

**SELECTIVE RECOVERY OF RARE EARTHS FROM  
KADABORA MULTIPLE OXIDES MINERAL  
CONCENTRATE (EASTERN DESERT, EGYPT) BY  
SULFATIZING ROASTING / CALCINATION**

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**ABSTRACT**

The working sample of Kadabora mineral concentrate (Eastern Desert, Egypt) assays an equivalent total of about 72 % economic metal oxides. The latter are present in the form of different refractory minerals including mainly fergusonite and columbite together with lesser amounts of samarskite, betafite, thorite beside a minor content of uranophane and zircon. Proper fusion with ammonium sulfate rendered the metal values to water-leachable products, however, to varying degrees. This is due to the heterogeneity of the input ore whose mineral constituents respond differently to the applied conditions. Control of the fusion temperature and time, the ammonium sulfate to ore ratio and with or without subsequent calcination would lead to insolubilization of the non-rare earth metal values. The relevant factors are studied to define the optimum conditions required for this separation.

**I- INTRODUCTION**

Both niobium and tantalum metals belong to the refractory rare metals group which essentially form hard and dense multiple oxides of the general formula  $A_mB_nO_{2(m+n)}$ . They can generally be described as the niobates, titanates and tantalates minerals of yttrium and rare earth elements. These minerals usually occur as accessory constituents of igneous rocks or else as resistant detrital grains in sedimentary rocks. Appreciable amounts of uranium, thorium, tin, tungsten, zirconium, etc. might replace for some of the mentioned cations. These complex

minerals can indeed be classified into the following three mineral series namely:

i) columbite-tantalite series, ii) euxenite-polycrase series and iii) pyrochlore-microlite series.

Beside Ti presence, the second series of euxenite ( $Nb+Ta>Ti$ ) - polycrase ( $Ti>Nb+Ta$ ) can be characterized by more replacement. Thus, samarskite  $\{(Y,Ce,U,Fe^{3+})_3(Nb,Ta,Ti)_5O_{16}\}$  and betafite  $(Y,U,Ce)_2(Ti,Nb,Ta)_2O_6OH$  represent euxenite and polycrase respectively, but with even more substituents. On the other hand, the pyrochlore( $Nb>Ta$ )-microlite( $Ta>Nb$ ) series is characterized by the presence of Na and Ca. Fergusonite is a member in this series in which REE wholly replace Na and Ca and has the general formula of  $Y(Nb,Ta)O_4$ .

In the eastern desert of Egypt, **Ibrahim et al. (1997)** have revealed that the pegmatite bodies associated with Kadabora granitic batholith are hosting several rare metal mineralizations. These include mainly Nb, Ta, U, Th, REE beside Ti and Zr in the form of various refractory minerals. The latter were identified to include fergusonite, samarskite, betafite as well as yttrantalite, gadolinite and minor uranophane, zircon, etc.

The chemical processing of such mineral varieties require indeed severe breakdown procedures including for example gaseous chlorination, digestion with a sulfuric-hydrofluoric acid mixture or sulfuric acid alone for partial recovery. However, the latter is characterized by severe operating conditions and long digestion periods. According to **Shaw and Landstrom (1967)**, the acid frequently presents corrosion problems and handling difficulties. Although, anhydrous fusion techniques (using sodium or potassium sulfate) would eliminate many of such problems, the presence of gross quantities of sodium and potassium in the product causes serious problems. Therefore, these authors have studied the anhydrous fusion of Idaho 86% euxenite concentrate with ammonium sulfate under various conditions for bulk or selective dissolution of REE.

The main objective of the present work is to investigate the behaviour of the refractory minerals of Kadabora concentrate when fused (sulfatizing roasting) with anhydrous ammonium sulfate under various conditions. The purpose is to render some or all the contained rare metal

values soluble, a matter which would facilitate the separate recovery of the rare earth metal fraction.

## II-EXPERIMENTAL

From the chemical composition of the working concentrate shown in Table (2), it was found that it consists essentially of 31.77 % RE<sub>2</sub>O<sub>3</sub>, 20.78 % Nb<sub>2</sub>O<sub>5</sub>, 9.09 % ZrO<sub>2</sub>, 6.45 % ThO<sub>2</sub>, 2.20 % U<sub>3</sub>O<sub>8</sub> and 1.06 % Ta<sub>2</sub>O<sub>5</sub> while the non-economic constituents assay about 28 %.

