Efficient Coagulation Removal of Fluoride Using Lanthanum Salts: Distribution and Chemical Behavior of Fluorine

Xiaocong Zhong¹,², Chen Chen¹, Kang Yan¹, Shuiping Zhong¹, Ruixiang Wang¹* and Zhifeng Xu³*

¹Faculty of Materials Metallurgy and Chemistry, Jiangxi University of Science and Technology, Ganzhou, China, ²State Key Laboratory of Separation and Comprehensive Utilization of Rare Metals, Guangzhou, China, ³Jiangxi College of Applied Technology, Ganzhou, China

Abstract: La-loaded absorbents have been widely reported for fluoride removal due to the strong affinity of La³⁺ towards fluoride ion. Herein, chemical removal of fluoride from flue gas scrubbing wastewater using lanthanum salt is investigated. The retaining free F⁻ concentration, phase composition and morphology of filtration residues, and the distribution of fluorine have been investigated using ion-selective electrode, analytical balance, scanning electron microscopy, and X-ray diffractor. The results show that at La/F molar ratio ≥ 1:3.05, the majority of fluorine exists as LaFx³−x complexes, leading to the failure of fluoride removal. At 1:3.20 ≤ La/F molar ratio ≤ 1:3.10, the formation of LaF₃ is facilitated. However, co-existing LaFx³−x tends to absorb on the surface of LaF₃ particles, leading to the formation of colloidal solution with large numbers of LaF₃·LaFx³−x suspended solids. At an optimized La/F molar ratio of 1:3.10, a fluoride removal of 97.86% is obtained with retaining fluorine concentration of 6.42 mg L⁻¹. Considering the existing of positively charged LaFx³−x and LaF₃·LaFx³−x, coagulation removal of fluoride is proposed and investigated using lanthanum salts and negatively charged SiO₂·nH₂O colloidal particles, which is in-situ provided via Na₂SiO₃ hydrolysis at pH near 5.5. At a La/F molar ratio of 1:3.00 and Na₂SiO₃ dose of 0.50 g L⁻¹, a fluoride removal of 99.25% is obtained with retaining fluorine concentration of 0.80 mg L⁻¹.

Keywords: fluoride removal, LaFx³−x complexes, coagulation, colloidal particles, precipitation

INTRODUCTION

Fluorine is one of the main contaminants in ground water and industrial effluents (Kong et al., 2020; Wan et al., 2021). Long-term intake of high-fluoride level water may lead to dental fluorosis, bone fluorosis and even neurological damage (Díaz-Flores et al., 2021). According to a standard issued by the World Health Organization (WHO), the fluorine content in drinking water should be less than 1.5 mg L⁻¹ (Kim et al., 2020).

Following the large-scale exploitation of sphalerite ores in recent decades, the available sphalerite ores present a decreasing grade and contain complicated components (Hu et al., 2017). Among the typical impurities in sphalerite ores, the fluoride has attracted extensive attention due to its
detrimental effects on the peel-off of cathodic product (O’Keefe and Han, 1992) and the corrosion of lead-based anodes during the zinc electrowinning process (Zhong et al., 2015; Zhong et al., 2017). During the roasting of sphalerite ores, about 70% of the fluoride and chlorine in the ores enter the flue gas, and the others incorporate into the zinc calcine. In order to further reduce the content of fluoride and chlorine, the zinc calcine is usually treated in a rotary/tube furnace at elevated temperature, where fluoride and chlorine would be volatilized into flue gas in the form of HF and HCl, respectively (Çinar Şahin et al., 2000; Kahvecioğlu et al., 2013). Similarly, the zinc recovery processes from Waelz oxide, zinc oxide fumes, electric arc furnace dust, and other zinc-bearing dusts also discharge flue gas containing HF and HCl (Wei et al., 2010; Martins et al., 2021). During the scrubbing of above-mentioned flue gas, fluoride and chlorine transfer into the liquid phase, yielding a large amount of fluoride-containing acidic scrubbing wastewater. Due to the potential threat of fluoride on human’s health, the fluoride ions must be selectively removed before being discharged. According to China’s ‘Emission Standard of Pollutants for Copper, Nickel and Cobalt Industries’ (GB25467-2010), the fluoride ion content in discharge water should be below 5.0 mg L$^{-1}$ (Liu, 2021).

Varied literatures have reported methods to efficiently remove fluoride from aqueous solutions, such as chemical precipitation (Turner et al., 2005; Chang and Liu, 2007; Huang et al., 2017), coagulation (Sandoval et al., 2019), adsorption (Ravuru et al., 2021; Yang et al., 2020; Sadhu et al., 2021), ion exchange (Samadi et al., 2014) and membrane separation (Feng et al., 2008; Arahmana et al., 2016). Among these methods, chemical precipitation has been widely used in metallurgical industry due to its advantages of simple operation, low cost, and applicability for high-fluoride wastewater. At present, the most widely used precipitant for fluoride removal is lime. However, due to the limitation of solubility product of CaF$_2$, it is difficult to achieve a retaining fluoride content below 7.5 mg L$^{-1}$ (Wajima et al., 2009) via lime precipitation, which is higher than the regulation limit of fluoride level.

