Study on Treatment of acidic and highly concentrated fluoride waste water using calcium oxide-calcium chloride chloride

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Abstract. There are problems with treating acidic waste water containing high concentration fluorine by chemical precipitation, including the low sludge setting velocity and the high difficulty of reaching the criterion. In Heilongjiang province, a graphite factory producing high-purity graphite generates acidic waste water with a high concentration of fluorine. In this paper, the effect of removals on the concentration of fluoride with the combined treatment of calcium oxide and calcium chloride were discussed with regard to acid waste water. The study improved the sludge characteristics by using polyacrylamide (PAM) and polymeric aluminum chloride (PAC). The effect of different coagulants on sludge was evaluated by the sludge settlement ratio (SV), sludge volume index (SVI) and sludge moisture content. The results showed that the optimal combination for 100 ml waste water was calcium oxide addition amount of 14 g, a calcium chloride addition amount of 2.5 g, a PAM addition amount of 350 mg/L, and the effluent fluoride concentration was below 6 mg/L. PAM significantly improved the sludge settling velocity. The sludge settlement ratio reduced from 87.6% to 60%. The process for wastewater treatment was easily operated and involved low expenditure.

1. Introduction

Fluorine in the environment can be accumulated into the human body, creating a serious threat to people’s health and life. The hydrofluoric acid method is widely applied in many domestic enterprises that produce high-purity graphite at present. After this treatment, the carbon content in the scaly graphite is increased to 99.94% [1]. The method that is used commonly has some advantages, such as its low production cost and the high quality of the product. However, acidic waste water containing a high concentration of fluorine is produced during production of high-purity graphite.

At present, waste water defluoridation is accomplished by several methods, including chemical precipitation, adsorption, chemical deposition, nanofiltration and other methods. Li Li applied lime-fly ash spectrometry technology in the treatment of 100mg/L fluoride wastewater [2]. The chemical deposition method is characterized by simple equipment, easy controls and low operation cost. It often chooses quicklime and hydrated lime as precipitants. However, in practical application, chemical precipitation still faces many problems, such as its difficulty keeping fluoride concentrations below 10mg/L [3] and its low sludge setting velocity.

To solve these problems, in this paper, acidic waste water containing a high concentration of fluorine was treated by the combined treatment of calcium oxide and calcium chloride. Calcium oxide reacted with both acids and fluorine ions to form calcium fluoride, which is insoluble in water.
Because of the common-ion effect, calcium chloride effectively reduced the concentration of fluoride. PAM and PAC were used to increase the settling rate and shorten the time required for settling. The study of treatment technologies of fluorine-containing waste water is favorable to the popularization of the hydrofluoric acid method, and it promotes the development of the graphite industry.

2. Materials and methods

2.1. Main instruments and reagents

Instruments: HJ-4magnetic stirrer, fluoride ion-selective electrode with lanthanum fluoride single crystal membrane, 217calomel electrode.

Reagents: AR grade calcium oxide made in Tianjin bodi chemical co., LTD., AR grade calcium chloride made in Tianjin bodi chemical co., LTD., AR grade non-ionic PAM, AR grade PAC.

The fluoride aqueous solution used in this study came from a graphite factory in Heilongjiang province. The concentration of fluoride was $3 \times 10^4 \text{mg/L}$, with a pH around 1. The mud used in this study came from the treatment of a fluoride aqueous solution using calcium oxide-calcium chloride.

2.2. Experimental methods

2.2.1. Defluoridation by calcium oxide. A designated amount of calcium oxide was added to 100ml of fluoride solutions. The solutions were vigorously stirred for 40min on at a rate of 300 rpm. There were two ways to add calcium oxide: dry powder, or emulsion (emulsion concentration was 20%). The dosage of calcium oxide had an influence on the treatment. In the experiment, the effect of dosing calcium oxide on pH, concentration of fluoride and sludge production was studied, and the treatment effects of dry powder and emulsion were compared. Fluoride ions were measured in the solution after 24h using a selective electrode for fluoride ions.

