



Recovery of fluorine from bastnasite as synthetic cryolite by-product

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ABSTRACT

This paper investigates the development of a new environment friendly approach for treatment of bastnasite. A new process was developed to recover fluorine from bastnasite as synthetic cryolite by-product. The conditions affecting the fluorine removal and recovery in the process, including contact time, acidity, Al^{3+} concentration, Al/F molar ratio and different kinds of aluminum salts being used, were investigated. The results indicate that high acidity and large Al/F molar ratio were beneficial to fluoride removal, and that the reaction reached equilibrium after 15 min. The effect of the initial Al^{3+} concentration at a certain total Al^{3+} amount was slight. Aluminum nitrate was more efficient than aluminum sulfate for the removal of fluoride. Optimum operation parameters for synthesizing cryolite have been obtained and proposed for industrial applications.

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1. Introduction

There are about 200 rare earths (RE) minerals worldwide, including halides, carbonates, oxides, phosphates, silicates, etc. Among them only a few minerals, such as bastnasite $((\text{Ce},\text{La})(\text{CO}_3)\text{F})$, monazite $((\text{Ce},\text{La})\text{PO}_4)$, xenotime (YPO_4) , and RE-bearing clay, can be economically used for RE production [1]. Bastnasite containing about 50 wt% cerium, 0.2–0.3 wt% thorium and 8–10 wt% fluorine is one of main sources of RE in China [2]. Light RE, such as lanthanum, cerium, praseodymium, neodymium and small amounts of samarium, europium and gadolinium, are the main components of minerals, while heavy RE are in very small amount. Exploitation of bastnasite began in the early 1980's in China. Process involving oxidation roasting by passing air, leaching by sulfuric acid, separating and recovering by double salt precipitation had been employed before the end of the last century. At present, the process involving oxidation roasting, hydrochloric acid leaching and solvent extraction is widely conducted in industry [3]. In this process RE in concentrates are converted into RE oxides by oxidation roasting. Hydrochloric acid is used to dissolve the oxides in the subsequent leaching step (Fig. 1). After elimination of solid residues by filtration, the rare earths pregnant leach solutions are subjected to solvent extraction to recover pure RE products. As thorium remains in the solid residues, there are no radiation concerns for the RE productions during this process.

During the common process of bastnasite treatment, however, some environmental issues still remains. One is the discharge of fluorine via waste liquid or waste solid. Fluorine element accounts for 8–10 wt% in bastnasite concentrate. About 22,500 tons [4] of bastnasite concentrate were treated annually in recent years. Therefore, about 2000 tons of fluorine would be produced and discharged to the environment. The discharge of such wastes leads to the fluoride contamination of surface and ground water. Fluoride contamination in groundwater has been recognized as one of the serious problems worldwide. Therefore, fluoride is classified as one of the contaminants of water for human consumption by the World Health Organization (WHO), which causes large-scale health problems [5]. Due to the fluoride adverse effects in human health and also in other living organisms its release to the environment is focusing increasing attention in the last decades [6]. In order to treat bastnasite in a more environment-friendly way, Li et al. [2,7] invented a new method to recover RE and fluorine from roasted bastnasite sulfuric leaching liquor with Cyanex 923. However, in the process, Cyanex 923 is more expensive than other common extractants, such as di-2-ethylhexyl phosphoric acid (D2EHPA) and 2-ethylhexylphosphonic mono-2-ethylhexyl ester (HEHEHP), resulting in the high cost for commercialization. Furthermore, the solid CeF_3 formed in the mixer-settler equipment during the stripping step of the process, thus likely resulting in organic lose and difficult operation. These are two factors leading to the high operation cost. Keeping the view of toxic effects of fluoride on human health, there is an urgent need to find out an effective and robust technology for the removal and recovery of fluoride from bastnasite. Recently, more attention has been paid to develop a process of bastnasite treatment in a beneficial

