_2\text{SO}_4
\]  

A suction filtration device was used to perform solid—liquid separation after a certain reaction period. The precipitate separated from FGD gypsum was dried at 60 °C to a constant weight for additional analysis.

4.3. Sulfur Separation Rate of FGD Gypsum. The sulfur separation of FGD gypsum under different experimental conditions was studied, and the separation rate was calculated as follows

\[
r = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

where \( r \) is the separation rate, \( C_0 \) (wt %) is the initial sulfur content in the FGD gypsum sample, and \( C_t \) (wt %) is the sulfur content of the sample after sulfur separation.

4.4. Analytical Methods. X-ray fluorescence (XRF-1800, Shimadzu Corporation) with a scan area of \( \phi = 30 \text{ mm}^2 \) was used to obtain the sulfur content change of FGD gypsum before and after sulfur separation. Before the test, the peak

### Table 6. Chemical Composition of FGD Gypsum (wt %)

| O   | Ca   | S    | Si   | Al  | Fe  | K   | Sr  | Ti  | F   |
|-----|------|------|------|-----|-----|-----|-----|-----|-----|
| 51.07 | 27.64 | 16.02 | 2.20 | 0.75 | 0.25 | 0.20 | 0.11 | 0.04 | 1.22 |
value of sulfur was calibrated with an analytically pure CaSO$_4$·2H$_2$O sample to ensure the accuracy of the sulfur content measurement in the experimental samples.

X-ray diffraction (D/Max 2500pc, Nippon Science Co., Ltd.) using Cu Kα radiation at a scanning rate of 2° min$^{-1}$ in the 2θ range from 10 to 70° was used to determine the phase change of the samples.

According to the theoretical analysis, the sulfur in FGD gypsum was completely separated into the solution during the separation process, and most of the elemental sulfur exists in the form of SO$_4^{2-}$. In order to estimate the concentration of H$_2$SO$_4$ in the separated liquid, an ion chromatograph (IC-2010, Tosoh, Japan) was used to measure the concentration of SO$_4^{2-}$ in the liquid. The pH meter (FE28, Mettler Toledo, Shanghai) was used to measure the pH of the solution.

To avoid random errors, three parallel experiments were conducted during the whole leaching and precipitation experiments, and the average values would be taken as the final results.

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