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SOLVENT EXTRACTION OF THORIUM FROM RARE EARTH ELEMENTS IN MONAZITE THORIUM CONCENTRATE

(Pengekstrakan Pelarut Torium daripada Unsur Nadir Bumi dalam Pekatan Torium Monazit)

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Abstract

Solvent extraction is a powerful separation technique in the preparation of nuclear grade thorium. In this study, monazite thorium concentrates produced from Malaysian monazite were used. Thorium was extracted from an aqueous nitric acid medium with TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene, respectively. Constant experimental conditions were used for the extraction in terms of the molarity of nitric acid, concentration of extractants in kerosene, organic/aqueous volumetric ratio, mixing time, and contact time between phases. The stripping process was carried out with distilled water. The determination of thorium and rare earth elements (REEs) in the monazite thorium concentrates and aqueous solutions were performed by using inductively coupled plasma mass spectrometry (ICP-MS). The concentrations of thorium in the thorium concentrate samples were in the range of 11.58 – 83.56%. Three stages of extraction and three stages of stripping were carried out for the extraction of thorium from the REEs in the nitrate solution. The results of the study showed that the thorium extraction efficiency was in the range of 60.96 – 99.75% using TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene. Thorium was stripped from the loaded TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene at an average stripping percentage of 89.04% and 75.75%, respectively. The stripped aqueous solutions were analysed, and it was shown that the thorium content was in the range of 29.49 – 91.28%. This study indicated that both extractants can be successfully used to recover thorium from REEs, but in order to increase the purification of thorium, the extraction and stripping process cycle should be increased.

Keywords: thorium, rare earth elements, solvent extraction, monazite thorium concentrate

Abstrak

Pengekstrakan pelarut adalah teknik pengasingan yang kuat digunakan untuk mengasingkan torium bergred nuklear. Dalam kajian ini, pekatan torium monazit yang dihasilkan daripada monazit Malaysia telah digunakan. Torium diekstrak daripada medium akues asid nitrik dengan TBP (30%) dalam kerosin dan Aliquat-336 (10%) dalam kerosin. Kondisi eksperimen digunakan iaitu molariti asid nitrik, kepekatan pengekstrak dalam kerosin, nisbah isipadu organik/akues, masa percampuran dan masa sentuhan antara fasa dikekalkan. Proses pelucutan dilakukan menggunakan air suling. Torium dan unsur nadir bumi (REEs) dalam pekatan torium monazit dan larutan akues ditentukan menggunakan spektrometri jisim plasma gandingan teraruh (ICP-MS). Kepekatan torium dalam sampel pekatan torium ditentukan adalah dalam julat 11.58 – 83.56%. Tiga peringkat pengekstrakan dan pelucutan dilakukan untuk mendapatkan torium dari REEs dalam larutan nitrat. Hasil kajian menunjukkan kecekapan pengekstrakan torium adalah dalam julat 60.96 – 99.75% menggunakan TBP (30%) dalam kerosin dan Aliquat-336 (10%) dalam kerosin. Torium telah dilucutkan daripada muatan TBP (30%) dalam kerosin dan Aliquat-336 (10%) dalam kerosin dengan purata peratus pelucutan masing – masing adalah 89.04% dan 75.75%. Larutan akues yang dilucutkan telah dianalisis dan menunjukkan bahawa kandungan torium adalah dalam julat 29.49 – 91.28%. Kajian ini menunjukkan bahawa kedua – dua pengekstrak boleh digunakan dengan berkesan untuk mendapatkan torium daripada REEs tetapi untuk meningkatkan kemurnian torium, pengekstrakan dan kitaran proses pelucutan harus dipertingkatkan.

Kata kunci: torium, unsur nadir bumi, pengekstrakan pelarut, pekatan torium monazit

Introduction

High-purity thorium is required in nuclear technology applications. Nuclear grade thorium is obtained by several industrial processes such as solvent extraction, ion exchange and direct precipitation. Solvent extraction is a powerful separation technique compared to ion exchange and precipitation due to its speed, ease of operation and large throughput [1, 2]. The basis of thorium purification by solvent extraction depends on the solubility of thorium in water and organic solvents by forming complex ions, chalets and solvated species. The sequential transfer between the aqueous and organic phases leads to the purification of thorium.

