

Leaching Study of Lanthanides from its Mineralized Rocks at Gebel Gattar, Eastern Desert, Egypt

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Abstract:- Gebel Gattar area is considered one of the most promising uranium mineralization occurrence located in the northern Eastern Desert of Egypt, located at the intersection of latitude $27^{\circ} 7' 30''$ N and longitude $33^{\circ} 17' 5''$ E covering about 2 km². Hydrothermal alterations of Gabal Gattar granitic mass at GII occurrence exhibited an increase in Ni, Cu, Zn, Pb, Mo, Nb, Rb beside HREEs.

A technological sample from G II occurrence was subjected to extraction of REEs through both leaching and precipitation processes. The optimum leaching conditions achieved were as follows: 40 g/l HNO₃ acid, 12 hours contact time, 1/2 S/L ore/acid ratio, - 60 mesh grain size and room temperature (25 °C) giving REEs leaching efficiency of about 97%. REEs were directly precipitated using sodium hydroxide (20%) where REEs hydroxide was obtained at pH 8.5.

Keywords:- Gebel Gattar, leaching, precipitation, REEs

I. INTRODUCTION

Lanthanides ions are used as the active ions in luminescent materials used in optoelectronics applications, most notably the Nd:YAG laser. Erbium-doped fiber amplifiers are significant devices in optical-fiber communication systems. Phosphors with rare earth dopants are also widely used in cathode ray tube technology such as television sets. Rare earth elements have an important application in nuclear power industry (Haexl et al., 2006).

Monazite, bastnasite and xenotime are considered the most famous sources of lanthanides (Cotton, 2006). The lanthanides become important elements ; they are now used in a great variety of applications such as in petroleum cracking crystals in its refining, in flint stones, ignition device, superconductor, hydrogen storage, polishing powder, laser materials and special optical glasses. Also, lanthanides compounds containing lanthanum are extensively used in carbon lighting applications, especially by the motion picture industry for studio light and projection and as electron dense tracer in molecular biology (Chau and Lu, 1995).

In addition, lanthanides have a variety of nuclear application. Because they absorb neutrons, they have been employed in control rods used to regulate nuclear reactors. They has also used as shielding materials and as structural components in reactors. Some lanthanides have unusual magnetic properties. For instance, cobalt – samarium magnets are very strong permanent magnets (Lagowski, 2009).

Gebel Gattar area is one of the most promising uranium mineralization occurrence located in the northern Eastern Desert of Egypt at about 35 km west of Hurghada city. This prospect is located at the intersection of latitude $27^{\circ} 7' 30''$ N and longitude $33^{\circ} 17' 5''$ E covering about 2 km² (Fig. 1). Gabal Gattar granitic mass forms sharp serrated and very rugged topographic scenery that may attain 1963 m above sea level. It is characterized by its sharp peaks and deep narrow fractures in contrast to the surrounding relatively lowland countries. The younger granites of G. Gattar have an intrusive relation to the different country rocks surrounding it. Granite under investigation in most of its exposures, is nearly fresh, hard, massive and light pink to reddish pink color (Fig. 2).

The GII uranium prospect is located in the northwestern part of G. Gattar (Fig. 3). Uranium mineralization extends along a highly sheared, silicified and hematitized zone following NNE-SSW and NW-SE trends, where mineralization intensifies at the intersection zones. Recent surface exploration activities led to the discovery of new promising uranium mineralized zones on the surface of the G-II occurrence. These zones were investigated at depth by mapping the surface features and projecting the geometry to the subsurface. Primary uranium mineralization was first time discovered in the tunnel by the geological team of G. Gattar prospect (El-Feky et al., 2004). However, studies of field geology indicated that visible secondary uranium mineralization of bright yellow and orange colors are recorded at various levels of exposures.

