Recovery of fluorine utilizing complex properties of cerium(IV) to obtain high purity CeF$_3$ by solvent extraction

Kai Li[a,b], Ji Chen[a,*], Dan Zou[a]

[a] *State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, PR China*
[b] *University of Science and Technology of China, Hefei, Anhui 230026, China*

ABSTRACT

Utilizing complex properties of cerium(IV) with fluorine(I), this paper investigated the recovery of fluorine from nitrate solutions in the form of CeF$_3$ by solvent extraction. The extraction mechanism was studied firstly, and then CeF$_3$ was obtained from the extracted organic phase by reductive stripping. The effects of the main parameters such as HNO$_3$ concentration, extractant concentration, F(I) concentration, salting-out agent concentration and the temperature were examined and discussed. Showing that HNO$_3$ concentration, salting-out agent concentration and the temperature did not affect the extraction of Ce(IV). The presence of F(I) can decrease the extraction of Ce(IV). The extraction of HNO$_3$, Ce(IV) and Ce(IV)-F have been studied respectively, and the extracted complexes are considered to be HNO$_3$·Cyanex923, Ce(NO$_3$)$_4$·2Cyanex923 and Ce(HF)(NO$_3$)$_4$·Cyanex923 individually. The extraction mechanisms were concluded according to slope analysis, and the loading capacities of Ce(IV) had been obtained. The Infrared Spectra of extracted complexes was determined, showing that the NO$_3^-$ ion is a bidentate ligand. High purity CeF$_3$ nanoparticle was obtained and the size distribution, SEM and TEM images of the nanoparticle were given, CeF$_3$ nanoparticle was acquired also in H$_2$SO$_4$ system and the difference between the two CeF$_3$ were compared.

1. Introduction

Bayan Obo ores is the largest light rare earth (RE) sources in the world, mainly composed of bastnaesite (REFCO$_3$) and monazite (REPO$_4$) [1]. There are 7–8% F and 4–6% P in Bayan Obo mixed RE concentrate. The classical process of decomposing mixed RE concentrate by roasting with concentrated sulfuric acid at low temperature cannot recover F and P, which could cause environmental pollution and waste of resources [2]. Fluoride was considered a hazardous element which can cause serious health problems [3]. Due to the harmful effects in human health, the recovery of fluoride has attracted more and more attention in the last decades [4]. So a green and clean process to treat Bayan Obo mixed RE concentrate should be explored.

Our group proposed a process for Bayan Obo mixed RE concentrate by utilizing the property of valence change of Cerium. When Ce(III) was oxidized to Ce(IV), F(I) can be easily recovered from leaching liquor by solvent extraction in virtue of the complex properties of Ce(IV) with F(I) [5,6]. Many literatures reported that Ce^{4+} can complex with F$^-$ in different forms at different acidic solution [7–10]. In perchloric acid medium, species of [CeF^{3+}], [CeF$_2^{2+}$], [CeF$_3^+$], and [CeF$_4$] were

formed and the complexation stability constants were reported to be 107, 1014, 1020 and 1024 respectively [9]. In sulfuric acid medium, Ce^{4+} and F$^-$ can also form stable complex species of [CeF$_2^{2+}$] and [CeF$_3^+$] [10]. Those studies indicate that F$^-$ can be stabilized by Ce^{4+}. The acidic solution containing Ce(IV) and F(I) can be co-extracted by some appropriate extractants. After extraction, CeF$_3$ which has been widely used in inorganic scintillating crystal [11], optoelectronics [12], and solid lubricant [13] etc. can be obtained by reductive stripping.

So solvent extraction is the key to the whole process and many kinds of extractants have been investigated and applied to recover Ce(IV) and F(I) in nitrate acid or sulfuric acid medium, such as acidic organophosphorous extractants [14–19], neutral organophosphorous extractants [20–28], amines [29] and bifunctional ionic liquid extractants (Bif-ILEs) [30–32] etc. Among these extractants, neutral organophosphorous extractants were applied widely in recently years for Ce(IV) extraction. TBP was used to recover Ce(IV) and F(I) from high acidic HNO$_3$ solutions by adding an appropriate quantity of H$_3$BO$_3$ [33]. However, the extraction of Ce(IV) by TBP has some disadvantages, such as low extraction efficiency, high extraction acidities, serious co-extraction of mineral acids, and so on. Zhao et al. had investigated the

extraction and recovery of Ce(IV) and F(I) from HNO_3 solutions using Di-(2-Ethylhexyl) 2-Ethylhexyl Phosphonate (DEHEHP) and the extraction mechanism was given[20,21]. The extraction of Ce(IV) by DEHEHP has some disadvantages, such as lower extractability and low loaded capacity. Moreover, reduction problem in the process of extracting Ce(IV) by DEHEHP should be taken into account. Compared to other neutral organophosphorous extractants, Cyanex923 (mixture of four tri-alkylphosphine oxides) has significant advantages for Ce(IV) extraction because of its poor aqueous solubility, complete miscibility with common organic diluents and resistance to hydrolysis[34]. Lu et al. [23] studied the separation of Ce(IV) and Th(IV) from trivalent rare earths in nitrate medium, but the data given in this report couldn't reveal the nature of the extraction in detail. Besides, this study did not refer to the recovery of F(I). Liao et al. have investigated the extraction mechanism of Ce(IV) and F(I) by Cyanex923 from H_2SO_4 solution, and indicated the extraction species of $Ce(HF)(HSO_4)_2(SO_4)\cdot2(Cyanex923)$ [25,26].