The most common thorium extraction process is the extraction of thorium nitrate from a solution of nitric acid with TBP (tributyl phosphate) diluted with an aliphatic hydrocarbon such as kerosene or xylene/toluene to reduce the viscosity of the mixture [3]. The purified thorium nitrate, which can be used as a feed material to produce thorium compounds, is converted to thorium oxide or thorium tetrafluoride. Nuclear grade thorium nitrate is obtained with 99% thorium recovery by the solvent extraction process [4].

The extraction of thorium from monazite by solvent extraction was carried out with various organic solvents, e.g. the secondary amine, Adogen 283 [5], Aliquat-336 [6], TBP [7] and primene JM-T [8]. Sato studied the partition of thorium (IV) between aqueous sulphuric acid and solutions of di-(2-ethylhexyl)-phosphoric acid (DEHPA) in kerosene, and also between aqueous sulphuric acid and solutions of long-chain aliphatic amines [9, 10]. Several methods of stripping thorium and rare earths from solvents have been frequently performed. Furthermore, the optimum experimental conditions for the extraction of thorium from a number of elements have been determined in some studies, while the effects of the types and concentrations of the extractants, the settling time between phases, the types and concentrations of the stripping solutions, and the aqueous/organic volumetric ratio have been studied in detail [7, 8].

In this study, thorium concentrates were obtained from Malaysian monazite, which, according to a previous study, contains approximately 2% of thorium [11, 12], where a range of between 6.5 – 7.5% for thorium concentrations and 53.6 – 57.8% for rare earth oxides have also been documented in Malaysian monazite [13]. The objectives of this study were to extract thorium from REEs by TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene, and to determine the thorium purification percentage.

Materials and Methods

Materials

All the reagents and chemicals used in this work were of analytical grade, and the extractants used were TBP (tributyl phosphate), which was from Merck Schuchardt OHG, and Aliquat-336 (tricaprylmethylammonium chloride) from Alorich Chemistry. Both extractants were used without further purification. Kerosene, which was used as a diluent, was supplied by R&M Chemicals. Thorium nitrate was obtained from the nuclear science stockpile of Universiti Kebangsaan Malaysia (UKM), and distilled water was used in all the experiments for aqueous solutions**.**

Solvent extraction procedure

The extraction and stripping experiments were performed using glass bakers and the magnetic stirrer, and then the separation of the organic/aqueous phases was done using a separatory funnel. The sample of Malaysian monazite used in this study was originally from *'amang'* factory in Perak, while the thorium concentrate was obtained from the selective precipitation of a sulphate leach solution of Malaysian monazite using ammonia at a pH of 1.8. Prior to that, the Malaysian monazite was initially processed using hot concentrated sulphuric acid (98%). The concentrations of thorium, uranium and REEs in the aqueous solutions were determined using ICP-MS (ELAN 9000 – Perkin Elmer SCIEX), and the concentration percentages of the elements were calculated from the total concentrations of the elements, which were in µg/g.

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An aqueous solution of thorium was prepared by weighing about 0.10 g of thorium concentrate and dissolving it in 4 M of HNO_3 in a 100-ml volumetric flask at room temperature. A solution of thorium nitrate was prepared by dissolving 0.10 g of thorium nitrate in 4 M nitric acid in a 100-ml volumetric flask at a molarity of 1.85×10^{-3}. TBP and Aliquat-336 were prepared by diluting 30% of TBP (v/v) in kerosene and 10% Aliquat-336 (v/v) in kerosene, respectively. The extraction experiments were carried out at room temperature.

Constant experimental conditions were maintained for each extractant, whereby the aqueous/organic volumetric ratio was 1:1, and the shaking and settling time was 10 minutes. About 5 ml. of the aqueous solution was mixed with 5 ml. of the organic solvents, and shaken for 10 minutes in bakers. The phases were allowed to settle, and were separated after 10 minutes in a separatory funnel. Three stages of extraction and three stages of stripping were carried out for the extraction of thorium from REEs in a nitrate solution. Each extraction experiment was triplicated.

The concentrations of thorium in the aqueous phase before and after the extraction were determined by ICP-MS, and the extraction percentage, E, was calculated from the distribution ratio, D, using equations 1 and 2, respectively as follows:

$$D = \frac{Co - C}{C}, \tag{1}$$

$$E\% = \frac{DVo}{DVo + Vaq} . 100. \tag{2}$$

where C_o and C are the thorium concentrations in the aqueous phase before and after the extraction, respectively, and V_{aq} and V_o are the volumes of the aqueous and organic phases, respectively [6, 7, 14].