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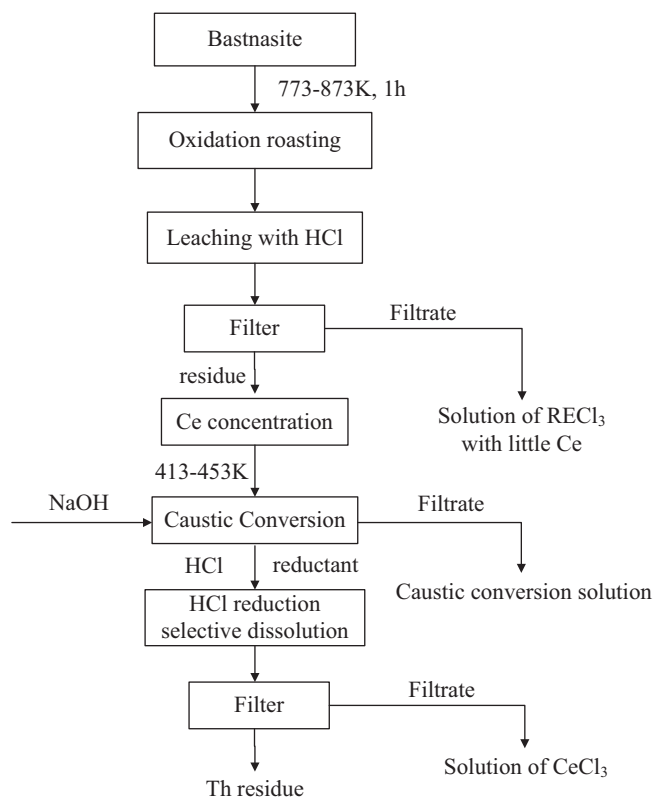


Fig. 1. Schematic flowsheet of bastnasite treatment by oxidization roasting, hydrochloric acid leaching and caustic conversion.

way economically and environmentally, especially in the process of recovering fluorine from bastnasite as valuable resources [3,8].

Previous investigations [9,10] show that F^- coordinated with $Ce(IV)$ to form CeF_2^- complex, which can be extracted into the organic phase easily with D2EHPA by the following reaction: $Ce^{4+} + 2F^- + 2(HA)_2 = CeF_2 \cdot 2(HA)_2 + 2H^+$. Similar results were also reported in other investigations [2,7,11–13]. It is known that Al^{3+} can form complex with F^- strongly [14]. Due to its high electronegativity and small ionic size, the fluoride ion is classified as a hard base, which has a strong affinity towards metal ions including $Al(III)$, $Fe(III)$, $La(III)$. Al^{3+} ions have good affinity with fluoride anions, because of the hard–hard combination, in agreement with the soft–hard acid base (SHAB) concept. Therefore, $Al(III)$ is frequently used in defluorination. [15–18] Plankey [19] conducted a kinetics study on formation of AlF_2^{2+} in pH range of 2.9–4.9 (which is normal in natural water resources). The thermodynamic calculation shows that fluoride complexes are generally the dominant species of aluminum in the studied systems.

In this study, a novel process was developed to recover fluorine from bastnasite in the form of cryolite. Solution of aluminum salt was used as the coordination reagent of fluoride to scrub the fluoride from the loaded organic phase into the aqueous phase and then separate it from cerium. The resultant scrubbing solution containing aluminum fluoride complexes was subjected to a subsequent step to produce cryolite. Cryolite (Na_3AlF_6) is an important industrial chemical which is widely applied in industry, especially in the Hall–Héroult process (a process for production of aluminum) [20,21]. Recovery of the fluoride in the form of synthetic cryolite from the bastnasite could increase the economical value of the bastnasite and also mitigate the environmental concerns via reducing the discharge of waste containing fluoride.

2. Experimental

2.1. Reagents and solution preparation

The 2-ethylhexyl phosphoric acid mono 2-ethylhexyl ester (HEHEHP), without further purification, was mixed with kerosene to the required concentration (1.0 mol L^{-1}). Kerosene was sulfonated before use. Sulfuric acid leaching solution of bastnasite contains $0.124 \text{ mol L}^{-1} Ce^{4+}$, $0.225 \text{ mol L}^{-1} F^-$ (4.24 g/L) and $0.47 \text{ mol L}^{-1} H^+$. The F^- and Ce^{4+} loaded organic solution was obtained by mixing the 1.0 mol L^{-1} HEHEHP and the sulfuric acid leaching solution of bastnasite at the phase ratio (O/A) of 2 to reach equilibrium, and the extraction rate of $Ce(IV)$ and F is over 99% and 95%, respectively. The caustic conversion solution containing 5–6 g/LF, $0.3 \text{ mol L}^{-1} OH^-$ and $0.6 \text{ mol L}^{-1} Na^+$ was obtained from bastnasite treatment by oxidization roasting, hydrochloric acid leaching and caustic conversion (Fig. 1). Unless indicated otherwise, all reagents were reagent grade.

