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Synthesis of new extractant P113 for cerium(IV) extraction and higher separation over thorium from bastnaesite

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ABSTRACT

Cyanex923 (a mixture of four trialkyl (hexyl and octyl) phosphine oxides) has been extensively employed in the recovery of cerium (Ce(IV)) and fluorine (F), as well as the separation over thorium (Th(IV)) from bastnaesite. However, rigorous production conditions and involvement of highly toxic raw materials (PH_3) have been critical problems to be solved during the synthesis of Cyanex923. Meanwhile, its extraction performance remains to be improved. Therefore, we attempted to adjust the feed ratio to increase the proportion of short carbon chain components, successfully synthesized a novel extractant (P113, a mixture of four trialkyl (hexyl and octyl) phosphine oxides) with contents of each component different from Cyanex923 using an environmentally benign method. The comparison with Cyanex923 revealed obvious improvement of P113 in terms of extraction efficiency, selectivity and saturation capacity. The extraction efficiency and saturation capacity of Ce(IV) were increased by 10% and 10 g L^{-1}, respectively. Separation factor of Ce(IV)/Th(IV) was increased from 16 to 27 at 2 mol L^{-1} H_2SO_4. Furthermore, P113 presented excellent regenerability. The superiority of P113 was theoretically explored using the density functional theory (DFT) and polarizable continuum model (PCM), and the results indicated that THPO (trihexyl phosphine oxide) had lower extraction phase transfer energy than TOPO (trioctyl phosphine oxide) from aqueous phase to organic phase. The comprehensive evaluation of P113 demonstrated the feasibility employed in the recovery of Ce(IV)-F and the separation of Th(IV) from bastnaesite, which advanced industrial application of the novel extractant, and held significant value for the utilization of resources and environmental protection.

1. Introduction

China has abundant rare earth mineral resources, supplying over 95% of the world's output of rare earth with its products and exports [1,2]. Bastnaesite, as the most important light rare earth resource, occupies a dominated position in the rare earth industry of China, in which $CeO_2/\Sigma REO$ accounts for as high as 50% of the total. In addition, 8–10 wt% fluorine (F) and 0.2–0.3 wt% thorium (Th) commonly coexist with cerium (Ce) [3–5]. As a precious strategic resource, Ce along with its compounds have been extensively applied in high-tech fields such as catalysis, laser, glass, electrochemistry and so on due to its unique physicochemical properties [6–9]. Fluorine compounds are viewed as important industrial raw materials while thorium is a vital element for conducting a nuclear energy program. However, direct emissions of fluorine containing waste gas as well as the residue of radioactive thorium (Th(IV)) could lead to negative impacts on human health and the environment during the process of bastnaesite treatment [10,11]. Accordingly, the recovery of Ce(IV) and F(I) as well as the separation of Th(IV) has been extremely urgent, which holds important practical significance for comprehensive utilization of rare earth resources and environmental protection.

Liquid-liquid solvent extraction has certain inherent advantages in the extraction of REEs due to its high-performance extraction, excellent selectivity, large loaded capacity and regenerability of the organic

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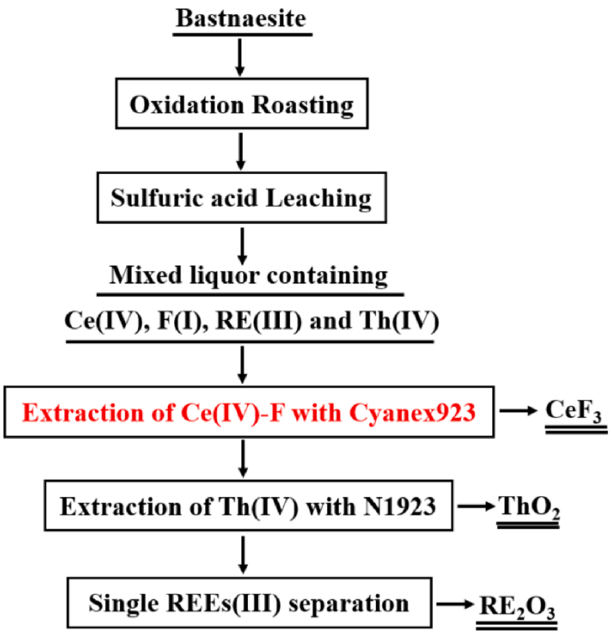

Fig. 1. The current technique for the extraction of rare earths and thorium from bastnaesite.

phase, and considered as an ideal technique to separate REEs from ores. So far, a significant amount of extractants have been used to recover Ce (IV) and Ce(IV)-F(I) from acidic solutions, such as acidic organophosphorous extractants [2,12–17]. However, difficulty of stripping, the weaker extraction ability of F(I) and selectivity of Ce(IV)/Th(IV) have been the main problems for this type of extractants, which is adverse to the practical application. In addition, numerous neutral organophosphorous extractants have been reported [18–27]. For instance, TBP (tributyl phosphate) was first put forward by Warf to recover Ce(IV) from HNO_3 medium. However, the extraction process still confronted with a series of problems, such as high extraction acidity and water solubility, poor extraction ability and serious co-extraction of mineral acids. Zhao et al. had attempted to extract and recover Ce(IV)-F(I) from HNO_3 liquor using DEHEHP (di-(2-ethylhexyl) 2-ethylhexyl phosphonate). Unfortunately, DEHEHP suffered from some drawbacks such us poor extractability toward F(I) and low saturation capacity. In addition, reduction problem in the extraction process limited the large-scale industrial applications of DEHEHP. TRPO (trialkyl phosphine oxide)-type extractants had obvious advantages in Ce(IV) extraction due to higher electron cloud density at the $P = O$ bond. e.g., TOPO (trioctyl phosphine oxide) had strong extraction ability for Ce(IV), but poor solubility in aliphatic diluents severely constrained its saturation capacity. EHBEHP (2-ethylhexyl bis(2-ethylhexyl) phosphinate) and TEHPO (tris(2-ethylhexyl) phosphine oxide) had considerable extraction ability for Ce(IV) and F(I) in HNO_3 medium [28,29]. However, few F(I) was extracted into the organic phase in H_2SO_4 medium, which was not suitable for the recovery of Ce(IV)-F(I) from practical bastnaesite H_2SO_4 leaching liquor. Cyanex923 had been considered as a promising extractant for the recovery of Ce(IV)/Ce(IV)-F from acidic solution because of rapid phase disengagement, complete miscibility with common aliphatic diluents, poor aqueous solubility and good resistance to hydrolysis. The extraction ability of Ce(IV) with Cyanex923 is excellent in the range of 0.5–4.0 mol L^{-1} H_2SO_4, while separation coefficient of Ce(IV)/Th(IV) is higher at sulfuric acid concentration of 0.5–2.5 mol L^{-1} [22]. Our group developed and completed a new clean technique based on high efficiency recovery of Ce(IV)-F and the separation of Th during the bastnaesite treatment in the last 30 years [30]. The process flowchart was shown in Fig. 1. Cyanex923 can simultaneously recover Ce(IV)-F and separate them from Th(IV) in sulfuric acid medium, playing a vital role in this process. The recovery of REEs and associated resources as well as the residue of radioactive element can be effectively solved. However, high toxicity of raw material PH_3 and rigorous synthesis conditions had been existed in Cyanex923 as serious problems, and its extraction performance also remained to be improved. Therefore, continued effort to develop more outstanding extractant for comprehensive treatment of bastnaesite had been extremely urgent.

In this work, a novel extractant P113 was synthesized by a greener method. In order to verify the industrial application potential of the novel extractant for the recovery of Ce(IV) and F from bastnaesite, its extraction performance had been systematically evaluated and compared with the analogue Cyanex923, involved extractability, interfacial phenomenon, selectivity, stripping ability and saturation capacity.

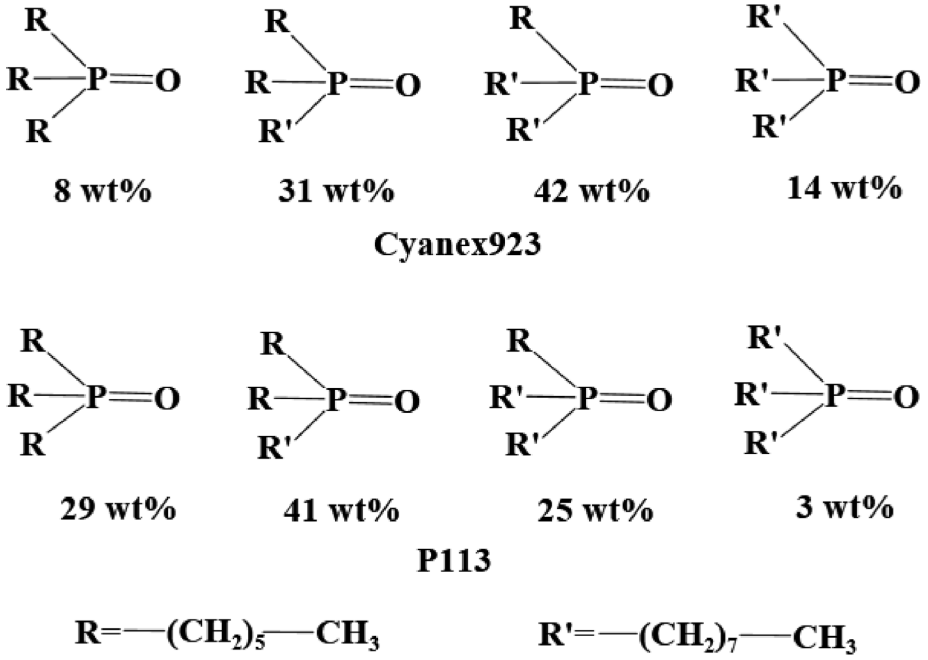

Fig. 2. The chemical structures of two extractants.

