



# Preparation of Pure Nb<sub>2</sub>O<sub>5</sub> from Gabal El-Faliq Pegmatite, South Eastern Desert, Egypt

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## Abstract

The present work is concerned with selective dissolution of niobium from Gabal El Faliq concentrate sample by using fluoride-free process. The chemical analysis of concentrate sample revealed the presence of high amount of ZrO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, Re<sub>2</sub>O<sub>3</sub>, and HfO<sub>2</sub> assaying 33.6, 1.99, 4.8, and 1.2%w/w respectively. Several economic minerals including zircon, samarskite, fergusonite, and xenotime were recorded in the studied sample. About 98% of Nb content was selectively dissolved at the optimum conditions of 1:2 concentrate sample: KOH weight ratio, 2.5 h fusion time, and fusion temperature of 550 °C. Organic solvent extraction process using Aliquat 336S in xylene was effectively used for preparing pure Nb<sub>2</sub>O<sub>5</sub> (98.95%).

**Keywords** Alkaline fusion · Niobium · Solvent extraction · Aliquat 336S

## 1 Introduction

Gabal (G.) El-Faliq area, southeastern Desert of Egypt, is located between latitude 24° 35' and 24° 42' N and longitude 34° 28' and 34° 35' E. This area is covering about (250 km<sup>2</sup>) and it is composed mainly of ophiolitic mélange, gneisses, older, younger granitoids, post granitic dykes, and veins which include pegmatites [42]. The most important rock unite in the studied area is the post granitic dykes and veins. The younger granitoids and post granitic dykes and veins also attracted the interest of many authors because they are typically associated with anomalous concentrations of rare and some economically important elements such as Sn, W, Mo, U, Nb, Ta, REE, Zr, and Rb. It is worthy to mention herein that all the granitoid rocks of G. El Faliq area are cut and crossed by several pegmatite bodies. These bodies are trending (NNE-SSW) and ranging in length from 50 m to several meters. Also, they occur as pockets or lenses (10–20 m in length) at the margin and the core of the gneisses rocks as well as

ophiolitic mélange. The present minerals of G. El Faliq area are classified into (a) secondary uranium minerals (uranophane and meta-autunite), (b) niobium–tantalum minerals (columbite, euxenite, and fergusonite), (c) sulphide minerals (pyrite and barite), and (d) accessory minerals (allanite and zircon) [35, 42, 43].

Niobium and tantalum are widely used in today's technology due to their unique properties; they have been utilized widely in the steel, electronic, and other high-tech industries [7, 22]. Chemical separation or purification of these metals from their ores and concentrates has been studied using different methods. Among these methods, alkali fusion using sodium hydroxide and sodium carbonate (or the potassium salts) were used as leaching agents [6, 7, 12, 50, 53], and KHSO<sub>4</sub> roasting [3]. Some niobium–tantalum ore types can also be processed using chlorination, fusion with ammonium fluoride and bifluoride [20, 25, 37], direct acidic dissolution with either H<sub>2</sub>SO<sub>4</sub> [15], or a combination of H<sub>2</sub>SO<sub>4</sub> and HF [23, 27, 39]. Also, most niobium–tantalum ores were dissolved with concentrated HF [14, 20, 40, 41]. Due to high volatility of HF, about 6–7% of it is lost during the decomposition process which is hazardous [10, 11, 21, 22]. Furthermore, a large amount of wastewater containing fluoride is generated that needs to be treated. More importantly, this method is only appropriate for high-grade niobium–tantalum ores [32].

With respect to pure Nb and Ta recovery from their leach liquors, many researchers studied in details the separation and purification of Nb and Ta via liquid–liquid extraction

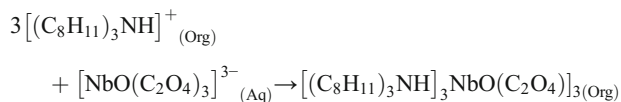
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processes. In this regard, several solvents were applied for this purpose. One of the most important and widely industrially applied is tri-*n*-butyl phosphate (TBP) [4, 5, 20, 36]. Also, many workers as Salles [44], El-Hussaini [14], Agulyansky et al. [2], Nikolaev and Maiorov [34], Yang et al. [52], Toure et al. [47], and Htwe and Lwin [23] used methyl isobutyl ketone (MIBK) for separating pure compounds of Nb and Ta, while Mayorov and Nikolaev [31], Agulyansky et al. [2], and El-Hazek et al. [13] used octanol. In this target, Tertiary amines, e.g., trioctyl amine, Alamine 336, and Aliquat 336S, were effectively applied by Sato et al. [45, 46], Deblonde et al. [8], Mishra et al. [33], and Zhu and Cheng [54]. The following equation illustrates the extraction process of Nb and Ta from oxalate media with tertiary amines [54].



The main purpose of the present work is the selective alkaline dissolution of Nb from Gabal El Faliq concentrate sample depending essentially on the fluoride-free process with breakdown of the associated refractory minerals, e.g., zircon and xenotime. Finally, the preparation of pure Nb<sub>2</sub>O<sub>5</sub> using Aliquat 336S in xylene was carried from the prepared leach solution.

**Table 1** XRF chemical analysis of Gabl El-Faliq concentrate sample

Compound formula	Concentration (% w/w)	Compound formula	Concentration (% w/w)
SiO <sub>2</sub>	38.905	Tb <sub>4</sub> O <sub>7</sub>	0.069
Al <sub>2</sub> O <sub>3</sub>	5.215	Dy <sub>2</sub> O <sub>3</sub>	0.470
Fe <sub>2</sub> O <sub>3</sub>	10.023	Ho <sub>2</sub> O <sub>3</sub>	0.05
CaO	0.628	Er <sub>2</sub> O <sub>3</sub>	0.390
MgO	0.333	Tm <sub>2</sub> O <sub>3</sub>	0.02
Na <sub>2</sub> O <sub>3</sub>	0.233	Yb <sub>2</sub> O <sub>3</sub>	0.403
K <sub>2</sub> O	0.524	Lu <sub>2</sub> O <sub>3</sub>	0.03
MnO	1.111	U	0.08
TiO <sub>2</sub>	0.468	ThO <sub>2</sub>	0.0335
P <sub>2</sub> O <sub>5</sub>	0.389	Rh	0.025
ZrO <sub>2</sub>	33.621	ZnO	0.058
HfO <sub>2</sub>	1.201	CuO	0.036
Nb <sub>2</sub> O <sub>5</sub>	1.985	PbO	0.020
Ta <sub>2</sub> O <sub>5</sub>	0.045	SrO	0.011
Y <sub>2</sub> O <sub>3</sub>	1.998	Cl	0.095
La <sub>2</sub> O <sub>3</sub>	0.177	SO <sub>3</sub>	0.102
CeO <sub>2</sub>	0.392	F	0.086
Pr <sub>2</sub> O <sub>3</sub>	0.04		
Nd <sub>2</sub> O <sub>3</sub>	0.312		
Sm <sub>2</sub> O <sub>3</sub>	0.144		
Gd <sub>2</sub> O <sub>3</sub>	0.307		

## 2 Experimental

### 2.1 Materials

All the utilized chemicals in the experimental work were analytical grade including potassium hydroxide pellets (99%) [Prolabo], sulfuric acid (97%) [Adwic], oxalic acid (99%), ammonium hydroxide (30%) and xylene (99%) [Adwic], nitric acid (69%) [BDH], and Aliquat 336S (99%) [Sigma Aldrich]. On the other hand, the working concentrate sample of Gabal El Faliq area was subjected to both mineralogical and chemical specification and also to processing procedures.

