การสกัดยูเรเนียมในเค้กเหลืองจากแร่โมนาไซต์ให้มีความบริสุทธิ์สูง โดยใช้ TBP และ D2EHPA ในน้ำมันก๊าด

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บทคัดย่อ

ในการแปรสภาพแร่โมนาไซต์เพื่อแยกยูเรเนียม ทอเรียม และธาตุหายากที่เป็นองค์ประกอบอยู่ในแร่ ยูเรเนียมถูกแยกออกมาในรูปของแอมโมเนียมไดยูเรเนตหรือเค้กเหลือง ซึ่งพบว่ายังมีการปนเปื้อนของทอเรียมและธาตุหายากอยู่บางส่วนในเค้กเหลืองที่ได้ จำเป็นต้องทำให้ยูเรเนียมมีความบริสุทธิ์สูงขึ้นอีก งานวิจัยนี้ได้ศึกษาการใช้ตัวสกัดไตรบิวทิลฟอสเฟต (TBP) ความเข้มข้น 5 10 และ 15% ในน้ำมันก๊าด และไดเอทิลเฮกซิลฟอสฟอริกแอซิด (D2EHPA) ความเข้มข้น 3 5 และ 10% ในน้ำมันก๊าด เพื่อสกัดยูเรเนียมจากสารป้อนที่มีกรดไนตริกความเข้มข้น4 N และมีทอเรียมและซีเรียมปนเปื้อน ผลการศึกษาพบว่าการกระจายตัวของยูเรเนียมใน D2EHPA มีค่าสูงกว่าใน TBP โดยความสามารถในการสกัดของตัวสกัดทั้งสองมีค่ามากขึ้นตามความเข้มข้นที่สูงขึ้นของตัวสกัด สำหรับสารป้อนที่มียูเรเนียมต่ำกว่า 20,000 กรัมต่อลิตร ตัวสกัด 10% D2EHPA และ15% TBP สามารถสกัดยูเรเนียมได้สูงกว่า 90% สัมประสิทธิ์การแยกยูเรเนียมจากทอเรียมของ TBP มีค่าเฉลี่ยประมาณ 20 - 50 ในขณะที่สัมประสิทธิ์การแยกยูเรเนียมจากทอเรียมของ D2EHPA มีค่าต่ำกว่า 0.1 ส่วนสัมประสิทธิ์การแยกยูเรเนียมจากซีเรียมของตัวสกัดทั้งสองมีค่าเฉลี่ยสูงกว่า 100 นอกจากนี้ได้ทดลองชะล้างทอเรียมและซีเรียมที่ติดอยู่ในตัวสกัด TBP โดยใช้กรดไนตริกความเข้มข้น 1.0 - 2.5 N เพื่อเพิ่มความบริสุทธิ์ของยูเรเนียมด้วย

คำสำคัญ : ยูเรเนียม เค้กเหลือง แร่โมนาไซต์ การสกัดด้วยตัวสกัด

Purification of Uranium in Yellow Cake from Monazite Ore with TBP and D2EHPA in Kerosene

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Abstract

In the processing of monazite ore to separate uranium, thorium and rare earth elements from the ore, uranium is produced in the form of ammonium diuranate or yellow cake. This yellow cake requires further purification to remove thorium and rare earth impurities from the cake. The purification of uranium by solvent extraction was investigated using 5, 10 and 15% tributyl phosphate (TBP) in kerosene and 3, 5 and 10% di(2-

ethylhexyl) phosphoric acid (D2EHPA) in kerosene as the extractants. The prepared uranium feed solution was in 4 N HNO_3 with the presence of thorium and cerium as the impurities. The distribution ratio of uranium in D2EHPA was found to be higher than that of TBP and the distribution ratios in both extractants increased with the increasing concentration of extractants. For the feed of uranium concentration less than 20,000 mg/L, the extraction efficiencies of 10% D2EHPA and 15% TBP were higher than 90%. The separation factor of U-Th in TBP was in the average of 20-50 while this factor in D2EHPA was lower than 0.1. The separation factors of U-Ce in both extractants in the average were higher than 100. Using nitric acid of 1.0 - 2.5 N as the scrubbing solution, the purity of the extracted uranium in the TBP extractant could be further increased.