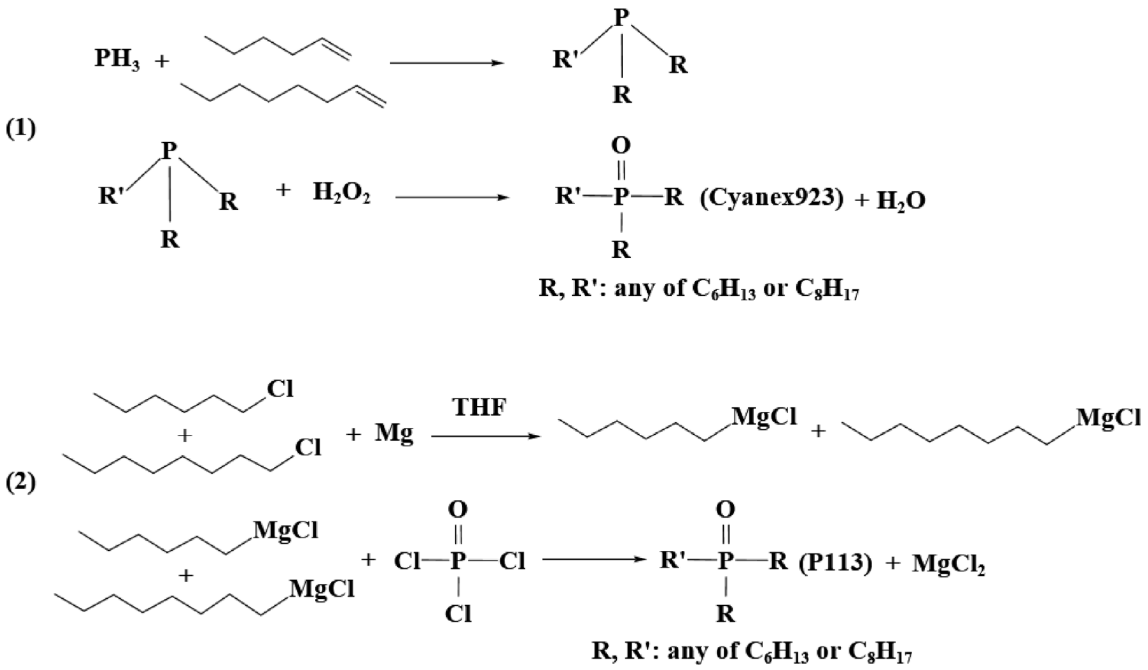

Fig. 3. Synthesis schemes of extractants.

Meanwhile, five extraction-stripping-washing cycle experiments were carried out. Furthermore, the density functional theory (DFT) and polarizable continuum model (PCM) were performed to comprehend the effect of alkyl substituents of extractants on the phase transfer energy of extraction process, which theoretically explained the superiority of P113 with regard to Cyanex923. The novel extractant P113 was equipped with ability to recover Ce(IV)-F(I) and separate Th(IV) from bastnaesite and revealed the high potential in industrial application.

2. Experiment.

2.1. Reagents and solutions

P113 (a mixture of four trialkyl (hexyl and octyl) phosphine oxides, purity ≥ 98%) and THPO (trihexyl phosphine oxide, purity ≥ 98%) were synthesized in accordance with the patent [31] proposed by Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. P113 industrial products used in this experiment were produced and supplied by JiangXi JieXin Technology Co., Ltd. Characterization analysis including TG analysis, FT-IR spectra, ESI-MS spectra, GC–MS spectra as well as physical properties of P113 were presented in Supplementary Material (Fig. S1 ~ Fig. S6 and Table S1 ~ Table S3). Cyanex923 (a mixture of four trialkyl (hexyl and octyl) phosphine oxides, purity ≥ 93%) was provided by Cytec Industry Canada Inc, and the comparison for chemical structures of two extractants was shown in Fig. 2. The extractants were successively washed with 2 wt% Na_2CO_3, 2 wt% H_2SO_4 and deionized water to remove reductive impurities before using. TOPO (trioctyl phosphine oxide, purity ≥ 98%) was purchased from Shanghai Macklin Biochemical Co., Ltd. In addition, F(I) was provided by NaF. $Ce(OH)_4$ (purity ≥ 99.95%) were purchased from Shanghai Aladdin Industrial Corporation. $Th(NO_3)_4$ (purity ≥ 98%) and $La(NO_3)_3{\cdot}6H_2O$ (purity ≥ 99%) were purchased from Shanghai Macklin Biochemical Co., Ltd. NaF and H_2SO_4 were obtained from Beijing Chemical Works. All other reagents were of analytical grade.

The extractants were dissolved in *n*-heptane (purity ≥ 99%) to obtain desired concentrations before experiments. The stock solution was prepared by dissolving $Ce(OH)_4$ in H_2SO_4 media and diluted with deionized water to desired concentrations. The oxidation percentage of Ce(IV) in the stock solutions was over 95%.

For the convenience of subsequent writing, four components of extractants were simplified as THPO (trihexyl phosphine oxide), DHMOPO (dihexyl monooctyl phosphine oxide), DOMHPO (dioctyl monohexyl phosphine oxide), TOPO (trioctyl phosphine oxide), respectively.

2.2. Apparatus

The concentrations of Ce(IV) and Ce_{total} in aqueous phase were measured by complexometric titration with standard $(NH_4)_2Fe(SO_4)_2$ solution and counterparts in organic phase were determined based on material balance. Besides, the concentrations of La(III) and Th(IV) were determined by inductively coupled plasma atomic emission spectrometer (ICP Spectrometer Thermo iCAP 6000). The acidity in aqueous phase was titrated with standard NaOH solution, using phenolphthalein as an indicator. The concentrations of F(I) in aqueous phase were measured using ion-selective electrodes with a pHs-3C acidimeter (Shanghai Rex Instrument Factory). Mass Spectra were obtained by a Bruker Daltonics Flex mass spectrum analyzer. Gas Chromatography-Mass Spectrometry (GC–MS, 7000D GC/TQ) was provided by Agilent. Analysis of Fourier transform Infrared (FT-IR) Spectra was recorded on a Bruker IFS 66 V/S spectrometer utilizing the KBr pellet method in the region of 4000–500 cm^{-1}. Thermogravimetric analysis (TGA) was performed on a simultaneous thermogravimetric analyzer (Netzsch STA449F3). High-resolution nuclear magnetic resonance (NMR) spectroscopy was conducted on a Bruker AVANCE III 400 MHz spectrometer equipped with a 4 mm standard bore CPMAS probe head for high power decoupling in the case of ^{31}P measurements. The obtained CeF_3 product was verified by Powder X-ray Diffractometer (D8 Advance) with Cu Kα radiation. Besides, the morphology of CeF_3 particles was characterized by field emission scanning electron microscope (SEM, S-4800).

2.3. Synthesis of P113

Alkene-phosphine method is a major production process of Cyanex series extractant produced by Cytec Industry Canada Inc and shown as Fig. 3(1). However, commercial Cyanex923 synthesized by virtue of this method still has some defects. For instance, the raw material PH_3 is easy to decompose and highly toxic, and the H_2O_2 has strong oxidability and is explosive with low safety factor. Especially, high equipment requirements result in expensive process cost.

In this context, we made some improvements in terms of the above synthesis method. Grignard reagent-phosphorus oxychloride method has been attempted to obtain a novel extractant (P113, a mixture of four trialkyl (hexyl and octyl) phosphine oxide) [31]. The method avoided the involvement of highly toxic substance PH_3, and eliminated the need to operate without water or oxygen. In addition, cheap and readily available raw materials and mature synthesis technology lessened expenditure to a certain extent. The synthesis scheme of P113 was presented in Fig. 3(2), and the specific synthesis procedures were as follows: (a) *n*-hexane chloride and *n*-octane chloride were dissolved in tetrahydrofuran (THF) at a molar ratio of 2:1 to prepare a mixed halogenated hydrocarbon THF solution with a mass fraction of 35 wt%. At the same time, magnesium scraps (particle size 2–10 mm) were filled in the solid feeding device that was filled every 5 h in the subsequent reaction. Then the prepared mixed halogenated hydrocarbon THF solution was dropped into the reaction chamber at a rate of 2.5 L h^{-1}, and the reaction initiated. The temperature in the reaction chamber kept at 40–45 ℃, and the molar ratio of magnesium scraps to "*n*-hexane chloride and *n*-octane chloride" was 1.05:1. The reaction solution was introduced into the filter to remove residual magnesium, resulting in a solution of 2 mol L^{-1} Grignard reagent. The purity of Grignard reagent was above 95%, and the yield reached 85%; (b) Introduce 50 L the above Grignard reagent solution into reaction kettle and dropwise add $POCl_3$ to 4.26 kg. Cool with ice water bath and keep the internal temperature not exceeding 50 ℃. After adding, stir for 2 h. Finally, THF was removed first using distillation at atmospheric pressure and then decompress distillation, and control the internal temperature not to exceed 110 ℃; (c) Add 2 mol L^{-1} HCl solution drop by drop to neutralize the excess Grignard reagent, stir for 1 h and then stratify at rest. The aqueous phase was removed and the organic phase was rinsed twice with 10 L × 2 deionized water; (d) The organic phase was transferred into a 10 L glass bottle and distilled under reduced pressure to obtain 7.3 kg product.

Experimental conditions of distillation products: temperature of collected products (top temperature): 150–240 ℃; internal temperature: 260 ℃; oil temperature: 270 ℃; vacuum: 98 Pa.

2.4. Extraction procedures

All the extraction experiments were performed at 298 ± 1 K except for the temperature experiment. The extraction procedures were operated in the 10 mL centrifuge tube equipped with equal volumes (4 mL) of organic phase and aqueous phase, which was then shaken in a desktop constant temperature oscillator (TH2-318, Shanghai Jinghong Equipment Co. Ltd.) for 30 min to reach equilibrium. The aqueous phase was separated for the analysis of the concentrations of target ions. With regard to temperature experiment, equal volumes (4 mL) of aqueous phase and organic phase were synchronously placed in a desktop constant temperature oscillator to reach the extraction temperature, and then two phases were stirred in the 10 mL centrifuge tube for 30 min to achieve equilibrium. The *n*-heptane in the loaded organic phase was removed through vacuum rotary evaporation, and then vacuum drying at 80 °C to obtain extracted species for subsequent characterization. As for stripping experiment, 4 mL of loaded organic phase was contacted with the 8 mL of stripping agent (H_2O_2 + H_2SO_4) and the mixture was shaken vigorously for 30 min to reach a new equilibrium.

The extraction efficiency (*E*, %), distribution ratio (*D*), separation factor (*β*) and stripping rate (*S*, %) can be calculated as depicted in the following Equations 1–4, respectively.

