

Received June 10, 2021; reviewed; accepted August 25, 2021

Physical and chemical processes of Abu Rusheid cataclastic rocks for recovering niobium, zirconium and uranium compounds

Walid M. Abdellah, Mahmoud S. Khalafalla, Hanaa A. Abu Khoziem, Omneya M. El Hussaini

Nuclear Materials Authority P.O. Box: 530- El Maadi, Cairo, Egypt

Corresponding author: hn_abdelaal@yahoo.com (Hanaa Abu Khoziem)

Abstract: Cataclastic rocks of Abu Rushied area (South Eastern Desert, Egypt) characterized by the presence of niobium, tantalum, zirconium minerals as well as uranium-thorium minerals. Physical upgrading process was applied using gravity and magnetic separation techniques to concentrate these economic minerals mainly to obtain the magnetic niobium concentrate at 0.2- 0.5 ampere, beside the non-magnetic Zr and U at 1.5 ampere. The chemical processing upon niobium concentrate was performed using NH_4F roasting process at 250°C followed by selective precipitation of Nb as Nb-sulfide. An alkaline fusion using NaOH was applied upon zirconium concentrate at the optimum conditions of: zircon concentrate/ NaOH mass ratio 1/2, fusion temperature of 650°C and 2.5h fusion time followed by selective precipitation of Zr as Zr- tartrate. Finally, two flowsheets were drawn summarizing the whole recovery processes.

Keywords: physical and chemical processes, cataclastic rocks, separation, niobium, zirconium, uranium

1. Introduction

Abu Rushied area is considered as one of the most promising rare-metal mineralization in South Eastern Desert of Egypt. This mineralization is mainly associated with muscovite, chlorite, quartz, fluorite, pyrite, magnetite, and rare biotite of the psammitic gneiss. The recorded economic minerals mainly include columbite-tantalite, pyrochlore (var. betafite), and ferrocolumbite. The U-Th and REE minerals (uraninite, thorite, uranothorite, ishikawaite, cheralite, monazite, and xenotime) and Hf-rich zircon ones are also recorded (Sabet et al., 1976; El-Gemmizi, 1984; Ibrahim et al., 2004; Raslan, 2008; Ali et al., 2011; Ali and Abd El- Razeq, 2020 and Fawzy et al., 2021). Physical beneficiation is the first step in the extraction of metal from natural resources. The objectives of physical beneficiation are: increasing the metal grade of ore, reducing the amount of associated gangue minerals (quartz, feldspar, hematite, and goethite), reducing leaching plant costs as well as increasing the productivity. Most of rare metal minerals are beneficiated through a combination of unit operations such as gravity concentration, magnetic separation, and froth flotation (Zhang et al., 2021 a&b; Han et al., 2021). Due to their relatively high specific gravities, gravity separation can be used to concentrate rare metal minerals by eliminating low specific gravity gangue minerals such as quartz and feldspar. In the context of mineral beneficiation, magnetic separation is typically used for two purposes: (1) removing of ferromagnetic gangue minerals such as iron oxides, and (2) separating of paramagnetic minerals from other heavy minerals (Jordens et al. 2014).

Hydrometallurgical processes are the most established technologies for separating Nb, Ta, Zr, Hf, and U. The dissolution of niobium mineral underwent flux fusion methods with molten salts (Xiaohui et al., 2009; Senda, et al., 2014; Purcella, et al., 2018; Abd el Wahab et al., 2019), acid dissolution (El Hussaini and Mahdy, 2008), fusion with NH_4F and NH_4HF (Kabangu and Crouse, 2012; Purcell et al., 2018), and microwave digestion (Nete et al., 2010). Also, most Nb-Ta ores were dissolved with concentrated HF (Rodriguez et al., 2007 & 2015). The mainly frequently procedures used for separating

Zr and Nb dissolved species are extraction utilizing organic compounds such as tributyl phosphate and methyl isobutyl ketone (Sadigzadeh et al., 2009; Xu et al., 2014; Nguyen and Lee, 2019). In order to extract Zr, extreme processes like alkaline breakdown have to be applied upon zircon mineral (Zolfonoun, et al., 2010; Nel et al., 2011; Amalia and Nugraha, 2016). The fused matrix should be leached in water in order to separate quartz as soluble sodium silicate (Na_2SiO_3) and the residue from water leaching was used for further leaching with HCl acid to have zirconium oxy-chloride (Setyadji and Susiantini, 2020). The fractional crystallization process of the latter was operated for many years on an industrial scale (Xu et al., 2015). Also, zirconium tetrachloride is produced by carbo-chlorination of zircon at $>800^\circ\text{C}$ (Nel et al., 2011).

Uranium is a naturally occurring radioactive element that is primarily used in the production of nuclear energy (Uranium, 2018). Depending on the mineral composition of uranium-bearing ores, leaching procedures may be carried out using an alkaline or an acidic route (Kim et al., 2014; Abdel Wahab et al., 2019), However, in most cases, U is extracted by acidic leaching (Abu Elatta et al., 2018; Xu et al., 2019) The acid way is usually considered non-selective and produces multi-metal solutions such as thorium, rare earth elements (REE), in addition to uranium. The treatment of acidic leach solution may involve a wide range of techniques including selective precipitations (Bhowmik et al., 2009 and El-Ansary et al., 2018), solvent extraction (Singh and Gupta 2008, Zhu et al., 2013; Avelar et al., 2017; Abdoul-Rachid, 2018 and Abdellah, 2020), and ion exchange resins (Danko et al., 2017; Abdel Aal and Abdel Samad, 2019).

Consequently, the present work aimed to investigate the potentiality of physical upgrading of Abu Rushied cataclastic rocks using mainly gravity and magnetic separation methods, as well as to determine the optimum leaching conditions for subsequent recovery of Nb, Zr, and U with highest possible purity. To achieve this goal, a representative sample was properly collected and firstly subjected to mineralogical examination and physical upgrading to identify its mineral constituents. Nb was recovered from fluoride leach liquor as Nb-sulfide while, selective separation of Zr from U was carried out using ammonium tartrate.

2. Materials and methods

The experimental work of the present study includes applying physical beneficiation and chemical processes upon the studied cataclastic rock sample. The former includes mineralogical identification and physical procedures using shaking table and a laboratory Carpco high intensity lift-type magnetic separation techniques. The obtained two concentrates were subjected to chemical processing, the concentrate of 0.2- 0.5 ampere subjected to ammonium fluoride roasting. The latter includes alkaline fusion upon the non- magnetic concentrate of 1.5 ampere.

2.1. Mineralogical characterization

To identify the main mineral constituents, the rock sample was first ground and then sieved into the size -0.5 to +0.063 mm. The light and heavy fraction were separated by bromoform (sp. gr. $2.8\text{gm}/\text{cm}^3$, Merk- Germany). The heavy mineral particles were picked under a binocular microscope (Optech, LFZT-Germany) and identified by Environmental Scanning Electron Microscope (ESEM) a Philips Model XL 30 supported by an energy dispersive X- ray unit (EDAX) for semi-quantitative analysis.

2.2. Physical beneficiation studies

A bulk sample weight 6 kg representing Abu Rushied cataclastic rocks was subjected to size reduction using a combination of jaw crushers and a roll mill crusher to obtain a sample less than 1mm, and the oversized (+1 mm) fraction was recycled to the secondary jaw crusher step. The deslimed fraction was fractionated using a set of screens starting from -1.000 down to +0.063 mm which is suitable for the gravity technique. In this context, the laboratory wet Wilfely shaking table (No.13, Germany) was firstly used to separate the light (gangue minerals) from the heavy minerals (carrier the valuable and interested elements). The operating conditions were 5Kg/h feed rate with water flow equal 4L/min, stoke length of 10mm and table inclination of 8. Then, the Carpco high- intensity lift-type magnetic separator Model MLH (13) III-5 (USA) was used for the magnetic separation.

2.3. Chemical analysis

The chemical composition of the representative raw material beside the obtained fractions at different magnetic amperes was carried out using the XRF technique for their major and trace elements. Microwave Plasma Atomic Emission Spectrometer (4200 MP-AES, Agilent Technologies) was employed for chemical analysis of Zr, Nb, and Ta during all experimental work. On the one hand, a visible-ultra violet spectrometer (Shimadzu UV-160) was used for the quantitative analysis of both of Th and REE (Marczenko, 2000). U was determined using an oxidometric titration method against NH_4VO_3 in the presence of diphenyl amine-4-sulfonic acid sodium salt (99.9%, Merck-Germany) as an indicator (Mathew et al., 2009). The zircon concentrate was prepared for ICP chemical analysis via digestion of approximately 0.2 g of zircon concentrate with 2 g of lithium tetraborate fluxing reagent at 1 100°C for at least 4 hours in a platinum crucible. After complete digestion, the platinum crucible was removed from the oven and immediately cooled by direct contact with distilled water in a water bath in order to crack the melt, facilitating faster dissolution times (Lötter et al., 2012). With respect to Niobium concentrate: 5 cm³ of HF was added to 0.1 g of Nb concentrate, an aqueous solution of HNO_3 (volume ratio = 1:1) was admixed drop by drop till a complete dissolution of the concentrate (Kubová et al., 1993).

