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Liquid – liquid extraction of uranium from sulfate leach liquor of Ramlet Hemeyir, ferruginous sandstone ore material, Southwestern, Sinai, Egypt

N.A.Abdelfattah[1]*, S.M.Mahmoud[1], H.M.Salman[2]

[1]Nuclear Materials Authority, P.O. Box: 530 El Maadi, Cairo, (EGYPT)

[2]Faculty of Science, South Valley University, Qena, (EGYPT)

ABSTRACT

The Ferruginous sandstone ore was obtained from Ramlet Hemeyir area, Southwestern Sinai, Egypt. It was found to contain 0.26 % U and 10 % REE (rare earth elements). A representative sample has been subjected to acid agitation leaching using H_2SO_4 by which 89% U and 93% REE were released by mixing the sample with concentrated H_2SO_4 at solid/liquid (S/L) ratio of 1/2 for 5h at a temperature range (250 - 300^{o}C). After precipitation of rare earth elements and lead. Uranium was separated from the filtrate by liquid – liquid extraction using a synergistic system of D2EHPA/TBP in kerosene as a diluent under the following conditions: a solvent concentration of 0.5 M at pH 1, an A/O ratio of 1:1 and a contact time 10 min. The loaded organic solvent was stripped with 10% sodium carbonate at ratio 3:1. Then NaOH was added to the stripped solution to precipitate U-cake at pH 12.0.

KEYWORDS

Uranium;
Rare Earth elements;
Separation;
Precipitation.

INTRODUCTION

The studied sample of Ramlet Hemeyir area consists of white to pale brownish pebbly and ferruginous sandstones from the topmost of El Adedia Formation. El Adedia Formation in the study area is up to 72 m thick. The uppermost beds of this formation are highly ferruginous and usually stained by manganese and iron oxyhydroxides[8].

Depending upon the nature of the pregnant solution and the element concentration several techniques could be used to recover uranium and REE from its ores by different leaching processes followed by some separation techniques among which are direct precipitation, ion-exchange and solvent extraction.

Several methods have been studied that industrially applied for the breakdown of the most common rare earth minerals (monazite, bastnasite and xenotime). The economic treatment upon high grade concentrates of these minerals should be achieved by physical beneficiation methods such as: (gravimetric, magnetic, flotation and electrostatic). Extraction of rare earths from xenotime can be achieved using sulfuric acid digestion at temperature range of 250-300 ^{o}C for 1-2 h followed by water leaching; such leaching is uneconomic for concentrates containing less than 10% xenotime[9].

The choice of an economic suitable technique depends upon many factors such as the element's concentration in the leach liquors, the amount and the concentration of the co-dissolved impurities as well as the purity of desired final product. For example, solvent extraction is preferred for a uranium concentration greater than 0.9 g U_3O_8/L while ion-exchange is the best choice for a concentration below 0.35 g U_3O_8/L[2]. whereas direct precipitation requires a uranium concentration much higher than that required for solvent extraction.

The present work is concerned with studying the recovery of REEs and lead followed by recovery of U by using solvent extraction using a synergistic system of D2EHPA/ TBP in kerosene as a diluent under the following conditions: a solvent concentration of 0.5 M at pH 1, an A/O ratio of 1:1 and a contact time 10 min. The loaded organic solvent was stripped with 10% sodium carbonate at ratio 3:1. Then NaOH was added to the stripped solution to precipitate U-cake at pH 12.0.

EXPERIMENTAL WORK

Mineralogical identification

To investigate the mineralogical composition of ferruginous sandstone ore; heavy liquid separation was performed upon a representative bulk sample. About 1 Kg of the ore sample was washed with excess amount of tap water to get rid of the slimes. The slimes -free sample was dried, properly sieved by a set of sieves ranging from 500 μm down to 100μm (35 to 140 mesh grain size) and the obtained size fractions were subjected to heavy liquid separation using bromoform (sp.gr. 2.84). The obtained heavy fractions were isodynamically separated at (0.2, 0.5, 1.0 and 1.5 Amp.) using Frantz isodynamic separator where the separated fractions were picked under the binocular microscope.

