

**SEPARATION OF NIOBIUM FROM ITS REFRACTORY
MINERALS BY FUSION WITH NON HAZARDOUS
FLUORIDE CONTAINING COMPOUNDS**

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ABSTRACT

The decomposition of Egyptian ore refractory minerals and the separation of niobium were performed in presence of fluoride containing compounds to avoid the difficult handling of hydrofluoric acid and allow the subsequent reactions to be done in conventional vessels.

Some fluoride containing compounds beside yttrium fluorite mineral were mixed with the ground ore sample at different weight ratios and fused at elevated temperatures. The fused cakes were then leached with sulfuric acid. Selecting the flux type has its influence in liberating the elements of interest (Nb, Ta, Ti, Ce, Y, etc.) into the sulfate leach liquor. Niobium was finally separated by liquid extraction using methyl isobutyl ketone (MIBK).

Keywords: niobium, fluoride containing compounds, fusion, leach liquor, recovery.

1. INTRODUCTION

As a common method, most of niobium minerals can be readily decomposed with hydrofluoric acid. The corrosion nature of hydrofluoric acid prohibits the use of metallic vessels or simple glass ware. The extent of leaching has been found to increase considerably utilizing a mixture of acids comprising hydrofluoric acid (e.g. carboxylic acid and fluosilicic acid) rather than hydrofluoric acid alone [Rodriguez et al., (2004)]. In addition, fluosilicic acid (H_2SiF_6) was found to improve the extraction of niobium by tributyl phosphate (TBP), [Mayorov & Nikolaev, (1996)

and Maiorov et al., (2004)]. Gupta and Suri (1994) reported that direct hydrofluoric acid is not preferred for decomposing niobium minerals containing high alkaline constituents because of large requirement of the acid.

The ore sample under study was attacked by acidic fluxes of fluoride containing compounds. Yttrium fluorite mineral, introduced as natural source of calcium fluoride was also fused with the ore sample to detect its influence compared to other fluoride chemicals in liberating the valuable elements during the subsequent sulfuric acid leaching upon the fused cake. The separation of niobium from the leach liquors was done by methyl isobutyl ketone (MIBK).

2. EXPERIMENTAL

2.1. Materials

All the chemical reagents employed were of analytical grade and the deionized water was used in the corresponding procedures. The ore sample obtained from eastern desert of Egypt was analyzed for its mineralogical and chemical compositions by X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively, (Table 1). Yttrium fluorite mineral obtained from El Missikat area was used as fluoride reagent as well. It was analyzed in the same manner, (Table 2).

2.2. Apparatus

The fusion process was performed in a Lenton muffle furnace model AWF 12/25 supplied with controller 2216e. The pH measurement was carried out using Cheker-1 pH meter from HANA instruments provided with HI1270 combined electrode. Identification of the ore minerals was done by XRD with Cu target model PW 223/20 operated at 40 KV and 20 mA. The chemical composition of the ore sample was analyzed in School of Process, Environmental and Materials Engineering, University of Leeds, U.K using a scanning electron microscope (CAM SCAN series 4 ISIS 200 E/X system with pentajet detector). Yttrium fluorite mineral was analyzed by Camera SX 100 at university of Texas at El Paso (UTEP- USA). The double beam UV-VIS recording spectrophotometer Shimadzu UV160A was used to determine the elements concentrations in the leach liquors and in the aqueous solutions after extraction and stripping experiments. Niobium and tantalum were analyzed without preliminary separation using pyrogallol in alkaline and acidic solutions, respectively. The rare earth elements

were determined by arsenazo(III) [Marczenko, (1986)], silicon was analyzed by ammonium molybdate blue while titanium analysis was done by hydrogen peroxide in presence of sulfuric and phosphoric acids.

Table (1): The mineralogical and elemental composition of the ore sample collected from Kadabora Batholiths - Eastern Desert of Egypt.

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

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

Table (2): The mineralogical and elemental composition of yttrium fluorite mineral collected from El Missikat area - Egypt.

Mineralogical composition	Elemental composition, (wt %)*	
Yttrium fluorite (ASTM No. 21-159)	F	47.07
	Ca	52.21
and Quartz (ASTM No. 5-490)	Y	0.04
	Ce	0.08
	Nd	0.05
	U	0.01

*Microprobe analysis in university of Texas at El Paso (UTEP- USA).

