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Separation of Th from leachate of monazite sulphation process using amine solvent extraction

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Astract: The solvent extraction is one of the most common method for separating Th from solution. Primary amine has higher selectivity for the extraction of Th(IV) than U(VI) and RE(III) in sulfate media. N1923 (a primary aliphatic amine with amino nitrogen linked to a secondary carbon consisting of branched alkyl groups in C19–23 range) is commonly used to extract Th. At room temperature using 0.1M N1923 amine as solvent in this work, the results showed that thorium maximum extraction capacity was about 2.5 g/L with concentration of sulfuric acid in the aqueous phase was 1 M and for 3 minutes shaking. At room temperature for 3 minutes shaking the best conditions for scrubbing process was using the mixture of acids H_2SO_4 0.2 M and HNO_3 0.1 M, result inover 75%, Th was scrubbed in the aqueous phase only 0.7%. The separation of Th from leachate of monazite sulphation process was carried out on a multistage continuous flow extraction device (12 boxes), the thorium purity was 98%. Therefore, the use of amine solvents can purify thorium from rare-earth solutions in a sulfate medium.

Keywords: *Monazite, Th, solvent extraction, amine solvent.*

I. INTRODUCTION

Of the 200 best known minerals containing rare earth elements (REEs), only three contain significant amount – bastnasite, monazite and xenotime in which monazite is the second most important source of rare earths. Monazite is a rare earth phosphate mineral containing thorium and uranium as associated metals [1]. The processing of monazite leads to the generation of RE concentrates containing thorium (Th), uranium (U) and phosphate. The sulphation process of monazite generates leachates containing the RE elements, Th and U [2]. Vietnamese monazite is a light rare earth-type phosphate ore and Th consist of 3.8%, of which the sulphation process is similar as [2].

In the conventional solvent extraction processes (i.e., Thorex and Amex process) [2,3], the recovery and separation of uranium and thorium are carried out in various ways after chemical interaction of the mineral with sulfuric acid.

The solvent extraction method is used to separate Th from solution. The agents commonly used for extraction are: tributyl phosphate (TBP), triizoamyl phosphate (TiAP), 2-ethylhexyl- alamine) [4]. Primary amine has higher selectivity for the extraction of Th(IV) than that of U(VI) and RE(III) in sulfate media. Mostly used commercial primary amines are Primene JMT (a primary aliphatic amine with amino nitrogen linked to a tertiary carbon consisting of highly branched alkyl groups in the C16–C22 range) and N1923 (a primary aliphatic amine with

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amino nitrogen linked to a secondary carbon consisting of branched alkyl groups in C19–23 range) [4,5]. In this environment the reactions occur completely and achieve high purity [6].

In the present study, the extraction and separation of thorium from a prepared stock solution containing rare earth and Th sulfate,and from leachate of monazite sulphation process have been investigated using neutral extractant N1923 as solvent.

II. CHEMICALS AND EXPERIMENTAL

A. Chemicals

N1923 was purchased from Shanghai Worldyang Chemical Co., Ltd.China. N1923 0.1 M was prepared by dilution N1923 with AlkanesC13-16, iso (IP2028) and 5% n-decanol. Stock aqueous solutions of thorium(IV) and rare earthswere prepared by dissolving oxides (ThO_2, La_2O_3, CeO_2 and Y_2O_3 with purity over than 99%) in sulfuric acid. The Th, La, Ce and Y concentrations of 13.3, 10.6, 40.9 and 20.0 g/L, respectively, were used as an initial solution for this research. The leachate from monazite sulphation has got composition as a rare earth elements and Th concentration were 52.6 g/L and 5 g/L, respectively.

Apparatus

The concentrations of thorium and rare earths in aqueousphases were determined by inductively coupled plasma opticalemission spectroscopy (ICP-OES) analyzer (Horiba, Japan). Mechanical shaker was used to mix organic and aqueous phases.A continuous multistage upflow consists of 12 boxes, with 15 L/box volume.

B. Experimental

Solvent extraction experiments were carried out on the mechanical shaker. The experimental parameters were fixed as follows: the volume ratio between organic and aqueous phases of 1:1, room temperature, shaking time of 3 min and phase volume of 25 mL. The two phases were separated by separatory funnel and the concentrations of the metallic ions in aqueous phases before and after extractions were determined using ICP.