2.4. Chemical processing procedures

Chemical processing procedures include the extraction of Nb and Ta from magnetic concentrate of 0.2-0.5 ampere beside Zr and U from non- magnetic concentrate of 1.5 ampere.

2.4.1. Recovery of niobium from magnetic concentrate

The magnetic concentrate of 0.2- 0.5 ampere was ground to 0.074 mm and treated with ammonium fluoride salt (98%, Merck- Germany) at ($\text{NH}_4\text{F}/\text{Nb}$) mass ratios in the range of (1.3– 10.0) at temperature ranged from 200 to 350°C for 1 h. The obtained cake (C) was washed with distilled water collected from Automatic water still-Human Lab.(L) to release the elements of interest at L/C ratios of 25, 50, and 100. The fluoride leach solution was contacted with sodium sulphide (60%, Adwic- Egypt) (Na_2S) at ($\text{Na}_2\text{S}/\text{leach liquor}$) volume ratios in the range of (0.5-2.5) to remove impurities. Then, the sulfide precipitate was finally washed with a nitric acid (65% Adwic-Egypt) solution. On the other hand, the sulfide filtrate was treated with conc. HCl (36%, Adwic- Egypt) to separate elemental sulfur as by-products. Finally, the obtained products were ignited at 900°C and were analyzed using both ESEM and XRD (a Philips X-ray diffractometer, model PW 223/20 at 40 kV and 20 mA).

2.4.2. Recovery of zirconium and uranium from non- magnetic concentrate

The non- magnetic concentrate of 1.5 ampere contains mainly Zr and U after grinding using disc mill (Germany Retsch-RM 200) to 0.074 mm was first mixed with solid NaOH (96%, Adwic- Egypt) at different mass ratios of concentrate sample/ NaOH for different time periods (1- 4h) and temperature ranging from 550-750°C. Moreover, the molten mass after cooling was then washed with distilled water at a water/fused mass ratio of 1/5 for dissolving its Si content. After the filtration using filter paper (185 mm made in France) and washing, the insoluble sodium zirconate and uranium salt were then dissolved in 9 mol/dm³ HCl for 20 min at 90°C. Finally, the pregnant chloride leach liquor was then subjected to the selective separation of Zr from U via precipitation by adding ammonium tartarate (98%, Sigma-Aldrich) at definite time and pH values. While, U in the filtrate was directly precipitated as ammonium diuranate.

3. Results and discussion

3.1. Mineralogical characterization of the studied mineralized cataclastic rock sample

It is worthy to mention herein that; the main target of the mineralogical studies was to identify the existing valuable minerals as well as identified their chemical composition and physical properties in order to choose the most appropriate physical beneficiation technique. The mineralogical examination revealed that, the heavy bromoform minerals in the studied Abu Rushied cataclastic sample represented about 30 Wt.% of the total bulk sample. The obtained heavy bromoform subjected to individual mineral

separation under the binocular microscope. The obtained data of EDX analyses revealed the presence of the following minerals:

- Uranothorite [(Th, U) SiO₄] - it is a thorium mineral contains high amount of uranium [14.55 wt. %] (Fig. 1a). The content of U and Th in uranothorite grains is variable depending upon the representative test sample. Also, other uranothorite picked grains showed content of REE and Zn (Fig.1b).
- Kasolite Pb (UO) SiO₄ (H₂O) and uranophane (Ca (UO₂) (SiO₃)₂ (OH). 5H₂O) - these uranium minerals were detected in the studied sample (Figs 1c and 1d), but in less amount than uranothorite mineral.

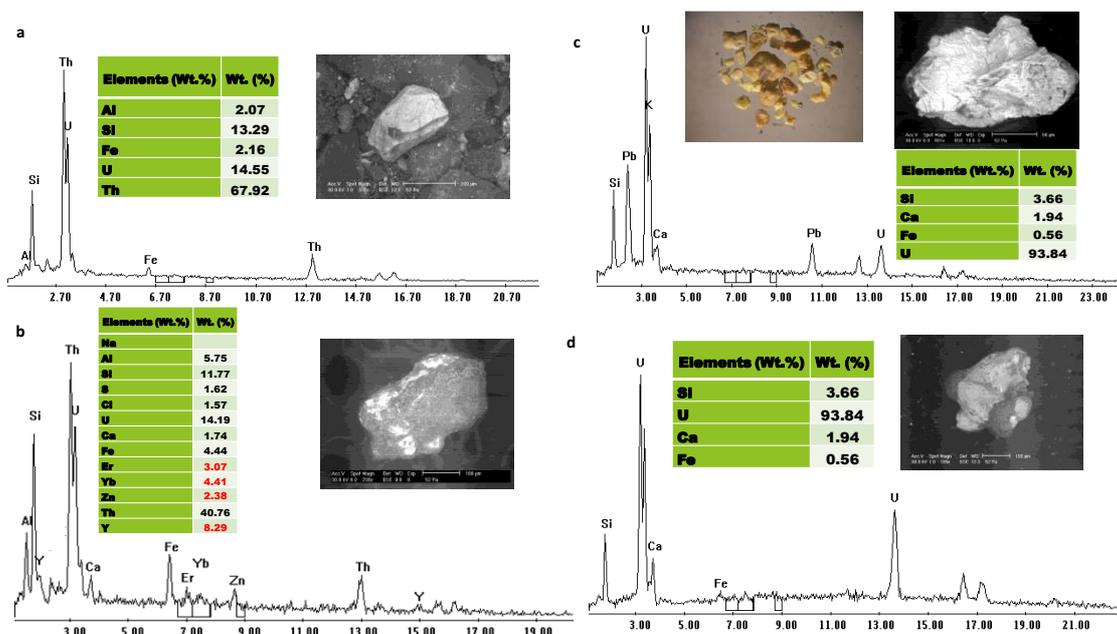


Fig. 1. EDX analysis data of uranothorite grains (a) uranothorite contain REE (b), kasolite (c) uranophane (d) with photograph showing its grain color and habit

- Columbite and ferrocolumbite minerals [(Fe, Mn) (Nb, Ta, Ti) O₄] - in the present work, ferrocolumbite [(Fe, Mn) (Nb, Ta, Ti)O₄] has dark pitchy to velvety black to dark brown color, irregular massive grains with metallic luster (Fig.2a). EDX analysis data confirm its presence in the separated grains from magnetic fraction showing U, Y and Fe as the main substitutions with different ratios (Fig. 2b).
- Ishikawite [(U, Fe, Ca, Y, Th) (Nb, Ta, Ti)₂O₆] - is a member of the samarskite group Hanson et al., 1999; Simmons et al., 2006 and Raslan et al., 2017). Ali et al. (2017) suggests that ishikawite is a variety of samarskite contains uranium and sometimes is a replacement with columbite minerals.
- Zircon (Zr SiO₄) - is common accessory mineral has radiogenic nature and mainly metamicted (radioactive zircon) and characterized by presence of radial and concentric fractures. These fractures are good path way for leaching or addition of U (Ali et al., 2011). EDX analysis data confirmed the presence of zircon with profit amount especially in non-magnetic fraction (Fig.4a). Some zircon grains showing the presence of U inclusion within its grain (Fig. 2c).
- Apatite mineral [Ca₅ (PO₄)₃F] - it is present in few amounts, its surfaces are pitted as the result of hydrothermal solutions, so that U, Th and REE are found on this surface as a result of the substitution among these cations, Ca²⁺, (REE)³⁺, U⁴⁺ and Th⁴⁺ (Förster, 1998). This fact is reflected by EDX analysis data of these surfaces where they are composed of 31.60 wt.% Y and about 11% REE (Fig. 2d), while U and Th contents reach about 6 and 30% wt.% respectively (Fig. 3a).
- Xenotime (YPO₄) - grain have high concentrations of HREE and significant concentrations of Th and U. EDX analyses of xenotime grain show about 56 wt.% Y, 1.5 wt.% Th and 0.4 wt.% U as

in Fig. (3b). Pyrite (Fe₂S): this sulfide mineral present in few amounts in the studied sample (Fig. 3c) separated mainly from non- magnetic fraction associated with zircon.

