

Research Article

Chloride Ion Removal from the Wet Flue Gas Desulfurization and Denitrification Wastewater Using Friedel's Salt Precipitation Method

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The desulfurization and denitrification wastewater (DDW) from the wet flue gas treatment project is difficult to be treated and recycled because of high chloride ion (Cl^-) concentration. Cl^- can cause equipment and piping corrosion. However, there is a lack of cost-effective treatment technologies for the removal of Cl^- from the DDW. In this research, the feasibility of Cl^- removal from the DDW using Friedel's salt precipitation method was evaluated. Factors affecting the Cl^- removal, such as $\text{Ca}(\text{OH})_2$ dosage, NaAlO_2 dosage, solution's initial pH, solution's temperature, reaction time, stirring speed, and anions (SO_4^{2-} , NO_3^- , and F^-), were investigated, and the optimal experimental conditions for Cl^- removal were determined. Experimental results showed that Friedel's salt precipitation method can remove Cl^- effectively and can achieve synergistic removal of SO_4^{2-} , F^- , and heavy metal ions. Under the best experimental conditions, the average removal efficiencies of Cl^- , SO_4^{2-} , F^- , and heavy metal ions reach more than 85%, 98%, 94%, and 99%, respectively. The Cl^- removal mechanism studies showed that Cl^- can be removed by precipitation as $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$. The purified wastewater and the precipitated solid can be reused to reduce the consumption of water and alkali. Friedel's salt precipitation method is an effective control technology for the synergistic removal of Cl^- , SO_4^{2-} , F^- , and heavy metal ions and has enormous potential to be applied in the industrial wastewater treatment field.

1. Introduction

The wet flue gas desulfurization (WFGD) technology is one of the world's most widely used flue gas desulfurization technology due to its high desulfurization efficiency and low investment and operation costs [1]. Meanwhile, in order to cost-effectively control SO_2 , NO_x and other pollutants in the flue gas, scholars have developed a variety of multipollutant cooperative control technologies based on the WFGD in recent years. The main principle of the technology is through adding an oxidizing agent to the WFGD system to achieve synergistic removal of multipollutants from the flue gas. Ozone [2], chlorine dioxide [3], potassium persulfate [4], potassium permanganate [5], sodium chlorite [6, 7], and other oxidizing agents [8], have all been tested for multipollutants

control, among which sodium chlorite (NaClO_2) has been shown to be one of the best-performing additives [7]. Industrial demonstration of the technology in which NaClO_2 is used as an oxidant has been completed in China's industrial boilers and furnaces, and multipollutant removal efficiencies are satisfactory. However, there are still some deficiencies in the technology that need to be improved. One of the more prominent problems is the corrosion of equipment and piping caused by Cl^- accumulation. The concentration of Cl^- in the absorption solution is generally 1000–3000 mg/L. The maximum can be more than 10000 mg/L. Cl^- can promote corrosion through destroying the passive film of metal and accelerating the growth of pitting corrosion [9]. Furthermore, most of the corrosion and scale inhibitors cannot really inhibit the Cl^- corrosion [10]. Therefore, part

of absorption solution must be discharged to regulate the concentration of Cl^- and other impurities in the solution and to form the wet flue gas DDW. Furthermore, the WFGD absorption solution, industrial cooling water, and other industrial wastewater also have the Cl^- accumulation problem, which leads to metal corrosion. However, the chemical precipitation method, which is usually used to treat desulfurization wastewater (DW), is difficult to remove Cl^- . As a result, the chlorine-containing wastewater cannot be directly discharged or reused [11]. Hence, in order to avoid Cl^- corrosion and promote DDW recycling, it is necessary to develop a cost-effective Cl^- removal technology.

Currently, various Cl^- removal technologies have been developed, mainly including evaporation crystallization [12], electrochemical method [13, 14], adsorption [15, 16], ion exchange [17, 18], and reverse osmosis [19]. However, these methods are complex and have high operating costs, and most of them are suitable for the treatment wastewater of a low Cl^- concentration. Chemical precipitation methods, such as silver salt precipitation [20], copper slag precipitation [21], and Friedel's salt precipitation (ultra-high lime with aluminum process, UHLA) [22], are all very suitable for the treatment of wastewater with high Cl^- concentration. Among them, Friedel's salt precipitation method is considered to be a cost-effective Cl^- removal technology. The fundamental of the UHLA method is through adding an excess of calcium salt and aluminum salt to the chlorine-containing solution, and the calcium and aluminum ions react with chloride ion to form a precipitate of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ which is called Friedel's salt at a certain reaction temperature and stirring speed, and finally the high efficient removal of chloride ion is achieved. Abdel-Wahab et al. [10, 22] evaluated Cl^- removal from recycled cooling water using the UHLA process and investigated the effect of aluminum dosage and lime dosage on Cl^- removal at room temperature. Experimental results showed that the UHLA process can effectively remove Cl^- by precipitation as calcium chloroaluminate [$\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$]. Cl^- removal was barely affected by the lime dosage, but significantly affected by the aluminum dosage. The optimal Ca/Al ratio to achieve maximum Cl^- removal was approximately 2.5.