### 2.2 Chemical and Mineralogical Specification

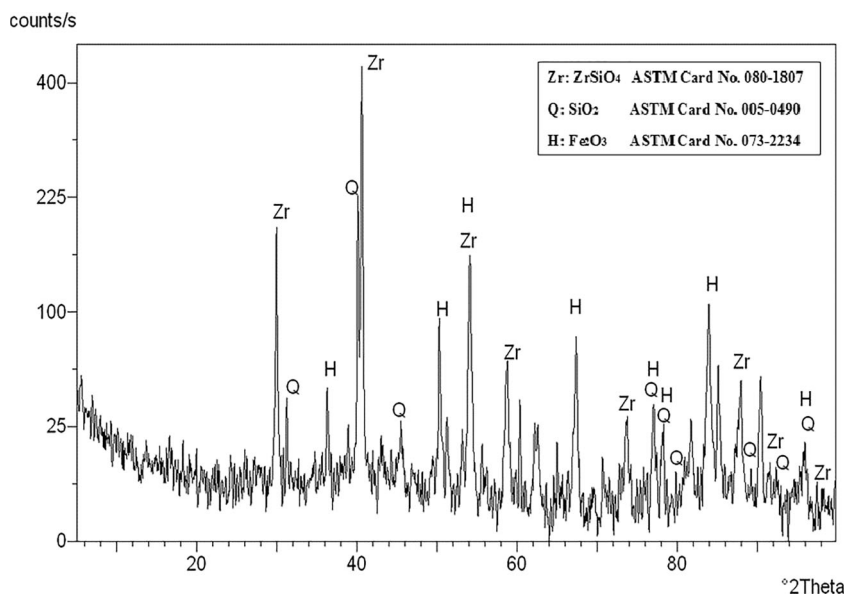
The sample under study was selected from Gabal El-Faliq, southwestern Desert, Egypt, and was subjected to physical upgrading process using shaking table. The concentrate sample was subjected to major and minor oxide chemical analysis together with analysis of Nb, REE, Zr, and Hf besides U and Th elements using Axios advanced WDXRF-PANalytical (Netherland). In this regard, the analysis of Nb and Zr during all experimental work was carried out by Microwave Plasma Atomic Emission Spectrometer (4200 MP-AES, Agilent Technologies). The REE were estimated using 0.05% Arsenazo III at λ<sub>654</sub> nm using Y as a reference ([29]), while U in all performed procedures was measured by oximetric titration against NH<sub>4</sub>VO<sub>3</sub> in the presence of diphenyl amine-4-sulfonic acid sodium salt as an indicator [30]. The scanning electron microscopy (CAM SCAN series 4 ISIS 200 E/X system with pentajet detector) (SEM-EDX) was used for confirming the Nb cake and ICP (720 ICP-OES, Agilent Technologies) was used for identifying of the Nb pure product.

To study the mineralogical composition of the studied concentrate sample, the latter was subjected to X-ray diffraction analysis (PHILIPS PW 223/30) for identification of mineral content. Moreover, heavy mineral separation procedures were applied; for this purpose, the sample was ground to 60 mesh size to liberate the heavy minerals. The ground sample was then washed with distilled H<sub>2</sub>O for removing slimes; then, it was sieved into the size interval of 0.4, 0.3, 0.2, and 0.1 mm. Heavy liquid separation procedures were applied using bromoform (sp.gr. 2.8) to bring out the heavy fraction. The mineral grains of the same color in the heavy fraction were separately picked up under the binocular microscope. The separated mineral grains were then investigated by X-ray diffraction analysis to identify the mineral crystals structure.

### 2.3 Optimization of the Fusion Process

Several experiments were performed by mixing constant weight (5 g) of the fine ground concentrate sample with a solid KOH (melting point 360 °C) as the fused reagent in a

**Fig. 1** XRD pattern of bulk concentrate sample



porcelain crucible. The mixture was then fused at different temperatures ranged from 300 to 650 °C for different periods of times (1–3 h). After cooling, the fused matrix was leached with distilled H<sub>2</sub>O in S/L ratio of 1/4 for 30 min at room temperature. The spent residue was washed twice with distilled H<sub>2</sub>O. After filtration using filter paper, Nb in the prepared alkaline solution was analyzed and its leaching efficiency (%) was calculated using the equation:

$$\text{Leaching efficiency(\%)} = \frac{\text{Metal content in the leach liquor}}{\text{Metal content in the ore}} \times 100$$

### 2.4 Preparation of Impure Niobium Cake

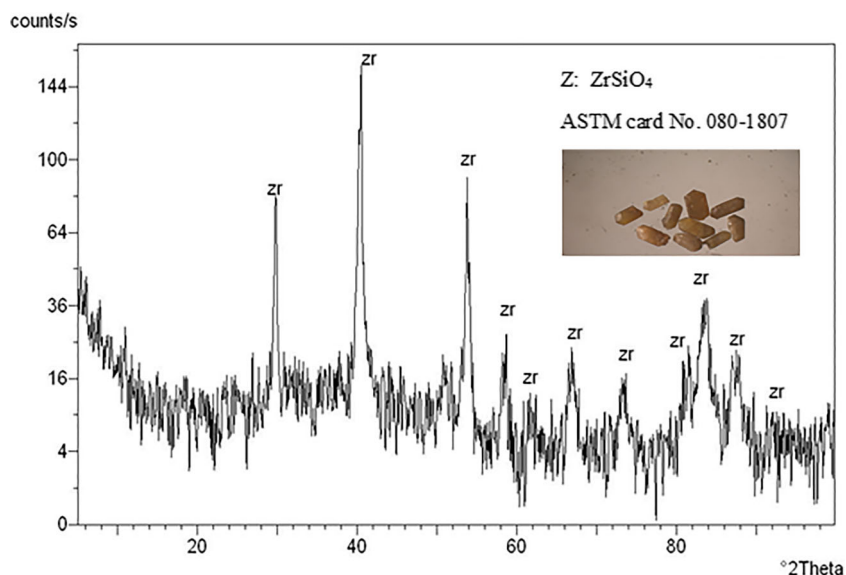
Nb ion species in the prepared alkaline leach liquor was completely precipitated by neutralization process using

diluted H<sub>2</sub>SO<sub>4</sub> to pH 8.5. The precipitated Nb cake was then leached with oxalic acid solution for the dissolution of its Nb content with some associated impurities. Aliquat 336S diluted in xylene was used at ambient temperature 35 ± 5 °C for extraction of Nb from its oxalate leach liquor.

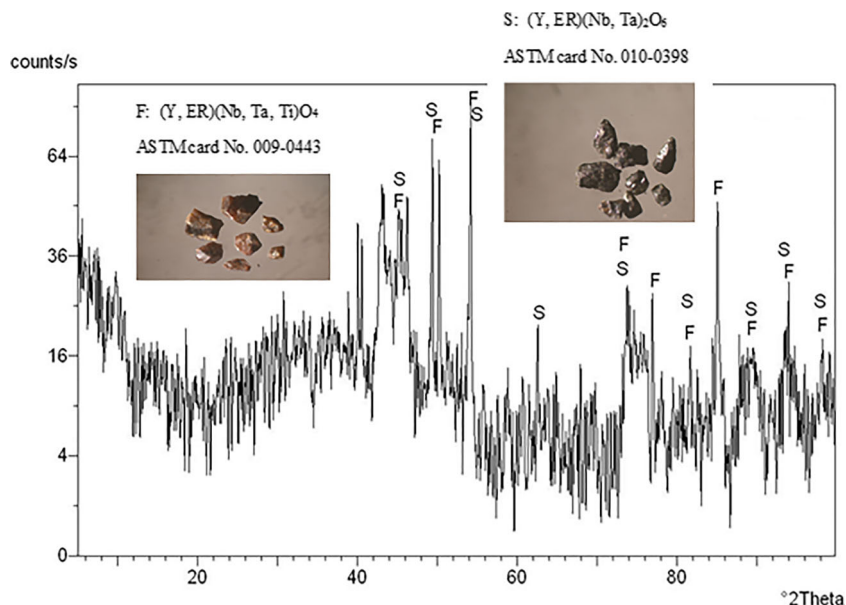
### 2.5 Optimization of Nb Extraction Process

Several relevant effective extraction parameters such as Aliquat 336S concentration, pH value, contact time, and phase volume ratios (O/A) were tested to optimize the loading process of Nb. The loaded Aliquat 336S was stripped with different mineral acids, e.g., H<sub>2</sub>SO<sub>4</sub>, HCl, and HNO<sub>3</sub> of 0.4 M concentration at A/O ratio of 1/1 and contact time of 5 min to optimize the Nb stripping process. All the experiments were carried out in shaking funnels. Finally, the concentrated Nb

**Fig. 2** XRD pattern of the identified zircon mineral grains



**Fig. 3** XRD pattern of the identified fergusonite- and smarskite-heated mineral grains



strip solution was treated with an ammonia solution to precipitate Nb as Nb-hydroxide cake. The latter was carefully washed with distilled water and then ignited at 650 °C to prepare a pure Nb<sub>2</sub>O<sub>5</sub> product which identified with XRD, while its purity was determined using ICP.