As a highly electropositive metal, La$^{3+}$ has a strong affinity towards fluoride ion (Nagaraj et al., 2017). Consequently, a large number of La-loaded absorbents have been reported for fluoride removal from ground water (G.J. Millar et al., 2017; Yan et al., 2017; Wang et al., 2018; He et al., 2019). Absorption has been regarded as one of the most effective methods to treat ground water with relative low fluoride concentration (<100 mg L$^{-1}$), which features low retaining fluoride concentration, low cost, and easy operation (Zhou et al., 2018). In a typical flue gas scrubbing wastewater, the fluoride content could be higher than 300 mg L$^{-1}$, La-loaded absorbents are not suitable to treat this aqueous solution because of its relatively small absorption capacity, which could lead to a large consumption of absorbents and long operation time. Hence, chemical precipitation of fluoride ion using lanthanum salt was proposed to remove fluoride in this work. In spite of extensive report on La-loaded absorbents, the distribution and chemical behavior of fluoride in the presence of La$^{3+}$ remains unclear.

In the present work, the aqueous equilibrium diagrams of F$^{-}$H$_2$O and La-F-Cl-H$_2$O systems were made to understand the species distribution of fluoride and lanthanum element in La-F-Cl-H$_2$O system at varied pH values. The retaining fluoride concentration, precipitate morphology and structure, and distribution of fluoride in La-F-Cl-H$_2$O system at different La/F molar ratios (1:3.20 ≤ La/F molar ratio ≤ 12.40) were investigated and analyzed. Based on the experimental results mentioned above, the distribution and chemical behavior of fluoride in the presence of La$^{3+}$ was discussed in detail. Furthermore, coagulation strategy was proposed to efficiently remove fluoride by adding Na$_2$SiO$_3$ and La(NO$_3$)$_3$·H$_2$O. The retaining fluoride in the equilibrium solution can be reduced to 0.80 mg L$^{-1}$.

### EXPERIMENTAL SECTION

#### Reagents

NaF, NaCl, La(NO$_3$)$_3$·6H$_2$O, Na$_2$SiO$_3$, NaOH, HNO$_3$, analytical grade were purchased (Sinopharm Group, China) and used without further purification. The fluoride-containing synthetic solutions were prepared to stimulate flue gas scrubbing wastewater with NaF, NaCl, and deionized water, and its pH was adjusted to 2.0 ± 0.1 using HNO$_3$.

#### Aqueous Equilibrium Diagram

The aqueous equilibrium diagrams of F$^{-}$H$_2$O and La-F-Cl-H$_2$O systems were made using Hydra database and MEDUSA© software. Specifically, the Hydra database (Puigdomenech, 2004) provided thermodynamic data such as composition data, possible solid phases formed, potential chemical reactions and their equilibrium constants. In the F$^{-}$H$_2$O system, the main species considered were HF, H$_2$F$_2$, HF$_2^-$, H$^+$ and OH$^-$. In the La-F-Cl-H$_2$O system, F$^-$, HF, H$_2$F$_2$, HF$_2^-$, La$^{3+}$, LaF$_2^+$, LaF$_3^-$, LaF$_5^-$, La(OH)$_2^+$, La(OH)$_3^-$, La(OH)$_4^-$, La$_2$(OH)$_6^{2-}$, LaCl$_2^+$, LaCl$_3^-$, H$^+$ and OH$^-$ were taken into account. The chemical reactions and corresponding equilibrium constants are listed in Table 1. These data were sent to MEDUSA© software to make

| Table 1 | Chemical reactions in La-F-Cl-H$_2$O aqueous system and their equilibrium constants. |
|---|---|
| Equation no | Reaction | $\log K$ |
| (1) | $2H^+ + 2F^- = H_2F_2$ | 6.77 |
| (2) | $HF + F^- = HF_2^-$ | 3.18 |
| (3) | $F^- = H^+ + F^-$ | 3.62 |
| (4) | $La^{3+} = H^+ + LaOH^{2+}$ | -6.86 |
| (5) | $La^{3+} + 2F^- = LaF_2^-$ | -18.14 |
| (6) | $La^{3+} + 3F^- = LaF_3^-$ | -27.91 |
| (7) | $La^{3+} + 4F^- = LaF_4^-$ | -40.86 |
| (8) | $5La^{3+} + 9F^- = LaF_4^{9-}$ | -71.20 |
| (9) | $La^{3+} + F^- = LaF_2^+$ | 3.85 |
| (10) | $La^{3+} + 2F^- = LaF_2^+$ | 6.65 |
| (11) | $La^{3+} + 3F^- = LaF_3^-$ | 8.69 |
| (12) | $La^{3+} + 4F^- = LaF_4^-$ | 10.35 |
| (13) | $La^{3+} + Cl^- = LaCl^+$ | 0.29 |
| (14) | $La^{3+} + 2Cl^- = LaCl_2^+$ | -0.03 |
| (15) | $H_2O = H^+ + OH^-$ | -14.00 |
diagrams based on principles of mass conservation, simultaneous chemical equilibrium, and electronic charge neutrality. The distribution of fluorine species in the F-H2O system, and the distribution of La or F species in the La-F-Cl-H2O system were analyzed.

