

Research Article

Removal of High-Concentration Sulfate Ions from the Sodium Alkali FGD Wastewater Using Ettringite Precipitation Method: Factor Assessment, Feasibility, and Prospect

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The feasibility of removal of sulfate ions from the sodium alkali FGD wastewater using the ettringite precipitation method was evaluated. Factors affecting the removal of sulfate ions, such as NaAlO_2 dosage, $\text{Ca}(\text{OH})_2$ dosage, solution temperature, anions (Cl^- , NO_3^- and F^-), and heavy metal ions (Mg^{2+} and Mn^{2+}), were investigated, and the optimal experimental conditions for the removal of sulfate ions were determined. Experimental results indicate that the ettringite precipitation method can effectively remove SO_4^{2-} with removal efficiency of more than 98%. All the investigated factors have influences on the removal of sulfate ions, and among them, the dosage of reagents, solution temperature, and fluoride ions have the strongest influence. In addition, the method can effectively synergistically remove F^- and heavy metal ions with removal efficiencies of more than 90% and 99%, respectively; meanwhile, Cl^- and NO_3^- also can be removed minimally by the method. The result of actual wastewater treatment shows that the method is feasible for treating high-concentration sulfate wastewater. The ettringite precipitation method has the potential to be a commercial application in the future.

1. Introduction

At present, the wet flue gas desulfurization (WFGD) is the most commonly used technology in the field of industrial flue gas desulfurization in China [1]. For power plant flue gas desulfurization, the main technology used in China is limestone-gypsum wet process. High desulfurization efficiency and gypsum recycling are the main advantages of this technology. However, some disadvantages, such as the complex system, higher investment cost, and requirement for a large area, have limited the application of this technology in the flue gas desulfurization of industrial boilers and furnaces in China. Therefore, the sodium alkali (NaOH) FGD technology with relatively simple process and high SO_2 removal efficiency (>95%) is widely used in the flue gas desulfurization of industrial boilers and furnaces. However, there are some shortcomings in this technology that need further improvement. One of the major problems is the disposal of complex and sulfate-rich wastewater.

The sulfate (SO_4^{2-}) concentration in the sodium alkali (NaOH) FGD wastewater is generally more than 10,000 mg/L; the maximum can be greater than 20,000 mg/L. In addition, the wastewater also contains a large number of inorganic anions (NO_3^- , Cl^- , and F^-) and heavy metal ions (Mg^{2+} and Mn^{2+}). Though SO_4^{2-} is a common and nontoxic component of various types of water bodies, high concentrations of SO_4^{2-} in the water can cause a series of serious environmental problems, leading to water mineralization, metal corrosion, pipes and equipment scaling, toxic hydrogen sulfide release, and disruption in the balance of the natural sulfur cycle [2–5]. In addition, high concentrations of SO_4^{2-} (>600 mg/L) in the water can cause laxative effects in mammals [6]. Hence, to protect the environment, the SO_4^{2-} concentration in the industrial effluents is set ranging from 250 mg/L to 500 mg/L in many countries [6]; for example, the sulfate ion concentration limit values in the industrial recycling water and surface water are all set as 250 mg/L in China. Hence, in order to meet the discharge standard or achieve the recycling of

desulfurization wastewater, it is necessary to remove the sulfate ion in the sodium alkali FGD wastewater.

Currently, several technologies, such as biological treatment [7, 8], membrane filtration [9], adsorption [10], ion exchange [11, 12], electrocoagulation [13], crystallization [14, 15], and chemical precipitation [16], have been developed to treat sulfate in water. However, these methods are not very suitable for the treatment of high concentration of SO_4^{2-} wastewater, except the chemical precipitation method. The chemical precipitation method mainly includes lime precipitation [6], barium chloride precipitation [17, 18], and ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) precipitation methods [19]. The limestone precipitation method is widely used in the field of water treatment; however, due to the relatively high solubility of gypsum [19], the SO_4^{2-} removal efficiency is low. The barium chloride precipitation method can reach high SO_4^{2-} removal efficiency, but a large number of corrosive chloride ions and toxic barium ions will be introduced into the water; besides, barium chloride is more expensive than lime, so the technology is rarely used in the field of flue gas desulfurization wastewater treatment.

Compared with the above methods, the ettringite precipitation method is considered as an effective method for treating high-concentration sulfate effluents. In this method, lime and aluminum salts are added into the wastewater to react with sulfate to form insoluble ettringite ($\text{pK}_{\text{sp}} = 111.6$) [20], and then sulfate is effectively removed. The ettringite precipitation method has become a preferred method due to its high removal efficiency and cost-effectiveness, and many studies have used this method to treat industrial wastewaters, such as aluminum anodizing, textile industries, and mine water [19–21]. However, in existing researches the sulfate concentrations in simulated or actual wastewaters were usually lower; hence, anions and heavy metal ions were not considered in the removal of sulfate; meanwhile, there exists little information on the removal of SO_4^{2-} from the sodium alkali (NaOH) FGD wastewater using the method in the literatures.

The aims of this study are to evaluate the feasibility of removal of high-concentration SO_4^{2-} from the sodium alkali FGD wastewater by using the ettringite precipitation method and investigate the influence of different parameters on SO_4^{2-} removal, in particular, anions and heavy metal ions. In addition, the removal of SO_4^{2-} and other ions in actual sodium alkali FGD wastewater by using ettringite precipitation method was also studied. Finally, the optimal experimental conditions for the removal of high-concentration sulfate ions were determined.

