

Pressure Leaching of some Niobium-Tantalum-Rare Earths Refractory Minerals

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Summary: The ore obtained from the Eastern-Desert of Egypt includes euxenite, betafite, thorite as well as the zirconium minerals zircon and baddeleyite. The refractory minerals containing niobium, tantalum and rare earths have been successfully digested by leaching, in a pressure reactor with hydrofluoric, sulfuric and hydrochloric acids.

X-ray diffraction, scanning electron microscope, atomic absorption and UV-VIS spectrophotometer were used to investigate the samples before and after leaching.

Recovery of over 90% of niobium and tantalum was achieved by leaching the ore concentrate ground to less than 200 mesh with 20 M hydrofluoric acid was mixed at the ore/acid ratio 1/10 and heated at 100 °C for two hours. The rare earths maximum recovery of 96.8% was obtained when the ground ore concentrate was mixed with concentrated hydrochloric acid at the ore/acid ratio 1/10 and temperature 150 °C for two hours.

Introduction

A relatively zircon–euxenite–rich variety of the multiple oxide ore has lately been discovered at central Eastern Desert. The identified ore minerals include mainly beside euxenite, betafite, thorite and the zirconium minerals zircon and baddeleyite. The gangue minerals are essentially represented by quartz and feldspar minerals which are highly stained by hematite.

The breakdown of niobium-tantalum ores could be performed by different methods involving fusion at elevated temperatures and leaching with mineral acids⁽¹⁾. Alkali or acid fusion processes are characterized by the formation of insoluble residue containing most of niobium and tantalum amounts, while the other constituents were removed by the subsequent water and acid leaching of the fused mass. On the other hand, the acid leaching

processes cause the dissolution of most of the ore constituents and high recovery of niobium-tantalum and rare earths.

Pressure leaching is a versatile tool for the extraction of metals from minerals and concentrates, as well as for metal refining and metal recovery from leaching solutions. Pressure reactors, or autoclaves are gradually gaining acceptance in hydrometallurgic operations, due to the fact that, being closed vessels, they are less air contaminant⁽²⁾. Among the advantages of pressure leaching are the reduced consumption of acid, fast kinetics and high recovery.

Experimental

The chemical composition of the host rock was done by the scanning electron microscope (SEM-CAM SCAN, Series 4, ISIS 200 EDAX) with pentagete detector, operated at 25 KV and 150 μ A.

A representative sample from the ore was ground to a grain size range -60 +140 mesh and was subjected to heavy liquid separation using bromoform (Sp. Gr. 2.84) to reduce the leaching costs of the refractory ore minerals⁽³⁾. The heavy fraction was examined for its mineralogical composition by X-ray diffraction (XRD- Philips model PW 223/20). The x-ray radiation from copper tube was operated at 40 kV and 20 mA. A portion of the separated heavy fraction was then finely ground to less than 200 mesh and was subjected to pressure leaching using HF (48%, BDH), H₂SO₄ (97%, BDH) or HCl (36%, BDH). The leaching conditions are given in Table (1).

Pressure leaching was carried out in a polytetrafluoroethylene bomb reactor with cover, suitable for use up to about 200 °C; temperature was easily measured and controlled. After leaching completion, the content was properly washed and filtered. The recovery of the interesting elements in the leach liquor was determined using atomic absorption (Varian Spect AA. 10) for analyzing Nb at $\lambda = 335$ nm and Ta at $\lambda = 272$ nm. The total rare earths were analyzed by arsenazo (III) method⁽⁴⁾ using UV-VIS spectrophotometer (Shimadzu 160 A).

Table (1): Experimental Conditions for the Recovery of Niobium, Tantalum and Rare Earths from the Ore Concentrate Applying Pressure Leaching Using Hydrofluoric Acid, Sulfuric Acid and Hydrochloric Acid.

Leachants	Experimental Conditions			
	Acid Conc. M	Temp., °C	Time, h.	Ore/Acid Wt./Vol. Ratio
A) Hydrofluoric Acid	1.9, 5.0, 9.9, 11.9, 14.9, 17.1, 20.0	60, 80, 100, 120, 150	1, 2, 3, 4, 5, 6	1/2.5, 1/5.0, 1/7.5, 1/10.0, 1/12.5
B) Sulfuric Acid	0.5, 3.0, 6.0, 9.0, 12.0, 15.0	60, 80, 100, 120, 150	1, 2, 3, 4, 5, 6	1/2.5, 1/5.0, 1/7.5, 1/10.0, 1/12.5
C) Hydrochloric Acid	0.5, 0.9, 2.4, 5.0, 9.5, 11.8	60, 80, 100, 120, 150	1, 2, 3, 4, 5, 6	1/2.5, 1/5.0, 1/7.5, 1/10.0, 1/12.5

Results and Discussion

Ore Analysis

The chemical composition of the representative ore material as determined by the SEM procedure is given in Table (2). A proper ore concentrate was physically prepared and the important metal values were found to assay 43.50% ZrO_2 , 3.70 RE_2O_3 , 2.11% Ta_2O_5 , 1.76% Nb_2O_5 beside 2.02% ThO_2 and 0.093% U_3O_8 , (Table 3). The mineralogical composition of the ore concentrate analyzed by XRD was found to include euxenite, betafite, thorite beside zircon and baddeleyite, while the main gangue minerals are represented by hematite stained quartz and feldspar, Table (4).