According to the above studies, Li et al. [35] established an important process to recover Ce(IV) and F(I) by Cyanex923 from roasted bastnaesite sulfuric acid leach liquor. High purity cerium products were obtained with purity of > 99.99% and high yield of 90% Ce(IV) and F(I). But this process would extract SO_4^{2-} into organic phase. CeF_3 obtained in this system would have high concentration of SO_4^{2-}, which is hard to be removed. When these CeF_3 were used, SO_4^{2-} would be concentrated and the applications of CeF_3 would be limited. Compared to bastnaesite sulfuric acid leach liquor, Bayan Obo mixed RE concentrate liquor contained P which caused the result that Ce-product was a mixture of CeF_3 and $CePO_4$ [6]. It would limit the application of Ce-products. Considering the low hydration of nitrate, recovering Ce(IV) by Cyanex923 in HNO_3 medium may not extract PO_4^{3-} to solve the problem that Ce-products was a mixture of CeF_3 and $CePO_4$. Hence, the extraction and recovery of Ce(IV) and F(I) using Cyanex923, especially in HNO_3 solutions, needed to be further studied. But until now, there was no systematic report on Cyanex923 as extractant to obtain CeF_3 from HNO_3 solution directly. This paper investigated the extraction and recovery of Ce(IV) and F(I) from HNO_3 solution using Cyanex923. The extraction mechanism was discussed and the CeF_3 nanoparticle was obtained. The results obtained may provide a potential method to treat bastnaesite and Bayan Obo mixed RE concentrate liquor.

2. Experimental

2.1. Reagent and solutions

Cyanex923 was kindly supplied by Cytec Industries (Canada) and analytical grade n-heptane was used as diluents in some cases. Cyanex923 was purified washed with 2% $NaCO_3$, 2% H_2SO_4 and distilled water successively. The stock solution of $Ce(NO_3)_4$ was prepared by dissolving its oxides (purity 99.9%) in HNO_3, and the oxidation percentage of Ce(IV) in stock solution was greater than 95%. Besides, NaF was used to provide F^-. All other chemicals were of analytical grade.

2.2. Method

Fourier transform infrared (FTIR) transmission spectroscopy of organic phase was recorded on a Perkin-Elmer Spectrum 100 spectrometer (USA) at room temperature using the KBr pellet method. The XRD patterns were performed on a Rigaku D/MAX-IIB diffractometer with Cu Kα radiation. The particle size of CeF_3 was measured by dynamic light scattering (DLS) using a 90 Plus particle size analyzer (Brookhaven, USA) at 25 °C, and the suspension was diluted with ethanol to a concentration of about 1 mg/ml. The morphology of CeF_3 was characterized by scanning electron microscopy (SEM) using a Model XL 30 ESEM (Philips). The sample was dropped on a silica surface and dried at rooms temperature, and then were covered by gold.

The TEM images were recorded using a transmission electron microscope (Hitachi H-800) at an acceleration voltage of 100 kV.

The concentrations of Ce(IV) and Ce_{total} in aqueous phase were determined by complexometric titration and in the organic phase was determined from material balance. Occasionally, data were also determined by an inductively coupled plasma atomic emission spectrometer (ICP Spectrometer Thermo iCAP 6000). The concentration of the F^- in the aqueous phase was measured by ion-selective electrodes with a pHs-3 C acidimeter (Shanghai Rex Instrument Factory) [36]. The nitric acid concentration in aqueous and organic phase was obtained by titrating with standard NaOH, using phenolphthalein as an indicator.

2.3. Experimental procedure

All the experiments were performed at room temperature except for the temperature experiment. Liquid-liquid extraction/stripping were carried out by shaken equal volumes (10 mL) of organic and aqueous solutions in 30 ml separatory funnels for 15 min. The n-heptane in saturated loaded organic phase was removal by vacuum rotary evaporation. Then vacuum drying at 120 °C to obtain the saturated extracted species.

The extraction efficiency (E), distribution ratio (D), and stripping ratio (S) are defined in Eqs. (1)–(3) as follows:

$$E\% = \frac{[M]_t - [M]_a}{[M]_t} \times 100 \tag{1}$$

$$D = \frac{[M]_t - [M]_a}{[M]_a} \tag{2}$$

$$S\% = \frac{[M]_{aq,a}}{[M]_{org,t}} \times 100 \tag{3}$$

where $[M]_t$ and $[M]_a$ represent the initial and final concentration of Ce(IV) or F(I) in aqueous phase. $[M]_{aq,a}$ is equilibrium concentration of metal ion in stripping solution and $[M]_{org,\ t}$ is initial concentration of metal ion in organic phase, respectively.