However, these studies focused on the Cl^- removal from the circulating cooling water and did not consider the effect of coexistent anions, such as SO_4^{2-} , NO_3^- , and F^- , on the Cl^- removal. Meanwhile, there is little information about the effect of process parameters, such as the solution's initial pH, reaction temperature, and reaction time on the Cl^- removal. The composition of the ions in the circulating cooling water is relatively simple, and the concentration of different kinds of ions is also lower compared to that of the DDW and the DW, but nowadays little information on the Cl^- removal from the DDW or the DW using Friedel's salt precipitation method can be found in the literatures. Therefore, the research aims to evaluate the feasibility of the Cl^- removal from the wet flue gas DDW using Friedel's salt precipitation method. A series of experiments to evaluate the influence of different factors on Cl^- removal were carried out, and the Cl^- removal mechanism by this process was hypothesized. In addition, removal of Cl^- and other ions in the actual DDW using Friedel's salt precipitation method was also studied.

2. Experimental Setup

2.1. Materials. NaAlO_2 , $\text{Ca}(\text{OH})_2$, Na_2SO_4 , NaOH , NaF , NaCl , KNO_3 , and HNO_3 were analytical grade, and directly used without purification. The authors tested Cl^- concentration in the actual DDW and found that the Cl^- concentration in the DDW was about 1000–3000 mg/L. So chloride-rich simulated wastewater used in this study was prepared by dissolving anhydrous NaCl in deionized water to get initial Cl^- concentration of 2000 mg/L. The solution's initial pH was adjusted using HNO_3 (0.1 mol/L) and NaOH (0.1 mol/L). The actual DDW was obtained from a ceramic production enterprise located in Guangdong province, China.

2.2. Analytical Methods. The solution's pH was measured with an MP511 pH detector (Shanghai Precision Instruments Co., Ltd.). Concentrations of NO_3^- , F^- , SO_4^{2-} , and Cl^- were measured with an ion chromatography system (Metrohm 883, Switzerland), and concentrations of heavy metal ions such as Ni^{2+} , Pb^{2+} , and Mn^{2+} were determined with an inductively coupled plasma emission spectrometer (ICP-AES 710, Agilent technologies). The precipitated solids were collected by filtering. The separated solids were then dried at room temperature. X-ray diffraction (XRD) was performed on the solids using an X-ray diffractometer (XRD-6000, Shimadzu, Japan).

2.3. Removal of Chloride Ions. Experiments were carried out on a six-league electric blender (ZR4-6, China). The experimental steps of Friedel's salt precipitation method are as follows: the first step was conducted by adding a certain amount of $\text{Ca}(\text{OH})_2$ and NaAlO_2 to the NaCl solution (2000 mg/L) with a volume of 1 L at the specified reaction temperature; then stirring for a certain time, at last samples were taken and filtered under vacuum through a $0.45\ \mu\text{m}$ microporous membrane filter. The filtrate was analyzed for Cl^- and other ions using related equipments, and finally the removal efficiencies of Cl^- and other ions were calculated by the following equation. The solid phases formed in precipitation experiments were identified by XRD spectroscopy.

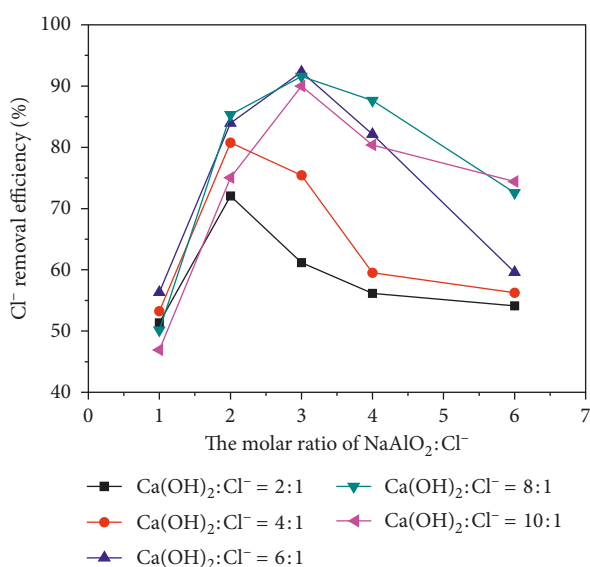
$$\eta = \frac{C_0 - C_t}{C_0} \times 100, \quad (1)$$

where η is the Cl^- or other ions removal efficiencies; and C_0 and C_t are the initial and final Cl^- or other ions concentrations of solutions (mg/L), respectively.

According to the characteristics of ion composition of actual DDW, the literatures [10, 20, 22, 23] and an analysis of main factors influencing Cl^- removal, a series of experiments were conducted to evaluate Cl^- removal from DDW using Friedel's salt precipitation method, and the optimal experimental conditions for Cl^- removal were determined by using single factor test. In addition, the removal experiments of chloride ions from a ceramic enterprise wastewater were carried out under the best experimental conditions. The experimental conditions of the individual experiments are shown in Table 1.

TABLE 1: Experimental conditions of the individual experiments.

Number	Experiment	Experimental conditions
1	The effect of NaAlO_2 dosage	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
2	The effect of $\text{Ca}(\text{OH})_2$ dosage	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
3	The effect of the solution's initial pH	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$.
4	The effect of the solution's temperature	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
5	The effect of reaction time	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, initial $\text{pH} = 7.0$.
6	The effect of stirring speed	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
7	The effect of SO_4^{2-} concentration	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
8	The effect of F^- concentration	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
9	The effect of NO_3^- concentration	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
10	The effect of precipitated solid reuse	$V_{\text{solution}} = 1 \text{ L}$, $[\text{Cl}^-] = 2000 \text{ mg/L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$, initial $\text{pH} = 7.0$.
11	Removal of chloride ion and other ions in actual DDW	Two-stage Freund's salt precipitation method: (1) First stage mainly removed SO_4^{2-} , $V_{\text{solution}} = 1 \text{ L}$, $\text{Ca}/\text{Al}/\text{S}$ molar ratio = 4 : 1 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$. (2) Second stage mainly removed Cl^- , $V_{\text{solution}} = 1 \text{ L}$, $\text{Ca}/\text{Al}/\text{Cl}$ molar ratio = 6 : 3 : 1, $T_{\text{reaction}} = 25^\circ\text{C}$, $v_{\text{stirring}} = 400 \text{ r/min}$, $t = 30 \text{ min}$.