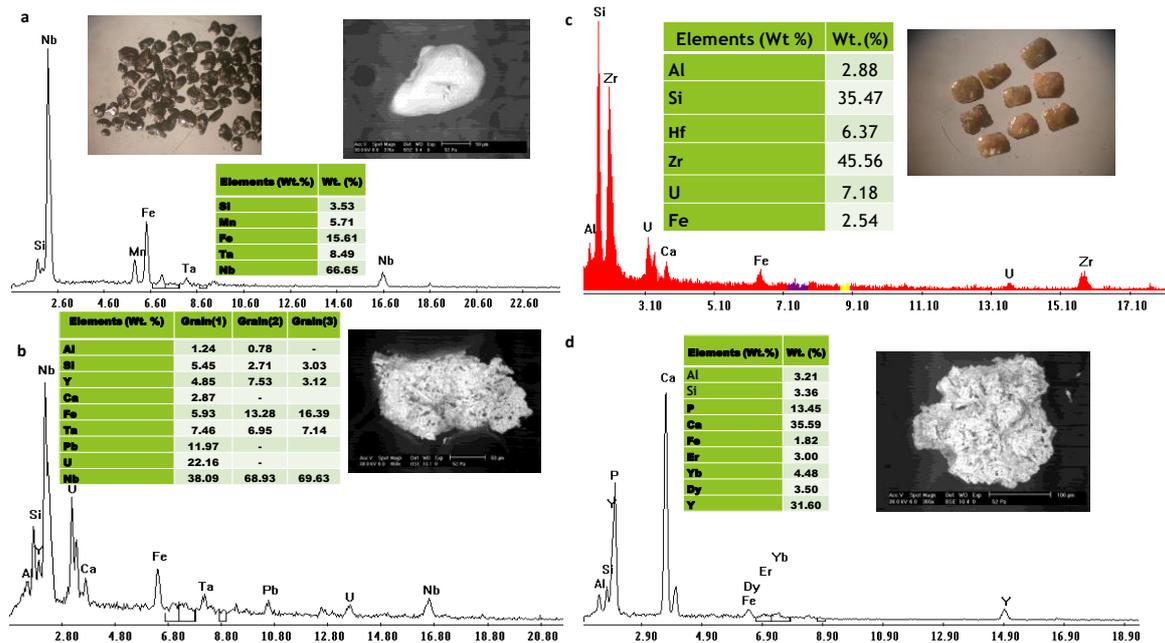


Fig. 2. EDX analysis data of columbite grain (a) and ferrocolumbite and ishakawite (b). Zircon grains(c) with photograph showing its grain color and habit and apatite mineral contains HREE

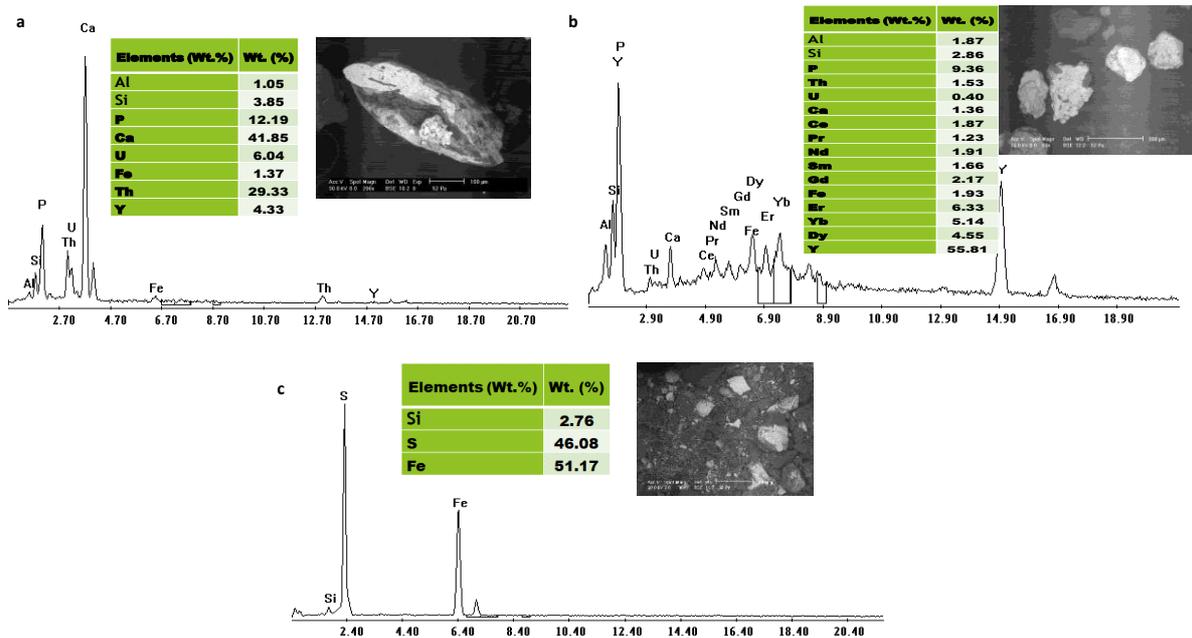


Fig. 3. EDX analysis data of apatite contain U and Th (a) and xenotime mineral enriched in REE (b) and of pyrite mineral (c)

3.2. Physical beneficiation of the studied cataclastic rock sample

3.2.1. Gravity separation

The bulk weight of 6 kg from Abu Rushied cataclastic rocks was sieved in different size fractions (-1 + 0.7 mm), (-0.7 + 0.5 mm), (-0.5 + 0.25 mm), and (-0.25 + 0.063 mm). Each feed size fraction was separated using the Wilfely shaking table No. 13 to obtain a primary concentrate (Table, 1). The obtained data showed differences in the specific gravities between the heavy minerals and the associated gangue

minerals that render the gravity concentration by shaking table as an efficient tool for their primary separation. Moreover, it was concluded from Table 1 that about 73% of the valuable mineral was concentrated in size fraction of (-1+0.063 mm) with a recovery of 81.6% from a heavy mineral content (30 wt. %) of the original feed sample.

Table 1. The particle size distribution and amount of heavy minerals in each size fractions

Particle size (mm)	Wt. (%)	Shaking table concentrate (%)	Heavy minerals assay (%)
+1	10.4	-	-
-1+0.7	14.7	3.5	97.1
-0.7+0.5	15.8	6.8	80.5
-0.5+0.25	25.1	9.1	84.8
-0.25+0.063	31.9	5.1	30.1
-0.063	2.1	-	-
Sum -1+0.063mm	87.5	24.5	73.1
Total (+1-0.063)	100		

3.2.2. Magnetic separation

The magnetic separation process was used in order to disperse the huge assemblages of valuable minerals obtained from the shaking table concentrate. The latter was subjected to laboratory Carpo high intensity lift-type magnetic separator model MLH (13) III-5 to obtain pure concentrates of each mineral fraction. The results presented in Table 2 showed that, about 48 wt. % of heavy minerals have magnetic susceptibility and concentrated between 0.2- 0.5 magnetic intensities.

Table 2. Distribution of minerals as weight % present at different magnetic intensities

Particle size	Magnetite	0.2	0.5	1	1.5	1.5 non- Magnetic
-1+0.063 mm	1.6	14.8	32.6	8.4	15.1	23.5
Distribution of valuable minerals						
Mica		85.5	100	2.5	-	-
Nb- minerals		50.4	100	0.6	-	-
U-Th minerals		10.5	15.2	7.3	8.5	10.7
Zircon		-	0.5	85.7	97.5	100
*Others		-	-	-	-	0.5

* Represent (pyrite, fluorite, and galena)

Microscopic identification and chemical analysis of each magnetic fractions (Table, 3) clarifies that; mica represented the majority of these fractions. Nb-Ta minerals (ferro-columbite and ishikawite) represented about 24 wt. % of the total 0.2- 0.5 magnetic fraction with significant amount of radioactive U-Th minerals (uranophane, uranothorite, and kasolite). Additionally, 97% of the total zircon mineral was concentrated at a non-magnetic fraction at 1.5 amperes with the remains U minerals, pyrite, and fluorite.

Finally, from the mineralogical and physical upgrading studies, the multiple-oxide minerals columbite, ferrocolumbite, ishikawite, and xenotime, were identified as the main refractory ones and were concentrated in the magnetic fraction of 0.2- 0.5 ampere. Meanwhile, zircon was concentrated in the non-magnetic fraction of 1.5 ampere. Indeed, uranothorite, uranophane, and kasolite as which were splitting during magnetic separation. A flowsheet represented the sequence of processes following the upgrading operation is shown in Fig. (4).