2. Experimental Section

2.1. Materials. $\text{Na}(\text{SO}_4)_2$, NaAlO_2 , $\text{Ca}(\text{OH})_2$, NaF , NaCl , KNO_3 , NaOH , MgSO_4 , MnSO_4 , and HNO_3 were of analytical grade and used directly without purification. NaAlO_2 and $\text{Ca}(\text{OH})_2$ were used as aluminum and calcium sources in this study. All reagents were purchased from Guangzhou Chemical Reagent Factory. The sulfate-rich simulated wastewater used in this study was prepared by dissolving Na_2SO_4 in deionized water to get initial SO_4^{2-} concentration of 10,000 mg/L. The initial pH of the solution was adjusted using HNO_3 (1.0 mol/L) and NaOH (1.0 mol/L).

TABLE 1: Results of anions removal.

	SO_4^{2-}	Cl^-	F^-	NO_3^-	pH
Actual wastewater, mg/L	15,274.8	205.56	101.43	58.30	7.8
Purified wastewater, mg/L	172.61	199.71	7.95	54.94	13.1
Average removal efficiency, %	98.87	2.85	92.16	5.76	—

TABLE 2: Results of heavy metal ions removal.

	Cr^{2+}	Mg^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
Actual wastewater, mg/L	3.55	15.48	22.76	5.53	5.15	5.29
Purified wastewater, mg/L	—	0.0102	0.0019	—	—	—
Average removal efficiency, %	100	99.93	99.99	100	100	100

The actual sodium alkali (NaOH) FGD wastewater was obtained from a ceramic production enterprise located in Guang Dong Province, China. The composition of the ions in the wastewater was analyzed and the results are shown in Tables 1 and 2 (in Section 3.8).

2.2. Analytical Methods. The concentrations of SO_4^{2-} , NO_3^- , F^- , and Cl^- in the solution were analyzed with an ion chromatography system (Metrohm 883, Switzerland). The concentrations of heavy metal ions, such as Mg^{2+} and Mn^{2+} , were measured using an inductively coupled plasma emission spectrometer (ICP-AES 710, Agilent Technologies). An MP511 pH detector (Shanghai Precision Instruments Co., Ltd.) was used to determine the pH of the solution.

2.3. Removal of Sulfate Ions. Experiments were performed on a six league electric blender (ZR4-6, China). The experimental steps of the ettringite precipitation method are as follows: (1) 1 L of solution sample was taken in a glass reactor, and a certain amount of $\text{Ca}(\text{OH})_2$ and NaAlO_2 was added to the solution. (2) Then, the sample was stirred at a certain speed for a certain time. (3) Finally, the sample was taken and filtered under vacuum using a $0.45 \mu\text{m}$ microporous membrane filter. The filtrates were analyzed for SO_4^{2-} and other ions, and finally, the SO_4^{2-} and other ions removal efficiencies were calculated by (1). According to the above steps, batch experiments effecting different experimental conditions on SO_4^{2-} removal were implemented, including $\text{Ca}(\text{OH})_2$ dosage (the molar ratios of $\text{Ca}(\text{OH})_2$ to SO_4^{2-} of 1~6:1), NaAlO_2 dosage (the molar ratios of NaAlO_2 to SO_4^{2-} of 0.7~3:1), solution initial pH (3.0~11.0), solution temperature (25~80°C), reaction time (15~120 min), stirring speed (100~500 r/min), and the concentrations of Cl^- (500~4000 mg/L), NO_3^- (100~2000 mg/L), F^- (200~1000 mg/L), Mg^{2+} (50~1000 mg/L), and Mn^{2+} (50~1000 mg/L):

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\%, \quad (1)$$

where η is the SO_4^{2-} or other ions removal efficiency and C_0 and C_t are the initial and final SO_4^{2-} or other ions concentrations of solutions (mg/L), respectively.

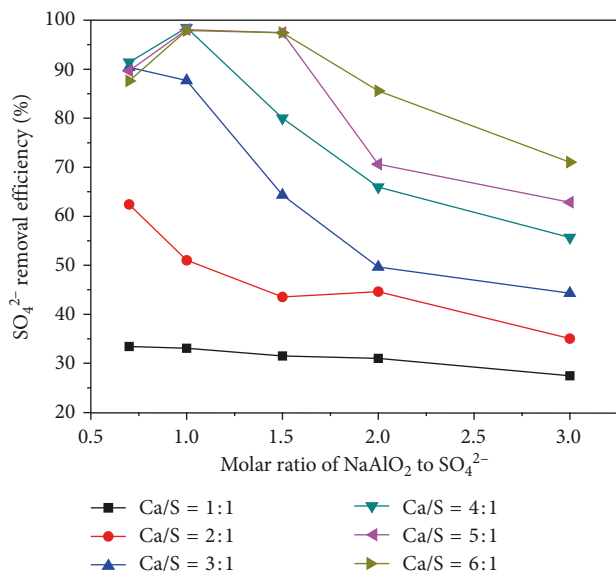


FIGURE 1: The effect of NaAlO_2 dosage. $V_{\text{solution}} = 1 \text{ L}$, $T = 25^\circ\text{C}$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, and $\text{pH} = 7.0$.