FIGURE 1: The effect of NaAlO_2 dosage.

3. Results and Discussion

3.1. Effect of NaAlO_2 Dosage and $\text{Ca}(\text{OH})_2$ Dosage. It was reported that Cl^- removal was primarily controlled by the formation of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ [22]. So NaAlO_2 dosage and $\text{Ca}(\text{OH})_2$ dosage have a significant effect on Cl^- removal. As shown in Figure 1, good Cl^- removal (>85%) was observed at reasonable ranges of NaAlO_2 dosage and $\text{Ca}(\text{OH})_2$ dosage. It was found that the Cl^- removal increased upon increasing the molar ratios of NaAlO_2 to Cl^- (Al/Cl) at first, then decreased with the Al/Cl increase when the molar ratio of $\text{Ca}(\text{OH})_2$ to Cl^- (Ca/Cl) was constant. For example, when the Ca/Cl was constant at 6:1, the Cl^- removal sharply increased from 56.3% to 91.6% when the Al/Cl varied from 1:1 to 3:1, then Cl^- removal decreased from 91.6% to 59.6% with an increase of Al/Cl between 3:1 and 6:1. Higher NaAlO_2 dosage is not conducive to the Cl^- removal. Addition of excess NaAlO_2 results in increasing $\text{Al}(\text{OH})_4^-$ and OH^- ions ((2) and (3)) in the solution, and the increases of OH^- and $\text{Al}(\text{OH})_4^-$ ions result in substitution of Cl^- with OH^- and $\text{Al}(\text{OH})_4^-$ ((6) and (7)) in the solid solution formation, thus increasing the fraction of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and

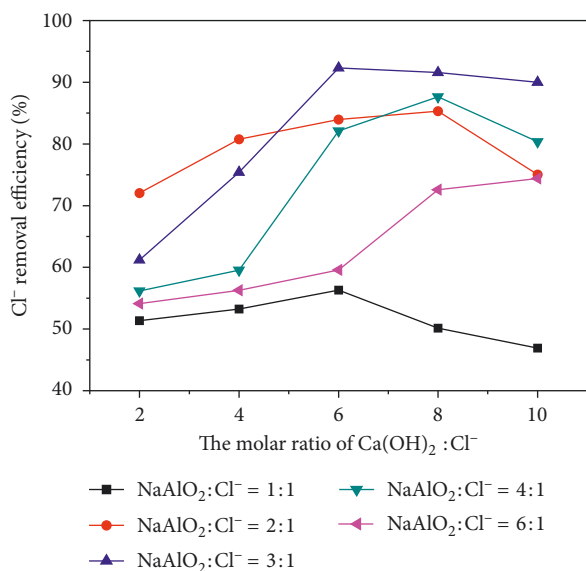


FIGURE 2: The effect of $\text{Ca}(\text{OH})_2$ dosage.

decreasing the fractions of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ and $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ in the solid solution. So, the results show that there is an optimum range of Al/Cl of 2–4:1.

Figure 2 shows the effect of $\text{Ca}(\text{OH})_2$ dosage on Cl^- removal. When the Al/Cl was 1:1, the $\text{Ca}(\text{OH})_2$ dosage had little effect on Cl^- removal. However, the Cl^- removal was greatly affected by the $\text{Ca}(\text{OH})_2$ dosage when the Al/Cl was more than 1:1. As depicted in Figure 2, when the Al/Cl was constant, Cl^- removal increased rapidly as the Ca/Cl increased at first, then decreased with the increase of Ca/Cl. This is because the $\text{Ca}(\text{OH})_2$ solubility is low, Ca^{2+} concentration in the solution increases with the increasing of $\text{Ca}(\text{OH})_2$ dosage, meanwhile OH^- concentration also increases in the solution. The increasing of Ca^{2+} concentration leads to increased Cl^- removal; however, the increase of OH^- concentration is not conducive to the Cl^- removal because the Cl^- in the $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ can be replaced by OH^- to form the $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ (6) under the higher OH^- concentration condition. So, the results show that there is an optimum range of Ca/Cl of 6–8:1.

In order to further determine the effect of the dosage of chemical reagents on Cl^- removal and to determine the reaction product type, XRD was used to examine the crystalline phases of the precipitated solids produced under different conditions, and the results are shown in Figure 3.