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

$$D = \frac{[M]_t - [M]_a}{[M]_a} \quad (2)$$

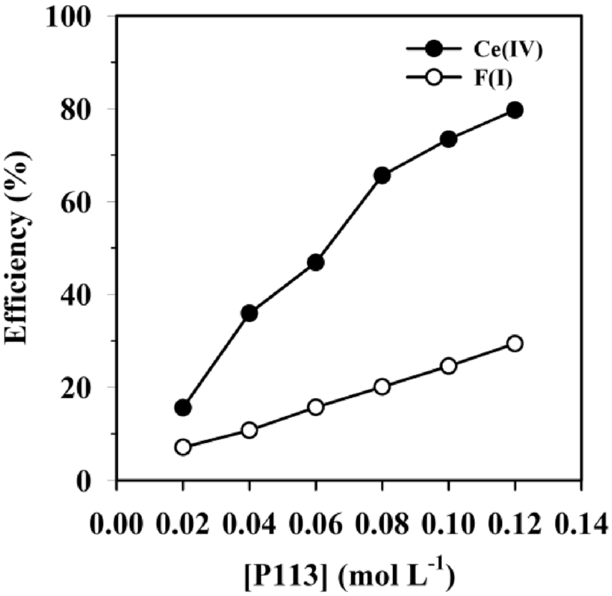

Fig. 4. Effect of the P113 concentrations on the extraction of Ce(IV) and F(I), $[Ce^{4+}]$ = 0.01628 mol L^{-1}, $[F^-]$ = 0.02829 mol L^{-1}, $[H_2SO_4]$ = 1.5 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

$$\beta = \frac{DM_1}{DM_2} \quad (3)$$

$$S\% = \frac{[M]_{aq,a}}{[M]_{org,t}} \times 100\% \quad (4)$$

where $[M]_t$ and $[M]_a$ represent the initial and equilibrium concentrations of target ions in the aqueous phase, respectively. D_{M1} and D_{M2} are the distribution ratios of ions. $[M]_{aq,a}$ stands for the equilibrium concentration of ions in the stripping solution, and $[M]_{org,t}$ is the initial concentration of ions in the loaded organic phase. The subscript "*org*" and "*aq*" refer to the organic phase and aqueous phase in a simplified form. The concentration of targets in the organic phase was calculated by mass balance, and the experimental error was calculated by repeating experiments where the values were lower than 5%.

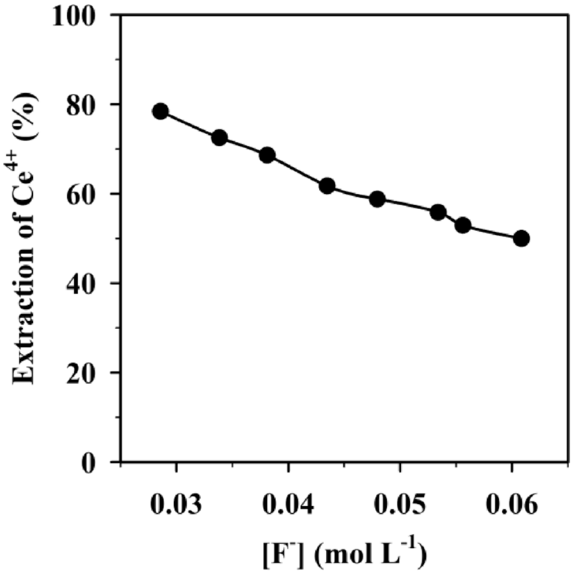

Fig. 5. Effect of the F(I) concentrations on the extraction of Ce(IV), [P113] = 0.1162 mol L^{-1}, $[Ce^{4+}]$ = 0.01359 mol L^{-1}, $[H_2SO_4]$ = 1.5 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

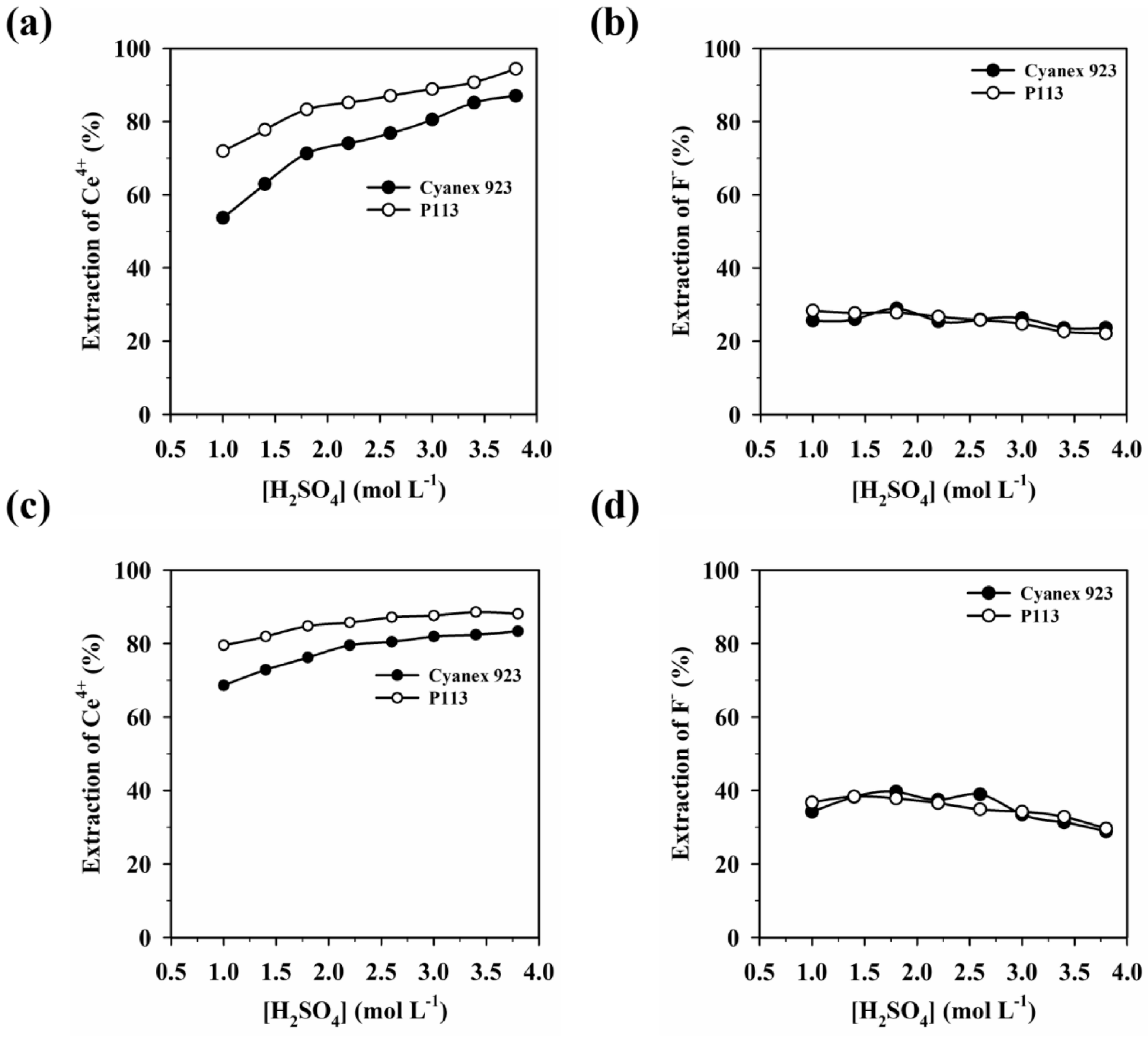

Fig. 6. Effect of sulfuric acid concentration on the extraction of Ce(IV) and F(I), (a) (b) [L] = 0.1162 mol L^{-1}, [Ce^{4+}] = 0.01434 mol L^{-1}, [F^-] = 0.02551 mol L^{-1}; (c) (d) [L] = 0.2012 mol L^{-1}, [Ce^{4+}] = 0.02398 mol L^{-1}, [F^-] = 0.04145 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min, L represents the extractant.

3. Results and discussion

3.1. *Ce(IV) and F(I) extraction from sulfuric acid solution*

3.1.1. *Effect of the P113 concentration*

The extraction behaviour of cerium(IV) and F(I) from sulfuric acid medium as a function of extractant concentration was investigated in the range of 0.02–0.12 mol L^{-1} P113. Fig. 4 depicted that the extraction efficiency increased with respect to the increasing concentration of P113. The progress in extraction efficiency was observed from 16% to 80% by varying the concentration of P113 from 0.02 mol L^{-1} to 0.12 mol L^{-1} at 1.5 mol L^{-1} H_2SO_4. According to the common ionic effect, the extraction efficiency of Ce(IV) will accordingly advance with the increase of H_2SO_4 concentration. Therefore, it is reasonable to select 0.12 mol L^{-1} extractant concentration for subsequent comparison of the extraction efficiency of Cyanex923 and P113.

3.1.2. *Effect of the F(I) concentration*

Fluorine (F) as an associated element co-exists with Ce(IV) in bastnaesite. Therefore, it is essential to explore the effect of different F(I) concentrations on the extraction of Ce(IV) in H_2SO_4 system. The results are shown in Fig. 5 that the increase of F(I) concentration restrained the Ce(IV) extraction in H_2SO_4 medium [32], which can be preliminarily inferred that a competitive relationship developed between F and Ce(IV) in the extraction process.

3.1.3. *Effect of the concentration of H_2SO_4*

Generally, sulfuric acid is considered as an appropriate medium for the leaching of bastnaesite. Then, it is of significance to explore the influence of sulfuric acid concentration in aqueous phase on the extraction efficiency of Ce(IV) and F(I) for the assessment of an extractant. Accordingly, the extraction ability of P113 to Ce(IV) and F(I) was simultaneously tested at various H_2SO_4 concentrations (1.0–3.8 mol L^{-1}), and compared with that of Cyanex923 under identical situation. It can be shown from the Fig. 6(a) and Fig. 6(c) that the extraction efficiency of Ce(IV) has an enhancement with the increase of initial H_2SO_4 concentration, and the reason for this phenomenon maybe attributed to the common ion effect [33]. The increase in acidity favors the formation of neutral extracted complexes, thereby elevating the extraction efficiency. Obviously, P113 has a stronger extraction ability for Ce(IV) than Cyanex923 in equivalent condition. On the contrary, extraction efficiency of F(I) slightly decreased as seen in Fig. 6(b) and Fig. 6(d), which resulted from a competitive effect between the F and Ce(IV) in the extraction process.

