Available online at www.sciencedirect.com

ScienceDirect

Trans. Nonferrous Met. Soc. China 19(2009) 474−478

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn

Extraction of niobium from sulfate leach liquor of Egyptian ore sample by triazoloquinazolinone

O. M. EL HUSSAINI

Nuclear Materials Authority, P.O. Box 530 El Maadi, Cairo, Egypt

Received 4 May 2008; accepted 6 October 2008

Abstract: 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 to 4.5 mol/ L. 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 extraction efficiency of 84% was achieved by contacting equal volumes of 0.32% extractant with 4.5 mol/L sulfate solution for 15 min. The stripping was performed by 0.5 mol/L HF with efficiency of 86.7%.

Key words: extraction; niobium; triazoloquinazolinone; stripping efficiency

---

1 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; and 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 situation, primarily by CBMM (Companhia Brasileira de Metalurgia e Mineração) with its further expansion to 185 t/a Nb_2O_5 scheduled in 2008[1].

Niobium is extracted from the source materials, imported concentrates, and tin slags[2−3]. 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 into two categories. One includes neutral oxygenated extractants, such as ketones, tributyl phosphate(TBP), triocytlphosphine oxide(TOPO), *N*-oxides, and sulfoxides. The other category includes 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 been found acceptance in industrial-scale operations[4−6].

Niobium ions form complex species with virtually all types of neutral and anionic donors. They form 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 suggested the formula of the complexes as $NbLCl_5$[7]. The neutral oxoniobium(V) complexes $ONbL_3$ was formed by reaction of bidentate 2-pyridinol-*N*-oxide with hydrated niobium(V) oxide[8]. IVŠIĆ and TAMHINA[9] separated niobium(V) from zirconium(IV) and hafnium (IV) in the 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 [10]. Heterocyclic nitrogen compounds were previously reported for extracting niobium by using 8-quinolinol and 5-nitro-8-quinolinol[11].

Synthesis of triazolo quinazolinone as condensed ring systems[12−13] is of considerable interest because of the diverse range of their biological properties. The present work deals with the synthesis of multidentate heterocyclic nitrogen ligand, namely 8,9-dihydro[1,2,4]-

---

Corresponding author: O. M. EL HUSSAINI; E-mail: omneya@link.net

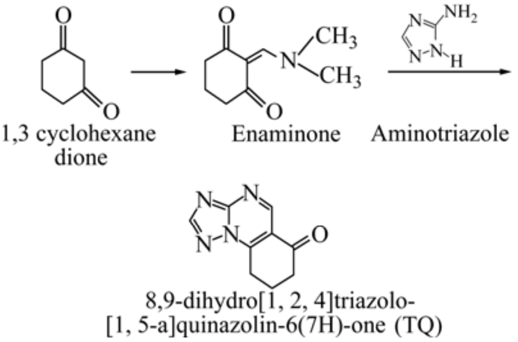
DOI: 10.1016/S1003-6326(08)60298-8

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.

2 Experimental

2.1 Synthesis of extractant

The *β*-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 1,3 cyclohexane dione (10 mmol) was heated under reflux with (11 mmol) dimethylformamide dimethyl acetal(DMF DMA) for 3 h. After cooling to room temperature, the obtained enaminone was properly crystallized from hexane. Next, it reacted under reflux with aminotriazole in ethanol for 6 h followed by the addition of catalytic amount of pipredine. The residual solid was taken in ethanol and washed with distilled water. After filtration, recrystallization from DMF/water was done to afford the corresponding fused heterocyclic 8,9 dihydro[1,2,4]triazolo[1,5-a]quinazolin- 6(7H)-one symbolized by TQ. The reaction is shown in the following scheme:



(1)

The multidentate ligand TQ has molecular mass of 188 g and melting point of 215 ℃. The yield of the synthesized TQ was 94%. Analytical calculation percentages of elements are: C, 57.44; H, 4.28; N, 29.77 and the percentages found are: C, 57.46; H, 4.31; N, 29.79.

2.2 Characteristic of ore sample

The ore sample used in this study was collected from a multiple oxide mineralization Kadabora Batholiths situated in the Eastern Desert of Egypt[14]. It was ground to <74 μm and was subjected to X-ray diffraction analysis using Philips X-ray diffractometer model PW 223/20 operated at 40 kV and 20 mA. It revealed the presence of multiple oxides refractory minerals. The elemental analysis was done using scanning electron microscope (CAM SCAN series 4 ISIS 200 E/X system with pentajet detector, University of Leeds, England). Table 1 summarizes the obtained minerals and the average elemental chemical composition of different sample spots.