2.2. Procedures for fluoride removal

Aluminum salt was used as coordination reagent of fluoride to scrub fluoride from the loaded organic phase into the aqueous phase and then separate it from cerium. At a room temperature ($298 \pm 1 \text{ K}$) and Al/F molar ratio of 2 (except for the tests of Al/F ratio effect), a volume of 15 mL aluminum salt solution and 15 mL fluoride loaded organic solution were mixed in a separation funnel for 15 mins by means of a mechanical shaker (except for the tests of contact time effect). After phase separation the aqueous solution was analyzed. Cerium concentration was determined by titration with standard $(NH_4)_2Fe(SO_4)_2$ using o-phenanthroline as indicator, and fluoride concentration was determined by fluoride-ion selective electrode [22]. The fluoride electrode was freshly calibrated using standard fluoride solution. The hydrogen ion concentration of the stock solution was determined by titration, using standard NaOH containing Ca–EDTA as the masking reagent (fixed $pH=4.5$) [23]. Reproducibility of the measurements was determined in triplicates and the average values are reported. Relative standard deviations were found to be within $\pm 3.0\%$.

2.3. Procedures for cryolite precipitation

The resultant scrubbing solution containing aluminum fluoride complexes was subjected to a subsequent step to produce cryolite. The cryolite particles were obtained by using caustic conversion solution to adjust the F/Al molar ratio and Na/Al molar ratio, aiming at neutralizing the aluminum fluoride complexes solution. The morphology of the cryolite particles (being dried at 383 K for 3 h) was analyzed by means of Scanning Electron Micrograph (SEM). The chemical compositions of the cryolite products were examined by X-Ray Fluorescence Spectroscopy (XRF), and the crystal phases of the cryolite particles were identified by X-Ray Diffraction (XRD).

3. Results and discussions

3.1. Defluorination from the loaded organic phase

3.1.1. Effect of contact time

Defluorination experiments were performed in order to determine the rate of fluoride removal from the loaded organic phase. Fig. 2 illustrates the fluoride removal at an O/A phase ratio of 1 and an Al/F molar ratio of 3. For all the substrates, fluoride removal was fast during the first 10 min and pseudo-equilibrium was reached at 15 min. At this time the maximum efficiency of fluoride removal is about 90%. Therefore, a quick action of aluminum ions could be expected when using it as an additive to removal fluoride from the

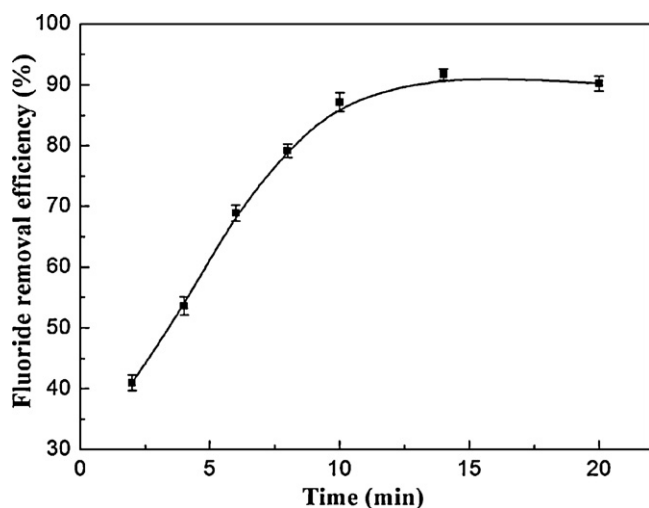


Fig. 2. Effect of contact time on the fluoride removal efficiency from fluoride loaded organic phase.

loaded organic phase. Kinetic curves also shows that after achieving the equilibrium period, much longer times of interaction did not give rise to release of fluoride retained amounts in the loaded organic phase, what proves the stability of the aluminum fluoride complexes $[AlF_n]^{(3-n)}$ in the solution under the pH conditions. Therefore, 15 min duration was considered as the optimum contact time for further defluoridation studies.

3.1.2. Effect of initial acidity

The tests of defluoridation from the loaded organic phase were carried out using the scrubbing solutions initially containing 0.01–1.0 mol L⁻¹ sulfuric acid. The efficiency of fluoride removal and cerium loss rate are shown in Table 1. From Table 1, it can be seen that the fluoride removal efficiency maintains at 85% when the initial acidity $[H^+]$ varies from 0.02 mol L⁻¹ to 0.5 mol L⁻¹, and then increases further with increasing initial acidity, reaching 90.9% at a $[H^+]$ concentration of 2.0 mol L⁻¹. This is probably attributed to the good stability of aluminum fluoride complexes $[AlF_n]^{(3-n)}$ with increased acidity. These results are consistent with those reported by Rietjens [24] and Townsend [25]. However, the cerium loss rate increases with increased initial acidity and reaches 3.6% when $[H^+]$ was raised to 2.0 mol L⁻¹. This observation can be attributed to the ion exchange reaction mechanism of the Ce(IV) extraction [9,10]. In addition, the acid consumption increases with the increased initial acidity. Therefore, a concentration of 0.2 mol L⁻¹ $[H^+]$ is considered to be the optimum acidity.

