



Selective extraction and separation of thorium from rare earths by a phosphorodiamidate extractant



Youcai Lu^{a,b}, Haiqin Wei^{a,b}, Zhifeng Zhang^a, Yanling Li^a, Guolong Wu^a, Wuping Liao^{a,*}

^a State Key Laboratory of Rare Earth Resource Utilization, ERC for the Separation and Purification of REs and Thorium, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 6 December 2015

Received in revised form 7 March 2016

Accepted 21 April 2016

Available online 23 April 2016

Keywords:

Thorium

Rare earths

Phosphorodiamidate

Solvent extraction

Separation

ABSTRACT

A novel phosphorodiamidate extractant has been designed and synthesized for the extraction and separation of thorium from rare earths. By introducing nitrogen element into the phosphate, the electron density of the P=O group in this novel extractant was increased, which would exhibit stronger affinity for the metals. The extraction of thorium in different mediums such as nitric acid, hydrochloric acid and sulfuric acid was investigated and the extraction of thorium with different extractants such as Cyanex923, TBP and DEHEHP was also compared. Thorium extraction in nitrate medium was more efficient, which indicates the novel extractant can be used to selectively extract and separate thorium from rare earths in nitrate medium. The stoichiometry of the extracted species of thorium was determined to be $\text{Th}(\text{NO}_3)_4 \cdot 2\text{L}$ and the thermodynamic functions ΔH , ΔG and ΔS were calculated. Furthermore, the extraction capacity of this new extractant toward thorium and the stripping of loaded thorium from the organic phase were studied.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Thorium is a potential nuclear fuel because ^{232}Th can convert to ^{233}U by absorbing slow neutrons (Ashley et al., 2012). Commonly, thorium is associated with rare earth elements which are some important elements for advanced materials and high technology industries (Du et al., 2009; Shen et al., 2009). For instance, the rare earth ores such as monazite and bastnaesite may contain thorium. Thus, the extraction and separation of thorium and rare earths have attracted considerable attentions due to the elimination of radioactive pollution caused by thorium and the wide usage of rare earths (Jain et al., 2001). Solvent extraction is a major technique for the separation of thorium and rare earths in industry due to its advantages such as straightforward continuous operation, high separation efficiency and simple equipment. Various extractants such as amines (Elyamani and Shabana, 1985; Ejaz, 1976; Li et al., 1987), neutral organophosphorus (Gupta et al., 2002; Pathak and Argekar, 1992) and acidic organophosphorus compounds (Dinkar et al., 2012; Wang et al., 2013a) have been developed for the extraction and separation of thorium and rare earths. For instance, Gupta et al. (2002) reported the potential application of Cyanex923 for the separation of thorium and lanthanides, Wang et al. (2013b) discussed the preparation of high-purity thorium with DEHEHP in nitrate medium. Singh et al. (2001) studied the extraction of

thorium by 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEHEHP) in nitrate medium. Tong et al. (2013) studied the synergistic effects of the mixtures of acidic organophosphorus extractants such as HEHEHP and DEHPA and neutral organophosphorus extractant Cyanex923 toward thorium. The amine extractants also exhibited high selective extraction toward thorium. Li et al. reported the extraction and separation of thorium and rare earths by primary amine N1923 in sulfate medium and successfully applied this technique to Panxi bastnaesite (Liu et al., 2008; Li et al., 2004; Li et al., 1987).

However, these extractants have some disadvantage such as high price of Cyanex923, complex chelates for primary amine, and high stripping acidity for HEHEHP (Wang et al., 2013a). Therefore, to explore some more efficient extractants is still a challenge (Turanov et al., 2014; Ren et al., 2014; Lu et al., 2013; Chu et al., 2014; Zuo et al., 2008). In the previous work, we synthesized a series of calixarene derivatives modified by neutral phosphonate groups on the upper rim (Lu et al., 2013; Li et al., 2012), carboxyl acid groups on the lower rim (He et al., 2008) and sulfonyl group on the bridge (Sun et al., 2013) for the extraction and separation of thorium and trivalent rare earths. All these extractants exhibit good extraction ability. However, the syntheses are more complicated which leads to difficult mass production. At the present work, a novel extractant (**L**, shown in Fig.1) is designed and synthesized for the separation of thorium from rare earths. Since nitrogen has weaker electron withdrawing ability than oxygen, the phosphoryl group of this extractant would exhibit stronger ability to donate its lone pair of electrons than those in other neutral phosphorus extractants with three P—O bonds such as TBP (Xu and Yuan, 1987).

* Corresponding author.

E-mail address: wpliao@ciac.ac.cn (W. Liao).

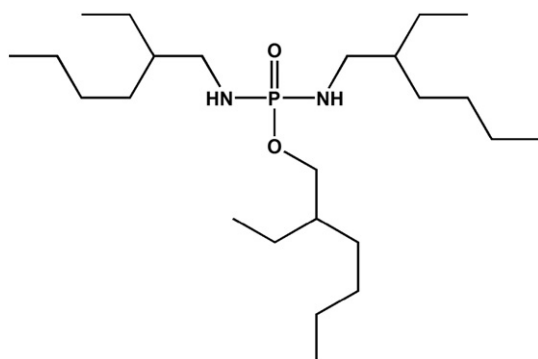


Fig. 1. Molecular structure of novel Extractant (L).

