

Article

Purification of CaF_2 from Fluorine-Containing Sludge: Optimization via Calcium Ion Coexistence Effect

Danyang Zhu ¹, Xiang Chen ^{2,3}, Hui Gong ^{1,*} , Xiankai Wang ^{2,3}, Xueyuan Qiao ^{2,3} and Xiaohu Dai ¹

¹ State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

² YANGTZE Eco-Environment Engineering Research Centre, China Three Gorges Corporation, Wuhan 430010, China

³ National Engineering Research Centre of Eco-Environment Protection for Yangtze River Economic Belt, Wuhan 430010, China

* Correspondence: gonghui001@tongji.edu.cn

Abstract: The rapid development of the photovoltaic industry has significantly increased fluorine-containing sludge production. Calcium fluoride (CaF_2), a vital non-renewable raw material used in optics, metallurgy, and chemical synthesis, holds immense significance for ensuring the sustainable supply of fluoride resources. This study focuses on purifying CaF_2 from fluorine-containing sludge using a systematic approach. Through characterization techniques such as XRF, SEM-EDS, XRD, FT-IR, and laser granulometry, the sludge's composition was thoroughly analyzed. An acid-leaching–alkali-leaching method was proposed and validated for CaF_2 purification. A key finding during acid leaching was the “calcium ion coexistence effect”, where the dissolution of other calcium salts influences CaF_2 dissolution equilibrium, reducing its loss. Leveraging this phenomenon, an optimized strategy was developed by increasing acid concentration while reducing acid volume. This approach effectively addresses two common challenges in traditional acid-leaching processes: high CaF_2 dissolution loss and difficulties in impurity removal. Experimental results revealed that under optimized acid-leaching conditions, the purity of CaF_2 increased significantly from an initial 36.7 wt% to 76.1 wt% after acid-leaching–alkali-leaching. This study demonstrates a successful method for purifying CaF_2 from fluorine-containing sludge, providing a sustainable solution for fluoride resource recovery.

Keywords: fluorine-containing sludge; CaF_2 ; acid-leaching–alkali-leaching; calcium ion coexistence effect; resource recovery



Academic Editors: Lucian-Ionel Cioca and Elena Simina Lakatos

Received: 28 January 2025

Revised: 12 February 2025

Accepted: 13 February 2025

Published: 16 February 2025

Citation: Zhu, D.; Chen, X.; Gong, H.; Wang, X.; Qiao, X.; Dai, X. Purification of CaF_2 from Fluorine-Containing Sludge: Optimization via Calcium Ion Coexistence Effect. *Processes* **2025**, *13*, 552. <https://doi.org/10.3390/pr13020552>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

China's photovoltaic industry accounts for more than 80% of the global market share [1], and its rapid growth has led to a significant increase in fluorine-containing wastewater generated during silicon wafer chemical etching, with concentrations reaching 10^2 – 10^4 mg/L [2–4]. As the discharge of high-concentration fluorine-containing wastewater continues to grow annually, various defluorination technologies have been developed, including coagulation–flocculation, crystallization precipitation, adsorption precipitation, membrane processes, electrodialysis, electrocoagulation, and biological treatments [5–10]. Among these methods, coagulation–flocculation is widely used in practical applications due to its simplicity and relatively low operational cost [11–13]. This approach involves adding inexpensive calcium salts, such as calcium oxide, calcium hydroxide, calcium sulfate, and calcium chloride, to facilitate the binding of fluoride ions with calcium ions,

forming CaF_2 precipitates. The process is further enhanced by coagulants, including alum, polyaluminium chloride (PAC), polyacrylamide (PAM), and magnesium oxide, which induce flocculation through charge neutralization and adsorption, achieving fluoride removal rates of over 95% [3,5,11,14]. However, the excessive use of calcium salts and coagulants in this method generates large amounts of fluorine-containing sludge, which has become a significant challenge in industrial applications [15].

CaF_2 is an indispensable core material in fields such as optics, metallurgy, and chemical synthesis [16–18]. In 2024, the global fluorspar production is estimated to be 9.5 million tons, while the reserves amount to only 95 million tons [19]. Due to the non-renewable nature of fluoride resources and the increasing consumption of fluorspar in recent years, ensuring a stable supply of CaF_2 has become a critical issue that many countries must urgently address [20,21]. In this context, recycling plays a crucial role in the sustainable supply of fluoride resources for the future. It serves as a key strategy for alleviating resource pressure and achieving resource recycling. At the same time, fluorides can accumulate in living organisms, and their release into the environment poses serious threats to human health [22–25]. The World Health Organization (WHO) has stated that when the concentration of fluoride in drinking water exceeds 1.5 mg/L, it can lead to a range of health issues, including dental fluorosis, skeletal fluorosis, and an increased risk of fractures [26]. Therefore, recovering fluoride from fluorine-containing sludge is essential for both the sustainable development of fluoride resources and the protection of human health.

However, the complex composition of fluorine-containing wastewater results in equally complex fluorine-containing sludge. In addition to containing 30–60% CaF_2 , it also includes added calcium salts and coagulants, as well as other calcium salts introduced or formed during the coagulation–flocculation process. The high impurity content significantly increases the difficulty of separating the target substances [27,28]. For low-purity metallurgical-grade fluorspar, the CaF_2 purity must be at least 60% to be useful in industrial applications [19]. Given that fluorine-containing sludge is primarily composed of inorganic materials, chemical methods show great potential for effectively addressing these challenges [28–30].

This study focuses on the key issue of purifying CaF_2 from fluorine-containing sludge. First, a comprehensive characterization of the sludge was conducted to guide the selection of an appropriate purification method. The acid-leaching–alkali-leaching method was proposed for the purification of CaF_2 from fluorine-containing sludge. To address the “calcium ion coexistence effect” observed during the acid-leaching process, where the dissolution of other calcium salts in the system reduces the dissolution loss of CaF_2 , a further optimization strategy for CaF_2 purification was introduced. The specific objectives of this study are (1) to analyze the composition of fluorine-containing sludge and apply chemical methods to recover CaF_2 , (2) to confirm the presence of the “calcium ion coexistence effect” in the selected purification methods, and to optimize the process to minimize CaF_2 dissolution loss. By recovering CaF_2 from low-quality fluorine-containing sludge, this study lays a solid theoretical foundation for the resource utilization of fluorine-containing sludge, promotes the development and application of sludge treatment technologies, and contributes to the progress and sustainable development of the photovoltaic industry.

2. Materials and Methods

2.1. Materials Preparation

The fluorine-containing sludge used in the experiments was sourced from a company located in Gansu Province, China. The company’s process involves adding excess calcium chloride (CaCl_2) and calcium hydroxide ($\text{Ca}(\text{OH})_2$), followed by sodium hydroxide (NaOH)

to adjust the pH. Then, polyaluminium chloride (PAC) and polyacrylamide (PAM) were added to form flocculates, which settle out as a precipitate. The resulting sludge was then concentrated in a settling tank and passed through a plate-and-frame filter press to produce a low-fluorine sludge cake. The filter cake was dried at 105 °C to a constant weight. After drying, the filter cake was ground and passed through a 200-mesh sieve to obtain a uniform sample particle size.

2.2. Characterization of Fluorine-Containing Sludge and Purified Sludge

The elemental composition and oxidation states of the fluorine-containing sludge and the purified sludge were measured using an X-ray fluorescence spectrometer (XRF, Rigaku ZSX Primus III+, Rigaku Corporation, Tokyo, Japan). The microstructure of the fluorine-containing sludge and purified sludge was observed using a scanning electron microscope (SEM, ZEISS GeminiSEM 300, Carl Zeiss AG, Oberkochen, Germany) equipped with an energy-dispersive X-ray spectrometer (EDS), operating in secondary electron mode. The phase composition of the fluorine-containing sludge powder was analyzed using an X-ray diffractometer (XRD, Bruker D2 Phaser, Bruker Corporation, Karlsruhe, Germany). XRD was performed with a copper target, scanning from 10° to 80° at a scanning speed of 10°/min.

2.3. Purification of Calcium Fluoride from Fluorine-Containing Sludge

Based on the composition data obtained from the characterization of fluorine-containing sludge and considering its predominantly inorganic nature, chemical methods were chosen for its treatment. The process involved two stages: an acid-leaching process was applied to remove impurities that react with the acid, followed by an alkali-leaching process to remove impurities. According to a previous study [28], hydrofluoric acid is considered the most effective for purifying CaF₂ due to its minimal dissolution of other impurities. Hydrochloric acid (HCl), while slightly less effective because of some dissolution loss of calcium fluoride, still provides a reasonable purification performance. In contrast, sulfuric acid is the least effective, as it reacts with calcium salts to form stable calcium sulfate, limiting the improvement in CaF₂ purity to only 50–60%. For this experiment, considering both the effectiveness and economic factors, HCl (AR grade, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) was selected as the acid solvent.