Experimental Procedure and Characterization

The pH of the fluorine-containing synthetic solution was firstly adjusted to 5.5 ± 0.1 using NaOH. Afterwards, different amounts of La(NO3)3·6H2O were added to 200 ml of synthetic solution under agitation (200 rpm) based on a specific La/F molar ratio. The fluoride removal reaction proceeded for 1 h at 30 ± 1°C. During the reaction, fluoride ion selective electrode and pH meter were used to monitor the variation of pF (-log(af-), measured continuously without pH adjustment) and pH value with reaction time. At the end of reaction, the solution was vacuum filtrated using inorganic filtration membrane (pore diameter of 0.22 μm, Jinteng®). The filtration time was recorded, and the filtration residue was collected. The final pF of the solution was measured using ion selective electrode after adjusting the pH of filtrate to 5.5 ± 0.1. The filtration residues collected were dried overnight in an oven at 80°C. After this, the weights of filtration residues were obtained using weight loss method. The morphologies and phase structures of filtration residues were investigated using scanning electron microscopy (SEM, MIRA 3) and X-ray diffraction (XRD, MiniFlex 600-C). At a La/F molar ratio ≥1:3.05, there was no precipitate obtained, extra NaF (0.133 g) was added into the filtrate to produce LaF3 precipitates, which were further collected, dried, weighed and analyzed as mentioned above.

Removal of fluoride from synthetic solution using Na2SiO3 and La3+ was also investigated. Firstly, different doses of Na2SiO3 (0.25–1.00 g L−1) were added into the synthetic solution under agitation (200 rpm). After 30 min of agitation, the solution pH was adjusted to 5.5 ± 0.1. Then La(NO3)3·6H2O was added to target a La/F molar ratio of 1:3.00. After 1 h of reaction, the solution was vacuum filtrated. The filtration residue and filtrate were analyzed as mentioned above. To confirm the presence or absence of LaFx3−x or LaFxLaF3·LaFx3−x, extra NaF (0.133 g) was added to the filtrate, and whether precipitate formed was checked.

RESULTS AND DISCUSSION

Aqueous Equilibrium Diagram

Figure 1A shows the distribution of fluorine species in F-H2O equilibrium system. At pH < 4.0, fluorine element exists in the form

---

**FIGURE 1 |** Aqueous equilibrium diagram: (A) fraction of fluorine species in F-H2O system at 298 K, [F]T = 0.01 M; fraction of fluorine species (B) and lanthanum species (C) in La-F-Cl-H2O system at 298 K, [La]T = 0.0053 M, [F]T = 0.0158 M, [Cl]T = 0.0338 M.
of HF, F\(^-\) and H\(_2\)F\(_2\). The proportion of H\(_2\)F\(_2\) decreases as pH increases from 1.0 to 4.0 and descends to zero at pH > 4.0. As a weak acid, most of fluorine exists as HF at low pH range (Li et al., 2013). Over the pH range 1.0–5.5, the proportion of HF descends rapidly as pH increases, while the proportion of F\(^-\) exhibits a reverse variation. At pH > 5.5, HF becomes negligible, and almost all the fluorine exists as free F\(^-\). Figures 1B, C show the distribution of F and La species in La-F-Cl-H\(_2\)O equilibrium system. The molar ratio of La/F in the system is set as 1:3.00, and the total concentration of F and Cl is 0.0158 and 0.0338 M, respectively, same as the synthetic solution. As shown in Figures 1B, C, at pH < 3.0, a small part of fluorine exists as H\(_2\)F\(_2\), while the majority of fluorine exists as LaF\(_3\). Over the pH range 3.0–8.3, almost all fluorine exists in the form of LaF\(_3\). Interestingly, as pH further increases (>8.3), La\(^{3+}\) tends to hydrolyze to La(OH)\(_3\), resulting in a decrease of LaF\(_3\) proportion. Based on the thermodynamic diagrams of La-F-Cl-H\(_2\)O equilibrium system, it can be confirmed that at acidic environment (pH < 3.0), part of fluorine exists in the form of H\(_2\)F\(_2\), which could hinder the combination of fluorine with La\(^{3+}\). Nevertheless, in the pH range over 8.3, La\(^{3+}\) hydrolysis reaction would compete with LaF\(_3\) precipitation reaction, resulting in a low fluoride removal and a high retaining fluorine concentration. Therefore, the pH range for fluoride removal using La\(^{3+}\) should be controlled between 5.5 and 8.3. Given the pH of the synthetic solution is about 2.0, in order to reduce the neutralization cost, the pH for fluoride removal is optimized to 5.5. Similarly, several literatures have also reported the largest adsorption capacity and highest defluorination efficiency of La-loaded adsorbents near pH of 5.5 (Cai et al., 2018).