2.3 Recovery of niobium

The ground ore sample (15 g) was mixed with 100 mL sulfuric acid (8.8 mol/L). The obtained slurry was agitated for 2 h at 150 ℃ 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 mol/L HF or 1.0 mol/L HF) were shaken for 15 min to back extract niobium. The final step in the treatment 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 kV accelerating voltage and 60−120 s count time, Nuclear Materials Authority(NMA) 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[15]. The analysis was performed with a double beam UV-VIS recording Shimadzu UV160A spectrophotometer.

3 Results and discussion

3.1 Extraction experiments

Cyclohexone was previously used for extracting 70% niobium from sulfate leach liquor in presence of

Table 1 Mineralogical and elemental composition of ore sample collected from Kadabora Batholiths in Eastern Desert of Egypt

<table>
<tr><td colspan="14">Mineralogical composition</td></tr>
<tr><td colspan="4">Samarskite
(ASTM card No.13−524)</td><td colspan="3">Fergusonite
(ASTM card No. 9−443)</td><td colspan="3">Betafite
(ASTM card No. 8−300)</td><td colspan="4">Pyrochlore
(ASTM card No.2−674)</td></tr>
<tr><td colspan="14">Mass fraction of elemental composition*/%</td></tr>
<tr><td>C</td><td>O</td><td>Na</td><td>Al</td><td>Si</td><td>Ca</td><td>Ti</td><td>Fe</td><td>Y</td><td>Nb</td><td>Ce</td><td>Nd</td><td>Ta</td><td>U</td></tr>
<tr><td>14.11</td><td>47.89</td><td>0.61</td><td>1.34</td><td>4.01</td><td>25.28</td><td>0.34</td><td>1.20</td><td>0.87</td><td>1.70</td><td>1.12</td><td>0.45</td><td>0.61</td><td>0.46</td></tr>
</table>

* Conducted in School of Process, Environment and Materials Engineering, University of Leeds, England.

Table 2 Some elements of interest composed (100 mL) of sulfate leach liquor

Element	Concentration/(g·L^{-1})	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

ammonium nitrate[16−17]. In the present study, 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 mol/L H_2SO_4) containing 2.33 g/L Nb for 15 min. This *β*-diketone was used as start for synthesizing 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.

3.2 Effect of sulfuric acid concentration

Four leach liquors were prepared by digesting the ground ore sample with sulfuric acid of 17.6, 8.8, 6.25 and 4.5 mol/L. Equal volumes of these solutions were shaken for 15 min 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 to the ability of TQ to extract sulfuric acid. The maximum distribution coefficient(D_a^0) was 2.05 at 4.5 mol/L. It is worth mentioning that this acid concentration satisfied the highest decomposition of the ore sample.

Fig.1 shows the plot of lg *D* versus lg [H_2SO_4], which is found to be linear with slope of about 3.0. It is probable that the following reaction may occur:

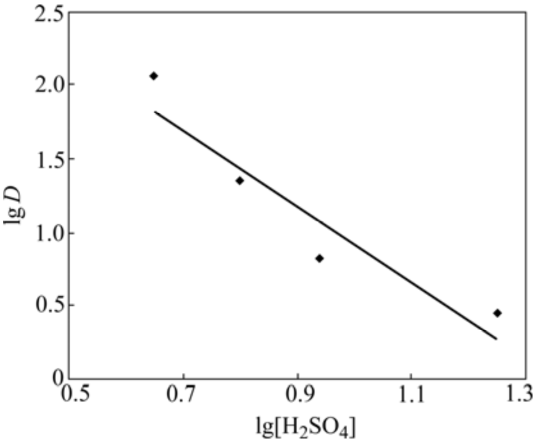


Fig.1 Logarithmic plot of Nb distribution ratio lg *D* vs lg[H_2SO_4]

$$Nb_2O_5+6H_2SO_4+5/2O_2 \rightarrow 2NbO_2(SO_4)_3+6H_2O \qquad (2)$$

3.3 Effect of contact time

The aqueous leach liquor of 4.5 mol/L 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 min. The results showed that increasing the contact time had little influence on increasing the extraction efficiency of niobium and 15 min was adequate for the maximum extraction of niobium where 67.2% was achieved.

3.4 Effect of aqueous/organic (A/O) ratio

The sulfate leach liquor of 4.5 mol/L acid concentration containing 2.33 g/L Nb was shaken with 0.06% TQ in methylene chloride for 15 min 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 the maximum Nb loading was occurred at ratio of 3/1.