The relatively zircon-euxenite rich ore material containing various interesting metal values is subjected to a hydrometallurgical study for Nb, Ta and RE elements recovery.

Table (2): Complete Chemical Analysis of the Host Rock.

Element	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): Chemical Analysis of Valuable Oxides in the Heavy Fraction.

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

* ZrO₂ is present as zircon and baddeleyite

Table (4): Mineralogical Composition of the Ore Concentrate as Analyzed by X-Ray Diffraction.

Gangue Minerals	Economic Minerals⁽¹⁾	Associated Minerals
Quartz	Euxenite	Hematite
Feldspar	Betafite	
	Thorite	
	Zircon	
	Baddeleyite	

(1) The grains were heated at 1000°C before XRD analysis

Study of Leaching Factors

The dissolution of multiple oxides minerals under pressure using hydrofluoric, sulfuric or hydrochloric acids was studied by varying, acid concentration, temperature, leaching time and ore to acid ratio. The leachability of niobium, tantalum and rare earths from their minerals is represented as follows:

Leaching with hydrofluoric acid

Effect of acid concentration

Hydrofluoric acid concentration has great influence on leaching niobium-tantalum and rare earth bearing minerals. When the ore mixed with the acid of concentrations varied from 1.9 M to 20 M (3.3- 34.8%) at the ore/acid ratio 1/10 and heated in a bomb reactor at 100 °C for 2 hours, the dissolution of both niobium and tantalum reached the maximum values of 94.3 and 97.4%, respectively. On the other hand, the rare earths relatively show low solubility in hydrofluoric acid due to the formation of insoluble fluorides.

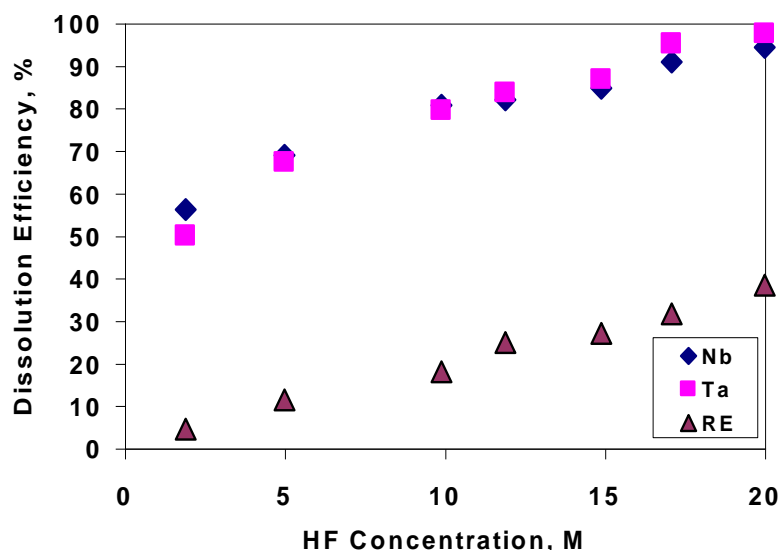


Fig. 1a: Effect of HF concentration on the dissolution efficiency of Nb, Ta and RE at 100 C for 2 hr and ore/acid ratio 1/10.

Maximum dissolution of 38.3% was obtained at 20 M HF. The results are shown in Figure (1a).

Ruiz et al.⁽²⁾ performed the pressure leaching on Columbo-tantalites

mineral using hydrofluoric acid. They found that increasing the acid concentration from 2.9 M to 8.6 M (5-15%) increases the amount of niobium and tantalum in the leach solution.

As reported by Krismer and Hoppe⁽⁵⁾, the recovery of 92% Nb and 98% Ta in the leach liquor was obtained by leaching fergusonite (Nb-Ta-RE bearing mineral) with 70% HF under nitrogen pressure. The rare earths remained insoluble in the residue.

