

Technical Note

## Removal of radioactive elements from niobium and tantalum ores

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### ABSTRACT

The production of niobium and tantalum elements from their ores requires separating from the accompanying elements and purification. The ore material obtained from the Eastern-Desert of Egypt consists of euxenite, betafite, thorite and zircon. It was decomposed by sulfuric acid digestion and portions of its constituents were transferred to the leach liquor as given: 66.8% Nb<sub>2</sub>O<sub>5</sub>, 38.7% Ta<sub>2</sub>O<sub>5</sub>, 76% rare earths, 28.9% TiO<sub>2</sub>, 86.5% ThO<sub>2</sub> and 91.1% U<sub>3</sub>O<sub>8</sub>; while ZrO<sub>2</sub> remained in the unattacked residue. Liquid-liquid extraction was performed to remove the radioactive elements from the leach liquor, leaving niobium, tantalum and rare earths unextracted. The system sulfuric acid -diethylhexyl phosphoric acid/tributyl phosphate in kerosene was efficient to extract both thorium and uranium. The extraction was performed by contacting the sulfate leach liquor of pH=1.0 and 6.6M SO<sub>4</sub><sup>2-</sup> with 0.2M D<sub>2</sub>EHPA/TBP in the ratio A:O=3:1 for 15 minutes. The separation of thorium from uranium was performed by two different stripping steps to obtain recovery of 99.6% ThO<sub>2</sub> and 91.2% U<sub>3</sub>O<sub>8</sub>. On the other hand zircon of 96% purity was separated from the unattacked residue by successive chemical treatments. © 2005 SDU. All rights reserved.

Keywords: Niobium; Tantalum; Rare earth elements; Leaching; Liquid-liquid extraction

### 1. INTRODUCTION

A relatively zircon – euxenite – rich variety of the multiple oxide ore has lately been discovered at central Eastern Desert of Egypt. The identified ore minerals include mainly zircon beside euxenite, betafite and thorite. The gangue minerals are essentially represented by quartz and feldspar minerals which are highly stained by hematite. Beside Zr, the interesting metal values thus involve Nb, Ta, REE as well as Th and minor uranium. Before chemical processing, the ore must be physically upgraded in order to reduce the leaching costs of the refractory ore minerals. On the other hand, such an array of metal values would not economically respond to one leaching process i.e. more than one leaching circuit might be required.

Accordingly, the present work is concerned with a concentrated sulfuric acid leaching of the ore concentrate. Apart from zircon, leaching with sulfuric acid causes actually the dissolution of the different ore constituents in varying degrees. Rare earths, thorium and uranium are however highly leached by this acid (Krismer and Hoppe, 1984). Therefore, application of a proper solvent extraction method to the sulfate leach liquor would separate both Th and U. Subsequent leaching of the ore residue by hydrofluoric acid would bring the Nb/Ta leaching to completion while zircon would be partially leached.

A method for controlling the radioactive contents through the production of niobium and tantalum by fluoridation process was performed by Sohama *et al.* (2003). In this method, an ore or concentrate containing 70% Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> as well as 0.05% U<sub>3</sub>O<sub>8</sub> and ThO<sub>2</sub> was leached with 80% hydrofluoric acid after mixing with gypsum and stirring this mixture with concentrated sulfuric acid at 85°C for 16 hours. After completion, the radioactive elements were collected and concentrated in the residue while niobium and tantalum products were confirmed to have high purity.

A study for removing the radioactive elements with recovery of 95% uranium and 98% thorium was done by using tributyl phosphate of 10 and 40% concentrations to separate uranium and thorium respectively from rare earth elements through processing of Malaysian monazite by the acidic and alkali digestion (TRS, 2003). On the other hand D<sub>2</sub>EHPA was used for cleaning the rare earth elements residue which was found to contain 1.79% ∑ REE.

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## 2. EXPERIMENTAL

The chemical composition of the host rock was done by the scanning electron microscope (CAM SCAN, Series 4, ISIS 200 EDAX) with pentaget detector. A representative sample from the ore material was subjected to physical upgrading process to separate the economic ore minerals from the gangue minerals. For this purpose, the ore was ground to a grain size of  $-250 + 100\mu\text{m}$  ( $-60 + 140$  mesh) and subjected to heavy liquid separation using bromoform (sp. gr. = 2.84g/ml). The separated heavy fraction was examined by means of XRD Philips model PW 223/20 for its mineralogical composition. An aliquot portion of the separated heavy fraction was then finely ground to  $-50\mu\text{m}$  ( $-200$  mesh) and was subjected to severe leaching using concentrated  $\text{H}_2\text{SO}_4$  acid at  $100^\circ\text{C}$  for 4h and S/L=1/3.