Keywords: uranium, yellow cake, monazite ore, solvent extraction

1. Introduction

Uranium is an important element for making nuclear fuel of nuclear power plant. It has been found that monazite ore in the tailings of tin mines in the South of Thailand contains about 0.24-0.79% of uranium (U) in the form of phosphate compounds.[1] Monazite ore also contains 4.5-10.6% thorium (Th) and 37-58% rare earth elements (Ce, La, Nd, Pr, Sm, Gd, Dy and Y). As part of research activities at the Research and Development Division, Thailand Institute of Nuclear Technology (TINT), the study on the break-down monazite ore using alkaline process to separate and purify each composed element has been conducted. Solvent extraction process with tributyl phosphate (TBP)/kerosene extractant has been used to separate uranium from thorium. Uranium was precipitated in the form of ammonium diuranate ($(NH_4)_2U_2O_7$) or yellow cake which still contains a few impurities of thorium and some rare earth elements.

Uranium purification by the TBP process has been employed in several countries. Other processes using organophosphoric compounds such as alkyl phosphine oxide and phosphonate, phosphinate, and ketones, ethers were also reported but TBP process was seen to have more advantages and was widely chosen.[2-6] The equilibrium constant of the extraction reaction of uranium nitrate by TBP is shown as the following reaction:

$$UO_2^{+2} + 2NO_3^{-} + 2TBP \leftrightarrow UO_2(NO_3)^2 \cdot 2TBP$$

The typical purification process normally includes the scrubbing step using appropriate solution to scrub some impurities which may be extracted into the extractant along with the uranium to ensure the purification of uranium before being stripped to the product.

The present work investigated the purification of uranium in yellow cake obtained from monazite ore using TBP/kerosene and D2EHPA/kerosene extractants with uranium in nitric acid solution having thorium and cerium as impurities.

2. Materials and Methods

Feed solution of uranium was prepared by dissolving standard uranium oxide (Spex Industries) with concentrated nitric acid and the acidity of HNO_3 was adjusted to 4 N. Thorium and cerium from standard nitrate solution of Accustandard were added as impurities. TBP and D2EHPA used for the extractants were from Fluka and BDH respectively. The extraction was carried out using separatory funnels on a shaking machine at room temperature (32 ± 2°C) with a setting speed of 200 rpm and contact time of 10 min to ensure the equilibrium state.[2-3] The feed to extractant ratio used in the experiment was 1:1 or 5 mL each. The concentrations of elements in aqueous phase were determined with ICP-AES spectrometer (Optima 5300 DV, Perkin Elmer).

2.1 Extraction with TBP/Kerosene

Extractant solution of 5, 10 and 15% TBP in kerosene were prepared and saturated with 4 N HNO_3 before being used to extract uranium from feed solution with uranium concentration of 100-35,000 mg/L. Concentration of uranium in aqueous raffinate (C_A) after each extraction was determined with ICP-AES spectrometer. The concentration of uranium in organic extractant (C_O) was calculated from the mass balance between each phase. The distribution ratio or distribution coefficient of uranium (D_U) was then determined from the ratio of C_O to C_A as C_O / C_A. The uranium extracted in each extraction condition was also calculated.

2.2 Extraction with D2EHPA/Kerosene

Solution of 3, 5 and 10% D2EHPA in kerosene were prepared and saturated with 4 N HNO_3 before being used as uranium extractant with feed solution of uranium concentration 500-25,000 mg/L. The concentration of uranium in aqueous raffinate (C_A) was determined as well as the concentration of uranium in organic extractant (C_O) and they were used to calculate for the distribution ratio of uranium and the uranium extracted in each extraction condition.