On the other hand, identification of the mineralogical composition of the ore sample and analysis of the prepared products were detected by the X-ray diffraction (XRD) model Phillips X- ray (PW3710) with a generator (PW1830), and Cu target tube (PW 223/20) and it was operated at 40 Kv and 30 mA.

Methods of analysis

A number of analytical methods have been used during the present work. Beside the analysis of leaching and separation experiments, the host rock was first analyzed for its major and some trace elements' contents.

(a) Major and trace elements analyses

The major and minor oxides were analyzed as reported by[7] for rapid silicate analytical procedure. This procedure includes the preparation of two main solutions; namely an alkaline solution for SiO_2 determination and an acid solution for determination of other oxides like CaO, MgO, Al_2O_3, TiO_2, P_2O_5, total iron oxides, etc.

Uranium was analyzed by an oxidimetric titration method against ammonium metavanadate[3].

Concerning the total REE, a UV-VIS spectrphotometer (Shimadzu UV-160) was used for its quantitative analysis using 0.015 % arsenazo (III) at 654 nm taking Y as reference[5].

The economic metal values namely; Zn, Ni, Mn, Pb and Cu were measured using a Unicam atomic absorption spectrophotometer model-969 (AAS) flame type at λ 213.9, 232, 279.5, 217 and 324.8 nm respectively.

The produced $Na_2U_2O_7$ concentrate after purification was examined under X-ray microanalyzer (Module Oxford 6587 INCA x-sight) attached to JEOL JSM-5500 LV scanning electron microscope at 20KV after gold coating using SPI-Module sputter coater.

Procedures for metal values separation

The hydrometallurgical processing of the ore material is represented by two main stages, leaching then separation of the studied metal values.

(a) Preparation of sulfate leach liquor

Acid digestion was performed by mixing different concentrations of H_2SO_4 with 100g ore sample and agitating at various S/L ratio, temperature and agitation time. The optimum conditions were applied to prepare a pregnant leach liquor of about 1.5liters.

(b) Separation procedures

(A) Separation of total REE

The prepared leach liquor was subjected to the precipitation of the total REE as their oxalates. For this purpose, different experiments were carried out to determine the optimum oxalic acid concentration, as well as the pH and the temperature required for achieving the highest precipitation efficiency.

(B) Separation of lead

The sulfate leach liquor almost free from REE was then subjected to Pb precipitation; a solution of 1%Na2S at pH 0.8 was added in order to obtain selective precipitation of Pb.

(C) Separation of uranium

The leach liquor free from lead was filtered, then underwent oxidation step by addition of drops of H2O2. This acidic solution was adjusted to have pH of 1.0 by using ammonia hydroxide. The extraction process of U from the sulfate liquor was performed using diethyl hexyl phosphoric acid D2EHPA (sp. gr. = 0.98). Tributylphosphate (TBP) (sp.gr.0.979 g/ml) was used as modifier with similar concentration as the solvent. A commercial grade of kerosene was used as a diluent. The working conditions for the extraction process of U from sulfate / D2EHPA system are given in TABLE 1. The stripping of U was done by 10% sodium carbonate and its precipitation was done by sodium hydroxide.

RESULTS AND DISCUSSIONS

Mineralogical composition

The binuclear microscope investigation revealed that most of magnetic fractions are highly mineralized where xenotime which was the dominant mineral and had a wide distribution in 0.5 Amp., 1.0 Amp., and 1.5 Amp. magnetic fractions. It represented 32-40 % of these magnetic fractions while zircon was dominant in 1.5 Amp. non-magnetic fraction. Iron oxides (hematite, goethite and rarely magnetite) separated at 0.2 Amp. magnetic fraction were widely dispersed in these heavy magnetic fractions. The obtained minerals as analyzed by XRD are shown in Figure 2. These are kaolinite $Al_2Si_2O_5(OH)_4$, quartz (SiO_2), goethite FeO(OH), hematite Fe_2O_3, magnetite Fe_3O_4 and xenotime YPO_4.