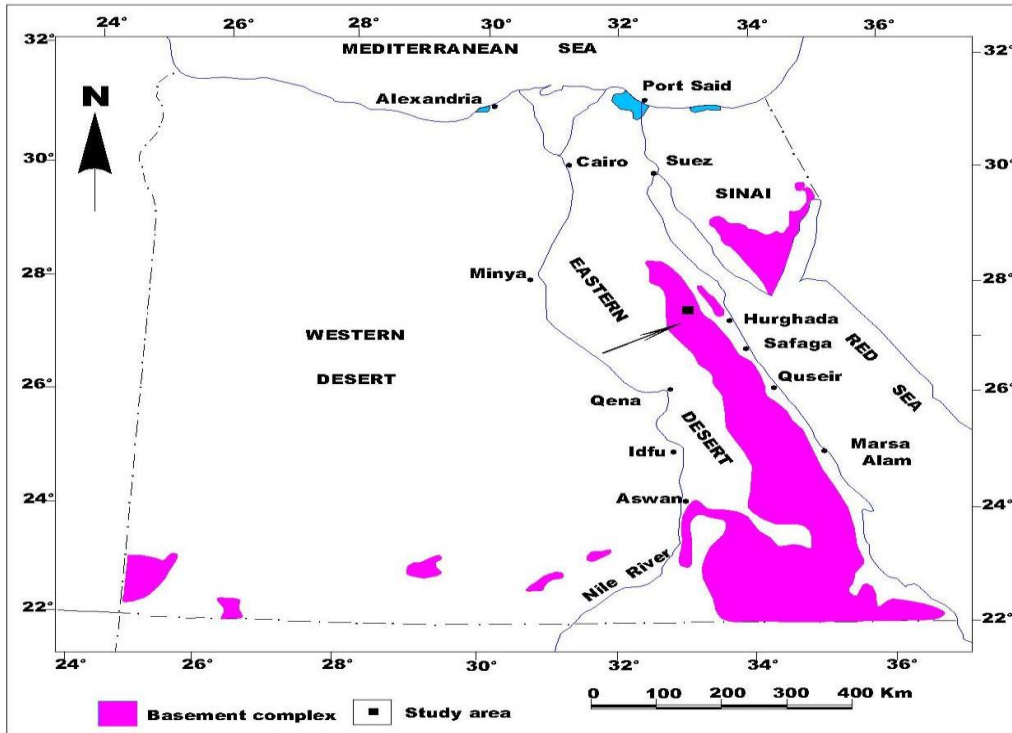


Fig. (1): Location Gabal Gattar area in the northern Eastern Desert of Egypt

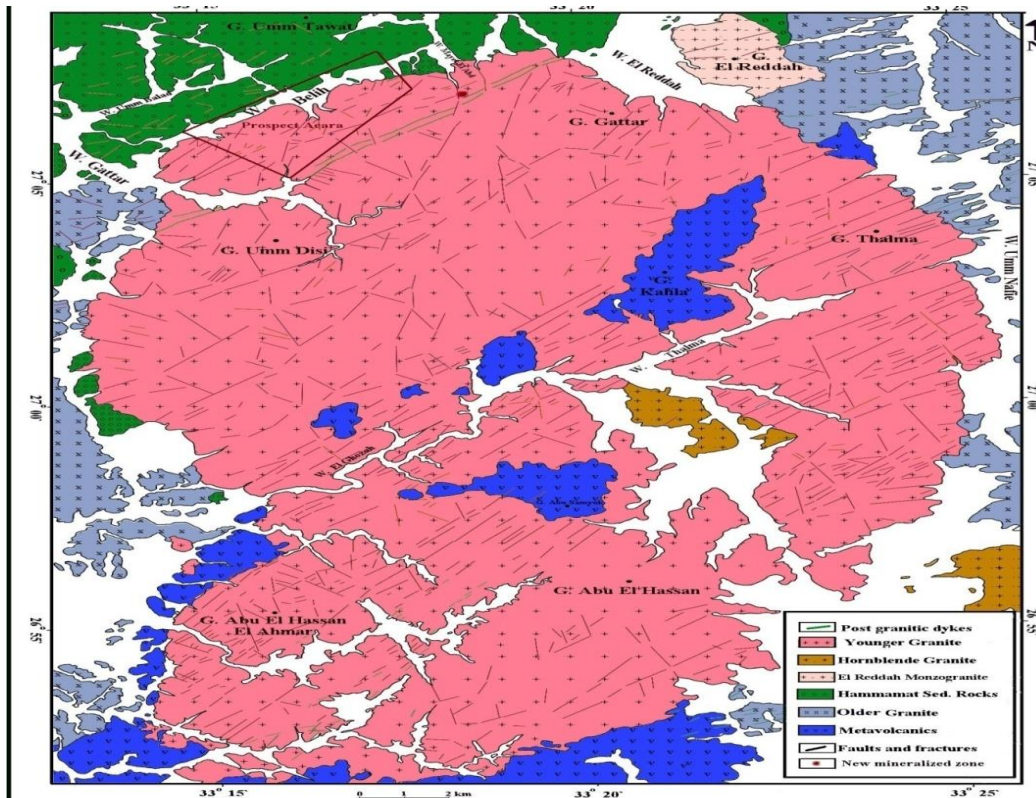


Fig. (2): Location of the study area and regional geological map of G. Gattar batholith and its environs (satellite image)

