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Potash Breakdown of Poly-Mineralized Niobium-Tantalum-Lanthanides Ore Material

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Abstract

The potentiality of the alkali breakdown of the poly mineralized ore material south Gabal El-A'urf area, central Eastern Desert, Egypt is investigated. It includes the multiple oxide mineral tanteuxenite, monazite, bastnasite, anatase, as well as zircon. This ore material assaying lanthanides (RE_2O_3 1.9%), niobium (Nb_2O_5 1.25%) as well as titanium and zirconium (TiO_2 and ZrO_2 1.23% and 1.12%) respectively besides tantalum (Ta_2O_5 0.13%), were used for the present work. This sample has thus been subjected to two alkali breakdown techniques using potash; namely agitation leaching and fusion. The latter technique was found to be preferred as it gives higher leaching efficiency. The optimum leaching conditions are weight ratio of the ore/potassium hydroxide 1/2 at 400˚C for 1 h. The realized leaching efficiencies attained 95.0% and 93.7% for Nb and Ta respectively as well as 96% for lanthanides and 75% for Ti while that for Zr did not exceed 10%.

Keywords

Lkali Fusion, Agitation Leaching, Niobium-Tantalum-Lanthanides Ores, Polymineralized Ore Material

1. Introduction

A poly mineralized ore material from south Gabal El-A'urf area, central Eastern Desert, Egypt [1] includes several interesting minerals; namely tanteuxenite, monazite, bastnasite, anatase and zircon. The corresponding interesting rare metals of these minerals in a properly prepared technological sample for the present work include RE_2O_3 1.9%, Nb_2O_5 1.25% as well as TiO_2 and ZrO_2 1.23%

and 1.12% respectively besides Ta_2O_5 0.13%. Several leaching studies have been performed upon comparable ore materials from different locations, but with different constituents and grades of the economic metal values. These studies include those of Shaw and Lindstrom [2] who reported that euxenite was recovered by fusing the ore material with $(NH_4)_2SO_4$ or $(NH_4)HSO_4$ at 400˚C for 4 hours. Shaw [3] indicated that euxenite from Arizona is amenable to REE recovery by digestion with HF-H_2SO_4 acid mixture. On the other hand, Shaw and Bauer [4] treated Idaho euxenite by H_2SO_4 acid alone for REE recovery. However, Pittuck *et al.* [5] performed a caustic fusion process for a concentrate of euxenite and fergusonite that assayed 9.4% U_3O_8 and 12.4% Nb_2O_5 at 700˚C for 10 - 15 min with an ore/reagent ratio of 1/3. Xiaohui Wang *et al.* [6] have also studied the leaching of Nb and Ta from a low-grade ore using KOH roast-water leach system. They achieved 95% and 94% leaching efficiencies for Nb and Ta with 80% for Si and Sn, 50% for Ti and <20% for Fe and Mn. Silva *et al.*, [7] investigated a Brazilian zircon concentrate fusion with NaOH followed by a two-step leaching. The effects of NaOH/zircon mass ratio, temperature and time were determined. The best fusion conditions were: NaOH/$ZrSiO_4$ mass ratio = 1.5:1; temperature, 575˚C; reaction time, 30 min. Water leaching was best conducted with a water/fused mass ratio = 3.75 at 25˚C. Acid leaching required 100 mL 3 $mol\cdot L^{-1}$ H_2SO_4 g^{-1} water-insoluble solid at 25˚C. 97 wt% of $ZrSiO_4$ was decomposed and around 91.5 wt% of Zr was recovered in the final product.