Effect of temperature

The decomposition of niobium-tantalum ores by hydrofluoric acid leaching is exothermic⁽⁶⁾, so heat must be controlled to keep the solution not below the reaction temperature of about 60 °C after most of the acid has been used. The leaching temperature was varied from 60 to 150 °C to study its effect on the dissolution of niobium, tantalum and rare earths when the ground ore of

-200 mesh was mixed with 20 M hydrofluoric acid in the ore/acid ratio 1/10. The data obtained showed that the leaching ability of these elements increased to reach its maximum at 100 °C then decreased with increasing the temperature as shown in Figure (1b).

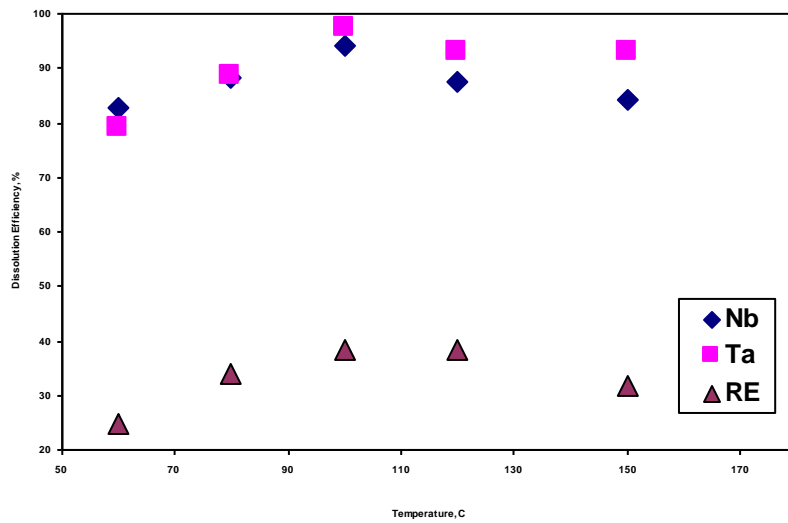


Fig. 1b: Effect of temperature on dissolution efficiency of Nb, Ta and RE by using 20M HF for 2 hr and ore/acid ratio 1/10.

II-A-3. Effect of leaching time

The leaching extent of niobium, tantalum and rare earths reached their maximum values within a few hours. Figure (1c) shows that two hours are sufficient

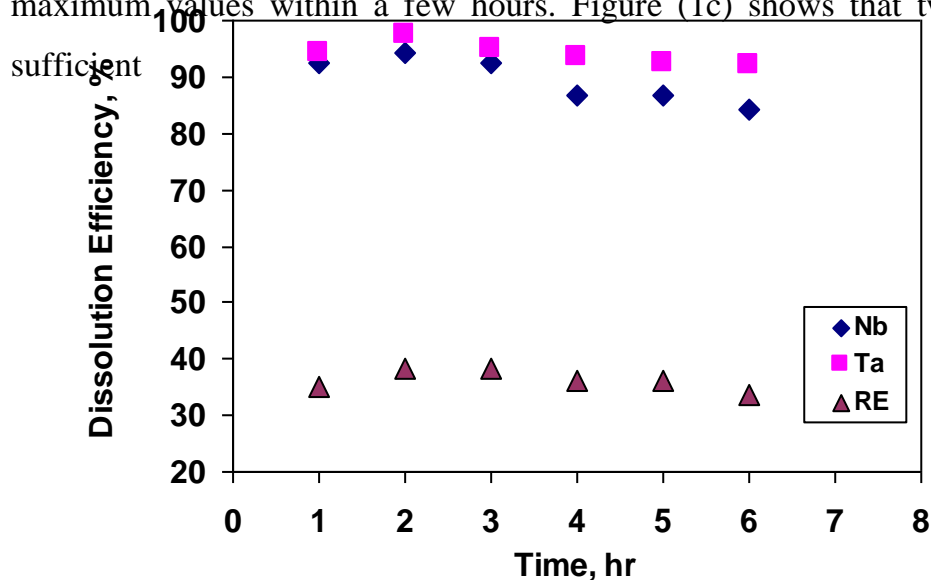


Fig. 1c: Effect of time on the dissolution efficiency of Nb, Ta and RE by

to dissolve 94.3% Nb and 97.4% Ta. The maximum dissolution of rare earths was attained within two to three hours. These results were obtained by mixing the ground ore of -200 mesh with 20 M HF in the bomb reactor at the ore/acid ratio 1/10 at 100 °C.

II-A-4. Effect of ore to acid ratio

A set of experiments was carried out to examine the effect of ore to acid ratio while using 20 M HF to leach the ground ore at 100 °C for two hours. Varying the ore/acid ratio from 1/.5 to 1/12.5 improves the dissolution of the rare earths to reach a maximum recovery of 43.9% at 1/12.5. Niobium and tantalum maximum leaching extent of 94.3% and 97.4%, respectively was obtained at the ore/acid ratio 1/10, Figure (1d).