The obtained ore slurry was properly filtered and the ore residue left behind was thoroughly washed by distilled water. The filtrate and washes were adjusted to a final volume of one litre to represent the obtained sulfate liquor. On the other hand, the ore residue was subjected to a further digestion step using concentrated HF acid to dissolve the remaining Nb and Ta values.

The sulfate leach liquor and the aqueous phases after the extraction and stripping processes were analyzed using UV-VIS Spectrometer Shimadzu 160 A to determine the concentration of U, Th, REE, Nb, Ta, Ti and  $\text{SO}_4^{2-}$ . Zirconium was analyzed by AAS Unicam 969 A at  $\lambda = 360.1\text{nm}$ . Also iron and the free acidity of the sulfate liquor were detected by titration methods (Vogel, 1989).

The extraction process of U and Th from sulfate liquor was performed using diethyl hexyl phosphoric acid  $\text{D}_2\text{EHPA}$  (sp. gr. = 0.98g/ml).

Tributyl phosphate TBP was used as modifier of sp. gr. 0.979g/ml. A commercial grade of kerosene was used as a diluent. The working conditions for the extraction process of U and Th from sulfate/ $\text{D}_2\text{EHPA}$  system are given in Table 1. To prevent the influence of iron during the extraction, the sulfate liquor was passed through a column containing iron dust to reduce ferric to ferrous (Vacariu *et al.*, 1999). The emf of the solution was checked at  $-300\text{mV}$ .

The measurements of pH, emf were performed using HANNA pH meter HI 8424 supplied by combined electrode and redox electrode.

The stripping and precipitation of Th was first done by using 6% ammonium fluoride while the stripping of U was done by 10% sodium carbonate and its precipitation was done by sodium hydroxide.

Table 1  
 Working conditions for the extraction process of U and Th from sulfate/ $\text{D}_2\text{EHPA}$  system

Factors	Range values	Fixed conditions				
		$\text{SO}_4^{2-}$ , M	pH	Time, min.	Solvent conc., M	A/O ratio
pH	0.5, 1.0, 1.5, 2.0, 2.5, 3.0	9.1		15	0.1	1/1
Contact time min.	1/2, 1, 2, 5, 10, 15	6.6	1		0.2	1/1
Solvent conc. M	0.01, 0.05, 0.08, 0.1, 0.15, 0.20	6.6	1	15		1/1
Volume ratio A/O	1/3, 1/2, 1/1, 2/1, 3/1, 4/1, 6/1	6.6	1	15	0.2	

## 3. RESULTS AND DISCUSSION

### 3.1. Ore analysis

The chemical composition of the representative ore material as determined by the SEM procedure is given in Table 2.

The ore concentrate obtained as the heavy fraction in bromoform (sp. gr. = 2.84g/ml) was analyzed to find out its mineralogical components (Table 3). On the other hand, the chemical composition of the heated heavy fraction is given in Table 4.

From the obtained chemical results shown in Table 4, it is clear that the economic metal values are mainly represented by  $\text{ZrO}_2$  (43.50%),  $\text{RE}_2\text{O}_3$  (3.70%),  $\text{Ta}_2\text{O}_5$  (2.11%),  $\text{Nb}_2\text{O}_5$  (1.76%) beside  $\text{ThO}_2$  (2.02%) and  $\text{U}_3\text{O}_8$  (0.093%). The present zirconia content occurs in the form of the two main Zr minerals; namely zircon and most probably baddeleyite. Although the latter is not reflected in the performed X-Ray diffraction pattern, its presence is expected from the acid digestion results. Thus about 45% of  $\text{ZrO}_2$  total content ( i.e. about 19.58%) has been dissolved in  $\text{H}_2\text{SO}_4$  but did not report in the sulfate liquor due to hydrolysis (El-Hazek, 2001).

Table 2  
Complete chemical analysis of pegmatite host rock

Element	Concentration, %
C	31.60
O	43.70
Si	7.96
Al	2.42
Fe	9.09
Mn	0.27
Mg	0.16
Na	0.65
K	0.49
Zr	1.37
Ce	1.30
Th	0.90
Nb	0.05
Ta	0.07

Table 3  
Mineralogical composition of the heavy fraction

Sample		Euxenite 14-643		Betafite 8-300		Zircon 6-0226		Thorite 11-172	
DA	I/lo	DA	I/lo	DA	I/lo	DA	I/lo	dA	I/lo
4.66	8	-	-	-	-	-	-	4.66	35
4.41	32	-	-	-	-	4.43	45	-	-
4.25	9	-	-	-	-	-	-	-	-
4.04	1	-	-	4.04	10	-	-	-	-
3.66	6	3.69	20	-	-	-	-	-	-
3.53	12	-	-	-	-	-	-	3.53	12
3.42	8	-	-	-	-	-	-	-	-
3.34	55	3.38	10	-	-	-	-	-	-
3.29	100	-	-	-	-	3.30	100	-	-
3.11	10	-	-	3.11	10	-	-	-	-
2.99	9	3.01	100	2.99	9	-	-	-	-
2.83	2	-	-	-	-	-	-	2.84	20
2.64	13	-	-	-	-	2.65	8	2.64	40
2.52	63	-	-	-	-	2.52	45	-	-
2.33	10	-	-	-	-	2.33	10	-	-
2.21	6	-	-	-	-	2.22	8	2.21	16
2.06	16	-	-	-	-	2.06	20	-	-