Fluoride Removal at La/F Molar Ratios ≥1:3.00

Figure 2 shows the variation of solution pF and pH with time during the reaction at La/F molar ratios ≥1:3.00. At the initial stage, pF increased rapidly, indicating a sharp decreasing of free F\(^-\) concentration (Figure 2A). Meanwhile, the solution pH value exhibits a quick drop (Figure 2B). The decreasing pH could be explained by the enhanced ionization of HF due to the decreasing concentration of free F\(^-\), which results in a larger H\(^+\) activity. When the reaction time exceeds 300 s, the solution pF and pH change slightly, suggesting an equilibrium state obtained between La\(^{3+}\) and fluorine species. As the La/F molar ratio increases from 1:3.00 to 1:2.85, the stable pF increases apparently, and the pH exhibits a reverse change. This result indicates that addition of excessive La\(^{3+}\) can promote the combination of F\(^-\) and La. However, when the La/F molar ratio further increases, the stable pF increases slightly, indicating that increasing lanthanum dose has a small effect on the stable pF at La/F molar ratio ≥1:2.85.

As mentioned above, during the fluoride removal at La/F molar ratios ≥1:3.00, the stable pF is larger than 4.5, namely, the free F\(^-\) concentration could be reduced to below 0.5 mg L\(^{-1}\). However, after 1 h of reaction the solutions with La/F molar ratios ≥1:3.00 remained clear and transparent (shown in Supplementary Figure S1). During the vacuum filtration using inorganic membranes with a pore diameter of 0.22 μm, the mass of filtration residue collected from five solutions with different La/F molar ratios (≥1:3.00) is negligible.

Due to the low free F\(^-\) concentration and the absence of precipitate, it is reasonable to assume that most of fluorine retains in the solution as soluble species. In order to verify this assumption, extra NaF (0.133 g) was added to each solution. The digital photos of solutions after adding extral NaF are shown in Supplementary Figure S1. Interestingly, flocculent precipitates formed immediately upon the addition of extra NaF. The XRD pattern and SEM image of the precipitates are shown in Supplementary Figure S2. It is apparent that characteristic peaks of LaF\(_3\) are observed in the XRD pattern of the precipitates (Supplementary Figure S2A), signifying the formation of LaF\(_3\) with extra addition of NaF. As shown in Supplementary Figure S2B, LaF\(_3\) precipitates exist as irregular crystalline bulks and amorphous particles simultaneously. The crystalline bulks may be resulted from the recrystallization of amorphous floccules during the vacuum filtration and drying process (Hermans and Weidinger., 1946). The mass of precipitates formed by adding extra NaF in different solutions is shown in Supplementary Figure S3. It is found that the mass of
precipitates is close to the theoretical LaF₃ production. These results confirm that at La/F molar ratio ≥1:3.00, fluorine retains in the solution as soluble species. However, reducing the La/F molar ratio by adding extra NaF could facilitate the formation of LaF₃.

Considering the fact that fluoride ion could complex La³⁺, which results in the formation of LaF₂⁺ and LaF₂⁺⁺, it could be inferred that in aqueous solutions with La/F molar ratios ≥1:3.00, most of fluorine retains in solution as LaFₓ⁻⁻ complexes. Similarly, Antuñano et al. (2016) and Liu et al. (2020) reported the presence of AlFₓ⁻⁻ complexes in Al-F-H₂O system. Table 2 shows the distribution of fluorine in the solution after 1h of reaction with La/F molar ratios ≥1:3.00. It could be found that over 99% fluorine retains in the solution as LaF₃. As the La/F molar ratio increases, the proportion of LaFₓ⁻⁻ slightly increases. Since all fluorine retains in the solution in the form of LaF₃ or free F⁻, the fluoride removal efficiencies of solutions with La/F molar ratios ≥1:3.00 are all zero.

**Fluoride Removal at La/F Molar Ratios ≤1:3.00**

It is confirmed that at La/F molar ratios ≥1:3.00 the fluorine could be not removed in the form of LaF₃ precipitates. Therefore, it is necessary to investigate the chemical behavior of fluorine at La/F molar ratios ≤1:3.00.