## 3. Results and discussion

3.1. Extraction of HNO_3

Many evidences [23,37] had proved that Cyanex923 can extract HNO_3 through the P=O group and the general equilibrium of HNO_3 extraction in a simplified form can be represented as follow:

$$HNO_3 + mCyanex923 \xrightarrow{K} HNO_3\cdot mCyanex923 \tag{4}$$

From this equation can be obtained:

$$logD_{HNO_3} = mlog[Cyanex923] + logK \tag{5}$$

Extraction isotherm of HNO_3 by [Cyanex923] is shown in Fig. 1. From the result, we calculate the value of $[HNO_3]_{(O)}/[Cyanex923]_{(O)}$. These values indicate that with the increase of initial nitric acid concentration, the extracted species have different forms. When the concentration of $[HNO_3]$ is below 2 mol/L, the extracted specie is Cyanex923·HNO_3; when the concentration of $[HNO_3]$ is 2–4.5 mol/L, the extraction of HNO_3 reached saturated; and when the concentration of $[HNO_3]$ is higher than 4.5 mol/L, Cyanex923·2HNO_3 begin to appear. Besides, we studied the extraction of HNO_3 under different concentrations of Cyanex923. The result is shown in Fig. 2. From the plot slope we can include that m equals about 1 at these initial acid concentrations. So the extraction mechanism of HNO_3 with Cyanex923 can be written as follow:
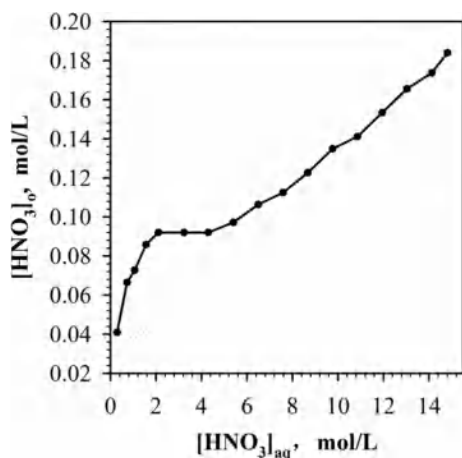
$$HNO_3 + Cyanex923 \xrightarrow{K} HNO_3\cdot Cyanex923 \tag{6}$$
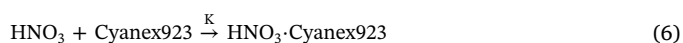
Fig. 1. Extraction isotherms of HNO_3 by Cyanex923, [Cyanex923] = 0.1 mol/L.

Fig. 2. Extraction of HNO_3 at different [Cyanex923] concentrations.

Fig. 3. Effect of HNO_3 concentration on the extraction of Ce(IV), [Ce^{4+}] = 0.02012 mol/L, [Cyanex923] = 0.01 mol/L.

Fig. 4. Effect of Cyanex923 concentration on the extraction of Ce(IV), [Ce^{4+}] = 0.02012 mol/L, [HNO$_3$] = 1 mol/L.
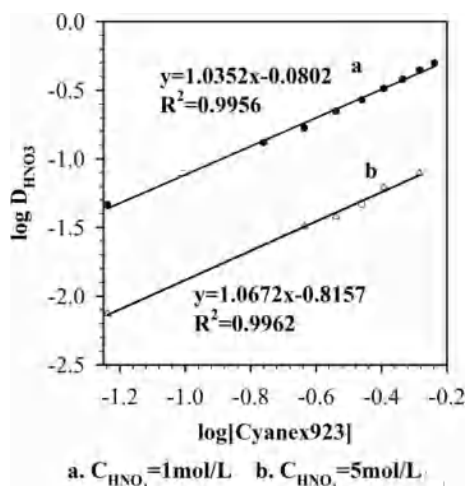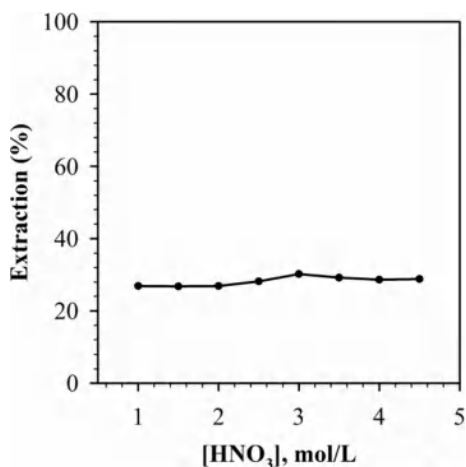

Fig. 5. Effect of nitrate ion concentration on the extraction of Ce(IV), [Cyanex923] = 0.01 mol/L, [Ce^{4+}] = 0.01714 mol/L, [HNO$_3$] = 1 mol/L.
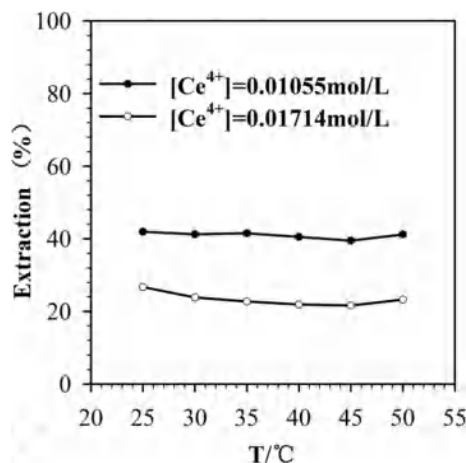

Fig. 6. Effect of the Temperature on the extraction of Ce(IV), [Cyanex923] = 0.01 mol/L, [HNO$_3$] = 1 mol/L.

3.2. Extraction of Ce(IV) in HNO_3 solution

3.2.1. Effect of nitric acid concentration

The effect of aqueous acidity on the extraction of Ce(IV) by Cyanex923 has been studied, and the result is shown in Fig. 3. It is clear that the concentration of HNO_3 has no evidently effect on the extraction of Ce(IV). This phenomenon is also exist in extraction Ce(IV) in H_2SO_4 solution by Cyanex923 [25].