Chemical analysis

The chemical analysis is given in TABLE 1 for

TABLE 1 : The working conditions for the extraction process of U from sulfate D2EHPA/TBP system

Contact time (min.)	pH	Solvent conc., (M)	A/O ratio
1, 5, 10, 15 & 20	1	0.2	1:1
10	0.5, 1, 1.5 & 2	0.2	1:1
10	1	0.2, 0.5, 1 &1.5	1:1
10	1	0.5	1:1, 1:2, 1:3, 2:1, 3:1 & 4:1

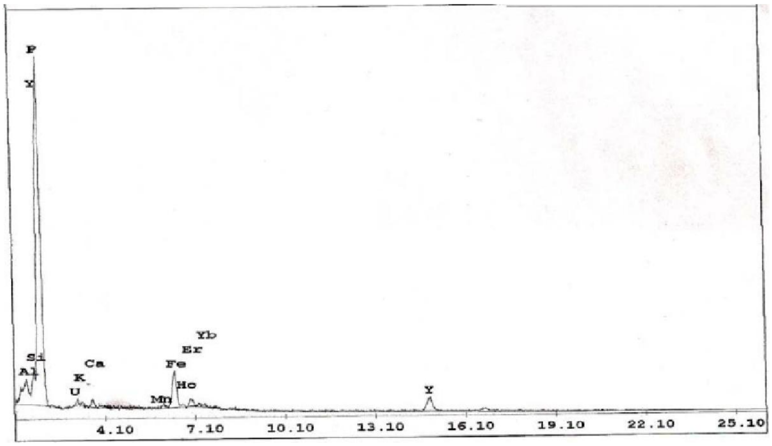


Figure 1 : The mineralogical composition as analyzed by EDAX

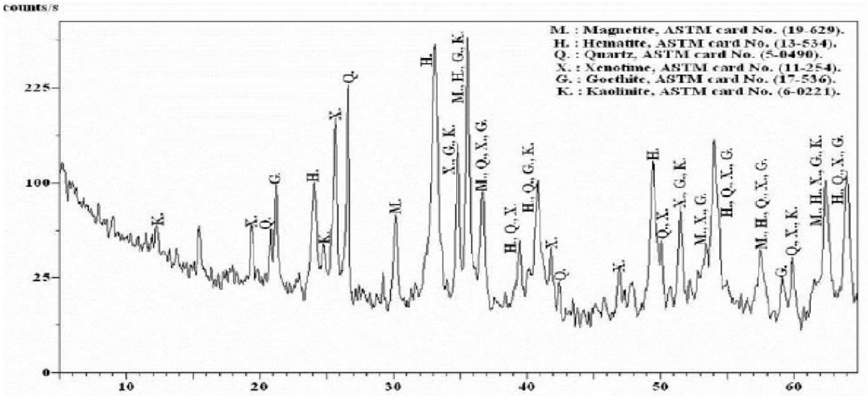


Figure 2 : The mineralogical composition as analyzed by XRD

TABLE 2 : Chemical composition of the ferruginous sandstone ore material

Major Oxides	Conc., (%)	Trace Elements	Conc. (ppm)
SiO_2	40.0	U	2600
TiO_2	0.33	Ni	138
Al_2O_3	3.40	Pb	900
Fe_2O_3	23.30	B	200
CaO	1.20	Cu	165
MgO	3.20	V	150
MnO	1.80	Zr	180
Na_2O	0.90		
K_2O	0.70		
P_2O_5	6.30		
RE_2O_3*	12.60		
L.O.I**	4.06		
Total	97.79		

RE_2O_3*: representing Y_2O_3[5]; L.O.I: loss of ignition**

major oxides and some trace elements. The chemical composition reflects the previously mentioned mineralogical composition.

Preparation of sulfate leach liquor

Sulfuric acid digestion was done upon a representative ferruginous sandstone sample under the following optimum conditions: mixing 100g ore sample with concentrated H_2SO_4 at 1/2 S/L ratio for 5h at temperature range of 250-300 °C. A pregnant solution of 1.5liters was prepared by adding the washings to the original filtrate. The pH of the produced sulfate leach liquor was 0.2. This liquor was analyzed mainly for its content of rare earth, iron and uranium, TABLE 2.

