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Extraction and recovery of cerium(IV) and thorium(IV) from sulphate medium by an α-aminophosphonate extractant†

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Abstract: In the present work, a novel α-aminophosphonate extractant (Cextrant 230) was synthesized for the extraction and recovery of cerium and thorium from sulphate medium. The introduction of amine group into the phosphate molecule would enhance the extraction of Ce(IV) and Th(IV). The effects of extractant concentration, H_2SO_4 concentration and temperature on the metal extraction were investigated in detail. It was found that the extraction of Ce(IV), Th(IV) and REs (La, Gd, Yb) in sulphate medium decreased in the following order: Ce(IV)>Th(IV)>REs(III). A solvent extraction process to extract and recover cerium and thorium from bastnasite leaching was proposed, in which the purities of cerium and thorium products reached 99.9% and 99% with yield of 92% and 98%, respectively.

Keywords: thorium; rare earths; α-aminophosphonates; solvent extraction; separation

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Rare earths are a kind of important and strategic resource in high-tech fields for their excellent optical, magnetic, acoustic and electrical properties[1–2]. Due to the increasing global demand for rare earths, the recovery of rare earths from a variety of resources has drawn great attention in the world[3,4]. Among a large number of rare earth minerals, only four are economically used for rare earth commercial production, i.e., bastnasite ((RE)(CO_3)F), monazite ((RE)PO_4), xenotime (YPO_4) and RE-bearing clay[5,6]. Panxi bastnasite is an important rare earth resource in China which contains about 50 wt.% cerium, 0.2 wt.%–0.3 wt.% thorium and 8 wt.%–10 wt.% fluorine[7]. At present, the process with the procedures of oxidizing roasting, hydrochloric acid selected leaching and solvent extraction is widely used in the bastnasite metallurgy[8,9]. However, there are some problems found in the industrial practice such as low recovery and purity of rare earths, pollution arising from the storage of radioactive precipitate and the fluorine-containing wastewater.

In order to overcome the drawbacks mentioned above and improve comprehensive utilization of bastnasite resources, Li et al.[10,11] invented a metallurgical process based on a commercially available extractant Cyanex 923 for the extraction and separation of Ce, F, Th and REs from Panxi bastnasite. Cyanex 923 was used to extract Ce(IV) and F(I) from the sulphuric acid leaching. And then the loaded cerium(IV) can be stripped by some reductive reagents and F(I) stripped as CeF_3 nanoparticles. However, Cyanex 923 is more expensive than other commercial extractants such as TBP and P507. Huang et al.[12] investigated the recovery of Ce(IV), Th(IV) and F(I) from sulphuric acid leaching of bastnasite by 2-ethylhexylphosphonic acid mono-(2-ethylhexyl) ester (P507). However, the separation of Ce(IV) from Th(IV) is difficult and the stripping of thorium from the loaded organic phase needs rather high acidity. Thus, it is necessary to develop new efficient extractants[13–15].

Recently, aminophosphonate compounds have attracted attention of researchers, and been widely used as anticancer agents, herbicides, antibacterial, extractants, etc.[16–20], α-aminophosphonic oxide showed superior extractive properties[21] over the corresponding phosphonate compounds. For example, bis(dihexylphosphinylmethyl) octylamine[18] was employed for the extraction of rare earths[22]. High selectivity for the extraction of Sc(III) ion from the ions of satellite metals was found. There are some advantages of this kind of extractants such as easy synthetic route, high thermal stability, low emulsifying ability during extraction, and high extraction capacity of metal ions.

However, the solvent extraction and separation of cerium, thorium and rare earths with aminoalkylphosphoryl compounds has not been studied. Our group designed and synthesized a novel extractant (shown in Fig. 1) for the extraction of Ce(IV), Th(IV) and RE(Ⅲ) from sul-

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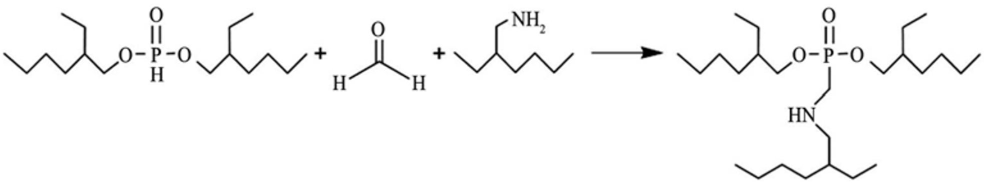

Fig. 1 Scheme for the synthesis of the extractant Cextrant 230
Cextrant 230: di(2-ethylhexyl) [N-(2-ethylhexyl)aminomethyl]phosphonate

phuric acid medium. This new extractant can be easily synthesized[23] with a high yield by the Kabachnik-Fields reaction of bis(2-ethylhexyl)hydrogen phosphite, paraform and 2-ethylhexylamine. Here we presented the extraction and stripping behavior of Ce(IV) and Th(IV) by this new extractant and discussed the separation properties of Ce(IV), Th(IV) from REs(III) from sulphuric acid leaching of roasted bastnasite.