3. Results and Discussion

3.1. Effect of NaAlO_2 Dosage and $\text{Ca}(\text{OH})_2$ Dosage. Previous researches have shown that SO_4^{2-} removal was significantly affected by NaAlO_2 dosage and $\text{Ca}(\text{OH})_2$ dosage [21, 22]. So the effects of NaAlO_2 dosage and $\text{Ca}(\text{OH})_2$ dosage on SO_4^{2-} removal were investigated and the results are shown in Figures 1 and 2.

As depicted in Figure 1, the SO_4^{2-} removal was greatly affected by the NaAlO_2 dosage, but the effect of NaAlO_2 dosage on the removal of sulfate was different under different molar ratios of $\text{Ca}(\text{OH})_2$ to SO_4^{2-} (Ca/S ratio). The SO_4^{2-} removal decreased with increasing NaAlO_2 dosage, when the Ca/S ratio was less than 3 : 1. However, it was found that the SO_4^{2-} removal increased with the increase of the molar ratios of NaAlO_2 to SO_4^{2-} (Al/S ratio) at first, then decreased rapidly with the increase of NaAlO_2 dosage when the Ca/S ratio was more than 4 : 1. The theoretical Al/S ratio found in $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ is about 0.67; the NaAlO_2 dosage was added in excess (Al/S ratio ≥ 0.7) in the series of experiments. It was found that the amount of ettringite generated was reduced with an increase of NaAlO_2 dosage; meanwhile, the monosulfate ($\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12}$) generation increased [21]. The Al/S ratio in the monosulfate is 2 : 1 higher than the ettringite (2 : 3), and the Ca/S ratio in the monosulfate is 4 : 1 higher than the ettringite (2 : 1). Therefore, sulfate ions are mainly removed in monosulfate form at the high NaAlO_2 dosage condition, resulting in large consumption of calcium and aluminum, and reduction of sulfate ion removal. The results have shown that overdosing of NaAlO_2 is not conducive to sulfate ions removal; the preferred Al/S ratio is 1 : 1.

The effect of $\text{Ca}(\text{OH})_2$ dosage on SO_4^{2-} removal is shown in Figure 2. The results show that SO_4^{2-} removal increased with an increase of $\text{Ca}(\text{OH})_2$ dosage at first, then decreased slowly with the $\text{Ca}(\text{OH})_2$ dosage further increasing, when

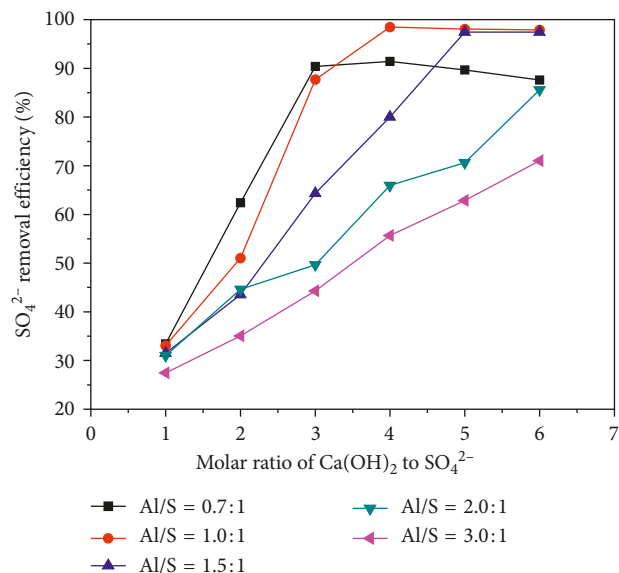
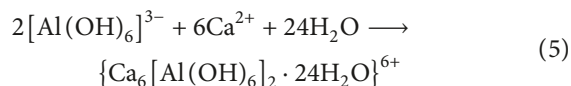
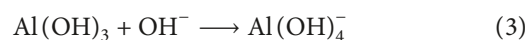
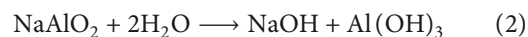


FIGURE 2: The effect of $\text{Ca}(\text{OH})_2$ dosage. $V_{\text{solution}} = 1 \text{ L}$, $T = 25^\circ\text{C}$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, and $\text{pH} = 7.0$.

the Al/S ratio was less than 1.5 : 1. This is because Ca^{2+} concentration in the solution increased with an increase of $\text{Ca}(\text{OH})_2$ dosage, which facilitated the SO_4^{2-} removal. However, the pH of the solution increased with an increase of $\text{Ca}(\text{OH})_2$ dosage. The reaction of NaAlO_2 hydrolysis could be inhibited by hydroxide ions; meanwhile, the hydroxide ions could promote the formation of monosulfate, and finally, the SO_4^{2-} removal decreased with the increase of the solution pH. When the Al/S ratio was higher than 1.5 : 1, SO_4^{2-} removal increased with the increase of $\text{Ca}(\text{OH})_2$ dosage. The main reason is that sulfate ions are mainly removed in the monosulfate form at the high NaAlO_2 dosage condition. The molar ratio of Ca^{2+} to SO_4^{2-} in the monosulfate is twice as much as that in the ettringite, and the concentration of Ca^{2+} in the solution increased with the $\text{Ca}(\text{OH})_2$ dosage increasing, leading to generate a large amount of ettringite. Thus, the SO_4^{2-} removal increased. However, it is deduced that SO_4^{2-} removal will decrease with further increase in the $\text{Ca}(\text{OH})_2$ dosage, as a large number of hydroxide ions are not conducive to the formation of ettringite. So overdosing of $\text{Ca}(\text{OH})_2$ is neither desirable nor cost-effective; the preferred Ca/S ratio is 4 : 1.