### 3 Results and Discussion

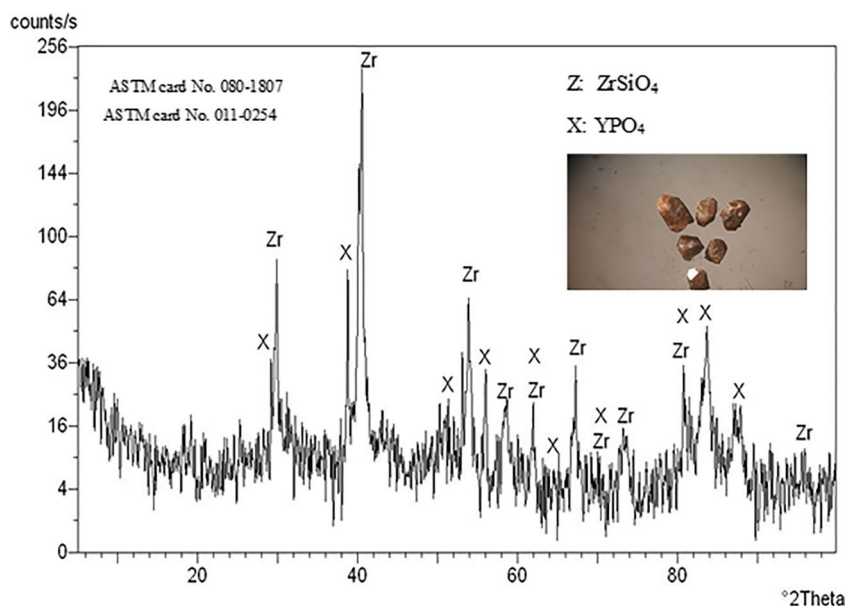
#### 3.1 Chemical and Mineralogical Characterization of the Sample

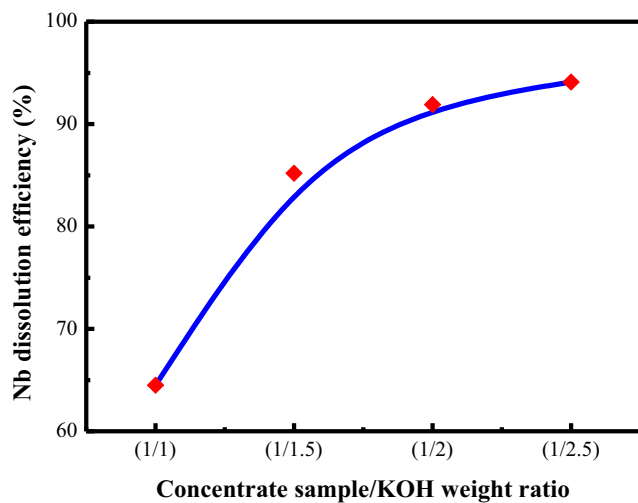
Complete chemical composition of Gabl El-Faliq concentrate sample is represented in Table 1. From this table, it is clearly

evident that the concentrate is mainly composed of ZrO<sub>2</sub> together with SiO<sub>2</sub> as well as Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> which assaying 33.6, 39, 10, and 5.9%w/w, respectively. In the meantime, there are considerable concentrations of valuable economic oxides, e.g., Re<sub>2</sub>O<sub>3</sub> [sum of all rare earth elements oxides (La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, etc...)], Nb<sub>2</sub>O<sub>5</sub>, Ta<sub>2</sub>O<sub>3</sub>, and HfO<sub>2</sub> assaying 4.8, 1.99, 0.045, and 1.2%w/w, respectively. Moreover, the present concentrate sample contains remarkable concentrations of radioactive nuclear elements, e.g., U and Th assaying 800 and 340 ppm, respectively.

For mineral identification, the bulk concentrate sample was characterized by means of XRD analysis as shown in Fig. 1; it revealed the presence of zircon, silica, and hematite as main components, while the obtained data of XRD analysis of

**Fig. 4** XRD pattern of the identified zircon and xenotime mineral grains



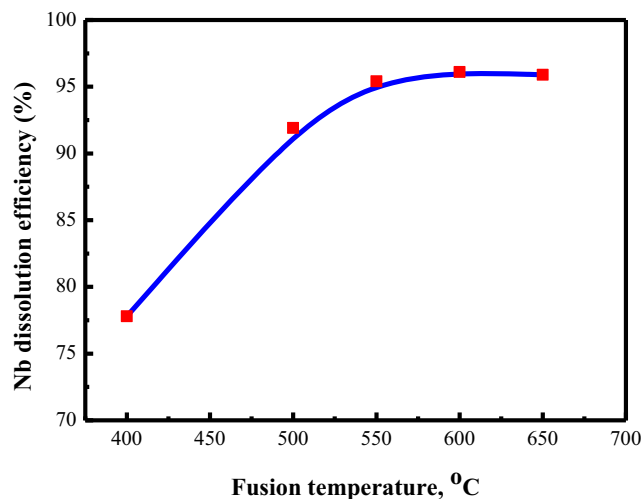


**Fig. 5** Effect of concentrate sample/KOH weight ratio upon dissolution efficiencies of niobium (2 h fusion time and 550 °C fusion temperature)

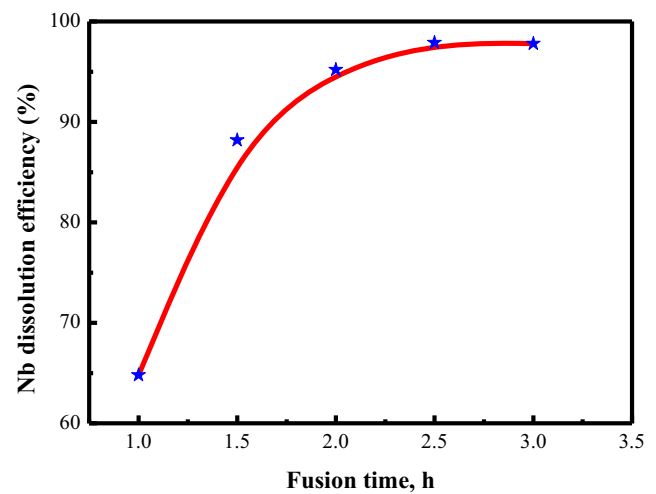
separated mineral grains revealed the presence of valuable minerals in close association with non-notable (gangue) minerals. Accordingly, the studied sample refers to the presence of the following mineral association (Figs. 2, 3, and 4).

### 3.1.1 Zircon Mineral

Zircon ( $ZrSiO_4$ ) is a common accessory mineral in igneous, metamorphic, and sedimentary rocks. It may form large well-developed crystals in granites and pegmatites. This mineral is extremely resistant to chemical and physical weathering. Zircon was identified by XRD analysis (Fig. 2) in association with xenotime and separated in abundant amounts from pegmatite sample of G. El Faliq. Some crystals show corrosion, zonation, and overgrowth phenomena; they have varying shades of honey color due to the effect of radioactivity.



**Fig. 6** Effect of fusion temperature upon dissolution efficiencies of niobium (2 h and 1/2 concentrate sample/KOH weight ratio)



**Fig. 7** Effect of fusion time upon dissolution efficiencies of niobium (1/2 concentrate sample/KOH weight ratio and 550 °C fusion temperature)

### 3.1.2 Nb, Ta, and REE Minerals

Samarskite is common and locally abundant enough that it has the potential to be a valuable source of REE. It is usually associated with fergusonite as Nb, Ta, and REE mineral. Samarskite has dark pitchy to velvety black to dark brown color, irregular massive grains with sub-conchoidal fracture. XRD data confirmed its presence in the separated grains from the pegmatite of G. El Faliq (Fig. 3).