3.3. Recovery of niobium from magnetic concentrate

The separated magnetic fractions at 0.2 - 0.5 amperes represented mainly the niobium concentrate. It

Table 3. Chemical composition of ore and separated heavy fractions (wt. %) at different magnetic intensities

	Different magnetic intensities					
	Ore	0.2	0.5	1	1.5	3
SiO ₂	71.82	28.3	21.9	37.5	43.9	45.06
TiO ₂	0.03	0.9	0.56	0.47	0.37	0.3
Al ₂ O ₃	12.59	4.81	4.32	3.52	2.55	1.9
Fe ₂ O ₃	3.11	18.3	13.35	7.29	3.1	0.9
MnO	0.79	1.71	2.4	2.47	0.01	0.03
MgO	0.50	2.14	2.51	1.2	0.34	0.58
CaO	0.89	0.48	0.53	0.42	0.29	0.15
Na ₂ O	4.39	0.24	0.45	0.31	0.45	0.23
K ₂ O	3.15	1.22	0.99	0.51	0.42	0.38
P ₂ O ₅	0.85	0.92	0.85	0.64	0.55	0.42
L.O. I.	1.00	0.89	0.93	0.88	0.9	0.95
Total	99.11	59.61	48.49	55.11	52.88	50.90
ZrO ₂	0.31	2.3	2.6	29.4	38.47	39.52
HfO ₃	0.03	0.2	0.45	0.34	2.61	3.6
Nb ₂ O ₅	0.21	24.2	33.5	9.9	0.34	0.25
Ta ₂ O ₅	0.02	2.77	4.31	0.13	U.L.D.	U.L.D.
U ₃ O ₈	0.09	1.5	1.8	2.4	2.7	3.9
ThO ₂	0.06	0.25	0.25	0.25	0.29	0.26
REE ₂ O ₃	0.07	3.8	3.6	1.14	0.15	0.19
PbO	0.09	0.12	0.54	0.3	0.4	0.35
Total	0.88	37.14	47.05	43.86	44.96	48.07

* L.O.I. - loss of ignition ** U.L.D. - under limit of detection

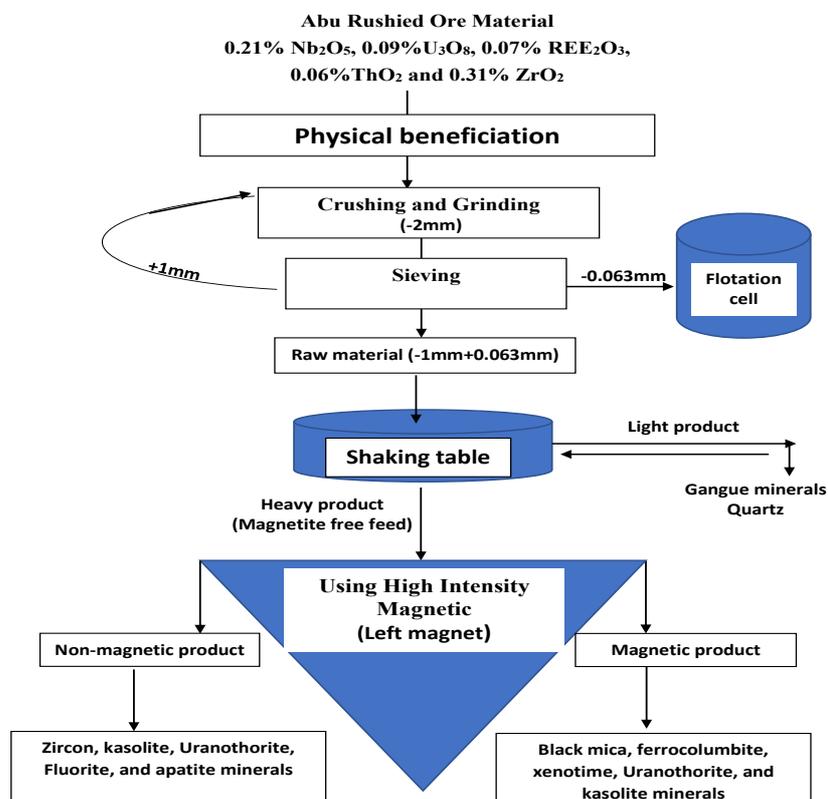


Fig. 4. A flowsheet illustrates physical beneficiation process upon Abu Rushied ore material

contains columbite and ferrocolumbite minerals in association with U-Th minerals and REE-minerals which satisfied the chemical composition for major and economic elements as summarized in Table 3. In order to separate niobium from this fraction in the soluble leach liquor leaving most of the other elements in the residue (U, Th, and REE), the decomposition was done by mixing with ammonium fluoride (NH_4F) at 250°C for an hour in a closed system. NH_4F was selected, because of its availability beside all its elements would be volatile while, ignition to obtain niobium oxide compound (not sodium or calcium salts). Also, for the solubility of Nb and Ta in fluoride solutions is far higher than in other aqueous acids. The factors controlling the dissolving efficiency were studied to optimize the recovery of Nb.

3.3.1. Effect of ammonium fluoride (NH_4F) amount

The variation of NH_4F weight mixed with the ground Nb fraction as (wt./wt.) was studied at ratios 1.3/1.0 to 10.0/1.0 to find its influence upon decomposition of niobium minerals or concentrate at 250°C (Fig. 5A). As the ammonium fluoride amount decreased with respect to the ground Nb concentrate, the released elements were found to decrease by leaching with water (L) of 25 times the fused cake weight (C). Thus, there is a direct, proportional relationship between the (wt./wt.) ratio and the dissolution of elements.

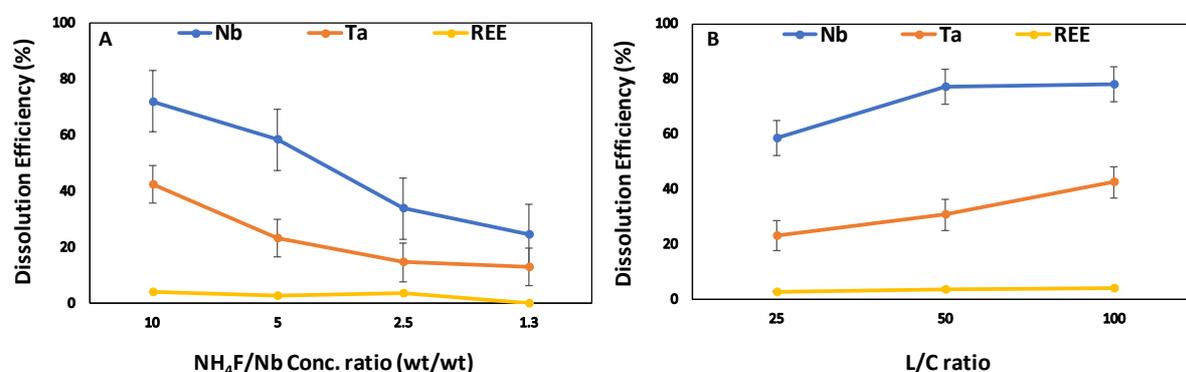


Fig. 5. Effect of $\text{NH}_4\text{F}/\text{Nb}$ conc. Ratio (A) and (L/C) ratio (B) upon elements dissolution efficiencies

3.3.2. Effect of water volume leach to the fused fluoride cake

The volume of distilled water (L) used for the leaching the fluoride cake was studied versus the fused cake (C) at $\text{NH}_4\text{F}/\text{Nb}$ concentrate ratio of (wt./wt.) 5.0/1.0 and 250°C . It was found that, by increasing water's volume, the ability of elements transferred to the leach liquor increased (Fig. 5b). Accordingly, varying the temperature around 250°C showed a negligible influence upon the dissolution of elements from the fused cake. Similarly, the variation in fusing time showed little influence upon the dissolution of elements. It is clear that most of the rare earth elements and uranium, as well as thorium remained in the solid residue

3.3.3. Preparation of pure niobium oxide from fluoride leach liquor

The leach liquor containing the given elements of interest in g/dm^3 : 4.58 Nb, 0.3 Ta, 1.4 Fe, 0.1 Ti, and 0.25 Zr underwent sulfide precipitation using 15% sodium sulfide precipitant at different ratios. Iron and niobium rather than the other elements were mainly affected by adding the precipitant. Fig. (6) shows the addition of sulfide solutions at different pH values to completely precipitate all iron from the leach liquor. In the meantime, niobium was also found to precipitate in this media where its concentration was gradually decreased till it reached only 47 ppm at pH of 9.3.

Consequently, the sulfide precipitate was washed with diluted nitric acid at (S/L) ratio of 1/10 to remove the iron, leaving niobium in the solid residue (Fig.7). The latter was washed three times with distilled water and ignited at 900°C to obtain niobium oxide as analyzed by XRD given in Fig. (8) and its purity was 85% with associated 11% Ta and 4% Si as analyzed by ESEM. On the other hand, the

filtrate separated from iron and niobium sulfide precipitate was treated with concentrated HCl. This leads to the formation of pure sulfur precipitate as a by-product detected by XRD (Fig.9) analyses.