**Figure 3** shows the variation of pF and pH with time in solutions with La/F molar ratios ≤1:3.00. Similar to the results obtained in solutions with La/F molar ratios ≥1:3.00, the reaction between La³⁺ and fluorine get an equilibrium state in 5 min. The stable pF decreases as the La/F molar ratio decreases, while the final pH shows the reverse change. Notably, at La/F molar ratio ≤1:3.00, the La/F molar ratio has a more significant influence on the stable pH and pF of the solutions. Specifically, as La/F molar ratio decreases from 1:3.00 to 1:3.05, the stable pF decreases from 4.50 to 3.75, indicating a much higher concentration of free F⁻ retaining in the solution.

**Supplementary Figure S4** shows the photos of the solutions with different La/F molar ratios (≤1:3.00) after 1 h of reaction. It is apparent that a large number of white floccules suspend in the solutions with La/F molar ratios ≤1:3.05. As La/F molar ratio decreases, the solution becomes more and more turbid. It is worth noting that after standing for 2 h, the suspended solids could not settle. Therefore, it can be inferred that colloidal solutions were formed at La/F molar ratio ≤1:3.05. The formation of colloidal solution could be explained as follows. As mentioned above, in solutions at La/F ≥ 1:3.00, the insufficient fluorine results in formation of LaFₓ⁻⁻, such as LaF₄⁺⁺ and LaF₅⁺. In solution of La/F ≤ 1:3.05, the presence of sufficient fluorine promotes the formation of LaF₃. However, the coexisting LaFₓ⁻⁻ tends to adsorb on the surface of LaF₃, resulting in negative charges on
the surface of suspended solids (LaF$_3$-LaF$_{3-x}$). This would enhance the stability of suspended solids and result in the formation of a colloidal solution.

The suspended solids were collected by vacuum filtration using inorganic membrane. Interestingly, filtration residues could only be obtained from solutions with La/F molar ratio $\leq$1:3.10. The XRD patterns and SEM images of the filtration residues obtained from solutions with La/F molar ratio of 1:3.10, 1:3.15 and 1:3.20 are shown in Figures 4, 5, respectively. It can be found that the main phase of the filtration residues obtained in three solutions is LaF$_3$. There is no other apparent characteristic peak, signifying the high purity of LaF$_3$ precipitates. As shown in Figure 5, the LaF$_3$ residues presents two kinds of structures, part of LaF$_3$ exists as irregular bulks with high crystalline, while the others exhibit amorphous structures. As La/F molar ratio decreases, excessive fluoride accelerates the formation of LaF$_3$, resulting in smaller particle size and a larger crystalline degree of LaF$_3$. It is noteworthy that, at La/F molar ratio of 1:3.15 and 1:3.20, the filtrate obtained in vacuum filtration remains light pale, suggesting a small number of suspended solids remain in the solution. This could be explained with the smaller size of colloid particles formed with large fluorine excess coefficient, which could not be intercepted by the filtrate cake and membrane. Table 3; Figure 6 show the distribution of fluorine in solutions with La/F molar ratios $\leq$1:3.00 after 1 h of reaction. It could be found that, as La/F molar ratio decreases (the excess coefficient of fluorine increases), the free F$^-$ concentration of the equilibrium solution increases. At La/F molar ratio of 1:3.00 and 1:3.05, no fluorine is removed from the solution in the form of filtration residues, and over 98% fluorine retains in solution as LaF$_{3-x}$ or LaF$_3$LaF$_{3-x}$. Remarkably, at La/F molar ratio of 1:3.10, about 97.86% fluorine is removed from the aqueous system in the form of filtration residue, and the retaining fluoride concentration is about 6.42 mg L$^{-1}$, slightly higher than the emission standard established in GB25467-2010. As La/F molar ratio further decreases, the proportion of free F$^-$ increases obviously, while the proportion of filtration residues decreases, resulting in a higher retaining free F$^-$ concentration and a decreasing fluoride removal efficiency. Specifically, when La/F molar ratio increases to 1:3.20, the retaining fluoride concentration is about 32.16 mg L$^{-1}$, much higher than the emission standard. Although the presence of excess fluorine could facilitate the precipitation of LaF$_3$, it leads to a significant increase in the retaining free F$^-$ concentration and fine suspended colloid particles
(LaF$_x$-LaF$_{3-x}$). Therefore, the La/F molar ratio is optimized as 1:3.10 for precipitating fluoride using lanthanum salts.

