Removal of fluoride from zinc sulfate solution by *in situ* Fe(III) in a cleaner desulfuration process

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ABSTRACT

The desulfuration of fume gas using ZnO slurry is a cleaner process because the SO₂ from exhaust is transformed to a valuable ZnSO₄ solution, and the ZnSO₄ solution can then be reused in industrial processes. However, the existence of fluoride (F) in the cleaner process severely hinders the reuse of the ZnSO₄ solution. In this study, an innovative, targeted and simple technique using *in situ* Fe(III) in the actual ZnSO₄ waste liquid for the removal of F was proposed. The results indicated that *in situ* Fe(III) exhibited a good performance in the removal of F and an increase of Fe concentration is beneficial to the removal of F. The active component in the removal of F was identified as a type of hydroxylation ferric sulfate, schwertmannite, which formed under the strong acidic condition. The removal mechanism of F was recognized as an ionic-exchange with the OH[−] groups from coordinated FeOH^{−1/2} and Fe₂OH⁰ and SO₄^{2−} groups in schwertmannite as well as electrostatic adsorption interactions. Based on above principle, the concentration of F in the actual ZnSO₄ solution was successfully reduced to below 50 mg/L, bringing the ZnSO₄ solution up to the recycling standard. This research can be used to guide the effective removal of F from the waste liquid with high acidity, salinity and heavy metals, in the practice.

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1. Introduction

Wet absorption desulfurization technology as a sustainable method have been preferably selected because of their high desulfurization efficiency, high utilization rate of reagents and recycling the substances generated. The absorption of SO₂ using ZnO slurries is a cleaner and sustainable desulfuration method, especially in the zinc hydrometallurgy industry (Fig. S1). After a series of chemical reactions, hundreds of g/L of ZnSO₄ solution with a low pH (~1–2) is produced and then the high concentration ZnSO₄ solution can be reused for producing valuable zinc ingots and other Zn-bearing products (Zhang, 2003). Through the above treatment process, the SO₂ in exhaust gas is transformed into valuable ZnSO₄ resources, which are recycled in the production of

zinc products with almost no waste discharge.

However, the inevitable existence of F in the cleaner desulfuration process causes significant adverse impacts on the recycling of ZnSO₄, thus impeding the normal practice production process. Fluoride in the ZnSO₄ solution is detrimental to the production of electrolytic zinc because of its severe corrosive reaction to both the cathode and anode plates, leading to not only the peeling failure of zinc sheets from the pole plates but also debasing the quality of zinc products (Hu et al., 2015). Only when the concentration of F in ZnSO₄ electrolytes is reduced to less than 50 mg/L can the zinc electrolysis process can run smoothly (Tan et al., 2015). There is approximately 0.38% F contained in the natural zinc ore. It can be transferred into the intermediate product ZnO and the SO₂ flue gas from the zinc smelting process, and then enters the ZnSO₄ solution. Although various techniques have been used for the removal of F from zinc ore and ZnO, unfortunately there are still high concentrations of 100–200 mg/L F in ZnSO₄ solutions. And in the practice, there is currently almost no effective technology to reduce F to less than 50 mg/L from complex solution with hundreds of g/L of ZnSO₄.