### 3.1.3 Rare Earth Minerals

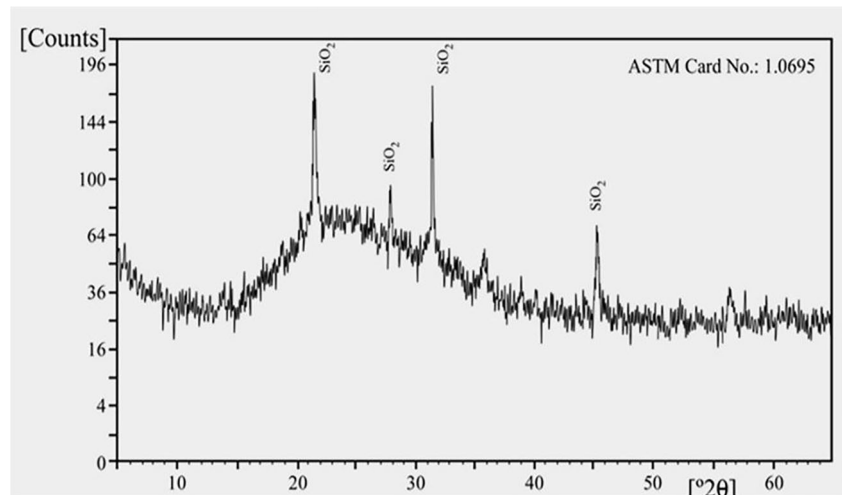
In the study area, fergusonite (Y, Er) (Nb, Ta, Ti)  $O_4$  and xenotime were recorded as parent REE minerals in pegmatite of G. El Faliq. It is worthy to mention herein that fergusonite is mainly associated with samarskite. Fergusonite-Formanite series of chemical formula (Y, Er) (Nb, Ta)  $O_4$ -(Y, Er) (Nb, Ta)  $O_4$  have brown color with no specific crystal shape but usually metamictized (Fig. 3). Fergusonite end member is the most common mineral. The chemical heterogeneity of fergusonite is represented by the variation in  $Re_2O_3$  and  $Nb_2O_5$  [49]. Fergusonite, ideally  $YNbO_4$ , occurs as an accessory mineral

**Table 2** Chemical composition of the working alkaline leach liquor

Element	Conc., g/L	Dissolving efficiency, %
K	109	78.4
Si	11.76	65.1
Nb	1.36	97.9
Y	0.178	11.3
Fe	0.25	3.7
Zr	0.29	1.2
Th	U.D.	–
U	U.D.	–



**Fig. 8** XRD patterns for the confirmation of  $\text{SiO}_2$



in granitic pegmatites, mostly in rare earth element (REE)-enriched pegmatites [17, 18, 38], and often in combination with one or more Y, Th, Nb, Ta, and Ti oxide accessory minerals [28]. The XRD data confirmed the detection of fergusonite mineral (Fig. 4).

On the other hand, xenotime is an  $(\text{YPO}_4)$  REE-phosphate mineral; Eu, Er, Tr, and Yb, as well as metal elements such as Th and U (all replacing Y), are the expressive secondary components of xenotime. Xenotime is used chiefly as a source of yttrium and HREE (Dy, Yb, Er, and Gd). It is found in pegmatites and other igneous rocks, as a minor accessory mineral. Associated minerals include biotite, quartz, and zircon; xenotime is typically translucent to opaque in shades of brown to brownish yellow and has a variable habit. It may form as minute grains or as extremely thin (less than  $10 \mu$ ) coatings on detrital zircon grains (Fig. 4).

In this context, oxy-hydroxy minerals are either primary phases (e.g., magnetite) or oxidation products of the mineralized rocks occurring at different ratios in the studied area (e.g., hematite and goethite) in close association with quartz and

kaolinite minerals and also with the valuable minerals which refer to hematization process.

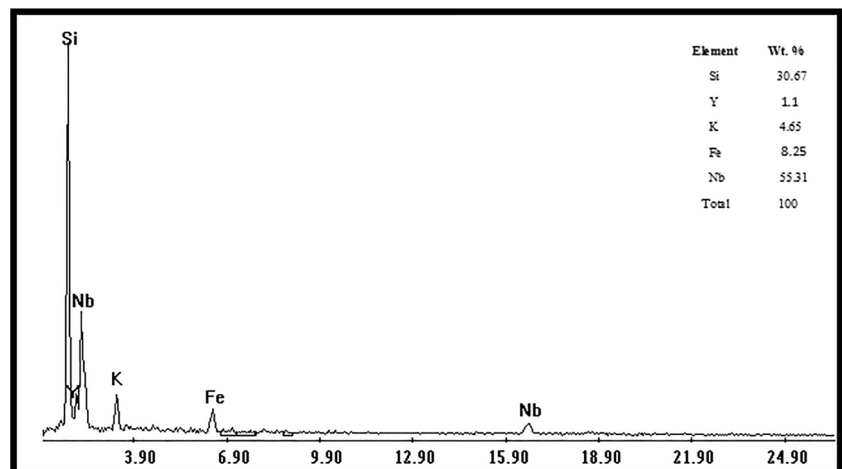
### 3.2 Alkaline Fusion of the Concentrate Sample

The mentioned chemical and mineralogical composition of Gabl El-Faliq concentrate sample reflected the significant high-grade type of mineralization and reflected also the importance of the processing of such concentrate sample for recovering its valuable elements. According to the huge assemblage of mineral constituents in the working concentrate, it was found necessary to apply the alkaline breakdown using KOH due to:

\*Selective dissolution of Nb away from Zr and REE, where it forms water-soluble K-niobates and insoluble (Zr-REE) hydrous oxides.

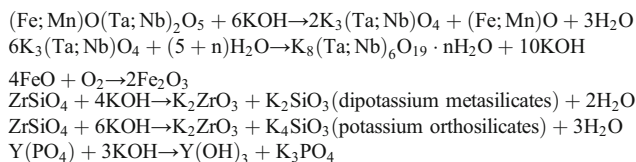
\*\*Molten KOH forms with zircon mineral ( $\text{ZrSiO}_4$ ), a water-soluble K-silicates and K-zirconate. It also forms

**Fig. 9** SEM-EDAX chart for identification of Nb precipitated cake



with xenotime mineral (YPO<sub>4</sub>), soluble K-phosphate, and acid soluble RE-hydroxide.

All of these can be summarized by the following equations which represented the chemical reactions between the molten KOH and the studied sample [1, 19, 50].



In this context, several relevant factors such as sample/KOH mixed weight ratios, fusion time, and fusion temperature were properly studied in a manner to optimize the Nb dissolution process.

### 3.2.1 Effect of Concentrate Sample/KOH Weight Ratios

The effect of concentrate sample/KOH weight ratios upon the leaching efficiency of niobium was studied in the range between 1/1 to 1/2.5, while the other fusion conditions were fixed at 2 h as fusion time and fusion temperature of 550 °C. The obtained data (Fig. 5) showed that Nb dissolution efficiency improved obviously with decreasing the concentrate sample/KOH weight ratio, where it increased from 64.5 to 91.9% with decreasing the ratio from 1/1 to 1/2. However, further decreasing in the weight ratio more than 1/2 reflected very slight improvement in Nb dissolution efficiency. This may be attributed to the consumption of KOH in the dissolution of interfering metal ions especially Si<sup>4+</sup> during the dissolution of niobium [50]. Thus, 1/2 weight ratio is preferred as the optimum ore concentrate/KOH weight ratio.