2.3. Procedure

Two grams of the ground ore to - 200 mesh were mixed at different ratios with the fluoride compounds. The mixtures were fused in 50 ml covered platinum crucible and the temperature was raised gradually to prevent spattering then maintained for two hours at the required temperature. Table (3) shows the working conditions of the fusion experiments. The fused cakes were transferred after cooling to teflon container to be leached under reflux at 100° C with concentrated sulfuric acid at solid /liquid ratio of 2/1 for 2 hours. The leached liquors were separated from the residues by filtration and subjected to a single stage liquid extraction step using MIBK at aqueous to organic ratio of (1/1) for 15 minutes. This was followed by scrubbing and stripping steps using sulfuric acid and distilled water, respectively. The extraction conditions are given in Table (4).

3. RESULTS AND DISCUSSION

3.1. Decomposition of ore sample

Fluoride fusions are usually used for the silicon removal and destruction of multiple oxides minerals of niobium, tantalum, titanium and zirconium. The soluble niobium fluoride will be next separated from other metallic contaminants by water immiscible organic solvent commonly MIBK [Gupta & Suri, (1994)].

In the present work, the ore sample containing niobium refractory minerals (Table 1) was fused at high temperatures with fluorine containing compounds: NH_4F , mixture of NH_4F and potassium pyrosulfate, CaF_2 and yttrium fluoride mineral. The subsequent sulfuric acid leaching in the case of calcium fluoride fluxes yielded the insoluble sulfates as in the following equation: $\text{CaF}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4\downarrow + 2\text{HF}\uparrow$. The evolved HF in the closed vessel turns some elements into soluble species as will be shown below. The type of the fluoride containing compound (flux) as well as its weight ratio to the ore sample have great influence on the liberation of elements by the subsequent sulfuric acid leaching, (Table 3).

3.1.1. Ammonium fluoride

Fusing the ore sample with ammonium fluoride at any given ratios allowed better dissolution of Nb and Ta than other elements, (Table 3). As the flux to ore ratio increased, tantalum dissolution

increased. This may be due to the formation of hydrated ammonium tantalum oxide which is soluble in sulfuric acid [Singh & Miller, (2002)]. At fluoride to ore ratio of 0.8, the leaching efficiency of cerium and yttrium from the fused cake reached 41.0% and 33.7%, respectively. Increasing the ratio lowered both elements dissolution due to the formation of insoluble fluorides. The poor uranium solubility may be due to its precipitation as fluoride [Woyski & Harris, (1963)]. It was mentioned [Gupta & Suri, (1994)] that samarskite behaved similarly upon fusion with ammonium fluoride, in which niobium, tantalum and titanium were transferred into the leach liquor, leaving most of rare earths and almost all uranium in the residue.

3.1.2. Ammonium fluoride and potassium pyrosulfate

Using the mixed flux of potassium pyrosulfate and ammonium fluoride had good influence in fusing the ore sample as well as improving its elements dissolution. This may be attributed to the ability of alkaline pyrosulfate to dissolve most oxygen -bearing niobium tantalum compounds beside the other elements in its minerals [Dolezal et al., (1968)]. Mixing equal portions of the ore sample and the mixed flux resulted in complete cerium and yttrium dissolution and more than 90% of niobium and tantalum contents (Table 3). Increasing the ratio of ore sample / ammonium fluoride / potassium pyrosulfate to 1 / 4 / 8, respectively, decreased cerium and yttrium dissolution upon leaching the fused cake with sulfuric acid. This may be due to the formation of less soluble rare earths double salts in presence of excess potassium ions. The lower titanium dissolution may be referred to the formation of double salts $K_2SO_4Ti(SO_4)_2$ in molten potassium hydrogen sulfate [Prakash, (1986a)]. On the other hand, slight improvement in uranium dissolution (37.2%) was observed in presence of higher potassium pyrosulfate.

The X-ray diffraction analysis of the residue remained after leaching the fused cake was found to contain: plaster of Paris (ASTM card No. 2-675), fluorite (ASTM card No. 4-864) and Gypsum (ASTM card No. 6-46).