In the subsequent HF digestion of the sulfuric attack residue, the hydrolyzed ZrO<sub>2</sub> content was probably reported in the form of ZrF<sub>4</sub>·3H<sub>2</sub>O (Mathur and Tandon, 1986). The remaining 55% of the input ZrO<sub>2</sub> content (i.e. 23.92%), is that present as zircon mineral, its presence is confirmed by X-Ray diffraction pattern and its purity reached 96% as obtained from chemical analysis. In other words, the zircon content would be equivalent to 35.57% in the input studied ore. Accordingly, 23.92% equivalent to ZrO<sub>2</sub> and 11.65% SiO<sub>2</sub> from the total silicate (32.62%) reported in Table 4, were involved in the formation of zircon.

Table 4  
Chemical analysis of valuable oxides in the heavy fraction

Valuable oxide	Wt., %
ZrO <sub>2</sub> *	43.50
RE <sub>2</sub> O <sub>3</sub>	3.70
Ta <sub>2</sub> O <sub>5</sub>	2.11
Nb <sub>2</sub> O <sub>5</sub>	1.76
ThO <sub>2</sub>	2.02
U <sub>3</sub> O <sub>8</sub>	0.09
Fe <sub>2</sub> O <sub>3</sub>	8.20
Silica and Silicates	32.62
Total	100.00

\*ZrO<sub>2</sub> is presented as zircon and baddeleyite

It can be mentioned that the total silica and silicates content in the gangue mineral are reduced to 20.97%. Apart of this, SiO<sub>2</sub> is presented in thorite which is confirmed from the XRD shown in Table 3. From these data, it is also indicated that apart from zircon and thorite, the principal economic mineral constituents include euxenite and betafite. It can thus be concluded that Th is partially presented in thorite as silicate beside its occurrence as oxide in the two multiple oxide minerals. The analyzed Nb, Ta, REE as well as Ti and U are most probably presented wholly in euxenite and betafite. Finally, the main gangue minerals are represented by quartz and albite.

### 3.2. Chemical composition of the sulfate liquor

The sulfate liquor obtained by sulfuric acid digestion of the ground heavy ore fraction was chemically analyzed for the interesting metal values.

From the obtained results shown in Table 5 it is clearly evident that most uranium and thorium values have been dissolved (95.7% and 86.1% respectively) while the dissolved RE<sub>2</sub>O<sub>3</sub> amounted to 76.2%. On the other hand, Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> showed different behavior where about 67% and 39% were respectively brought into solution. The different dissolution percent of the interesting ore components might reflect their presence in more than one mode of occurrence beside the relatively rapid hydrolysis of Nb and in particular Ta (Gupta and Suri, 1994). In this regard, it has been shown that Th is partially present as thorite beside its incorporation in the multiple oxide ore minerals euxenite and betafite.

Table 5  
Chemical analysis of valuable oxides in sulfate leach liquor

Valuable oxide	Conc., g/l	Recovery, %
RE <sub>2</sub> O <sub>3</sub>	2.82	76.2
Ta <sub>2</sub> O <sub>5</sub>	0.82	38.9
Nb <sub>2</sub> O <sub>5</sub>	1.18	67.0
ThO <sub>2</sub>	1.74	86.1
U <sub>3</sub> O <sub>8</sub>	0.08	95.7
H <sub>2</sub> SO <sub>4</sub>	470.40	-
*Total SO <sub>4</sub> <sup>2-</sup>	585.50	-

\*6.1 M

It is worth mentioning that the obtained sulfate liquor is relatively high in iron due to severe dissolution conditions. Thus about 47% iron dissolution was obtained which resulted in about 3.86g/l as Fe<sub>2</sub>O<sub>3</sub>. It is also interesting to mention that zircon did not show any dissolution rate in concentrated H<sub>2</sub>SO<sub>4</sub> acid whatsoever. However, as previously mentioned, 45% of the input zirconia content was dissolved in sulfuric acid but was completely hydrolyzed to be later reported in the hydrofluoric acid leach steps.