2.3 Extraction with Thorium and Cerium Impurities

Feed solutions of uranium concentration at 100-20,000 mg/L were added separately with thorium at 500 and 1,000 mg/L and with cerium at 100 and 200 mg/L. These feed solutions were

then extracted with 5, 10 and 15% TBP/kerosene and 3, 5 and 10% D2EHPA/kerosene extractants. After phase separation, the concentrations of elements in the aqueous raffinates were determined and calculated for their distribution coefficients. The separation factor between element A and B (SF_{A-B}) was determined from the ratio of distribution coefficient of A (D_A) to distribution coefficient of B (D_B) as D_A / D_B.

2.4 Effect of Nitric Acid Concentration for Scrubbing

Extractants of 10 and 15% TBP/kerosene were loaded with uranium, thorium and cerium by mixing with feed solution containing 10,000, 1,000 and 200 mg/L of uranium, thorium and cerium respectively. The loaded extractants then were scrubbed with nitric acid solution of 1.0, 1.5, 2.0 and 2.5 N. The concentrations of elements in the scrubbing solution were determined and used to calculate for the recovery and purification of uranium.

3. Results and Discussions

The equilibrium distributions of uranium in 4 N HNO_3 and 5, 10 and 15% TBP/kerosene are shown in Fig. 1 and their distribution ratios as well as the extraction efficiencies are presented in Table 1. The equilibrium distributions of uranium in 4 N HNO_3 and 3, 5 and 10% D2EHPA/kerosene are shown in Fig. 2 as well as their distribution ratios and the extraction efficiencies are presented in Table 2.

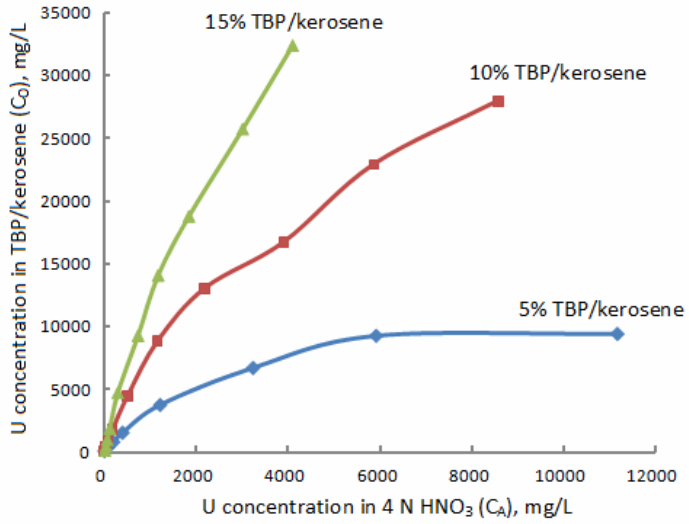

Fig. 1 Equilibrium distribution of uranium in 4 N HNO_3 and TBP/kerosene.

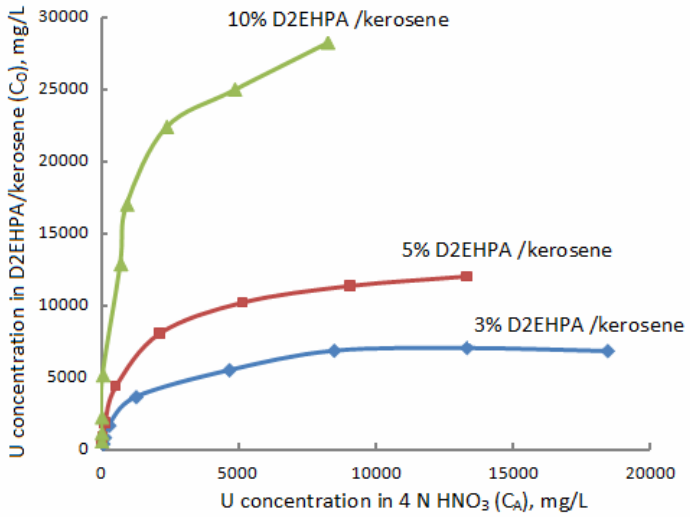

Fig. 2 Equilibrium distribution of uranium in 4 N HNO_3 and D2EHPA/kerosene.