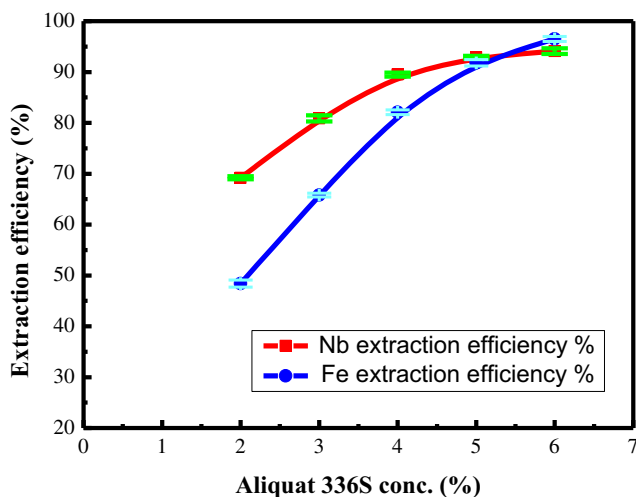


Fig. 10 Effect of Aliquat 336S conc. upon Nb and Fe extraction efficiencies [pH 3, O/A volume ratio of 1/1 and contact time of 10 min at ambient temperature (35 ± 5)]

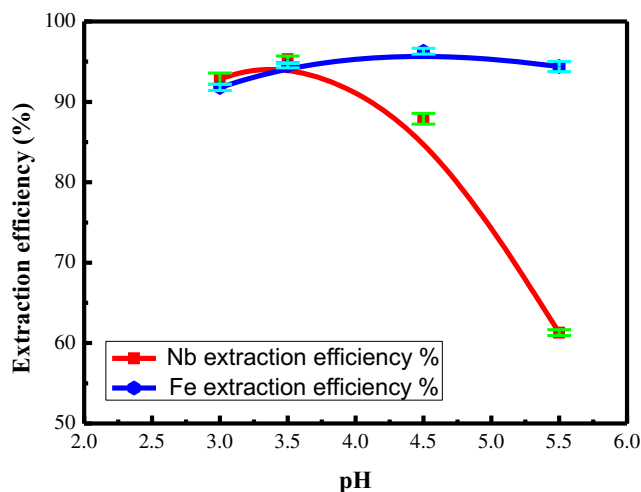


Fig. 11 Effect of pH values upon Nb and Fe extraction efficiencies (5% Aliquat 336S, O/A volume ratio of 1/1 and contact time of 10 min at ambient temperature)

### 3.2.2 Effect of Fusion Temperature

Data in Fig. 6 indicated the effect of changing fusion temperature from 400 to 650 °C upon Nb dissolution efficiency from the working ore material concentrate at ore concentrate/KOH weight ratio of 1/2 and fusion time of 2 h. It was observed that the best Nb dissolution efficiency (95.4%) was achieved at the suitable fusion temperature of 550 °C. Also further increase in fusion temperature up to 650 °C did not show any significant change in Nb dissolution efficiency, where the reaction between Nb<sub>2</sub>O<sub>5</sub> and KOH occurred much more readily than other reactions and was complete at only 550 °C [50].

### 3.2.3 Effect of Fusion Time

This effect was studied in the time periods ranged between 1 to 3 h, where the other parameters were fixed at fusion

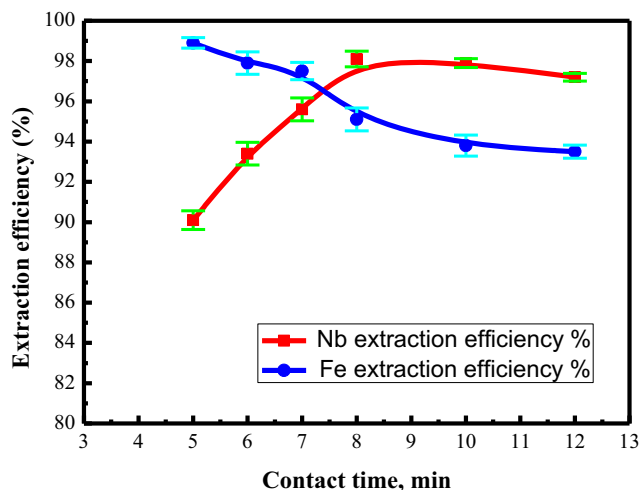


Fig. 12 Effect of time values upon Nb and Fe extraction efficiencies (pH 3.5, 5% Aliquat 336S, and O/A ratio 1/1 at ambient temperature)

**Table 3** Effect of O/A ratio upon the extraction efficiency of Nb

O/A ratio	Organic phase conc. (ppm)	Aqueous phase conc. (ppm)	$D_A^O$	Nb extraction efficiency (%)
3/1	1048	6	175	99.8
2/1	1555	41	38	98.7
1/1	3080	70	44	97.8
1/2	5046	627	8	80.1
1/3	6539	970	7	69.2

Where  $D_A^O$  is the distribution coefficient between organic and aqueous solutions

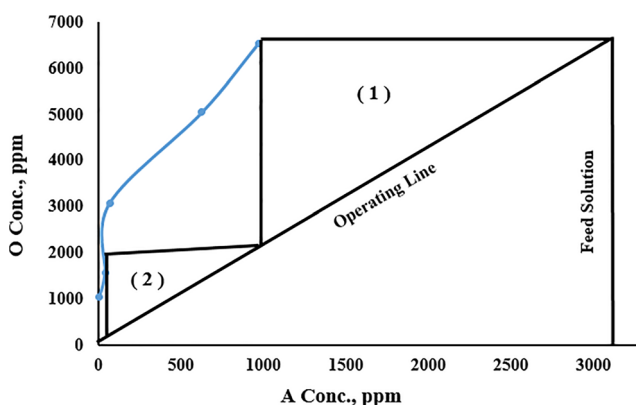
temperature of 550 °C and concentrate sample/KOH weight ratio of 1/2. Data represented in Fig. 7 emphasized that Nb dissolution efficiency reached its maximum value (97.9%) at the time period of 2.5 h.

### 3.3 Preparation of the Alkaline Leach Liquor

In the light of the foregoing mentioned alkaline fusion process of Gabal El-Faliq concentrate sample, it could be concluded that the optimum fusion conditions required for dissolving 97.9% of niobium are as follows:

Concentrate sample/KOH weight ratio: 1/2  
 Roasting time: 2.5 h  
 Roasting temperature: 550 °C

On the other hand, it is worthy to mention herein that the other associated metal values, e.g., REE, Zr, U, and Th, were left in the spent residue as insoluble hydrous cake. These determined optimum fusion conditions were used to prepare the pregnant leach liquor for subsequent recovery of niobium. Accordingly, 200 g of the concentrate sample was used to yield 2 L of alkaline leach liquor. The latter was found to assay 1.36 g/L of Nb and 0.03 g/L of Ta with chemical composition as shown in Table 2 and its pH value higher than 12. Yttrium showed small solubility with potassium hydroxide (11.3%) and this may be attributed to the technical viability of the alkaline leaching of yttrium [48, 51]. The prepared alkaline

**Fig. 13** Macabe-Thiele diagram for Nb extraction

leach liquor was first subjected to silica gel precipitation. This was carried out by adjusting the pH value of the prepared leach liquor via H<sub>2</sub>SO<sub>4</sub> (97%) to be 10. Almost Si<sup>4+</sup> ions were precipitated as gelatinous Si(OH)<sub>4</sub> with precipitation efficiency of 93%, while small amounts of Nb<sup>5+</sup> ions (not exceed 0.95% of total Nb content) were lost. After filtration, the precipitate of gelatinous Si(OH)<sub>4</sub> was then ignited at 850 °C for 1 h and identified using XRD (Fig. 8).

### 3.4 Extraction and Purification of Niobium

The filtrate of the working alkaline solution which contains almost niobium (1.34 g/L) and the remains of silicon (0.8 g/L) was subjected for further acidification to pH 8.5, where almost Nb<sup>5+</sup> ions (99.8%) were already precipitated via hydrolysis process [50]. After filtration and washing, the prepared Nb cake was collected and a small amount of the cake was examined using SEM-EDAX, where it revealed that its purity attained only 55.3% with the interfering impurities of Si, Fe, K, and Y as shown in Fig. 9.