3.1.3. Effect of Al/F molar ratio

In order to evaluate the effect of Al/F molar ratio on the defluoridation of fluoride loaded organic phases, a series of experiments were carried out at an Al/F molar ratio of 1:6–2:1. The results in Fig. 3 indicates that the increase of Al/F molar ratio leads to the

Table 1

The fluoride removal efficiencies from the fluoride loaded organic phase under various initial acidities. ($T=298\text{ K}$, $[HEHEHP]=1.0\text{ mol L}^{-1}$, $[F^-]_{org}=0.11\text{ mol L}^{-1}$, $O/A=1$, mixing time = 15 min and Al/F (molar ratio) = 2).

$[H^+]$ (mol L ⁻¹)	Fluoride removal efficiency (%)	Cerium loss rate (%)
0.02	85.54	–
0.20	85.63	–
0.50	85.81	0.03
1.00	86.37	0.23
2.00	90.87	3.57

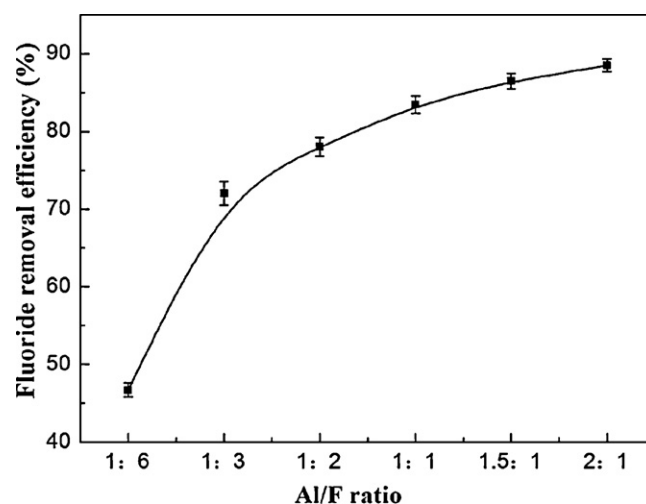


Fig. 3. Effect of Al/F ratio on the fluoride removal efficiency from fluoride loaded organic phase.

significant increase in fluoride removal efficiency. It reaches 46.7% at an Al/F molar ratio of 1:6, then goes up to 72.0% at 1:3, and shows a continuing increase with the Al/F molar ratio increasing further. The aluminum fluoride complexes exist as $[AlF_n]^{(3-n)}$ in acidic solution [14,19]. When the Al/F molar ratio is larger than 1:3, the fluoride removal efficiency tends to increase slowly due to the subsequent reactions involving $2AlF_3 + Al^{3+} \rightarrow 3AlF_2^+$ and $AlF_2^+ + Al^{3+} \rightarrow 2AlF^{2+}$.

3.1.4. Effect of Al^{3+} concentration

Tests on the effect of $[Al^{3+}]$ were carried out with the concentration of Al^{3+} from 0.12 mol L⁻¹ to 0.24 mol L⁻¹, keeping a pH of 2–3 and a total Al^{3+} ions amount of 3.3 mmol in solution. The obtained results in Fig. 4 shows that the initial $[Al^{3+}]$ has slight effect on the fluoride removal efficiency. However, higher $[Al^{3+}]$ leads to a good comprehensive utilization in downstream process. The preferred $[Al^{3+}]$ is suggested to be about 0.24 mol L⁻¹, at which a fluoride removal efficiency of 87.0% could be achieved.