It is seen that distribution ratios of uranium in both extractants increase with the increasing extractant concentration in kerosene and decrease with the increasing uranium concentration in the feed solution. The distribution ratio and the extraction efficiency of D2EHPA are found to be higher than those of TBP. In the feed solution with uranium concentration less than 2,000 mg/L, the distribution ratio of 10% D2EHPA is higher than 400 and the distribution ratio of 15% TBP is about 17. For the feed solution of uranium concentration less than 20,000 mg/L, the uranium extraction efficiencies of 10% D2EHPA and 15% TBP are higher than 90%. The uranium extracted by both extractants as shown in Table 1 and 2 increase with the increasing extractant concentration in kerosene which is in accord with the uranium distribution ratio. The uranium extracted by 10% D2EHPA is more than 99% in the feed solution with uranium concentration less than 5,000 mg/L.

Table 1 Distribution ratios of uranium and uranium extracted in 4 N HNO_3 and TBP/kerosene

Uranium concentration in feed (mg/L)	Distribution ratio, D_U			Uranium extracted (%)		
	5% TBP/K	10% TBP/K	15% TBP/K	5% TBP/K	10% TBP/K	15% TBP/K
104	4.32	11.23	17.48	81.20	91.82	94.59
502	4.19	10.45	17.00	80.73	91.27	94.45
1029	3.90	10.70	17.38	79.58	91.45	94.56
1972	3.79	10.29	16.67	79.11	91.14	94.34
5008	3.08	8.89	16.52	75.48	89.89	94.29
9998	2.08	7.65	12.74	67.52	88.44	92.72
15247	1.58	5.97	12.06	61.17	85.64	92.35
20637	0.85	4.28	10.22	45.92	81.06	91.08
28775	-	3.90	8.54	-	79.61	89.52
36520	-	3.26	7.90	-	76.53	88.76

Table 2 Distribution ratios of uranium and uranium extracted in 4 N HNO_3 and D2EHPA/kerosene

Uranium concentration in feed (mg/L)	Distribution ratio, D_U			Uranium extracted (%)		
	3% D2EHPA/K	5% D2EHPA/K	10% D2EHPA/K	3% D2EHPA/K	5% D2EHPA/K	10% D2EHPA/K
520	9.41	22.05	425.12	90.40	95.66	99.77
1053	8.97	21.24	553.91	89.97	95.50	99.82
5054	2.96	8.70	119.70	74.73	89.69	99.17
11872	1.19	3.84	45.86	54.38	79.32	97.87
16648	0.81	1.99	18.42	44.84	66.53	94.85
22583	0.53	1.26	9.47	34.70	55.67	90.44
27050	0.37	0.90	4.93	27.11	47.44	83.12

The separation factors of U-Th and U-Ce determined from their distribution ratios of TBP and D2EHPA extractants are shown in Table 3 and 4, respectively. It is found that on the average the separation factor of U-Th in D2EHPA is much lower than 0.1 while this separation factor in TBP is in the average of 20-50. The separation factor of U-Th in D2EHPA extractant is much lower than that in TBP extractant which means TBP is more suitable extractant than D2EHPA. The average separation factors of U-Ce in both extractants are higher than 100. In the case of U-Th mixture, the separation factor seems to decrease with the increasing TBP concentration.

