Research on Advanced Treatment Technology of Fluorine Containing Wastewater from Graphite Production

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Abstract. With the gradual improvement of environmental emission requirements in China, the graphite industry is facing environmental pressure from advanced treatment. This article first conducted a study on the current status of advanced treatment technology for fluorinated wastewater. Subsequently, a single defluorination agent experiment was conducted, and it was found that compared to several agents used in the experiment, such as PAC, PAFS, and CaCl2, PAC had the best defluorination effect. The optimization of PAC conditions showed that its optimal reaction pH was 7, and equilibrium could be achieved after 3 minutes of reaction. The study also conducted orthogonal experiments with mixed salts, and the best conditions for the combination of fluoride removal agents were found to be PAC adding 400 mg/L, CaCl2 adding 400 mg/L, PAFS adding 200 mg/L, which can remove fluoride to 0.92 mg/L, below 1 mg/L, meeting the Class III water standard in the " Environmental quality standards for surface water ".The SEM image of the sludge generated by the reaction between the composite fluoride removal agent and fluoride containing wastewater shows a larger particle size of up to 50 μm which is beneficial for the separation and removal of sludge. The generated sediment sludge is mainly composed of Al, Fe, Ca, O, and Si according to EDS results, and belongs to general industrial solid waste.

Keywords: Electrostatic precipitator; Cathode frame; Anti bending deformation; Anti slip collapse; high safety and stability.

1. Background

With the increasing demand for graphite deep processing products in both domestic and international markets, the amount of production wastewater discharged by graphite processing enterprises is also increasing. The treatment of fluorinated wastewater has become a major challenge. In the process of processing high carbon graphite to purify the content of graphite, 200-250kg of hydrofluoric acid, 200-300kg of sodium hydroxide, and 1000kg of hydrochloric acid are required for every ton of graphite product processed. The total water consumption is 100-150t. If all added chemicals, as well as a small amount of graphite and trace metal elements, are discharged into the surrounding water through the water washing process, it will cause serious damage to the surrounding environment [1]. At present, the use of chemical precipitation method and its upgraded high-density sludge (HDS) induced crystallization process can basically meet the Integrated wastewater discharge standard (GB18918-2002, grade1). With the increasingly strict national discharge standards for industrial fluorinated wastewater, local governments have also continued to increase their comprehensive environmental law enforcement efforts and raised the fluoride concentration limits in emission standards for key watersheds and industries. Local standards such as the " Integrated wastewater discharge standard of Yellow river basin in Shanxi province " all stipulate a fluoride discharge standard of 5 mg/L. Among them, the special discharge limit in the " and the " Integrated wastewater discharge standard of Yellow river basin in Henan Province" is 2 mg/L. In the Integrated wastewater discharge standard for basin (DB37/3416.1~DB37/3416.5), fluoride has been added as a control indicator for urban sewage treatment plants, set its limit to 2mg/L. Therefore, it is urgent to develop deep fluoride removal processes for graphite deep processing wastewater containing fluorine to meet increasingly strict environmental discharge requirements.