Various technologies are being used to remove F from water but

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still the problem has not been rooted out. Meenakshi and Maheshwari (2006) provided a broad overview of the available technologies, such as adsorption (Biswas et al., 2009), precipitation–coagulation (Deng et al., 2016), ion-exchange (Viswanathan and Meenakshi, 2009), membrane separation process (Sehn, 2008), for the removal of F and advantages and limitations of each one. Based on the consideration of treatment cost and efficiency for industrial wastewater from factories, precipitation and adsorption are the most practical methods. However, specific to solutions with high ZnSO_4 concentrations and strong acidities, above methods for the removal of F are not working that well: either the removal efficiency of F is extremely limited, or the valuable ZnSO_4 cannot be recycled due to the introduction of foreign elements. Take, for example, the precipitation method in which an inexpensive CaO slurry is the most popular precipitant reagent and is used for the removal of F through the formation of CaF_2 (s). However, for a solution with hundreds of g/L of ZnSO_4 and a strong acidity, a lot of SO_4^{2-} ions will react with a large amount of free Ca^{2+} , forming a CaSO_4 precipitate. Then, the formation of CaF_2 (s) is hampered, causing the removal efficiency of F to greatly decrease. Moreover, the strong acidity of the solution and the relatively high solubility-product constant ($K_{\text{sp}} = 3.95 \times 10^{-11}$) of CaF_2 require use of excessive amounts of CaO , leading to the generation of large quantities of sludge and an extremely limited removal efficiency of F. In addition, through numerous preliminary tests, it can be found that the concentration of F in an 80 g/L ZnSO_4 solution could only be decreased from 200 mg/L to 105 mg/L or more using CaO slurry. When the concentration of ZnSO_4 is increased to 200 g/L, the remaining F concentration increased to 170 mg/L, which is much higher than the required 50 mg/L. For adsorption technique, because both F^- and SO_4^{2-} are negatively charged ions and the concentration of SO_4^{2-} is much higher than F^- in solution, a strong, competitive adsorption on the surface of the adsorbent will occur between the F^- and SO_4^{2-} ions, leading to an extremely low removal efficiency of F. And the regeneration of adsorbent is required after every 4–5 months and effectiveness of adsorbent for F removal reduces after each regeneration. Disposal of F laden sludge and concentrated regenerant is also a problem. Given all this, innovative and targeted techniques for the removal of F from high acidity, salinity and heavy metals should be proposed based on the characteristics of an actual solution.

Through sampling and preliminary analysis, the main ingredients of an actual ZnSO_4 solution from the desulfuration process were obtained: 250–300 g/L ZnSO_4 , 100–200 mg/L F, 7–9 g/L dissolved Fe(II) and a pH of 1–2. To recycle the ZnSO_4 to the greatest extent on the premise of not introducing foreign elements, the F concentration needs to be reduced to < 50 mg/L and the Fe(II) concentration needs to be reduced to < 10 mg/L. To achieve the above requirements, an innovative and low-cost strategy for the simultaneous removal of F and Fe(II) was proposed in this study. The key step in this method is the formation of *in situ* Fe(III) from the pre-oxidation of coexisting Fe(II). This type of Fe(III), formed in the original place of Fe(II) in aqueous solution, has performed much better in the ability to remove contaminants such as arsenic (Guan et al., 2009; Sun et al., 2013) and phosphate (Mao and Yue, 2016) than *pre* Fe(III) [e.g., $\text{Fe}_2(\text{SO}_4)_3$]. Thus, it may be more efficient for *in situ* Fe(III) to reduce the F concentration to below 50 mg/L in high concentration ZnSO_4 solutions. In this study, the green oxidant H_2O_2 is used in the pre-oxidizing process of Fe(II). The removal efficiency of F in a simulated solution under different conditions, such as low pH, Fe concentration, ZnSO_4 concentration and F concentration, was investigated. A removal mechanism for F was proposed, based on the characterization of attenuated total reflection infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS). As a comparison, the removal of F using

pre Fe(III) and Fe(II) were also performed. In addition, the removal of F from an actual solution collected from a zinc smelting plant was studied.

2. Materials and methods

2.1. The removal of F

All chemicals are analytical-grade or higher and were used without further purification. All solutions were prepared with deionized water. Two types of simulated feed solution were prepared in advance: (1) a solution containing F^- , ZnSO_4 and Fe(II); and (2) a solution containing F^- , ZnSO_4 and Fe(III). F concentrations of 49, 96, 134 and 190 mg/L were prepared by dissolving NaF. The Fe(II) and Fe(III) concentrations of 2, 5, 10, 20 and 40 mmol/L were prepared by dissolving $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$, respectively. ZnSO_4 with concentrations of 0, 25, 75, 125 and 250 g/L were prepared by dissolving $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