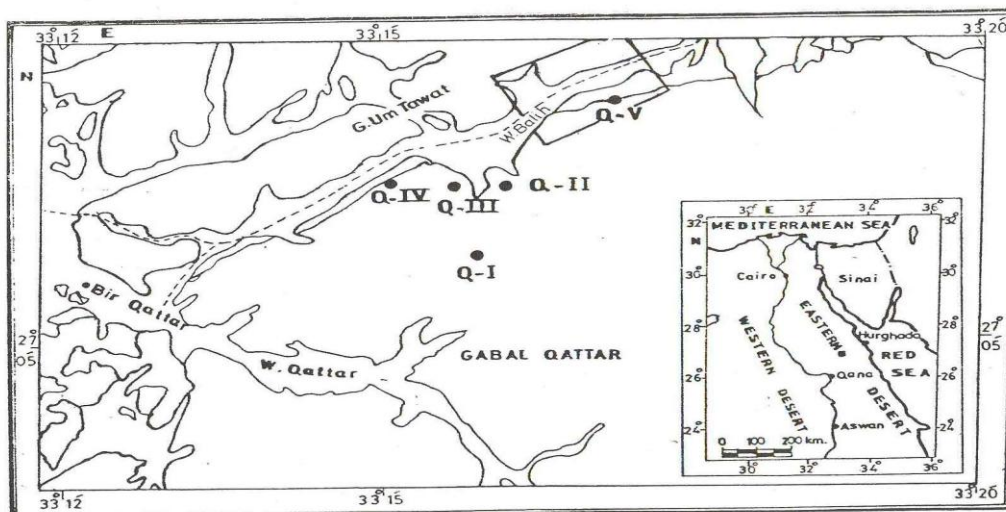


Fig. 2.9: Location map of Qattar-II and V prospect area, Gabal Qattar, North Eastern Desert, Egypt.

Fig. (3): Location of GII and GV occurrences located in the northwestern part of G. Gattar

The altered granites at the GII and GV occurrences show more alkaline nature than hypersolvus granites (El-Sayed et al., 2003), where the former are more enriched in (HFSE) such as Nb, Zr, Th, U, Y and HREEs than the latter.

Hydrothermal alterations at the GII occurrence exhibit an increase in Ni, Cu, Zn, Pb, Mo, Nb, Rb beside HREEs and a decrease in Ba, Co, Sr, and V. Hydrothermal alteration during the late magmatic stage is also identified through the development of unusual REEs patterns and fractionation of ratios like Zr/Hf and Y/Ho out of the CHARAC (Charge Radius Controlled) range (El-Feky, 2011).

Depending on EDX analyses, the concentrations of uranium in uraninite from the Gattar Uranium Prospect are highly variable, with UO₂ ranging from 54.87 wt% to 69.98 wt%. Total REE (ΣHREEs and ΣLREEs oxides in both uraninite and coffinite) are also recorded. All other elements also vary significantly (Table 1) (El Feky, 2011).

Ghazala (2015), performed the recovery study of the rare earth elements from the uranium concentrate obtained from the uraniferous granite of G. Gattar (G II) using ion exchange technique. Dwex 50WX8 was the cation resin used under the following optimum conditions: 1:30 solid/liquid (S/L), 100 rpm stirring speed and pH 1 for 120 min. contact time at room temperature. The total REE oxide cake obtained assayed 74.72%.

The present work mainly concerned with the leaching of the high content of REEs present in Gebel Gattar (GII occurrence) radioactive ore. The radiometric investigations show that the study radioactive granite is enriched in U and lanthanides (relative to their hosting granite).