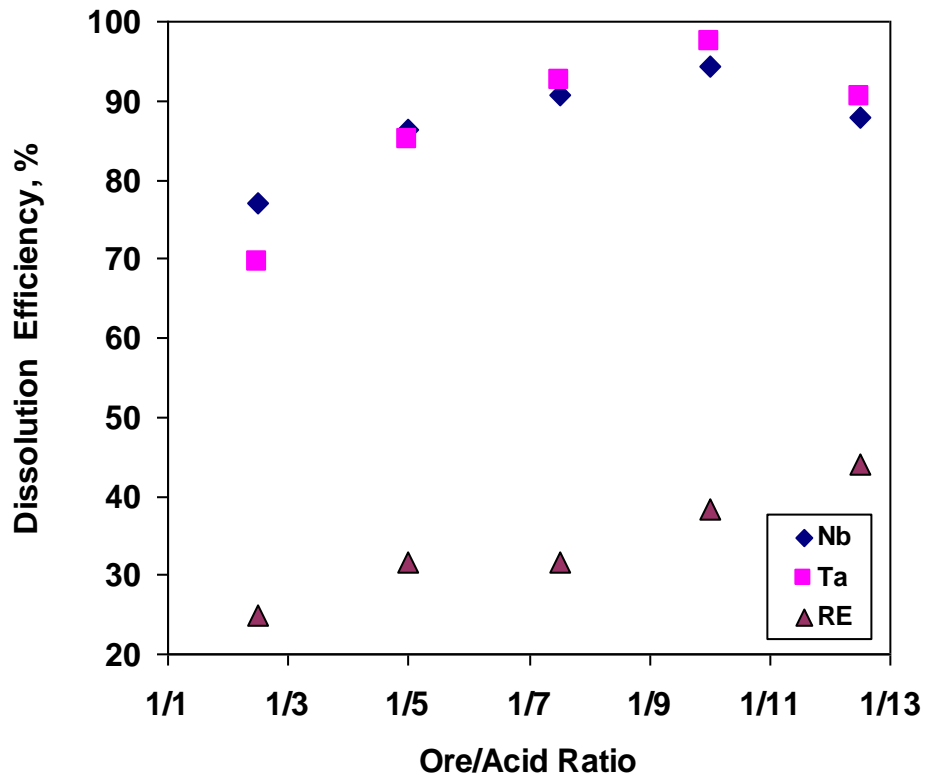


Fig. 1d: Effect of ore:acid ratio on the dissolution efficiency of Nb, Ta and RE by using 20M HF at 100 C for 2hr.

Leaching with sulfuric acid

Effect of acid concentration

Increasing sulfuric acid concentration from 0.5 M to 15.0 M shows a good influence on leaching both niobium and rare earths rather than tantalum. The concentrated sulfuric acid did not bring more than 46% of tantalum into the leach liquor while 82.1% and 75.3% of niobium and rare earths were dissolved,

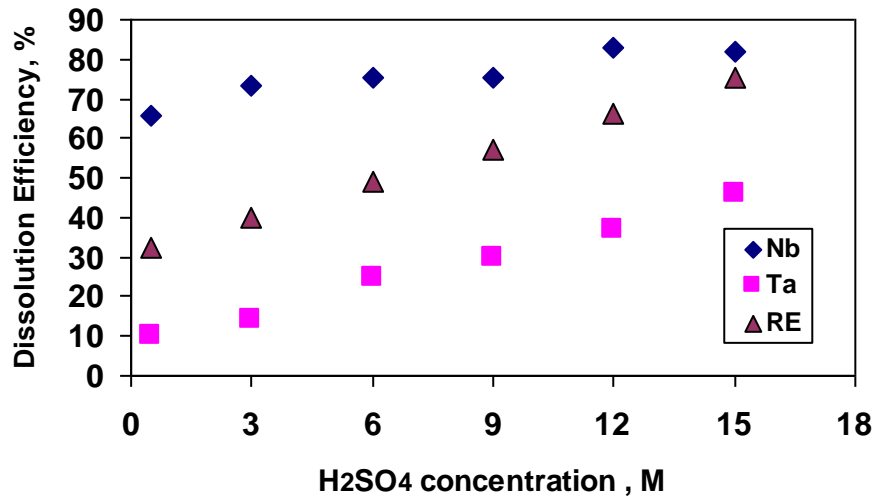


Fig. 2a: Effect of H₂SO₄ concentration on the dissolution efficiency of Nb, Ta and RE at 100 °C for 2hr and ore/acid ratio 1/10.

respectively. Figure (2a) shows the results of varying sulfuric acid concentration when mixed with the ground ore of -200 mesh at the ore/acid ratio 1/10 and leached under pressure at 100 °C for 2 hours.