Jar tests were performed using a 350 mL simulated solution in 500 mL beakers that were mixed (200 r/min) on a programmable magnetic stirring apparatus under ambient temperatures. For the *in situ* Fe(III) system, a certain amount of H_2O_2 was first added to the simulated solution containing Fe(II) and then stirred for 20 min. Subsequently, the pH of the *in situ* Fe(III) solution was adjusted to pH 3.5–5.5 using diluted sodium hydroxide. After 30 min, samples were allowed to quiescently settle for 1 h. The supernatant was sampled and then immediately filtered through a 0.45 μm membrane filter. Each experiment was carried out in duplicate (at least). The amount of H_2O_2 added, approximately 0.55 times that of Fe(II), was determined on the condition that almost all of the Fe(II) was oxidized to Fe(III). For the control experiments, the processes were as above but without the pre-oxidizing process. For the removal of F from an actual ZnSO_4 solution, the experimental procedures were the same as in the simulated solution, except that the pH was adjusted to 4.5, 5.0 and 5.5 using ZnO . Additionally, the effect of the addition dosage of H_2O_2 (3, 6, 9, 12, 15, 30, and 45 mL/L-solution), with a purity of 30% on the removal efficiency of F, were also performed.

2.2. Analytical methods

The total F was determined using a PXSJ-216F ion meter with a PF-2-01 F ion selective electrode (Shanghai INESA Scientific Instrument Ltd., China) in the total ionic strength adjuster and buffer solution (TISAB; 1 mol/L NaNO_3 and 0.2 mol/L Na-citrate, adjusted to pH 5–6 with 1 mol/L HCl). To eliminate the interference of high Zn^{2+} , SO_4^{2-} and Fe^{2+} or Fe^{3+} , a standard addition method was used. The analytical steps were as follows. (1) A 1.00 mL filtrate sample was transferred to a 50 mL volumetric flask. (2) The pH of the solution was adjusted to near-neutral using either ammonia or a diluted solution of sulfuric acid. (3) Ten milliliters of TISAB was added into the 50 mL of volumetric flask, and the mixed solution was then diluted with deionized water to a final volume of 50 mL. (4) Under stirring conditions, the electric potential of the above prepared solution was determined as E_1 . (5) An additional 1.00 mL of the standard 0.01 mol/L F^- solution was added to the above 50 mL solution. Then, the electric potential of the new solution was determined as E_2 . The concentration of F can be calculated using equation (1).

$$C_x = \frac{C_s \cdot \left(\frac{V_s}{V_x + V_s} \right)}{10^{(E_2 - E_1)/S} - \left(\frac{V_s}{V_x + V_s} \right)}, \quad (1)$$

where C_s is the concentration of the added F standard solution, 0.01 mol/L; V_s is the volume of the added F standard solution,

1.00 mL; V_x is the volume of the sample, 50 mL; and S is the sensitivity of the F ion selective electrode, which was determined by the slope of the regression equation for $\log C_F$ vs. E (mV).

The concentrations of Fe and Zn were determined using an inductively coupled plasma optical emission spectrometer (NexION 300X, PerkinElmer, USA). The floc size in the strong acidic *in situ* Fe(III), *pre* Fe(III) and Fe(II) solutions were determined by a laser particle analyzer (Mastersizer, 2000; Malvern Instruments Ltd., UK). The crystal texture of the hydrolysis floc of Fe(III) was recorded by X-ray diffraction (XRD) on an X'Pert PRO MPD diffractometer (PANalytical, Holland) at 40 kV and 40 mA (Cu K radiation). The valence state of Fe in the hydrolysis floc was taken on the X-ray photoelectron spectra (XPS) with an ESCALAB MK II apparatus (VG Scientific Ltd. UK), using Mg K radiation and the carbon 1s peak at 284.6 eV as standard. The surface property of the Fe(III) floc was recorded on the attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) measurements using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co., USA) spectrometer equipped with a single-bounce diamond crystal and a deuterated triglycine sulfate detector. The FTIR spectra of all samples were determined in the range of 500–4000 cm^{-1} with a resolution of 4 cm^{-1} . The points of zero charge (PZC) of *in situ* Fe(III) and *pre* Fe(III) were determined by immersion technique (Bourikas et al., 2003). The surface roughness of *in situ* Fe(III) and *pre* Fe(III) were analyzed using the contact mode on a multimode atomic force microscope (AFM) (Nanoscope IIIa, Digital Instruments, Italy). A scanning frequency of 1.5 Hz, and a scanning size of 5 nm $\times$ 5 nm for *pre* Fe(III) floc and 10 nm $\times$ 10 nm for *in situ* Fe(III) were employed.