3.1.5. Effect of different kinds of aluminum salts

In general, aluminum sulfate, aluminum nitrate and aluminum chloride are common salts available commercially. Aluminum chloride was not considered for the defluoridation use in the developed

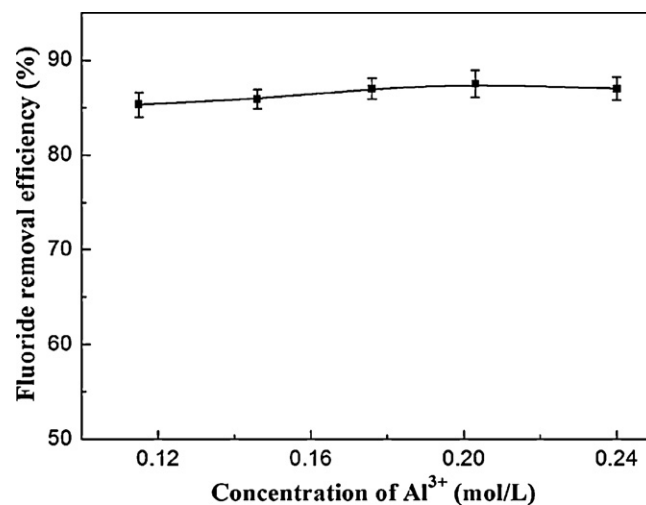


Fig. 4. Effect of Al^{3+} concentration on the fluoride removal efficiency from fluoride loaded organic phase.

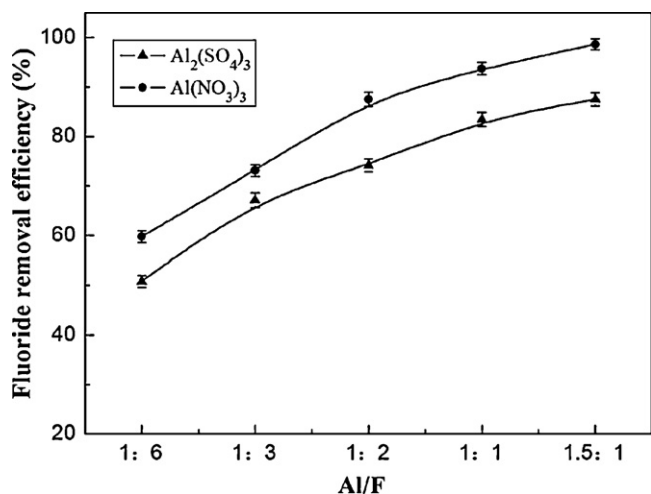


Fig. 5. Effect of different aluminum salts on the fluoride removal efficiency from fluoride loaded organic phase under various Al/F molar ratios.

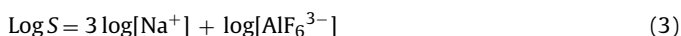
process because chloride ion can reduce Ce(IV) to Ce(III) in the organic phase, resulting in the loss of cerium by forming CeF₃ particles which went into the aqueous phase. Thus, the effect of aluminum sulfate and aluminum nitrate on the fluoride removal efficiency was studied with a fluoride concentration of 0.11 mol L⁻¹ in loaded organic phase. The Al/F molar ratio varied from 1:6 to 2:1 when the O/A ratio was maintained at 1. As shown in Fig. 5, aluminum nitrate performs better than aluminum sulfate. At an Al/F molar ratio of 1.5, a fluoride removal efficiency of 95% was achieved when aluminum nitrate was adopted, while only 85% being obtained when aluminum sulfate was used. This is probably due to the fact that nitrate ion is low-affinity ligand. Thus, its presence in solution would have no effect on fluoride removal since fluoride removal through formation of strong bonds with aluminum at the inner Helmholtz plane, i.e. inner-sphere complexation [26]. At 293 K, the log of equilibrium constants of [AlF_n]⁽³⁻ⁿ⁾ K₁–K₄ is 6.69, 5.35, 3.68 and 2.75, respectively, which corrected to zero ionic strength by the application of some theoretical or empirical formula. While at 293 K, in the 0.2 mol L⁻¹ KNO₃ solution medium, the log of equilibrium constants of [AlF_n]⁽³⁻ⁿ⁾ K₁–K₄ is 6.32, 5.16, 3.85 and 3.30, respectively [27]. In the present fluoride removal system, the sulfate ion reduces the fluoride removal efficiency slightly. This behavior could be explained taking into account that sulfate ion may have competed fluoride ion for the aluminum complexes since sulfate ion is partially inner-sphere complex forming species [26]. At 293 K, the log of equilibrium constants of aluminum sulfate K₁, K₂ is 3.01 and 1.89, respectively [27]. Similar observations were reported for fluoride removal studies by aluminum-based materials [16,26,28–31].

3.2. Precipitation of cryolite

3.2.1. Principles of cryolite formation

The conditions applicable for precipitation of fluoride chemicals from leaching/synthetic solutions can be understood by the theoretical estimation of the solubility of the fluorides at any pH or fluoride/metal ion concentration.