Table (1): ESEM-EDAX semi-quantitative chemical compositions of uraninite and coffinite oxides (El Feky, 2011)

	Uraninite (wt%)				Coffinite (wt%)			
SiO ₂	05.80	05.06	04.51	11.97	26.14	30.50	28.15	38.77
Al ₂ O ₃	01.47	00.63	02.51	03.49	03.95	03.88	05.58	09.96
Fe ₂ O ₃	04.20	04.35	06.68	09.24	03.09	03.77	03.79	08.11
CaO	02.68	02.88	02.95	03.61	06.45	07.62	05.08	03.70
K ₂ O	03.19	03.36	03.00	03.06	03.67	03.95	03.36	03.39
P ₂ O ₅	00.33	00.38	n.d.	01.19	n.d.	n.d.	n.d.	n.d.
MoO ₃	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	01.10	01.10
Nb ₂ O ₅	n.d.	n.d.	01.00	n.d.	n.d.	00.88	n.d.	01.92
PbO	04.73	05.55	03.23	03.70	00.99	n.d.	n.d.	n.d.
Bi ₂ O ₃	02.01	02.18	02.43	02.03	n.d.	n.d.	n.d.	n.d.
ThO ₂	00.57	00.76	00.50	00.91	02.22	00.65	05.04	02.80
UO ₂	69.98	69.05	68.29	54.87	43.46	42.79	36.42	21.31
□ LREE oxide	00.78	01.37	n.d.	n.d.	02.77	01.32	03.93	01.106
□ HREE oxide	04.27	04.44	04.89	05.93	07.65	04.63	07.56	07.84

Note: n.d. Not determined

II. MATERIALS AND METHODS

1. Reagents and solutions

Most of the used reagents and solutions are as follows: Hydrochloric acid (37%, POCH, Poland), nitric acid (65 % Merck, Germany), sulfuric acid (95.97%, Sigma, Germany), oxalic acid, sodium hydroxide (98%, Winlab, U.K.), arsenazo I (pure, Sigma chem. C. O. USA), ferrous sulphate, salfosalysilic acid (pure, Kochlight labs Ltd., England), diphenylamine-4- sulfonic acid sodium salt (Merck, Germany) and boric acid (99%, Hungary).

2. Lanthanides determination

Lanthanides determination was carried out by Arsenazo (I) method where it reacts in neutral medium with tetravalent REEs ions to form a water soluble pink violet 1:1 complex, which is stable between pH 4 and 9. A solution of the reagent alone is red. With Arsenazo (I) the REEs are usually determined in solutions buffered at pH 7-8 with borax and boric acid (Merchzenko, 1976).

The total REEs analysis was conducted by addition of suitable volume 1ml of solution contains total REEs and put it in 25 ml volumetric flask put 1.5 ml of 0.05 % Arsenazo (I) to the sample and complete the flask with buffer solution and measure at wavelength 580 nm.

3. Uranium determination

Uranium was determined in the pregnant leach solution and the crude uranium concentrate using titration method which was performed using few drops of diphenyl-amin-4-sulfonic acid sodium salt as indicator. Titration of 5 ml sample solution against 1 M of NH_4VO_3 till the appearance of a purplish red color represents the end point (Davies, W. and Gray, W. 1964).

Uranium concentration in the working sample solution is then calculated according to the following equation:

$$U \text{ (g/L)} = T.V_1.1000/V$$

T: titration intensity of NH_4VO_3

V_1 : consumed NH_4VO_3 (ml)

V: Volume of sample (ml)

- Leaching experiments were performed using a three openings flask 250 ml, where 10 g of the ore were subjected to all the studied experiments.

Recovery of the lanthanides from the radioactive granite of the study area was generally achieved through two stages namely; leaching and precipitation stages.

In the present work, the first stage was performed using acid agitation leaching technique where the most effective factors controlling leaching efficiency were studied. The studied sample contained total iron 1.84 wt.% , U= 0.55% and total lanthanides 4630 ppm.

III. RESULTS AND DISCUSSION

1. Effect of acid type

Different acids were studied such as sulfuric, nitric and hydrochloric acid for maximum leaching of lanthanides. The experimental conditions were fixed at 40 g/l acid concentration, 4 hrs agitating time, 1/2 solid / liquid ratio at room temperature (25 °C) and -60 mesh grain size. The obtained lanthanides analysis revealed that nitric acid is the most effective leaching agent (Fig.4).