3. Results and discussion

3.1. Effect of pH

The effect of pH test was conducted in 350 mL simulated solution containing 10 mmol/L F, 20 mmol/L Fe(III) or Fe(II), and 125 g/L ZnSO_4 . The removal efficiency of F and the remaining concentration of Fe at different pH are shown in Fig. 1a and Fig. S2a, respectively. The following was found: (1) pH 4.0 is the optimal pH for the removal of F by *in situ* Fe(III) and *pre* Fe(III). With the increase of pH from 4.0 to 5.5, the removal efficiency of F decreases from 30.9% to 16.4%. This is because the hydrolysis of Fe(III) is uncompleted at pH 3.5, and the complexation ion $[\text{FeF}_6]^{3-}$ forms due to the reaction between Fe^{3+} and F^- , thus lowering the removal efficiency of F. The decrease in removal efficiency when pH is above 4.0 can be explained by pH_{ZPC} . The pH_{ZPC} of *in situ* Fe(III) and *pre* Fe(III) was measured as 3.0 and 3.4, respectively (Fig. S3). The electrostatic repulsion between F^- and the negatively charged surface of *in situ* Fe(III) and *pre* Fe(III) floc as a $\text{pH} > \text{pH}_{\text{ZPC}}$ leads to the decrease of the removal efficiency of F. (2) At the studied pH values, the removal efficiency of F by *in situ* Fe(III) is higher than that by *pre* Fe(III) by approximately 6 percentage points. (3) The removal efficiency of F by Fe(II) increased with the increase of pH, but the by only up to a value of at most 4% at pH 5.5. This is because almost no Fe(II) floc was generated at $\text{pH} < 5.5$. Additionally, (4) at $\text{pH} > 4.5$, almost no dissolved Fe was detected in the supernatant while there is 120–170 mg/L Fe in the Fe(II) system. In addition, almost no loss of Zn is found in the *in situ* Fe(III), *pre* Fe(III) and Fe(II) systems at the studied pH values.

Fig. 1. The effect of pH, Fe concentration, Zn concentration and initial F concentration on the removal efficiency of F. Conditions: (a) 10 mmol/L F, 20 mmol/L Fe(III) or Fe(II), and 125 g/L ZnSO_4 ; (b) pH 4.0, 10 mmol/L F, and 125 g/L ZnSO_4 ; (c) pH 4.0, 10 mmol/L F, and 20 mmol/L Fe(II) or Fe(III); (d) pH 4.0, 40 mmol/L Fe(II) or Fe(III), and 125 g/L ZnSO_4 .

3.2. Effect of the concentration of Fe(II) and Fe(III)

The effects of the concentration of Fe(II) and Fe(III) on the removal efficiency of F and the remaining Fe were determined at pH 4.0 in a 350-mL simulated solution containing 10 mmol/L F, 125 g/L ZnSO₄ and Fe(II) or Fe(III) with different concentrations (2, 5, 10, 20 and 40 mmol/L). The results are shown in Fig. 1b and Fig. S2b: (1) when the concentration of Fe increases from 2 to 40 mmol/L, the removal efficiency of F increases from 0 to 55% and 35% for *in situ* Fe(III) and *pre* Fe(III) systems, respectively, while almost no F is removed from the Fe(II) system. This is because with the increase of Fe concentration, more Fe(III) floc is formed, providing more adsorption and exchange sites for the removal of F. (2) The removal efficiency of F in the *in situ* Fe(III) solution is higher than that in the *pre* Fe(III) solution, and the difference widens from 0 to 20% with the increase in Fe concentration. (3) The remaining Fe in the *in situ* Fe(III) and *pre* Fe(III) solutions decreases from 60 mg/L to 5 mg/L with the increase of initial Fe, while an inverse trend is found in the Fe(II) solution. There is approximately 350 mg/L Fe remaining in the Fe(II) system when the initial Fe concentration is 40 mmol/L.