Table 3 Effect of A/O ratio upon extracting niobium by 0.06% TQ from aqueous solution of 4.5 mol/L sulfuric acid and 15 min contact time

A/O ratio	Concentration in aquor/(g·L^{-1})	Concentration in organics/(g·L^{-1})	D_a^0
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

3.5 Effect of 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 min and using the leach liquor of 4.5 mol/L 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 TQ (0.4%). The logarithmic plot of niobium distribution ratio versus TQ concentration given in Fig.2 yielded a molar ratio of 3:1. Hence, the extracted species probably had the composition of TQ [$NbO_2(SO_4)_3$]$_3$.

3.6 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 min. Regarding the molar ratio, the maximum loading capacity was found to be 4.7 g/L. It is worth to mention that contacting three

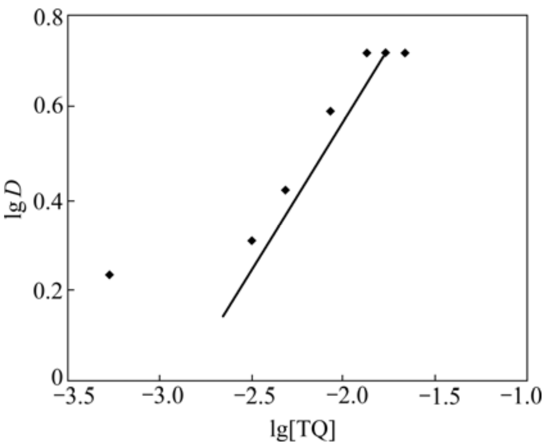


Fig.2 Logarithmic plot of Nb distribution ratio lg *D* vs lg[TQ]

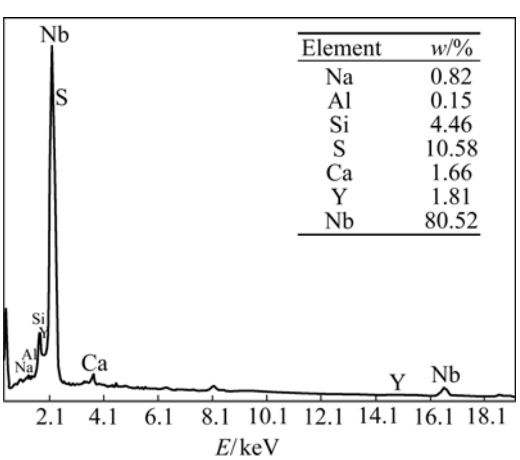
volumes of the feed solution with one volume of 0.06% TQ yielded 4.46 g/L (Table 3), which is 94.8% of the maximum loading capacity.

3.7 Stripping and precipitation experiments

The loaded organic phase assaying 19.58 g/L niobium was shaken with the same volume of the following stripping agents: distilled water, 0.5 mol/L HF and 1.0 mol/L HF. The results given in Table 4 showed that 0.5 mol/L HF stripped 86.7% of the loaded niobium. Two volumes of ammonia solution (33%) were mixed with one volume of 0.5 mol/L HF strip solution to yield 92.0% precipitation efficiency. The solid product was filtered and thoroughly washed; then it was ignited at 900 ℃. The analysis by SEM showed that its purity reached 80.52%; and it was mainly contaminated with sulfur, calcium and yttrium (Fig.3).

Table 4 Stripping of niobium from loaded extractant 0.32% TQ at O/A ratio of 1/1 for 15 min

Stripping agent	H_2O	0.5 mol/L HF	1.0 mol/L HF
Stripping efficiency/%	69.2	86.7	81.1



Element	w/%
Na	0.82
Al	0.15
Si	4.46
S	10.58
Ca	1.66
Y	1.81
Nb	80.52

Fig.3 Elemental composition of precipitate formed from strip solution as analyzed by scanning electron microscope

3.8 Interfering elements extracted by TQ

The major elements extracted by TQ from the sulfate leach liquor were cerium and yttrium with efficiency of 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 was transferred to the extractant while 4% uranium and 0.2% iron were extracted but none of the mentioned elements were stripped with 0.5 mol/L HF.

4 Conclusions

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 mol/L H_2SO_4 for 15 min. The extraction of niobium by TQ assumed to form the complex $TQ[NbO_2(SO_4)_3]_3$ in the organic phase. The 0.5 mol/L HF was used to strip 86.7% niobium, which was precipitated by ammonium hydroxide with efficiency of 92.0%. The purity of the final product reached 80.52%.