1 Experimental

1.1 Reagents and apparatus

Bis(2-ethylhexyl)phosphite was kindly supplied by Shang Hai Rare-earth Chemical Co., Ltd., China and used without further purification. All other chemical reagents were of reagent grade. Standard solutions of rare earths and thorium were prepared by dissolving corresponding oxides (99.99%) with concentrated sulphuric acid. All work solutions were obtained by appropriate dilution of the standardized stock solutions. The extractant was dissolved in n-heptane to the required concentrations.

The metals were analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optimal 8000). FT-IR spectra (KBr pellets) were obtained on a Bruker Vertex 70 spectrometer. ^{1}H-NMR spectra were performed on a Bruker AV 400. Elemental analyses were carried out on a varioEclube machine. pH measurement was processed with a model PHS-3C digital pH meter made by Shanghai REX Instrument Factory. Mass spectra were recorded on a Bruker Daltonics Flex Analysis instrument.

1.2 Synthesis of the extractant

Fig. 1 presents a synthetic scheme[23] for di(2-ethylhexyl)[N-(2-ethylhexyl)amino methyl] phosphonate (Cextrant 230). The mixed solution of 2-ethylhexylamine (50 mmol, 6.45 g), bis(2-ethylhexyl)phosphite (50 mmol, 15.30 g), paraformaldehyde (52.5 mmol, 1.58 g) and *p*-toluenesulfonic acid (100 mg) in toluene were refluxed with a Dean-Stark trap until water no longer released. At the end of the reaction, 0.5 g K_2CO_3 was added in the solution and refluxed for 15 min. The mixture was washed with HCl (1 mol/L) to remove unreacted catalyst and then washed with water for three times. Then the organic phase was removed by rotary evaporation after drying with anhydrous magnesium sulphate. Yield: 80%. GC-MS: 447; ^{1}H-NMR (400 MHz, $CDCl_3$): 0.89(t, 18H, CH_3), 1.29–1.37 (m, 24H, CH_2), 1.70–1.57 (m, 3H, CH), 2.87 (d, 2H, CH_2), 3.37 (d, 2H, CH_2), 4.03 (t, 4H, CH_2). IR (KBr): 1250, 1014 cm^{-1}.

1.3 Extraction procedures

The solvent extraction experiments were carried out in temperature-controlled shaker bath for 30 min at 298 K (unless stated), which was sufficient to reach equilibrium. Both of the volumes of organic and aqueous phases in tube were 5 mL. After phase separation, the concentration of rare earths in the aqueous phase was determined by ICP-OES and the concentration of metals in organic phase was obtained by mass balance:

$$[M]_{(o)}=[M]_{ini}-[M]_{(a)} \tag{1}$$

"o" , "a" and "ini" represent organic, aqueous and initial, respectively.

1.4 Elution of the loaded thorium

After extraction, a majority of rare earths were transferred into the organic phase at proper condition. The loaded organic phase was equilibrated with nitric acid of different concentrations. The mixtures were shaken at 298 K for 30 min. After the split of the phases by gravity, the metal concentration in the aqueous phase was quantified to evaluate the stripping ratio.

$$St=\frac{[M]_{(a)}}{[M]_{(o,\ ini)}}\times 100\% \tag{2}$$

2 Results and discussion

2.1 Extraction of Ce(IV), Th(IV) and other REs(III) using Cextrant 230

The effect of sulfuric acid concentration on the extraction of Ce(IV), Th(IV) and other RE(III) (RE=La, Gd, Yb) was investigated and the results are shown in Fig. 2. Compared with the extractant DEHEHP which also has two P–O bonds and one P–C bond and exhibits poor extraction properties towards cerium(IV) in sulphate medium[24], Cextrant 230 exhibits stronger extraction ability towards cerium(IV), which would be attributed to the fact that the introduced nitrogen element in Cextrant 230 would be involved into the coordination of metals. With the increasing of the sulfuric acid concentration, the extraction of cerium decreased slowly and that of thorium