3.3. Effect of ZnSO₄ concentration

The test was performed at pH 4.0 in 350 mL simulated solution containing 10 mmol/L F, 20 mmol/L Fe(II) or Fe(III) and ZnSO₄ with different concentrations (0–250 g/L). The results are shown in Fig. 1c and Fig. S2c: (1) The existence of ZnSO₄ clearly reduces the removal efficiency of F. When the concentration of ZnSO₄ increases from 0 to 250 g/L, the removal efficiency of F decreases by approximately 20% in the *in situ* Fe(III) and *pre* Fe(III) systems. A large amount of sulfate ions inhibits the removal efficiency of F, mainly by competing for adsorption sites with F, as both sulfate ions and F can form partially inner-sphere complex species on the surface of Fe(III) floc (Goswami and Purkait, 2014; Kumpulainen et al., 2008). (2) The removal efficiency of F in the *in situ* Fe(III) system is still higher by approximately 10% than in the *pre* Fe(III) system, while almost no F is removed in the Fe(II) solution. (3) The concentration of ZnSO₄ has little impact on the remaining Fe concentration.

3.4. Effect of F concentration

The test was performed at pH 4.0 in 350 mL simulated solution containing F at the initial concentrations of 49, 96, 134 and 190 mg/L; 40 mmol/L Fe(II) or Fe(III); and 125 g/L ZnSO₄. The results are shown in Fig. 1d. In the *in situ* Fe(III) system, the removal efficiency of F remained almost unchanged at 60%, which is irrelevant to the initial F concentration. Thus, when the initial F concentration is below 125 mg/L, the remaining F can be reduced to below 50 mg/L; and when the initial F concentration is 310 mg/L, through a two-step treatment by *in situ* Fe(III), the remaining F can also be reduced to below 50 mg/L. While in the *pre* Fe(III) system, as the initial F concentration increases from 49 mg/L to 190 mg/L, the removal of F decreases from 64% to 34%. This is because different removal mechanisms of F are in the *in situ* Fe(III) and *pre* Fe(III) systems, which will be discussed in the next section. In the Fe(II) system, the removal efficiency of F was maintained at 1%–6%, much less than that in the *in situ* Fe(III) system.

3.5. Characterization of the hydrolysis species of Fe and suggested removal mechanisms of F

From the above results, it can be found that *in situ* Fe(III) plays an important role in the removal of F because of the hydrolysis floc characteristics of *in situ* Fe(III). Although both hydrolysis products

Fig. 2. The XRD patterns of *in situ* Fe(III) and *pre* Fe(III) flocs.

in the *in situ* Fe(III) and *pre* Fe(III) systems are Fe(III) floc, there are two obvious differences in the removal of F: (1) In general, the *in situ* Fe(III) showed a much better performance in the removal of F than *pre* Fe(III); and (2) When the amounts of surface OH[−] and SO₄^{2−} are sufficient in the *in situ* Fe(III) system, the removal efficiency of F is irrelevant to the initial concentration of F, while the removal efficiency of F decreased with the increase of the initial F concentration in the *pre* Fe(III) system. This indicated that some differences existed between the hydrolysis floc of *in situ* Fe(III) and *pre* Fe(III), resulting in different removal mechanisms and efficiencies of F.