2. Introduction to the advanced treatment technologies for fluoride containing wastewater

The main treatment methods for fluorinated wastewater include calcium salt precipitation method, resin adsorption method, defluorination agent method, and membrane separation method [2]. For high concentration fluoride wastewater (F^-≥20mg/L), chemical precipitation method is usually used, which involves adding calcium salts or lime and using calcium ions and fluoride ions to generate calcium fluoride precipitation to remove fluoride ions. It can basically adapt to the emission limits (6 mg/L to 20 mg/L) specified by national, local, and industry standards [3] [4], but the deep treatment capacity is limited. For low concentration fluorinated water (F^-≤20 mg/L), coagulation precipitation method is generally adopted, which involves adding aluminum salt coagulant and using the coagulant to form positively charged colloidal particles in the water to adsorb fluorine, causing the colloidal particles to aggregate with each other and form larger flocculent precipitates, in order to achieve the goal of fluoride removal. The coagulation sedimentation method has the advantages of simple principle, convenient treatment, low cost, and good effect, but it has disadvantages such as large equipment, difficulty in meeting effluent standards, and slow sedimentation. The membrane separation method can be used for the advanced treatment of fluorine containing wastewater, but the fluorine containing wastewater from graphite deep processing contains a large amount of calcium and a small amount of ferrosilicon, and the total dissolved solids (TDS) are high. The operating pressure of the membrane sys is high, which is easy to cause fouling and scaling of the membrane which resulted in short service life and high operating. Although ion exchange resin has a high adsorption capacity for anions in water, its selectivity for F^- is poor. It is difficult to achieve the ideal fluoride removal effect for graphite production wastewater systems with high salt content and a large number of competing ions [6]. The adsorption method utilizes a filling matrix for ion exchange or surface chemical reaction with pollutants in wastewater to remove fluoride. This method is easy to operate and has a stable fluoride removal effect [7]. The commonly used fluoride removal adsorbents mainly include activated alumina, bone char, zeolite, bentonite, activated carbon, activated fly ash, coconut shell, magnesium oxide, hydroxyapatite, zirconia, rare earth compounds, etc. Under certain conditions, adsorption methods can achieve deep fluoride purification, but commonly used adsorbents have low adsorption capacity, poor adsorption selectivity, and problems such as decreased adsorption capacity after desorption regeneration[8]. The defluorination agent method is a defluorination method based on chemical flocculation and defluorination precipitation agent, which has the advantages of wide applicability, fast reaction speed, and high removal rate. This study intends to use the defluorination agent method based on aluminum salt, calcium salt, and compound salt to investigate the deep treatment effect of graphite deep processing fluorine-containing wastewater, explore the best reagent process conditions. The study will provide supporting technical requirements for the upgrading need of fluoride containing wastewater in the graphite industry.

3. Experimental Materials and Methods for Advanced Fluorine Removal

3.1 Experimental Purpose

In response to the actual fluorine containing wastewater generated in the graphite deep processing industry that has already reached the " Integrated Wastewater Discharge Standard (GB8978-1996)." through preliminary chemical precipitation treatment, further laboratory research on the fluorine removal agent method for deep treatment will be carried out to explore the optimal types and process conditions of fluorine removal agents, providing technical support for the deep treatment of fluorine containing wastewater in the graphite industry.

3.2 Experimental chemicals

Experimental chemicals: $CaCl_2$, PAC, PAFC, $Al_2(SO_4)_3$, industrial grade.

3.3 Experimental water sample

Taken from a graphite deep processing plant in Shandong, the water sample was preliminarily treated using sludge induced crystallization method at room temperature~20℃, and the concentration of fluoride ions after treatment was about 7~10 mg/L.

4. Research results of deep fluoride removal experiment

4.1 Experimental study on deep defluorination with a single defluorination agent

Data shows that inorganic salt defluorination agents such as polyaluminum chloride (PAC), aluminum sulfate ($Al_2(SO_4)_3$), and polyaluminum iron (PAFS) are effective methods for defluorination through coagulation precipitation.By adding aluminum salts and adjusting the pH, the generated hydroxide colloid adsorbs fluoride ions together, forming an insoluble complex that can remove fluoride ions from water. On the other hand, adding aluminum salt coagulants can promote the destabilization and coagulation of colloidal particles, accelerate the sedimentation rate of sludge, and have a positive effect on reducing sludge volume. This experiment investigates the process conditions for adding aluminum salt coagulants and other defluorination agents to treat fluoride containing wastewater.

4.1.1 Experimental results of aluminum salt defluorination

Add PAC to the supernatant of the graphite purified fluoride wastewater sample treated by the sediment reflux induced crystallization method to further remove the concentration of fluoride ions. The dosages were 500mg/L, 1000mg/L, 1500mg/L, and 2000mg/L, respectively. After stirring for 30 minutes, PAM was added for flocculation and sedimentation. The supernatant was taken to test the fluoride ion concentration. The experimental results are shown in Table 1.