Examination of the samples indicates the presence of mixed phases, the major crystalline phases are $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ (ICDD PDF card # 35-0105, $2\theta = 11.4^\circ, 22.8^\circ, 23.6^\circ, 31.1^\circ, 35.6^\circ$, and 42.7°), $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ (ICDD PDF card # 33-0255, $2\theta = 11.4^\circ, 31.1^\circ, 38.9^\circ$, and 64.5°), $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ (ICDD PDF card # 24-0217, $2\theta = 17.4^\circ, 20.0^\circ, 26.7^\circ, 28.5^\circ, 31.9^\circ, 36.5^\circ, 39.3^\circ, 44.5^\circ, 52.6^\circ, 54.6^\circ$, and 66.4°), and $\text{Ca}(\text{OH})_2$ (ICDD PDF card # 04-0733, $2\theta = 18.3^\circ, 34.3^\circ, 47.4^\circ$, and 51.0°). As shown in Figure 3(a), the intensities of characteristic diffraction peaks of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ and $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ all increased with the increasing $\text{Ca}(\text{OH})_2$ dosage at first, then decreased slowly with the increase of $\text{Ca}(\text{OH})_2$ dosage. On the contrary, the intensities of characteristic diffraction peaks of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ decreased as

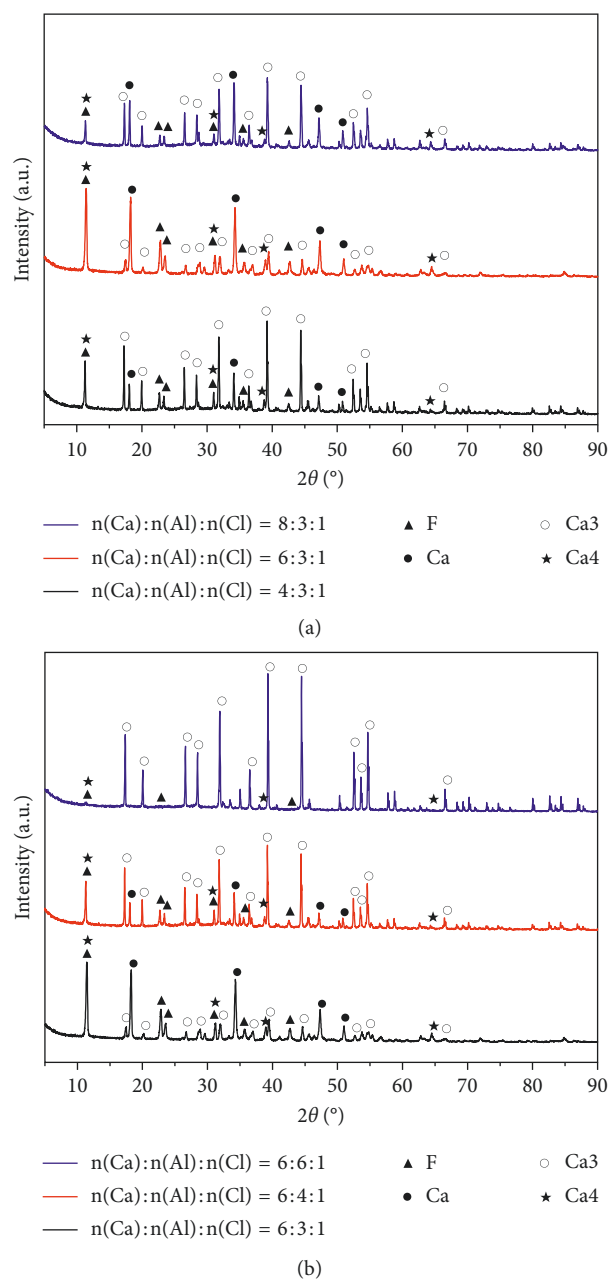


FIGURE 3: XRD patterns of precipitated solids: (a) different $\text{Ca}(\text{OH})_2$ dosage; (b) different NaAlO_2 dosage. F($\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$), Ca3 ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$), Ca4($\text{Ca}_4\text{Al}_2(\text{OH})_{14}$), $\text{Ca}(\text{Ca}(\text{OH})_2)_2$.

the $\text{Ca}(\text{OH})_2$ dosage increased at first, then increased with the increase of $\text{Ca}(\text{OH})_2$ dosage. This may be attributed to the increase in concentration of Ca^{2+} in solution with $\text{Ca}(\text{OH})_2$ dosage increase, thus promoting the $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ and $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ generation ((4), (5) and (6)). However, higher $\text{Ca}(\text{OH})_2$ dosage contributes to the OH^- concentration increase in solution and promote the progress of the reactions ((7) and (8)), resulting in an increase of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ and decrease of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ and $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$ in the solids. In addition, the intensities of characteristic diffraction peaks of $\text{Ca}(\text{OH})_2$ increased with the increasing $\text{Ca}(\text{OH})_2$ dosage. The results of

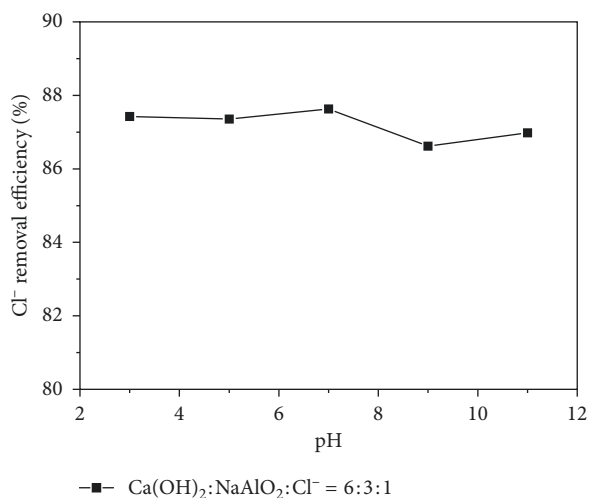


FIGURE 4: The effect of the solution's initial pH.