A 2 g sample of the fluorine-containing sludge was mixed with 30 mL of 1 M HCl and shaken at 160 rpm for 1 h. After the leaching process, solid–liquid separation was carried out via vacuum filtration, and the solid portion was dried. To remove insoluble impurities such as silica (SiO₂), 20 mL of a 15 wt% NaOH solution was added to dissolve 1 g of the dried powder treated by acid leaching. This mixture was shaken under the same conditions for 2 h. After the alkali-leaching process, solid–liquid separation was again performed via vacuum filtration, and the solid part was dried.

The waste generated from both the acid and alkali leaching processes, including the wash water and residual solutions, was carefully handled to minimize the environmental impact. The acid solution used for the leaching process, after treatment, was neutralized with a suitable base (e.g., NaOH) to adjust its pH to a safe, non-corrosive level. The neutralized solution was then subject to disposal according to local environmental regulations. Additionally, the wash water used during solid–liquid separation was treated using standard filtration and neutralization procedures before being discharged. These measures ensured that all by-products and residuals were managed in an environmentally responsible manner, in line with sustainable practices.

2.4. Optimization of CaF₂ Extraction from Fluorine-Containing Sludge

2.4.1. Verification of the Optimization Approach

The “simulated sludge” was used to verify the potential coexistence effect of calcium ions during the actual treatment process and to optimize the treatment process based on this concept. It was prepared by mixing CaF₂ with other calcium sources, such as calcium carbonate (CaCO₃) and CaCl₂, in specific ratios. The proportion of other calcium sources was increased to enhance the visibility of experimental phenomena.

To determine the appropriate acid dosage, the CaCO₃ in the sample is used as the baseline. The critical acid value was defined as the amount required for the complete reaction of CaCO₃ with acid: values below this threshold were considered “non-excessive acid”, while those above were classified as “excessive acid”.

Six experimental groups were designed to study the dissolution behavior of different simulated sludges under various acid quantities and concentrations. The simulated sludge compositions included pure CaF₂, a mixture of CaF₂ and CaCO₃ (molar ratio 1:1), and a mixture of CaF₂ and CaCl₂ (molar ratio 1:1). The purpose of varying the sludge compositions was to investigate how different calcium sources affect the dissolution of CaF₂ during acid leaching, thereby enhancing the understanding of the dissolution mechanisms and the reactivity of CaF₂ as well as its co-existing calcium-based compounds in actual fluoride-containing sludge treatments.

In this experiment, CaCl₂ represents a calcium source that does not react with acid, while CaCO₃ represents a calcium source that does react with acid. The amount of CaCO₃ used was 1.28 g (0.0128 M), and the critical value for acid usage was 0.0256 M HCl.

Considering that the commonly used concentration of hydrochloric acid for leaching fluorine-containing sludge ranges from 0.5 M to 2 M, this experiment selected a concentration range of 0.5 M to 3.5 M [28]. Each experiment involved adding 5 mL/60 mL of HCl with concentrations of 0.5 M, 1.0 M, 1.5 M, 2.0 M, 2.5 M, 3.0 M, and 3.5 M to the simulated sludge. The mixture was then stirred at 160 rpm for 1 h. Detailed experimental parameters are provided in Table 1. By simulating the addition of both excessive and non-excessive amounts of acid, the experiment mimicked real production scenarios where acid quantity may be either excessive or limited. The reaction characteristics of different calcium sources were observed under conditions of both excessive and non-excessive acid, with a particular focus on the solubility loss of CaF₂. Each experiment was repeated three times to minimize errors caused by random factors.

Table 1. Experimental setup for verifying the “calcium ion coexistence effect”.

Experimental Group	CaF ₂ (g)	CaCO ₃ (g)	CaCl ₂ (g)	HCl Concentration (M)	HCl Volume (mL)
CaF ₂	1	-	-	0.5–3.5	60
	1	-	-	0.5–3.5	5
CaF ₂ + CaCO ₃	1	1.28	-	0.5–3.5	60
	1	1.28	-	0.5–3.5	5
CaF ₂ + CaCl ₂	1	-	1.42	0.5–3.5	60
	1	-	1.42	0.5–3.5	5

2.4.2. Optimization of the Extraction Process for Fluorine-Containing Sludge

The extraction process for actual fluorine-containing sludge was optimized based on the verified approach. Since the solid-to-liquid ratio for leaching fluorine-containing sludge is 1:30 at a 1 M acid concentration, the optimization strategy involves increasing the acid concentration while reducing the volume of acid added, keeping the total amount of acid constant. If the concentration is increased to 2 M, the solid-to-liquid ratio becomes 1:15 with the total acid amount unchanged. If the concentration is increased to 4 M, the

solid-to-liquid ratio would be 1:3.75, again maintaining the same total amount of acid. The alkali-leaching conditions remained unchanged. The experiment was carried out under these optimized conditions shown in Table 2, and the resulting products were compared and analyzed to evaluate the effectiveness of the process.

Table 2. Optimized experimental conditions for extracting CaF_2 from fluorine-containing sludge.

Experimental Group	Sample Mass (g)	HCl Concentration (M)	HCl Volume (mL)	Shaking Speed (rpm)	Shaking Time (h)	Alkali Solution Concentration (NaOH)	Alkali Solution Volume (mL)	Shaking Time (h)
1	2	2	7.5	160	1	15 wt%	20	2
2	2	4	3.75	160	1	15 wt%	20	2

2.5. Composition Calculation of Fluorine-Containing Sludge

To calculate the composition of fluorine-containing sludge, it was assumed that the sludge is primarily composed of CaF_2 , CaCO_3 , Ca(OH)_2 , SiO_2 , Al_2O_3 , and CaSO_4 . These components were considered to account for the entire composition of the sludge, and their quantities were estimated based on the elemental content.

The content of CaF_2 was calculated based on the fluoride (F) content using stoichiometric relationships.

$$\text{CaF}_2 \text{ wt\%} = \text{F wt\%} \times \frac{M_{\text{CaF}_2}}{M_{\text{F}_2}} = \text{F wt\%} \times \frac{78.08}{38.00} \quad (1)$$

The content of SiO_2 was calculated based on the silicon (Si) content.

$$\text{SiO}_2 \text{ wt\%} = \text{Si wt\%} \times \frac{M_{\text{SiO}_2}}{M_{\text{Si}}} = \text{Si wt\%} \times \frac{60.08}{28.09} \quad (2)$$

The content of Al_2O_3 was calculated based on the aluminum (Al) content.

$$\text{Al}_2\text{O}_3 \text{ wt\%} = \text{Al wt\%} \times \frac{M_{\text{Al}_2\text{O}_3}}{M_{\text{Al}_2}} = \text{Al wt\%} \times \frac{101.96}{53.96} \quad (3)$$

The content of CaSO_4 was calculated based on the sulfur (S) content.

$$\text{CaSO}_4 \text{ wt\%} = \text{S wt\%} \times \frac{M_{\text{CaSO}_4}}{M_{\text{S}}} = \text{S wt\%} \times \frac{136.14}{32.07} \quad (4)$$

Other calcium-based reagents, such as CaO , CaCO_3 , and Ca(OH)_2 , were considered as residual components. Their combined content was determined by subtracting the calculated amounts of the other components from the total composition. Since the calculation is primarily based on XRF quantification and XRD qualification, and XRF detects elements such as O, Ca, F, Si, Al, Na, Mg, P, S, Cl, K, Ti, Mn, Fe, Zn, Sr, and Zr but does not include H, hydrates are not considered. It should be noted that under drying conditions at 105 °C, calcium sulfate typically exists in its hemihydrate form ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$).

$$\text{CaO/CaCO}_3/\text{Ca(OH)}_2 \text{ wt\%} = 1 - \text{CaF}_2 \text{ wt\%} - \text{SiO}_2 \text{ wt\%} - \text{Al}_2\text{O}_3 \text{ wt\%} - \text{CaSO}_4 \text{ wt\%} \quad (5)$$

This method simplifies the complex sludge composition into a few main components. It relies on elemental content as a reference and uses molecular weight ratios for estimation. Through this approach, a quantitative evaluation of the sludge composition can be achieved.

3. Results and Discussion

3.1. Characterization of Fluorine-Containing Sludge

3.1.1. Elemental Composition Analysis

In the field of fluorine-containing sludge research, there is currently no standardized method for characterization. To address this, this study employed a variety of characterization techniques to perform a comprehensive and systematic analysis of the fluorine-containing sludge samples [31,32]. The goal was to investigate their intrinsic properties and material composition, providing a solid data foundation and theoretical basis for subsequent treatment and research.