### Chemical Reactions Between F$^-$ and La$^{3+}$

Based on the above results, it can be found that the chemical reactions between F$^-$ and La$^{3+}$ are sensitive to the La/F molar ratio. As shown in Figure 7, at La/F molar ratio ≥1:3.05, the fluoride is relatively insufficient, there is not enough fluoride participate in the precipitation reaction (Eq. 16), resulting in the formation of LaF$_x^+$ (Eq. 17), or even LaF$_x^{2+}$ (Eq. 18). Under this condition, although the free F$^-$ concentration in the aqueous system can be reduced to a very low level, most of fluoride retains in the solution in the form of LaF$_{3-x}^-$ complexes, resulting in the failure of fluoride removal. At 1:3.20 ≤ La:F < 1:3.05, sufficient fluoride enhances the precipitation of LaF$_3$. However, coexisting LaF$_x^{3-x}$ in the aqueous solution could adsorb on the surface of LaF$_3$, resulting in the formation of colloidal solution with LaF$_3$:LaF$_x^{3-x}$ suspended solids (Eqs 19–20).

### Coagulation Removal of Fluoride Using La$^{3+}$ and Na$_2$SiO$_3$

At the optimized La/F molar ratio of 1:3.10, the retaining fluoride concentration in the filtrate is 6.42 mg L$^{-1}$, exceeding the emission standard level (GB25467-2010). Therefore, chemical precipitation using lanthanum salt fails to sufficiently remove fluoride from aqueous solution. Given that fluoride could exists in the form of positively charged LaF$_x^{3-x}$ or LaF$_3$:LaF$_{3-x}^-$ (x = 1 or 2), SiO$_2$·nH$_2$O, as a well-known negatively charged colloidal particle (Lin et al., 2018), is introduced to facilitate the coagulation of LaF$_3$:LaF$_{3-x}$ and LaF$_3$:LaF$_{3-x}$ based on electrostatic interaction. In practice, Na$_2$SiO$_3$ was firstly added into the synthetic solution. After 0.5 h of agitation, the solution pH was adjusted to 5.5 ± 0.1 to produce active colloidal particles (SiO$_2$·nH$_2$O) in situ. Afterwards, the lanthanum salt is added to target a La/F molar ratio of 1:3.00, rather than 1:3.10 in order to reducing the retaining free F$^-$ concentration.
Supplementary Figure S5 shows the digital photos of solutions with different doses of Na$_2$SiO$_3$ after 1 h of reaction. In the absence of Na$_2$SiO$_3$ (Supplementary Figure S5A), the solution remains clear and transparent. Correspondingly, during the vacuum filtration, there is no filtration residues obtained from this solution. In the presence of 0.25 g L$^{-1}$ Na$_2$SiO$_3$ (Supplementary Figure S5B), about 0.10 g L$^{-1}$ filtration residues were collected from the solution. As Na$_2$SiO$_3$ dose further increases, the solutions at equilibrium state become more and more turbid, signifying the formation of suspended particles. Consequently, much more filtration residues were obtained from these solutions.

The XRD patterns and SEM images of the filtration residues were shown in Figures 8, 9. In the XRD patterns of filtration residues obtained from solutions with 0.50–1.00 g L$^{-1}$ Na$_2$SiO$_3$, only the featured peaks of LaF$_3$ appears, demonstrating the main phase of the filtration residues is LaF$_3$. The absence of characteristic peaks of SiO$_2$ may be explained by the low content of SiO$_2$·nH$_2$O or the amorphous structure of SiO$_2$·nH$_2$O. The morphologies of filtration residues obtained with Na$_2$SiO$_3$ addition are shown in Figure 9. It can be found that the presence of Na$_2$SiO$_3$ has an obvious effect on the structures of filtrate residues. A large number of fine irregular particles agglomerates, resulting in the lumps in large size (≥5 μm). However, the dose of Na$_2$SiO$_3$ does not show obvious influence on the morphologies of filtration residues.

Figure 10 shows the distribution of F, Si and La element on the surface of filtration residues obtained from solution with La/F molar ratio of 1:3.00 and 0.50 g L$^{-1}$ Na$_2$SiO$_3$. It is observed that the F and La element is uniformly distributed on the surface of filtration residues, further demonstrating the formation of LaF$_3$ precipitates. In spite of the absence of featured peaks of SiO$_2$ in the XRD pattern, the Si element is detected on the surface of filtration residues, which testifies the participation of colloidal particles (SiO$_2$·nH$_2$O) in the coagulation of LaF$_3$. The EDS results indicate that the contents of Si in filtration residues are 2.87 wt%, 3.67 wt% and 4.25 wt%, corresponding to the addition of 0.50 g L$^{-1}$, 0.75 g L$^{-1}$, and 1.00 g L$^{-1}$ Na$_2$SiO$_3$, respectively.

Table 4; Figure 11 shows the distribution of fluorine element in solutions with La/F molar ratio of 1:3.00 and different doses of Na$_2$SiO$_3$. In the absence of Na$_2$SiO$_3$, even though free F$^-$ concentration could be reduced to 0.51 mg L$^{-1}$, nearly 99.83% fluorine retains in the solution as LaF$_{3-x}$. When Na$_2$SiO$_3$ dose
fluorine is removed from the solution in the form of filtration residues, and 79.25% remains in the solution in the form of LaF$_3$$^{-x}$.