The experimental conditions used for the stripping were similar to the conditions for extraction. Distilled water was used as the stripping solution to strip the thorium from the organic phase to the aqueous phase. The stripping percentage was calculated using the concentration of thorium in the aqueous phase after stripping and the concentration of thorium in the organic phase. The flowchart for the solvent extraction of thorium by TBP (30%) in kerosene and by Aliquate-336 (10%) in kerosene is illustrated in Figure 1.

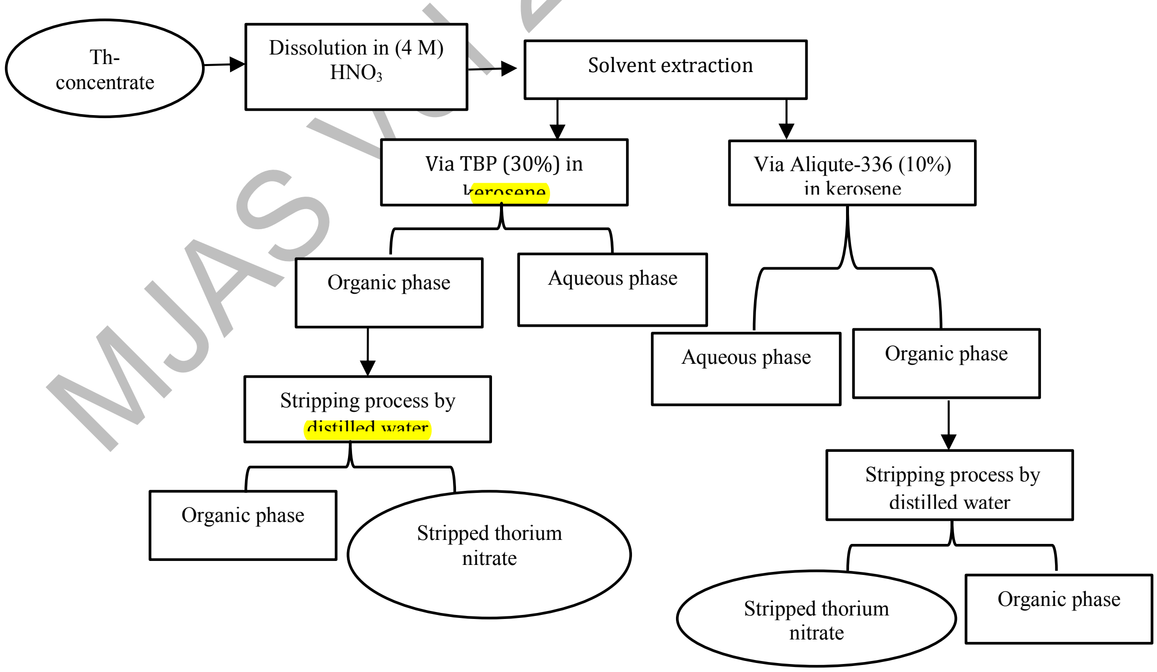

Figure1. Solvent extraction of thorium via TBP (30%) in kerosene and via Aliquate-336 (10%) in kerosene

Results and Discussion

Monazite, which is a rare-earth and thorium phosphate mineral ((Ce, La, Nd, Th) PO_4), are the best primary sources of thorium. Monazite contains 2.5% of thorium and the concentrations of light rare earth elements (LREEs) are more than the concentrations of heavy rare earth elements (HREEs) [15, 16]. Furthermore, monazite concentrates usually contain 5.0 – 10.0% of thorium oxide (ThO_2), 0.2 – 0.4% of uranium oxide (U_3O_8), 55.0 – 60.0% of rare earth metal oxides, and 24.0 – 29.0% of phosphate (P_2O_5) [17].

The results of the analysis of eight monazite thorium concentrate samples are shown in Table 1. It was noticed that the thorium concentration was in the range of 11.58 – 83.56% in the monazite thorium concentrates and the uranium concentration was in the range of 0.04 – 0.63%, which was much lower than the concentrations of thorium and REEs. Meanwhile, the light rare earth elements (LREEs) were in high concentrations compared to the heavy rare earth elements (HREEs) because monazite is originally rich with LREEs and thorium. The Ce content was the highest among the LREEs, and its range was between 4.62 – 41.68%. The La, Nd and Pr contents were lower at 17.86%, 17.54% and 4.83%, respectively. In addition, the rest of the REE concentrations were less than 3.50%.