Therefore, further purification using solvent extraction Aliquat 336S in xylene was needed. For this purpose, the previously prepared hydrous Nb cake was completely dissolved in 8% oxalic acid solution and stirring for 30 min at 80 °C to form the corresponding stable anion Nb-oxalate complexes [Nb(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>-</sup> and/or [Nb(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> at pH 0.3–4.3 [24]. Complete dissolving of Nb, Fe, and small portion of Si was attained, while Y was kept as insoluble Y-oxalate [16]. The prepared Nb-oxalate solution of pH 2.8 was found to assay 3.15 g/L of Nb and 0.39 g/L of Fe as well as 0.25 g/L

**Table 4** Effect of O/A ratio upon the extraction efficiency of Fe

O/A ratio	Organic phase conc., ppm	Aqueous phase conc., ppm	$D_A^O$	Fe extraction efficiency, %
3/1	129	4	30	98.9
2/1	190	10	19	97.5
1/1	367	23	16	94.1
1/2	513	133	4	65.8
1/3	565	202	3	48.3



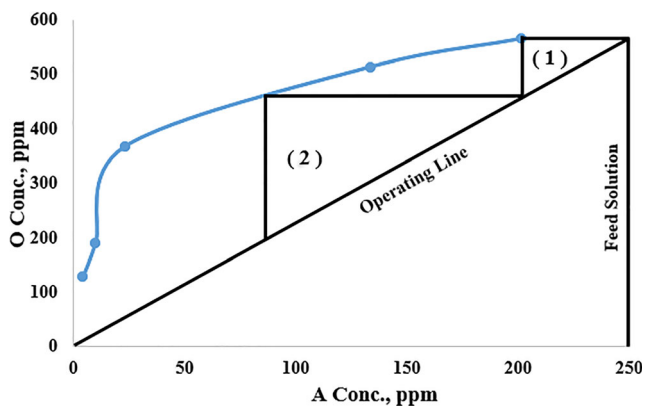


Fig. 14 Macabe-Thiele diagram for Fe extraction

of Si with leaching efficiencies of 98.9, 84.7, and 14.3% respectively.

### 3.4.1 Optimization of Loading Step

The maximum loading of  $[\text{Nb}(\text{C}_2\text{O}_4)_3]^{3-}$  anion complex from the aqueous phase of Nb-oxalate solution to the organic phase of Aliquat 336S required the investigation of several effective loading parameters as follows:

**Effect of Aliquat 336S Concentration** This effect was already studied using the Aliquat 336S concentrations ranged between 2 and 5% in xylene from the prepared oxalate leach liquor of pH 3 at O/A volume ratio of 1/1 and contact time of 10 min at ambient temperature ( $35 \pm 5$ ). After separation, Nb and Fe were analyzed in the raffinate to calculate their extraction efficiencies. The obtained data conducted in triplicate with low standard deviation of  $1 \pm 0.4\%$  (Fig. 10) revealed that Nb and the interfering Fe loading efficiencies were progressively improved from 69.2 and 48.4% to 92.9 and 91.8%, respectively, as the Aliquat 336S concentration increased from 2–5%, where further increase to 6% showed a limit increase in the Nb loading efficiency to 94.1%, while that of the interfering Fe increased to 96.5%. Indeed, Aliquat 336S concentration of 5% was very suitable to apply for Nb extraction process. Thus, the optimum conc. of Aliquat 336S was 5%.

**Effect of pH Value** Data given in Fig. 11 represented the effect of increasing pH values of the prepared oxalate solution from

Fig. 15 Effect of reagents type upon Nb and Fe stripping efficiencies (A/O ratio 1/1 and contact time 5 min)

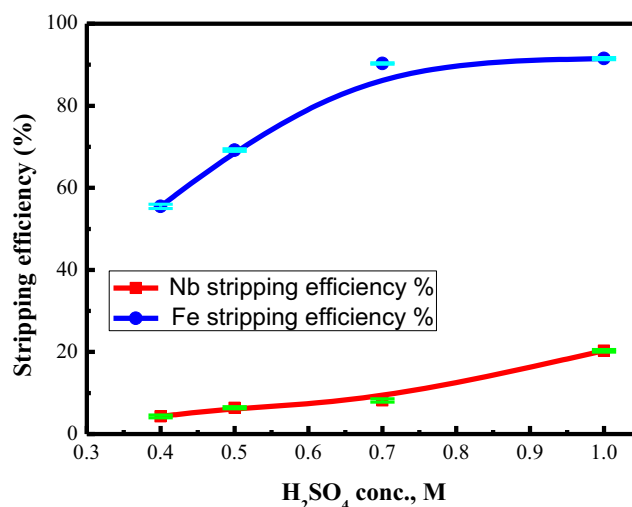
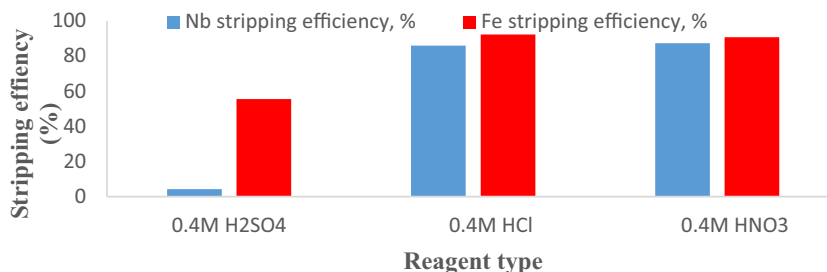


Fig. 16 Effect of H<sub>2</sub>SO<sub>4</sub> conc. upon Nb and Fe stripping efficiencies (A/O ratio 1/1 and contact time 5 min)

pH 3 to pH 5.5 upon Nb and Fe loading efficiencies using 5% (v/v) Aliquat 336S at O/A volume ratio of 1/1 and contact time of 10 min. It was noticed that Nb loading efficiency increased up to 95.3% at the pH 3.5 and decreased gradually up to 61.3% at pH 5.5. This may be explained that the present soluble anion Nb complex  $[\text{Nb}(\text{C}_2\text{O}_4)_3]^{3-}$  would be hydrolyzed to  $[\text{Nb}(\text{C}_2\text{O}_4)_2(\text{OH})_2]^{3-}$  precipitated, at higher pH values more than pH of 4.5 [54]. In an opposite manner, the loading efficiency of Fe increased gradually with increasing the solution pH values. So, the pH value 3.5 was considered the optimum value due to the highest extraction efficiency of Nb.

**Effect of Contact Time** The effect of contact time (shaking time) upon the extraction efficiencies of Nb and Fe from the oxalate leach liquor adjusted to pH of 3.5 was investigated by contacting 5% (v/v) Aliquat 336S at different contact time ranging from 5 to 10 min at O/A ratio 1/1. The obtained results (Fig. 12) emphasized that the loading efficiency of Nb achieved its maximum value (97.9%) at the contact time of 10 min [26]. It was also noticed that further increase in the contact time to 12 min had an opposite effect. With respect to Fe loading, efficiency was found inversely proportional to the contact time.

**Effect of Organic/Aqueous Volume Ratio and Constriction of Macabe-Thiele Diagram** This effect was studied at different O/

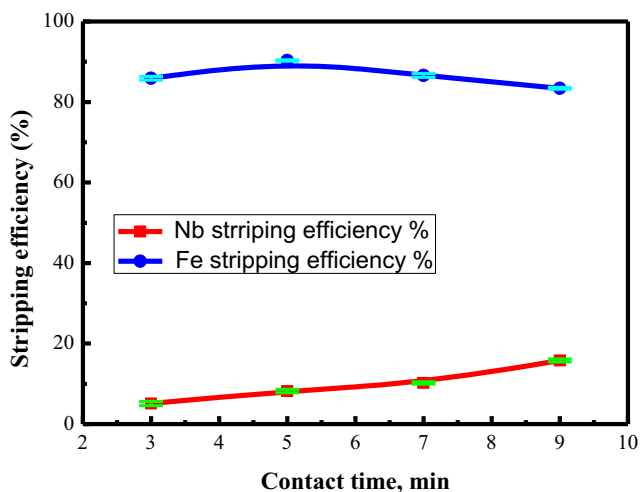


Fig. 17 Effect of contact time upon Nb and Fe stripping efficiencies (0.7 M H<sub>2</sub>SO<sub>4</sub> and A/O ratio 1/1)

A ratios 3/1,... 1/1,... 1/3 using 5% Aliquat 336S at a contact time of 10 min and pH of 3.5. From the obtained data (Table 3 and Fig. 13), it was observed that the Nb loading efficiency at O/A ratios 2/1 (98.7%) and 1/3 (99.8%) was higher than O/A of 1/1 (97.9%). But these ratios were not applied because they yielded lower Nb concentrations in the organic phase. On the other hand, the Nb loading efficiencies at O/A ratios 1/2 and 1/3 are 80.1 and 69.7%, respectively, which were lower than that of 1/1 (97.9%). The same manner was already found for the loading efficiency of Fe; it was 98.9% and 97.5% at O/A ratios of 2/1 and 3/1 and lower to be 65.8% and 48.3% at the ratios 1/2 and 1/3 (Table 4 and Fig. 14). Indeed, the suitable O/A ratio applied for the best Nb and Fe loading efficiencies was 1/1.