XRF was employed to precisely measure the elemental composition of the sludge samples. The analysis revealed that the primary components of the sample were oxygen (O, 36.2 wt%), calcium (Ca, 31.3 wt%), and fluorine (F, 17.9 wt%), with the remaining 14.6 wt% comprising other elements, mainly silicon (Si), aluminum (Al), and trace amounts of heavy metals (Figure 1). Based on these measurements, the CaF_2 content was estimated to be approximately 36.8 wt%. XRF is a non-destructive and highly accurate technique for elemental analysis, making it particularly suitable for the quantitative analysis of complex solid samples like fluorine-containing sludge. The method operates by exciting atoms in the sample using high-energy X-rays, causing them to emit characteristic fluorescence. By measuring the energy and intensity of these emitted X-rays, the types and quantities of elements present in the sample can be determined. Consequently, XRF analysis provides a comprehensive overview of the elemental composition of the fluorine-containing sludge. The XRF results, combined with an understanding of material formation mechanisms during the coagulation–flocculation process, revealed the coexistence of components such as CaF_2 , CaCO_3 , and other calcium-based substances.

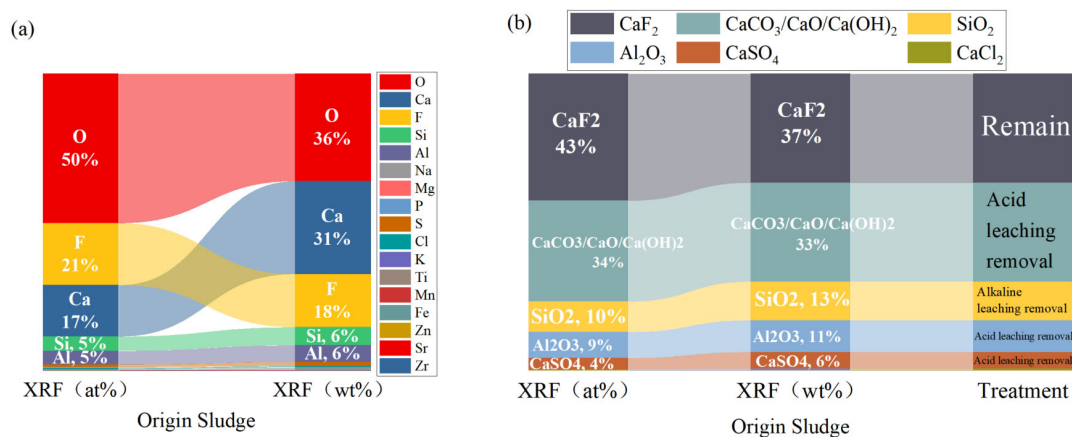


Figure 1. Percentage bar chart of XRF results for the original sample, showing elements (a) and compositional compounds (b). Note: CaCl_2 is detected only in the original sludge, with a proportion below 1% in both at% and wt%. Due to its low abundance, it is not distinctly visible in (b), and its chemical formula is not labeled.

The crystalline structure of the sample was analyzed using XRD. The results (Figure 2) displayed distinct characteristic diffraction peaks for CaF_2 , confirming the presence of highly crystalline CaF_2 in the sample. To quantify minor mineral phases more accurately, the phase quantification of the fluorine-containing sludge was carried out using XRD, with Al_2O_3 as an internal standard, and the K-value method was used for the quantitative analysis of the phase structure. This method successfully identified minor mineral phases including CaCO_3 , Al_2O_3 , SiO_2 , and trace amounts of calcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$). The non-crystalline form of SiO_2 often appears as a broad peak in the XRD spectrum, typically

between 20° and 30° in the 2θ range. The K-value method, which uses the internal standard to account for the intensity of diffraction peaks, enabled the quantitative determination of SiO_2 content, even in its non-crystalline form, by analyzing the broad peak in combination with the crystalline phases present. The presence of SiO_2 is likely due to the introduction of sand or silicate compounds from earlier stages of the process.

Compared to conventional XRD and XRF, the XRD internal standard recovery method offers higher accuracy in quantifying mineral phases, particularly for highly crystalline substances.

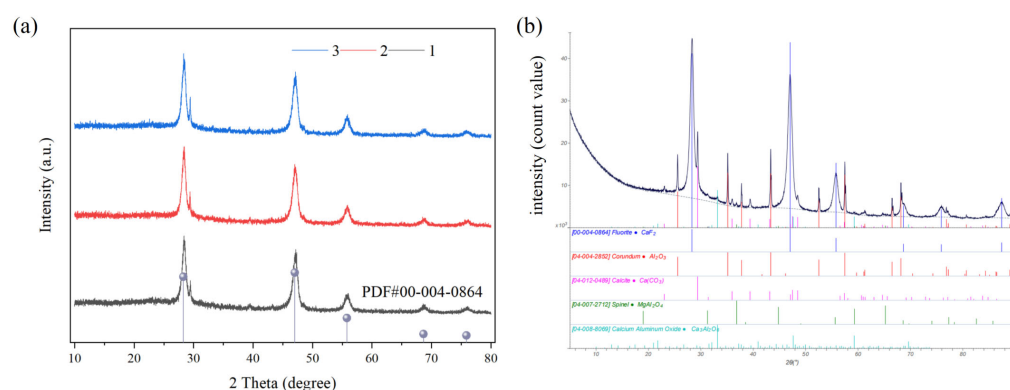


Figure 2. XRD spectra of fluorine-containing sludge: conventional XRD spectrum (a) and XRD internal standard recovery analysis spectrum (b).

3.1.2. Organic Functional Group Analysis

Due to the prior addition of the flocculant PAC, the fluoride-containing sludge may contain organic matter. Thermogravimetric analysis at 600°C revealed that the organic matter content was 14.6%. FTIR was employed for the further analysis of the organic functional groups in the sample (details provided in Supplementary Materials). The absorption peaks at 1083 cm^{-1} and 876 cm^{-1} correspond to the O-S-O stretching vibrations of SO_4^{2-} and the O-P-O stretching vibrations of PO_4^{3-} , indicating the presence of sulfates and phosphates. The absorption peak at 574 cm^{-1} is attributed to the Al-OH bond, confirming the presence of PAC flocculant residues. The broad peak at 3448 cm^{-1} corresponds to O-H stretching vibrations, which may be associated with alcohols, phenols, water molecules, or inorganic hydroxides. The absorption peak at 1636 cm^{-1} is related to C=O bond vibrations, suggesting the presence of carbonyl compounds such as ketones, acids, esters, or amides. Peaks at 1427 cm^{-1} and 876 cm^{-1} further confirm the presence of CO_3^{2-} in the sample.

Since the sludge is primarily composed of inorganic materials, acid leaching was selected as the preferred purification method due to its cost-effectiveness and efficiency. In this study, HCl was used to dissolve CaCO_3 , CaO , Ca(OH)_2 , and Al_2O_3 , while NaOH was applied to dissolve SiO_2 , removing impurities in sequence.

3.1.3. Particle Size and Microscopic Morphology Analysis

The particle size range of the sample was measured using a laser diffraction particle size analyzer, revealing a range of 1–142 μm with good dispersion and fine particle characteristics (details provided in Supplementary Materials). During the coagulation–flocculation process, the materials did not distribute evenly but formed a system where flocculent aggregates coexisted with particulate matter. SEM analysis revealed spherical particle structures on the surface of the sample, encapsulated by the flocculent material (Figure 3). The SEM-EDS analysis of the elemental distribution on the surface showed that the primary elements were O (26.7 wt%), Ca (21.2 wt%), and F (22.0 wt%), with significant amounts of Si (13.4 wt%) and a small amount of Al (1.9 wt%). EDS further confirmed that

these spherical particles were enriched with F and Ca, while Si and Al were uniformly distributed throughout the sample. The calculated surface concentration of CaF_2 was approximately 45 wt%, significantly higher than the overall average determined via XRF analysis. This suggests that CaF_2 is primarily concentrated in the surface region of the particles, with the flocculent material likely enclosing these fluorite-rich particles.