The dissociation of Na₃AlF₆ can be represented as:



Where *S* is the solubility products of Na₃AlF₆ (4×10^{-10}) [20].

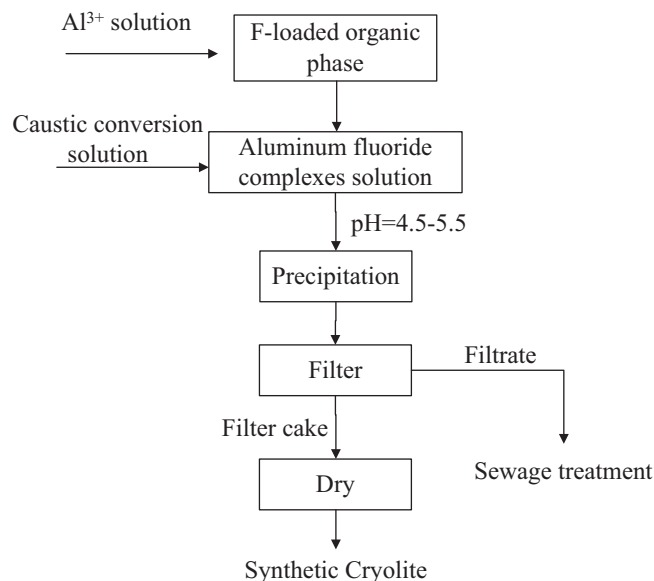


Fig. 6. Schematic flowsheet of the formation of synthetic cryolite.

3.2.2. Procedures for the cryolite formation

A solution containing 0.6 mol L⁻¹ H⁺, 5–6 g/L F⁻, 20 g/L Al³⁺ (calculated as Al₂O₃), and small amounts of Fe³⁺, Ce³⁺, which were generated at the fluoride removal step as mentioned above, was used to investigate the formation of cryolite. Previous investigation work [8] shows that at maximum precipitation efficiency more than 95% Na₃AlF₆ was obtained after the aluminum fluoride complexes solution was neutralized to pH 5.0 at 368 K by 1 mol L⁻¹ NaOH. These conditions were employed to precipitate Na₃AlF₆ to recover fluorine and aluminum. The procedure is shown in Fig. 6.

Pilot tests for fluorine recovery from bastnasite as cryolite were carried out based on the flow sheet in Fig. 6. Results were obtained and shown in Table 2. Recovery efficiencies of the fluorine and aluminum reached to about 97% and 99% for each batch test, respectively. This indicates a very good repeatability of the operation conditions. When the pH of the supernatant liquor was controlled at 5.0, [F⁻] remaining in the liquor is in the range of 70–170 mg/L, and then it could be reduced to less than 10 mg/L via lime and/or flocculant to be removed further, thus, meeting environmental discharge requirement. Treatment of wastewater containing fluoride ions requires a suitable and effective method. The precipitation and

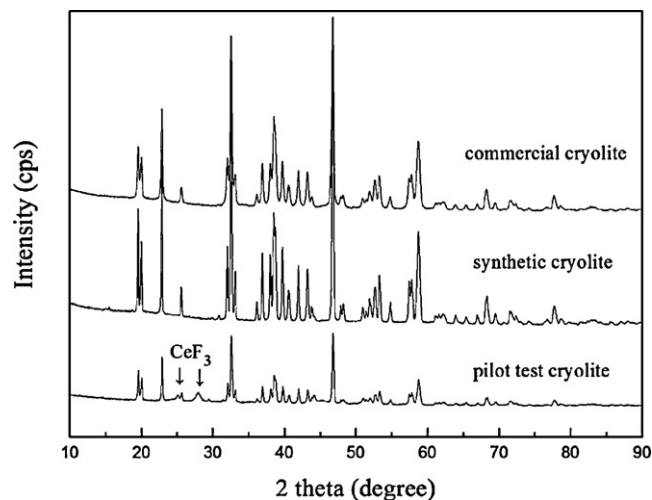


Fig. 7. The XRD patterns of cryolite.