Effect of temperature

Figure (2b) shows that the maximum recovery of tantalum by varying the leaching temperature from 60 °C to 120 °C did not exceed 46% while it attained 95.4% for niobium at 120 °C and 91.7% for rare earths at 150 °C. This set of experiments was carried out by mixing the ground ore with 15 M sulfuric acid in the ore/acid ratio 1/10 and leached under pressure for 2 hours. It was reported by Krismer and Hope⁽⁵⁾ that leaching such type of niobium-tantalum rare earth minerals at atmospheric pressure needs severe conditions of temperature raised up to 350 °C and concentrated sulfuric acid (18 M) to bring out 95% rare earths into the leach liquor.

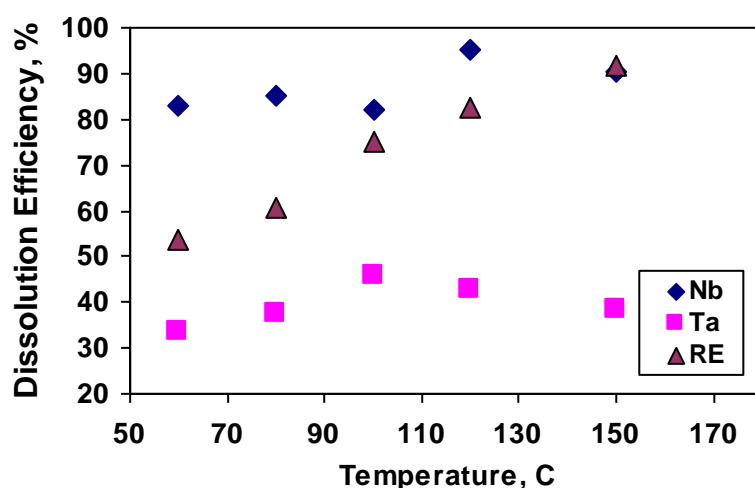


Fig. 2b: Effect of temperature on the dissolution efficiency of Nb, Ta and RE by using 15M H₂SO₄ for 2 hr and ore/acid ratio 1/10.

Effect of time

The effect of increasing the leaching time from 1 hour to 6 hours was studied when mixing the ground ore of -200 mesh with 15 M sulfuric acid at the ore/acid ratio 1/10 and heating the mixture in the bomb reactor at 100 °C. The results shown in Figure (2c) indicate that the dissolution of niobium and rare earths improve with increasing time. The dissolution of 46% of tantalum was achieved within 2 hours. Increasing the leaching time to 6 hours leads to 10% decrease in tantalum dissolution due to hydrolysis.

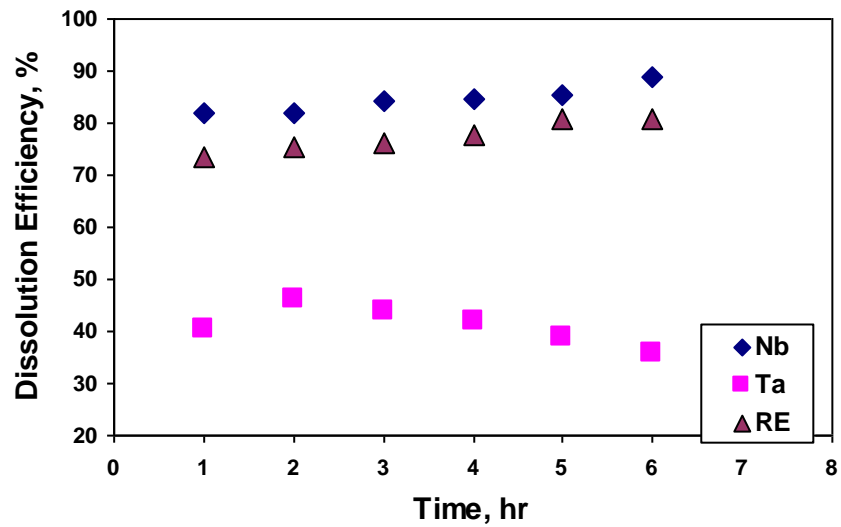


Fig. 2c: Effect of time on the dissolution efficiency of Nb, Ta and RE by using 15M H₂SO₄, at 100 C and ore/acid ratio 1/10.

Effect of ore to acid ratio

From Figure (2d), it is clear that niobium and tantalum dissolution increases by increasing the ore to acid ratio from 1/2.5 to 1/12.5. At the ratio 1/10, the rare earths attained the maximum dissolution of 75.3% then the dissolution decreased at 1/12.5.