### 3.3. Results of D<sub>2</sub>EHPA extraction for uranium and thorium

In the present work, it was decided to recover both thorium and uranium from the obtained sulfate liquor by liquid – liquid extraction. For this purpose, the di –2- ethyl hexyl phosphoric acid (D<sub>2</sub>EHPA) diluted in kerosene was used. The different relevant extraction factors were studied in detail to determine their optimum values. These include contact time, pH and SO<sub>4</sub><sup>2-</sup> concentration in the aqueous feed beside solvent concentration in the organic phase. Furthermore, an extraction McCabe – Thiele diagram was properly constructed for Th and U to determine the necessary number of extraction stages.

#### 3.3.1. Study of extraction factors

##### 3.3.1.1. Effect of contact time

The effect of contact time between the sulfate leach liquor and D<sub>2</sub>EHPA organic solvent was studied in the range of 0.5 min. up to 15 min. at fixed conditions of pH 1 and SO<sub>4</sub><sup>2-</sup> concentration of 6.6M, a solvent concentration of 0.2M and an A/O ratio of 1:1. From the obtained data given in Table 6, it is clearly evident that 15 min. is the best contact time which achieve 86.0% and 84.0% extraction efficiencies of Th and U respectively.

##### 3.3.1.2. Effect of pH

The effect of pH of the sulfate leach liquor upon the extraction efficiencies of both Th and U by D<sub>2</sub>EHPA was studied in the range of 0.5 to 3 at fixed conditions of SO<sub>4</sub><sup>2-</sup> concentration of 9.1M, a solvent concentration of 0.1M, an A/O ratio of 1:1 and a contact time 15 min. From the obtained data tabulated in

Table 7, it is concluded that as the pH of sulfate leach liquor increase, the extraction efficiencies of both Th and U increased.

Table 6

Effect of time upon Th and U extraction efficiencies by D<sub>2</sub>EHPA at fixed conditions of SO<sub>4</sub><sup>2-</sup> concentration 6.6M, pH 1, solvent concentration 0.2M and A/O ratio 1/1

Time, min.	Extraction efficiencies, %	
	Th	U
0.5	49.1	35.5
1.0	55.6	42.0
2.0	63.2	49.5
2.5	70.8	52.5
5.0	77.3	62.0
10.0	82.7	77.1
15.0	86.0	84.0

Table 7

Effect of pH upon Th and U extraction efficiencies by D<sub>2</sub>EHPA at fixed conditions of SO<sub>4</sub><sup>2-</sup> concentration 9.1 M, solvent concentration 0.1M, contact time 15 min and A/O ratio 1/1

pH	Extraction efficiencies, %	
	Th	U
0.5	88.0	60.9
1.0	92.1	63.0
1.5	93.3	69.5
2.0	94.0	75.8
2.5	94.5	87.4
3.0	95.0	89.3

### 3.3.1.3. Effect of SO<sub>4</sub><sup>2-</sup> concentration

A series of experiments were done using the sulfate leach liquor adjusted at different values of SO<sub>4</sub><sup>2-</sup> concentration ranging between 6.6M to 9.4M at fixed conditions of pH 1 and a solvent concentration of 0.1M while A/O ratio was fixed at 1/1 and the contact time at 15 min. The obtained data are tabulated in Table 8. From these data, it is noticed that as SO<sub>4</sub><sup>2-</sup> concentration increases, the extraction efficiencies of both Th and U are increased.

Table 8

Effect of SO<sub>4</sub><sup>2-</sup> concentration upon Th and U extraction efficiencies by D<sub>2</sub>EHPA at fixed conditions of solvent concentration 0.1M, pH 1, A/O ratio 1/1 and contact time 15 min

SO <sub>4</sub> <sup>2-</sup> conc., M	Extraction efficiencies, %	
	Th	U
6.6	67.5	55.9
6.9	71.8	57.5
7.1	78.2	59.1
7.6	80.9	59.2
8.1	81.9	61.0
8.6	85.3	62.8
9.1	92.1	63.0
9.4	93.0	70.2

### 3.3.1.4. Effect of solvent concentration

To study the effect of the solvent molarities ranging between 0.01 and 0.20M six equilibrium experiments were performed at fixed conditions of SO<sub>4</sub><sup>2-</sup> concentration of 6.6M and pH 1 and using an A/O ratio of 1/1 for a contact time of 15 min. The obtained data are summarized in Table 9. From the latter, it is clear that as the solvent concentration increases, the extraction efficiencies of both Th and U are increased. Thus at a solvent concentration of 0.2M, Th and U extraction efficiencies attained 86.0 and 84.0% respectively.