III. RESULTS AND DISCUSSION

A. Effect of Th concentrations in the initial solution, shaking time andH_2SO_4 concentration on Thorium extraction

25 mL of thorium sulfate solutions with concentrations in range of 0.3 to 6 g/L were shaken with 25 mL of N1923 (0.1M) and 1 M H_2SO_4, within 3 mins. After shaking, the organic phase was stripped twice by using HNO_3. After that, organic phase and aqueous phase were analyzed. The figure 1 showed that the Th maximum extraction capacity using 0.1 M N1923 in 1 M H_2SO_4 mediawas 2.5 g/L.

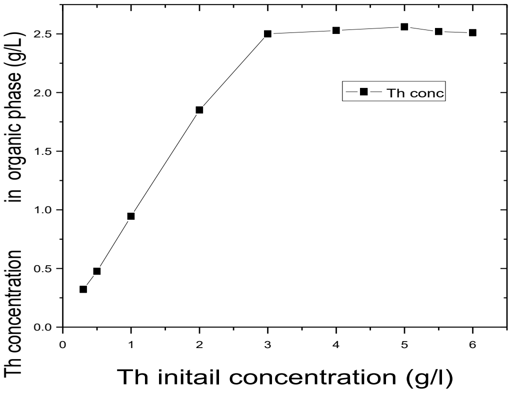

Fig. 1. Dependence of the concentration of Th in the organic phase on the initial concentration of Th.

In this work, the shaking time (contact between organic phase and aqueous phase) was set in the range of 0.5 to 5 minutes, with aqueous phases 5 g/L [Th] and 1 M H_2SO_4. The results were shown in figure 2. Then one minute shaking time was sufficient for extraction. This showed that the thorium extraction process by the N1923 extraction agent occurs rapidly. In order to facilitate the sample preparation and the experimental process in subsequent studies, selected shaking time was 3 minutes.

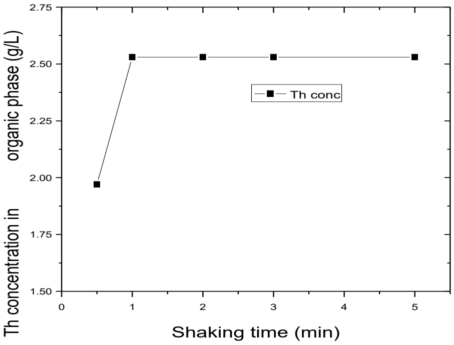

Fig. 2. Dependence of the concentration of Th in the organic phase on shaking time.

The concentration of H_2SO_4 in the initial solution was varied in the range of 0.2 - 2 M. The concentration of thorium in the aqueous phase before shaking was 5 g/L, shaking time was 3 minutes at room temperature. When the concentration of sulfuric acid increased from 0.2 to 1 M, the concentration of Th in the organic phase increased, but did not increase significantly. When the concentration of sulfuric acid increased from 1 to 2 M, the concentration of Th decreased very little. Thus, it can be said that the acid concentration does not significantly affect the extraction efficiency (Figure 3).

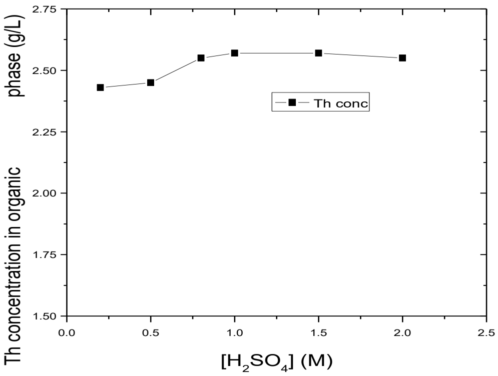

Fig. 3. Dependence of the concentration of Th in the organic phase on sulfuric acid concentration.