2.2.2. Defluoridation by calcium chloride. At 20°C, in order to increase the pH of the reaction system to neutral (pH=7), 14g calcium oxide was added to 100ml of fluoride solutions. The concentration of fluoride decreased to 12mg/L. The solutions were vigorously stirred for 40min at a rate of 300rpm. Then, designation calcium chloride was added to the solutions. The solutions were vigorously stirred for 10min at a rate of 300 rpm. The concentration of fluoride in the supernatant was measured after 24h.

2.2.3. Flocculation experiment. The PAC solution concentration was 4%, PAM 0.1%. The flocculant was added to 200ml of mud. The mixture was vigorously stirred at a rate of 120 rpm for 1min, then stirred at a rate of 40 rpm for 10min. The sludge volume was recorded at 5min, 10min, 20min, 30min, 60min and 120min. In the paper, the sludge settlement ratio (SV), sludge volume index (SVI) and sludgemoisture content were used to evaluate the sludge settleability.

3. Results and discussion

3.1. Defluoridation by calcium oxide

The waste water has strong acidity. When calcium oxide dissolves in water, the liquid will have alkalinity, and emit heat. Calcium oxide reacts with acid to form a salt. It increases the pH value to make the effect better. In the waste water, $F^{-}$ reacts with Ca$^{2+}$. Then, the fluoride ion will be reduced by forming CaF$\text{2}$, which is hardly dissolved by water. The reaction equation is: $\text{CaO} + 2\text{H}^{+} = \text{Ca}^{2+} + \text{H}_2\text{O}$, $\text{Ca}^{2+} + 2F^{-} = \text{CaF}_2\downarrow$. The results are shown in figure 1 and figure 2.

The results showed that with the increasing of calcium oxide, the concentration of fluoride in the waste water decreased sharply. When n(Ca$^{2+}$/F-) was more than 0.8, the concentration of fluoride tended to be constant at about 15mg/L. Whether calcium oxide was added as dry powder or emulsion, the concentration of fluoride was not lower than 10mg/L. At the same time, from figure 2, the higher
the calcium oxide dosage was, the higher the pH of the solution was. When \( n(\text{Ca}^2+/\text{F}^-) \) was 0.8, the solution was neutral, with a pH value of 7. The proper treatment condition obtained from the experiment results was: \( n(\text{Ca}^2+/\text{F}^-) \) of 0.8.

### 3.2. Defluoridation by calcium chloride

Calcium fluoride is difficult to dissolve in water. In theory, because its solubility product (Ksp) is \( 4.0 \times 10^{-11} \) at 25 degrees Celsius, the concentration of fluoride is 8.17mg/L. Waste water from the factory is characterized by complicated components and many salts, so the solubility of calcium fluoride is improved. If calcium oxide alone is added to waste water, the concentration of fluoride has difficulty reaching the criterion. According to the common ion effect, when calcium chloride is added to a saturated calcium fluoride solution, the calcium ion concentration is increased. The solubility equilibrium of precipitation to calcium fluoride can occur with an increase in the calcium ion concentration. The concentration of fluoride is therefore reduced [4].

The best dosing quantity was determined by comparing the treatment effects. The results are shown in figure 3 and figure 4.

![Figure 1. Influence of calcium oxide dosage on F- removal efficiency.](image1)

![Figure 2. Influence of calcium oxide dosage on pH.](image2)

![Figure 3. Influence of calcium chloride dosage on F- removal efficiency.](image3)

![Figure 4. Influence of calcium chloride dosage on pH.](image4)

The results showed that with the increasing of calcium chloride, the concentration of fluoride in the waste water was significantly reduced. When the added calcium chloride was 2.5g, the concentration of fluoride was reduced to 5.7mg/L. When the added calcium chloride was more than 2.5g, the
concentration of fluoride tended to be constant at about 6mg/L. The reasons could be attributed to the following. Overmuch calcium ion caused the formation of a complex, such as CaCl\(^+\) and CaF\(^+\) \[^5\], which made it unable to further reduce the concentration of the fluoride in the solution.