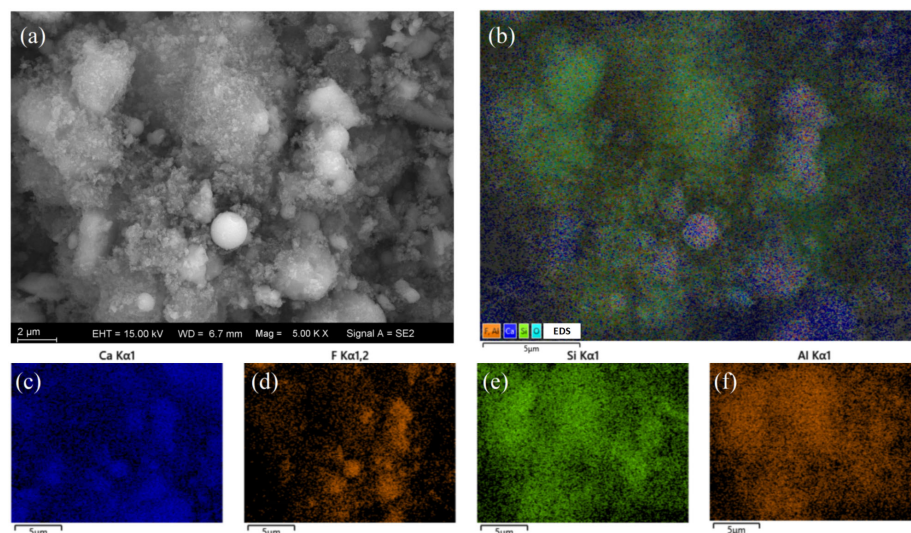


Figure 3. SEM-EDS analysis results of the original sludge: SEM image (a), EDS results (b), elemental distribution maps for Ca (c), EDS of F (d), EDS of Si (e), and EDS of Al (f).

3.2. Purification of CaF_2 from Actual Fluorine-Containing Sludge

To purify CaF_2 from actual fluorine-containing sludge, a combined acid-leaching and alkali-leaching method was employed. The experimental results (Figure 4) indicate that after acid leaching, the proportion of CaF_2 in the sludge significantly increased. However, it is noteworthy that the proportion of SiO_2 impurities also rose as a result of this process.

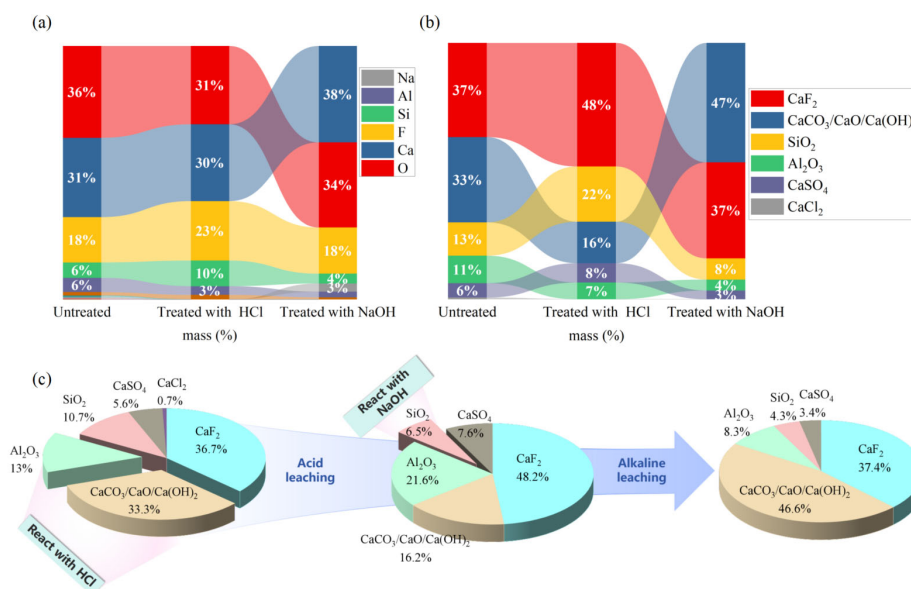


Figure 4. Composition of actual fluorine-containing sludge samples before and after CaF_2 purification, percentage bar chart of elemental composition (a), percentage bar chart of compositional compounds (b), and schematic diagram of treatment process (c). Note: CaCl_2 is detected only in the original sludge, with a proportion below 1% in both at% and wt%. Due to its low abundance, it is not distinctly visible in (b), and its chemical formula is not labeled. Percentages may not sum to 100% due to rounding.

The subsequent alkali-leaching step did not produce the expected outcomes. Although the proportion of Si was reduced during the alkali treatment, the proportion of impurities such as CaCO_3 increased significantly. This unexpected increase in CaCO_3 content reduced the overall purity of CaF_2 instead of improving it, creating a bottleneck in the purification process. Further optimization of process parameters is needed to explore more effective purification routes in order to achieve efficient CaF_2 purification from fluorine-containing sludge, meeting the purity requirements for practical applications.

3.3. Optimization of CaF_2 Purification from Actual Fluorine-Containing Sludge

3.3.1. Effect of Coexisting Calcium Ions in the Acid Treatment of Simulated Sludge

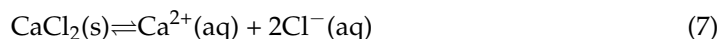
The dissolution rate of 1 g of CaF_2 doped with CaCO_3 or CaCl_2 in 60 mL of an acid solution demonstrated distinct linear relationships with acid concentration. Experiments were conducted using seven different concentrations of HCl (0.5 M, 1 M, 1.5 M, 2.0 M, 2.5 M, 3 M, and 3.5 M). As shown in Figure 5, the CaF_2 loss rate increased linearly with the acid concentration, indicating that the higher acid concentration led to a greater CaF_2 loss rate. For pure CaF_2 , the CaF_2 loss rate increased from 16.7% at a 0.5 M acid concentration to 49.4% at a 3.5 M acid concentration, with a fitted linear equation of $y = 0.0496x + 0.132$ ($R^2 = 0.9744$). For the CaF_2 doped with CaCl_2 , the CaF_2 loss rate increased from 8.2% at a 0.5 M acid concentration to 27.6% at a 3.5 M acid concentration, with a fitted linear equation of $y = 0.0322x + 0.0817$ ($R^2 = 0.9107$). For the CaF_2 doped with CaCO_3 , the CaF_2 loss rate increased from 10.6% at 0.5 M acid concentration to 28.2% at 3.5 M acid concentration, with a fitted linear equation of $y = 0.0302x + 0.0774$ ($R^2 = 0.9855$).

As acid concentration increases, the ionic strength of the solution also increases, which can affect the dissolution behavior of CaF_2 . Ionic strength is known to influence the activity coefficients of ions in a solution, particularly for charged species like Ca^{2+} and F^- . At higher acid concentrations, the increased ionic strength can enhance the solubility of CaF_2 by reducing the electrostatic repulsion between ions, which facilitates the dissolution process.

Additionally, the presence of additional calcium sources decreased the dissolution loss rate of CaF_2 . This is attributed to the “coexisting calcium ion effect,” where the dissolution equilibrium (Equation (6)) is shifted to the left by the increased concentration of calcium ions in the solution.



When CaCl_2 dissolves, it contributes additional calcium ions through the reaction (Equation (7)), suppressing CaF_2 dissolution.



The CaF_2 loss rate in the CaCl_2 -doped group is notably less sensitive to increasing acid concentration compared to the pure CaF_2 group. This trend is visually evident in Figure 5, where the rate of CaF_2 loss rises more slowly in the CaCl_2 -doped group despite higher acid concentrations, resulting in a smaller slope for the fitted linear equation. When CaCl_2 is added, the concentration of calcium ions in the solution increases, which dilutes the acid's effect on F^- dissolution. Two main equilibrium reactions are involved in this system: dissolution equilibrium (Equation (6)) and acid–base equilibrium (Equation (8)).