Table 1. Th, U and REEs concentrations (%) in monazite thorium concentrates samples

Analyte/ Sample ID	**Thc1**	**Thc2**	**Thc3**	**Thc4**	**Thc5**	**Thc6**	**Thc7**	**Thc8**	**Pure Th Nitrate**
Th	17.05	18.38	11.58	16.09	21.89	9.81	83.56	73.02	99.86
U	0.09	0.18	0.30	0.12	0.07	0.04	0.63	0.23	0.00
LREEs									
La	13.11	12.28	14.19	15.73	14.31	17.86	2.65	4.07	0.03
Ce	38.09	37.88	36.50	36.44	36.11	41.68	4.62	10.53	0.05
Pr	4.62	4.50	4.12	4.26	4.29	4.83	0.65	1.33	0.01
Nd	17.38	15.51	13.92	16.65	15.89	17.54	3.16	4.91	0.03
Sm	3.67	2.66	2.99	3.02	2.74	3.05	0.48	1.24	0.00
HREEs									
Eu	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.01	0.00
Gd	2.55	2.09	2.72	0.45	0.24	0.23	0.48	1.09	0.00
Tb	0.23	0.24	0.36	2.38	1.96	2.38	0.07	0.15	0.00
Dy	0.85	1.18	2.08	0.26	0.18	0.21	0.39	0.87	0.00
Ho	0.11	0.20	0.40	1.09	0.64	0.70	0.09	0.16	0.00
Er	0.33	0.57	1.27	0.16	0.08	0.08	0.33	0.49	0.00
Tm	0.03	0.08	0.20	0.05	0.02	0.02	0.06	0.08	0.00
Yb	0.22	0.54	1.38	0.32	0.14	0.12	0.40	0.54	0.00
Lu	0.03	0.07	0.19	0.04	0.02	0.02	0.06	0.08	0.00
Y	1.60	3.61	7.78	2.92	1.41	1.41	2.37	1.21	0.01

First, thorium was extracted from thorium nitrate solution dissolved in nitric acid by two extractants. The efficiency of the extraction of thorium by the two extractants is displayed in Table 2. The results indicated that under constant experimental conditions, both the TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene were able to successfully extract thorium from pure thorium nitrate solution with an extraction efficiency of 96.92 and 99.84%, respectively, and the extraction efficiency from the thorium concentrates was in the range of 60.96 – 99.75%. From the comparison between the two extractants, Aliquat-336 (10%) in kerosene was more efficient than TBP for the extraction of thorium, and achieved an average extraction efficiency of 95.47% from the thorium concentrates, while the average extraction efficiency of TBP (30%) was 89.02%. Basically, the extraction of thorium depends on the stability of the thorium-ligand complex in the aqueous phase, and the solubility of the extracted thorium in the organic phase. The extractant type and concentration, mixing time, settling time and organic/aqueous volumetric ratio have an effect on the extraction of thorium.

Table 2. Extraction efficiency % of thorium using TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene

Sample ID	**TBP (30%)**	**Aliquat-336 (10%)**
	E%	**E%**
Pure thorium nitrate	96.92	99.84
Thc1	94.95	99.75
Thc2	90.59	94.22
Thc3	89.44	97.72
Thc4	88.97	97.43
Thc5	96.12	95.05
Thc6	95.13	98.48
Thc7	96.02	99.70
Thc8	60.96	81.38

Furthermore, the stripping results showed that distilled water was a good stripper with TBP (30%) in kerosene and with Aliquat-336 (10%) in kerosene, and it was more successful in stripping thorium from loaded TBP than from loaded Aliquat-336 with an average stripping percentage of 89.04% and 75.75%, respectively (see Figure 2). However, the use of different strippers will increase the efficiency of the stripping, especially when the process involves Aliquat-336. The stripping process depends on the type of stripping agent, the concentration, mixing time, settling time and the organic/aqueous volumetric ratio.