### 3.3. Flocculation settling experiment

Sludge was a by-product of the wastewater-treatment system. In the combined treatment system of calcium oxide and calcium chloride, a large amount of complicated ingredient sludge was formed. It mainly contained calcium hydroxide and calcium fluoride. If the sludge was not being disposed of properly, the factory would be affected. During the experimental process, the sludge settling velocity was slow. In order to improve the sludge behaviour of the precipitation, flocculant was used in this paper. The flocculation mechanisms include the interaction of hydroxides, the compression of double charged and so on \[^6\]. Flocculation was applied to add to the instability and aggregation of suspended particles. The effect of the flocculant type and agent dosage on the settling speed was studied in the flocculation settling experiment.

#### 3.3.1. Settleability improved by PAC

PAC is an inorganic cationic polymeric coagulant, which has the very good characteristics of coagulation and precipitation \[^7\]. PAC can flocculate the suspended particles in the solution by the function of gathering, adsorbing and unwrapping. The results were shown in figure 5 and table 1.

| PAC (mg/L) | SV (%) | SVI (ml/g) | Moisture content(%) |
|-----------|--------|------------|--------------------|
| 0         | 90.8   | 9.5        | 89                 |
| 200       | 88.4   | 9.2        | 88                 |
| 1000      | 83.2   | 8.7        | 85                 |

The dose of PAC was 200mg/L and 1000mg/L, which was 1.3‰ and 6.7‰ of the dried sludge. From figure 4, when no PAC was added in the sludge, the sludge volume reduced to 4/5 after 2h. After PAC was added, the curve showed an obvious decreasing trend. This showed that the sludge sedimentation velocity increased with the growth of the dose. When 1000mg/L PAC was added, the sludge settlement ratio decreased to 83.2%, the sludge volume index to 8.7ml/g and the sludge moisture content to 85%. The sludge volume reduced to 3/5 after 2h.

**Figure 5.** Settlement curve of different PAC dosage.

**Figure 6.** Settlement curve of different PAM dosage.
3.3.2. Settleability improved by PAM. PAM, as a linear high polymer, floculates the suspended particles though charge neutralization and bridging action. In the paper, sludge settlement ratio (SV), sludge volume index (SVI) and sludge moisture content were used to evaluate the sludge settleability. The results are shown in figure 6 and table 2.

Table 2. Effect of PAM dosages on the characteristics of sludge.

| PAC (mg/L) | SV (%) | SVI (ml/g) | Moisture content(%) |
|------------|--------|------------|---------------------|
| 0          | 87.6   | 8.2        | 86                  |
| 100        | 85.3   | 8          | 85                  |
| 350        | 60     | 5.6        | 83                  |

The dose of PAM was 100 mg/L and 350 mg/L, which was 0.7‰ and 2.3‰ of the dried sludge. The results indicate that when 100mg/L PAM was added in the sludge, there was no obvious change in the sludge settleability. When 350mg/L PAM was added, the curve showed an obvious decreasing trend. The sludge settlement ratio decreased to 60%, the sludge volume index to 5.6ml/g and the sludge moisture content to 83%. The sludge volume reduced to 1/2 after 2h. This showed that the sludge sedimentation velocity increased with the growth of the dose.

4. Conclusion

- In the treatment of acidic and highly concentrated fluoride waste water using calcium oxide-calcium chloride, the optimum dosage for the 100 ml waste water was a calcium oxide addition amount of 14 g, calcium chloride addition amount of 2.5g, PAM addition amount of 350mg/L. The effluent fluoride concentration is 5.7mg/L, which met the integrated wastewater discharge standard (GB8978-1996).
- Both PAC and PAM could accelerate the settlement velocity, but the treatment effects were better with PAM. When 350 mg/L PAM was added, the sludge settlement ratio decreased from 87.6% to 60%, the sludge volume index from 8.2 ml/g to 5.6ml/g and the sludge moisture content from 86% to 83%. The sludge volume reduced to 1/2 after 2h.
- The process featured simple operation, low cost of operation and easy maintenance. Its effects were satisfactory. PAM was used to solve the low settlement velocity.

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