In the *in situ* Fe(III) system, an interesting and complex hydrolysis phenomenon was observed. Unlike *pre* Fe(III), at pH 2.5, a hydrolysis product with *d*_{0.5} = 1200 μm formed following the addition of H₂O₂ after 5 min (Fig. S4), and the amount of the product gradually increased with time. The products were collected after 10 min, 30 min, 1 h and 4 h of reaction; dried in a vacuum; and analyzed by XRD, ATR-FTIR and XPS. The XRD patterns (Fig. 2) of the *in situ* Fe(III) floc show a weak crystalline structure and four peaks at 17.27, 35.16, 47.30 and 66.14°, which are consistent with the peak positions for schwertmannite (PDF 47–1775), an amorphous Fe-oxyhydroxy sulfate mineral (Fe₈O₈(OH)_x(SO₄)_y; x = 8–2y, 1 < y < 1.75) commonly reported as a brownish yellow precipitate in acid mine drainage precipitates and acid sulfate soil environments (Eskandarpour et al., 2008). The formation of schwertmannite is accompanied by the oxidation of Fe(II) (Bigham et al., 1994; Burton et al., 2007; Wang et al., 2013). Thus, in the Fe(II)/H₂O₂ system, the oxidation of Fe(II) and reduction of Fe(III) occurred continuously (Eqs. (2)–(6)), steadily producing schwertmannite.

The XPS patterns of the *in situ* Fe(III) floc at pH 2.5 at different times were consistent with the above analysis. In Fig. 3a, little difference is seen in the patterns of the *in situ* Fe(III) and *pre* Fe(III) flocs. The binding energy of Fe 2p_{1/2} and Fe 2p_{3/2} in the *in situ* Fe(III) system shift approximately 0.2 eV to the left compared with the binding energy of the Fe(III) in *pre* Fe(III). However, through the peak fitting of Fe 2p_{3/2} for the three representative samples, the same three peaks at 712.5 ± 0.1 eV, 711.0 ± 0.1 eV and 710.0 ± 0.1 eV can be found assigned to the Fe(III) binding energy (NIST, 2016), independent of reaction time, pH and Fe(III) species (Fig. 3b–c). This indicates that the complete oxidation of Fe(II) to Fe(III) occurred in the first 10 min or less.

Furthermore, the ATR-FTIR (Fig. 4c) confirms the existence of OH^- and SO_4^{2-} groups in schwertmannite. These measured samples are dominated by a broad OH^- -stretching band centered at 3430 cm^{-1} and a H_2O deformation band at 1625 cm^{-1} . The band at 1123 cm^{-1} is from a bidentate bridging complex between SO_4^{2-} and Fe, which may result from the replacement of OH^- groups by SO_4^{2-} on the surface of schwertmannite through ligand exchange. Bands at 973 and 619 cm^{-1} are assigned to $\nu_1\text{SO}_4^{2-}$ and $\nu_4\text{SO}_4^{2-}$, respectively. Vibration at 701 cm^{-1} is attributed to a Fe–O stretch (Goswami and Purkait, 2014; Wang et al., 2013). Goswami and Purkait (2014) verified that schwertmannite could remove F from drinking water and that the adsorption efficiency (%) of F was maximum at pH 4–9. Schwertmannite can also be used to remove As(III) from acidic waters and arsenate retention, which is controlled by ligand exchange with surface adsorbed SO_4^{2-} (Dou et al., 2013; Fukushima et al., 2003, 2004; Paikaray et al., 2011).

Thus, it can be speculated that schwertmannite will play an important role in the removal of F from high ZnSO_4 and the mechanism may be the exchange of F^- with surface SO_4^{2-} .