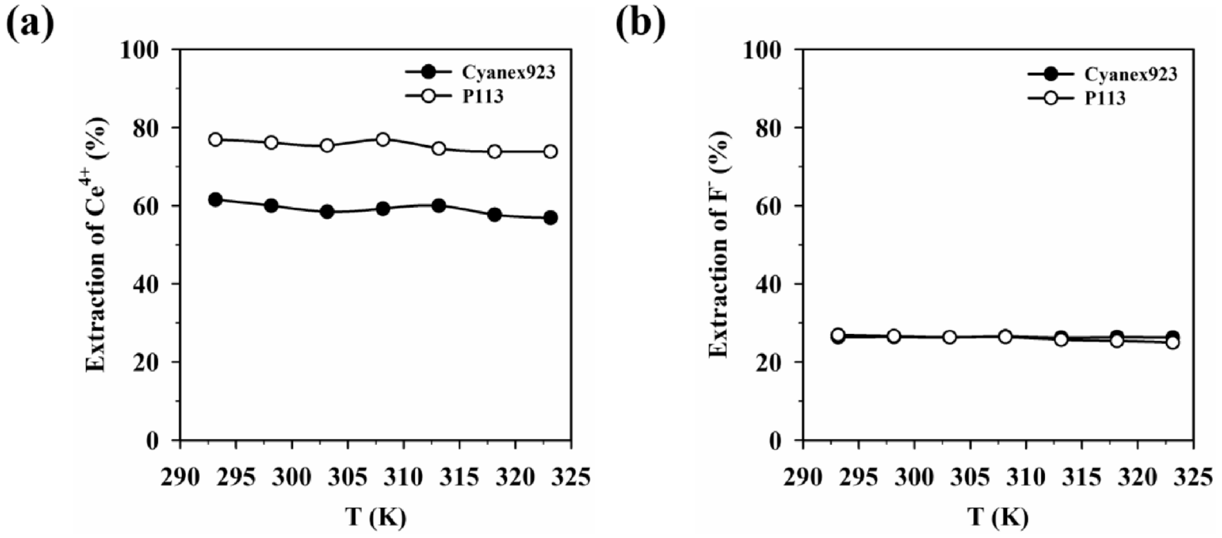

Fig. 7. Effect of the temperature on the extraction of Ce(IV) and F(I), [L] = 0.1162 mol L^{-1}, [Ce^{4+}] = 0.01685 mol L^{-1}, [F^-] = 0.03045 mol L^{-1}, [H_2SO_4] = 1.5 mol L^{-1}, O/A = 1:1, T = 298 K and t = 30 min.

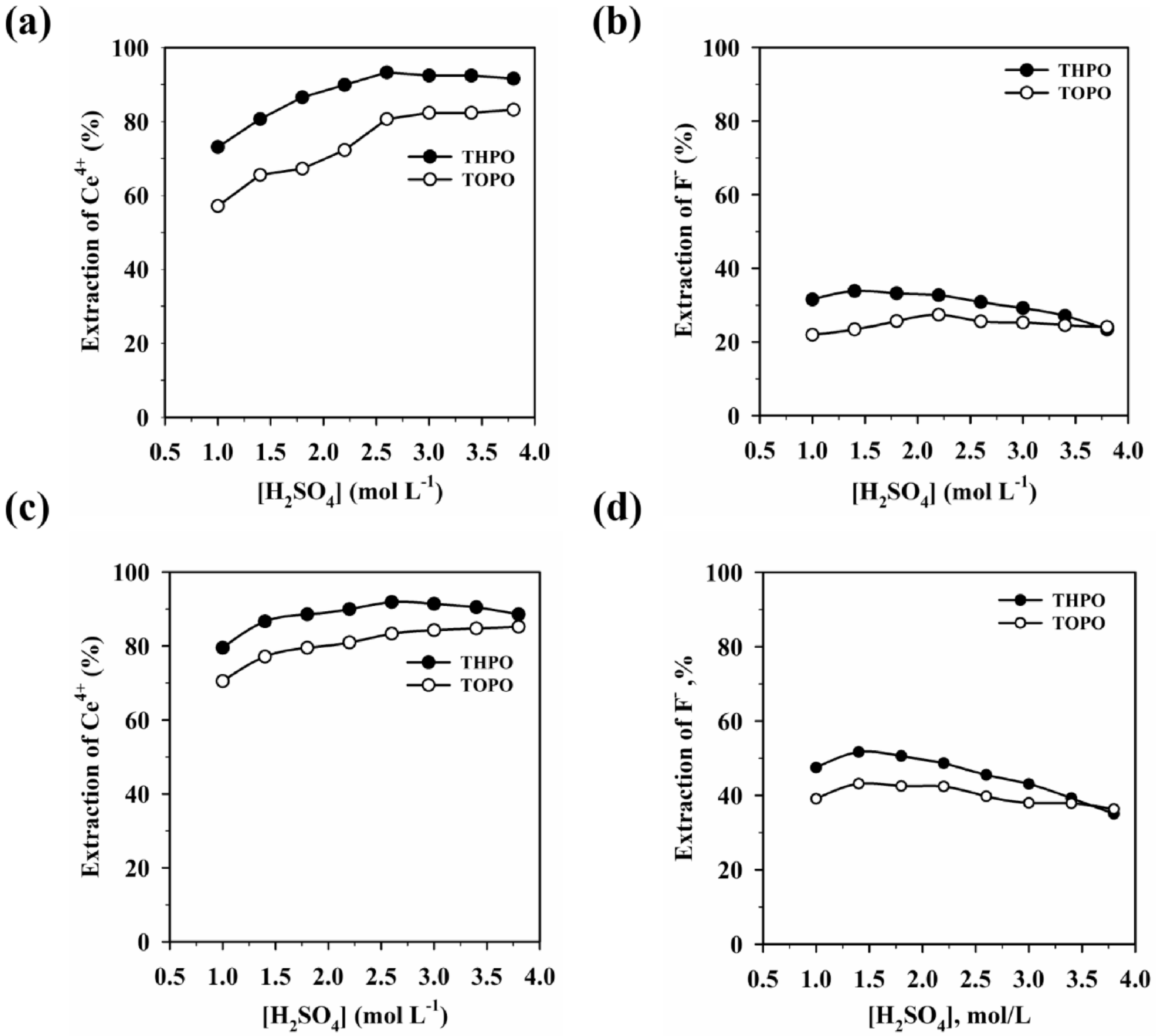

Fig. 8. Effect of sulfuric acid concentration on the extraction of Ce(IV) and F(I), (a) (b) [L] = 0.12 mol L^{-1}, [Ce^{4+}] = 0.01357 mol L^{-1}, [F^-] = 0.02448 mol L^{-1}; (c) (d) [L] = 0.2173 mol L^{-1}, [Ce^{4+}] = 0.02398 mol L^{-1}, [F^-] = 0.04145 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min, L represents THPO and TOPO, respectively.

3.1.4. *Effect of temperature*

Temperature is also a considerable parameter for extraction process. Subsequently, the effect of temperature on the extraction of Ce(IV) and F(I) was investigated by varying the temperature from 293 to 323 K. As seen in Fig. 7, no significant effect on the extraction of Ce(IV) and F(I) was observed with the variation of temperature [32,34]. In addition, P113 had obviously higher extraction ratio of Ce(IV) than the Cyanex 923 in the entire experimental temperature range.

3.2. *Extraction ability comparison*

3.2.1. *Ce(IV) and F(I) extraction from the H_2SO_4 solution with THPO and TOPO*

It can be seen from the above results established that P113 has certain inherent advantages on extraction ability of Ce(IV) compared with Cyanex923. It was reasonably inferred that resulted from the differences in the contents of each component between two extractants. As shown in Fig. 2, THPO content in P113 is more than that in Cyanex923 while TOPO content in P113 is relatively less in comparison with that in Cyanex923. Based on the situation, we speculate that the increasing content of THPO is beneficial to the extraction of Ce(IV). Meanwhile, the relatively less TOPO may also promote the process. For that, the extraction efficiencies of Ce(IV) and F(I) with THPO and TOPO was systematically compared under identical conditions.

The results of Fig. 8 revealed that THPO had a stronger extraction ability than TOPO, which could be explained three reasons: (1) The increase of length of alkyl chain linked to $P = O$ gave rise to the stronger hydrophobicity of extractant molecules, which weakened the extraction capability. Meanwhile, small molecules were liable to keep higher activity at the interface between the two phases, which was greatly conducive to the extraction process [5]. (2) The steric hindrance effect from bulky substituents inhibited the extraction with the increase in the carbon chain length. Though in principle the favorable electronic effect increased in the order of substituents H < Me (methyl) < Et (ethyl). The further extension of the alkyl chain (for instance Pr (propyl)) had no influence on the electronic density of the reaction centers, which may be the substituents longer than ethyl had practically the same electronic properties as ethyl [35–38]. (3) Additionally, to further understand the effect of alkyl substituents of extractants on the extraction process, a theoretical study had been performed based on the density functional theory (DFT) and polarizable continuum models (PCM), and the detail was presented in calculation sections of Supplementary Material. In terms of the chemical structures of four components that made up two extractants, they had the same functional group, $P = O$. Therefore, the bond energy between $P = O$ and Ce(IV) was almost identical for the four components. While the difference of extraction energy was primarily caused by the phase transfer process. The calculation results revealed that the phase transfer energy of THPO, DHMOPO, DOMHPO, TOPO was 27.17, 27.45, 27.98, 28.45 kJ mol^{-1}, respectively, and the phase transfer energy of their corresponding extracted complexes was 96.15, 97.73, 98.51 and 99.39 kJ mol^{-1}, respectively. Obviously, the compound with longer alkyl chain was more difficult to transfer the Ce(IV) from aqueous phase to organic phase, which agreed well with the experimental results shown in Fig. 8.

Compared with TOPO, the increase in the extraction ability of THPO can be attributed to the weaker hydrophobicity and steric hindrance effect of the straight chain of hexyl as well as lower phase transfer energy of THPO. To sum up, THPO played a relatively decisive role in the extraction process, and further corroborated superior extraction performances of P113 based on structural effect.