Another series of experiments were done for studying the solvent molarity at the same fixed conditions, and at an input SO<sub>4</sub><sup>2-</sup> concentration of 9.1M. From the obtained data summarized in Table 10, it is noticed that at the solvent concentration of 0.01M and a SO<sub>4</sub><sup>2-</sup> concentration of 9.1M, Th extraction attains 82.0% while U extraction was only 1.0%. Thus, it would be possible to achieve a high degree of separation

between Th and U at these conditions, Table 10. It is noticed that about 86% Th extraction was obtained at 0.05M solvent concentration a result which was obtained by 0.20M in the first series. Thus, it can be concluded that increase in  $SO_4^{2-}$  concentration from 6.6M to 9.1M is quite beneficial, probably behaving as a salting out agent. This effect can be utilized in almost high separation between Th and U by further decreasing solvent concentration to 0.01M.

Table 9  
 Effect of solvent concentration upon Th and U extraction efficiencies by  $D_2EHPA$  at fixed conditions of  $SO_4^{2-}$  concentration 6.6M, pH 1, A/O Ratio 1/1 and contact time 15min

Solvent conc., M	Extraction efficiencies, %	
	Th	U
0.01	51.1	19.9
0.05	55.2	45.4
0.08	60.3	50.0
0.10	67.5	55.9
0.15	77.7	82.5
0.20	86.0	84.0

Table 10  
 Effect of solvent concentration. upon Th and U extraction efficiencies by  $D_2EHPA$  at fixed conditions of  $SO_4^{2-}$  concentration 9.1M, pH 1, A/O ratio 1/1 and contact time 15min

Solvent conc., M	Extraction efficiency, %	
	Th	U
0.01	82.0	1.0
0.05	85.7	13.3
0.08	89.3	32.6
0.10	92.1	63.0
0.15	93.2	80.3
0.20	94.4	80.6

### 3.3.2. Construction of McCabe - Thiele extraction diagram

For uranium and thorium bulk extraction from the studied sulfate leach liquor, Table 5, solvent extraction using 0.2M  $D_2EHPA$  in kerosene was actually used. This was found beneficial to ensure complete extraction of both Th and U. For this purpose, the feed liquor assaying 6.6M  $SO_4^{2-}$  was first adjusted to pH 1. The organic phase was also pretreated by contacting it with a sulfuric acid of the same pH as the feed liquor.

On the other hand, REE, Nb and Ta metal values were analyzed in the aqueous Th/U raffinate phase to check their possible co-extraction. It was actually found that these metal values have been completely left behind in the raffinate aqueous phase. Accordingly, the obtained loaded organic solvent does not need any scrubbing step. To construct the corresponding McCabe - Thiele diagram and to ensure bulk Th/U extraction, seven equilibrium experiments were performed at different A/O phase ratios ranging from 1/3 to 6/1. In these experiments, the shaking time was fixed at 15min and the mixed phases were left 5 min. for settling. The obtained equilibrium concentration for both Th and U under these conditions are shown in Tables 11 and 12, respectively. From these data, it is clearly evident that extraction of both Th and U is almost identical as reflected from either their  $D_a^o$  or their extraction efficiencies. Besides, it has been shown that at an A/O ratio of 1/1 the distribution coefficient of Th and U attained to 6.15 and 5.30 respectively and which are equivalent to 86% and 84% for Th and U extraction efficiency respectively. This indicates that the used solvent molarity is quite suitable for this bulk extraction. The similar behavior of Th and U is further manifested in their constructed McCabe- Thiele diagrams, Figures 1 and 2.

Table 11  
 Effect of A/O ratio upon Th extraction efficiencies by  $D_2EHPA$  at fixed conditions of  $SO_4^{2-}$  concentration 6.6M, pH 1, solvent concentration 0.2M and contact time 15min

A/O ratio	Thorium conc., g/l		$D_a^o$	Extraction efficiency,%
	Aqueous phase	Organic phase		
1/3	0.070	0.558	8.00	96.0
1/2	0.105	0.820	7.85	94.0
1/1	0.244	1.501	6.15	86.0
2/1	0.436	2.617	6.00	75.0
3/1	0.596	3.446	5.78	65.8
4/1	0.721	4.097	5.69	58.7
6/1	0.901	5.066	5.63	48.4

Table 12

Effect of A/O ratio upon U extraction efficiencies by D<sub>2</sub>EHPA at fixed conditions of SO<sub>4</sub><sup>2-</sup> concentration 6.6M, pH 1, solvent concentration 0.2M and contact time 15min

A/O ratio	Uranium conc., mg/l		D <sub>a</sub> <sup>o</sup>	Extraction efficiency,%
	Aqueous phase	Organic phase		
1/3	3.57	28.58	8.00	96.8
1/2	5.91	41.70	7.10	93.4
1/1	14.25	75.05	5.30	84.0
2/1	24.81	129.01	5.25	72.2
3/1	32.60	170.14	5.21	63.5
4/1	38.83	201.94	5.18	56.5
6/1	48.02	247.76	5.15	46.2