As Na$_2$SiO$_3$ dose increases to 0.50 g L$^{-1}$, a fluorine removal efficiency of 99.25% could be obtained. When adding extra NaF into the filtrate, the solution keeps clear and transparent, proving the absence of LaF$_3$$^{-x}$ or LaF$_3$·LaF$_x$$^{-x}$. The retaining fluoride concentration in equilibrium solution is 2.24 mg L$^{-1}$, lower than the emission standard established in GB25467-2010. As Na$_2$SiO$_3$ dose further increases, the retaining fluoride concentration could be reduced to 0.8 mg L$^{-1}$, lower than the limited fluoride level established by the WHO. However, it is noteworthy that, at a Na$_2$SiO$_3$ dose $\geq$0.50 g L$^{-1}$, the filtration time is longer than 5 h, which could be explained by the formation of a large amount of sticky SiO$_2$·nH$_2$O colloidal particles.

Above results verify our assumption that the presence of negatively charged SiO$_2$·nH$_2$O colloidal particles could interact with positively charged LaF$_3$$^{-x}$ and LaF$_3$·LaF$_x$$^{-x}$, promoting their aggregation and settlement. It is demonstrated that coagulation removal of fluoride could be achieved through adding Na$_3$SiO$_3$ and lanthanum salts. However, the presence of SiO$_2$·nH$_2$O colloidal particles render the difficulty in solid/liquid separation, the operation parameters for coagulation removal of fluoride could be achieved through adding Na$_3$SiO$_3$ and lanthanum salts. However, the presence of SiO$_2$·nH$_2$O colloidal particles render the difficulty in solid/liquid separation, the operation parameters for coagulation

### TABLE 4 | Distribution of fluoride element in aqueous solutions (La:F molar ratio = 1:3.00) after 1 h of reaction in the presence of Na$_2$SiO$_3$.

| Na$_2$SiO$_3$ dose (g L$^{-1}$) | Free F$^{-}$ | LaF$_{3-x}$ or fine LaF$_3$·LaF$_x$$^{-x}$ | Filtration residues | Retaining fluoride$^d$ | Removal |
|--------------------------|-------------|---------------------------------|-----------------|------------------|---------|
|                          | C$^a$ (mg L$^{-1}$) | Mass (mg) | (%) | Mass (mg) | (%) | Mass (mg) | (%) | Mass (mg) | (%) | Mass (mg) | (%) | (mg L$^{-1}$) | % |
| 0                       | 0.51         | 0.10   | 17.07 | 59.90$^p$ | 99.83 | 0          | -    | 0         | -    | 300.00     | 0   |
| 0.25                    | 1.89         | 0.38   | 63.05 | 47.55$^p$ | 79.25 | 12.07     | 2.3  | 0         | 0    | 271.15     | 20.12 |
| 0.50                    | 2.24         | 0.45   | 75.00 | 0        | 0     | 59.53$^q$ | 362  | 99.22     | 2.33 | 99.22      | 99.25 |
| 0.75                    | 2.33         | 0.47   | 78.00 | 0        | 0     | 59.84$^q$ | 325  | 99.73     | 0.80 | 99.73      | 99.73 |
| 1.00                    | 0.80         | 0.16   | 27.00 | 0        | 0     | 59.90$^p$ | 99.83 | 0         | -    | 300.00     | 0   |

$^a$Calculated with final pH of filtrate measured at pH 5.5 ± 0.1.
$^b$Calculated with the fluoride balance (60 mg massfree F$^{-}$ - massfiltration residues $\times \frac{57}{196}$) based on the assumption that precipitate contains LaF$_3$ only (Si is neglected).
$^c$Calculated with the fluoride balance (60 mg massfree F$^{-}$), the absence of LaF$_{3-x}$ or LaF$_3$·LaF$_x$$^{-x}$ is proved by adding extra NaF.
$^d$Including free F$^{-}$, LaF$_{3-x}$ and fine LaF$_3$·LaF$_x$$^{-x}$.
removal of fluoride using Na2SiO3 and lanthanum salts should be optimized in future works.

CONCLUSION

Pyrometallurgical treatment of low-grade sphalerite ores and zinc-bearing dusts discharges a large amount of flue gas containing HF and HCl. During the flue gas scrubbing step, fluorine and chlorine transfer into the liquid phase, yielding a large amount of fluorine-containing scrubbing wastewater. In this work, precipitation removal and coagulation removal of fluoride from flue gas scrubbing wastewater (300 mg L\(^{-1}\) fluoride) using lanthanum salt is investigated.