Although schwertmannite formed at pH 2.5, there was still approximately 60% dissolved Fe(III) and 95% F in solution. Once the pH of a solution is adjusted to 4.0–5.5, the remaining dissolved Fe(III) rapidly transformed to *in situ* Fe(III) floc. The XRD patterns (Fig. 2) for *in situ* Fe(III) and *pre* Fe(III) flocs have indicated that both schwertmannite and $\text{Fe}(\text{OH})_3$ exist in the *in situ* Fe(III) floc. In addition, extra vibrations at 1377 and 1123 cm^{-1} ($\nu_3\text{SO}_4^{2-}$), as well as 701 and 505 cm^{-1} (Fe–O stretch), are found in the ATR-FTIR (Fig. 4c) of *in situ* Fe(III) floc when compared with *pre* Fe(III) floc (Fig. 4a). Additionally, vibrations at 973 cm^{-1} ($\nu_1\text{SO}_4^{2-}$) and 619 cm^{-1} ($\nu_4\text{SO}_4^{2-}$) disappeared in the *in situ* Fe(III) floc when compared with schwertmannite. This indicates that the SO_4^{2-} groups in schwertmannite are replaced by OH^- through ligand exchange with the increase of pH. Thus, it can be concluded that the *in situ* Fe(III) floc is comprised of schwertmannite formed under acidic conditions and $\text{Fe}(\text{OH})_3$ floc due to the hydrolysis of the remaining Fe^{3+} .

The removal of F by *in situ* Fe(III) floc can be described as an exchange reaction against OH^- and SO_4^{2-} surface groups. From Fig. 4d, it can be seen that the number of OH^- groups decrease when compared with the control group, while the corresponding removal efficiency of F is increased. Thus, OH^- groups in the floc are thought to be exchanged by F^- , forming the coordinated surface groups $\text{FeF}^{-1/2}$ and Fe_2F^0 (Eq. (7) and (8)) (Hiemstra and Van Riemsdijk, 2000).

Fig. 3. The XPS patterns of Fe in hydrolysis products under different conditions.

Fig. 4. The ATR-FTIR patterns for (a) *in situ* Fe(III) and *pre* Fe(III) flocs; (b) *pre* Fe(III) floc before and after the removal of F at pH 4.5 and 5.5; (c) hydrolysis products from *in situ* Fe(III) at pH 2.5 for different times; and (d) *in situ* Fe(III) floc before and after the removal of F at pH 4.5 and 5.5.

Moreover, the vibration at 973 cm^{-1} ($\nu_1\text{SO}_4^{2-}$) disappeared after reaction (Fig. 4d), which indicated that some surface adsorbed SO_4^{2-} was also exchanged by F^- .

As a comparison, the *pre* Fe(III) floc and the removal mechanism were analyzed. When the pH of $\text{Fe}_2(\text{SO}_4)_3$ solution was adjusted to $\text{pH} \geq 3.5$, a reddish-brown floc was generated from the hydrolysis of Fe^{3+} (Eq. (9)).

The XRD patterns in Fig. 2 show an amorphous *pre* Fe(III) floc. The XPS patterns in Fig. 3 show the +3 state of Fe is in the *pre* Fe(III) floc. The IR patterns of *pre* Fe(III) in Fig. 4a show some typical absorption bands at 3430 cm^{-1} (OH^- -stretching band), 1625 cm^{-1} (H_2O deformation band), 1123 cm^{-1} (Fe–OH stretch), and 600 cm^{-1} (Fe–O stretch) (Goswami and Purkait, 2014; Paikaray et al., 2011).

The removal mechanism of F by *pre* Fe(III) floc is regarded as surface adsorption and coprecipitation. From the ATR-FTIR of before and after reaction in the *pre* Fe(III) system in Fig. 4b, the number of OH^- groups at pH 5.5 is higher than at pH 4.5, and both of them are higher than at pH 4.0. The increase of OH^- groups at pH 5.5 is attributed to a higher hydrolysis degree of dissolved Fe(III) than at lower pH values. This indicated that the removal of F does not consume the OH^- groups. In addition, the F can also be

removed by coprecipitation with the *pre* Fe(III) floc.

In summary, the distinctions of surface properties of the *in situ* Fe(III) and *pre* Fe(III) flocs determine their different removal mechanisms of F. In the *in situ* Fe(III) system, the key factor is schwertmannite. The removal of F is mainly attributed to ionic-exchange with the OH^- and SO_4^{2-} surface groups in schwertmannite, as well as electrostatic adsorption interactions. When the amounts of surface OH^- and SO_4^{2-} are sufficient, the removal efficiency of F is independent of the initial F concentration. In the *pre* Fe(III) system, the removal of F is attributed to the electrostatic adsorption interactions between Fe(III) floc and F^- . This is why the removal efficiency of F decreased with the increase in initial F concentration. Additionally, the surface roughness of the *in situ* Fe(III) floc is much larger than the *pre* Fe(III) floc (Fig. S5), which may result in a much better performance in the removal of F than *pre* Fe(III) floc.