3.2.2. Effect of extractant concentration

The effect of Cyanex923 concentration, in the range of 0.01–0.04 M, on the extraction of Ce(IV) was studied in 1 M HNO_3 and the result is shown in Fig. 4. The functional relationship between log D and log

Table 1
Ce(IV) loading capacity of Cyanex923 in HNO$_3$ system.

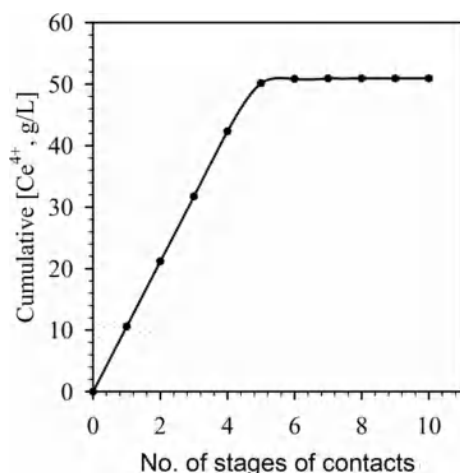| No. of stages of contacts	1	2	3	4	5	6	7	8	9
Cumulative [Ce^{4+},g/L]$_{org}$	10.58	21.17	31.75	42.34	50.16	50.87	50.94	50.94	50.94

Fig. 7. Ce(IV) loading capacity of Cyanex923 in HNO$_3$ system.

Fig. 10. Effect of Nitric Acid Concentration on the extraction of Ce(IV) and F(I), [Cyanex923] = 0.01 mol/L, [Ce^{4+}] = 0.0196 mol/L, [F$^-$] = 0.03722 mol/L.
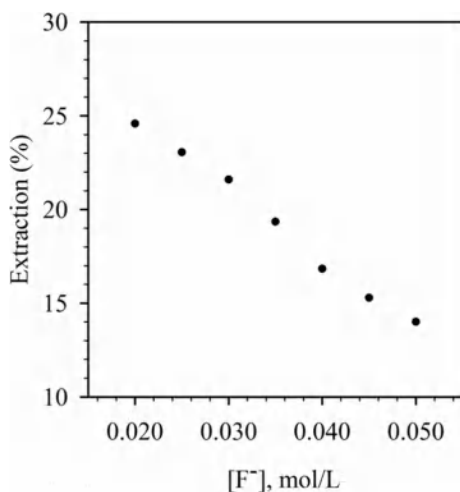

Fig. 8. Effect of the F$^-$ concentration on the extraction of Ce(IV) and F(I), [Cyanex923] = 0.01 mol/L, [HNO$_3$] = 1 mol/L, [Ce^{4+}] = 0.01055 mol/L.
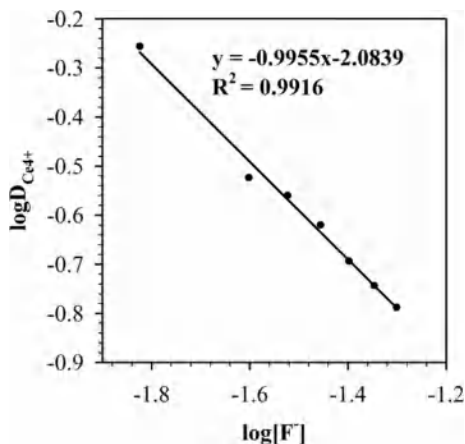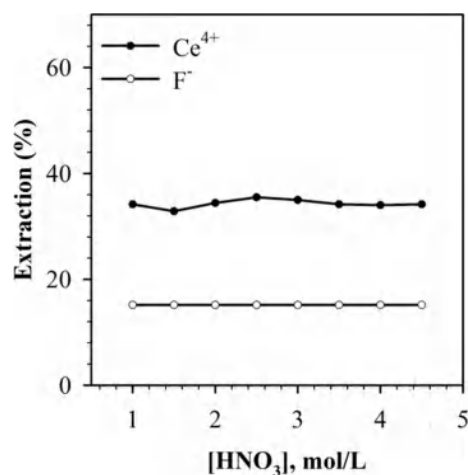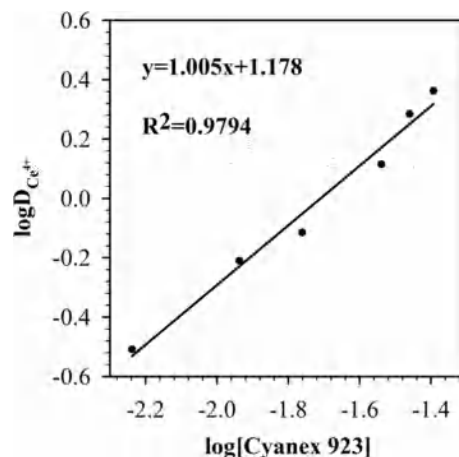

Fig. 11. Effect of Extractant Concentration on the extraction of Ce(IV), [Ce^{4+}] = 0.0196 mol/L, [HNO$_3$] = 1 mol/L, [F$^-$] = 0.03158 mol/L.
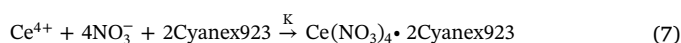
[Cyanex923] is showed linearly and the slope is nearly two. It is obvious that association between the two moles of Cyanex923 for each mole of Ce(IV) extracted into organic phase.