Separation of REE by direct precipitation

The prepared leach liquor was subjected to selective precipitation for the total REE by means of oxalic acid. This is due to the fact that, the REE form stable insoluble oxalates and thus can be used for their separation[4].

$$2RE^{3+} + 3H_2C_2O_4 \longrightarrow RE_2(C_2O_4)_3\ (solid) + 6H^+$$

The obtained REE-oxalate was filtered and washed properly with distilled water to get rid of any impurities. After dryness, the precipitate was ignited at 850°C for 2h. The latter was subjected to XRD analysis to identify its content. It is clearly evident that the obtained rare earth oxide concentrate is mostly composed of heavy rare earth oxides mainly yttrium oxide and terbium oxide Figure 3. The purity was found to be 88% as analyzed by UV-VIS spectrophotometer, while the total recovery of REE from the ore was found to be 75.7%.

Separation of lead

In the present work, Pb was almost completely precipitated at pH 0.8 from the filtrate obtained after REE precipitation by drop wise addition of a 1% Na2S solution to the latter with continuous stirring at room temperature; viz,

TABLE 3 : Analysis of the ferruginous sandstone sulfate leach liquor

Metal ion	Conc. (gm/l)
REE	6.20
U	0.154
Fe	10.60
Ca	0.384
Pb	0.05

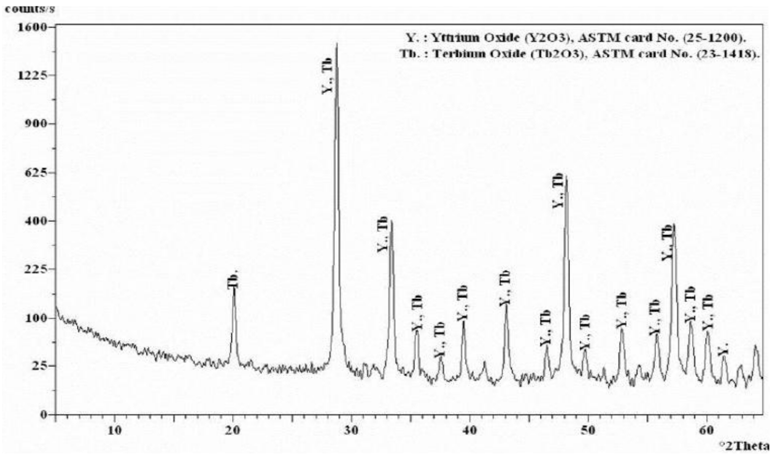


Figure 3 : XRD analysis of the produced RE_2O_3 concentrate

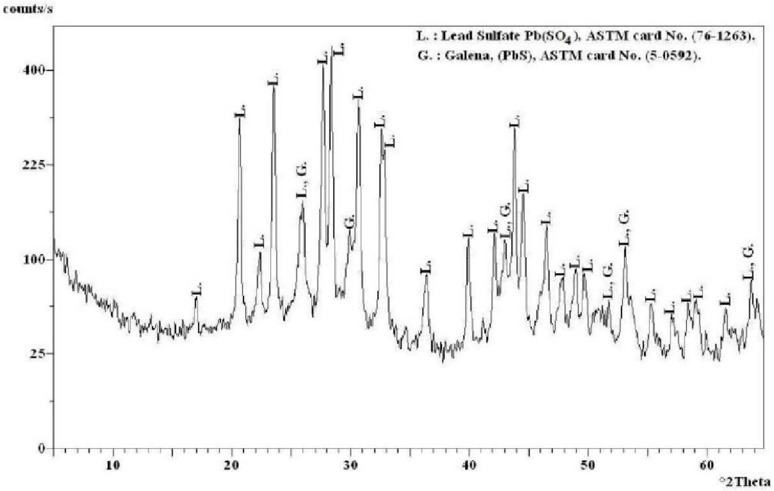


Figure 4 : XRD analysis of the PbS precipitate

$PbSO_4 + Na_2S \rightarrow PbS\downarrow + Na_2SO_4$

According to Abdel Wahab, (2008) the precipitation of lead sulfide can be better realized with a high recovery of the metal ion in a lower retention time and at low pH values as compared to the metal hydroxide. After filtration, the precipitate was properly washed several times and identified by means of XRD analysis Figure 4. It was found that a mixture of lead sulfate and lead sulfide were obtained, where 100% precipitation efficiency was achieved as determined by AAS analysis.