Concerning local ore materials, El Hazek [8] has studied the recovery of valuable metals from polymineralized ore material containing samarskite, betafite, thorite, uranophane and zircon. The ore concentrate assayed 31.77% RE_2O_3, 20.78% Nb_2O_5, 9.09% ZrO_2, 6.45% ThO_2, 2.2% U_3O_8 and only 1.06% Ta_2O_5 as well as 0.33% TiO_2. This ore material was subjected to H_2SO_4 agitation leaching to dissolve U, Th and REE while keeping Nb, Ta, Ti and Zr in the residue for subsequent leaching by HF. El Hussaini and Mahdy [9] have also studied the recovery of valuable metals from ore material containing fergusonite and euxenite besides the refractory U mineral davidite. Using H_2SO_4/HNO_3 acid mixture agitation leaching, almost complete dissolution of Nb and Ta was achieved together with 86% of Th and 70% of the REE; however, U and Ti leaching efficiencies did not exceed 60%. On the other hand, El Hazek *et al.* [10] have applied different breakdown techniques including agitation with conc. H_2SO_4 and potassium bisulfate fusion upon a polymineralized material to dissolve its metal values. The latter technique has realized maximum leaching efficiencies for all the metal values where Nb and Ta attained 98% and 99.3% as well as complete dissolution for REE and 94% for Ti while that of Zr didn't exceed 20%. The relevant optimum fusion conditions were 1/3 as the ore/reagent ratio at 650˚C for 3 h.

In the light of these givings, the present work was so planned to study the potentiality of potash breakdown of these minerals either by agitation or fusion at relatively high temperature. For this purpose, several experiments have been performed in both techniques to attain the optimum conditions that achieve highest dissolution with least cost.

2. Experimental

2.1. Analytical Procedures

The ore material from south Gabal El-A'urf area, central Eastern Desert, Egypt is subjected to complete chemical analysis for both major oxides and the economic metal values. Representative sample portions of the collected sample were properly obtained by proper quartering of the working sample after its grinding to −200 mesh size (−65 um). The major oxides have been analyzed using Shapiro and Brannock [11] rapid silicate analytical procedure. For Ca and Mg, a titrimetic method with EDTA using Eriochrome black T and Murexide as indicators was used [12]. The spectrometric analysis was used for SiO_2, Al_2O_3, and Fe_2O_3 (total) [11] [12], while for Na_2O and K_2O, flame photometry was applied using JENWAY flame photometer. The total loss of ignition (obtained at 1000˚C) is corresponding to humidity, combined water, CO_2 as well as possible organic matter [11].

On the other hand, the total REEs content was analyzed by a UV-Visible Spectrophotometer model Shimadzu UV-160A using Arsenazo III at wavelength 650 nm Marczenko [13]. The other metal values Ti, Nb, Ta and Zr were analyzed by the atomic absorption technique using a Unicam model 969 auto gas box at the wavelengths 365.4 nm, 334.4 nm, 271.5 nm and 360.1 nm respectivly Weltz and Sperling [14].

2.2. Alkali Breakdown Procedures

In both studied techniques, all the experiments have been performed using sample portions of the ground ore material. The interesting factors affecting both potash agitation leaching and potash fusion techniques have been examined.

1) KOH agitation leaching

Each leaching experiment has been performed by agitating a weighed amount of the ground ore sample with the alkali using different concentrations with different solid/liquid ratios for different periods of time at different temperature degrees. In these experiments, a hot plate fitted with a magnetic stirrer was used and the required precautions were taken to avoid evaporation. For high temperature degrees, an oil bath was used. At the end of each experiment, the obtained slurry was cooled, filtered, washed with distilled water and made up to volume. The obtained solution is then analyzed for the different metal values (Nb, Ta, REE, Ti and Zr) to calculate the leaching efficiency percent according to the equation:

$$\%\ \text{leaching efficiency} = \frac{\text{Metal content in the leach solution}}{\text{Original metal content in the ore sample}} \times 100$$

2) KOH fusion

Several fusion experiments have been performed using different amounts of KOH which were mixed with the sample portions in porcelain crucibles and heated in a muffle furnace for different periods of time at different temperature degrees. The obtained melt was then cooled and leached with distilled water, while the remaining ore residue was filtered and properly washed while the filtrate and washings were made up to volume for analyzing the interesting metal values for calculating their leaching efficiency percent.

3. Results and Discussion

3.1. Ore Composition

The results of the complete chemical analysis of the working technological ore material is shown in Table 1 where it is clearly evident that it is mainly composed of SiO_2 besides Al_2O_3 and Fe_2O_3. The relatively high K_2O content (4.92%) is indeed due to K-metasomatism while Na is markedly depleted (2.13%). On the other hand, the assay of the economic rare metal values including U (100 ppm) and Th (40 ppm) can be increased by some conventional physical techniques.