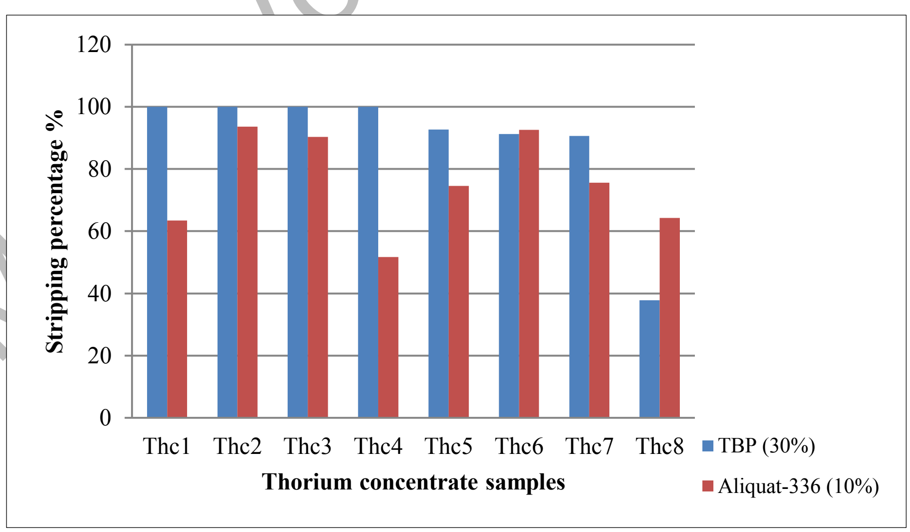

Figure 2. Stripping percentage of thorium by distilled water from loaded TBP (30%) in kerosene and Aliquate-336 (10%) in kerosene

The results of the analysis of the stripped aqueous solutions from loaded TBP and loaded Aliquat-336 for eight thorium concentrate samples are shown in Table 3. It can be seen the thorium purification range using TBP was good at approximately 30.65 – 91.28% compared to 29.49 – 86.90% for Aliquat-336. For uranium, slightly similar concentrations were shown using two extractants, while the REEs were high in the stripped solutions from Aliquat-336 compared to TBP. The study indicated that TBP was more efficient in the purification of thorium from REEs, and three stages of extraction and three stages of stripping were insufficient to obtain high-purity thorium. Therefore, the higher the number of cycles, the higher will be the level of purification.

Table 3. Th, U and REEs ranges content (%) in stripped thorium nitrates from TBP (30%) in kerosene and Aliquat-336 (10%) in kerosene

Analyte	Aqueous Stripped from TBP (30%)	Aqueous Stripped from Aliquat-336 (10%)
Th	30.65 - 91.28	29.49 - 86.90
U	0.20 - 1.97	0.21 - 1.18
LREEs		
La	1.01 - 12.73	2.68 - 18.27
Ce	2.37 - 26.26	5.24 - 33.73
Pr	0.29 - 4.15	0.51 - 3.52
Nd	1.15 - 18.16	1.72 - 14.51
Sm	0.28 - 3.76	0.30 - 2.52
HREEs		
Eu	0.01 - 1.77	0.01 - 0.31
Gd	0.02 - 2.21	0.16 - 1.50
Tb	0.05 - 2.37	0.04 - 1.84
Dy	0.15 - 1.52	0.08 - 0.98
Ho	0.06 - 0.95	0.04 - 0.58
Er	0.06 - 0.73	0.05 - 0.65
Tm	0.01 - 0.47	0.02 - 0.27
Yb	0.08 - 0.58	0.13 - 0.66
Lu	0.03 - 0.11	0.02 - 0.26
Y	0.07 - 4.76	0.09 - 3.39

Conclusion

This study proved that pure thorium can be produced from monazite thorium concentrates by solvent extraction using TBP (30%) and Aliquat-336 (10%) in a nitric acid solution. Thorium was extracted successfully with an extraction efficiency in the range of 60.96 – 99.75% under constant experimental conditions. Aliquat-336 (10%) in kerosene was more efficient than TBP (30%) for thorium extraction, and achieved an average extraction efficiency of 95.47% compared to 89.02% with TBP (30%). Distilled water was able to strip thorium from TBP (30%) and Aliquat-336 (10%), and it was successful in the recovery of thorium, especially from TBP. Thorium purification of up to 91.28% was obtained in the stripped aqueous solutions. The results of this study indicate that both extractants can be used successfully to recover thorium from REEs, but to increase the purification of thorium, the number of extraction and stripping process stages should be increased.

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