From the previous mineralogical and upgrading studies, the non-magnetic fraction obtained concentrate of 1.5 amper containing mainly zircon with a small amount of uranothorite, uranophane, and kasolite minerals was subjected to the alkaline breakdown process using sodium hydroxide as illustrated by the following equations:

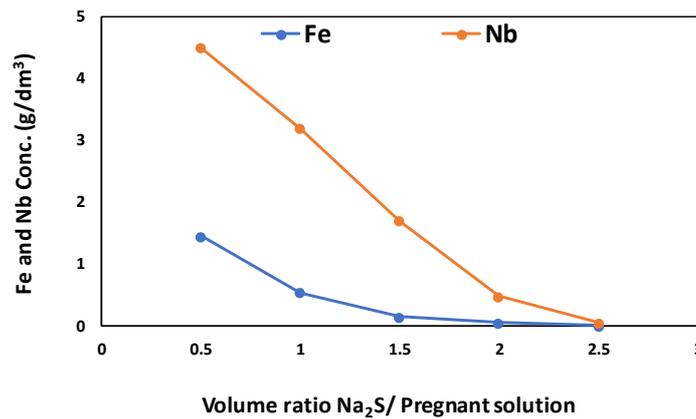


Fig. 6. Effect of volume ratio (Na₂S/ pregnant solution) upon precipitation of niobium and iron

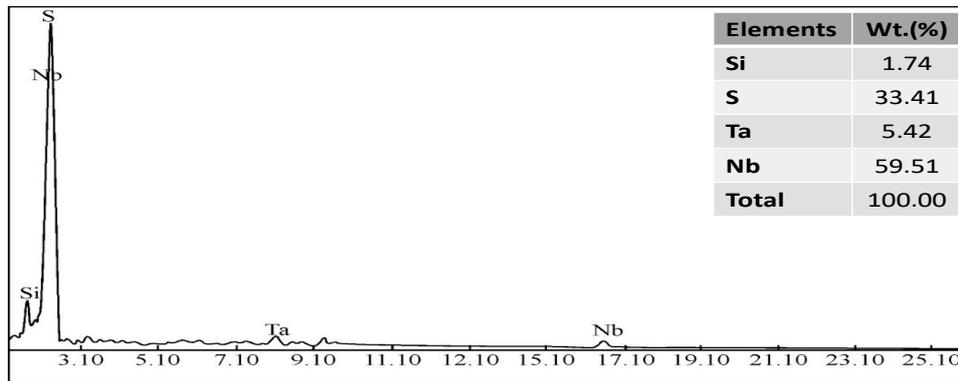


Fig. 7. EDX analysis of Niobium sulfide precipitate after iron removal

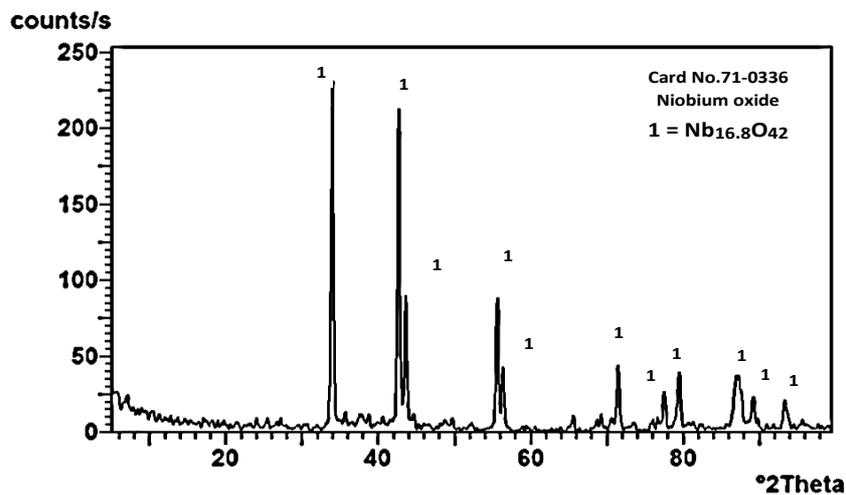


Fig. 8. XRD result of niobium oxide product

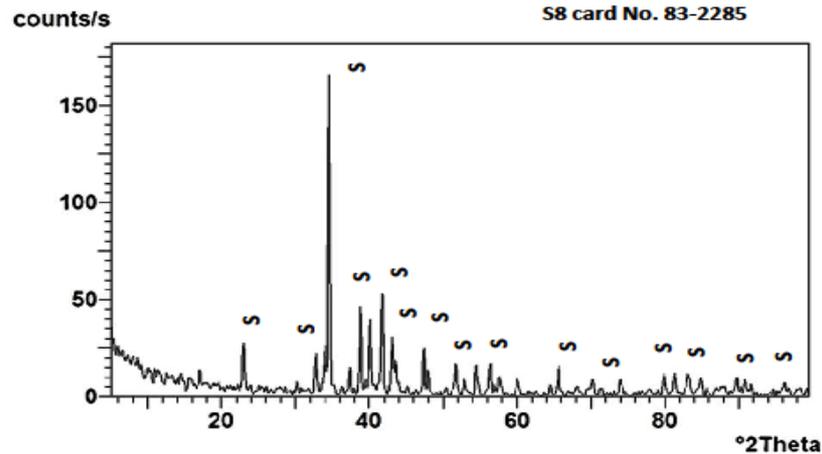
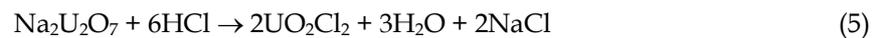
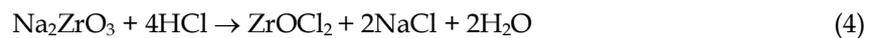


Fig. 9. XRD result of sulfur precipitate as a by-product

3.4. Recovery of zirconium and uranium from the non-magnetic concentrate

The fused matrix was then leached with water to dissolve its silica content as water-soluble sodium silicates, while both uranium and zirconium were kept insoluble. After the filtration and washing, the residue was then dissolved in 9 mol/dm³ HCl for 20 min. at 90°C (Eqs. 4 and 5), and the leaching efficiencies were then calculated. The effect of zircon concentrate /NaOH(w/w) mixed mass ratios, fusion time and fusion temperature were studied.



3.4.1. Effect of zircon concentrate /NaOH mass ratios (w/w)

The effect of zircon concentrate /NaOH (S/R) mass ratios was studied in the range between 1/1 to 1/2.5 at 550°C and 2h as the fusion temperature. The results of dissolving the fused matrix in HCl after the water removal of silica (Fig.10A) showed that, the dissolution efficiencies of both of Zr and U were improved obviously from 69.9 and 75.4% to 88.9 and 90.4%, respectively, with the decreasing S/R mass ratio from 1/1 to 1/2. However, the decreasing the mass ratio to 1/2.5 showed very a slight increase in the dissolution efficiencies for both of Zr and U. This may be attributed to the insufficient temperature for breaking down of zircon mineral (Song et al., 2020).

3.4.2. Effect of fusion temperature

This effect was studied in temperatures ranging from 550 to 750°C at S/R mass ratio of 1/2 and fusion time 2h. The results shown in Fig. (10B) emphasized that, the dissolution efficiencies of interested elements increased from 88.9 to 95.1% for Zr and from 90.4 to 95.3% for U with the increasing the fusion temperature from 550 to 650°C. However, further increase in temperature to 750°C showed a very slight change in the dissolution efficiencies of both of Zr and U.

3.4.3. Effect of fusion time

The effect of fusion time was studied in the range from 2 to 4h. The other factors were fixed at fusion temperature of 650°C, and S/R mass ratio of 1/2. The obtained data seen in Fig. (10C) showed that the dissolution efficiencies of Zr and U increased with the increasing the fusion time and reached its maximum value 97.9% for Zr and 98.5% for U after 2.5 h.

In the light of the foregoing mentioned study, the optimum conditions required for alkaline breakdown of Abu Rushied non-magnetic concentrate of 1.5 ampere were: S/R mass ratio of 1/2, fusion temperature of 650°C, and 2.5h fusion time. Under these conditions, 97.9% of Zr and 98.5% of U were dissolved using 9 mol/dm³ HCl for 20 min at 90°C. Consequently, the pregnant chloride leach solution

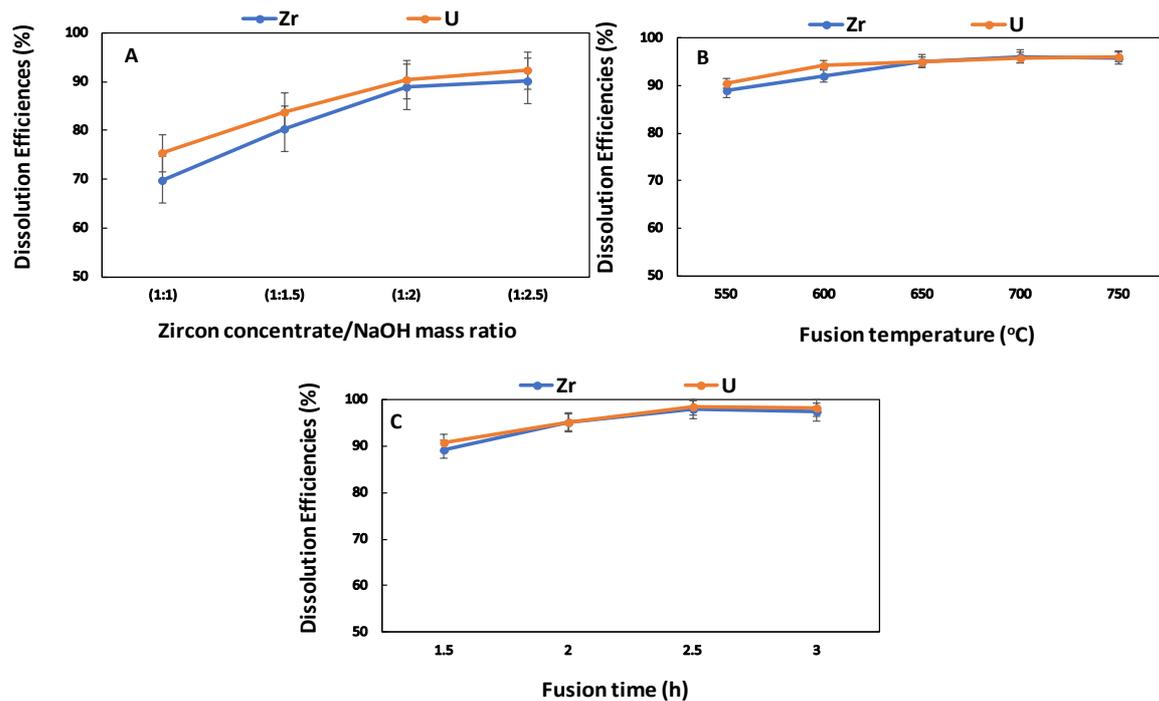


Fig. 10. Effect of zircon concentrate/NaOH mass ratio (A), fusion temperature (B) and fusion time (C) upon dissolution efficiencies of zirconium and uranium

was properly prepared upon 100 g of the concentrate sample. The total volume of the pregnant solution was 2 dm³ with the chemical composition (g/ dm³): 14.2 Zr, 58 Cl⁻, 1.29 Hf, 1.47 U, 0.119 Th, and 0.07 REE while its pH was 0.2.