Separation of uranium using D2EHPA/TBP

One of the main concern of this work is to recover the U content from the ferruginous sandstone sample. The filtrate free of lead containing 10.38g/L Fe and 0.15g/L U beside other contaminants was subjected to liquid – liquid extraction. For this purpose, synergistic system of D2EHPA/TBP in kerosene as diluents was used. It is worth mentioning that to prevent the third phase formation of alkaline stripping of U[6], tributylphosphate (TBP) was used as modifier. It was mixed with the same volume (1:1) and concentration (0.5M) as the solvent D2EHPA. The back extraction of the loaded solvent was done by stripping with Na2CO3 then precipitation with NaOH.

Extraction using D2EHPA/TBP

The different relevant extraction factors were studied in detail to determine their optimum values for loading U. These include: contact time, pH, solvent concentration and A/O ratio.

(a) Effect of contact time

The sulfate leach liquor of pH 1.0 was contacted with equal volume of the solvent D2EHPA/TBP of 0.2M concentration. The contact time was varied in the range of 1-20 minutes. The obtained data were given in

TABLE 4 : Effect of contact time upon the extraction efficiencies of U and Fe by D2EHPA/TBP of 0.2M and the feed solution of pH 1.0 at O/A of 1:1

Time, min	Extraction Efficiencies, %	
	U	Fe
1	40.2	53.5
5	67.5	72.2
10	81.2	88.0
15	82.3	91.0
20	83.0	92.0

TABLE 5 : Effect of pH of the sulfate feed solution upon U and Fe extraction efficiencies by D2EHPA/TBP of 0.2 M, an O/A ratio of 1:1 and a contact time 10 min

pH	Extraction Efficiencies,%	
	U	Fe
0.5	69.0	84.0
1.0	81.2	88.0
1.5	77.4	90.0
20	73.0	91.0

TABLE 4. The extraction of both U and Fe increased by increasing the contact time.

(b) Effect of pH

The effect of pH of the sulfate leach liquor upon the extraction efficiencies of U and Fe was studied in the range of 0.5 to 2.0 at fixed conditions of a solvent concentration of 0.2 M and an O/A ratio of 1:1 and a contact time 10 min. From the obtained data given in TABLE 5, it is clearly evident that, the extraction efficiency of U increased from 69 to 81.2% by increasing pH from 0.5 to 1. Further increasing in pH 1.5 led to decrease in the extraction efficiency of U to 77.4%. On the other hand, the extraction efficiency of Fe increased as the pH of the sulfate leach liquor increase.

TABLE 6 : Effect of solvent concentration upon U and Fe extraction efficiencies by D2EHPA/TBP at pH 1, an O/A ratio of 1:1 and contact time 10 min

solvent conc., M	Extraction Efficiencies,%	
	U	Fe
0.2	81.0	88.0
0.5	89.5	92.0
1.0	91.0	94.0
1.5	93.0	95.0

TABLE 7 : Effect of O/A ratio upon U and Fe extraction efficiencies by D2EHPA using a solvent concentration of 0.5 M, pH 1, and a contact time 10 min

O/A ratio	Extraction Efficiencies,%	
	U	Fe
1/1	89.0	92.0
1/2	90.0	94.0
1/3	92.0	95.0
2/1	76.0	90.5
3/1	68.0	91.0
4/1	59.3	92.0

(c) Effect of solvent concentration

To study the effect of the solvent molarities ranging between 0.2 to 1.5 M, four equilibrium experiments were performed at fixed conditions of pH 1, an A/O ratio of 1:1 and a contact time 10 min. The obtained data are summarized in TABLE 6. It is clear that as the solvent concentration increases, the extraction efficiencies of both U and Fe are increased (see TABLE 32). Thus, at a solvent concentration of 1.5 M in presence of TBP 1.5M U and Fe extraction efficiencies attained 93.0 and 95.0% respectively.