3.2.2. *Ce(IV) and F(I) extraction from the H_2SO_4 solution with Cyanex923-THPO/TOPO*

To further confirm the above statement, different proportions of THPO or TOPO were added to Cyanex923 to indirectly obtain several TRPO (trialkyl phosphine oxide)-type extractants with different proportions of components. The contents of each component at different molar ratios of Cyanex923-THPO/Cyanex923-TOPO were listed in Table 1 and Table 2. Then the variation trend of extraction efficiency of these extractants with different compositions was observed. The results of Fig. 9 demonstrated that extraction ratio of binary mixed extractants toward Ce(IV) was weakened with the decrease of proportion of THPO. On the contrary, the extraction efficiency advanced with the decrease of proportion of TOPO. This phenomenon can be explained by the fact that THPO had a greater extraction affinity than TOPO for Ce(IV), which absolutely conformed to above speculation. Meanwhile, the superior extraction capability of P113 to Ce(IV) was explained from the side.

Table 1
The contents of each component at different molar ratios of Cyanex923-THPO.

[Cyanex923]:[THPO]	THPO	DHMOPO	DOMHPO	TOPO
0:10	100%	—	—	—
2:8	81.6%	6.2%	8.4%	2.8%
4:6	63.2%	12.4%	16.8%	5.6%
6:4	44.8%	18.6%	25.2%	8.4%
8:2	26.4%	24.8%	33.6%	11.2%
10:0	8%	31%	42%	14%

Table 2
The contents of each component at different molar ratios of Cyanex923-TOPO.

[Cyanex923]:[TOPO]	THPO	DHMOPO	DOMHPO	TOPO
0:10	—	—	—	100%
2:8	1.6%	6.2%	8.4%	82.8%
4:6	3.2%	12.4%	16.8%	65.6%
6:4	4.8%	18.6%	25.2%	48.4%
8:2	6.4%	24.8%	33.6%	31.2%
10:0	8%	31%	42%	14%

3.2.3. *FT-IR study*

The prepared organic phases were characterized by comparing the FTIR spectra of mixed extractants with different proportion. In this study, the vibrational spectra were obtained in Fig. 10(a), curves n_1–n_6 corresponded to the IR spectra of Cyanex923-THPO with various molar ratios. Fig. 10(b) presented the enlarged view of $P = O$ band of different organic phases. The band at 1150.94 cm^{-1} was attributed to the $P = O$ stretching vibration of THPO. Obviously, the FTIR band of $P = O$ stretching vibration slightly shifted to higher frequency from 1150.94 to 1158.42 cm^{-1} with the variation of the THPO molar fraction from 1.0 to 0 with the fixed total concentration of 0.1851 mol L^{-1}. Accordingly, we presumed that there existed certain interaction between Cyanex923 and THPO molecules. Also, the FTIR band of $P = O$ stretching vibration in Fig. 11 shifted by 13 cm^{-1} from 1145.83 cm^{-1} to 1158.42 cm^{-1} (curve n_1 and n_6). Considering the reason for the remarkable blueshift of $P = O$ stretching vibration was probably because of the interaction between Cyanex923 and TOPO.

3.2.4. *NMR spectroscopy analysis*

High-resolution nuclear magnetic resonance (NMR) spectroscopy is a powerful tool to obtain information of phosphorus spectrum in detail. ^{31}P NMR spectra of the mixed extractants with different molar ratios were characterized to verify the interaction between Cyanex923 and THPO/TOPO. As indicated by the results from Fig. 12 and Fig. 13 that chemical shift of ^{31}P accordingly changed with variation of composition of the mixed extractants, which was consistent with FTIR results and provided further evidence about the interaction between Cyanex923 and THPO/TOPO.

3.3. *Saturation capacity and interfacial phenomenon*

Generally, the saturation capacity is defined as the maximum amount of target ions concentration that an extractant can uptake under

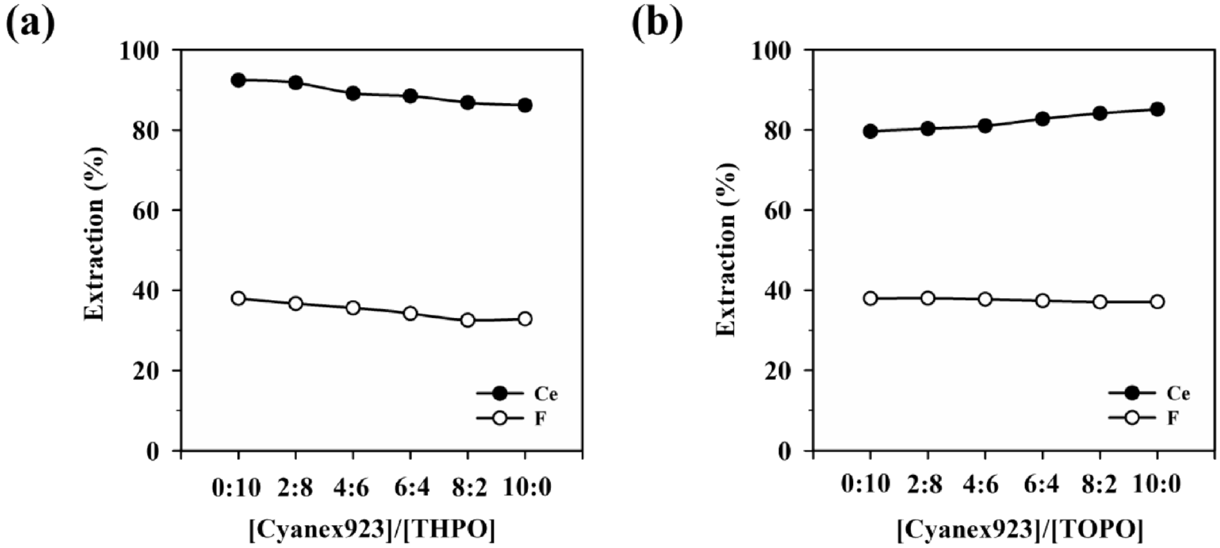

Fig. 9. Effect of different molar ratios on the extraction of Ce(IV) and F(I) of binary extractants, (a) [Cyanex923] + [THPO] = 0.1851 mol L^{-1}, [Ce^{4+}] = 0.02079 mol L^{-1}, [F^-] = 0.03595 mol L; (b) [Cyanex923] + [TOPO] = 0.1851 mol L^{-1}, [Ce^{4+}] = 0.01984 mol L^{-1}, [F^-] = 0.03589 mol L^{-1}, [H_2SO_4] = 2 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

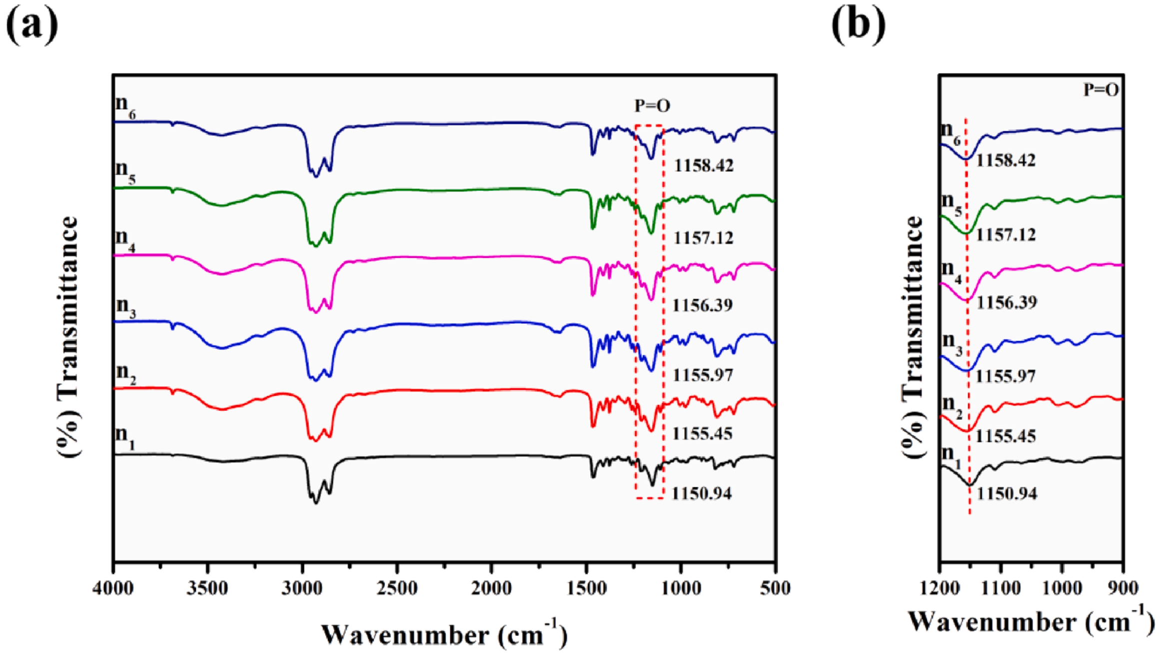

Fig. 10. FTIR spectra of the organic phases in different molar ratios, (a) n_1: [Cyanex923]: [THPO] = 0: 10; n_2: [Cyanex923]: [THPO] = 2: 8; n_3: [Cyanex923]: [THPO] = 4: 6; n_4: [Cyanex923]: [THPO] = 6: 4; n_5: [Cyanex923]: [THPO] = 8: 2; n_6: [Cyanex923]: [THPO] = 10: 0; (b) Enlarged view of P = O region.

the specified condition, which is a key parameter to evaluate industrial applicability of novel extractant. Therefore, the saturation capacity of 30 vol% extractant (0.8414 mol L^{-1}) was determined through successively contacting organic phase with the fresh aqueous solution containing 0.06502 mol L^{-1} Ce(IV) and 0.07883 mol L^{-1}F(I) at fixed O/A phase ratio of 1:1 (15 mL: 15 mL) for each experiment. The results were shown in Fig. 14 that the saturation capacity of P113 for Ce(IV) and F(I) was 44.0 g L^{-1} and 2.8 g L^{-1}, respectively. Apparently, P113 had approximately 10 g L^{-1} higher than that of Cyanex923 for Ce(IV) in same conditions. The possible explanation can be concluded that P113 contained more THPO which has stronger extraction ability for Ce(IV). As evinced through the experiment phenomenon that the new system still maintained clear phase interface during the extraction process.