**Table (1):** Kadabora Mineral Fractions Separated by Frantz Isodynamic Separator [after El Hazeek (2001)].

Current Intensity, Amp.	Wt. %	Major Minerals
0.2	6.82	Samarskite; Betafite
0.5	86.20	Fergusonite; Columbite
1.0	5.06	Thorite
Non Magnetic	1.85	Zircon, Uranophane

**Table(2):** Chemical Composition of Kadabora Multiple Oxide Mineral Concentrate

Component	Wt. %	Component	Wt. %
RE <sub>2</sub> O <sub>3</sub> *	31.77*	Fe <sub>2</sub> O <sub>3</sub>	1.50
Nb <sub>2</sub> O <sub>5</sub>	20.78	MnO	1.50
ZrO <sub>2</sub>	9.09	CaO	8.40
ThO <sub>2</sub>	6.45	H <sub>2</sub> O lattice H <sub>2</sub> O	3.41
U <sub>3</sub> O <sub>8</sub>	2.20	humidity	0.56
Ta <sub>2</sub> O <sub>5</sub>	1.06	Others**	12.95
TiO <sub>2</sub>	0.33		
<b>Total</b>	<b>71.68</b>	<b>Total</b>	<b>28.32</b>

\* Measured as equivalent Ce<sub>2</sub>O<sub>3</sub>

\*\* Mostly Na<sub>2</sub>O and to a much less extent K<sub>2</sub>O and SiO<sub>2</sub>

The technological sample representing these ore minerals was ground to a size ranging from -250 to + 63  $\mu\text{m}$  before being subjected to a heavy liquid separation (bromoform: sp. gr. 2.84) to obtain a proper concentrate suitable for studying the recovery of the required metal values. To identify the mineral composition of this concentrate, a weighed amount was subjected to magnetic separation using Frantz Isodynamic Separator. The obtained mineral fractions at different current intensities were weighed and examined under the binocular microscope Table (1).

The sulfatizing roasting experiments were carried out in a nickel crucible using a weight ratio of Kadabora concentrate to anhydrous ammonium sulfate of 1:6 unless otherwise stated. After thorough mixing, the reactants were roasted in a pre-heated furnace for a specified time and the evolved ammonia was allowed to escape. The roasted mass was allowed to cool to room temperature and was then leached with water for 1 h at 90° C. Some experiments were performed by keeping the reacting mass covered while in others, the reacting mass was leached into ice-cooled water. The residue left behind was filtered and washed while the filtrate and washings were made to volume 100 ml.

Analysis of the dissolved metal values of REE, Th, Nb and Ta were carried out using a Shimadzu double beam UV-Visible spectrophotometer, Model UV-160 A. For REE and Th, arsenazo III was used as a chromogenic reagent and absorbance of the formed complex in either case was measured at 650 and 660 nm, respectively [Marczenko (1986)]. For Nb and Ta, pyrogallol was used and absorbance of the formed complex in either case was measured at 372 and 392 nm, respectively [Welz and Sperling (1999)].

A GM Fluorometer manufactured by Advanced Technical Services, GmbH of Germany was used for U assay.

The leaching efficiency of the investigated metal values were calculated as follows:

$$\% \text{Leaching efficiency} = \text{Dissolved metal content} / \text{Input metal content} \times 100$$

### III-RESULTS AND DISCUSSION

#### III-1- Effect of Ammonium Sulfate Ratio

The effect of the weight ratios (2/1, 4/1 and 6/1) of ammonium sulfate to Kadabora refractory mineral concentrate was studied. In these experiments, the roasting temperature was fixed at 400° C for 4h. After

cooling to room temperature, the obtained mass was leached with water at 90 °C for 1h and the residue left behind was filtered and washed. By analysis of the different metal values in the obtained pregnant solution, it was possible to calculate their leaching efficiencies as shown in Table (3). From the data, it is evident that increase in the amount of the sulfating reagent resulted in increasing the rate and amount of the dissolved metal values. At the weight ratio of 6/1, a leaching efficiency exceeding 91 % was obtained for REE and U beside about 84 and 80 % for Th and Ta, respectively.

**Table (3):** Effect of Ammonium Sulfate Ratio during Roasting on the Water Leaching Efficiency (%) of Kadabora Metal Values (Roasting Temperature 400 °C; Roasting Time 4 h).

Concentrate/(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> Wt. Ratio	REE	Th	U	Nb	Ta
1/2	53.84	38.59	37.52	39.65	10.08
1/4	74.43	66.16	55.75	47.12	24.77
1/6	91.29	83.80	91.88	58.06	79.20

Although the leaching efficiency of Nb amounted to about 40 % at 2/1 weight ratio of the sulfate reagent, it only increased to about 47 and 58 % by increasing the weight ratio to 4/1 and 6/1, respectively. On the contrary, the leaching efficiency of Ta was quite low at 2/1 weight ratio and slightly increased to about 25 % at 4/1 weight ratio while at the weight ratio of 6/1 it sharply increased to about 80 %. It can thus be concluded that if Nb and Ta are found in the same mineral structure, difference in their leaching efficiencies might be due to differences in the extent of hydrolysis of the two metals. However, if both metals belong to different minerals in Kadabora concentrate, the achieved differences in their leaching efficiencies would be due to varying degrees of mineral sulfation.