Moreover, this extractant has some advantages such as convenient synthesis, easy obtaining raw materials, high yield and easy industrialization. Here, we studied and compared the extraction of thorium and rare earths by this new extractant in different medium. The extraction stoichiometry, stripping behavior of the loaded organic phase and the extraction capacity of this extractant in nitrate medium were also investigated.

2. Experimental

2.1. Reagents and apparatus

All chemical reagents except **L** were of reagent grade and used without further purification. All work solutions were obtained by appropriate dilution of the standardized stock solutions. The extractant was dissolved in *n*-heptane to the required concentrations. Standard solutions of metal ions were prepared by dissolving corresponding oxides (99.99%) with concentrated nitric acid and diluting with distilled water.

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. ¹H NMR spectra were performed on a Bruker AV 400. Mass spectra were recorded on a Bruker Daltonics Flex Analysis instrument. pH measurement was processed with a model PHS-3C digital pH meter made by Shanghai REX Instrument Factory.

2.2. Synthesis of the extractant

2-ethylhexyl-N,N'-di(2-ethylhexyl) phosphordiamidate (**L**) was synthesized by a similar method to that described in a previous article (Roth and Lenig, 1982) and the synthetic scheme was shown in Fig. 2. 2-ethyl hexanol (0.1 mol) was added dropwise to phosphoryl chloride (0.1 mol) in dichloromethane (100 mL) below 5 °C. The resulting mixture was slowly warmed to room temperature and stirred for 3 h. The generated HCl gas was removed by vacuuming. After that, the reaction mixture was transferred to a dropping funnel and added slowly to 2-ethylhexylamine (0.4 mol) in 100 mL dichloromethane below 5 °C.

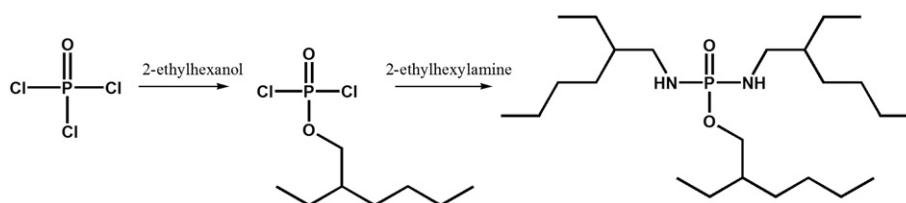


Fig. 2. Scheme for the synthesis of the extractant **L**: 2-ethylhexyl-N,N'-di(2-ethylhexyl) phosphordiamidate.

After complete addition, the reaction mixture was allowed to slowly warm to room temperature and stirred for 4 h. The mixture was washed first with dilute hydrochloric acid twice and then with distilled water until the washing gives no chloride tested. The solvent was removed by rotary evaporation and the residue was dried in vacuum as yellow oil. Yield: 92%. MS: *m/z*, 434.3 (*M* + 2); ¹H NMR (400 MHz, CDCl₃): 0.92 (m, 18H, CH₃), 1.34–1.39 (m, 24H, CH₂), 1.77 (s, 3H, CH), 2.08 (br, 2H, NH), 2.93 (br, 6H, CH₂). IR (KBr): 3230, 1206, 1037 cm⁻¹.

2.3. Procedures

Solvent extraction experiments were carried out in a temperature-controlled shaker bath for 0.5 h at 298 K (unless stated), which was sufficient to reach equilibrium. The volumes of organic and aqueous phases were 5 mL. After phase separation, the concentration of the metal ions in the aqueous phase was determined by ICP-OES and the concentration of metals in organic phase was obtained by mass balance.

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

“o”, “ini” and “a” represent organic, initial and aqueous, respectively.

2.4. Elution of the loaded thorium

After extraction, most of thorium was transferred into the organic phase at proper condition. The organic phase loaded with thorium was equilibrated with different stripping agents at various 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.

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

3. Results and discussion

3.1. Extraction of thorium in different medium

In order to reach higher extraction efficiency, the thorium extraction was studied with the acid concentration ranging from 0.01 mol/L to 7 mol/L in different medium. As shown in Fig. 3, the extraction of thorium from different medium decreases in the order: HNO₃ > HCl > H₂SO₄, which is in according with the increase in the hydration energy of their anions (Xu and Yuan, 1987) and the decrease in the hydrophobicity of the extracted complex. It is obvious that thorium can be completely extracted from nitrate medium in the studied range of acid concentration while there are two minima at 2.5 mol/L H⁺ for chloride medium and 1.5 mol/L H⁺ for sulfate medium, respectively. Similar results have also been observed in the extraction of thorium by raw Cyanex 923 (Gupta et al., 2002; Das et al., 2015). However, compared with the commercial extractant Cyanex 923, this extractant has some advantages such as convenient synthesis, easy obtaining raw materials, high yield and easy industrialization.

Download English Version:

<https://daneshyari.com/en/article/211873>

Download Persian Version:

<https://daneshyari.com/article/211873>

[Daneshyari.com](https://daneshyari.com)