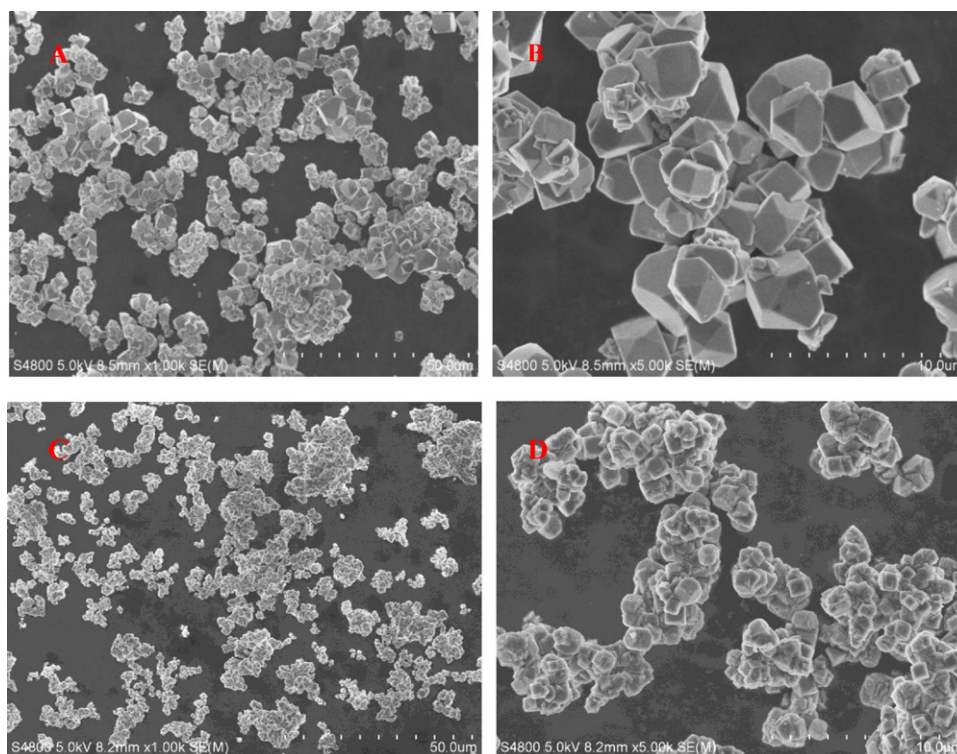


Fig. 8. SEM photograph of the cryolite precipitated from synthetic solution and the pilot test.

coagulation processes were widely used. However, the precipitation method leads to an increase of total dissolved solids in treated water, resulting in a supplementary difficulty in eliminating residual chemicals in excess. In this process, fluorine in the bastnasite was recovered effectively in a valuable form of Na_3AlF_6 (synthetic cryolite), to achieve a comprehensive utilization of bastnasite. As a result, it increased the economical benefits. And additionally, it also reduced the discharge of fluoride contained waste. Furthermore, the technique is relatively low in cost, robust, environmentally benign and simple.

(1) Crystal phases

The crystal phases of the precipitates were identified by XRD analysis (Fig. 7), which shows that the phases in the precipitate obtained from a synthetic solution under optimum conditions match very well with the phases of the sample

achieved commercially. It can be seen that some crystal phases are assigned to the CeF_3 contaminants, which appeared in the cryolite obtained from the pilot solutions. It is probably caused by the reduction of Ce(IV) to Ce(III) due to the unsaturated hydrocarbon in the diluents, thus forming of CeF_3 precipitation. Therefore, sulfonation of kerosene to remove the unsaturated hydrocarbons is necessary to avoid the Ce(IV) reduction [32].

(2) Particle morphology

The SEM images of the cryolite formed from synthetic solution and from the pilot test are shown in Fig. 8. The cryolite obtained from synthetic solution in optimum conditions was found to have a rectangular shape ($2\text{--}5\ \mu\text{m}$ size) with some agglomeration, while the cryolite derived from pilot test had a smaller size ($1\text{--}2\ \mu\text{m}$ size). This demonstrates a good repeatability of the operation conditions and a good filter performance of the cryolite.

Table 2
Recovery efficiency of fluorine and aluminum in pilot tests by forming cryolite precipitation.