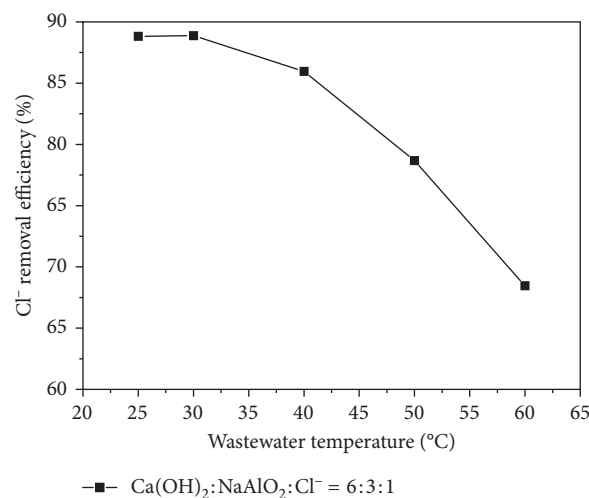


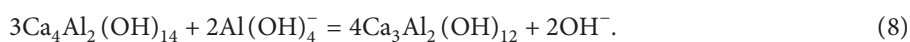
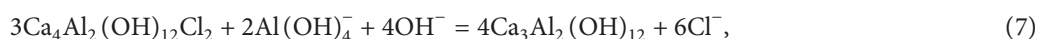
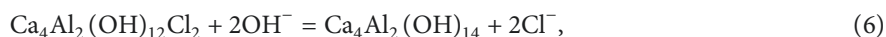
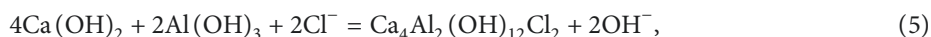
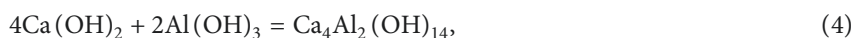
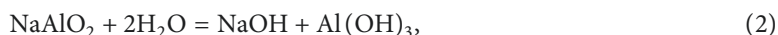
FIGURE 5: The effect of the solution's temperature.

XRD test are in good agreement with the results of Cl^- removal (Figure 1).

Figure 3(b) shows that additions of NaAlO_2 had significant influences on the distribution of solids in the solid solution. When the Ca/Cl was constant at 6:1 and the Al/Cl was more than 3:1, the intensities of characteristic diffraction peaks of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$, $\text{Ca}_4\text{Al}_2(\text{OH})_{14}$, and $\text{Ca}(\text{OH})_2$ all decreased rapidly with the increasing NaAlO_2 dosage; however, the intensities of characteristic diffraction peaks of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ increased rapidly as the NaAlO_2 dosage increased. Especially,

examination of the sample ($n(\text{Ca}) : n(\text{Al}) : n(\text{Cl}) = 6 : 6 : 1$) indicated that phases related to crystalline $\text{Ca}(\text{OH})_2$ were not observed, suggesting that almost no $\text{Ca}(\text{OH})_2$ was contained in the solids. The results of XRD test are in good agreement with the results of Cl^- removal (Figure 2).

Based on the experimental results, composition of the solids, and the literatures [10, 20, 22, 23], Cl^- removal reaction equations and the interactions among the solids during formation of the solid solution can be described by using the following chemical equilibrium reactions:



Considering the Cl^- removal and economic costs, in the next series of experiments, the molar ratio of $\text{Ca}(\text{OH})_2$ to NaAlO_2 to Cl^- were constant at 6:3:1.

3.2. Effect of the Initial pH. The effect of the solution's initial pH ranging from 3.0 to 11.0 on Cl^- removal has been studied. Figure 4 shows that the initial pH of solution had negligible effects on the Cl^- removal, and the average removal efficiencies of Cl^- remained at around 87% when the solution's initial pH changed from 3.0 to 11.0. The reason is that the addition of

$\text{Ca}(\text{OH})_2$ was excessive in this series of experiments, and regardless of whether the solution was acidic or alkaline, the solution's pH all increased to about 13.0 after adding excessive $\text{Ca}(\text{OH})_2$. The initial pH of solution has little effect on Cl^- removal, so the effect of wastewater pH need not be considered when using the method to control the Cl^- in practical engineering applications.

3.3. Effect of Solution's Temperature. Figure 5 presents the effect of the solution's temperature on Cl^- removal. The Cl^-

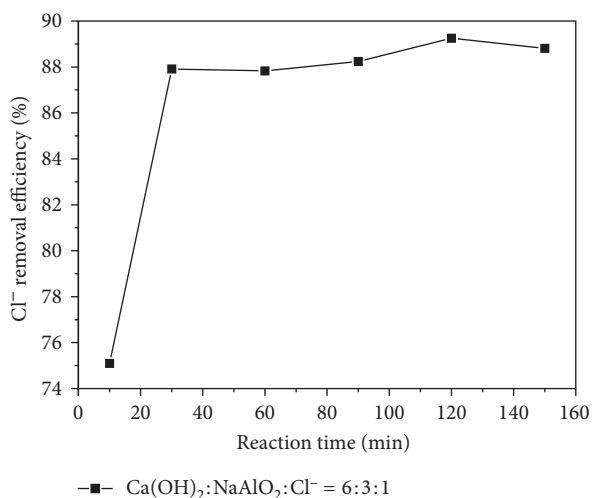


FIGURE 6: The effect of reaction time.