3.4.4. Selective precipitation of zirconium

Zirconium was selectively precipitated from the pregnant solution containing mainly Zr and U by the treatment with a precipitant of ammonium tartarate. White precipitate of Zr- tartarate was formed while U, Th, and REE remained soluble (Henry, 1982). The parameters, such as pH, precipitation time, and the added amount of ammonium tartrate were studied to optimize the recovery of Zr.

3.4.4.1. Effect of pH of the solution

A series of precipitation experiments were carried out at pH values ranging from 0.3 to 1.5 at room temperature while the added amount of ammonium tartarate was 1g/100 cm³ of chlorine bleach liquor with 15min stirring time. The obtained data summarized in Fig. 11A indicated that the pH 1.0 represented the optimum value for recovering about 98% of Zr.

3.4.4.2. Effect of ammonium tartrate weight addition to leach solution

This effect was studied in the range of 0.3- 5g solid ammonium tartrate/ 100 cm³ of leach solution at pH of 1.0 and 15-min precipitation time. Data shown in Fig. 11B emphasized that the amount of 0.5g/100 cm³ solution was sufficient for the recovering 98.9% Zr. On the other hand, the increasing the amount of precipitant led to a decrease in the precipitation efficiency of Zr, and this may be attributed to the re-dissolution of Zr with excess ammonium tartrate.

3.4.4.3. Effect of precipitation time

A series of precipitation experiments were performed at different periods of time (5- 30 min) while the other parameters were fixed at pH of 1.0 and 0.5g ammonium tartrate per 100 cm³ leach solution. It was evident from the obtained results seen in Fig. 11C that the precipitation of Zr was almost complete

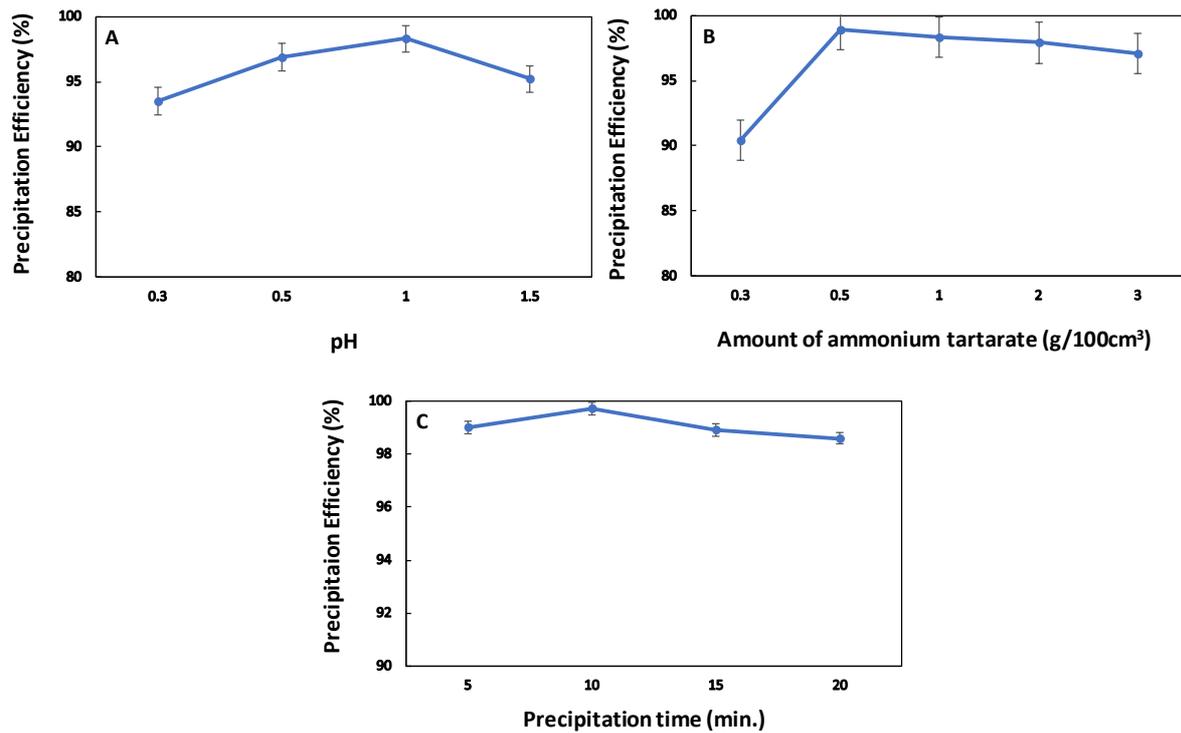


Fig. 11. Effect of pH (A), amount of ammonium tartarate (B) and precipitation time (C) upon precipitation efficiency of zirconium

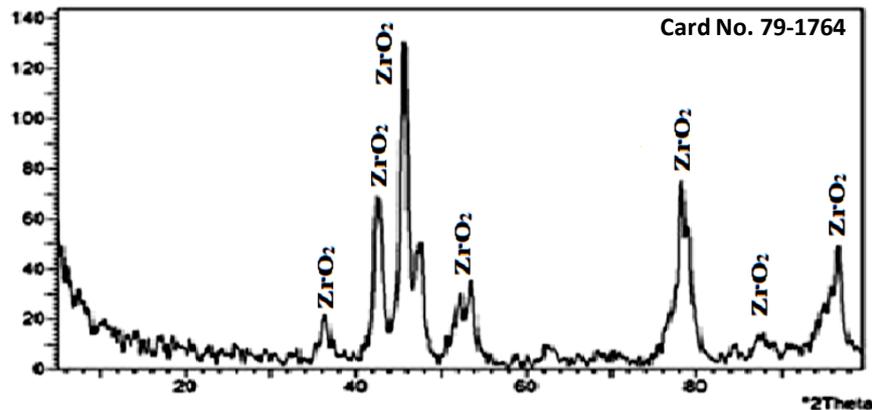
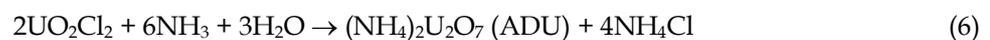


Fig. 12. XRD result for zirconium oxide product

From the above study, almost complete precipitation of Zr was carried out at the following optimum conditions: pH 1.0, precipitation time 10 min, 0.5g ammonium tartarate/ 100 cm³ pregnant solution at room temperature. Finally, Zr- tartarate precipitate was converted to ZrO₂ by conventional means such as roasting, then it was identified using the XRD technique (Fig.12), the chemical analysis of prepared ZrO₂ emphasized the purity of Zr was 90.3% associated with 5 % of Hf and 1.9% of Si.

3.4.5. Direct precipitation of uranium

The filtrate solution free from Zr was subjected to the U recovery via its precipitation as ammonium diuranate (ADU) using 25% of aqueous ammonia solution at room temperature and pH of 7.5 with stirring time for 2h (Eq. 6). The ADU precipitate was filtered, washed, dried, and analyzed by EDX analysis (Fig. 13).



On the other hand, the chemical analysis of the prepared yellow cake proved its purity about 98% with associated impurities of Fe, Si, Ca, and K. It is important to mention herein that both Th and REE did not precipitate and were found in the filtrate solution due to their lower concentrations. Therefore, a further recovery procedure will be done for their recovery using ion exchange resin.

Finally, a technical flowsheet shown in Fig. 14 was proposed on the assumption of both physical and chemical treating of the studied Abu Rushied cataclastic rock.