3.1.3. Calcium fluoride

Calcium fluoride was recommended by [Silva (1990)] for opening niobium-tantalum ore at high temperature of 1500° C. The ore sample under study was fused with calcium fluoride at 1000° C followed by sulfuric acid leaching of the fused cake. As the fluoride to ore ratio

increased, the dissolution of elements of interest decreased (Table 3). The formation of rare earths double sulfates decreased the solubility of cerium and yttrium during the leaching process. In addition, the precipitation of niobium and tantalum may be due to the formation of oxyfluoroniobates and oxyfluorotantalate that resulted from the reaction of calcium fluoride with niobium and tantalum oxides at high temperature [Prakash, (1986b)]. The XRD analysis of the insoluble residue revealed the presence of NbO_2F (ASTM card No. 9-22) beside anhydrite (ASTM card No. 6-226) as its main component.

It follows from Table (3) that Ti(IV) behavior was related to both Nb(V) and Ta(V) in fluoride-sulfate media. As reported by Lebdev (2005), titanium is a stronger fluoride acceptor; it formed soluble stable complexes with niobium and tantalum. The destruction of these complexes resulted in precipitation of 70% niobium, 60% tantalum and 60% titanium at fluoride to ore ratio of 2.0.

3.1.4. Yttrium fluoride

Yttrium fluorite mineral which is composed chemically of CaF_2 was used as flux. It exhibited different behavior than the chemical CaF_2 when mixed with the ore sample at different ratios and fused at 1000°C (Table 3). The elements dissolution increased by leaching the fused cake to values more than 65% especially at higher fluoride to ore ratio except uranium which remained insoluble. In addition, yttrium fluoride flux was distinguished by 27% silicon dissolution while not more than 4% of Si was leached in case of other fluxes. This was explained by the reaction of the evolved HF with quartz that associated yttrium fluorite mineral (Table 2) to form the fluosilicic acid according to the equation: $\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$

The presence of H_2SiF_6 in the digesting solution increased the solubility of Nb, Ta and Ti from the fused cake [MARLAP, (2004)]. The insoluble residue analyzed by XRD was found to contain fluorite as a major component beside anhydrite. This may be attributed to the reaction of the liberated calcium from both the flux and the ore sample with the evolved hydrofluoric acid and sulfuric acid, respectively.

From the above results it is possible to say that acidic fusion with fluoride containing compounds and yttrium fluorite mineral were effective in decomposing the ore sample as well as transferring the elements of interest into the sulfate leach liquor. This was independent on

the flux to ore ratio; also it had no effect on selective isolation of elements except uranium that remained almost insoluble.

The dissolution of niobium and tantalum from the ore sample depends upon the used flux in the order: $\text{CaF}_2 < \text{NH}_4\text{F} < \text{yttrium fluoride} < \text{mixture } \text{K}_2\text{S}_2\text{O}_7 \text{ and } \text{NH}_4\text{F}$. The separation of niobium and tantalum from other elements in the leach liquors was done by solvent extraction.

3.2. Niobium recovery

Niobium and tantalum were separated from the sulfate-fluoride media by selective extraction of their fluoro complexes with methylisobutylketone (MIBK), where equal volumes of aqueous and organic solutions were contacted for 15 minutes in a single stage extraction. The scrubbing was done by 12 N H_2SO_4 to remove impurities (especially titanium) before going to the stripping experiments with distilled water. Selecting the flux type has its influence in varying both sulfuric acid and fluoride ions concentrations as well as the ratio of Nb/Ta in the leach liquors. This in turn affected the extraction and the separation of niobium from tantalum (Table 4).

The leach liquor resulted from fusing equal weight ratio of the ore sample, ammonium fluoride and potassium pyrosulfate had 0.54M H_2SO_4 , 0.51M fluoride ions and Nb/ Ta ratio of 3.3/1.0. It was contacted with MIBK at aqueous/organic ratio of 1/1 for 15 minutes. The extraction of both elements did not exceed 50% because of the low acids concentrations of the leach liquor. Stripping equal volumes of the loaded solvent and distilled water for 15 minutes leads to back-extraction of niobium more than tantalum.