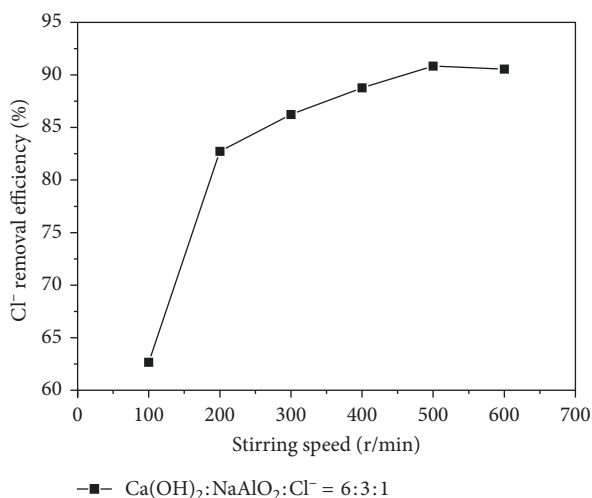
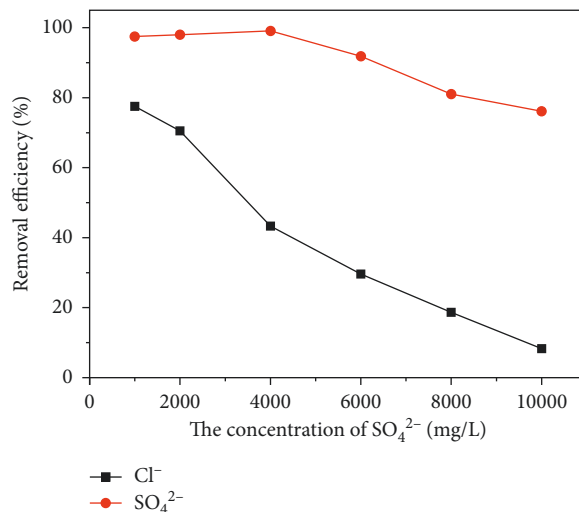


FIGURE 7: The effect of stirring speed.

removal decreased with the increasing temperature of the solution. Cl^- removal efficiencies were 88.8%, 88.9%, 86.0%, 78.7%, and 68.5% when the solution's temperatures were 25, 30, 40, 50, and 60°C, respectively. As Figure 5 illustrates, Cl^- removal decreased slowly with the solution's increasing temperature when the solution's temperature was less than 40°C, but when the solution's temperature was more than 40°C, the Cl^- removal decreased rapidly with the increase of the solution's temperature. Because the stable existence temperature of $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ is 40°C [23], a partial $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ will breakdown to form more stable solids such as $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ when the solution's temperature is more than 40°C. So, it is necessary to reduce the wastewater temperature in practical engineering applications to achieve a higher Cl^- removal.

3.4. Effect of Reaction Time. The effect of reaction time on Cl^- removal is shown in Figure 6. Results show that the reaction time has a certain effect on Cl^- removal. The NOx

FIGURE 8: The effect of SO_4^{2-} concentration.

removal sharply increased from 75.1% to 87.9% with the increase of reaction time from 10 min to 30 min and thereafter remained almost constant at about 88%–89%. The contact time of ions in the solution increased, resulting in a more complete reaction and an increase of Cl^- removal; however, limited by the low solubility of $\text{Ca}(\text{OH})_2$, the increase of contact time had a little effect on Cl^- removal. Taking into account the economic factor and Cl^- removal, the optimum reaction time is selected as 30 min.

3.5. Effect of Stirring Speed. Stirring speed has a significant effect on Cl^- removal. As shown in Figure 7, when stirring speed increased from 100 r/min to 200 r/min, Cl^- removal sharply increased from 62.7% to 82.7% and then gradually increased. When the stirring speed was more than 400 r/min, the Cl^- removal was little affected by the stirring speed and maintained between 89% and 91%. Increasing the stirring speed contributes to the dispersion and dissolution of the reagents and increases the probability of collision of various ions in the solution, resulting in higher Cl^- removal. However, excessive stirring speed not only cannot significantly improve the Cl^- removal, but also leads to increased operating costs, so the optimum stirring speed is selected as 400 r/min.

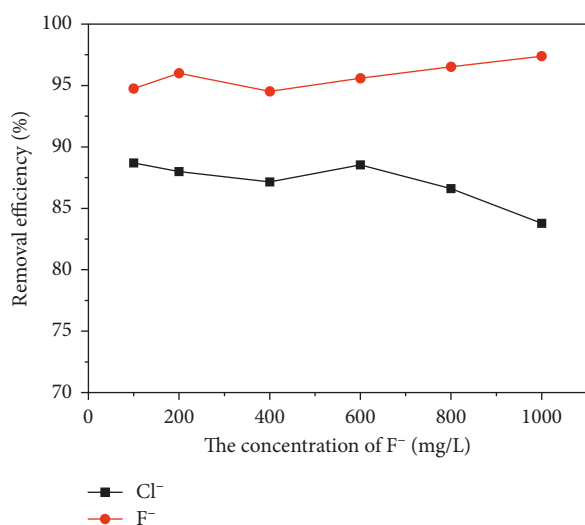
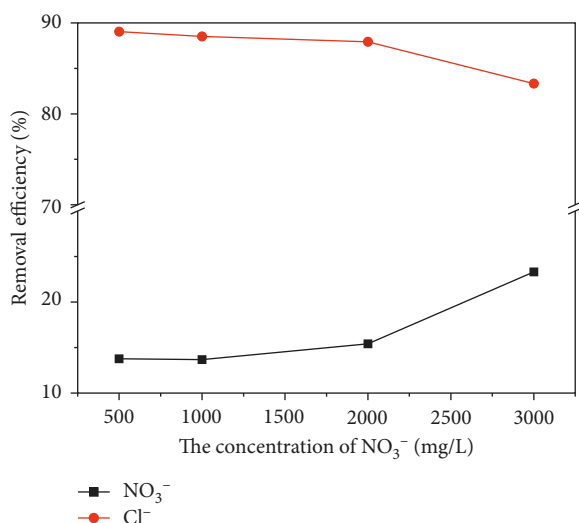
3.6. Effect of Anions. Various types of anions such as SO_4^{2-} , NO_3^- , and F^- exist in the DDW and DW, and the concentrations of these anions are often high. So, coexistent anions in the solution have a certain effect on Cl^- removal. In this paper, the effect of anions on Cl^- removal has been studied, and the results are shown in Figures 8–10.