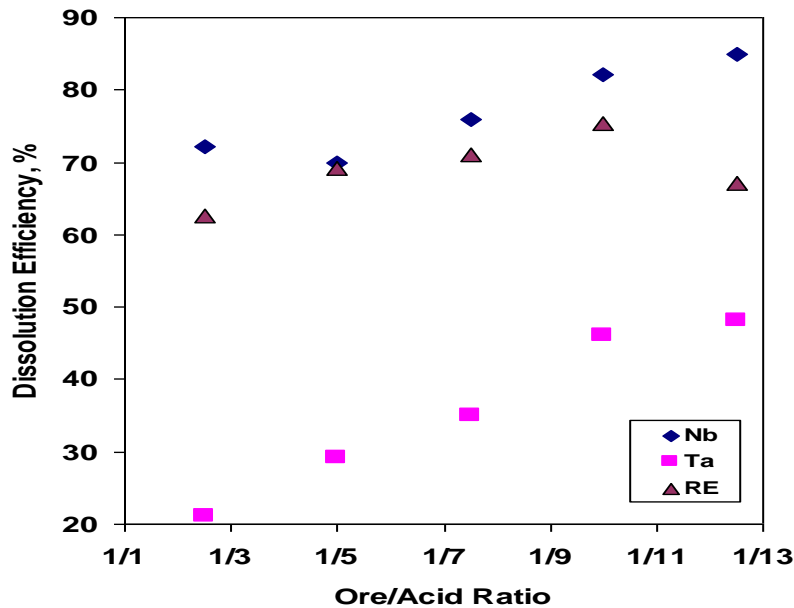


Fig. 2d: Effect of ore/acid ratio on the dissolution efficiency of Nb, Ta and RE by using 15 M H₂SO₄ for 2 hr at 100 C.

These results was obtained by mixing the ore ground to less than 200 mesh with the concentrated sulfuric acid in the bomb reactor and heating at 100 °C for 2 hours.

Leaching with hydrochloric acid

Effect of acid concentration

The reaction between the ground ore of –200 mesh and hydrochloric acid of different concentrations varying from 0.5 M to 11.8 M was performed in a bomb reactor at 100 °C for two hours where the ore to acid ratio was kept constant at 1/10. Figure (3a) reveals that the increase of acid concentration leads to increase in the solubility of niobium, tantalum and rare earths of euxenite and betafite minerals. It is also noticed that the rare earths leaching ability is higher than that of niobium and tantalum. Toromaroff and Habashi⁽⁷⁾ found that the decomposition of pyrochlore concentrate increased by increasing hydrochloric acid concentration from 2 – 10 M.

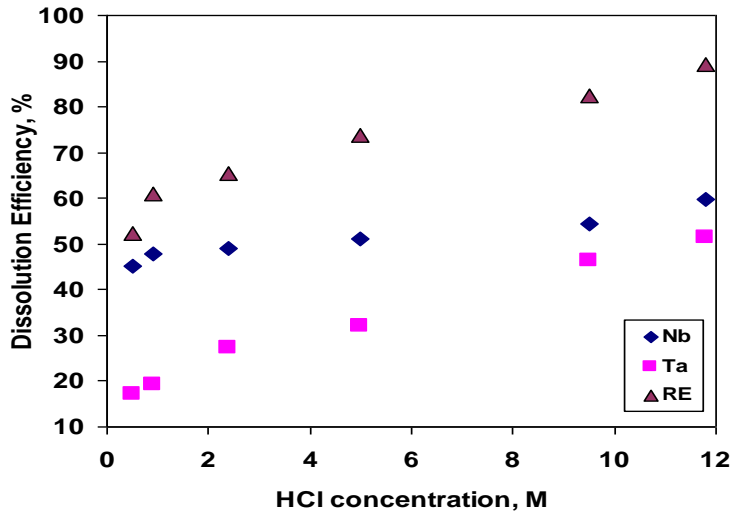


Fig. 3a: Effect of HCl concentration on the dissolution efficiency of Nb, Ta and RE at 100 C for 2 hr and ore/acid ratio 1/10.

Effect of temperature

The leaching tests were done by mixing the ore concentrate ground to less than 200 mesh with 11.8 M HCl at the ore/acid ratio 1/10 under pressure for 2 hours. Raising the temperature from 60 to 150 °C shows good influence on the recovery of niobium, tantalum and rare earths in the leach liquor, Figure (3b).