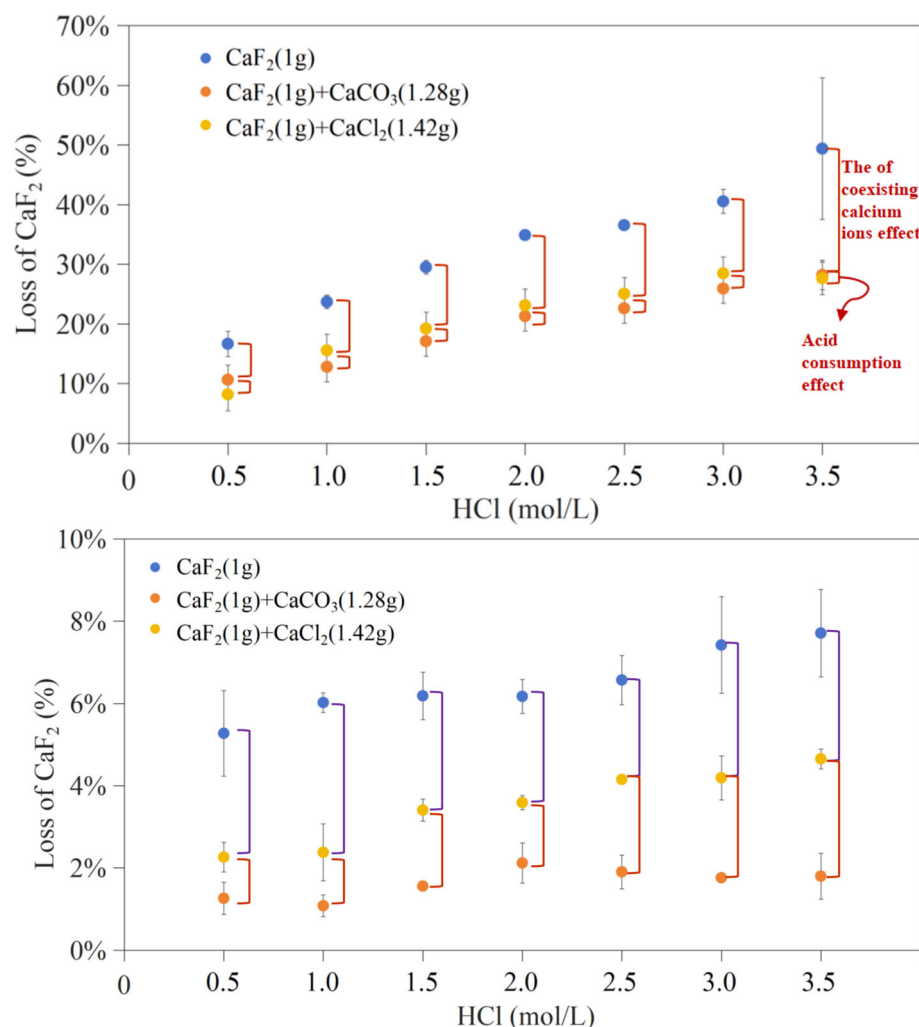


Figure 5. Effect of acid concentration on the fluoride loss rate under 60 mL HCl conditions (**top**) and 5 mL HCl conditions (**bottom**). Data shown are the mean values of triplicate experiments with error bars representing the standard deviation.

When the acid concentration increases, the increased H^+ reacts with F^- to form HF; however, in the $CaCl_2$ -doped group, the increased calcium ions inhibit the CaF_2 dissolution loss, reducing the availability of F^- . This inhibition limits the reaction between H^+ and F^- . As a result, despite the increase in acid concentration, the solubility of F^- is constrained by the calcium ion effect, leading to a smaller increase in the CaF_2 dissolution loss rate.

The calcium ion effect can be validated using the solubility product K_{sp} for CaF_2 and the ion activity coefficients for the involved ions. The dissolution of CaF_2 is governed by its solubility product, which is expressed as

$$K_{sp} = [Ca^{2+}][F^-]^2 \quad (9)$$

The addition of $CaCl_2$ increases the concentration of Ca^{2+} in the solution. According to Le Chatelier's principle, this increase in Ca^{2+} shifts the dissolution equilibrium of CaF_2 to the left, reducing F^- available for reaction. The shift in equilibrium is thermodynamically driven by the common ion effect, where the increase in Ca^{2+} suppresses the dissolution of CaF_2 .

Furthermore, the ion activity coefficients (γ) can be used to account for the influence of ionic strength on the solubility equilibrium. As the Ca^{2+} increases, the activity coefficient

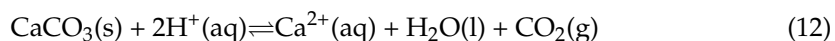
of F^- decreases, further reducing its effective concentration and solubility. The activity of Ca^{2+} ions can be expressed as

$$a_{Ca^{2+}} = \gamma_{Ca^{2+}} [Ca^{2+}] \quad (10)$$

$$a_{F^-} = \gamma_{F^-} [F^-] \quad (11)$$

where $a_{Ca^{2+}}$ and a_{F^-} are the activities of Ca^{2+} and F^- , respectively. The presence of additional Ca^{2+} ions from $CaCl_2$ reduces the availability of F^- , which further inhibits the dissolution of CaF_2 .

Furthermore, the dissolution rate slope of the $CaCO_3$ group is lower than that of the $CaCl_2$ group, and its overall CaF_2 dissolution loss rate is also lower. This phenomenon is attributed to the chemical reaction between $CaCO_3$ and an acid, which not only consumes H^+ but also generates $CaCl_2$, similar to the reaction occurring in the CaF_2 - $CaCl_2$ group. This further suppresses the dissolution loss of CaF_2 . Specifically, the reaction between $CaCO_3$ and an acid consumes H^+ ions through the following reaction:



By consuming H^+ , the reaction reduces the concentration of free H^+ in the solution, which shifts the acid–base equilibrium (Equation (8)) to the left. This shift decreases the availability of F^- ions for reaction, thus limiting the formation of HF and suppressing the dissolution of CaF_2 . Additionally, the calcium ions released from the dissolution of $CaCO_3$ also contribute to shifting the dissolution equilibrium of CaF_2 (Equation (6)) to the left.

In the $CaCO_3$ -doped system, the increased Ca^{2+} in the solution reduces the availability of F^- by competing for F^- . This further suppresses the dissolution of CaF_2 by causing the dissolution equilibrium to shift leftward, as predicted by Le Chatelier's principle.

Thus, the combined effects of acid consumption by $CaCO_3$ and the increased concentration of calcium ions due to $CaCO_3$ dissolution work synergistically to limit the dissolution of CaF_2 , resulting in a lower overall dissolution loss rate. This is in contrast to the $CaCl_2$ -doped system, where the calcium ions from $CaCl_2$ dissolution directly contribute to the shift in the CaF_2 dissolution equilibrium, but without the additional acid consumption effect provided by $CaCO_3$.

In summary, the difference in CaF_2 dissolution loss rates between the pure CaF_2 group and the CaF_2 - $CaCl_2$ group is due to the coexisting effect of calcium ions, while the difference between the CaF_2 - $CaCl_2$ group and the CaF_2 - $CaCO_3$ group is attributed to acid consumption.

In low-volume acid conditions (5 mL), the relationship between acid concentration and CaF_2 dissolution loss deviated from the typical linear trend observed under excess acid conditions. The dissolution loss rates were generally below 10%, significantly lower than those in high-volume acid scenarios. For pure CaF_2 , the CaF_2 dissolution loss rate increased from 5.27% at 0.5 M HCl to 7.71% at 3.5 M HCl. For the CaF_2 doped with $CaCl_2$, the rate increased from 2.26% at 0.5 M HCl to 1.80% at 3.5 M HCl.

This nonlinear behavior is attributed to the combined effects of acid concentration and calcium ion generation from $CaCO_3$ dissolution. Under non-excess acid conditions, the reaction between $CaCO_3$ and HCl generates calcium ions, shifting the dissolution equilibrium (Equation (6)) to the left. As the concentration of HCl increases, more calcium ions are released, enhancing the coexisting calcium ion effect and further suppressing the dissolution of CaF_2 . Additionally, the consumption of H^+ during the reaction shifts the acid–base equilibrium (Equation (8)), reducing the release of F^- .

The acid effect can be divided into two parts: Part A represents the effect of calcium ions in the CaF_2 - CaCl_2 group, while Part B represents the synergistic effect of acid consumption and coexisting ions in the CaF_2 - CaCO_3 group. As the acid concentration increases, the ratio of Part A to Part B decreases, indicating that the synergistic effects of acid consumption and coexisting ions increasingly dominate over the coexisting ion effect alone on the CaF_2 dissolution rate. Under high acid concentration conditions, the synergistic effects of acid consumption by CaCO_3 and the coexisting ion effect become more pronounced, resulting in a smaller increase in CaF_2 dissolution loss.

These findings suggest that during the acid leaching of fluoride-containing sludge, using higher concentrations of acid under non-excess acid conditions can reduce wastewater generation and lower the CaF_2 dissolution loss. This approach offers a more efficient and environmentally friendly pathway for the purification of fluorine-containing sludge.

3.3.2. Effect of Acid Concentration on the Removal of Simulated Impurities

Al_2O_3 was selected as the impurity for the simulation experiment (Table 3), because the actual fluoride-containing sludge contains a relatively high Al content (6 wt%) and Si content. Since the acid-leaching step does not remove SiO_2 , Al_2O_3 was chosen to study the effect of acid concentration on impurity removal under high acid conditions. At room temperature, the reaction of Al_2O_3 proceeds slowly. However, as the acid concentration increases, the removal rate of impurities improves. This indicates that higher acid concentrations facilitate the dissolution or breakdown of impurities, promoting their separation from the sample. In other words, the higher the acid concentration, the more impurities are removed. Based on these findings, it is suggested that during the acid leaching of fluoride-containing sludge, employing a higher concentration of acid under low acid conditions can achieve dual benefits: reducing wastewater generation and improving impurity removal, all while minimizing the loss of CaF_2 .

Table 3. Effect of acid concentration on the removal of Al_2O_3 .