3.2. Result of Alkali Breakdown Techniques

1) KOH agitation leaching

a) Effect of KOH concentration

This factor was studied using different concentrations of KOH ranging from 6 to 12 M while the other leaching conditions were fixed at 200˚C for 3 h with a S/L ratio of 1/2. The obtained leaching efficiencies (Table 2) show that Nb and Ta dissolution increased from 81.0% to 87.5% and from 80.0% to 85.0% respectively whereas REE and Ti dissolution increased from 81.0% to 89.0% and from 73.0% to 79.0% respectively by increasing the alkali conc. from 8 to 10 M. Further increase in alkali concentration to 12 M keeps comparable results for all metals leaching efficiencies. However, Zr leaching efficiency didn't exceeds 9% as it requires a temp. higher than 200˚C.

Table 1. Chemical composition of the ore material.

Major constituent	Wt%	trace constituent	Wt%
SiO_2	74.00	RE_2O_3	1.90
TiO_2	1.23	Nb_2O_5	1.25
Al_2O_3	5.00	Ta_2O_5	0.13
Fe_2O_3	5.10	ZrO_2	1.12
CaO	1.64	U_3O_8	0.01
MgO	0.80	ThO_2	0.04
MnO	0.05		
Na_2O	2.03		
K_2O	4.90		
P_2O_5	0.06		
LOI*	0.74		
Total		100.0	

LOI* includes $H_2O^{crystalline}$ and CO_2.

Table 2. Effect of KOH conc. on the leaching efficiencies of the metal values.

Conc. KOH, M	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
6	72	73	75	66	5
8	81	80	81	73	6
10	87.5	85	89	79	9
12	87	84	86	74	9

b) Effect of solid/liquid ratio (S/L)

The effect of the S/L ratio (ore weight/KOH solution ratio) upon the leaching efficiency of the interesting metals was studied with ratios ranging from 1/1 to 1/3 using 10 M KOH at 200˚C for 3 h. The leaching efficiencies (**Table 3**) indicate that at 1/2 S/L ratio, the leaching efficiencies for Nb and Ta were 87.5% and 85% respectively together with 89% and 79% for REE and Ti whilst Zr leaching efficiency didn't exceed 9%. The realized leaching efficiencies have almost been kept steady at the S/L ratio of 1/3.

c) Effect of leaching temperature

This factor was studied in the range from 80 up to 240˚C while the other conditions were fixed at 10 M KOH conc., a S/L ratio of 1/2 and a leaching time of 3 h. The obtained data (**Table 4**) indicate that the working polymineralized ore material requires a relatively high temp. to be broken due to its refractory nature. However, the leaching efficiencies for all the study metal values (except Zr) increased sharply by increasing the temp. till 200˚C where the leaching efficiencies for Nb and Ta attained 87.5% and 85% while REE and Ti leaching efficiencies attained 89% and 79% while the Zr leaching efficiency attained only 9%. Further increase in temperature beyond 200˚C was found to have an adverse effect.

d) Effect of leaching time

The effect of leaching time was studied in the range of 1 to 4 h while the other leaching conditions were fixed at 10 M KOH conc., S/L ratio of 1/2 at 200˚C. The corresponding leaching efficiencies (**Table 5**) of Nb and Ta attained 69.0% and 68.0% at 1 h and extending the leaching time up to 3 h increased these values up to 87.5% and 85% respectively. The leaching efficiencies of the lanthanides and Ti at this leaching time attained 89.0% and 79.0%. On the other hand, the Zr leaching efficiency was only 9%. Extending the leaching time for 4 h was found to have an adverse effect upon the dissolution of Nb, Ta, REEs and Ti.

2) KOH fusion

a) Effect of ore/KOH ratio (O/R ratio)

A set of alkali fusion experiments using potash has been performed using different O/R weight ratios ranging from 1:1 to 1:4 while the other two fusion conditions were fixed at 400˚C for 1 h. The results shown in **Table 6** proved that the leaching efficiencies of the interesting metals have been markedly increased at 1/2 ore/KOH ratio up to about 94% or more for Nb, Ta & REEs and to 75% and

Table 3. Effect of S/L ratio on the leaching efficiencies of the metal values.

S/L ratio	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
1/1	79	75	80	71	6
1/2	87.5	85	89	79	9
1/3	85.5	84	88	77	9

Table 4. Effect of temp. on the leaching efficiencies of the metal values.

