

## **Extraction of Niobium from Sulfate Leach Liquor of Egyptian Ore Sample by Triazoloquinazolinone**

Omneya M. El Hussaini

Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt  
e-mail:omneya@link.net

**Summary.** The refractory niobium bearing minerals: Samarskite, Fergusonite, Betafite and Pyrochlore of the ore sample obtained from Kadabora-Egypt, was subjected to sulfuric acid leaching using acid concentrations varied from 17.6 M to 4.5 M. The extraction of niobium from the sulfate leach liquors was done using the synthesized 8,9-dihydro[1,2,4]triazolo[1,5-a]quinazolin-6(7H)-one dissolved in methylene chloride. It has been found that 84% extraction efficiency was achieved by contacting equal volumes of 0.32% extractant with 4.5 M sulfate solution for 15 minutes. The stripping was performed by 0.5 M HF with 86.7% efficiency.

### **Introduction**

In nature, niobium almost invariably occurs as complex oxide minerals in association with tantalum. The most common geological occurrence of both suits of minerals is in association with Pegmatites. Niobium ores are processed by physically and chemically breaking down the ore to form salts or oxides; these may be sold, or further processed to reduce the salts to the respective metals. Niobium is considered to cover the vast majority of material in the industry. Its demand is at all time high and continue to rise. Mining and processing capacity is being increased to satisfy this, primarily by CBMM (Companhia Brasileira de Metalurgia e Mineração) with its further expansion to 185 M lb p.a.  $\text{Nb}_2\text{O}_5$  scheduled 2008<sup>(1)</sup>.

Niobium is extracted from the source materials, imported concentrates, and tin slags. A large number of solvent extraction processes using different combinations of various organic reagents and mineral acids have been investigated for the extraction and separation of niobium. The reagents that have been shown to be suitable for the extraction and separation of niobium can be grouped broadly under two categories. One includes neutral oxygenated

extractants, such as ketones, tributyl phosphate (TBP), triocylphosphine oxide (TOPO), N-oxides, sulfoxides, etc. In the other category are long chain aliphatic and aromatic amines that contain basic nitrogen capable of forming amine salts; i.e. trioctylamine (TOA) and tribenzylamine (TBA). Processes based on ketones and TBP have found acceptance in industrial-scale operations (2,3).

Niobium ions form complex species with virtually all types of neutral and anionic donors. It formed complex with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases in dry chloroform under a nitrogen atmosphere. The analytical data of the complexes suggest the formulae of the complexes as  $\text{NbLCl}_5^{(4)}$ . The neutral oxoniobium (V) complexes  $\text{ONbL}_3$  was formed by reacting bidentate 2-pyridinol-N-oxide with hydrated niobium (V) oxide<sup>(5)</sup>. Ivšić and Tamhina<sup>(6)</sup> separated niobium (V) from zirconium (IV) and hafnium (IV) in aqueous hydrochloric and sulphuric acid solutions by 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone (HY) dissolved in chloroform. More than 90% of niobium (V) was separated at around pH 5.4 by Amberlite XAD-7 resin impregnated with *p-tert*-butylsulfinylcalix[4]arene<sup>(7)</sup>. Heterocyclic nitrogen compounds were previously reported for extracting niobium by using 8-quinolinol and 5-nitro-8-quinolinol<sup>(8)</sup>.

The present work deals with the synthesis of multidentate heterocyclic nitrogen ligand namely 8,9 dihydro[1,2,4]triazolo[1,5-a]quinazolin-6(7H)-one for extracting niobium from acidic solution. For this purpose, sulfate leach liquor was prepared from leaching a multiple oxides niobium bearing minerals obtained from Kadabora-Central Eastern of Egypt.

## Experimental

### Synthesis of the extractant

The  $\beta$ -diketone 1,3 cyclohexane dione was selected as starting material to prepare a heterocyclic nitrogen compound to be used as an extractant for niobium ions. A suspension of 1,3cyclohexane dione (10 mmoles) was heated



**Table 1. The mineralogical and elemental composition of the ore sample collected from Kadabora Batholiths – Eastern Desert of Egypt**

<b>Mineralogical composition</b>	<b>Elemental composition, (wt %)*</b>	
Samaraskite, (ASTM card No. <b>13-524</b> )	C	14.11
	O	47.89
	Na	0.61
Fergusonite, (ASTM card No. <b>9-443</b> )	Al	1.34
	Si	4.01
	Ca	25.28
Betafite (ASTM card No. <b>8-300</b> )	Ti	0.34
	Fe	1.20
	Y	0.87
and	Nb	1.70
	Ce	1.12
	Nd	0.45
Pyrochlore (ASTM card No. <b>2-674</b> )	Ta	0.61
	U	0.46