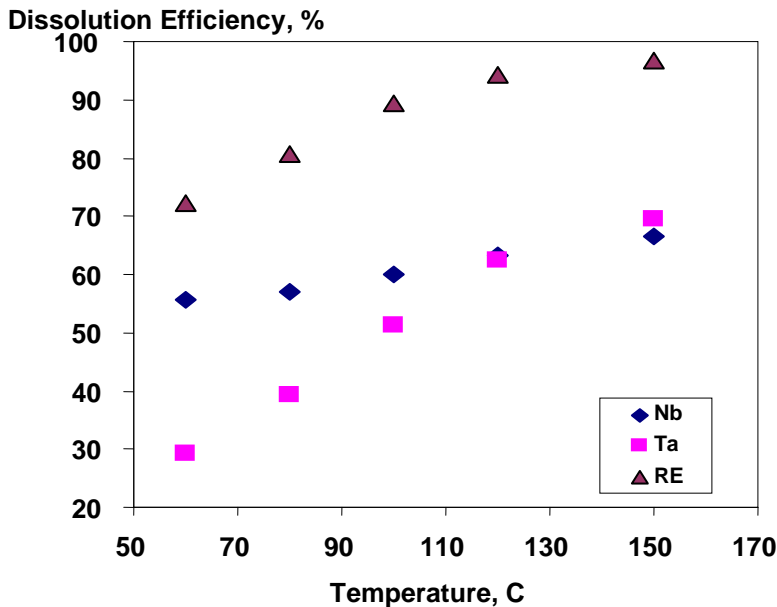


Fig . 3b: Effect of temperature on the dissolution efficiency of Nb, Ta and RE by using 11.8 M HCl for 2 hr and ore /acid ratio 1/10 .

The rare earths show the highest leaching ability of 97% at 150 °C. It was recommended that the boiled hydrochloric acid was used to decompose the rare earth minerals and turning them to soluble chlorides⁽⁸⁾. As reported by Derry, the pressure leaching of laporite concentrates with concentrated hydrochloric acid at 110-120 °C yields in 95-97% recovery of its metal values⁽⁹⁾.

Effect of time

As the leaching time increases to 4 hours, niobium and tantalum leaching increased to 63.1% and 49.4%, respectively then decreased by increasing the time to 6 hours. Five hours are needed to attain the maximum recovery of the rare earths of 93.3% in the leach liquor as shown in Figure (3c). The leaching time was studied by mixing the ore ground to less than 200 mesh with 11.8 M HCl in the bomb reactor at the ore/acid ratio 1/10 and heated at 100 °C.

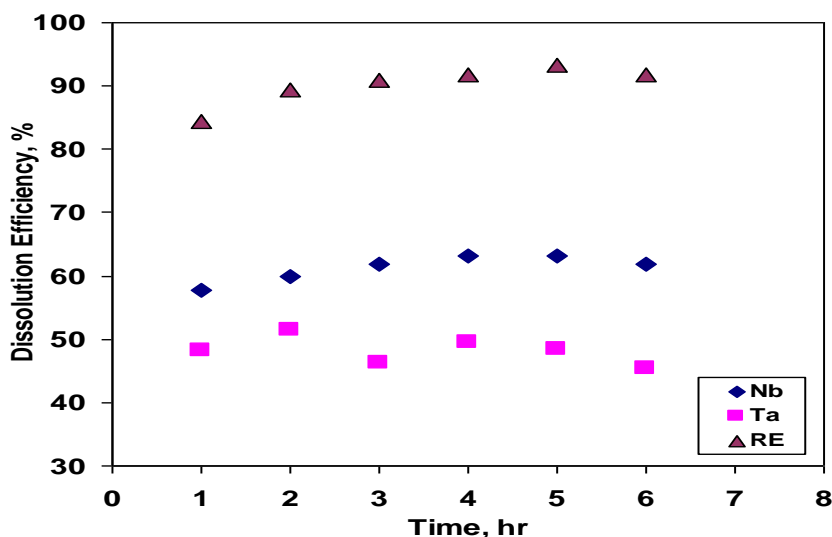


Fig.3c: Effect of time on the dissolution efficiency of Nb, Ta and RE by using 11.8M HCl, at 100 C and ore/acid ratio 1/10.

Effect of ore to acid ratio

Test was conducted in the bomb reactor by mixing the ore ground to less than 200 mesh with the concentrated hydrochloric acid at ratios varying from 1/2.5 to 1/12.5 and the leaching was done at 100 °C for 2 hours. As shown in Figure (3d) niobium and rare earths attained the maximum recovery of 64.8% and 91.8%, respectively at the ore to acid ratio 1/12.5, while the ore to acid ratio of 1/10 satisfies the maximum tantalum recovery of 51.4%.