The chemical reaction between La\(^{3+}\) and F\(^{-}\) has been discussed based on the distribution of fluorine in solutions with different La/F molar ratios. At acidic environment (pH ≤ 4.0), part of fluorine exists as HF and H\(_2\)F\(_2\)-retarding the combination of La\(^{3+}\) and fluorine. Nonetheless, at pH > 8.3, La\(^{3+}\) hydrolysis reaction would compete with LaF\(_3\) precipitation reaction, resulting in a low fluoride removal. Consequently, the pH for fluoride removal is optimized to 5.5. At La/F molar ratio ≥ 1:3.05, most of fluorine retains in the solution in the form of LaF\(_3\)\(_{3-x}\) complexes, resulting in the failure of fluoride removal. At 1:3.20 ≤ La/F ratio < 1:3.05, sufficient fluoride enhances the precipitation of LaF\(_3\). However, LaF\(_{x}\)\(_{3-x}\) coexisting in the aqueous solution could adsorb on the surface of LaF\(_3\), resulting in the formation of colloidal solution with large numbers of LaF\(_3\)/LaF\(_{x}\)\(_{3-x}\) suspended solids. In summary, at optimized La/F molar ratio of 1:3.10, about 97.86% fluoride is removed from the aqueous system in the form of filtration residue, and the retaining fluoride concentration is about 6.42 mg L\(^{-1}\), slightly higher than the emission standard established in GB25467-2010.

Considering the existing of positively charged LaF\(_x\)\(_{3-x}\) and LaF\(_{2}\)LaF\(_{x}\)\(_{3-x}\), coagulation removal of fluoride is proposed and investigated using lanthanum salts and negatively charged SiO\(_2\)·nH\(_2\)O colloidal particles (in-situ produced via Na\(_2\)SiO\(_3\) hydrolysis at pH near 5.5). At a La/F molar ratio of 1:3.00 and Na\(_2\)SiO\(_3\) dose of 0.50 g L\(^{-1}\), a fluoride removal of 99.25% is obtained with retaining fluoride concentration of 2.24 mg L\(^{-1}\). When Na\(_2\)SiO\(_3\) dose increases to 0.20 g, the retaining fluoride concentration could be further reduced to 0.80 mg L\(^{-1}\), lower than the limited fluoride level established by the WHO. During the coagulation removal of fluoride using lanthanum salts and Na\(_2\)SiO\(_3\), the presence of SiO\(_2\)·nH\(_2\)O colloidal particles render the difficulty in solid/liquid separation, the operation parameters for coagulation removal of fluoride should be optimized in future works.

Generally, coagulation removal of fluoride has a huge potential to be adopted in metallurgical industry due to high removal efficiency, low consumption of lanthanum salts, and relative low cost of lanthanum salts and Na\(_2\)SiO\(_3\). However, the influence of impurities, especially anions such as SO\(_4^{2-}\), Cl\(^{-}\), CO\(_3^{2-}\), and NO\(_3^{-}\), on the chemical behavior and distribution of fluoride during coagulation removal of fluoride should be fully evaluated before industrialized application of this process.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

RW: Writing review and editing, Funding acquisition. CC: Investigation, Writing original draft. XZ: Supervision, Methodology, Formal analysis, Writing review and editing. KY: Validation. SZ: Resources, Formal analysis. ZX: Supervision, Writing review and editing.

FUNDING

This work was financially supported by the National Key Research and Development Program of China (2019YFC1908405); Natural Science Foundation of Jiangxi Province (Youth Program; 20202BAB214015); Training plan for academic and technical leaders of major disciplines in Jiangxi Province (Youth Program; 20212BCJ23006, 20212BCJL23052); Program of Qingjiang Excellent Young Talents, Jiangxi University of Science and Technology (JXUSTQJYX2020015); Research Fund of State Key Laboratory of Rare Metals Separation and Comprehensive Utilization (GK-201905), China; Distinguished Professor Program of Jinggang Scholars in institutions of higher learning, Jiangxi Province.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.859969/full#supplementary-material
Zhou, J., Zhu, W., Yu, J., Zhang, H., Zhang, Y., Lin, X., et al. (2018). Highly Selective and Efficient Removal of Fluoride from Ground Water by Layered Al-Zr-La Tri-metal Hydroxide. *Appl. Surf. Sci.* 435, 920–927. doi:10.1016/j.apsusc.2017.11.108

**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

**Publisher’s Note:** All claims expressed in this article are solely those of the authors and do not necessarily represent those of their affiliated organizations, or those of the publisher, the editors, and the reviewers. Any product that may be evaluated in this article, or claim that may be made by its manufacturer, is not guaranteed or endorsed by the publisher.

Copyright © 2022 Zhong, Chen, Yan, Zhong, Wang and Xu. This is an open-access article distributed under the terms of the Creative Commons Attribution License (CC BY). The use, distribution or reproduction in other forums is permitted, provided the original author(s) and the copyright owner(s) are credited and that the original publication in this journal is cited, in accordance with accepted academic practice. No use, distribution or reproduction is permitted which does not comply with these terms.