Pilot test no.	11–12	11–14	11–17	11–18	11–21
$[\text{F}^-]$ of aluminum fluoride complexes solution (g/L)	4.92	5.60	5.60	5.60	5.11
Volume of aluminum fluoride complexes solution (m^3)	0.60	0.72	0.60	0.60	0.48
$[\text{F}^-]$ of caustic conversion solution (g/L)	5.61	6.43	6.60	6.87	5.12
Volume of caustic conversion solution (m^3)	4.05	4.63	3.40	3.63	3.89
$[\text{F}^-]$ of supernatant liquor (mg/L)	150.4	169.3	95.5	148.9	75.9
Volume of supernatant liquor (m^3)	4.60	7.26	5.8	5.05	5.05
Recovery efficiency of F (%)	97.3	96.4	97.9	97.3	98.3
$[\text{Al}^{3+}]$ of Aluminum fluoride complexes solution (g/L)	19.86	20.90	20.90	20.90	20.43
$[\text{Al}^{3+}]$ of supernatant liquor (mg/L)	26.1	1.2	70.0	3.0	20.2
Recovery efficiency of Aluminum (%)	99.0	99.9	96.8	99.9	99.0
$[\text{F}^-]$ of supernatant liquor after treatment (mg/L)	7.5	8.3	8.0	8.6	8.5
pH of supernatant liquor	5.0	5.1	4.8	5.0	4.9
Mass of synthetic cryolite (Kg)	46.8	61.9	44.7	51.8	39.0
Mass balance (%)	101.7	103.2	96.1	102.1	96.3

Table 3
Chemical analysis and physical properties of synthetic cryolite and Chinese National Standard of synthetic cryolite. (GB/T4291-2007.)

Grade/Pilot test no.	Chemical analysis (Mass fraction) (%)											Physical properties (%)	
	F	Al	Na	SiO ₂	Fe ₂ O ₃	SO ₄ ²⁻	CaO	P ₂ O ₅	La ₂ O ₃	CeO ₂	Hygroscopic water		Burning decrement (wt%)
	No less than			No more than									
CH-0	52	12	33	0.25	0.05	0.6	0.15	0.02	–	–	0.20	2.0	
CH-1	52	12	33	0.36	0.08	1.0	0.20	0.03	–	–	0.40	2.5	
CM-0	53	13	32	0.25	0.05	0.6	0.20	0.02	–	–	0.20	2.0	
CM-1	53	13	32	0.36	0.08	1.0	0.6	0.03	–	–	0.40	2.5	
11–12	52.23	12.55	30.35	0.31	0.08	0.96	0.09	0.03	0.08	0.92	–	2.40	
11–18	53.03	13.07	29.13	0.22	0.07	0.86	0.08	0.03	0.06	1.01	–	2.12	

(3) Chemical compositions of the cryolite products

By means of the analysis of the XRF, the chemical compositions of the synthesized cryolite are shown in Table 3. Fluorine, aluminum and sodium are the major components of the cryolites, which accounts for more than 52 wt%, 12 wt% and less than 33 wt%, respectively. In addition, the amounts of the burning decrement of the synthetic cryolites are all below 2.5 wt%, and the molecule ratio of synthetic cryolites (calculated as the mole ratio of NaF/AlF₃) varies from 2.6 to 2.8, which demonstrates that the cryolites belong to the common composition of the synthetic cryolite. In comparison with the corresponding data from Chinese National Standard of synthetic cryolite CH-1 (GB/T4291-2007, Table 3), the above results on chemical analysis match very well. However, it should be noted in mind that during the production of aluminum, the excess of AlF₃ in Na₃AlF₆/AlF₃ mixtures can not only be allowed but also be desired for the further processing [33]. Thus, synthetic cryolite of lower molecule ratio of NaF/AlF₃ is desired. Furthermore, the RE contaminant is around 1.0 wt%, which is beneficial to the aluminum electrolysis.

4. Conclusions

A defluorination process on Ce and F co-loaded organic phase containing HEHEHP as the extractant was studied. This process is a part of newly developed process for the bastnasite treatment by General Research Institute for Nonferrous Metals of China. With aluminum ion being used as fluoride complex reagent, fluoride could be removed and transferred into the aqueous phase from the loaded organic solution effectively, and the good separation of fluorine from cerium could be achieved in spite of its residues remaining in the organic phase. Higher initial acidity and larger Al/F molar ratio are favorable to fluoride removal, and the reaction reaches the equilibrium after a period of 15 min. At a certain total aluminum amount, the effect of initial Al³⁺ concentration on the defluorination process was slight. Aluminum nitrate is more effective for fluoride removal than aluminum sulfate. The recovery of fluorine and aluminum from aluminum fluoride complexes solutions was studied via the formation of synthetic cryolite particles. Optimum conditions have been obtained for practical applications, and a new environment friendly method for the bastnasite treatment was developed, which involves the recovery of fluorine as a synthetic cryolite. With fluorine recovery from the bastnasite in the form of synthetic cryolite, its economical values could be increased significantly and environmental concerns are also reduced to some extent by reducing the poisonous waste discharge.

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