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

Acknowledgements

The author gratefully acknowledge Professor Ahmad Farag and his colleagues (Chemistry Department, Faculty of Science, Cairo University) for their help in synthesizing the extractant. Deep thanks are expressed to Professor Adel El Affandi (Nuclear Materials Authority (NMA), Egypt) for supplying the ore sample. Thanks are also extended to the staff and members of X-ray department (NMA, Egypt) as well as SEM departments in NMA laboratories (Egypt) and Leeds University (England) for their help in analyzing the ore and the prepared samples. Special thanks are due to Mrs. Sahar Issa, Ms. Hayat Hussein and Mr. Saleh El Mahdi (NMA, Egypt) for their help in this work.

References

[1] Tantalum–Niobium International Study Center, T.I.C. Nibium, primary production [R]. Bulletin No. 132. 2007.

[2] GUPTA C K, SURI A K. Extractive metallurgy of niobium [M]. Chapter 3. CRC Press, 1994: 93.

[3] MILLER G L. Metallurgy of the rarer metals—6, tantalum and niobium [M]. Chapter 4. Scientific Publication, 1959: 90.

[4] CAMPDERROS M E, MARCHESE J. Transport of niobium (V)

through a TBP–Alamine 336 supported liquid membrane from chloride solutions [J]. Hydrometallurgy, 2001, 61: 89−95.

[5] International Atomic Energy Agency. Extent of environmental contamination by naturally occurring radioactive material (Norm) and technological options for mitigation. Appendix IV [R]. IAEA, 2003: 164.

[6] RITCEY G M, ASHBROOK A W. Solvent extraction principles and applications to process metallurgy (Part II) [M]. Chapter 4.11, Elsevier Publisher, 1979: 362.

[7] GUDASI K, MARAVALLI P, GOUDAR T. Thermokinetic and spectral studies of niobium(V) complexes with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases [J]. J Serb Chem Soc, 2005, 70(4): 643−650.

[8] SEFARIM M J S, BESSLER K E, LEMOS S S, SALES M J A. The preparation of new oxoniobium(V) complexes from hydrated niobium(V) oxide: The crystal and molecular structure of oxotris(2-pyridinolato-*N*-oxide)niobium(V) [J]. Transition Metal Chemistry, 2007, 32: 112−116.

[9] IVŠIĆ A G, TAMHINA B. Extraction and complex formation of niobium(V) with 3-hydroxy-2-methyl-1-(4-tolyl)-4-pyridone[J]. Talanta, 1991, 38(12): 1403−1407.

[10] MATSUMIYA H, YASUNO S, IKI N, MIYANO S. Determination of niobium(V) and tantalum(V) as 4-(2-pyridylazo)resorcinol-citrate ternary complexes in geological materials by ion-interaction reversed-phase high-performance liquid chromatography [J]. J Chromatography A, 2005, 1090: 197−200.

[11] RANE A T, NEPALI D R. Synergic extraction study of niobium with 8-quinolinol, its 5-nitro analogue and heterocyclic nitrogen compounds [J]. Hydrometallurgy, 1990, 24(1): 101−110.

[12] SHIKHALIEV K H S, KRYL'SKI D V, POTAPOV A Y, KRYSIN M Y. Synthesis of 8,8-R,R-8,9-dihydro[1,2,4] triazolo [1,5-a] quinazolin-6(7H)-ones [J]. Russian Chem Bull, 2005, 54(12): 2903−2904.

[13] MOURAD A E, ALY A A, FARAG H H, BESHI E A. Microwave assisted synthesis of triazoloquinazolinones and benzimidazoquinazolinones [J]. Beilstein Journal of Organic Chemistry, 2007, 3: 11.

[14] EL HAZEK M N. Recovery of uranium, niobium and tantalum from Kadabora uraniferous pegmatites, eastern desert of Egypt [D]. Ain Shams University, 2001, 15.

[15] EL-HUSSAINI O M. Extraction of niobium and tantalum elements from some egyptian ore materials [D]. Cairo University, 1996: 122.

[16] GOROSHCHENKO YA G, ANDREEVA M I, BABKIN A G. Cyclohexanone extraction of tantalum and niobium from sulfuric acid solutions [J]. Zhur Priklad Khim, 1959, 32: 1904−1913.

[17] YAGODIN G A, SINEGRIBOVA O A. Processes for zirconium-hafnium and niobium-tantalum. Handbook of solvent extraction [M]. Chapter 25.14, 1983: 812.

(Edited by YANG Bing)