B. Effect of H_2SO_4 concentration on simultaneous extraction of Th and rare earth elements (La, Ce, Y)

When extracting thorium from the monazite leachate, some of the rare earth elements were extracted simultaneously. Monazite leachate contains both light and heavy REEs. Therefore, La, Ce and Y were chosen for this study. The concentrations of Th, La, Ce and Y in solution were 5, 5, 5 and 2 (g/L), respectively. The concentration of sulfuric acid in the solution varies in the range of 0.2 – 2 M. The results in Table I indicated that the REEs were extracted with Th simultaneously to the organic phase but the extracted amount was negligible. The distribution coefficientof cerium was highest, in the range of 0.1 - 0.2 when the H_2SO_4 concentration varied in the range of 0.2 - 2M. The presence of REEs in the aqueous phase also caused reducing the thorium distribution coefficient from 1.06 (without REEs) to 0.8 (with REEs). The Th distribution coefficient was 1.06 equivalent 2.52 g/L of Th.

Table I. Effect of H_2SO_4 concentrations on thorium extraction out of RE solutions

[H_2SO_4] (M)	Distribution coefficient			
	Th	La	Y	Ce
0.2	0.72	$9.97x10^{-4}$	$7.31x10^{-4}$	0.01
0.5	0.75	$9.39x10^{-4}$	$6.73x10^{-4}$	0.02
0.8	0.84	$1.02x10^{-3}$	$6.61x10^{-4}$	0.02
1.0	0.86	$1.10x10^{-3}$	$6.94x10^{-4}$	0.02
1.2	0.79	$1.25x10^{-3}$	$6.81x10^{-4}$	0.02
1.5	0.75	$1.47x10^{-3}$	$6.85x10^{-4}$	0.02
2.0	0.7	$2.33x10^{-3}$	$7.38x10^{-4}$	0.02

The above results indicate that it is possible to remove REEs from organic phase into aqueous phase with diluted sulfuric acid without significantly changing thorium-concentrations in organic phase.

C. Study on the scrubbing process

Extracted phase containing Th, Y, La and Ce were prepared with concentrations of 2524.0; 5.4; 39.2 and 153.6 mg/L, respectively. The extracted phase was scrubbed by sulfuric acid and mixing H_2SO_4 andHNO_3. Table II showed that the amount of Th transferred to the aqueous phase was insignificant (less than 0.1% when the acid concentration less than 0.3 M). At the sulfuric acid concentration of 0.3 M, the amount of REEs was moved to the aqueous phase was about 55 - 60%.The amount of Th stripped increased rapidly when the HNO_3 concentration increased. The Th scrubbing efficiency was 7.5% using scrubbing solution 0.2 M H_2SO_4 and 0.15 M HNO_3, so the concentration of nitric acid added should only be controlled less than 0.1 M to gain the required scrubbing efficiency of REEs as well as to limit the loss of Th. The best conditions for scrubbing process was using the mixture of acids H_2SO_4 and HNO_3 at concentrations of 0.2 and 0.1 M, respectively, so REEs was removed over 75% and Th lost 0.7%.

D. Study on the stripping process of Th

NH_4Cl, HCl and HNO_3 were known to be good stripping agents of Th [2], so investigating the concentration of stripping agents was necessary. When HCl concentration was set at 1 M the effect of the stripping agents concentrations on Th stripping efficiency showed in Table III. At a concentration of NH_4Cl 0.5 M and when HNO_3 concentration was increased from 0.05 to 0.5 M, the stripping efficiency of Th increased from 58.3% to 94%. However, at a concentration of NH_4Cl 1 M, the HNO_3 content was ranged from 0.05 to 0.5 M, the stripping efficiency of Th increased from 61.5 to 99.8%. So, the concentrations of HCl, NH_4Cl and HNO_3 were chosen as 1 M, 1 M and 0.5 M to make sure that all Th was stripped in aqueous phase.

Table II. Effect of H_2SO_4 and HNO_3concentration on the scrubbing of Th and rare earth

[H_2SO_4] M	[HNO_3] M	Scrubbing efficiency of Th and RE (%)			
		Th	Y	La	Ce
0.2	0.05	0.03	43.7	77.3	91.1
0.2	0.1	0.7	44.6	80.4	92.4
0.2	0.15	7.5	46.3	81.1	97
0.1	0	0.1	38.9	45.4	54.1
0.2	0	0.1	42.6	53.6	57.6
0.3	0	0.1	55.6	55.6	59.4
0.4	0	0.2	59.2	58.7	63.3
0.5	0	0.3	62.4	61.5	67.6

Table III. Dependence of Th stripping efficiency on NH_4Cl, HCl and HNO_3concentrations