HCl Concentration		Al_2O_3 (0.5 g) Dissolution Rate
Room temperature 60 mL HCl	0.5 M	3.9%
	1.0 M	4.5%
	1.5 M	4.5%
	2.0 M	4.8%
	2.5 M	5.0%
	3.0 M	5.7%
	3.5 M	5.8%
	4 M	8.7%
	4.5 M	8.9%
	5 M	10.2%
	5.5 M	10.3%
	6 M	12.6%

3.3.3. Acid-Leaching Purification of Actual Fluoride-Containing Sludge

Based on the theoretical framework discussed earlier, two sets of acid leaching conditions were designed for the experiments, utilizing higher concentrations and smaller volumes of acid: one group utilized 2 M HCl with a liquid-to-solid ratio of 7.5 mL/g, while the other used 4 M HCl with a liquid-to-solid ratio of 3.75 mL/g. The conditions for alkaline leaching remained unchanged. Through this experimental design, a CaF_2 product with a purity of up to 76.1% was successfully obtained (Figure 6).

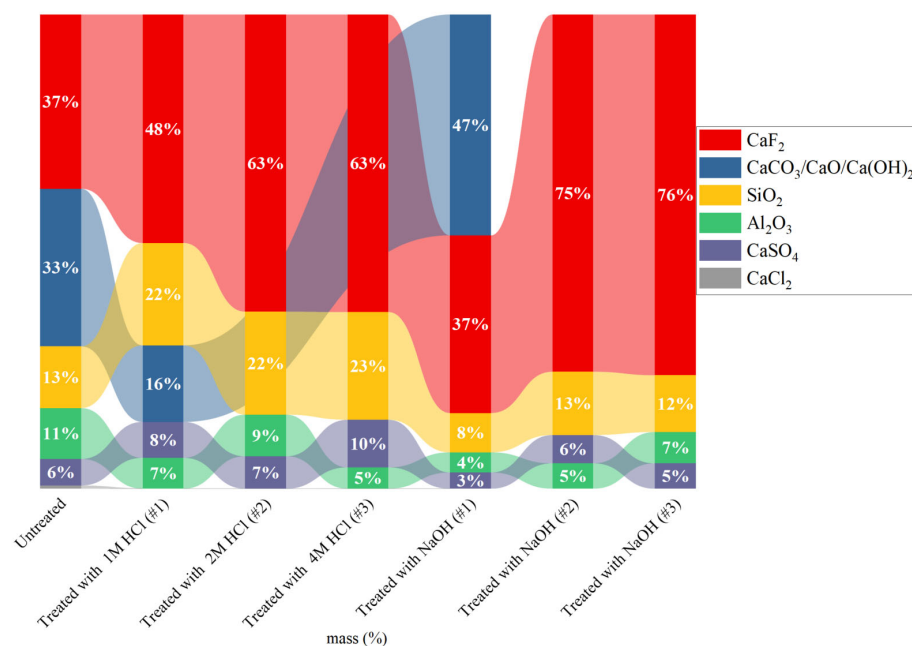


Figure 6. Percentage bar chart of the compound composition of the CaF₂ purified sample from actual fluoride-containing sludge. Note: CaCl₂ is detected only in the original sludge, with a proportion below 1% in both at% and wt%. Due to its low abundance, it is not distinctly visible in the figure, and its chemical formula is not labeled.

The process cleverly leveraged the co-ion effect generated by calcium salts. By increasing the acid concentration while reducing the volume of acid, the proportion of CaF₂ in the fluoride-containing sludge was significantly enhanced, and the impurities such as Al₂O₃ were more thoroughly removed. Specifically, as the acid leaching concentration increased, the proportion of CaF₂ exhibited a clear upward trend, from 48.2% at 1 M HCl to 52.8% at 2 M HCl, and further to 62.8% at 4 M HCl. Notably, under the 4 M HCl condition with a 3.75 mL/g liquid-to-solid ratio, the purity of CaF₂ was nearly 15% higher compared to the unoptimized conditions (1 M HCl and a 15 mL/g liquid-to-solid ratio). This strongly demonstrated the effectiveness of the optimization strategy.

Following the optimized acid-leaching step, the alkaline leaching process further increased the proportion of CaF₂. Both sets of optimized conditions achieved CaF₂ purity levels exceeding 75%. After optimizing the acid leaching conditions, the removal of calcium-based impurities was significantly enhanced, leading to a more efficient purification process. Although higher hydrochloric acid concentrations may increase waste acidity, this approach does not significantly raise costs and offers environmental benefits by reducing the volume of acid used and wastewater generated.

3.4. Microscopic Morphological Differences Before and After Treatment

The SEM observations of the raw sludge revealed spherical particle structures encased in the flocculent material on the sample surface. Upon further magnification and compositional analysis, these spherical particles were found to consist primarily of CaF₂ interspersed with CaCO₃, CaO, and other substances. As shown in Figure 7, the characterization of the raw sludge suggests that the formation of these components is closely linked to the coagulation–flocculation process.

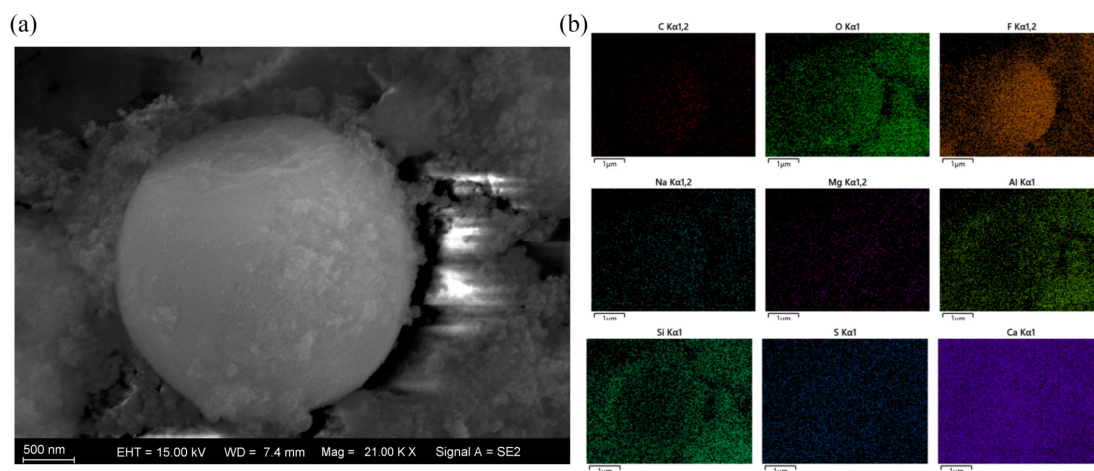


Figure 7. SEM image of spherical particles (a) and EDS element distribution map (b).

In fluoride-containing wastewater treatment, PAC works by neutralizing the charge, which disrupts the electrostatic repulsion between particles and promotes their aggregation. PAC adsorbs onto particle surfaces through a bridging mechanism and forms a structural core within the flocs. The outer layer of the floc incorporates sand particles trapped during the wastewater treatment, as well as CaF_2 generated by reactions with calcium salts. Additionally, the addition of $\text{Ca}(\text{OH})_2$ or CaO raises the pH of the system, promoting the precipitation of CaCO_3 and CaCl_2 .

In this complex physicochemical process, the enrichment of CaF_2 on the surface layer and the distribution of impurities together determine the final composition and phase characteristics of the sludge.

As shown in Figure 8, SEM-EDS point scan analysis was conducted on similar spherical particles. Figure 8a presents the SEM image with two marked points, 1 and 2, for analysis, while Figure 8b displays the corresponding elemental analysis. Similarly, in Figure 8c, another SEM image with three marked points (3, 4, and 5) was analyzed, with the elemental analysis shown in Figure 8d. The analysis revealed an interesting pattern: the F content was significantly higher near the outer layer of the spheres, while the C content was notably higher near the inner layers. Based on this observation, we hypothesize that this could be due to the gradual encapsulation of $\text{Ca}(\text{OH})_2$, CaCO_3 , and other substances by CaF_2 . This encapsulation process reflects both the physicochemical changes occurring in the sludge and the material migration patterns over time.

After the acid treatment of the sludge, the surface of the sample displayed a rough, pitted appearance, as shown in Figure 9a,b. These SEM images of the original sludge (before treatment) reveal a relatively smooth surface, indicating the initial state of the particles. However, after acid treatment, as seen in Figure 9c,d, the surface becomes significantly rougher, with numerous small pits formed due to the dissolution of substances such as CaCO_3 in the acidic environment. The acid treatment resulted in a clear increase in pore size, ranging from 40 nm to 100 nm, as quantitatively analyzed using the ImageJ software (version 1.54). These visible pits and the corresponding increase in pore size provide direct evidence of material dissolution and migration during the acid treatment process. Similarly, after alkali treatment, the SEM images in Figure 9e,f show further changes in the surface morphology, with the pores slightly enlarged compared to the acid-treated sludge, indicating additional material dissolution and the modification of the surface structure.