3.2.3. Effect of nitrate ion concentration

The extraction of Ce(IV) does not change with the increase in nitrate ion concentration from 0.1 to 2.4 M. The result is shown in Fig. 5. This probably has two reasons; first, HNO$_3$ is strong acid with entirely ionization, nitrate itself has certain effect of salting out, in addition, the ability of extraction of Ce(IV) in HNO$_3$ solution by Cyanex923 is so strong that nitrate ion concentration has no obviously effect.

3.2.4. Extraction equilibrium

From the results above and charge balance, the extraction equilibrium of Ce(IV) from HNO$_3$ solution by Cyanex923 can be described as follow:

Fig. 9. Plots of log D vs. log [F$^-$], [Cyanex923] = 0.01 mol/L, [HNO$_3$] = 1 mol/L, [Ce^{4+}] = 0.01055 mol/L.

$$Ce^{4+} + 4NO_3^- + 2Cyanex923 \xrightarrow{K} Ce(NO_3)_4 \cdot 2Cyanex923 \qquad (7)$$
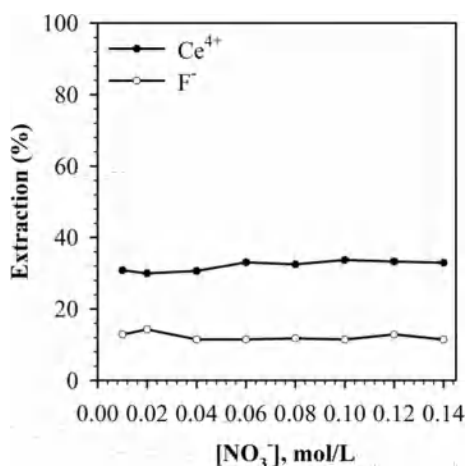
Fig. 12. Effect of nitrate ion concentration on the extraction of Ce(IV) and F(I), [Cyanex923] = 0.01 mol/L, $[F^-]$ = 0.02378 mol/L, $[Ce^{4+}]$ = 0.01055 mol/L, $[HNO_3]$ = 1 mol/L.
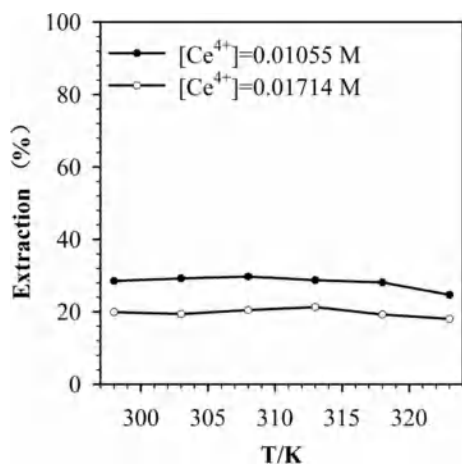

Fig. 13. Effect of the Temperature on the extraction of Ce(IV) as F^- existed, [Cyanex923] = 0.01 mol/L, $[F^-]$ = 0.02378 mol/L, $[HNO_3]$ = 1 mol/L.
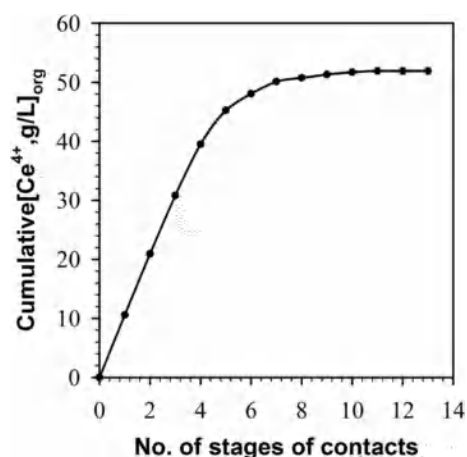

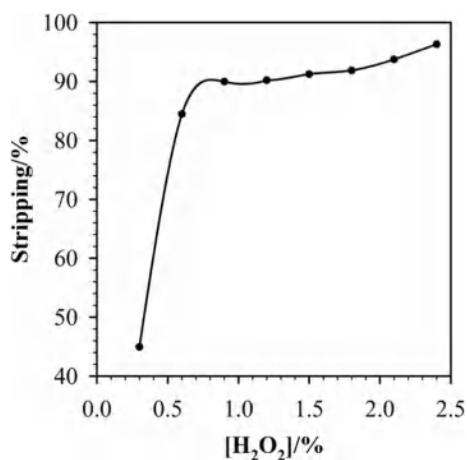**Fig. 14.** Ce(IV) loading concentration of Cyanex923 as F^- existed in HNO_3 system.

Fig. 15. Effects of $[H_2O_2]$ on the stripping of Ce(IV) and F(I) $[HNO_3]$ = 3 mol/L, V_{aq}/V_{org} = 1:1.

3.2.5. Effect of the temperature

The effect of temperature on the variable of Ce(IV) extraction by Cyanex923 was shown in Fig. 6. From The results, we can find that temperature didn't affect the extraction process clearly at these conditions.

3.2.6. Ce(IV) loading capacity of Cyanex923 in HNO_3 system

Equal volumes of organic phase (30% Cyanex923 in heptane) and aqueous phase ($[Ce^{4+}]$ = 0.0756 M) were contacted in a separatory funnel. After equilibrium for 15 min, the raffinate phase was measured to determine Ce(IV) concentration and the loaded organic phase was re-contacted with fresh aqueous phase until the Ce(IV) concentration in the raffinate phase remained unchanged. The Ce(IV) concentration in the saturated loaded organic phase was determined by mass balance. The result is shown in Table 1 and Fig. 7.