Figure 8 displays the effect of SO_4^{2-} concentration on Cl^- removal. As Figure 8 illustrates, SO_4^{2-} concentration has a significant effect on Cl^- removal. Cl^- removal sharply decreased from 77.5% to 8.3% when SO_4^{2-} concentration increased from 1000 mg/L to 10000 mg/L. Compared with the low Cl^- removal, SO_4^{2-} removal almost remained stable at more than 97% when SO_4^{2-} concentration varied from

TABLE 2: Results of Cl^- and SO_4^{2-} removal.

	Number			Average	Standard deviation
	1	2	3		
Average removal efficiencies of Cl^- (%)	85.49	87.56	86.26	86.44	0.138
Average removal efficiencies of SO_4^{2-} (%)	99.06	99.10	98.60	98.92	0.278

Two-stage Freund's salt precipitation method. (1) The first stage mainly removed SO_4^{2-} (4000 mg/L), the molar ratio of $\text{Ca}(\text{OH})_2$ to NaAlO_2 to SO_4^{2-} was constant at 4 : 1 : 1; the solution's temperature was 25°C, reaction time was 30 min, and the stirring speed was 400 r/min. (2) The second stage mainly removed Cl^- (2000 mg/L), the molar ratio of $\text{Ca}(\text{OH})_2$ to NaAlO_2 to Cl^- was constant at 6 : 3 : 1, respectively, and other operating conditions were the same as the first stage.

FIGURE 9: The effect of F^- concentration.FIGURE 10: The effect of NO_3^- concentration.

1000 mg/L to 4000 mg/L, then slowly decreased with the increase of SO_4^{2-} concentration. It has been reported that SO_4^{2-} can react with Ca^{2+} and Al^{3+} to form insoluble ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$). The solubility products of $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ and $\text{Ca}_4\text{Al}_2\text{Cl}_2(\text{OH})_{12}$ are about $10^{-109.9}$ and $10^{-27.10}$, respectively [10, 22]. So, Ca^{2+} and Al^{3+} in the solution are easier to react with SO_4^{2-} rather than Cl^- , leading to higher SO_4^{2-} removal and lower Cl^- removal.

Results show that the presence of SO_4^{2-} in the solution has a significant inhibitory effect on Cl^- removal. In order to achieve high Cl^- removal, it is necessary to remove the SO_4^{2-} from the solution first. Table 2 shows the results of SO_4^{2-} and Cl^- removal using two-stage Friedel's salt precipitation method, the average removal efficiencies of SO_4^{2-} and Cl^- can reach 98.9% and 86.2%, respectively.

Figure 9 shows that Cl^- removal almost remained stable at about 88% when F^- concentration increased from 100 mg/L to 600 mg/L, then decreased slowly from 88.5% to 83.8% when F^- concentration increased from 600 mg/L to 1000 mg/L, meanwhile F^- removal almost remained stable at the range of 94% to 98%. Due to the large amount of $\text{Ca}(\text{OH})_2$ dosage compared with the stoichiometric value, it is estimated that Ca^{2+} in the solution is excessive, so F^- can react with Ca^{2+} to form insoluble CaF_2 and not affect Cl^- removal when the F^- concentration is low. However, the further increase of F^- concentration causes competitive reactions of F^- and Cl^- for the Ca^{2+} and results in a decrease of Cl^- removal.

The effect of NO_3^- concentration on Cl^- removal is shown in Figure 10. The results indicate that the Cl^- removal was little affected when the concentration of NO_3^- in the solution was less than 2000 mg/L, and remained stable at about 88%; meanwhile, about 15% of NO_3^- removal was achieved. When the concentration of NO_3^- in the solution increased from 2000 mg/L to 3000 mg/L, the Cl^- removal slowly decreased from 87.9% to 83.3%, and the NO_3^- removal slowly increased from 15.4% to 23.3%. NO_3^- can react with Ca^{2+} and Al^{3+} to form the $\text{Ca}_4\text{Al}_2(\text{NO}_3)_2(\text{OH})_{12}$ that belong to AFm family of solids [24]; therefore, there is a certain negative impact on the Cl^- removal. Overall, NO_3^- has a certain inhibitory effect on Cl^- removal only under high NO_3^- concentration.

3.7. Determination of the Optimal Experimental Conditions.

The results indicate that using Friedel's salt precipitation method can effectively remove Cl^- in the solution. Cl^- removal depends primarily on the $\text{Ca}(\text{OH})_2$ dosage, NaAlO_2 dosage, the solution's temperature, and SO_4^{2-} concentration, and the solution's initial pH, reaction time, stirring speed, NO_3^- , and F^- concentrations all have a certain influence on NOx removal, but these factors have a relatively little influence on the Cl^- removal. Finally, considering the application to the practical engineering, the optimal conditions for Cl^- removal using Friedel's salt precipitation method were identified: (1) For sulfate-free wastewater, use one-stage Freund's salt precipitation method to remove Cl^- .