Considering the SO_4^{2-} removal and cost-effectiveness, in the next series of experiments the molar ratios of $\text{Ca}(\text{OH})_2$ to NaAlO_2 to SO_4^{2-} (Ca : Al : S) were constant at 4 : 1 : 1. In addition, based on the literatures and experimental results [19, 21], the following chemical equilibrium reactions can be used to describe the SO_4^{2-} removal reaction process:



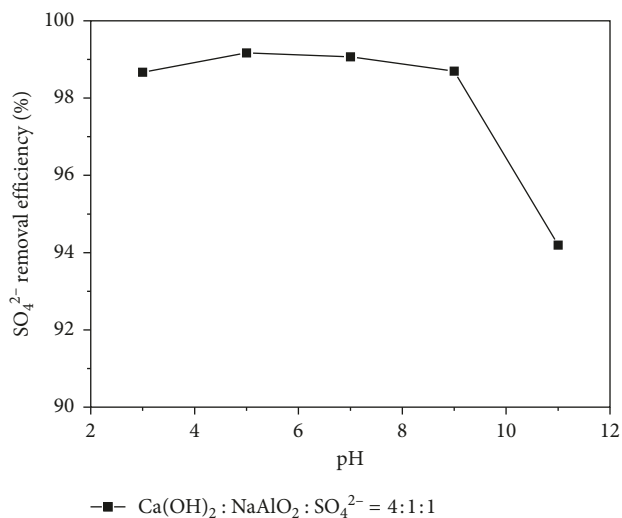
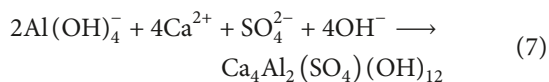
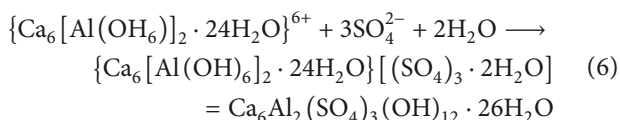


FIGURE 3: The effect of the solution initial pH. $V_{\text{solution}} = 1 \text{ L}$, $T = 25^\circ\text{C}$, $v = 200 \text{ r/min}$, and $t = 30 \text{ min}$.



3.2. Effect of the Solution Initial pH. It can be seen from Figure 3 that the removal of SO_4^{2-} was negligibly affected by the solution initial pH when the pH was ranging from 3.0 to 9.0 and the SO_4^{2-} removal efficiencies maintained at around 99% within the pH range. However, SO_4^{2-} removal efficiencies decreased slowly when the initial pH was more than 9.0; for example, the SO_4^{2-} removal efficiencies decreased from 98.69% to 94.19% in the pH range of 9.0~11.0. There are two main reasons for this outcome. One of the reasons is that $\text{Ca}(\text{OH})_2$ solubility decreased with the increase of solution pH, resulting in lower Ca^{2+} concentration in the solution and less ettringite production. Another reason is that the amount of CO_2 absorbed by the solution increased with increasing alkalinity of the solution, resulting in an increase of CO_3^{2-} concentration in the solution; thus CO_3^{2-} can react with ettringite to form hydrated carbonated calcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$) [19, 23], leading to decrease in SO_4^{2-} removal efficiencies. Therefore, it is necessary to control the wastewater pH in practical engineering applications in the range of 5.0~9.0 to achieve a higher SO_4^{2-} removal.

3.3. Effect of Solution Temperature. Solution temperature is one of the important factors in SO_4^{2-} removal. As Figure 4 shows, SO_4^{2-} removal sharply decreased from 99.29% to 37.62%, when the solution temperature increased from 25 to 80°C . The main reason is that the solubility of $\text{Ca}(\text{OH})_2$ increases with increasing temperature, and that the solution pH

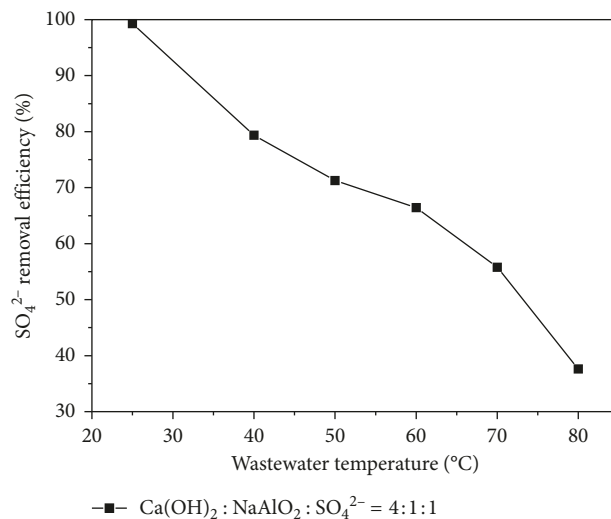


FIGURE 4: The effect of solution temperature. $V_{\text{solution}} = 1 \text{ L}$, $v = 200 \text{ r/min}$, $t = 30 \text{ min}$, and $\text{pH} = 7.0$.