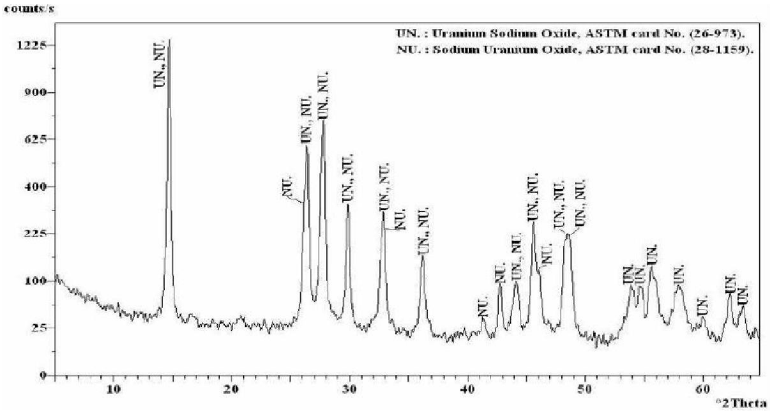


Figure 5 : XRD analysis of the U cake

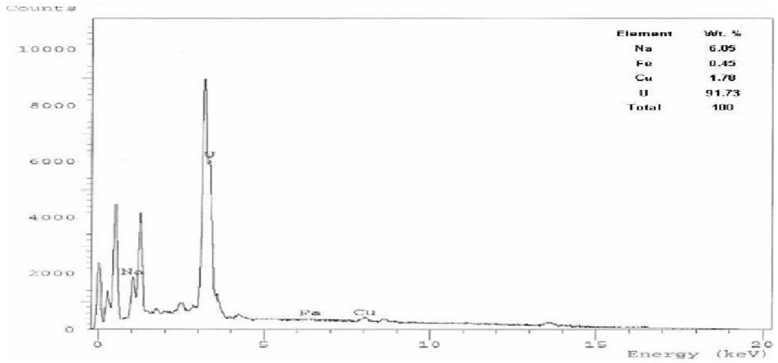


Figure 6: EDAX cake analysis of the U cake

(d) Effect of O/A ratio

The effect of O/A phase ratios upon the extraction efficiencies of U and Fe was studied in the range of 1/3 to 4/1 at fixed conditions of a solvent concentration of 0.5 M, pH 1, and a contact time 10 min. The obtained data are summarized in TABLE 7.

Results of U stripping and precipitation

Uranium was stripped by sodium carbonate as given by the equation (79).

$$UO_2R_4H_2 + 3Na_2CO_3 \rightarrow 2NaR_2H + Na_4UO_2(CO_3)_3$$

The loaded organic solvent was stripped with 10% sodium carbonate in the ratio 3:1. About 96% of uranium was stripped. Sodium hydroxide was used for precipitation as the following equation:

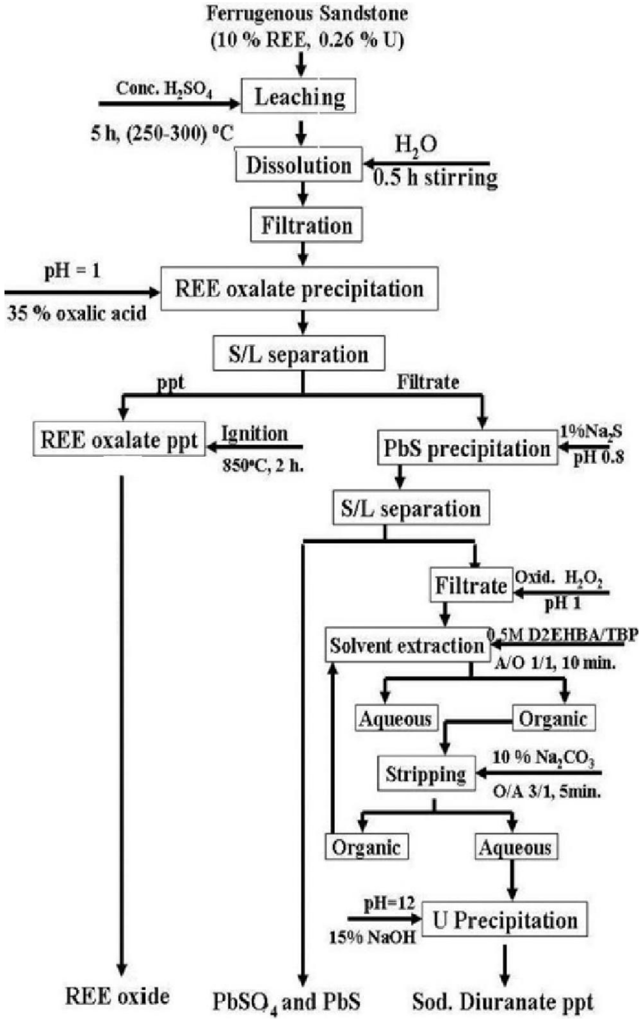
$$2Na_4UO_2(CO_3)_3 + 4NaOH \rightarrow Na_2U_2O_7 + 6Na_2C\ O_3 + 3H_2O$$