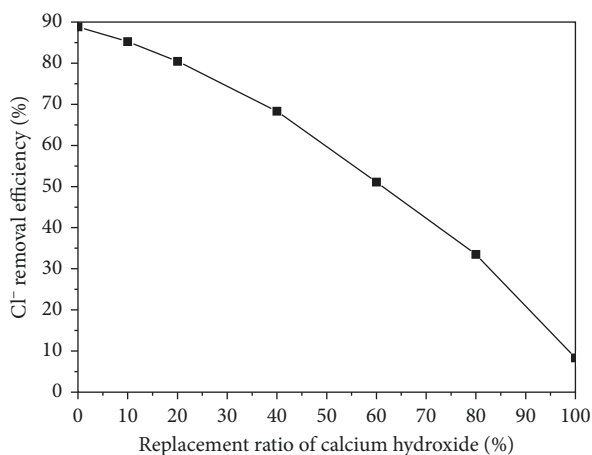


FIGURE 11: The effect of precipitated solid reuse.

TABLE 3: Results of anion removal.

	SO ₄ ²⁻	Cl ⁻	F ⁻	NO ₃ ⁻	pH
Actual wastewater (mg/L)	12309.5	1476.7	244.9	955.3	5.3
Purified wastewater (mg/L)	188.34	215.16	8.84	790.70	13.2
Average removal efficiency (%)	98.47	85.43	96.39	17.23	—

The optimal conditions were the molar ratio of Ca(OH)₂ to NaAlO₂ to Cl⁻ 6:3:1, solution's temperature of 25°C, reaction time of 30 min, and stirring speed of 400 r/min. (2) For sulfate-containing wastewater, use two-stage Freund's salt precipitation method to remove Cl⁻. First stage mainly removed SO₄²⁻, the optimal conditions were the molar ratio of Ca(OH)₂ to NaAlO₂ to SO₄²⁻ 4:1:1, solution's temperature of 25°C, reaction time of 30 min and stirring speed of 400 r/min. Second stage mainly removed Cl⁻, and the optimal conditions were the same as those used for sulfate-free wastewater.

3.8. Effect of Precipitated Solid Reuse. The XRD test (Figure 3) of the precipitated solids indicated that there existed a certain amount of Ca(OH)₂ in the precipitated solids, so it is possible to replace part of Ca(OH)₂ with the precipitated solids. As shown in Figure 11, Cl⁻ removal rapidly decreased with the increase of replacement ratio of Ca(OH)₂, the main reason is that the Ca(OH)₂ content of the precipitated solids was low, so it can't be achieved to use precipitated solids to replace an equivalent number of Ca(OH)₂. However, Cl⁻ removal can reach more than 80% when the replacement ratio of Ca(OH)₂ is controlled at less than 20%.

3.9. Removal of Chloride Ion and Other Ions in Actual DDW. Removal of Cl⁻ and other ions in actual wastewater by using Friedel's salt precipitation method was studied. The wastewater was the actual DDW from a ceramic plant. The NaClO₂/NaOH solution was used to remove the NO_x and SO₂ in the flue gas, and the wet flue gas desulfurization and denitrification system was operated under weak acid condition.

TABLE 4: Results of heavy metal ion removal.

	Cd ²⁺	Mg ²⁺	Mn ²⁺	Ni ²⁺	Pb ²⁺
Actual wastewater (mg/L)	4.332	10.88	23.85	37.62	9.20
Purified wastewater (mg/L)	—	0.086	0.006	—	—
Average removal efficiency (%)	100	99.21	99.97	100	100

So, the effluent from the system contained large amounts of Cl⁻ and other ions (Tables 2 and 3). Two-stage Friedel's salt precipitation method was used to purify the anion ions and other ions, and the results are shown in Tables 3 and 4. The results indicate that Friedel's salt precipitation method had high synergistic removal efficiencies for Cl⁻, SO₄²⁻, F⁻, and heavy metal ions, with average removal efficiencies of 85.43%, 98.47%, 96.39%, and more than 99%, respectively. The Cl⁻ concentration in the purified wastewater met the requirements for reuse of water which is 250 mg/L in China; meanwhile, SO₄²⁻, F⁻, and heavy metal ions were effectively removed. So the purified wastewater could be reused in the wet flue gas desulfurization and denitrification system. In addition, the pH of the purified water was about 13, so purified wastewater reuse could reduce the consumption of alkali in the flue gas treatment system.

4. Conclusions

In this study, Friedel's salt precipitation method was used to remove the Cl⁻, and the effects of different experimental conditions on Cl⁻ removal were mainly studied. Based on the results of the experiments, the following conclusions can be made:

- (1) Friedel's salt precipitation method is a very effective Cl⁻ removal technology, and Cl⁻ removal can reach more than 85%. Meanwhile, the method can effectively synergistically remove SO₄²⁻, F⁻, and heavy metal ions. The purified wastewater can be reused to reduce the consumption of water and alkali, and the precipitated solids can be used to replace part of Ca(OH)₂. Thus, it has a great potential to be applied in the industrial wastewater treatment field.
- (2) Ca(OH)₂ dosage, NaAlO₂ dosage, the solution's initial pH, the solution's temperature, reaction time, stirring speed, and anions (SO₄²⁻, NO₃⁻ and F⁻) have all effects on the Cl⁻ removal. Finally, considering the application to the practical engineering, the optimal conditions for Cl⁻ removal using Friedel's salt precipitation method were determined.
- (3) The removal mechanism of Cl⁻ was deduced based on the experimental results, composition of the precipitated solids, and the literatures. The results showed that Cl⁻ can be removed by precipitation as Ca₄Al₂Cl₂(OH)₁₂.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no competing interests.

Acknowledgments

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