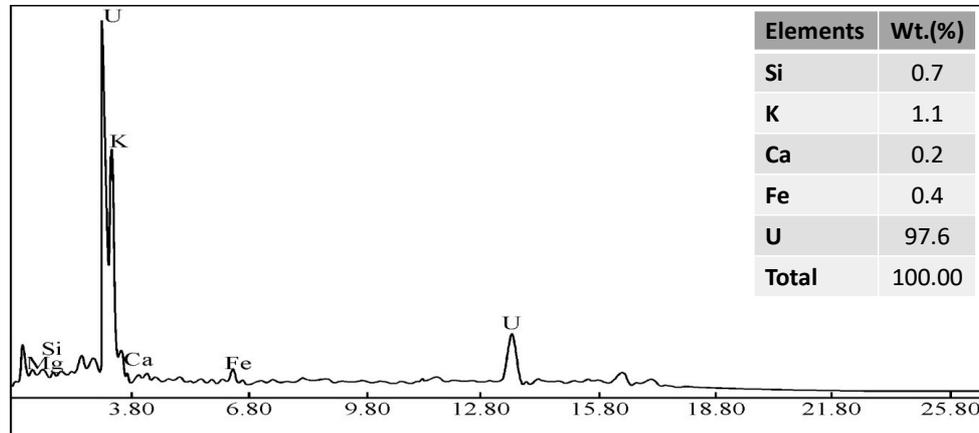


Fig. 13. EDX analysis of ammonium diuranate product

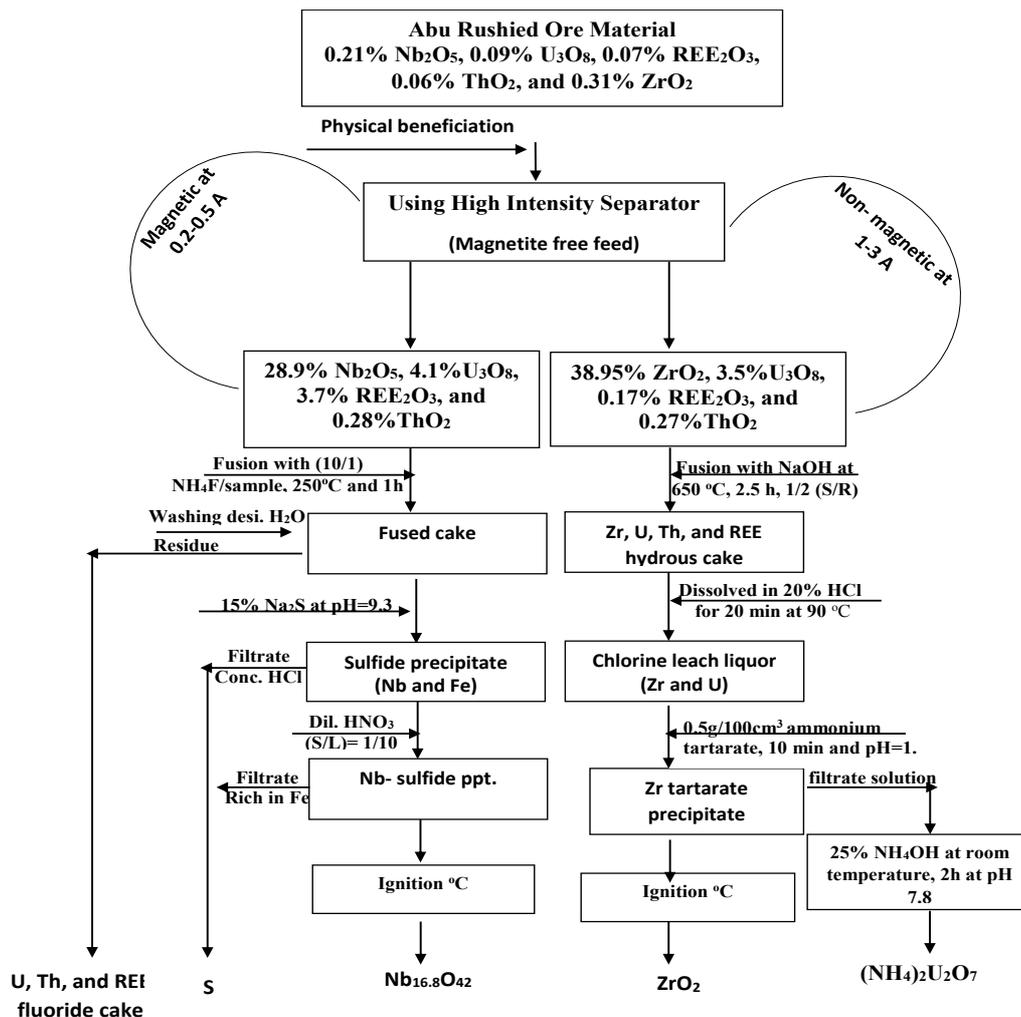


Fig. 14. The working flowsheet represented both physical and chemical treating of the studied Abu Rushied cataclastic rocks

4. Conclusions

Multiple-oxide minerals, namely columbite, ferrocolumbite, ishikawite, apatite, xenotime, uranothorite, and zircon, were identified in the studied ore material and were then concentrated using a gravity separation method (shaking table) followed by the magnetic separation. The heavy table concentrated mainly contained about 73% of valuable mineral with a recovery efficiency 81.6%. Nb–Ta minerals were concentrated mainly at 0.2- 0.5 magnetic fraction with a significant amount of radioactive U-Th minerals (uranophane, Uranothorite, and kasolite). While, 95% of total zircon mineral was concentrated at non-magnetic fraction at 1.5 amperes. Zr and U were recovered from the non-magnetic fraction at the optimum conditions of Zr concentrate /NaOH mass ratio 1/2, fusion temperature of 650 °C, and 2.5 h fusion time. 97.9% of Zr and 98.5% of U were dissolved using 9mol/ dm³ HCl for 20 min at 90 °C whereas Nb was recovered from the magnetic fraction by NH₄F roasting at 250°C. Finally, proper analyses of the obtained products of the Nb_{16.8}O₄₂, ZrO₂, and (NH₄)₂U₂O₇ as well as elemental S have revealed the potential of applying the mentioned procedures that has been summarized in the suggested two flow-sheets.

References

- ABDEL AAL, M. M., ABDEL SAMAD, A. A., 2019. *Comparative chemical studies between fixed bed and batch dynamic ion exchange techniques for extraction of uranium*. Arab J. Nucl. Sci. Appl. 52, 187-200.
- ABDELLAH, W. M., 2020. *Preparation of pure uranium, thorium and yttrium oxides from El-Garra El-Hamra sulfate leach liquor*. Radiochemistry 62, 347-358.
- ABDEL WAHAB, G. M., ABDELLAH, W. M., YOUSIF, A.M. MUBARK, A. E., 2019. *Preparation of Pure Nb₂O₅ from Gabal El-Faliq Pegmatite, South Eastern Desert, Egypt*. Mining, Metallurgy & Exploration. doi: 10.1007/s42461-019-00136-1
- ABDOUL-RACHID, C.Y., 2018. *Comparative Study of Solvent Extraction of Uranium with Alamine 336 and Aliquat 336: Application to the Uranium-Bearing Solutions of Niger Republic*. European Scientific J. 14, 1857– 7881.
- ABU ELATTA, S. A., ABDELLAH, W.M. ABU KHOZIEM, H. A., 2018. *Mineralogy, geochemistry and leaching characteristics of the high-grade Th-U-Y zone of altered syenite at El Garra El Hamra, Southwestern Desert, Egypt*. Minerals & Metallurgical Processing 53, 230-243.
- ALI, M. A., ABD EL- RAZEK, Y. A., 2020. *Study of the Geologic Features and Uranium Content of the Cataclastic Rocks at Wadi Sikait, South Eastern Desert, Egypt by SSNTDs*. J. Rad. Nucl. Appl., 5, 2, 11-118.
- ALI, M. A., LENTZ, D. R. HALL, D.C., 2011. *Mineralogy and geochemistry of Nb-, Ta-, Sn-, U-, Th-, and Zr-bearing granitic rocks from Abu Rusheid shear zones, South Eastern Desert, Egypt*. Chin. J. Geochem. 30, 226–247.
- AMALIA, Y.D., NUGRAHA, E. P., 2016. *Processing zirconia through zircon sand smelting with NaOH as a flux*. Indonesian mining journal 19, 39 – 49.
- DANKO, B., DYBCZYŃSKI, R., SAMCZYŃSK, Z., GAJDA, D., HERDZIK-KONIECKO, I., ZAKRZEWSKA-KOŁTUNIEWICZ, G., CHAJDUK, E., KULISA, K., 2017. *Ion exchange investigation for recovery of uranium from acidic pregnant leach solutions*. NUKLEONIKA 62, 213–221.
- AVELAR, E., ALVARENGA, C., RESENDE, G., MORAIS, C., MANSUR, M., 2017. *Modeling of the solvent extraction equilibrium of Uranium (VI) Sulfate with Alamine 336*. Brazilian J. Chem. Engin. 34, 355–362.
- BHOWMIK, K.A., SHANMUGAVELU, P., DHVAMURI, D., AGRAWAL, A., 2009. *Single stage purification of U refining*. World Intellectual Property Organization, International Bureau, International Publication No.Wo.2009/013759 A (PCT).
- EL-GEMMIZI, M.A., 1984. *On the occurrence and genesis of mud zircon in the radioactive psammitic gneisses of Wadi Nugrus, Eastern Desert, Egypt*. J. Univ. Kawait (Sci.). 2, 285–294.
- EL HUSSAINI, O., MAHDY, M., 2008. *Extraction of Niobium and Tantalum from Nitrate and Sulfate Media by Using MIBK*. Mineral Processing and Extractive Metallurgy Review 22, 633-650.
- FAWZY, M. M., KAMAR M. S. SALEH, G. M., 2021. *Physical processing for polymetallic mineralization of Abu Rusheid mylonitic rocks, South Eastern Desert of Egypt*. International Review of Applied Sciences and Engineering. 12, 2, 134–146 DOI: 10.1556/1848.2021.00200.
- FÖRSTER, H. J., 1999. *The chemical composition of uraninite in variscan granites Of the Erzgebirge, Germany*. Mineral. Mag. 63, 239–252.
- JORDENS, A., MARION, C., KUZMINA, O., WATERS, K.E., 2014. *Physicochemical aspects of allanite flotation*. Rare Earths 32, 476–486