Table 1 Table of Fluorine removal effect of different dosage of PAC.

Number	Chemicals	Dosage（mg/L）	F- (mg/L)
0	PAC	0	7.02
1	PAC	500	6.58
2	PAC	1000	7.21
3	PAC	1500	7.34
4	PAC	2000	6.82

The experimental results table show that the concentration of fluoride ions has decreased to around 7 mg/L after chemical precipitation treatment, and the concentration of fluoride ions does not significantly decrease with the increase of PAC dosage. At this time, the amount of PAC dosage is already large. Excessive addition of PAC not only increases the treatment cost, but also affects the water quality due to the residual Al3+in the effluent. The main reason for the poor fluoride removal effect is that the pH of the wastewater decreases to around 4.5 after adding PAC, and it is not easy to form flocs after adding PAM, which can also lead to pH exceeding the standard. Therefore, in subsequent experiments, after adding aluminum salt for fluoride removal, lime milk needs to be added to adjust to pH 7.0. The experimental results are shown in Tables 2 and 3.

Table 2 Table of Treatment Results of Fluorine by PAC

Number	Chemicals	Dosage(mg/L)	F^- (mg/L)
0	PAC	0	7.02
1	PAC	100	3.8
2	PAC	200	2.12
3	PAC	400	1.74

Table 3 Table of Treatment Results of Fluorine by $Al_2(SO_4)_3$

Number	Chemicals	Dosage(mg/L)	F^- (mg/L)
0	$Al_2(SO_4)_3$	0	7.02
1	$Al_2(SO_4)_3$	100	3.5
2	$Al_2(SO_4)_3$	200	3.12
3	$Al_2(SO_4)_3$	400	2.5

From Tables 2 and 3, it can be seen that both PAC and $Al_2(SO_4)_3$ have significant effects on treating low concentration fluoride wastewater. When PAC dosage is 400 mg/L, fluoride can be removed to 1.74 mg/L

The flocs generated from PAC and aluminum sulfate experiments are shown in the following figure：

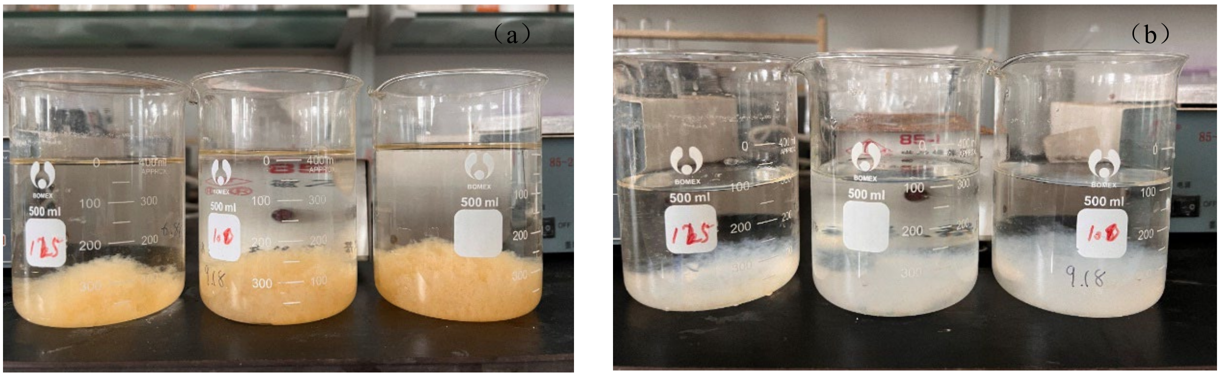

Figure 1 PAC defluorination (a), Al2 (SO4)3 defluorination (b)

It can be seen that adding lime adjust to pH 7.0 after aluminum salt defluorination and then adding PAM for flocculation and sedimentation has a better effect, and the supernatant is clear. PAC defluorinated sludge is more dense and settles faster than Al_2 $(SO_4)_3$.

4.1.2 Experimental Results of Fluorine Removal by PAFS

The treatment results of fluoride using other fluoride removal reagents PAFS are shown in Table 4.