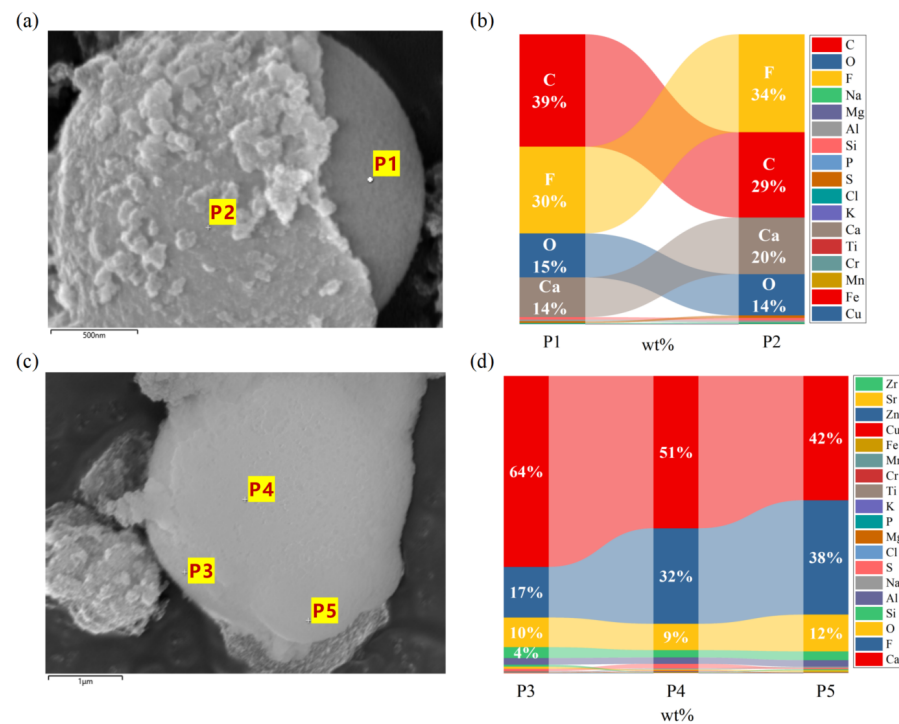


Figure 8. SEM-EDS point scanning results of the original sludge. (a) SEM image with points 1 and 2 marked for analysis and (b) elemental analysis of points 1 and 2; (c) SEM image with points 3, 4, and 5 marked for analysis and (d) elemental analysis of points 3, 4, and 5.

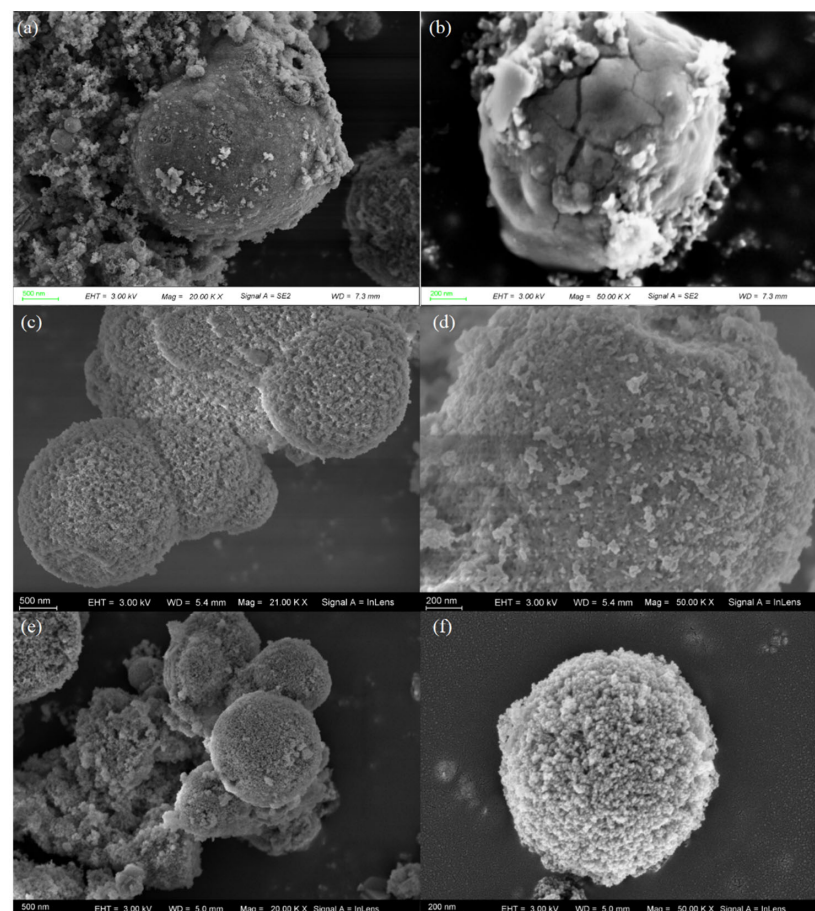


Figure 9. SEM analysis results: original sludge (a,b), after acid treatment (c,d), after alkali treatment (e,f).

4. Conclusions

This study systematically investigates the purification of CaF_2 from fluoride-containing sludge. Using a range of characterization techniques, including XRF, SEM-EDS, XRD, FT-IR, and laser particle size analysis, the composition of the fluoride-containing sludge was comprehensively analyzed. The results revealed that the sludge is primarily composed of elements such as O, Ca, and F, with smaller amounts of Si, Al, and trace heavy metals. The main phases identified were CaF_2 , CaCO_3 , Al_2O_3 , and $\text{Ca}_3\text{Al}_2\text{O}_6$, among others. For the CaF_2 purification process, the feasibility of an acid-leaching–alkali-leaching method was proposed and validated. A key phenomenon observed during the acid leaching stage, referred to as the “calcium ion co-existence effect”, indicated that the dissolution of other calcium salts in the system influences the dissolution equilibrium of CaF_2 , thereby reducing its loss. Building on this insight, an innovative strategy was developed that involved increasing the acid concentration while reducing the acid volume. This approach effectively utilized the co-ion effect of calcium salts, addressing the challenges of high CaF_2 loss and incomplete impurity removal typically associated with traditional acid-leaching processes. Experimental results demonstrated that under optimized acid-leaching conditions using 2 M HCl with a liquid-to-solid ratio of 7.5 mL/g or 4 M HCl with a liquid-to-solid ratio of 3.75 mL/g, the purity of CaF_2 significantly increased from 48.2% (achieved under 1 M HCl with a liquid-to-solid ratio of 15 mL/g) to 62.8%. Additionally, the removal of Al_2O_3 impurities was significantly improved, and the interference from calcium-based impurities during the alkali-leaching process was effectively eliminated. Consequently, the purity of CaF_2 consistently exceeded 75% under both optimized conditions. This study successfully achieved the efficient purification of CaF_2 from fluoride-containing sludge and offers a viable solution for the resource utilization of such sludge from both theoretical and practical perspectives. The findings hold promise for advancing fluoride-containing sludge treatment technology, providing substantial economic and environmental benefits to the environmental protection industry. However, challenges remain, particularly in scaling up the process and ensuring long-term stability under industrial conditions. Future research could focus on optimizing the process for large-scale applications, addressing issues such as energy consumption and waste management. Additionally, expanding the method’s applicability to other fluoride-containing industrial waste streams could further contribute to global resource recycling and environmental protection efforts. The potential to apply these purification strategies to related materials, such as calcium fluoride compounds in other industries, offers exciting prospects for further enhancing the efficiency and sustainability of the process.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr13020552/s1>, Table S1: Phase identification and internal standard quantification of fluorinated sludge; Figure S1: Fourier transform infrared spectroscopy of fluorinated sludge; Figure S2: Particle size analysis results of three parallel samples.

Author Contributions: Conceptualization, H.G.; methodology, H.G. and D.Z.; validation, D.Z.; formal analysis, H.G. and D.Z.; investigation, D.Z.; resources, H.G. and X.D.; data curation, H.G. and D.Z.; writing—original draft preparation, D.Z.; writing—review and editing, H.G.; visualization, D.Z.; supervision, X.D. and H.G.; project administration, X.D., X.C., X.W. and X.Q.; funding acquisition, H.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by China Three Gorges Corporation (No. 202403018).