Fusing similar weights of the ore sample and the mixed flux, then adding both sulfuric and hydrofluoric acids to the leach liquor to be 3.0M H_2SO_4 and 7.0M HF, lead to simultaneous extraction of both elements with preference to niobium (Table 4). The extraction of 84% Nb and 21.6% Ta allowed better separation in the subsequent stripping step. Contacting equal volumes of the loaded solvent and distilled water for 15 minutes lowered the acidity, thus back-extracting all the niobium with little tantalum. Niobium was then precipitated from the strip solution by ammonium hydroxide. The recovery of 78% Nb and 1.8% Ta was achieved.

On the other hand, the leach liquor resulted from fusing the ore sample with ammonium fluoride and potassium pyrosulfate at ratio of 1/4/8 respectively, was found to contain 1.08M H_2SO_4 , 2.05M fluoride

ions and Nb/Ta ratio of 2.7/1.0. Under these conditions, the higher tantalum extraction of 93.6% was obtained due to more fluoride concentration which enhanced the formation of the stable extractable species H_2TaF_7 [Gupta & Suri, (1994)]. As shown in Table (4), the back wash of the loaded solvent was not efficient to separate niobium from tantalum.

In the case of CaF_2 flux, its leach liquor contained 1.08M H_2SO_4 , 0.49M fluoride ions and Nb/Ta ratio of 2.7/1.0, (Table 4). The lower acids concentration did not allow higher niobium extraction; in the meantime no separation between the two elements in the stripping step.

The mineral yttrium fluorite was fused with the ore sample at ratio of 6/1 and the fused cake was leached with sulfuric acid. Niobium and tantalum leached at ratio of 0.8/1.0 were extracted by MIBK. The extraction efficiency of 97.7% Nb and 80.7% Ta were obtained in presence of 3.6M H_2SO_4 , 2.1M fluoride ions in addition to 0.4M Si. On the other hand, contacting MIBK with the leach liquor free of Si resulted from CaF_2 fusion and containing 3.8M H_2SO_4 , 2.0M fluoride ions gave an extraction efficiency of 51.2% Nb and 70.8% Ta. This indicated that, the higher extraction of both elements may refer not only to the concentrations of sulfuric acid and the evolved HF acid but possibly due to the presence of the fluosilicic acid that formed by leaching quartz associated yttrium fluorite mineral. Distilled water was used to strip 100% Nb and 17.1% Ta (Table 4). Separation of niobium was done by ammonium hydroxide precipitation to achieve 92.2% niobium recovery.

Thus, it is inferred that using the mineral yttrium fluoride is preferred as flux for decomposing niobium bearing refractory minerals due to the following reasons: a) It is naturally available. b) It is effective in decomposing niobium bearing minerals and liberating the economic elements from both the ore sample and yttrium fluorite (flux) into the leach liquor. c) The leached liquor of the fused cake was contaminated with minimum uranium concentration. d) The separation of niobium was achieved with 92.2% recovery.

Table (3): Working conditions of fusion experiments and their effects on elements dissolution.

Fluoride Flux	Experimental conditions		Elements dissolution in the leach liquor, (%)						Residue's content
	Fluoride to ore ratio	Temp. (° C)	Nb	Ta	Ti	Ce	Y	U	
NH ₄ F	i) 0.5 - 0.8	400	65.0	62.3	54.8	41.0	33.7	7.4	---
	ii) 1.0 - 1.5		60.7	64.8	45.2	35.4	20.9	2.4	
	iii) 1.5 - 2.0		60.0	71.8	42.3	18.2	10.4	0	
* NH ₄ F and K ₂ S ₂ O ₇	i) 0.5 - 0.8	750	94.4	90.3	49.6	100	100	33.3	Plaster of Paris, Fluorite & Gypsum
	ii) 1.5 - 2.0		92.4	93.3	42.2	83.3	78.2	37.2	
CaF ₂	i) 0.5 - 0.8	1000	65.1	68.3	53.3	45.9	54.4	2.6	Anhydrite & NbO ₂ F
	ii) 1.0 - 1.5		52.6	61.7	49.5	35.4	32.8	1.6	
	iii) 1.5 - 2.0		29.8	41.1	39.5	18.1	16.4	2.0	
Yttrium Fluorite	i) 0.5 - 0.8	1000	57.5	72.5	33.5	78.6	75.5	3.0	Fluorite & Anhydrite
	ii) 1.0 - 1.5		82.9	85.6	45.9	66.5	78.2	3.3	
	iii) 1.5 - 2.0		90.5	92.2	67.3	67.3	72.6	4.0	

* i) The ratio: ore / NH₄F / K₂S₂O₇ is 1/1/1 ii) The ratio : ore/NH₄F/ K₂S₂O₇ is 1/ 4/8.