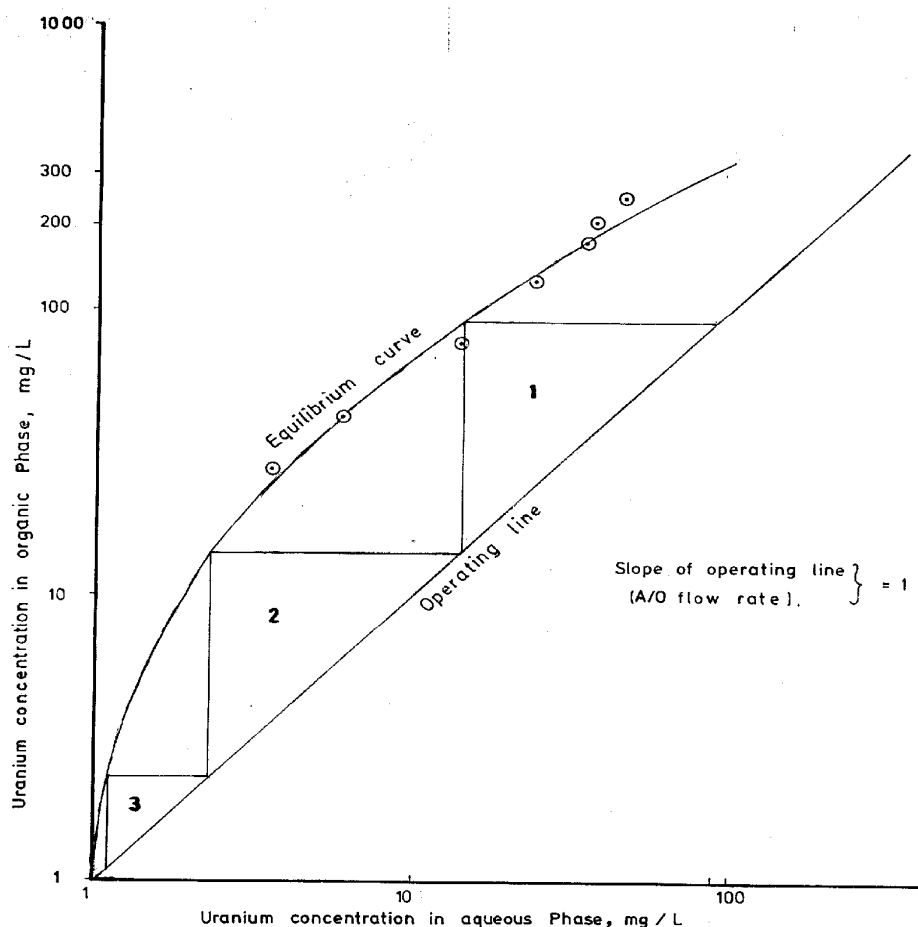


Figure 1. McCabe-Thiele diagram of uranium extraction from sulfate leach liquor

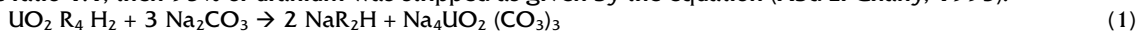
Thus, using an A/O ratio of 1:1 corresponding to a slope of unity for the operating line, three theoretical stages were found adequate for bulk extraction of Th and U.

### 3.4. Results of Th and U stripping and precipitation

The removal of Th from the loaded solvent occur in one step of simultaneous stripping and precipitation of Th product by ammonium fluoride. Uranium was stripped by sodium carbonate and precipitated by sodium hydroxide.

It is worth to mention that to prevent the third phase formation of alkaline stripping of U (Musikas and Schulz, 1992), tributyl phosphate (TBP) was used as modifier. It was mixed with the same volume (1:1) and concentration (0.2M) as the solvent D<sub>2</sub>EHPA.

Three volumes of the leach liquor of 6.6M  $\text{SO}_4^{2-}$  and  $\text{pH} = 1.0$  was conducted with one volume of 0.2M  $\text{D}_2\text{EHPA/TBP}$ . The loaded organic solvent was stripped with 6% ammonium fluoride, almost all the quantity was precipitated as  $\text{ThF}_4$ . Sodium carbonate (10%) was conducted with the same loaded organic solvent in the ratio 1:1, then 95% of uranium was stripped as given by the equation (Abd El Ghany, 1993).



Then the scrub carbonate solution was acidified with  $\text{H}_2\text{SO}_4$  acid to  $\text{pH}=3-5$  and was heated at 50-100°C to expel  $\text{CO}_2$ , then adding  $\text{NaOH}$  to precipitate U-cake at  $\text{pH}=12$  with a recovery of 91.2% according to the following equations.