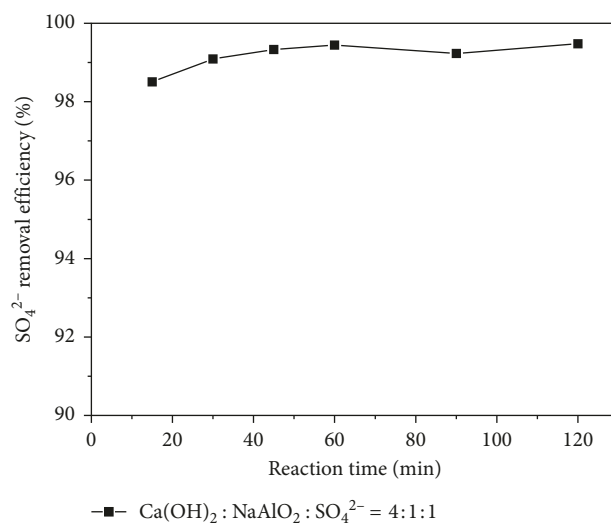


FIGURE 5: The effect of reaction time. $V_{\text{solution}} = 1 \text{ L}$, $v = 200 \text{ r/min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

increases significantly with the increase of temperature. For example, when the reaction temperatures were 25 and 80°C , the solution pH after the reaction were 12.8 and 13.5, respectively. However, previous studies have shown that the optimal pH range for producing stability of ettringite is about 11~12.5 [21, 24]. On the one hand, increasing the solution pH will inhibit the hydrolysis of sodium aluminate and further hinder the formation of $\text{Al}(\text{OH})_4^-$ and $\text{Al}(\text{OH})_6^{3-}$; on the other hand, increasing the pH will promote the decomposition of ettringite [21]. In addition, the solubility of ettringite increases with increasing temperature. Therefore, in order to achieve a higher SO_4^{2-} removal, it is necessary to reduce the wastewater temperature in practical engineering applications.

3.4. Effect of Reaction Time. Figure 5 displays the effect of reaction time on SO_4^{2-} removal. The results show that the

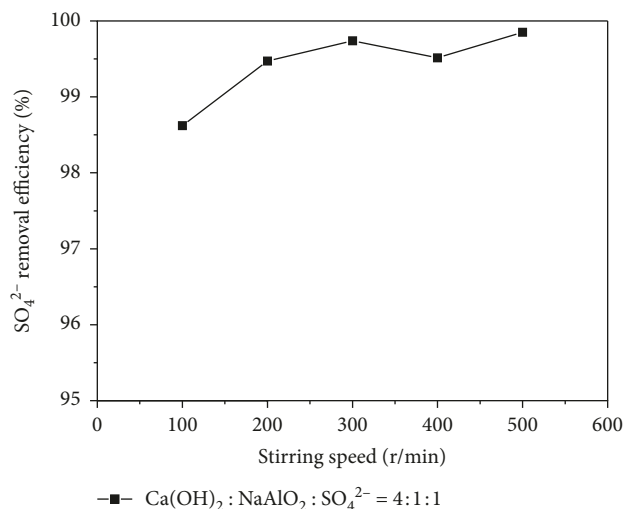


FIGURE 6: The effect of stirring speed. $V_{\text{solution}} = 1 \text{ L}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

reaction time has a minimal effect on SO_4^{2-} removal. SO_4^{2-} removal efficiencies were 98.51%, 99.09%, 99.33%, 99.45%, 99.23%, and 99.48% when the reaction time were 15, 30, 45, 60, 90, and 120 min, respectively. SO_4^{2-} removal slightly increased with the increase of the reaction time. However, due to the low solubility of $\text{Ca}(\text{OH})_2$, SO_4^{2-} removal was negligibly affected by the reaction time and remained almost constant at about 99%. The results show that the reaction of Ca^{2+} , Al^{3+} , and SO_4^{2-} is a rapid reaction under alkaline condition, being almost complete within 30 min. Taking into account the economic factor, area required, and SO_4^{2-} removal, the reaction time was selected as 30 min.

3.5. Effect of Stirring Speed. The influence of stirring speed on SO_4^{2-} removal was investigated and the results are shown in Figure 6. The results indicate that SO_4^{2-} removal was slightly affected by the stirring speed, and the SO_4^{2-} removal increased slowly from 98.62% to 99.5% with the increase of stirring speed from 100 to 500 r/min. In general, the increase of stirring speed helps promote the dissolution of the reagents by increasing the opportunities for contact and collision of ions and promote SO_4^{2-} removal. However, in this study the increase of stirring speed cannot significantly increase the SO_4^{2-} removal; the main reason is that the reaction of ettringite formation is a rapid reaction, and the appropriate stirring speed just can promote the completion of the reaction. Hence, it is not necessary to use high stirring speed to promote the reaction completion. Considering the cost and SO_4^{2-} removal, the stirring speed was selected as 200 r/min.

3.6. Effect of Coexisted Anions. The flue gas usually contains chloride, fluoride, nitrogen oxides, and other components; they can be absorbed by the washing liquid. Therefore, certain concentrations of chloride, fluoride, and nitrate ions will be present in the desulfurization wastewater. In this study, the effects of coexisted anions such as Cl^- , NO_3^- , and F^- on SO_4^{2-} removal have been investigated, and the results are shown in Figures 7–9.