From the above study, the co-extraction of both of Nb and Fe was already attained with achieved loading efficiencies of 97.9 and 93.8%, respectively, from the prepared Nb-oxalate

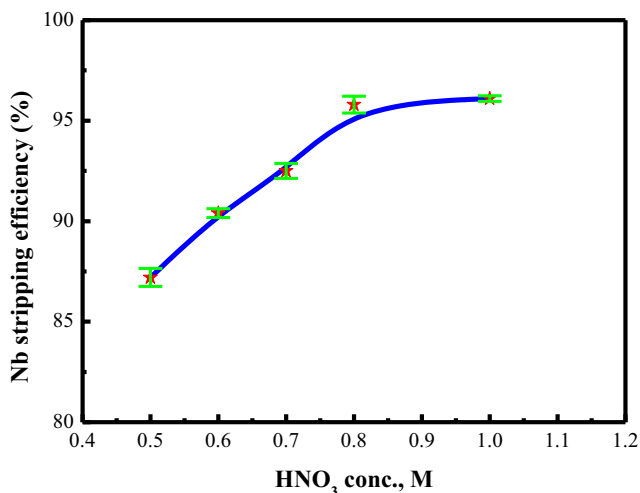


Fig. 18 Effect of HNO<sub>3</sub> conc. upon Nb stripping efficiency (5 min and A/O ratio 1/1)

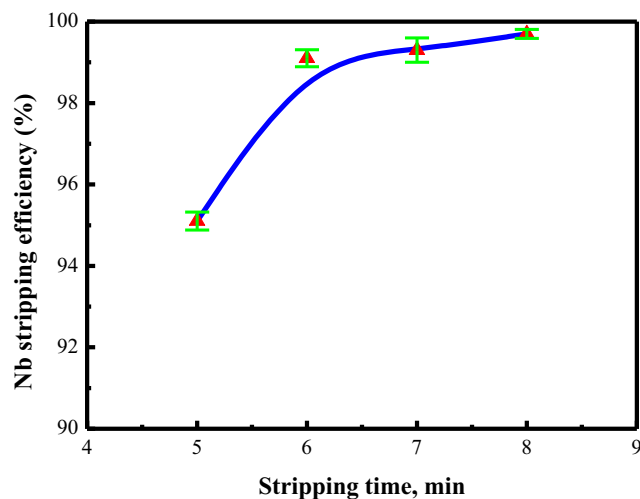


Fig. 19 Effect of stripping time upon Nb stripping efficiency (0.8 M HNO<sub>3</sub> and A/O ratio 1/1)

solution adjusted to pH 3.5 using 5% Aliquat 336S at O/A ratio of 1/1 and contact time of 10 min. The loaded organic solvent was then directed to the stripping process to bring out the loaded Nb and Fe to the aqueous solution until regeneration of the utilized organic solvent to be reused.

### 3.4.2 Optimization of Stripping Process

The stripping process was conducted to attain the maximum Nb stripping efficiency from one hand and for its separation from the co-extracted Fe from the other hand. For this purpose, the following stripping parameters would be investigated.

**Effect of Stripping Reagent Types** After separation and determination of both Nb and Fe in the strip solution, the obtained data (Fig. 15) showed that 0.4 M H<sub>2</sub>SO<sub>4</sub> acid gave very low Nb stripping efficiency (4.3%) with high Fe stripping efficiency (55.5%) from the loaded Aliquat 336S. Therefore, H<sub>2</sub>SO<sub>4</sub> acid would be firstly utilized and its effective stripping factors would be studied for selective stripping of Fe ([9]), while both HCl and HNO<sub>3</sub> acids yielded co-stripped Nb and Fe strip solution.

Table 5 Effect of A/O ratio upon the stripping efficiency of Nb

A/O ratio	Aqueous phase conc., ppm	Organic phase conc., ppm	$D_O^A$	Nb stripping efficiency, %
2/1	1446	0	$\infty$	100
1/1	2883	9	320	99.7
1/2	3696	1044	3.5	63.9
1/3	4563	1371	3.3	52.6

Where  $D_O^A$  is the distribution coefficient between aqueous and organic solutions

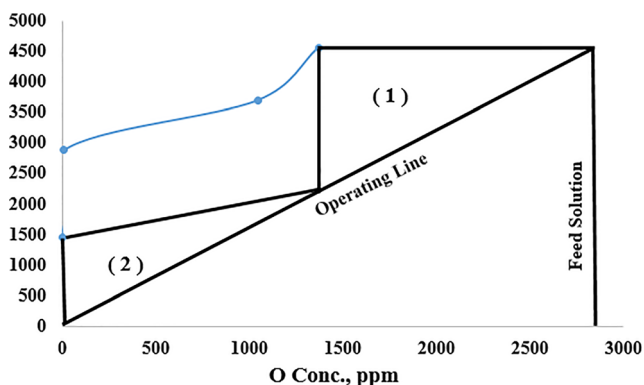


Fig. 20 Macabe-Thiele diagram for Nb stripping

**Effect of H<sub>2</sub>SO<sub>4</sub> Acid Concentrations** This effect was conducted via contacting the loaded solvent with H<sub>2</sub>SO<sub>4</sub> acid solution in different concentrations ranging from 0.2 to 1 M at A/O volume ratio of 1/1 and contact time of 5 min. A remarkable improvement of Fe stripping efficiency from 51.4 to 87.8% was attained with increasing H<sub>2</sub>SO<sub>4</sub> concentration from 0.2 to 0.7 M with maximum Nb stripping efficiency not exceeding 8.2% as presented in Fig. 16, while the further increase in the strip solution concentration to 1 M showed improvement in both Fe stripping efficiency to 91.5% and Nb stripping efficiency to 20.3%. Indeed, 0.7 M H<sub>2</sub>SO<sub>4</sub> acid was already chosen to remove almost of Fe from the loaded solvent.

**Effect of Contact Time** Figure 17 represents the influence of varying contact time periods from 3 to 9 min when 0.7 M H<sub>2</sub>SO<sub>4</sub> solution was contacted with the loaded Aliquat 336S at A/O ratio of 1/1. It was actually noticed that not less than 90.5% of the co-extracted Fe was removed with the smallest Nb efficiency (8.2%) which was attained at a contact time of 5 min.

It was concluded from the above study that 0.7 M H<sub>2</sub>SO<sub>4</sub> acid concentration should be firstly applied for removing 90.3% of Fe with a minimum amount of Nb (not exceeding 8.2%) at a contact time of 5 min and A/O ratio of 1/1. Another stripping process would be subsequently applied using HNO<sub>3</sub> solution for Nb stripping. Different Nb effective stripping factors should be studied as follows.

**Effect of HNO<sub>3</sub> Acid Concentration** The effect of HNO<sub>3</sub> acid concentration upon Nb stripping efficiency was studied in the range from 0.5 to 1.2 M with shaking time for 5 min at A/O ratio 1/1. Data (Fig. 18) reflected the great improvement of Nb stripping efficiency from 87.2 to 95.4% when HNO<sub>3</sub> acid concentration increased from 0.5 to 0.8 M, while the further increase in strip solution concentration more than 0.8 M had very limited improvement in stripping efficiency which increased to 96.2%.