Sodium hydroxide was added to the strip solution to precipitate U-cake at pH 12.

The precipitate was subjected to XRD analysis to identify its content as hown in Figure 5. Different spot images analysis of the obtained di-uranate precipitate were analyzed by EDAX, Figure 6. The purity attained 91.7% while the total recovery o U from the ore was found to be 78%.

CONCLUSION

A technical flowsheet for the recovery of U and REE was constructed Figure 7. For processing of Ramlet Hemeyir ferruginous sandstone ore material, the Ferruginous sandstone ore was subjected to acid agitation leaching using H2SO4. The studied optimum conditions involved containing 100g ore sample with 200ml conc. H2SO4 at solid/liquid (S/L) ratio of 1/2 for 5h stirring time at a temperature 250oC. From the prepared sulfate leach liquor REE had first been selectively precipitated at pH of 1.0 by addition of 35% oxalic acid to the sulfate leach liquor with precipitation efficiency (98%).. From the filtrate obtained after REE precipitation, Pb was almost completely precipitated at pH 0.8 by drop wise addition of a 1% Na2S solution to the latter with continuous stirring at room tempera-



ture. Uranium was separated after Pb precipitation from the filtrate by liquid – liquid extraction using a synergistic system of D2EHPA/TBP in kerosene as a diluent under the following conditions: a solvent concentration of 0.5 M at pH 1, an A/O ratio of 1:1 and a contacttime 10 min. The loaded organic solvent was stripped with 10% sodium carbonate at ratio 3:1. Then NaOH was added to the stripped solution to precipitate U-cake at pH 12.0.

REFERENCES

[1] G.M.Abdel Wahab; Extraction of some nuclear elements from Um-Ghieg Area Red Sea Coast, Egypt, Ph.D.Thesis, Chem.Dep., Fac.Of Sci., Ain Shams Univ., Cairo, Egypt **(2008)**.

[2] A.J.Brown, B.C.Hayden; A Comparison of Liquid and Resin Ion Exchange Processes for Purification and Concentration of Uraniferous Solutions, Mining Congr **(1964)**.

[3] W.Daveis, W.A.Gray; Rapid and Specific Titrametric Method for the Precise Determination of U using $FeSO_4$ as Reductant, Talanta, **11**, 1203-1211 **(1964)**.

[4] F.Habashi; A Textbook of Hydrometallurgy, Laval University, Quebec, Canada **(1993)**.

[5] Z.Marczenko; Separation and Spectrophotometric Determination of Elements, John Wiley and Sons, Harwood, New York **(1986)**.

[6] C.Musikasis, W.Sculz; Principles and practices of solvent extraction, Marcel Dekker Inc., New York, 418 **(1992)**.

[7] L.Shapiro, W.Brannock; Rapid Analysis of Silicate, Carbonate and Phosphate Rocks, U.S Geol. Surv.Bull., 114A **(1962)**.

[8] A.E.Shata, S.K.Aita, W.A.Hosni, A.A.El Sayed; Lithofacies and Radioactivity of the Adedia Formation in Ramlet Hemeyir Area, Southwestern Sinai, Egypt.J.of Sediment. of Egypt, **19**, 1-12 **(2011)**.

[9] R.Viyayalakshmi, S.L.Mishra, H.Singh, C.K.Gupta; Processing of Xenotime Concentrate by Sulfuric Acid Digestion and Selective Thorium Precipitation for Separation of Rare Earths, Hydrometallurgy, **61**, 75-80 **(2001)**.