3.4. Reductive stripping study

Stripping is a crucial property to evaluate the reusability of the extractant. Ce(IV) and F(I) from the loaded organic phase completely transfer into the aqueous phase can regenerate the extractant. Therefore, the stripping property of novel system was investigated. Ce(IV) may be stripped by reducing into Ce(III) from the organic phase due to the weaker interaction between Ce (III) and P113 in H_2SO_4 medium. Generally, H_2O_2 was selected as the reductive reagent and H_2SO_4 medium was added to control the acidity according to our previous work [32]. Therefore, the effect of H_2O_2 concentration on the stripping of Ce (IV) and F(I) was systematically explored. The results of Fig. 15 revealed that Ce(IV) could be completely stripped under experimental conditions, while the unstripped F(I) may be due to that some F^- ions were strongly

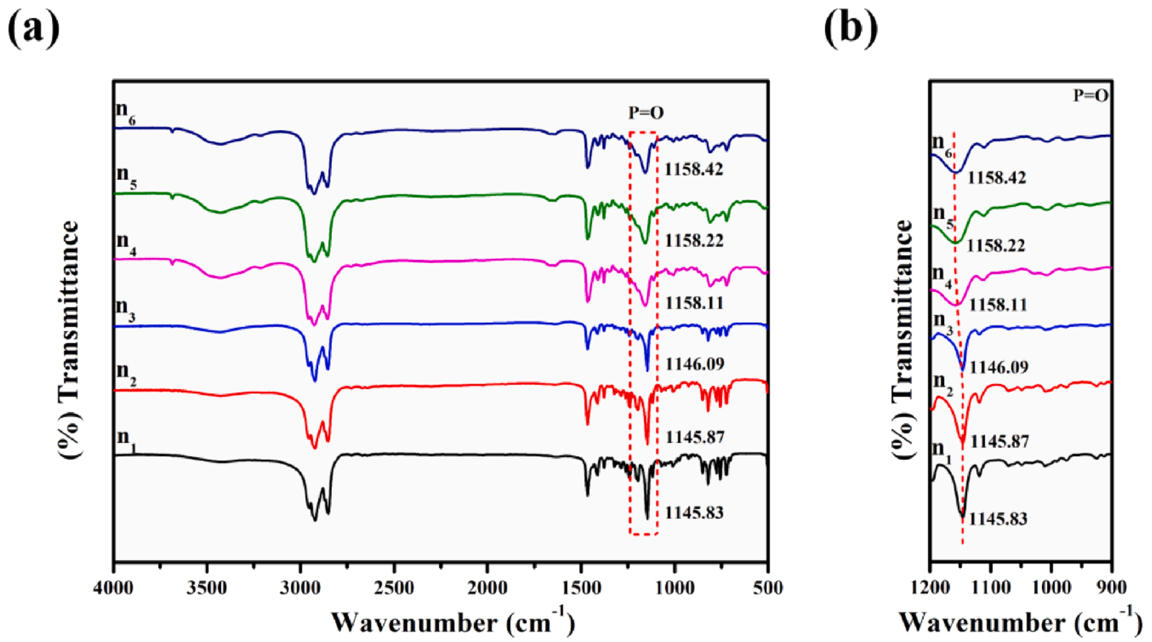

Fig. 11. FTIR spectra of the organic phases in different molar ratios, (a) n_1: [Cyanex923]: [TOPO] = 0: 10; n_2: [Cyanex923]: [TOPO] = 2: 8; n_3: [Cyanex923]: [TOPO] = 4: 6; n_4: [Cyanex923]: [TOPO] = 6: 4; n_5: [Cyanex923]: [TOPO] = 8: 2; n_6: [Cyanex923]: [TOPO] = 10: 0; (b) Enlarged view of P = O region.

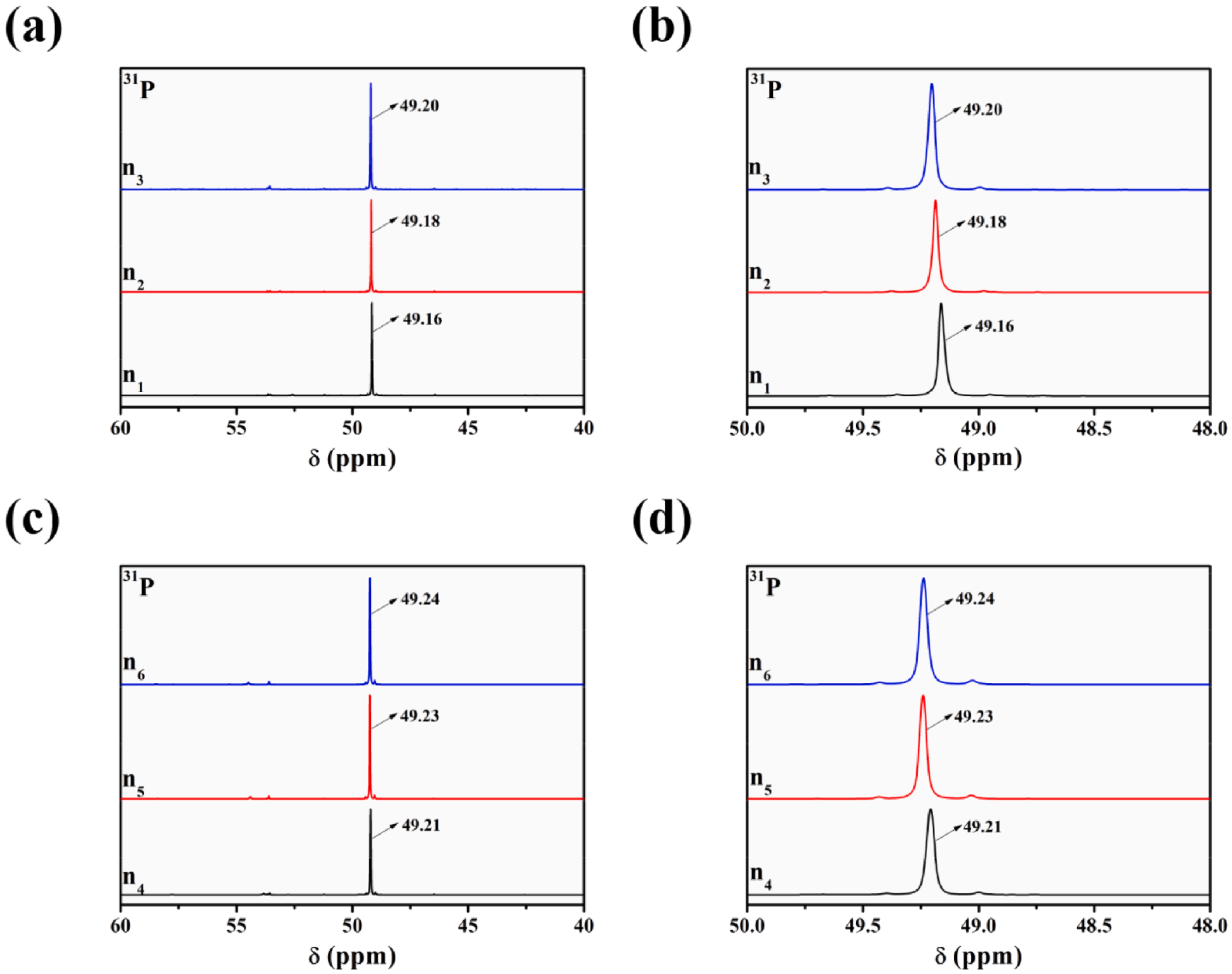

Fig. 12. ^{31}P NMR spectra of the organic phases in different molar ratios and corresponding enlarged view, (a) n_1: [Cyanex923]: [THPO] = 0: 10; n_2: [Cyanex923]: [THPO] = 2: 8; n_3: [Cyanex923]: [THPO] = 4: 6; (b) Enlarged view of phosphorus spectrum in (a); (c) n_4: [Cyanex923]: [THPO] = 6: 4; n_5: [Cyanex923]: [THPO] = 8: 2; n_6: [Cyanex923]: [THPO] = 10: 0; (d) Enlarged view of phosphorus spectrum in (c).