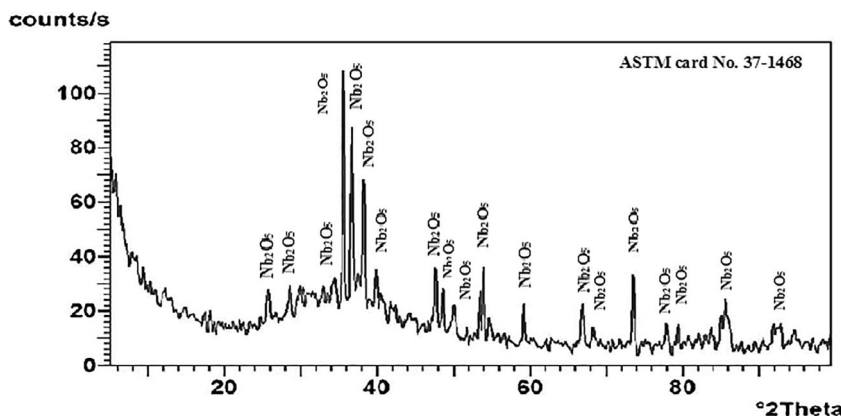
**Effect of Stripping Time** The effect of stripping time upon Nb stripping efficiency was studied in the range from 5 to 10 min using 0.8 M HNO<sub>3</sub> solution at A/O ratio of 1/1. The obtained results (Fig. 19) revealed that the stripping time 6 min is sufficient to regenerate not less than 99.1% of the loaded Nb.

**Effect of Aqueous/Organic (A/O) Ratio and Constriction of Macabe-Thiele Diagram** The equilibrium state of Nb stripping process from the loaded Aliquat 336S was investigated using 0.8 M HNO<sub>3</sub> solution at stripping time of 6 min via applying different A/O ratios of 2/1, 1/1, 21/2, and 1/3. Table 5 and Fig. 20 clearly reflected that almost 100% of the loaded Nb was stripped at A/O ratio of 2/1 compared with 99.1%, 63.9%, and 52.6% at A/O ratios of 1/1, 1/2, and 1/3, respectively. Indeed, the ideal applied A/O volume ratio was 1/1 which is also beneficial for Nb stripping with efficiency of 99.1%.

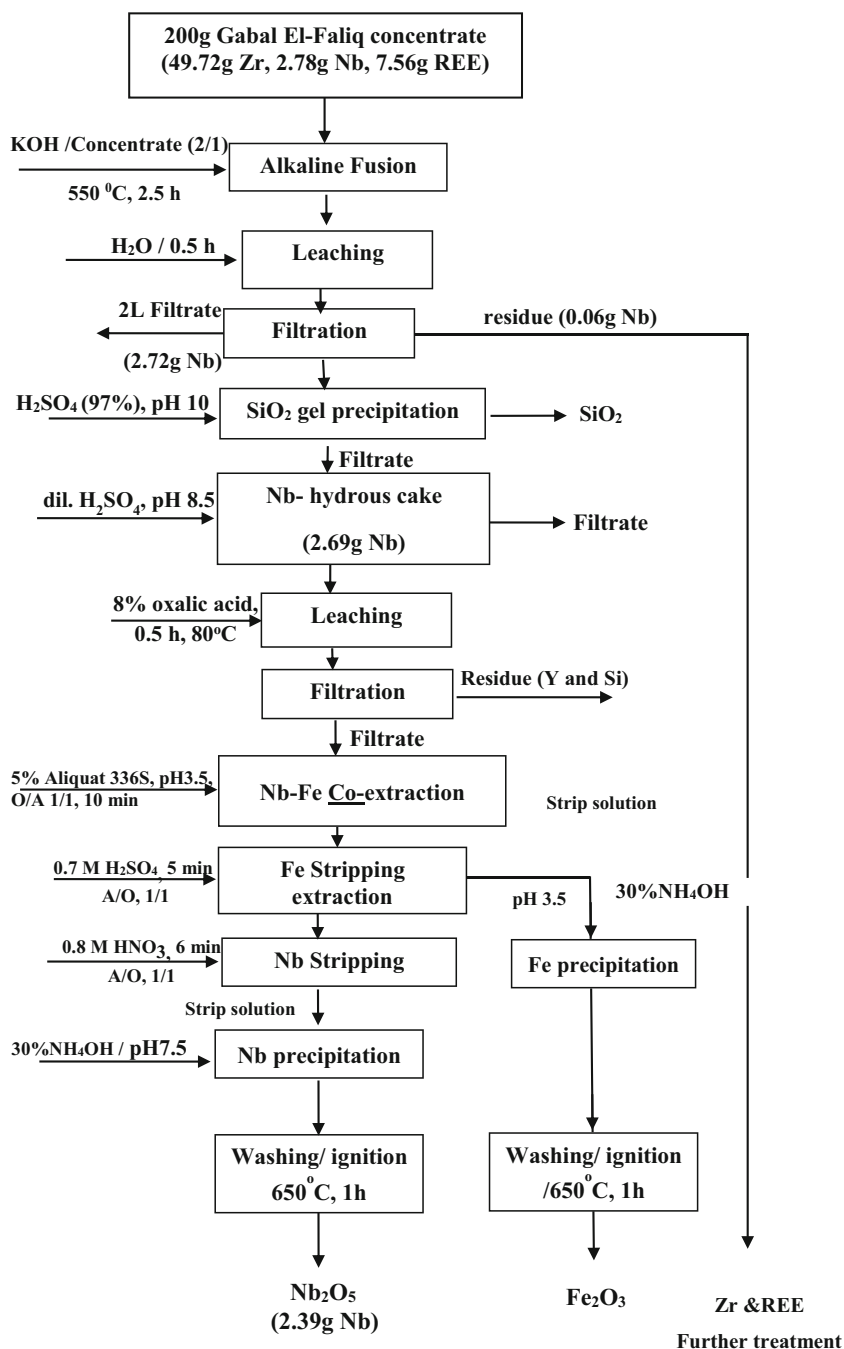
### 3.4.3 Preparation of Nb Product

From the previous data, it was found that the maximum value 99.1% of Nb stripping efficiency was achieved using 0.8 M HNO<sub>3</sub> solution at stripping time of 6 min and applied A/O ratio of 1/1. The strip nitrate solution rich in Nb was treated with 30% NH<sub>4</sub>OH solution where Nb was completely precipitated at pH 7.5 [13]. After filtration and washing, the obtained Nb hydroxide cake was ignited at 650 °C for 1 h. A small portion of the product was confirmed by XRD analysis (Fig. 21) and chemically analyzed for its purity. The final Nb<sub>2</sub>O<sub>5</sub> product was achieved with global recovery of 86% and purity

Fig. 21 XRD pattern of final pure Nb product



**Fig. 22** Proposed technical flowsheet for the processing Gabal El-Faliq concentrate sample



of 98.95% with low concentration of associated impurities, e.g., 0.9%  $\text{SiO}_2$ , 0.05%  $\text{Fe}_2\text{O}_3$ , and 0.1%  $\text{TiO}_2$ .

## 4 Conclusion

An alkaline fusion process using KOH followed by water leaching was applied for a selective dissolving of Nb as water-soluble potassium niobates from Gabal El-Faliq ore material concentrate, where 97.9% of the total Nb content was already dissolved at 1/2 concentrate sample/KOH weight ratio

and fusion temperature of 550 °C for a fusion time of 2.5 h. The prepared alkaline solution of pH higher than 12 was first neutralized at pH of 10 to remove almost of  $\text{Si}^{4+}$  as  $\text{Si}(\text{OH})_4$  gel, while complete precipitation of Nb and other associated impurities, e.g., Fe, Ti, and Y, were attained by further neutralization at pH 8.5.

The precipitated Nb-hydrous cake assaying 55.5% of Nb was dissolved in oxalic acid solution and subjected to Nb purification process using Aliquat 336S in xylene. The co-extracted Nb and Fe with loading efficiencies 97.9% and 93.8%, respectively, were attained using 5% Aliquat 336S concentration at

pH 3.5 and shaking time of 10 min at O/A ratio of 1/1. Two subsequent stripping processes were performed using both 0.7 M H<sub>2</sub>SO<sub>4</sub> for removing 90% of Fe away from the Aliquat 336S and 0.8 M HNO<sub>3</sub> for stripping 97.9% of Nb. Finally, this process was successfully applied to prepare Nb<sub>2</sub>O<sub>5</sub> product with purity of 98.95% and global recovery of 86% as summarized in the proposal flowsheet (Fig. 22).

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## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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