3.6. The removal of F from an actual ZnSO_4 solution

An actual solution with pH 2.0, containing 250 g/L ZnSO_4 , 124 mg/L F, and 8 g/L Fe(II) was collected from the desulfuration process to evaluate the removal efficiency of F by *in situ* Fe(III). The Fe(II) contained in the actual waste solution was directly used to form the *in situ* Fe(III) floc through pre-oxidizing by the green oxidant H_2O_2 . The effect of pH on the removal efficiencies of F and the remaining F are shown in Fig. 5a. When the addition of H_2O_2 was 6 mL/L-effluent, the removal efficiency of F increased from 32% to 56%; when the pH increased from 4.3 to 5.3, the remaining F

Fig. 5. The effect of the addition dosage of H₂O₂ and pH on the removal efficiency (%) of F and the remaining F (mg/L) in actual solution.

could reach approximately 50 mg/L at pH 5.3. The effect of the addition amount of H₂O₂ at pH 5.3 on the removal efficiency of F and the remaining F are shown in Fig. 5b. The removal efficiency of F increased from 35% to 65% when the addition amount of H₂O₂ increased from 3 to 9 mL/L-effluent and then remained approximately 65%, even though the addition amount of H₂O₂ above 9 mL/L-effluent. Thus, 9 mL/L-effluent H₂O₂ is an optimum, and at this point, the mole ratio of H₂O₂/Fe(II) is 0.55. Under the optimum condition, the remaining F and Fe in the actual waste solution was 45 mg/L and 5 mg/L, respectively, and only 4% or less of Zn was lost along with the elimination of F and Fe, meeting the recycling demand of ZnSO₄.

In summary, this removal method of F, which is based on the current production process and shows an effective removal effect of F, do not require any additional equipment but the addition of “green” oxidant H₂O₂. Thus, the treatment cost for high ZnSO₄ containing F solutions can be estimated by the price of H₂O₂. The current market price for H₂O₂ (with a volume/mass fraction of 30%) is approximately 1000 CNY per ton. Specific to an actual solution containing 250 g/L ZnSO₄, 124 mg/L F, and 8 g/L Fe(II) collected from the desulfuration process, the treatment cost is estimated to be 6–9 CNY per cubic meter. Additionally, if the concentration of co-existed Fe(II) in the solution cannot satisfy the removal efficiency of F, additional Fe(II) (in the form of FeSO₄·7H₂O) can be added in accordance with the mole ratio of H₂O₂/Fe(II) (0.55). The current market price for industrial-grade FeSO₄·7H₂O is approximately 200 CNY per ton. If 8 g/L Fe(II) (the optimum dosing amount) is added to the solution, it will increase the treatment cost only by approximately 0.1 CNY per cubic meter. Above all, this method achieves the recycling of high ZnSO₄ and ensures the smooth implementation of cleaner desulfuration process, producing immeasurable value.

4. Conclusion

This study provided an innovative, effective and simple removal technique of F from a high concentration ZnSO₄ solution. The effective removal of F not only ensures the reuse of high valuable ZnSO₄ solution to the greatest extent, but also solves a practical problem in the cleaner desulfurization application. Based on the removal mechanism of F, this research can also be used to guide the effective removal of F from the other waste liquid with high acidity, salinity and heavy metals in the practice. In addition, the operation parameters and identification of schwertmannite in the removal of F will inspire us to design better fluorine-removal reagents and processes. This study will also provide a theoretic and practical reference for the removal of analogous anions to F from complex

industrial solutions, thus promoting the recycling of highly valuable components and meanwhile reducing waste emissions.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jclepro.2017.06.213>.

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