Temp., ˚C	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
80	64	61	64	69	4
120	70	71	70	72	5
160	80	80	82	77	8
200	87.5	85	89	79	9
240	77	79	87	72	10

Table 5. Effect of time on the leaching efficiencies of the metal values.

Time, h	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
1	69	68	68	60.5	5
2	80	79	81	70.5	7
3	87.5	85	89	79	9
4	84	82	87	78	9

Table 6. Effect of O/R ratio on the leaching efficiencies of the metal values.

O/R ratio	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
1/1	72.1	70.5	78	61.5	5
1/2	95.0	93.7	96	75	10
1/3	90.2	88	91	71	10
1/4	88.8	82	87	68.2	9.5

10% for Ti & Zr respectively. Increasing the S/R ratio beyond 1/2 has progressively decreased the leaching efficiencies for all the study metals; a matter which is most probably due to hydrolysis.

b) Effect of fusion temperature

A second series of alkali fusion experiments has been carried out at temp. ranging from 300˚C to 600˚C while the other fusion conditions were fixed at an ore/KOH ratio of 1:2 for 1 h. The obtained leaching efficiencies of the study metals, Table 7 were found to increase gradually by raising the fusion temp. from 300˚C to 400˚C where they attained about 94% or more for Nb, Ta & REEs and 75% for Ti whereas only 10% for Zr. However, increasing the fusion temperature to 500˚C and 600˚C has an adverse effect on the leaching efficiencies of these metal values that might be due to hydrolysis. On the other hand, the leaching efficiency of Zr was markedly improved by increasing the fusion temp. where it attained 24.5% at 500˚C and 36.0% at 600˚C. This is most probably due to the refractory nature of the zircon mineral.

c) Effect of fusion time

A third set of alkali fusion experiments was performed for time periods ranging from 30 to 120 min. while the other fusion conditions were fixed at an ore/KOH ratio of 1:2 and a fusion temperature of 400˚C. From the leaching efficiencies of the studied interesting metal values (Table 8), it is clearly evident that increasing the fusion time from 30 to 60 min. increases the leaching efficiencies for all metals to become 96.0% and 93.7% for REE and Ta respectively and 95.0% and 75.0% for Nb and Ti respectively together with only 10% for Zr. Further increasing the fusion time to 90 and 120 min didn't improve the leaching efficiencies already obtained at 60min. for all the studied metal values.

4. Conclusion

The polymineralized ore material (real sample obtained from south Gabal El-A'urf area, central Eastern Desert, Egypt) has been subjected to two alkali breakdown techniques using potash; namely agitation leaching and fusion. Since alkali breakdown is highly selective and due to the refractory nature of this polymetallic ore material, sever conditions are necessary. In both techniques the

Table 7. Effect of the fusion temp. on the leaching efficiencies of the metal values.

Alkali fusion temp., ˚C	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
300	82	81	84	68	8
400	95	93.7	96	75	10
500	74.1	77	69	55	24.5
600	72	71	70	52	36

Table 8. Effect of the fusion time on the leaching efficiencies of the metal values.

Time, min	Leaching efficiency, %				
	Nb	Ta	REE	Ti	Zr
30	77	73	80	66	6
60	95	93.7	96	75	10
90	94	93.5	96	74.7	10
120	95	93.5	95	74	10

relevant conditions have been studied and optimized. Accordingly, for the agitation leaching, the determined optimum conditions involve 10 M alkali concentration with a solid/liquid ratio of 1/2 at 200˚C for 3 h using an ore size up to −60 mesh. Under these conditions, it was possible to achieve leaching efficiencies of 87.5% and 85.0% for Nb and Ta respectively together with 89.0% and 79.0% for REEs and Ti respectively while that of Zr didn't exceed 9% due to refractory zircon mineral. On the other hand, for the preferable alkali fusion technique, the optimum conditions involve a weight ratio of ore/potassium hydroxide of 1/2 at 400˚C for 1 h. The realized leaching efficiencies for the metal values have been attained 95.0% and 93.7% for Nb and Ta respectively as well as 96% for lanthanides and 75% for Ti while the leaching efficiency of Zr did not exceed 10% and hence would be concentrated in the residue left behind.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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