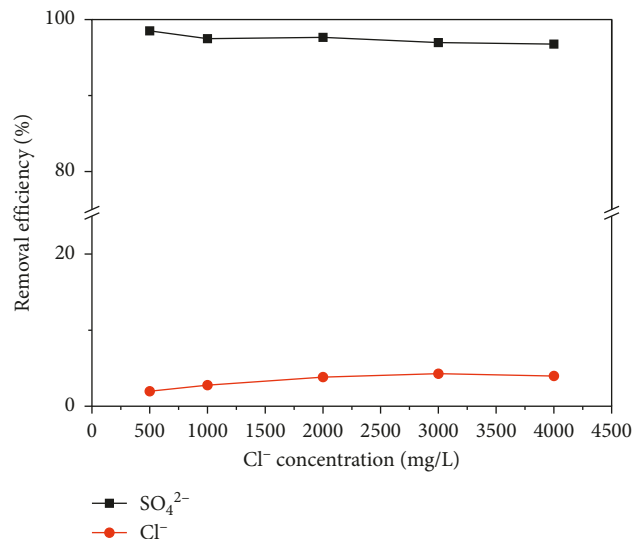


FIGURE 7: The effect of Cl^- concentration. $V_{\text{solution}} = 1 \text{ L}$, $n(\text{Ca} : \text{Al} : \text{S}) = 4 : 1 : 1$, $v = 200 \text{ r/min}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

As Figure 7 illustrates, SO_4^{2-} removal slowly decreased from 98.52% to 96.77% when the Cl^- concentration increased from 500 mg/L to 4000 mg/L. The results show that SO_4^{2-} removal is negligibly affected by the low Cl^- concentration (less than 2000 mg/L), but there is a certain negative impact on the SO_4^{2-} removal when the Cl^- concentration is high. It was reported that Cl^- can react with Ca^{2+} and Al^{3+} to form the $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ [25], though the solubility products of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ ($10^{-27.10}$) are much less than the solubility products of $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ ($10^{-111.6}$) [20, 25]; however, the high Cl^- concentration causes competitive reactions of Cl^- and SO_4^{2-} for the Ca^{2+} and Al^{3+} , resulting in a decrease of SO_4^{2-} removal. Overall, chloride ions have a minimal effect on the removal of sulfate ions. Compared with the high SO_4^{2-} removal, Cl^- removal is low. When Cl^- concentration varied from 500 mg/L to 4000 mg/L, Cl^- removal almost remained stable at the range of 2% to 5%. Hence, in the case of coexistence of SO_4^{2-} and Cl^- , SO_4^{2-} will be first effectively removed by using this method.

As demonstrated in Figure 8, the SO_4^{2-} removal was minimally affected when the NO_3^- concentration was less than 500 mg/L and remained stable at about 98%. However, when the NO_3^- concentration increased from 500 mg/L to 2000 mg/L, the removal of SO_4^{2-} decreased from 97.76% to 90.38%; meanwhile, the removal of NO_3^- almost remained stable at the range of 15% to 18% when the NO_3^- concentration increased from 500 mg/L to 2000 mg/L. The main reason is that high NO_3^- concentration causes severe competitive reactions of NO_3^- and SO_4^{2-} for the Ca^{2+} and Al^{3+} . NO_3^- can react with Ca^{2+} and Al^{3+} to form $\text{Ca}_4\text{Al}_2(\text{NO}_3)_2(\text{OH})_{12}$ [26]; hence, NO_3^- has a negative impact on SO_4^{2-} removal under high NO_3^- concentration.

It can be seen from Figure 9 that the presence of F^- in the solution has a significant inhibitory effect on SO_4^{2-} removal. SO_4^{2-} removal decreased rapidly from 98.49% to 61.39% when the F^- concentration increased from 200 mg/L to 1000 mg/L; meanwhile, the removal of F^- increased slowly from 92.24% to 96.34%. It is speculated that F^- could react with Ca^{2+} to form

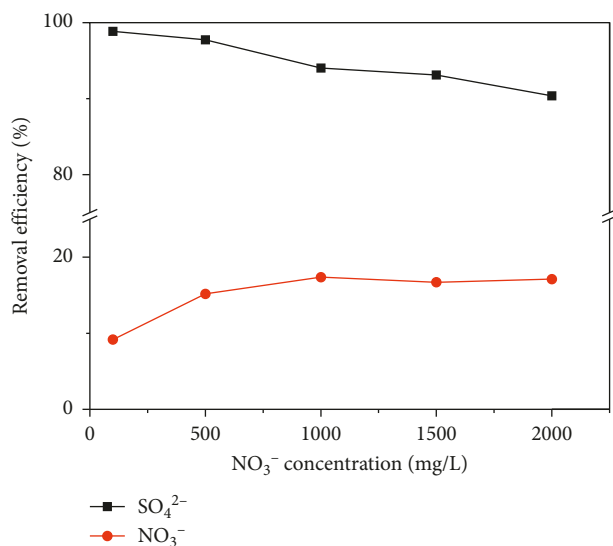


FIGURE 8: The effect of NO_3^- concentration. $V_{\text{solution}} = 1 \text{ L}$, $n(\text{Ca} : \text{Al} : \text{S}) = 4 : 1 : 1$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

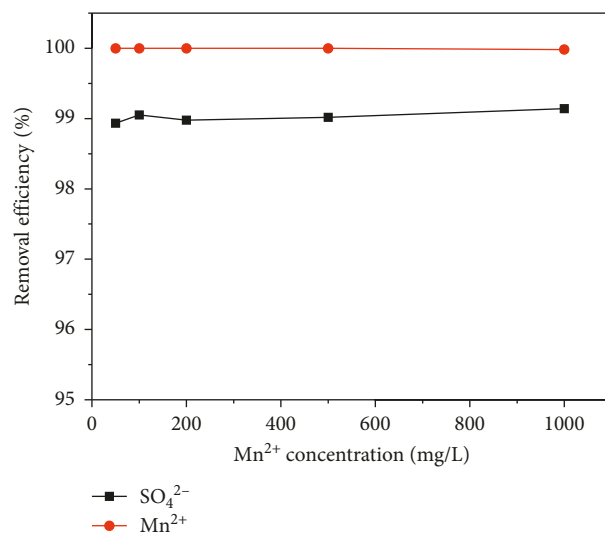


FIGURE 10: The effect of Mn^{2+} concentration. $V_{\text{solution}} = 1 \text{ L}$, $n(\text{Ca} : \text{Al} : \text{S}) = 4 : 1 : 1$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