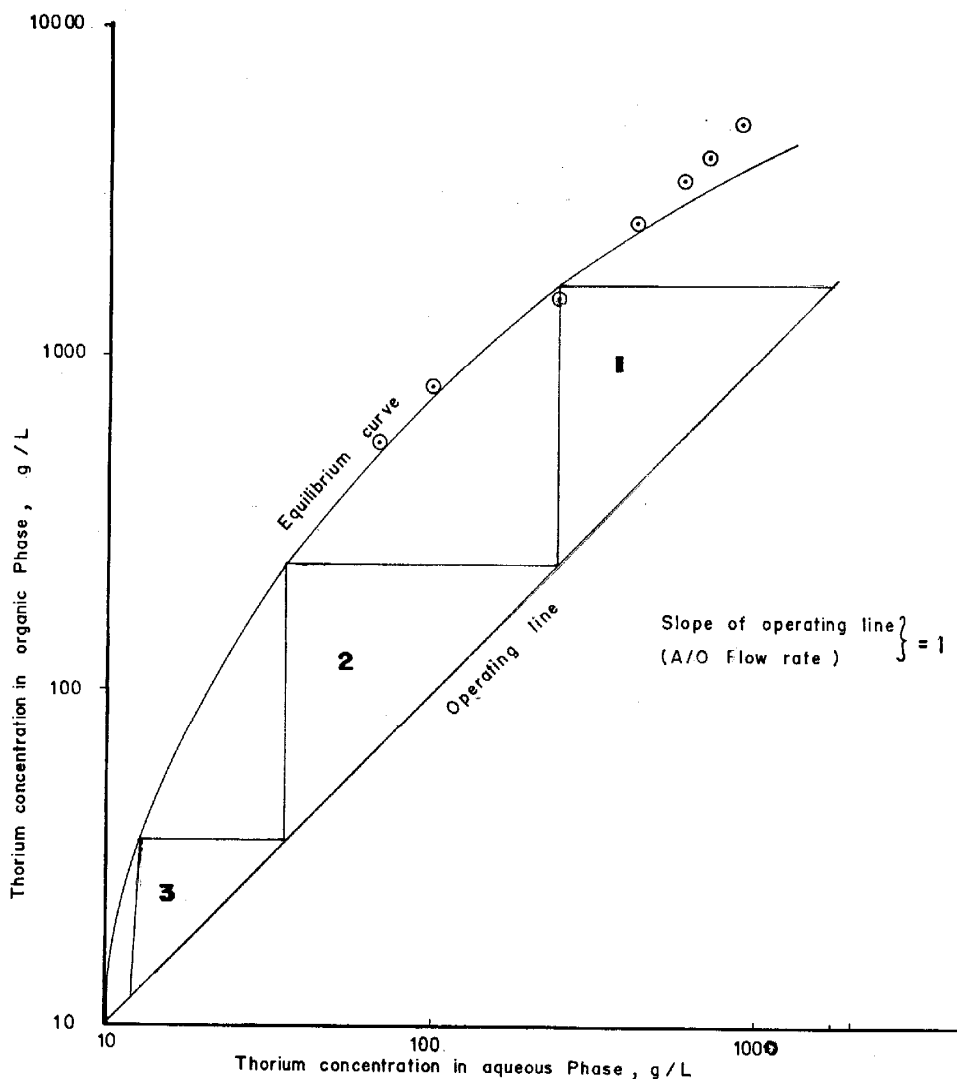
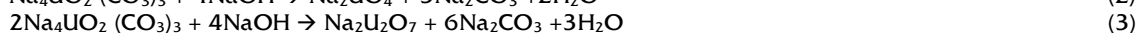
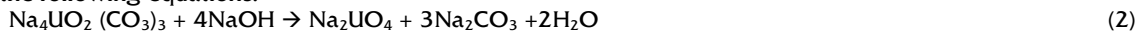


Figure 2. Mc Cabe-Thiele diagram of uranium extraction from sulfate leach liquor

#### 4. CONCLUSIONS

A relatively zircon-euxenite rich ore material containing various interesting metal values is subjected to a hydrometallurgical study for Th and U recovery. A proper ore concentrate was prepared and the important metal values were found to assay 43.50%  $\text{Zr}_2\text{O}_3$ , 3.70  $\text{RE}_2\text{O}_3$ , 2.11%  $\text{Ta}_2\text{O}_5$ , 1.76%  $\text{Nb}_2\text{O}_5$  beside 2.02%  $\text{ThO}_2$  and 0.093%  $\text{U}_3\text{O}_8$ . Mineralogically, the ore is composed of zircon, baddeleyite, euxenite, betafite, thorite while the main gangue minerals are represented by hematite stained quartz and feldspar.