Table 4 Table of Treatment Results of Fluorine by PAFS

Number	Chemicals	Dosage(ml.)	F^- (mg/L)
0	PAFS	0	14.60
1	PAFS	2.50	14.40
2	PAFS	5.00	13.60
3	PAFS	7.50	12.20
4	PAFS	10.00	14.60

Note: PAFS concentration is 5%.

From the above experiments it can be seen that PAFS has poor fluoride removal effect.

4.1.3 Experimental results of calcium salt deep defluorination

After $CaCl_2$ is dissolved in the water sample, it will increase the concentration of Ca^{2+}in the solution resulting in the same ion effect. This will promote the precipitation and dissolution equilibrium of CaF_2 in the solution to move towards the direction of generating CaF_2, effectively reducing the concentration of fluoride ions in the solution. Therefore, $CaCl_2$ is chosen as the fluoride precipitation agent.

The specific operation of the experiment is to take a mixture of fluorinated waste cement after chemical precipitation treatment, add $CaCl_2$ to it, react for 30 minutes, and then precipitate the supernatant to test the concentration of fluoride ions. Six experiments were conducted using 0g, 0.5g, 1.0g, 2.0g, and 2.5g, and the experimental results are shown in Figure 5.

Table 5 Table of Treatment Results of Fluorine by PAFS

Number	Chemicals	Dosage(g/L)	F^- (mg/L)
0	$CaCl_2$	0	7.02
1	$CaCl_2$	0.5	5.87
2	$CaCl_2$	1.0	4.96
3	$CaCl_2$	1.5	4.25
4	$CaCl_2$	2.0	4.11
5	$CaCl_2$	2.5	4.07

The experiment found that as the amount of $CaCl_2$ added increased, the concentration of fluoride ions gradually decreased. The optimal concentration was reached when 2.0g was added, resulting in a decrease of fluoride ion concentration to 4.07 mg/L, which to some extent improved the treatment effect.

4.1.4 Conclusion of single defluorination agent defluorination experiment

From the previous single defluorination agent test results, it can be seen that when using a single defluorination agent, $CaCl_2$ has average defluorination effect, PAFS has poor defluorination effect, $Al_2(SO_4)_3$ has better defluorination effect, and PAC has the best defluorination effect. Therefore, PAC was selected as the defluorination agent and subsequent condition optimization tests were conducted.

4.2 Experimental Study on Optimization of Fluorine Removal Conditions in PAC

Effect of pH value on the fluoride removal efficiency of PAC

The defluorination results of PAC with different dosages, pH values, and the same stirring reaction time (10 minutes) are shown in Table 6.

Table 6 The effect of pH value on the fluoride removal efficiency of PAC

Number	pH	Dosage(ml.)	F^- (mg/L)
1	9.0	2.50	12.8
2	8.00	5.00	10.75
3	7.0	10.00	1.74
4	6.0	15.00	1.75

Note: PAC concentration is 5%,water volume being tested is 500ml each.

According to Tables 4.2-1, the optimal pH values for PAC fluoride removal are pH 6 and pH 7. Considering that the emission standard is pH 6-9, pH 7 is chosen as the optimal pH value to ensure compliance.

Effect of reaction time on the fluoride removal efficiency of PAC

The defluorination results of the same dosage of PAC, the same pH value (pH7), and different stirring reaction times are shown in Tables 7.

Table 7 The Effect of Reaction Time on the Fluorine Removal Efficiency of PAC

Number	Time	pH	F^- (mg/L)
0	0	7	14.6
2	3	7	1.64
3	5	7	1.54

4	10	7	1.75

Note: PAC concentration is 5%, water volume being tested is 500ml each.

From Table 7 can be concluded that the reaction time for removing fluorine in PAC is relatively fast, and the equilibrium can be achieved by stirring for 3 minutes in the beaker bench test.