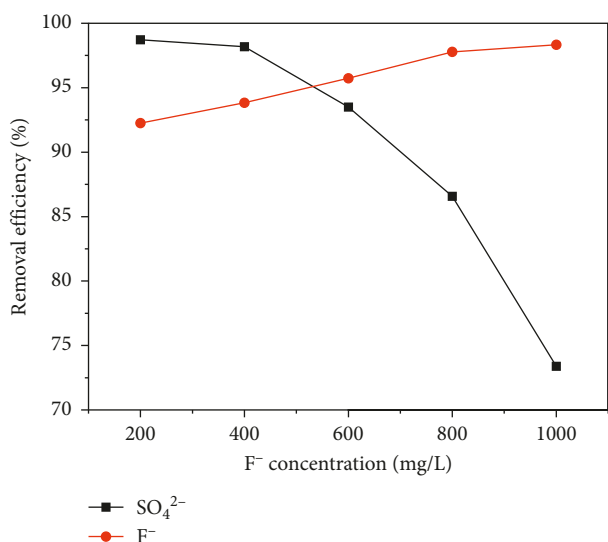


FIGURE 9: The effect of F^- concentration. $V_{\text{solution}} = 1 \text{ L}$, $n(\text{Ca} : \text{Al} : \text{S}) = 4 : 1 : 1$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

insoluble CaF_2 , so the competitive reactions of Ca^{2+} with F^- and SO_4^{2-} existed in the solution and the amount of Ca^{2+} was insufficient in the solution due to the low solubility of $\text{Ca}(\text{OH})_2$; hence, SO_4^{2-} removal decreased with the increase in the F^- concentration.

The research has shown that different types of anions in the solution had different effects on the removal of sulfate ions. The ability of three anions affected the SO_4^{2-} removal is $\text{F}^- > \text{NO}_3^- > \text{Cl}^-$. It suggests that if the wastewater contains high concentrations of F^- and SO_4^{2-} , F^- must first be removed in order to achieve high SO_4^{2-} removal.

3.7. Effect of Coexisted Heavy Metal Ions. A variety of heavy metal ions such as Pb^{2+} , Ni^{2+} , Mg^{2+} , and Mn^{2+} usually exist in the desulfurization absorption solution. The flue gas is

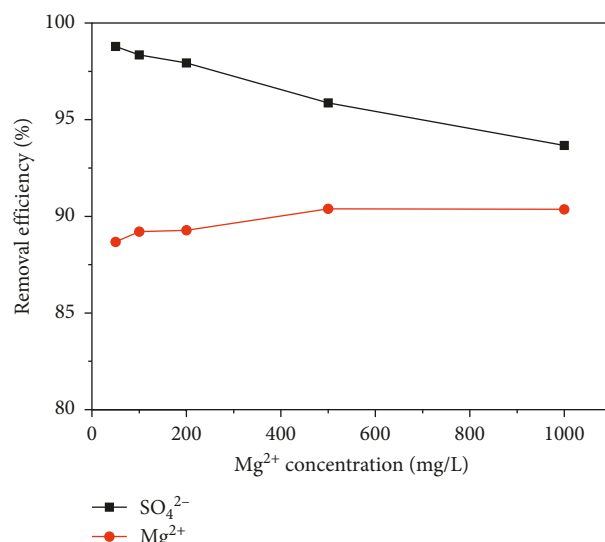


FIGURE 11: The effect of Mg^{2+} concentration. $V_{\text{solution}} = 1 \text{ L}$, $n(\text{Ca} : \text{Al} : \text{S}) = 4 : 1 : 1$, $\nu = 200 \text{ r/min}$, $t = 30 \text{ min}$, $T = 25^\circ\text{C}$, and $\text{pH} = 7.0$.

a major source of heavy metal ions; in addition to circulating water, the reagents also typically contain a certain amount of heavy metal ions. As the flue gas desulfurization absorption solution is usually alkaline in the sodium alkali (NaOH) FGD process, some types of heavy metal ions such as Pb^{2+} and Ni^{2+} easily react with OH^- to form hydroxide precipitates; therefore, the concentrations of these heavy metal ions in the solution are relatively low. It was found that Mn^{2+} and Mg^{2+} concentrations in the desulfurization wastewater were usually high. Hence, the study focused on the effect of Mn^{2+} and Mg^{2+} on SO_4^{2-} removal, and the results are displayed in Figures 10 and 11.

Data shown in Figure 10 indicate that manganese ions have no effect on SO_4^{2-} removal, when using the ettringite precipitation method. The removal of SO_4^{2-} and Mn^{2+}

almost remained stable at 99% and 100%, respectively, when Mn^{2+} concentration increased from 50 mg/L to 1000 mg/L. This is because the solution is strongly alkaline due to the addition of excess calcium hydroxide; Mn^{2+} can easily react with OH^- to form insoluble manganese hydroxide ($\text{pK}_{\text{sp}} = 13.40$) under strong alkaline conditions. Hence, Mn^{2+} preferentially converts to $\text{Mn}(\text{OH})_2$ under the experimental conditions and has no effect on SO_4^{2-} removal.