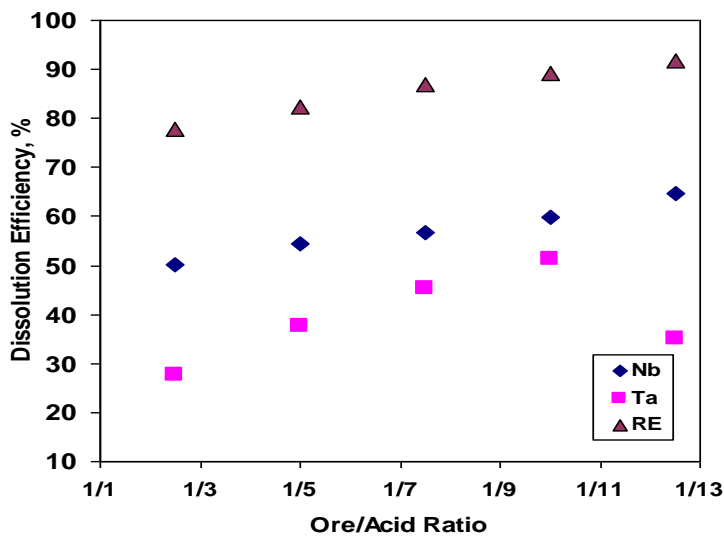


Fig. 3d: Effect of ore/acid ratio on the dissolution efficiency of Nb, Ta and RE by using 11.8M HCl for 2hr at 100 C.

Digesting the ore concentrate with hydrofluoric acid, sulfuric acid or hydrochloric acid in bomb reactor leads to 88%, 79% or 93% decomposition of the whole ore concentrate, respectively. In the meantime niobium, tantalum and rare earth elements are released from their refractory minerals euxenite and betafite.

From Figures (1a-1d), it is observed that niobium and tantalum have similar behavior when reacting with hydrofluoric acid with maximum recovery of 94.3% Nb and 97.4% Ta. The reaction causes the formation of the soluble species H_2NbF_7 or H_2NbOF_5 and $H_2TaF_7^{(10)}$. The rare earths remain in hydrofluoric acid residue as insoluble residue with 38.3% leachability. The

above results was achieved by leaching the ore concentrate with 20 M HF mixed at the ore /acid ratio 1/10 and heated at temperature 100 °C for 2 hours. The pressure leaching of Nb-Ta-RE minerals by sulfuric acid indicates that niobium and rare earths are highly affected by this acid rather than tantalum especially when the ore mixed with the acid in the ratio 1/10 and heated in the range 120 -150 °C. While about 95% of niobium content turns to soluble sulfate probably of the form $\text{Nb}_2\text{O}_5 \cdot \text{SO}_3$, it was found that about half of tantalum quantities may precipitated as tantalum hydroxide⁽¹¹⁾. The rare earths formed the soluble sulfates ($\text{RE}_2(\text{SO}_4)_3$) since 91.7% of its contents were determined in the leach liquor.

On the other hand, the ability of rare earths to form soluble species is higher than that of niobium and tantalum when the ore concentrate was leached under pressure with hot concentrated hydrochloric acid. About 97% of rare earths contents were dissolved from the ore concentrate mixed with 11.8M HCl at the ore /acid ratio 1/10 and heated at temperature 150 °C for 2 hours. Under these conditions the dissolution of both niobium and tantalum did not exceed 70% of each element contents, their dissolution may be accelerated by the addition of hydrofluoric acid⁽¹²⁾.

Thus, it possible to say that pressure leaching with hydrochloric acid satisfies both the maximum ore decomposition and the best total recovery of niobium, tantalum and rare earth elements in the leach liquor, while the separation of the insoluble rare earths from niobium and tantalum in the leach liquor may be achieved by varying the concentration of the hydrofluoric acid reacted with the ore concentrate under pressure.

Conclusion

Pressure leaching with hydrofluoric, sulfuric or hydrochloric acid shows good influence on the decomposition of the ore concentrate containing the refractory niobium-tantalum and rare earths bearing minerals, euxenite and betafite.

Pressure leaching turns the interesting elements to both soluble and insoluble species, the amount of each depends upon the acid used.

Varying hydrofluoric acid concentration while leaching the ore concentrate, may control the separation of both niobium and tantalum as soluble species from the insoluble rare earths. It is possible to leach 94% niobium and 97.4% tantalum of the ore minerals leaving more than 60% rare earths as insoluble fluorides. These results were obtained by reacting the ore concentrate in a bomb reactor with 20 M HF at the ore/acid ratio 1/10, temperature 100 °C and leaching time 2 hours.

The pressure leaching of the ore concentrate with hot concentrated hydrochloric acid decomposes 93% of its whole content. The rare earths reached its maximum leaching efficiency of 96.8% when the ore concentrate was leached under pressure with 11.8 M HCl at temperature 150 °C and ore/acid ratio 1/10 for 2 hours. The leaching ability of niobium and tantalum under these conditions was 66.4% and 69.6%, respectively.

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