3.3. Extraction of Ce(IV) and fluorine(I) in HNO_3 solution

3.3.1. Effect of the fluorine(I) concentration

The effect of F^- concentration on the extraction of Ce(IV) in HNO_3 system has been studied. The results are shown in Figs. 8 and 9. With the increase of the F^- concentration, the Ce(IV) extraction percentage decreases the F^- complexes with Ce(IV) in the aqueous phase. From Fig. 9, it can be concluded that association between the one molecule of fluorine(I) for each mole of Ce(IV) extracted into organic phase.

3.3.2. Effect of nitric acid concentration

The effect of nitric acid concentration on the extraction of Ce(IV) and F(I) by Cyanex923 has been studied, and the result is shown in Fig. 10. It is clear that the concentration of HNO_3 has no evidently effect on the extraction of Ce(IV) and F(I) in this system.

3.3.3. Effect of extractant concentration

The effect of Cyanex923 concentration, in the range 0.005 M − 0.04 M, on the extraction of Ce(IV) was studied in 1 M HNO_3 and the result is shown in Fig. 11. The functional relationship between

Table 2
Ce(IV) loading capacity of Cyanex923 in HNO_3 system.

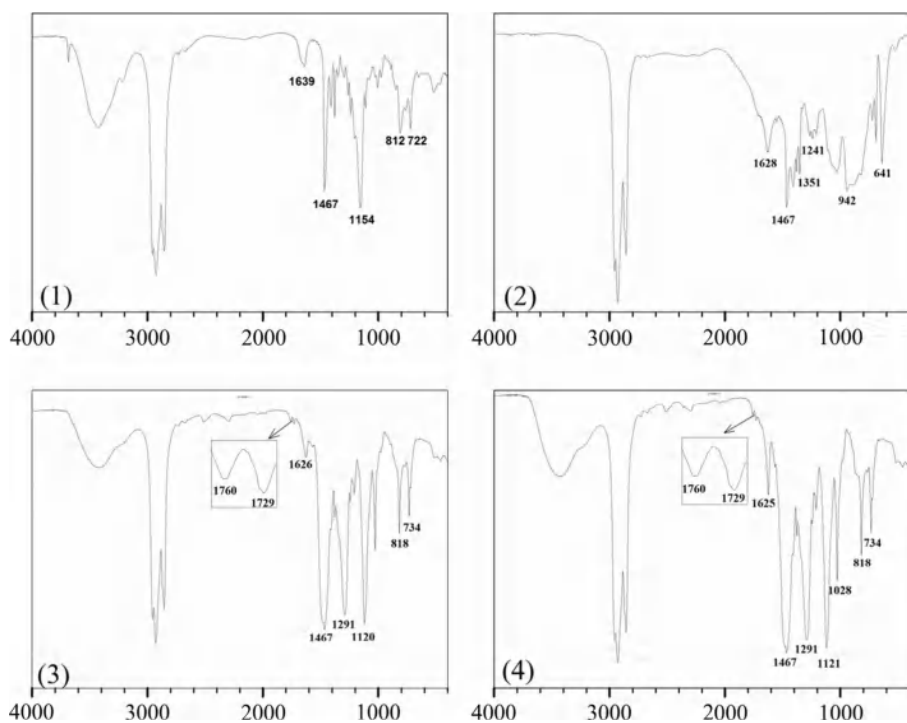| No. of stages of contacts	1	2	3	4	5	6	7	8	9	10	11	12
Cumulative$[Ce^{4+}$,g/L$]_{org}$	10.6	20.9	30.8	39.5	45.3	48.1	50.1	50.8	51.3	51.7	51.9	51.9

Fig. 16. (1) IR-Spectrum of purified Cyanex923; (2) IR-Spectrum of cyanex923 loaded with HNO₃; (3) IR-Spectrum of Cyanex923 loaded with Ce(IV); (4) IR-Spectrum of Cyanex923 loaded with Ce(IV) and F(I).
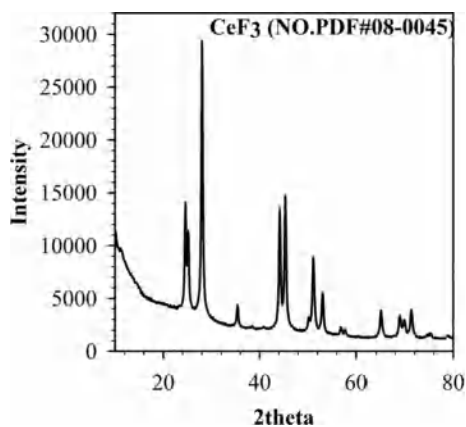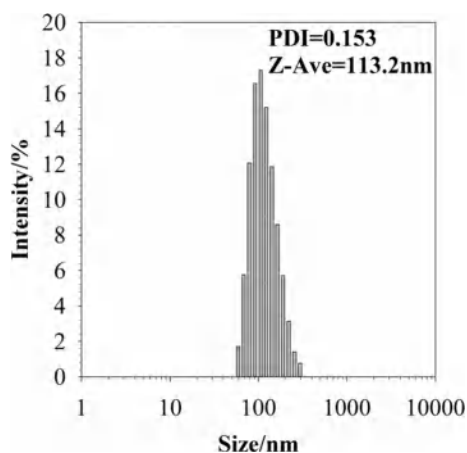

Fig. 17. XRD spectrum of stripping particle.