\*CAM SCAN - School of Process, Environmental and Materials Engineering, University of Leeds, England

### **Recovery of niobium**

The ground ore sample (15 g) was mixed with 100 mL sulfuric acid (8.8 M). The obtained slurry was agitated for 2 hours at 150° C and the insoluble residue left behind was separated by filtration. The chemical composition of the obtained leach liquor is given in Table 2. Several batch solvent extraction experiments were done by using the synthesized organic multidentate extractant TQ dissolved in methylene chloride as diluent. The extraction step was followed by the stripping step in which equal volumes of the loaded extractant and the stripping agents (distilled water, 0.5 M HF or 1.0 M HF) were shaken for 15 minutes to back extract niobium. The final step in the treatment of is represented by precipitation of niobium from the strip solution using (33%) ammonium hydroxide. The obtained final product was analyzed for its chemical composition and purity by SEM (EDAX 32 from Philips working at 15-52 accelerating voltages and 60-120 seconds count time, Nuclear Materials Authority laboratories – Egypt).

The determination of niobium concentration whether in the prepared leach liquors or in the aqueous raffinate solutions (after extraction) or else in the stripping solutions was performed by pyrogallol<sup>(9)</sup>. The analysis was performed with a double beam UV-VIS recording Shimadzu UV160A spectrophotometer.

**Table 2. Some elements of interest composing (100mL) of the sulfate leach liquor**

Element	Concentration, g/L	Recovery, %
Nb	1.54	91.6
Ta	0.48	78.8
Ti	0.30	90.1
Ce	0.95	69.8
Y	0.65	85.8
U	0.40	88.1
Fe	0.06	57.0

## Results and Discussion

### Extraction experiments

Cyclohexone was previously used for extracting 70% niobium from sulfate leach liquor in presence of ammonium nitrate<sup>(10)</sup>. In the present study the 1,3 cyclohexane dione was examined for extracting niobium. Its extraction efficiency did not exceed 5% by shaking equal volumes of the organic phase and sulfate leach liquor (4.5 M H<sub>2</sub>SO<sub>4</sub>) containing 2.33 g/L Nb for 15 minutes. This β-diketone was used as start for synthesizing 8,9 dihydro[1,2,4]triazolo[1,5-a]quinazolin-6(7H)-one symbolized by TQ. The latter was prepared as 0.06% in methylene chloride and was used to study the influence of different extraction conditions in improving niobium extraction efficiency from the sulfate leach liquor.

### Effect of sulfuric acid concentration

Four leach liquors were prepared by digesting the ground ore sample with sulfuric acid of concentration 17.6, 8.8, 6.25 and 4.5 M. Equal volumes of

these solutions were shaken for 15 minutes with the extractant 0.06% TQ. The extraction efficiency of niobium increased from 31.0% to 67.2% by decreasing the acid concentration which may be due the ability of TQ to extract sulfuric acid. The maximum distribution coefficient ( $D^0_a$ ) was 2.05 at 4.5 M. It is worth mentioning that this acid concentration satisfied the highest decomposition of the ore sample.

Figure (1) shows the plot of  $\log D$  versus  $\log [H_2SO_4]$  which found to be linear of slope  $\approx 3.0$ . It is probable that the following reaction may occur:



### **Effect of contact time**

The aqueous leach liquor of 4.5 M sulfuric acid and the extractant 0.06% TQ were shaken at A/O ratio of 1/1 for varying periods of time ranging from 1 to 30 minutes. The study showed that increasing the contact time had little influence on increasing the extraction efficiency of niobium and 15 minutes was adequate for maximum extraction of niobium where 67.2% was achieved.

### **Effect of aqueous/organic (A/O) ratio**

The sulfate leach liquor of 4.5M acid concentration containing 2.33 g/L Nb was shaken with 0.06% TQ in methylene chloride for 15 minutes at different A/O ratios varied from 1/4 to 3/1. As shown in Table 3, the distribution ratio of niobium increased by increasing volume ratio of aqueous phase over the organic phase, thus maximum Nb loading was occurred at ratio 3/1.