4.3 Experimental Study on Fluoride Removal with Compound Salts

PAC、PAFS and $CaCl_2$ were added to the supernatant of fluorine containing wastewater purified from graphite treated by chemical precipitation method. The synergic removal capacity of calcium, aluminum and iron compound salts was investigated. The reaction conditions were all 30 min, and then lime milk was adjusted to pH7.0 and PAM was added for flocculation and sedimentation. The experimental results are shown in Table 8.

Table 8 Fluoride removal effect of compound salt mixture of iron, aluminum and calcium

Numble	PAC^-(mg/L)	$CaCl_2^-$(mg/L)	$PAFS^-$(mg/L)	F^-(mg/L)
0	0	0	0	7.37
1	400	400	50	1.78
2	400	400	100	1.25
3	400	400	200	0.92
4	400	400	300	0.98
5	400	400	400	0.92

As can be seen from the above table, the optimal compounding conditions are 400 mg/L PAC, 400 mg/L $CaCl_2$ and 200 mg/L PAFS, and fluorine can be removed to 0.92 mg/L, which is lower than 1 mg/L and meets the Class III water standard in the " Environmental quality standards for surface water ".

4.4 Characterization of fluoride removal sediment using the compound salt method

SEM and EDS tests were conducted on the precipitate solids defluorinated by double salt method. The characterization results are shown in the following figure:

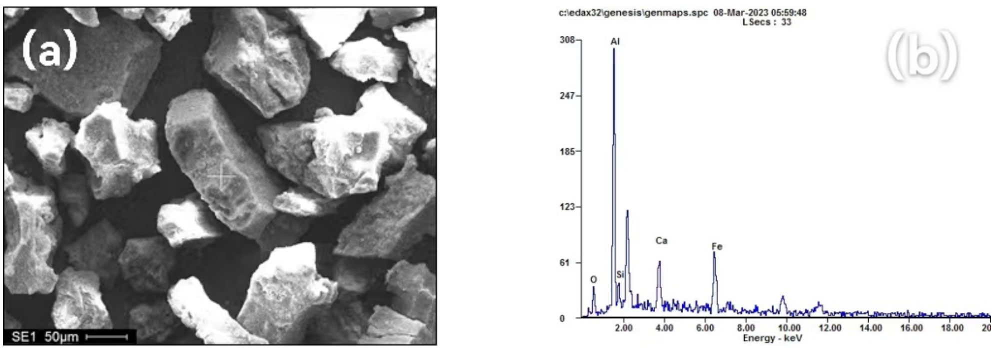

Figure 2 Characterization of compound salt defluoridation precipitated solids
(a. SEM image; b. EDS images)

As can be seen from Figure 4.3-1, the particle size of the precipitate formed by compound and salt defluorination is large, up to about 50μm, which is convenient for subsequent sludge settlement and removal. The supernatant during the experiment is relatively clear, and EDS results show that the composition of the sludge is mainly Al, Fe, Ca, O, and Si, which belongs to general solid waste.

5. Conclusion of Experimental Research on Deep Fluoride Removal

(1) When using a single fluoride removal agent for deep fluoride removal of graphite containing wastewater, PAC agent has the best effect, with pH 7 being the optimal pH value for the fluoride removal reaction. The reaction equilibrium can be reached when the reaction time is 3 minutes;

(2) When using a composite salt defluorination agent for deep defluorination of graphite wastewater, the treatment effect is better than that of a single defluorination agent. The optimal conditions for the composite agent are PAC adding 400 mg/L, $CaCl_2$ adding 400 mg/L, PFS adding 200 mg/L, which can remove fluoride to 0.92 mg/L, lower than 1 mg/L, and can meet the Class III water standard in the "Surface Water Environmental Quality Standard"

(3) SEM images show that the particle size of the precipitated sludge generated by using the experimentally developed compound salt defluorination agent for defluorination is relatively large, up to 50 μm is beneficial for the separation and removal of generated sludge;

(4) The EDS results show that the precipitated sludge generated by the experimental developed compound salt defluorination agent for defluorination is mainly composed of Al, Fe, Ca, O, Si, and belongs to the category of general solid waste.

Acknowledgments

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