Table 3 Separation factor of U-Th and U-Ce in 4 N HNO_3 and TBP/kerosene extractants

Th conc. in feed (mg/L)	Conc. ratio Th / U	Separation factor, $SF_{U\text{-}Th}$			Ce conc. in feed (mg/L)	Conc. ratio Ce / U	Separation factor, $SF_{U\text{-}Ce}$		
		5% TBP	10% TBP	15% TBP			5% TBP	10% TBP	15% TBP
500	5.000	15.0	22.8	19.1	100	1.000	26.2	70.6	114.9
	1.000	17.9	17.8	12.7		0.100	19.7	101.5	131.5
	0.500	61.1	37.9	27.4		0.050	26.6	119.6	157.7
	0.100	78.3	52.0	23.4		0.010	82.0	-	340.5
1000	10.000	83.4	27.1	21.9	200	2.000	31.1	219.6	281.0
	2.000	39.6	30.0	19.2		0.400	24.6	94.0	90.6
	1.000	12.4	20.6	14.2		0.100	34.8	150.9	221.9
	0.200	30.2	28.2	19.2		0.010	15.8	66.3	168.1

Table 4 Separation factor of U-Th and U-Ce in 4 N HNO_3 and D2EHPA/kerosene extractants

Th conc. in feed (mg/L)	Conc. ratio Th / U	Separation factor, $SF_{U\text{-}Th}$			Ce conc. in feed (mg/L)	Conc. ratio Ce / U	Separation factor, $SF_{U\text{-}Ce}$		
		3% D2	5% D2	10% D2			3% D2	5% D2	10% D2
500	1.000	0.009	0.005	0.012	100	1.000	> 500	166.1	> 500
	0.500	0.017	0.009	0.025		0.100	> 500	446.7	> 500
	0.250	0.030	0.017	0.044		0.050	> 500	> 500	> 500
	0.100	0.023	0.018	0.057		0.020	> 500	> 500	> 500
1000	2.000	0.006	0.014	0.002	200	2.000	19.4	22.3	56.9
	1.000	0.008	0.010	0.007		0.400	145.1	130.0	> 500
	0.500	0.009	0.012	0.030		0.100	50.0	104.6	367.4
	0.100	0.023	0.041	0.063		0.010	12.8	37.1	> 500

The effect of nitric acid concentration used for the scrubbing of the organic extractant is shown in Table 5. It is seen that purity of the uranium is increased by 2-3% and it seems to increase with the decreasing concentration of nitric acid. However, the uranium recovery is found to decrease with the decreasing concentration of nitric acid.

Table 5 Purity and recovery of uranium from 10 and 15% TBP in kerosene after scrubbing with 1.0 - 2.5 N HNO_3

Solution	Concentration (mg/L)			U Purity (%)	U Recovery (%)
	U	Th	Ce		
10% TBP/K	8966.7	212.6	13.7	97.54	-
1.0 N	3037.0	176.5	1.34	99.19	66.13
1.5 N	2237.0	159.3	0.71	99.02	75.05
2.0 N	1043.0	159.6	0.01	99.17	88.37
2.5 N	1353.0	148.8	0.24	99.00	84.91
15% TBP/K	9450.8	395.6	12.7	95.86	-
1.0 N	2055.0	336.5	0.57	99.05	78.26
1.5 N	1450.0	310.8	0.33	98.80	84.66
2.0 N	1728.0	259.8	0.48	98.12	81.72
2.5 N	995.3	264.7	0.01	98.33	89.47

4. Summary

The purification of uranium in 4 N HNO_3 with 5, 10 and 15% TBP/kerosene and 3, 5 and 10% D2EHPA/kerosene extractants has been investigated. Uranium feed solution was prepared from standard uranium, thorium and cerium to simulate the composition of yellow cake obtained from the processing of monazite ore. It has been found that the distribution ratio of uranium in both extractants increases with the increasing concentration of the extractant in kerosene and decrease with the increasing uranium concentration in the feed solution. The separation factor of U-Th in D2EHPA extractant is much less than 0.1 and is lower than that in TBP extractant which means TBP is more suitable extractant than D2EHPA. The purity of uranium can be increased by using appropriate concentration of nitric acid as scrubbing solution but the uranium recovery decreases with the increasing acidity of the scrubbing solution. The results can be further applied for the design of solvent extraction process in the purification of uranium from yellow cake obtained from monazite ore. The optimum conditions for the extraction process will need to consider a suitable multistage extraction to reduce the contamination of thorium as the main impurity.

5. References

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