A sulfate leach liquor was obtained by relatively severe concentrated  $H_2SO_4$  acid digestion using 1:3 ratio (ore : concentrated acid) at  $100^\circ C$  for 4h. After a proper washing, the obtained liquor assayed in g/L, 2.82  $RE_2O_3$ , 1.74  $ThO_2$ , 1.18  $Nb_2O_5$ , 0.82  $Ta_2O_5$  beside 0.089  $U_3O_8$ . From this liquor, bulk Th and U extraction was studied using  $D_2EHPA$  in kerosene. The relevant extraction factors were studied and the corresponding Mc Cabe – Thiele diagrams were constructed. The obtained results revealed that by using 0.2M  $D_2EHPA$  in kerosene, and after fixing pH and total  $SO_4^{2-}$  concentration of the liquor at 1.0 and 6.6M respectively, it was possible to extract both Th and U simultaneously using an A/O ratio of unity for 3 extraction stages. It is interesting to refer to the fact that neither REE nor Nb/Ta were extracted under the studied experimental conditions. Extraction of these metal values beside Zr will be later studied in a manner to be integrated in an overall flowsheet.

The loaded organic phase was first stripped for Th by 6%  $NH_4F$  solution resulting in  $ThF_4$  while U was later stripped using 10%  $Na_2CO_3$  solution. From the latter, uranium was precipitated by sodium hydroxide. A proposed flowsheet for the recovery of Zr, Th and U is given in Figure 3.

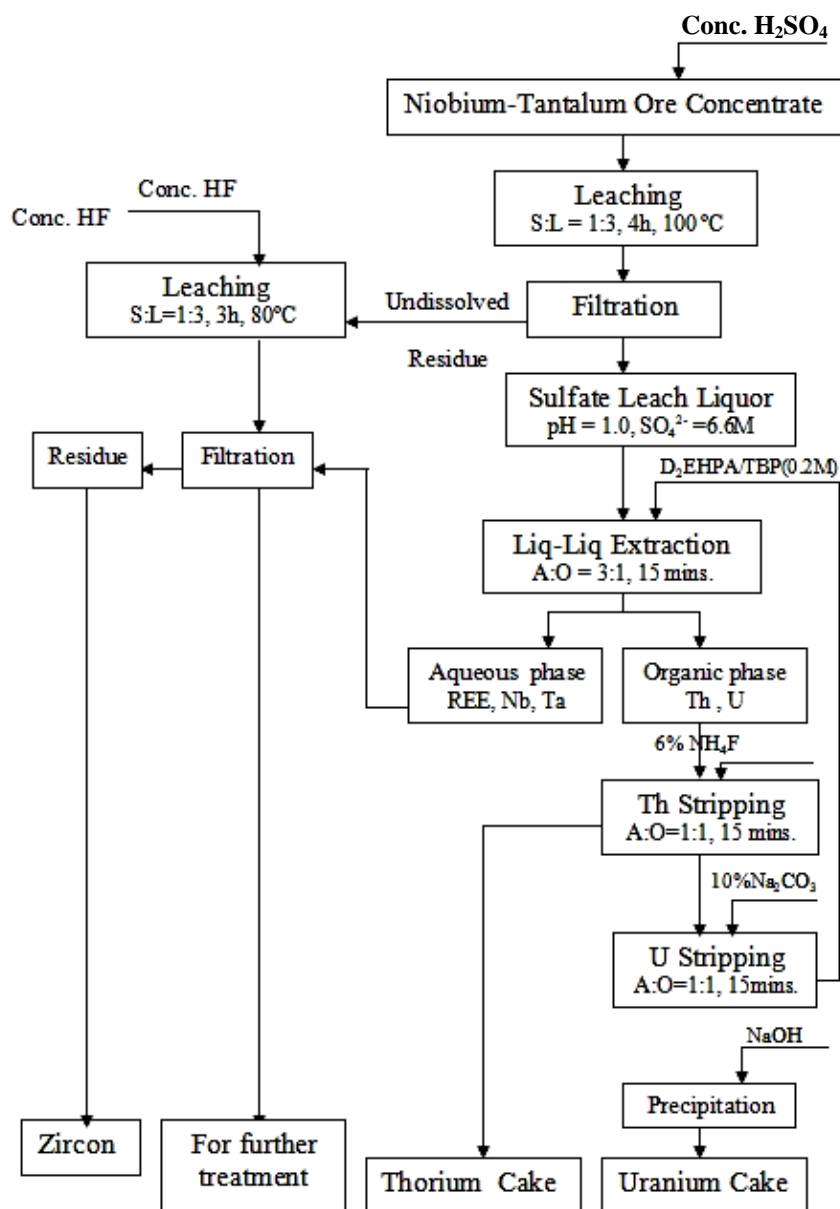


Figure 3. Flowsheet for the separation of zircon, thorium and uranium from niobium-tantalum ore concentrate

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