Fig. 18. Size distribution of CeF₃ nanoparticle.

log D and log [Cyanex923] is linearly and the slope is about one. It is obvious that association between the one mole of Cyanex923 for each mole of Ce(IV) extracted into organic phase.

3.3.4. Effect of nitrate ion concentration

The extraction of Ce(IV) and F(I) does not have any effect with the increase in nitrate ion concentration from 0.01 to 0.14 M. The result is shown in Fig. 12.

3.3.5. Extraction equilibrium

From the results above and charge balance, the extraction equilibrium of Ce(IV) and F(I)from HNO₃ solution by Cyanex923 can be simply described as follow:

$$Ce^{4+} + 4NO_3^- + F^- + H^+ + Cyanex923 \xrightarrow{K} Ce(HF)(NO_3)_4 \cdot Cyanex923$$

(8)
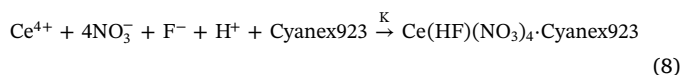
3.3.6. Effect of the temperature

The effect of temperature on extraction of Ce(IV) by Cyanex923 was shown in Fig. 13. From The results, we can find that temperature didn't affect the extraction process at these conditions.

3.3.7. Ce(IV) loading capacity of Cyanex923 as F⁻ existed in HNO₃ system

Equal volumes of organic phase (30% Cyanex 923 in heptane) and aqueous phase ([Ce^{4+}] = 0.0756 M; [F^-] = 0.15 M) were contacted in a separatory funnel. After equilibrium for 15 min, the raffinate phase was measured to determine Ce(IV) concentration and the loaded organic phase was re-contacted with fresh aqueous phase until the Ce(IV) concentration in the raffinate phase was the same as the initial concentration. The Ce(IV) concentration in the saturated loaded organic phase was determined by mass balance. The result is shown in Table 2 and Fig. 14.

3.3.8. Reductive stripping text

Owing to the weak extraction of Ce(III) by Cyanex923 in HNO₃ solution, it is possible to strip Ce(IV) by reducing Ce(IV) to Ce(III) in the organic phase. Many literatures [5,22,31] mentioned that H₂O₂ can reduce Ce(IV) to Ce(III) in this system. The effect of the concentration of
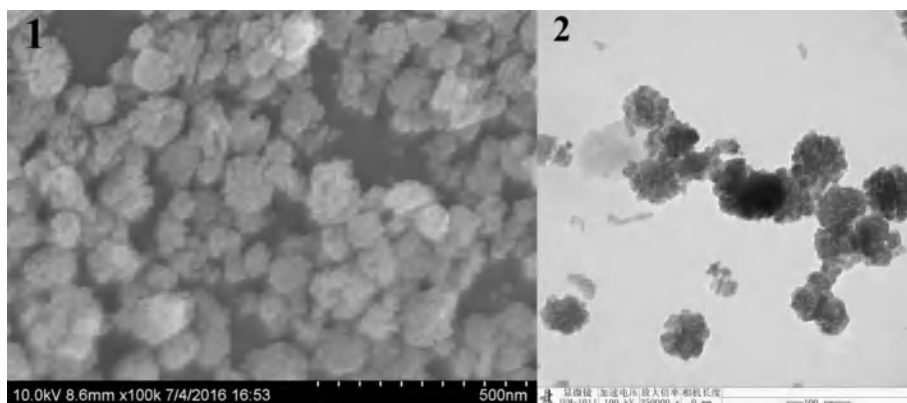
Table 3
Composition of the CeF$_3$.

Sample number	Ce (%)	F (%)	NO$_3^-$ (%)	SO$_4^{2-}$ (%)	Total (%)
1	68.34	27.46	1.2	\	97
2	71.07	28.79	0	\	99.86
3	61.06	18.26	\	17.61	96.87
4	62.97	18.87	\	17.95	99.79

Table 4
Composition of the HNO$_3$ liquor and the raffinate.

Element	La	Ce	Pr	Nd	F
Liquor (g/L)	33.58	48.45	3.27	9.39	8.16
After extraction (g/L)	33.45	24.69	3.27	9.48	4.68

H$_2$O$_2$ on the stripping of Ce(IV) was studied. HNO$_3$ was added to control the acidity, and the result was shown in Fig. 15. The stripping rate increases with an increasing concentration of H$_2$O$_2$, and 96.3% of stripping rate of Ce(IV) can be obtained with 2.4% H$_2$O$_2$.

3.4. Infrared Spectra of extracted complexes

To study the structure of extracted complexes, the IR spectra of the extracted complexes were investigated and the results are shown in Fig. 16.

The stretching frequency of P=O in Cyanex923 is 1155 cm^{-1}, this band almost disappears in HNO3·Cyanex923 complex. It may because this complex exists hydrogen bond between P=O bond and H-ONO$_2$. It caused the P=O bond was replaced by P−O−HO−NO$_2$ bond. This conclusion can be proved by the appearance of the band 942 cm^{-1}, which can be assigned to ν_{P-O-H} band. Furthermore, the bands at 1628 and 1351 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the −NO$_2$ group respectively. The band at 641 cm^{-1} is due to the bending vibration of −NO$_2$ group. These results demonstrate that HNO$_3$ combined with Cyanex923 by hydrogen bond.