Table (4): Extraction efficiency of niobium and tantalum from the leach liquors of different the fused cakes.

Flux	Ratio ore/flux	H ₂ SO ₄ conc. (M)	Fluoride conc. (M)	Ratio Nb/Ta in the leach liquor	Extraction Efficiency, (%)		Stripping Efficiency, (%)	
					Nb	Ta	Nb	Ta
NH ₄ F/K ₂ S ₂ O ₇	1 / 1 / 1	0.54	0.51	3.3 / 1.0	24.3	43.8	70	26.2
NH ₄ F/K ₂ S ₂ O ₇	1 / 1 / 1	3.0	7.0	3.3 / 1.0	84.0	21.6	100	9.2
NH ₄ F/K ₂ S ₂ O ₇	1 / 4 / 8	0.90	2.05	2.7 / 1.0	55.0	93.6	100	52.1
CaF ₂	1 / 0.5	1.08	0.49	2.7 / 1.0	30.0	75.4	0	26.8
Yttrium-fluorite	1 / 6	3.6	2.1	0.8 / 1.0	97.7	80.7	100	17.1

* Both sulfuric and hydrofluoric acid were added to the aqueous solution to obtain the given concentration.

4. CONCLUSIONS

In the acidic fusion process, the fluoride containing compounds: ammonium fluoride, calcium fluoride and yttrium fluoride mineral were selected as non hazardous materials to produce the hydrogen fluoride through the reaction of sulfuric acid with the fused cake; thus converting the refractory niobium-bearing minerals into soluble metal values.

Both niobium and tantalum exhibited higher dissolution efficiencies than the associated elements in the ore sample containing samarskite, fergusonite, betafite and pyrochlore. The maximum dissolution of 90.5 % niobium and 92.2% tantalum was achieved by fusing the ore sample with yttrium fluoride mineral at weight ratio of 1/6 respectively and 1000° C for two hours.

The dissolution of 100% cerium, 100% yttrium and 33.3% uranium were obtained by mixing equal weights of the ore sample and the mixed flux of potassium pyrosulfate and ammonium fluoride at 750°C.

The separation of niobium from the associated elements especially tantalum depends on both the flux type used in the fusion process and the acids concentrations in the leach liquor. The recovery of 92.2% niobium was achieved by contacting equal volumes of MIBK with the sulfate solution resulted from leaching the fused cake of the ore sample and yttrium fluoride mineral.

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فصل عنصر النيوبيوم من معادنه صعبة التفكك بطريقة الصهر
بمركبات الفلوريد قليلة الخطورة

أمنية محمد الحسيني

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يمكن إجراء عملية تحلل إحدى الخامات المصرية المحتوية على معادن صعبة التفكك في وجود أيونات الفلوريد دون اللجوء لاستخدام حامض الهيدروفلوريك شديد الخطورة ، بغرض فصل عنصر النيوبيوم من معادنه. ولتحقيق ذلك تم خلط نسب أوزان مختلفة من عينة الخام مع بعض مركبات عنصر الفلورين وكذلك مع معدن فلوريد الايتريوم ، ثم صهر الخليط عند درجات الحرارة المرتفعة. تتبع ذلك عملية إذابة للمصهور بحامض الكبريتيك ، فتحررت عناصر ذات قيمة اقتصادية عالية مثل : النيوبيوم ، التتاليوم ، التيتانيوم ، السيريوم.

هذا وقد استعمل المذيب العضوي ميثيل أيزوبوتيل كيتون (MIBK) لفصل النيوبيوم عن العناصر الأخرى المذابة في المحلول الحامضي.