### III-2- Effect of Roasting Time

To study the effect of roasting time upon the dissolution efficiencies of Kadabora metal values, a second series of experiments was performed fixing the roasting temperature at 400° C with a concentrate / reagent weight ratio of 1/6 and varying the roasting time from 15 min to 4h. From the corresponding dissolution efficiencies tabulated in Table (4) it is clear that as roasting time increases, the dissolution efficiency for all the metal values increases.

**Table (4):** Effect of Roasting Time on the Water Leaching Efficiency (%) of Kadabora Metal Values (Concentrate to  $(\text{NH}_4)_2 \text{SO}_4$  Weight Ratio, 1/6; Roasting Temperature 400° C)

Roasting Time, (h)	REE	Th	U	Nb	Ta
1/4	46.03	25.58	32.51	38.71	nil
2	77.34	67.92	74.37	55.48	43.20
4	91.29	83.80	91.88	58.06	79.20

As mentioned above, difference in the leaching efficiency attained for Nb and Ta are most probably due to their occurrence in different mineral constituents or to differences in the extent of their hydrolysis. However, as will be later shown, a leaching efficiency of about 95 and 90 % for Nb and Ta has respectively been obtained at a roasting temperature of 450° C.

### III-3- Effect of Roasting (Calcination) Temperature

To study the effect of the roasting temperature upon subsequent water leaching of the valuable metals of Kadabora concentrate, four experiments were conducted at temperatures ranging from 350 to 650° C. The other experimental conditions were fixed at a concentrate to reagent weight ratio of 1/6 and for a roasting time of 4h. From the obtained data summarized in Table (5), it is evident that a roasting temperature of 350° C is quite adequate for bringing most REE, Th, and U in solution (about 99, 93 and 96%, respectively). However, Nb and Ta were found to need

a higher roasting temperature of 450° C to attain dissolution efficiencies of about 95 and 90%, respectively. This behavior suggests that both metals belong to the same mineral species in Kadabora concentrate.

A further increase of the roasting temperature to 650° C decreased the dissolution efficiency of Nb sharply to about 7.7% while Ta was completely insolubilized. In the meantime, the dissolution efficiencies of both Th and U have also been adversely affected - by increasing the roasting temperature to 650° C, down to about 8 and 15%, respectively while that of REE was almost unchanged (about 88%). From these results, it is evident that it would be possible to achieve a relatively high selective dissolution of the REE content of Kadabora concentrate by its prior roasting at 650° C. To confirm these results, another roasting experiment was carried out at 400° C for 4h using a weight ratio of ammonium sulfate to Kadabora concentrate of 6/1. After cooling the roasted mass to room temperature, it was further subjected for 3h calcination at 650° C. Water leaching of the latter indicated that the dissolution efficiency of REE was not impaired, i.e. it remained at about 88% while the dissolution efficiency of Th and U decreased to about 4 and 10%, respectively and that of Nb decreased to about 6% while Ta remained insoluble.

**Table (5):** Effect of Roasting/Calcination Temperature on the Water Leaching Efficiency (%) of Kadabora Metal Values (Concentrate to (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> Weight Ratio, 1/6; Roasting Time, 4 h).

Roasting Temp. (°C)	REE	Th	U	Nb	Ta
350	98.96	92.62	95.52	34.84	34.56
400	91.29	83.80	91.88	58.06	79.20
450	88.02	74.10	90.05	94.97	90.14
650	87.46	7.94	15.01	7.74	nil
Roasting at 400 °C, 4h + Calcination at 650 °C, 3h	87.57	4.41	9.92	6.09	nil

Summing up, it can be mentioned that increase of roasting /calcination temperature to 650°C has proved quite advantageous to relative selective dissolution of REE vs. the non-rare earths of Kadabora constituents (Th, U and Nb) while Ta was completely insolubilized. This behavior might indeed be interpreted as due to the reformation of some insoluble oxide forms of Th, U, Nb and Ta. The latter may be individual and/or mixed oxide forms. The attained insolubilization might be also, at least partially, due to some hydrolysis effects.