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: Authors Xiang Chen, Xiankai Wang, and Xueyuan Qiao are employed by the China Three Gorges Corporation; the remaining 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. Furthermore, the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Abbreviations

The following abbreviations are used in this manuscript:

CaF ₂	Calcium fluoride
PAC	Polyaluminium chloride
PAM	Polyacrylamide
XRF	X-ray fluorescence spectrometer
SEM	Scanning electron microscope
EDS	Energy-dispersive X-ray spectrometer
XRD	X-ray diffractometer
FT-IR	Fourier transform infrared spectroscopy

References

1. IEA. Solar PV Global Supply Chains. Available online: <https://www.iea.org/reports/solar-pv-global-supply-chains> (accessed on 10 January 2025).
2. Liu, C.-C.; Liu, J.C. Coupled precipitation-ultrafiltration for treatment of high fluoride-content wastewater. *J. Taiwan Inst. Chem. Eng.* **2016**, *58*, 259–263. [CrossRef]
3. Wang, B.-y.; Chen, Z.-l.; Zhu, J.; Shen, J.-m.; Han, Y. Pilot-scale fluoride-containing wastewater treatment by the ballasted flocculation process. *Water Sci. Technol.* **2013**, *68*, 134–143. [CrossRef] [PubMed]
4. Tsai, S.-B.; Yu, J.; Ma, L.; Luo, F.; Zhou, J.; Chen, Q.; Xu, L. A study on solving the production process problems of the photovoltaic cell industry. *Renew. Sustain. Energy Rev.* **2018**, *82*, 3546–3553. [CrossRef]
5. Lacson, C.F.Z.; Lu, M.-C.; Huang, Y.-H. Fluoride-containing water: A global perspective and a pursuit to sustainable water defluoridation management -An overview. *J. Clean. Prod.* **2021**, *280*, 124236. [CrossRef]
6. Aldaco, R.; Garea, A.; Irabien, A. Calcium fluoride recovery from fluoride wastewater in a fluidized bed reactor. *Water Res.* **2007**, *41*, 810–818. [CrossRef]
7. Cao, X.; Peng, J.; Dong, W.; Wang, Y.; Di, Y. Theoretical study on the utilization of fluorine-containing wastewater in the aluminum industry: Crystallization characteristics and particle size control of cryolite prepared by carbonization. *J. Environ. Chem. Eng.* **2024**, *12*, 113572. [CrossRef]
8. Zhang, H.; Liang, J.; Li, Z.; Xiao, F.; Wu, Y.; Zhang, C. Preparation of Forward osmosis composite membrane with Chitosan/Tannic acid co-deposition interlayer and its fluoride removal performance. *Sep. Purif. Technol.* **2024**, *330*, 125300. [CrossRef]
9. Huang, H.; Liu, C.; Sun, Z. In-situ pyrolysis based on alkaline medium removes fluorine-containing contaminants from spent lithium-ion batteries. *J. Hazard. Mater.* **2023**, *457*, 131782. [CrossRef]
10. Zhou, G.; Meng, Q.; Li, S.; Song, R.; Wang, Q.; Xu, Z.; Xing, Z. Novel magnetic metal-organic framework derivative: An adsorbent for efficient removal of fluorine-containing wastewater in mines. *J. Environ. Chem. Eng.* **2022**, *10*, 108421. [CrossRef]
11. Fawell, J.; Bailey, K.; Chilton, J.; Dahi, E.; Fewtrell, L.; Magara, Y. *Fluoride in Drinking-Water*; IWA Publishing: London, UK, 2013. [CrossRef]
12. Saha, S. Treatment of aqueous effluent for fluoride removal. *Water Res.* **1993**, *27*, 1347–1350. [CrossRef]
13. Gao, X.; Wu, Q.; Zhou, B.; Yuan, Z.; Gai, N.; Yuan, R.; Chen, Z.; Luo, S.; Chen, H. Research status of typical wastewater treatment technology for photovoltaic cell production process. *Chem. Eng. J.* **2024**, *499*, 156523. [CrossRef]
14. Ayoob, S.; Gupta, A.K.; Bhakat, P.B.; Bhat, V.T. Investigations on the kinetics and mechanisms of sorptive removal of fluoride from water using alumina cement granules. *Chem. Eng. J.* **2008**, *140*, 6–14. [CrossRef]
15. You, S.; Cao, S.; Mo, C.; Zhang, Y.; Lu, J. Synthesis of high purity calcium fluoride from fluoride-containing wastewater. *Chem. Eng. J.* **2023**, *453*, 139733. [CrossRef]
16. Zhang, Y.; Song, S. Beneficiation of fluorite by flotation in a new chemical scheme. *Miner. Eng.* **2003**, *16*, 597–600. [CrossRef]
17. Dahhou, M.; El Hamidi, A.; El Moussaoui, M.; Arshad, M.A. Synthesis and characterization of belite clinker by sustainable utilization of alumina sludge and natural fluorite (CaF₂). *Materialia* **2021**, *20*, 101204. [CrossRef]
18. Nicoara, I.; Stef, M.; Vizman, D.; Negut, C.D. Gamma-rays induced color centers in Pb²⁺ doped CaF₂ crystals. *Radiat. Phys. Chem.* **2018**, *153*, 70–78. [CrossRef]

19. U.S. Geological Survey. *Mineral Commodity Summaries 2025*; U.S. Geological Survey: Reston, VA, USA, 2025; p. 212.
20. Gao, Z.; Wang, C.; Sun, W.; Gao, Y.; Kowalczyk, P.B. Froth flotation of fluorite: A review. *Adv. Colloid Interface Sci.* **2021**, *290*, 102382. [[CrossRef](#)]
21. Huang, J.; Zhang, Q.; Wang, S.; Wang, C.; Chen, M.; Li, H. Efficient selective flotation separation of fluorite from calcite using ferrous and ferric species as combined depressant. *Miner. Eng.* **2024**, *205*, 108451. [[CrossRef](#)]
22. Gómez-Hortigüela, L.; Pérez-Pariente, J.; García, R.; Chebude, Y.; Díaz, I. Natural zeolites from Ethiopia for elimination of fluoride from drinking water. *Sep. Purif. Technol.* **2013**, *120*, 224–229. [[CrossRef](#)]
23. Chen, J.; Wu, H.; Qian, H.; Gao, Y. Assessing Nitrate and Fluoride Contaminants in Drinking Water and Their Health Risk of Rural Residents Living in a Semiarid Region of Northwest China. *Expo. Health* **2017**, *9*, 183–195. [[CrossRef](#)]
24. Liu, J.; Peng, Y.; Li, C.; Gao, Z.; Chen, S. A characterization of groundwater fluoride, influencing factors and risk to human health in the southwest plain of Shandong Province, North China. *Ecotoxicol. Environ. Saf.* **2021**, *207*, 111512. [[CrossRef](#)] [[PubMed](#)]
25. Tiwari, K.K.; Raghav, R.; Pandey, R. Recent advancements in fluoride impact on human health: A critical review. *Environ. Sustain. Indic.* **2023**, *20*, 100305. [[CrossRef](#)]
26. WHO. WHO Guidelines Approved by the Guidelines Review Committee. In *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum*; World Health Organization: Geneva, Switzerland, 2017.
27. Aldaco, R.; Irabien, A.; Luis, P. Fluidized bed reactor for fluoride removal. *Chem. Eng. J.* **2005**, *107*, 113–117. [[CrossRef](#)]
28. Zhu, P.; Li, Y.; Xia, B.; Bilal, Xu, Y.; Zhang, Q.; Liu, Q. Purification mechanism of fluoride-containing sludge from different sources by hydrometallurgy. *J. Environ. Chem. Eng.* **2023**, *11*, 110304. [[CrossRef](#)]
29. Huang, C.J.; Liu, J.C. Precipitate flotation of fluoride-containing wastewater from a semiconductor manufacturer. *Water Res.* **1999**, *33*, 3403–3412. [[CrossRef](#)]
30. Zhu, H.; Qin, W.; Chen, C.; Chai, L.; Jiao, F.; Jia, W. Flotation separation of fluorite from calcite using polyaspartate as depressant. *Miner. Eng.* **2018**, *120*, 80–86. [[CrossRef](#)]
31. Chingo Aimacaña, C.M.; Pila, K.O.; Quinchiguango Perez, D.A.; Debut, A.; Attia, M.F.; Santos-Oliveira, R.; Whitehead, D.C.; Reinoso, C.; Alexis, F.; Dahoumane, S.A. Bimodal Ultrasound and X-ray Bioimaging Properties of Particulate Calcium Fluoride Biomaterial. *Molecules* **2021**, *26*, 5447. [[CrossRef](#)]
32. Sar, S.; Samuelsson, C.; Engström, F.; Ökvist, L.S. Experimental Study on the Dissolution Behavior of Calcium Fluoride. *Metals* **2020**, *10*, 988. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.