The stretching vibration frequency of P=O in Cyanex923 has shifted from 1155 cm^{-1} to 1120 cm^{-1} in Ce(NO$_3$)$_4$·2Cyanex923 complex and to 1121 cm^{-1} in Ce(NO$_3$)$_4$·HF·Cyanex923 complex. Coordination of P=O by Ce(IV) can result in the wave number removing from high to low. Besides, the stretching vibration frequency of P−C in Cyanex923 has shifted from 812 cm^{-1} to 818 cm^{-1} in the complexes. The band at 722 cm^{-1} assigned to out-of-plane bending vibration of −CH$_2$ groups next to the phosphorus atom in Cyanex923 is shifted to 734 cm^{-1} in these complexes. The results above can prove that Ce(IV) was coordinated with Cyanex923 by P=O. Compared to Cyanex923, appearance of the band at 1291 cm^{-1} in the complexes shows the coordination of NO$_3^-$ with Ce(IV). The coordination mode of

NO$_3^-$ is closely corresponds to the bands at 1700–1800 cm^{-1} region, Lever et al. [38] have concluded the relationship between combination band separation and coordination mode of nitrate, and for the mono-dentate nitrate group is 5–26 cm^{-1} and for bidentate nitrate is 20–66 cm^{-1}. As in the IR spectrum, Ce(NO$_3$)$_4$·2Cyanex923 complex and Ce(NO$_3$)$_4$·HF·Cyanex923 complexe show 31 cm^{-1} denotative of bidentate nitrate groups. The absorbance peak of HF in the complex of Ce(NO$_3$)$_4$·HF·Cyanex923 is inconspicuous may because the absorbance peak of H-F is weak.

3.5. CeF$_3$ nanoparticle obtained by reductive stripping

This paper used Cyanex923 to recover Ce(IV) and F(I) in HNO$_3$ solution, and CeF$_3$ nanoparticle was obtained by reductive stripping. The precipitate was washed three times with distilled H$_2$O and ethanol by using an ultrasonic bath to disperse, followed by centrifugation then dried 6 h at 60 °C in an oven. The X-ray diffraction spectrum of the nanoparticle was shown in Fig. 17. It is convinced that the main phase of nanoparticle is CeF$_3$ (No. PDF#08-0045). The size distribution of CeF$_3$ nanoparticle was measured by DLS. The result shown in Fig. 18 indicates that the average size of CeF$_3$ was 113 nm and the particle polydispersity index (PDI) was 0.153.

The morphology and microstructure of CeF$_3$ were investigated by the SEM and TEM observation and the results were shown in Fig. 19. The size of the particle is in accord with the result of DLS.

3.6. Compared to the two CeF$_3$ obtained in H$_2$SO$_4$ and HNO$_3$ system respectively

In order to further illustrate the merits of HNO$_3$ system, the composition of the CeF$_3$ obtained in HNO$_3$ system was compared with it acquired in H$_2$SO$_4$ system. CeF$_3$ obtained in H$_2$SO$_4$ system was treated with the same method described in 3.5. For further comparison, we burnt the two CeF$_3$ for two hours in a muffle furnace at 350 °C. The results were shown in Table 3.

Sample 1 and sample 2 are CeF$_3$ obtained in HNO$_3$ system, and sample 2 is the burnt one, similarly, Sample 3 and Sample 4 are CeF$_3$ obtained in H$_2$SO$_4$ system, and sample 4 is the burnt one. It can be concluded that the CeF$_3$ obtained in HNO$_3$ system has low impurity content, and the impurity could be removed by simply burning. But in H$_2$SO$_4$ system, SO$_4^{2-}$ content is very high and hard to be removed. CeF$_3$ obtained in HNO$_3$ system would have more potential applications as a result of low impurity content.

3.7. Application study

The extraction process discussed above was utilized in a practical system in order to study the application of this process. Bastnasite was placed in a muffle furnace held at a temperature of 500 °C for 2 h. The

roasted product was then removed from the furnace. After roasting, the powder was leached with 5 mol/L HNO_3 solution at 35 °C for 30 min.

The liquor was extracted with Cyanex923. And then Ce(IV) and F were extracted into organic phase, CeF_3 was obtained from the extracted organic phase by reductive stripping. The composition of the HNO_3 liquor and the raffinate was given in Table 4. From the results, we can find that about 43% F and 50% Ce were extracted into organic phase by one-time extraction. And the concentrations of other rare earth elements did not have significant changes. The results prove that this process is a potential method to treat bastnaesite and Bayan Obo mixed RE concentrate liquor.

4. Conclusion

The extraction and recovery of F(I) from nitrate solutions by Cyanex923 utilizing complex properties of Ce(IV) with F(I) have been investigated. Ce(IV) could be extracted efficiently by Cyanex923. Besides, F^- can decrease the extraction of Ce(IV). The extraction of HNO_3, Ce(IV) and Ce(IV)-F have been studied respectively, and the extracted complexes are considered to be $HNO_3 \cdot Cyanex923$, $Ce(NO_3)_4 \cdot 2Cyanex923$ and $Ce(HF)(NO_3)_2 \cdot Cyanex923$ individually. The extraction mechanism was studied by Infrared Spectra which demonstrate that the NO_3^- ion is a bidentate ligand. CeF_3 nanoparticle obtained in this extraction system by reductive stripping was compared with CeF_3 acquired in H_2SO_4 system. The results showed that CeF_3 obtained in HNO_3 system has low impurity content which could be removed by simply burning. The extraction process applied in the HNO_3 liquor of bastnaesite indicates a potential approach to recover Ce(IV) and F in light RE resources.

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