#### III-4- Effect of Roasting Under Ammonia Atmosphere

In a trial to check for potential selectivity of the studied metal values, the second and last experiments were roasted under ammonia atmosphere keeping crucibles covered. The subsequent water leaching results of the obtained products are shown in Table (6).

**Table (6):** Effect of Roasting/Calcination Temperature Under Ammonia Atmosphere on the Water Leaching Efficiency (%) of Kadabora Metal Values (Concentrate to  $(\text{NH}_4)_2\text{SO}_4$  Weight Ratio, 1/6).

Roasting Temp., °C / Time	REE	Th	U	Nb	Ta
400 °C for 4h	79.30	74.10	75.04	46.10	54.69
400 °C for 4h + Calcination at 650 °C for 3h	72.80	22.90	16.12	15.54	8.42

Comparing the values of data in Table (6) with the corresponding values in Table (5), it is evident that the presence of ammonia atmosphere at 400°C roasting has decreased the leaching efficiencies of all the metal values. Moreover, the data tabulated in Table (6) show that the calcination, of the roasted product (400 °C), for 3h at 650 °C, under ammonia atmosphere has, however, adversely affected the insolubilization percent of Th, U, Nb, and Ta. On the other hand, the REE leaching efficiency has been decreased to about 73%.



**III-5- Effect of Ice-Cold Water on the Solubilities**

A successful selective REE separation from Kadabora mineral concentrate has actually been possible by applying ice-cooled water leaching of the roasted/calcined product. This has been possible by air roasting the concentrate with six fold weight of  $(\text{NH}_4)_2\text{SO}_4$  at 400 °C for 4h followed by calcining the product at 650 °C for 3h. Any of the non-rare earth elements has not been detected in solution. Complete insolubilization of Th, U and Nb in cold water is most probably due to increased hydrolysis effects.

**IV- CONCLUSION**

The highly refractory complex oxide ore minerals of Kadabora (fergusonite, columbite, samarskite, betafite, thorite, etc.) require severe operating conditions for their breakdown. By careful control of roasting/calcination relevant factors using  $(\text{NH}_4)_2\text{SO}_4$ , it has been possible to achieve high breakdown rates of the ore minerals under study. Using 450 °C roasting temperature for 4h has resulted in a water subsequent leaching at 90 °C of about 90% of the REE, U, Nb and Ta contents and about 75% of the Th content of the investigated ore

Increasing the roasting/calcinations temperature to 650 °C for 4h has proved successful in achieving sharp decrease in the dissolution percent of Th, U, and Nb while Ta was completely insolubilized. Alternatively, roasting at 400 °C for 4h followed by calcination at 650 °C for 3h would not impair REE leaching efficiency but has resulted in further decrease of the leaching percent of Th, U and Nb. This behavior has been interpreted as due to possible re-formation of some insoluble oxide forms of the non-REE constituents. The latter may be individual and/or mixed oxide forms. Complete insolubilization of the latter was, however, achieved by using an ice-cold water for the subsequent leaching step.

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إستخلاص الأرضيات النادرة إنتقانيا من ركاز الأكاسيد المتعددة من منطقة كادابورا  
بالصحراء الشرقية ، مصر ، بطريقة التحميص بحامض الكبريتيك والكلسنة

يختص البحث بدراسة التحميص الحراري لعينة تكنولوجية من تمعدن النيوبيوم والأرضيات النادرة بمنطقة كادابورا بالصحراء الشرقية - مصر ونظرا لاحتواء العينة على العديد من المعادن المقاومة للذوبان مثل الفيرجوسونيت والكولومبيت والسمرسكيت والبيتايفيت والثوريت ... الخ ، فقد تمت دراسة التحميص المسبق لركاز من هذه العينة في وجود كبريتات الأمونيوم تحت ظروف مختلفة من درجة الحرارة ( ٣٥٠ - ٦٥٠ °م ) ومن نسبة العينة الى نسبة كبريتات الأمونيوم ( ٢:١ الى ٦:١ ) وكذلك باستخدام فترات تحميص مختلفة ( ربع ساعة - ٤ ساعات ) .

وقد تم تحديد الظروف المثلى للإذابة التي تعطي أكثر اذابة للعناصر المطلوبة . وقد أتضح من النتائج التي تم الحصول عليها امكانية اذابة كل من عناصر الأرضيات النادرة واليورانيوم والنيوبيوم والتتالوم ( ٨٨ - ٩٥ % ) وكذا الثوريوم بنسبة حوالى ٧٤ % في الماء .

وقد أمكن من خلال اجراء كلسنة عند ٦٥٠ °م لمدة ٣ ساعات للمنتج المحمص من خفض ذوبان جميع العناصر المذكورة ما عدا العناصر الارضية النادرة .