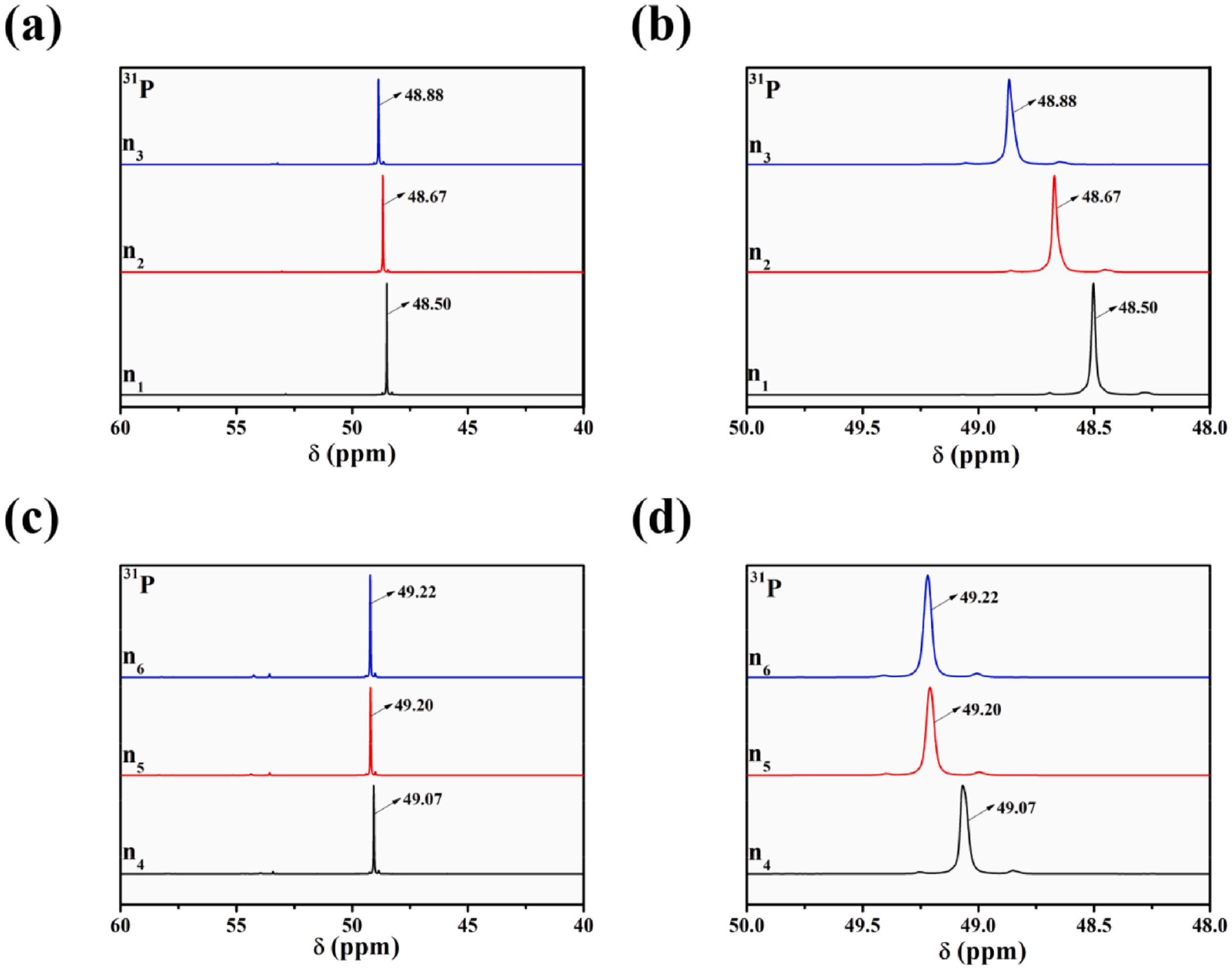

Fig. 13. ^{31}P NMR spectra of the organic phases in different molar ratios as well as corresponding enlarged view, (a) n_1: [Cyanex923]: [TOPO] = 0: 10; n_2: [Cyanex923]: [TOPO] = 2: 8; n_3: [Cyanex923]: [TOPO] = 4: 6; (b) Enlarged view of phosphorus spectrum in (a); (c) n_4: [Cyanex923]: [TOPO] = 6: 4; n_5: [Cyanex923]: [TOPO] = 8: 2; n_6: [Cyanex923]: [TOPO] = 10: 0; (d) Enlarged view of phosphorus spectrum in (c).

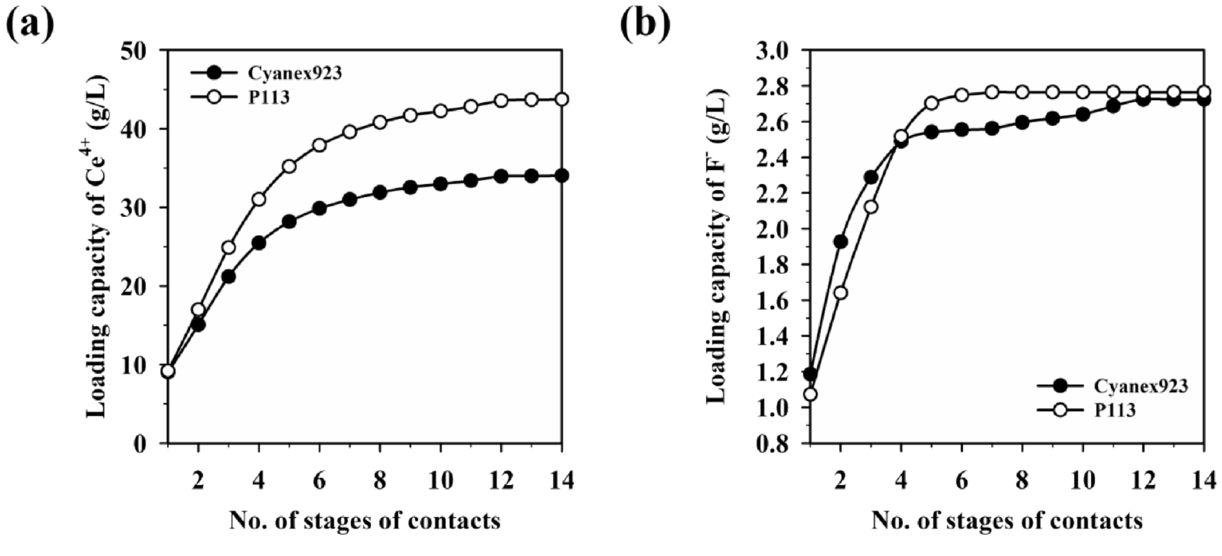

Fig. 14. Saturation capacity of Ce(IV) and F(I) in H_2SO_4 solution, [L] = 0.8414 mol L^{-1}, [Ce^{4+}] = 0.06502 mol L^{-1}, [F$^-$] = 0.07883 mol L^{-1}, [H_2SO_4] = 1.5 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

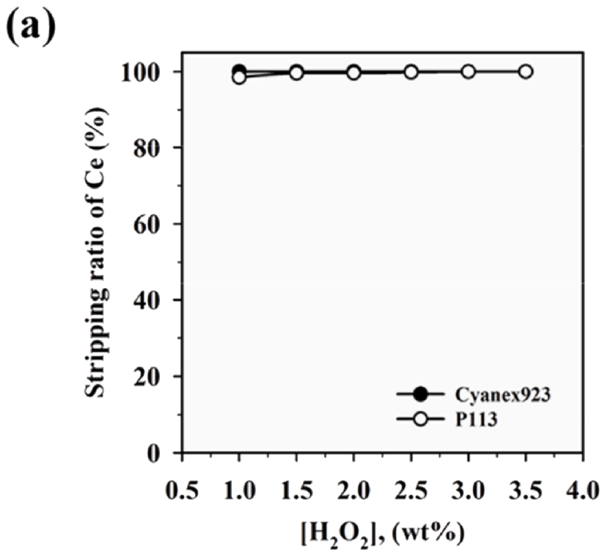

Fig. 15. Stripping ratio of Ce(IV) and F(I) from loaded organic phase as a function of the H_2O_2 concentrations, $[H_2SO_4] = 3$ mol L^{-1}, O/A = 1: 2, T = 298 K and t = 30 min.

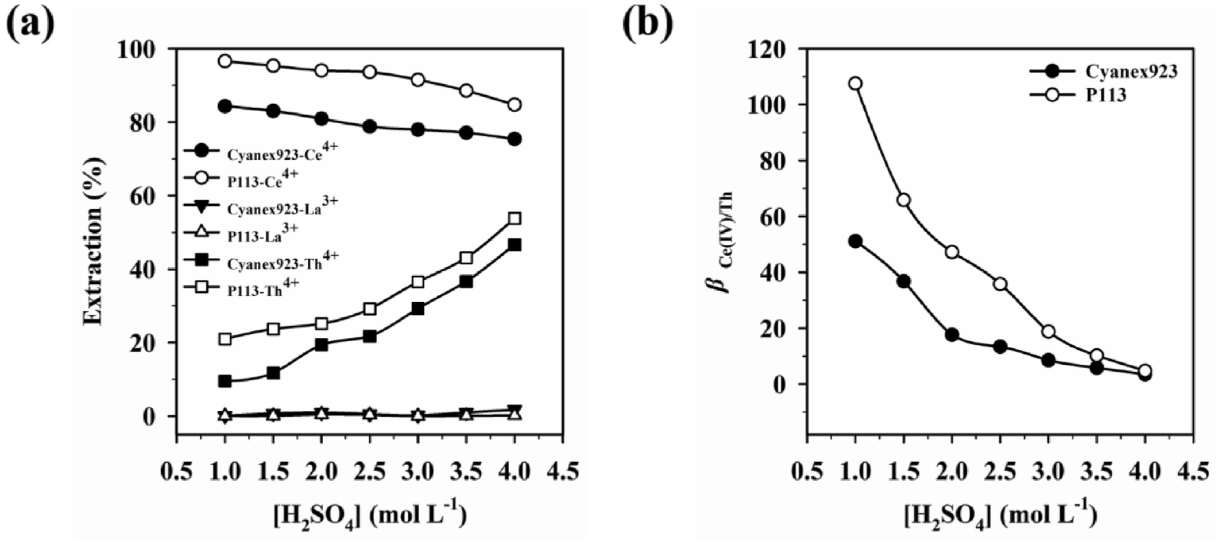

Fig. 16. (a) Extraction ratios of Ce(IV), Th(IV) and RE(III) and (b) separation factor of $\beta_{Ce(IV)/Th(IV)}$ under different acidity conditions, [L] = 0.12 mol L^{-1}, [Ce(IV)] = 0.01473 mol L^{-1}, [Th(IV)] = 0.005312 mol L^{-1}, [La(III)] = 0.005967 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

trapped by the organic phase due to its small ionic radius and low hydration energy. To improve stripping efficiency of F(I), the stripping rate could reach 100% after two times of stripping under the same conditions.

3.5. Selectivity over associated ions

The separation of Ce(IV) from bastnaesite ($REFCO_3$) was always interfered by some associated ions. Considering the similar property between trivalent light rare earth elements (LREEs), lanthanum (La(III)) was chosen for a representative of LREEs for subsequent studies. Therefore, the effect of associated ions (e.g., La(III), Th(IV)) on the separation of Ce(IV) should be taken into account, which had practical significance for the practical application of P113. Whereafter, the extraction ratios of Ce(IV), Th(IV) and RE(III) with P113 under different acidities were investigated and compared with that of Cyanex923. It can be seen from the results shown in Fig. 16(a) that the sequence of extractability of relevant ions using P113 was followed as: Ce(IV) > Th (IV) > > RE(III). Almost no RE(III) was extracted into organic phase in presence of Ce(IV), indicating the excellent selectivity of P113 toward Ce(IV)/RE(III). Moreover, P113 had significant superiority in selectivity compared with Cyanex923, and the separation factor of Ce(IV)/Th(IV)

Table 3
Chemical compositions of the H_2SO_4 leaching solution of bastnaesite and corresponding raffinate, g L^{-1}.

Element	CeO_2	TCeO	F	ThO_2	La	Pr	Nd	H+/M
Liquor	49.09	50.25	7.79	0.27	19.61	2.99	7.34	4.0
Raffinate-Cyanex923	14.67	/	5.54	0.23	19.59	2.98	7.33	3.99
Raffinate-P113	12.70	/	5.62	0.24	19.60	2.98	7.33	3.99

was increased from 17 to 47 at H_2SO_4 concentration of 2 mol L^{-1} as shown in Fig. 16(b). Based on these, P113 was qualified in the separation of Ce(IV)/RE(III) as well as Ce(IV)/Th(IV) from the bastnaesite as a decent extractant.