[NH_4Cl] M	[HCl] M	[HNO_3] M	Th(%)
0.5	1	0.05	58.3
0.5	1	0.1	59.6
0.5	1	0.3	89.5
0.5	1	0.5	94.8
1	1	0.05	61.5
1	1	0.1	70.1
1	1	0.3	96.3
1	1	0.5	99.8

E. Study on separating Th from leachate of monazite sulphation processusing multistage continuous flow extraction

Table IV showed the content of the feed solution from the roasted monazite with sulfuric acid. This indicates that the concentration of thorium was 5 g / l, the concentration of rare-earth elements was 52.6 g / l, and the concentration of H_2SO_4 was 1.1 M. Figure 4 showed a scheme for extracting thorium from rare-earth elements, which carried out on a multistage continuous flow extraction device. volume of each box is 15 L, consisting of 4 boxes of extraction, 4 boxes of washing and 4 boxes of the stripping. The operating parameters were shown in Figure 4, where the feed solution was supplied on box number 4, the scrubbing solution on box number 8, the stripping solution on box number 12. The thorium product was obtained at box 9 and analyzed on ICP-OES and showed that the thorium purity was 98% (Table V).

Table IV. The content of feed solution from the roasted monazite with sulfuric acid

Ele	La	Ce	Pr	Nd	Y	REEs	Th	U
g/L	12.6	22.6	2.7	10.0	2.9	52.7	5.1	0.03

Table V. The concentration of Th on the solution after purification by solvent extraction.

Ele	La	Ce	Pr	Nd	Sm	Y
mg/L	<0,05	0,71	<0,08	<0,05	<0,18	<0,27
Ele	Th	U	Pb	Al	Mn	Fe
mg/L	6924	<0,05	<0,01	54,3	<0,1	<0,003

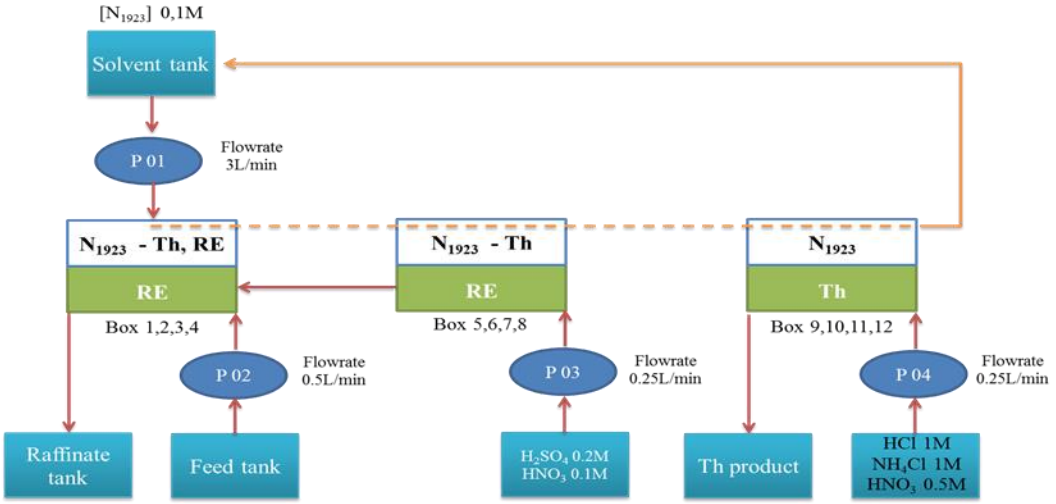

Fig. 4. Extraction Th fromleachate of monazite sulphation processby N1923 solvent on multistage continuous flow extraction.

IV. CONCLUSIONS

Separation of Th from leachate of monazite sulphation process by amine solvent and REEs scrubbing and Th stripping processes have been investigated. The maximum extractability of thorium using 0.1 M N1923 amine was 2.5 g/L; the extraction efficiency of thorium did not depend on the concentration of sulfuric acid (0.3-2 M). The time for separating phaseswas only about 1 minute. Rare earths were extracted together with thorium only small amountand they were easily scrubbed by sulfuric acid and nitric acid. The extraction of thoriumfromleachate of monazite sulphation processwas carried out on a multistage continuous flow extraction device (12 boxes), the thorium purity was 98%. Therefore, the use of amine solvents can purify thorium from rare-earth solutions in a sulfate medium.

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