As shown in Figure 11, magnesium ions have a certain impact on the removal of sulfate ions. The removal of SO_4^{2-} decreased from 98.78% to 93.67%, when the Mg^{2+} concentration increased from 50 mg/L to 1000 mg/L; meanwhile, the Mg^{2+} removal was almost maintained at between 88.68% and 90.36%. Previous researches have revealed that Mg^{2+} can react with OH^- to convert to $\text{Mg}(\text{OH})_2$ which preferentially reacts with $\text{Al}(\text{OH})_4^-$ and SO_4^{2-} to form hydrotalcite-type compound ($\text{Mg}_6\text{Al}_2\text{SO}_4(\text{OH})_{16}\cdot n\text{H}_2\text{O}$) rather than ettringite ($\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3\cdot 26\text{H}_2\text{O}$) [19, 27]. Comparing the two chemical formulas, it can be found that the Al/S ratio is 2:1 in hydrotalcite-type compound, which is three times of that in ettringite, and the molar ratio of OH^- to SO_4^{2-} in hydrotalcite-type compound is four times of that in ettringite. It can be derived from the results that hydrotalcite-type compound consumes more Al^{3+} and OH^- compared with ettringite, resulting in the decrease of Al^{3+} and OH^- concentrations in the solution, and finally, resulting in a decline of SO_4^{2-} removal. Thus, in the coexistence of Mg^{2+} and Ca^{2+} , Mg^{2+} can compete with Ca^{2+} for Al^{3+} to form hydrotalcite-type compound, and the higher the concentration of magnesium ions, the stronger the inhibitory effect of magnesium ion on the SO_4^{2-} removal.

3.8. Feasibility and Application Prospect of the Method.

The removal of sulfate ions and other ions in actual flue gas desulfurization wastewater by using the ettringite precipitation method was evaluated. The composition of wastewater and the results of purification various ions are shown in Tables 1 and 2. The results indicate that the ettringite precipitation method had high removal efficiencies for SO_4^{2-} , F^- , and heavy metal ions, with average removal efficiencies of more than 98%, 90%, and 99%, respectively. In addition, Cl^- and NO_3^- could also be removed minimally by the method.

The results show that the removal of high-concentration sulfate ions from the sodium alkali FGD wastewater is feasible by using the ettringite precipitation method. The SO_4^{2-} concentration in the purified wastewater met the requirements for reuse of water which is 250 mg/L in China; meanwhile, F^- and heavy metal ions were effectively removed. As displayed in Table 1, the pH of the purified wastewater was 13.1; thus, the water could be reused to decrease the consumption of water and alkali in the flue gas treatment system and to reduce the operating costs. In addition, the solid sediment produced by wastewater treatment can be used as a raw material for ceramics and other building materials production. Therefore, considering the cost-effectiveness, pollutant removal efficiencies, and resource reuse, the ettringite precipitation method has the potential to be a commercial application in the field of removal of high-concentration sulfate ions from the industrial wastewater in the future.

4. Conclusions

In this paper, the ettringite precipitation method was used to remove the sulfate ions, and the influences of experimental parameters on SO_4^{2-} removal were investigated. Based on the results of the experiments, the following conclusions can be obtained:

- (1) The ettringite precipitation method can effectively synergistically remove SO_4^{2-} , F^- , and heavy metal ions with removal efficiencies of more than 98%, 90%, and 99%, respectively. In addition, Cl^- and NO_3^- also can be removed minimally by the method.
- (2) NaAlO_2 dosage, $\text{Ca}(\text{OH})_2$ dosage, solution initial pH, solution temperature, reaction time, stirring speed, anions (Cl^- , NO_3^- and F^-), and heavy metal ions all have effects on the Cl^- removal. Finally, the optimal experimental conditions (Al/S ratio, 1:1; Ca/S ratio, 4:1; solution temperature, 25°C; reaction time, 30 min; and stirring speed, 200 r/min) were determined.
- (3) The ettringite precipitation method is feasible for treating high-concentration sulfate wastewater and has the potential to be a commercial application in the high-concentration sulfate wastewater treatment field in the future.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

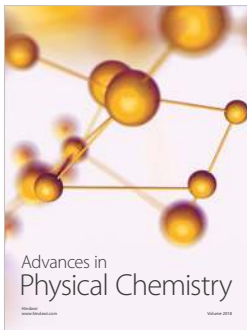
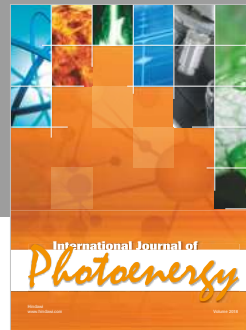
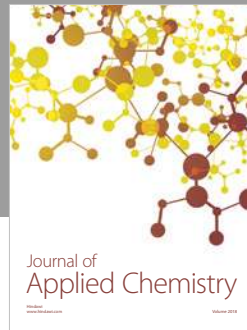
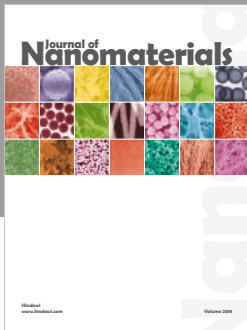
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