Table 4
Comparison of saturation capacity between P113 and Cyanex923 from H_2SO_4 leaching liquor of bastnaesite, g L^{-1}.

Element	Ce(IV) loaded capacity, g/L					F(I) loaded capacity, g/L				
Time	1	2	3	4	Total	1	2	3	4	Total
Cyanex923	23.87	9.21	2.90	0.51	36.49	2.25	0.47	0.3	0.04	3.06
P113	25.84	14.08	4.46	1.43	45.81	2.17	0.45	0.32	0.03	2.97

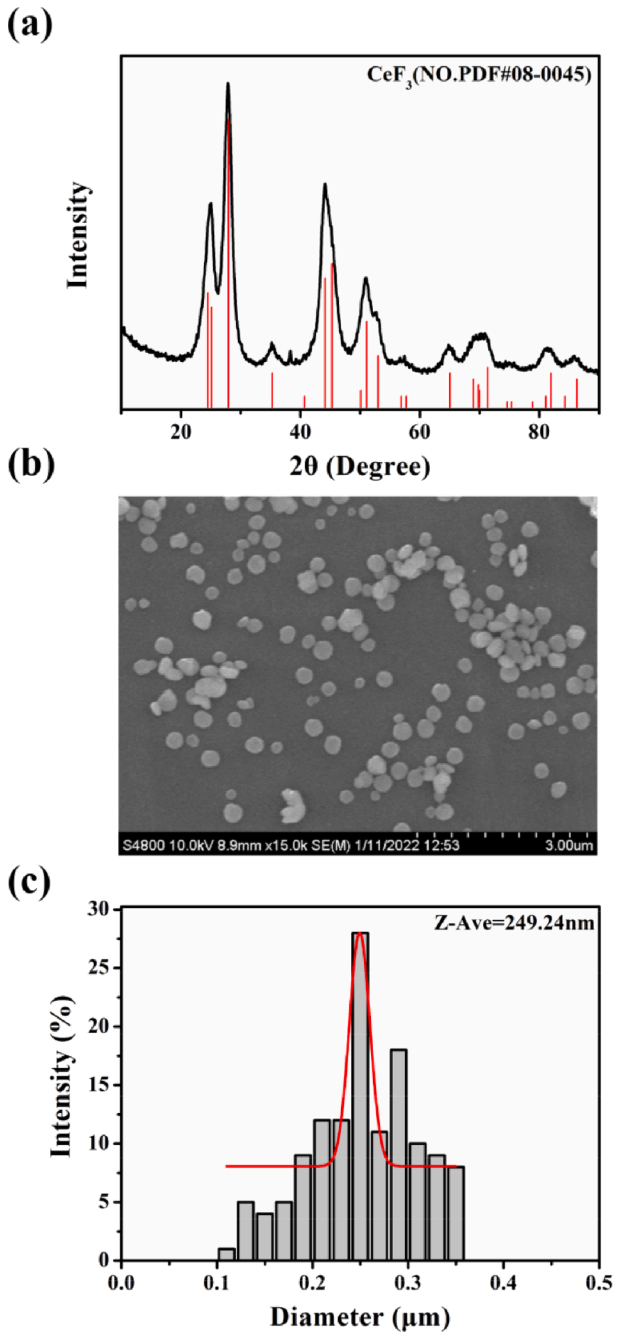

Fig. 17. Practical application with P113 for the recovery of Ce(IV) and F(I) from H_2SO_4 leaching liquor of bastnaesite. (a) XRD spectrum of stripping product; (b) SEM images of the CeF_3 nanoparticle; (c) Size distribution of CeF_3 nanoparticle. [L] = 0.90 mol L^{-1}, [Ce^{4+}] = 0.2852 mol L^{-1}, [F^-] = 0.41 mol L^{-1}, [H_2SO_4] = 2.0 mol L^{-1}, O/A = 1: 1, T = 298 K and t = 30 min.

3.6. *Practical application-recovery of Ce(IV) and F from bastnaesite*

To gain a profound understanding on the potential industrial value of synthetic P113 in practical application, we carried out systematic studies on the separation and recovery of Ce(IV) and F(I) from H_2SO_4 leaching liquor of bastnaesite. Bastnaesite was kindly provided by Mianning Fangxing Rare Earth Company and handled through oxidation roasting and sulfuric acid leaching method. Firstly, bastnaesite was placed in a muffle furnace with a temperature of 500 ℃ for 2 h, and the roasted product was kept acid leaching with 2.5 mol L^{-1} H_2SO_4 at 80 ℃ for 30 min, liquid solid ratio was 8 [39]. The obtained H_2SO_4 liquor was mingled with 30 vol% (0.90 mol L^{-1}) extractant. Table 3 listed the main compositions of sulfuric acid leaching solution and corresponding raffinate. The single-stage extraction efficiencies of P113 for Ce(IV) and F (I) were calculated to be 74.13% and 27.86%, respectively. Meanwhile, P113 performed excellent selectivity between Ce(IV) and associated ions. LREEs(III) was hardly extracted by organic phase, and the separation factor of Ce(IV)/Th(IV) increased from 16 to 27 compared with Cyanex923 at 2.0 mol L^{-1} H_2SO_4 from practical liquor of bastnaesite. Additionally, P113 embodied higher saturation capacity for Ce(IV) as shown in Table 4.

Ce(IV) and F(I) could be reductively stripped using 3% H_2O_2 solution from loaded organic phase as a product of CeF_3 powder which has been widely used in inorganic scintillating crystal, optoelectronics and solid lubricant etc. The X-ray diffraction spectrum verified that the main phase of the stripping product was CeF_3 (No. PDF#08–0045) (Fig. 17 (a)), and SEM image presented the morphology of product as spherical particles with nanoscale (Fig. 17(b)). Also, Fig. 17(c) revealed a smaller size distribution (ZAve = 249.24 nm) of the CeF_3 product. To sum up, synthetic novel extractant successfully recovered Ce(IV)-F(I) and separated Th(IV) from light rare earth resources, suggesting the high potential application value.

3.7. *Reusability of extractant*

Whether the extractant can be recycled is an important parameter to evaluate economic feasibility. Therefore, the reusability of P113 was further explored. The actual H_2SO_4 leaching solution of bastnaesite was selected as aqueous phase. Five cycles of experiments of extraction and stripping was carried out using 3 mol L^{-1} H_2SO_4 + 3% H_2O_2 as stripping agent. As can be seen from Fig. 18(a) that extraction efficiency of P113 still remained at the initial level after five cycles treatment, and P113 presented stronger extraction ability of Ce(IV) over Cyanex923 in actual liquor of bastnaesite. Fig. 18(b) depicted the excellent reusability of P113. Above results demonstrated the superiority of P113 towards industrial application in the future.

4. Conclusion

In conclusion, P113 was introduced as an outstanding performance novel extractant that is effective for the extraction of Ce(IV)-F(I) and the separation over Th(IV) in H_2SO_4 medium. Compared with Cyanex923,

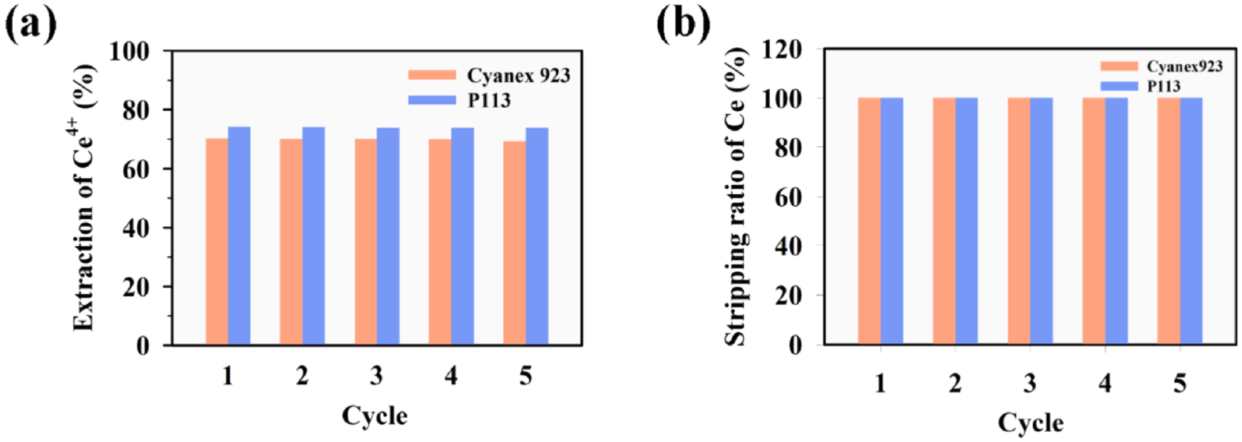

Fig. 18. (a) Extraction of Ce(IV) from H_2SO_4 leaching liquor of bastnaesite, [L] = 0.90 mol L^{-1}, [Ce^{4+}] = 0.2852 mol L^{-1}, [F^-] = 0.41 mol L^{-1}, [H_2SO_4] = 2.0 mol L^{-1}, O/A = 1: 1; (b) Stripping: 3 mol L^{-1} H_2SO_4 + 3% H_2O_2 as stripping agent, O/A = 1: 2, T = 298 K and t = 30 min.

the P113 synthesized using an environmentally benign scheme had a significant improvement in extraction efficiency, selectivity and saturation capacity due to the change of contents of each component (higher content of THPO). In addition, P113 had favourable reusability and interfacial phenomenon even after five cycles. As a novel extractant, P113 was qualified in recovering Ce(IV)-F(I) and separating Th(IV) from the H_2SO_4 leaching liquor of bastnaesite, which held significant value for comprehensive utilization of resources and environmental protection. Finally, this study provided useful information for the relationship between structure of straight chain trialkyl phosphine oxide (TRPO)-based extractants and their extraction abilities, and will promote industrial applications of the novel extractant.

CRediT authorship contribution statement

Mingyang Liu: Conceptualization, Methodology, Validation, Data curation, Writing – original draft, Investigation, Visualization, Writing – review & editing. **Dan Zou:** Writing – original draft, Funding acquisition, Methodology, Methodology. **Donghai Yu:** Funding acquisition. **Shaoji Xiang:** Methodology. **Yuefeng Deng:** Methodology. **Ji Chen:** Writing – review & editing, Supervision, Funding acquisition, Project administration. **Jichang Xiao:** Writing – review & editing, Supervision, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.123909.

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