- HANSON, S.L., SIMONS, W.B., FALSTER, A.U., FOORD, E. E., LICHTER, F. E., 1999. *Proposed nomenclature for samarskite-group minerals: new data on ishikawaite and calciosamarskite*. Mineralogical Magazine 63, 27–63.
- HAN, G., WEN, S, WANG, H., FENG, Q., 2021. *Surface sulfidization mechanism of cuprite and its response to xanthate adsorption and flotation performance*. Miner. Eng. 169, 106982.
- HENRY, H.G., 1982. *Separation of zirconium and uranium*. USA patent no, 4,330-509.
- IBRAHIM, I., SALEH, G.M., AMER, T., MAHMOUD, F., ABU EL HASSAN, A., ALL, M.A., AZAB, M.S., RASHED, M., KHALEAL, F., MAHMOUD, M., 2004. *Uranium and Associated Rare Metals Potentialities of Abu Rusheid Brecciated Shear Zone II, South Eastern Desert, Egypt*. Internal Report, Nuclear Materials Authority, Cairo, Egypt.
- KABANGU, M. J. CROUSE, P. L., 2012. *Separation of niobium and tantalum from Mozambican tantalite by ammonium bifluoride digestion and octanol solvent extraction*. Hydrometallurgy 129-130, 151–155.
- KIM, J. S., CHUNG, K.W., LEE, H.I., YOON, H.-S. KUMAR, J.R., 2014. *Leaching behavior of uranium and vanadium using strong sulfuric acid from Korean black shale ore*. J. Radioanal. Nucl. Chem. 299, 81–87.
- KUBOVA, J., POLAKOVICOVA, J., STRESKO, V., MEDVED, J., 1993. *Determination of Niobium and Tantalum in Geological Materials by Atomic Emission Spectroscopy with Inductively Coupled Plasma*. Chem. Papers 47, 225-229.
- LÖTTER, S.J., PURCELL, W., NEL, J.T., SNYDERS, E., 2012. *Alternative dissolution of zircon samples and simultaneous analysis of major and trace components*. J. S. Afr. Inst. Min. Metall. 112, 69-76.
- MARCZENKO, Z., 2000. *Spectrophotometric determination of elements*. John Wiley and Sons, Harwood, New York.
- MATHEW, K. J., BURGER, S., OGT, S. V., MASON, P. M., NARAYANAN, U. I., 2009. *Uranium assay determination using Davies and Gray titration*. Processing the Eighth International Conference on Methods and Applications of Radioanalytical Chemistry (Marc Viii) Kaailua-Kona, Hawaii, P.5.
- NEL, J.T., DU PLESSIS, W., NHLABATHI, T.N., PRETORIUS, C.J., JANSEN, A.A., CROUSE, P.L., 2011. *Reaction kinetics of the microwave enhanced digestion of zircon with ammonium acid fluoride*. Journal of Fluorine Chemistry 132, 258–262.
- NETE, M., PURCELL, W., SNYDERS, E. NEL, J., 2010. *Alternative dissolution methods for analysis of niobium containing samples*. S. Afr. J. Chem. 63,130–134.
- NGUYEN, T. H. LEE, M-S., 2019. *A Review on the Separation of Niobium and Tantalum by Solvent Extraction*. Mineral Processing and Extractive Metallurgy Review 40, 265-277.
- PURCEL, L.W., POTGIETE, R.H., NETE, M., MNCULWANE, H., 2018. *Possible methodology for niobium, tantalum and scandium separation in ferrocolumbite*. Miner. Eng. 119, 57–66.
- RASLAN, M.F., 2008. *Occurrence of Ishikawaite (Uranium-rich Samarskite) in the Mineralized Abu Rushied Gneiss, Southeastern Desert, Egypt*. International Geology Review 50, 1132–1140.
- RASLAN, F.M., FAWZY, M.M., ABU KHOZIEM, H. A., 2017. *Mineralogy of mineralized pegmatite of Ras Mohamed granite, Southern Sinai, Egypt*. Inter. J. of Geology, Earth & Environmental Sciences 7, 65-80.
- RODRIGUEZ, M., QUIROGA, O., DEL, M., RUIZ, C., 2007. *Kinetic study of ferrocolumbite dissolution in hydrofluoric acid medium*. Hydrometallurgy 85, 87–94.
- RODRIGUEZ, M.H., ROSALES, G.D., PINNA, E.G., SUAREZ, D.S., 2015. *Extraction of niobium and tantalum from ferrocolumbite by hydrofluoric acid pressure leaching*. Hydrometallurgy 156, 17–20.
- SABET, A.H., TSOGOEV, V.B., BORDONOSOV, V.P., SHOBLOVSKY, R.G., KOSSA, M., 1976. *On the geologic structures, laws of localization and prospects of Abu Rusheid rare metals deposit*. Annl. Geol. Surv., Egypt 7, 181–197.
- SADIGZADEH, A., CHEHRENAMA, S., SHOKRI, H., 2009. *Solvent extraction of zirconium from nitric-hydrochloric acid solutions using TBP*. Journal of Theoretical and Applied Physics 3, 20-26.
- SENDA, R., KIMURA, J., CHANG, Q., 2014. *Evaluation of a rapid, effective sample digestion method for trace element analysis of granitoid samples containing acid-resistant minerals: Alkali fusion after acid digestion*. Geochemical Journal 481, 99 - 103.
- SETYADJI, M., SUSIANTINI, E., 2020. *Leaching kinetics of Sodium Zirconate in Hydrochloric Acid based on shrinking core models*. IOP Conf. Series: Journal of Physics: Conf. Series 1436, 1-12.
- SIMMONS, W.B., HANSON, S.L., FALSTER, A.U., 2006. *Samarskite-(Yb) A new species of the samarskite group from the Little Pasty Jefferson County, Colorado*. Can. Mineral. 44, 1119–1125.
- SINGH, H., GUPTA, C.K., 2008. *Solvent Extraction in Production and Processing of Uranium and Thorium*, Mineral processing and Extractive Metallurgy Review 21, 307-349.
- SONG, J., FAN, J-F., LIU, J-C., LIU, R., QU, J-K., QI, T., 2020. *A two-step zircon decomposition method to produce zirconium oxychloride: alkali fusion and water leaching*. Rare metals 39, 448–454.

- URANIUM. 2018. *Resources, Production and Demand*. Nuclear Energy Agency Organization (NEA). 7413, for Economic Co-Operation and Development.
- XU, L., XIA, Y., VAN SANDWIJK A., XU, Q., YANG, Y., 2014. *Separation of Zirconium and Hafnium: A Review*. The Chinese Society for Metals (CSM) and The Minerals. Metals & Materials Society (TMS), 451-457.
- XU, L., XIAO, Y., VAN SANDWIJK, A., XU, Q., YANG, Y., 2015. *Production of nuclear grade zirconium: A review*. Journal of Nuclear Materials 466, 21-28.
- XU, L., YANG, H., LIU, Y., ZHOU, Y., 2019. *Uranium leaching using citric acid and oxalic acid*. J. Radioanal. Nucl. Chem. 321, 815-822.
- XIAOHUI, W., ZHENG, S., XU, H., ZHANG, Y., 2009. *Leaching of niobium and tantalum from a low-grade ore using a KOH roast-water leach system*. Hydrometallurgy 98, 219-223.
- ZHANG, Q. , WEN S., FENG, Q., LIU, J., 2021 (a). *Surface modification of azurite with lead ions and its effects on the adsorption of sulfide ions and xanthate species*. Appl. Surf. Sci. 543, 148795.
- ZHANG, Q. , WEN S., FENG, Q., LIU, J., 2021 (b). *Activation mechanism of lead ions in the flotation of sulfidized azurite with xanthate as collector*. Miner. Eng. 163, 106809.
- ZHU, Z., PRANOLO, Y., CHENG, C.Y., 2013. *Uranium Solvent Extraction and Separation From Vanadium in Alkaline Solutions*. Separation Science and Technology 48, 1402-1408.
- ZOLFONOUN, E., BOVEIRI, A., TAGHIZADEH, M., AHMADI, S., 2010. *Selective and direct sorption of zirconium from acidic leach liquor of zircon concentrate by rice bran*. Minerals Engineering 23, 755-756.