### **Loading capacity of TQ**

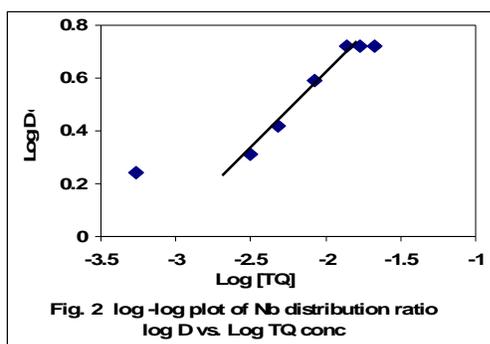
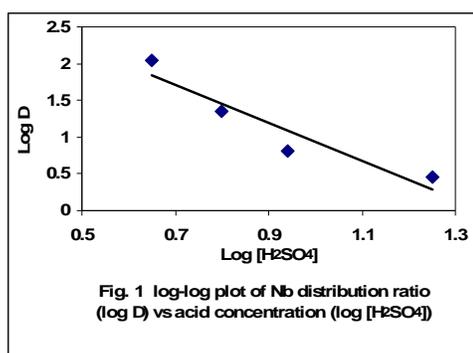
The loading capacity of TQ was determined by contacting the feed solution and 0.32% TQ in methylene chloride at an A/O ratio of 1/1 for 15 minutes. Regarding the molar ratio, the maximum loading capacity was found to be 4.7 g/L. It is worth to mention that contacting three volumes of the feed solution with one volume of 0.06% TQ yielded 4.46 g/L (Table 3), which is 94.8% of the maximum loading capacity

**Table 3. Effect of A/O ratio upon extracting niobium by 0.06% TQ from the aqueous solution of 4.5M sulfuric acid and 15 minutes contact time**

A/O Ratio	Conc. in Aq., (g/L)	Conc. in Org., (g/L)	$D^{\circ}_a$
1/4	0.61	0.43	0.70
1/3	0.66	0.55	0.83
1/2	0.72	0.81	1.12
1/1	0.76	1.57	2.07
2/1	0.81	3.03	3.74
3/1	0.84	4.46	5.31

### Effect of the TQ concentration

To study this factor, the TQ concentration in methylene chloride was varied from 0.01% up to 0.4% while the other extraction conditions were fixed at an A/O ratio of 1/1, contact time 15 minutes and using the leach liquor of 4.5 M sulfuric acid. The extraction efficiency increased from 63.5% till it reached 84% at the extractant concentration of 0.32% and no further extraction occurred by using an excess of TQ (0.4%). The log-log plot of niobium distribution ratio versus TQ concentration given in Figure (2) yielded a molar ratio of 3:1. Hence, the extracted species probably had the composition: TQ  $[\text{NbO}_2(\text{SO}_4)_3]_3$ .



### Stripping and precipitation experiments

The loaded organic phase assaying 1.938 g/L niobium was shaken with the same volume of the following stripping agents: distilled water, 0.5 M HF or 1.0 M HF. The results given in Table (4) showed that 0.5 M HF stripped 86.7% of the loaded niobium. Two volumes of ammonia solution (33%) were mixed with one volume of 0.5 M HF strip solution to yield 92.0% precipitation efficiency. The solid product was filtered and thoroughly washed; it was then ignited at 900° C. The analysis by SEM showed that its purity reached 80.52%; it was mainly contaminated with sulfur, calcium and traces of yttrium.

**Table 4. Stripping of niobium from the loaded extractant 0.32%TQ at O/A ratio of 1/1 for 15 minutes**

Stripping agent	Stripping Efficiency, (%)
H <sub>2</sub> O	69.2
0.5 M HF	86.7
1.0 M HF	81.1

### Interfering elements extracted by TQ

The major elements extracted by TQ from the sulfate leach liquor were cerium and yttrium with efficiency 63% and 55.2%, respectively. Both elements were stripped with 20% sodium hydroxide. The extraction process was also interfered by 1.6% calcium, which was detected in the final product. Only 4.3% tantalum were transferred to the extractant while 4% uranium and 0.2% iron were extracted but none of the mentioned elements were stripped with 0.5 M HF.

### Conclusion

This study demonstrated the potentiality of 8,9 dihydro[1,2,4]triazolo[1,5-a]quinazolin-6(7H)-one (TQ) in the extraction of niobium from sulfate leach liquor of Egyptian ore sample. The results of the bench scale extraction experiments showed that 84% of niobium was extracted

by shaking equal volumes of 0.32% TQ in methylene chloride with leach liquor of 4.5 M H<sub>2</sub>SO<sub>4</sub> for 15 minutes. The extraction of niobium by TQ assumed to form the complex TQ[NbO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>]<sub>3</sub> in the organic phase. The 0.5 M HF was used to strip 86.7% niobium which was precipitated by ammonium hydroxide with efficiency 92.0%. The purity of the final product reached 80.52%.

Thus, it is possible to utilize TQ as an extractant in hydrometallurgical processes for separating niobium from sulfate liquor of Egyptian ore sample.

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