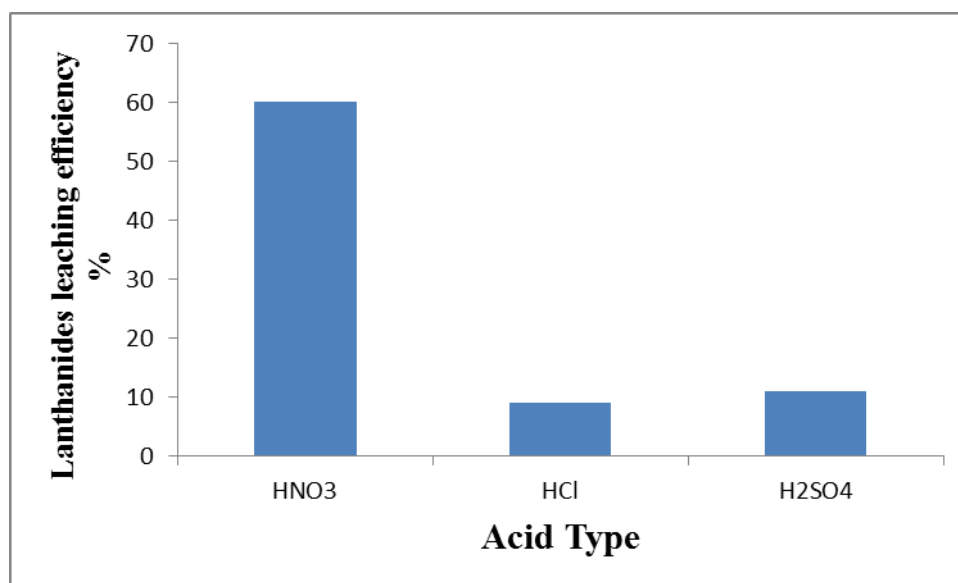
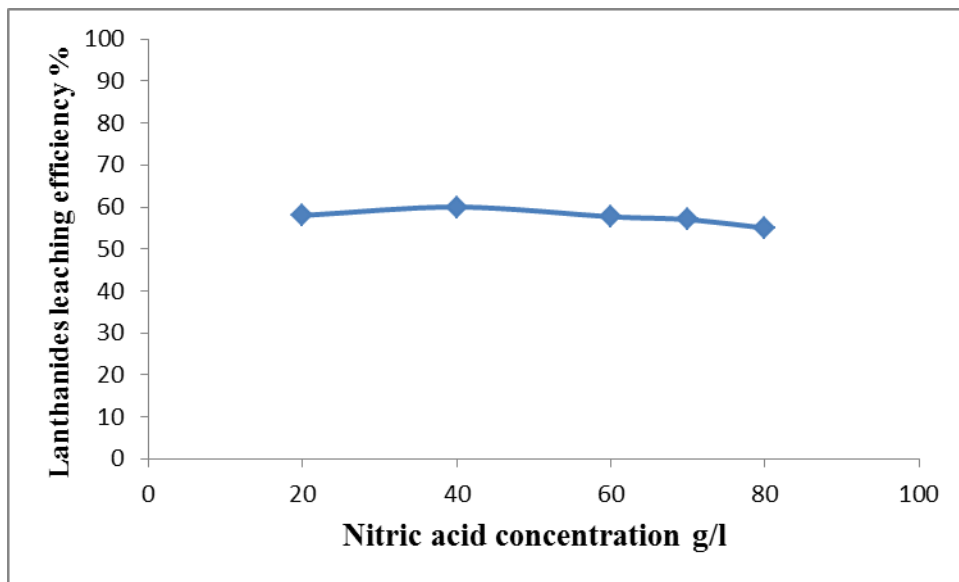


Fig. (4): Effect of acid type upon REE leaching from Gattar mineralized rocks (GII)

2. Effect of different nitric acid concentration

Different concentrations of the nitric acid were used (20, 40, 60, 70 and 80 g/L) as a leaching agent of lanthanides with fixing the other leaching conditions. The obtained results indicated that a concentration of 40 g/L was the optimum one (60 % leaching efficiency) (Fig. 5), while the leaching efficiency of the lanthanides slightly decreased at 80 g/L due to some complexes formed.



(Fig. 5): Effect of nitric acid concentration on lanthanides leaching from Gattar (GII) mineralized rocks

3. Effect of contact time

This factor was studied where different contact times (2, 4, 6, 8, 10 and 12 hours) and the other leaching conditions were fixed at 40 g/l nitric acid, 1/2 solid /liquid ratio, at room temperature (25 °C) and – 60 mesh grain size. It was concluded that 12 hours contact time was the optimum for maximum lanthanides leaching (Fig. 6), as the nature of the study ore (hard and massive granite) needs strong acid and long contact time.

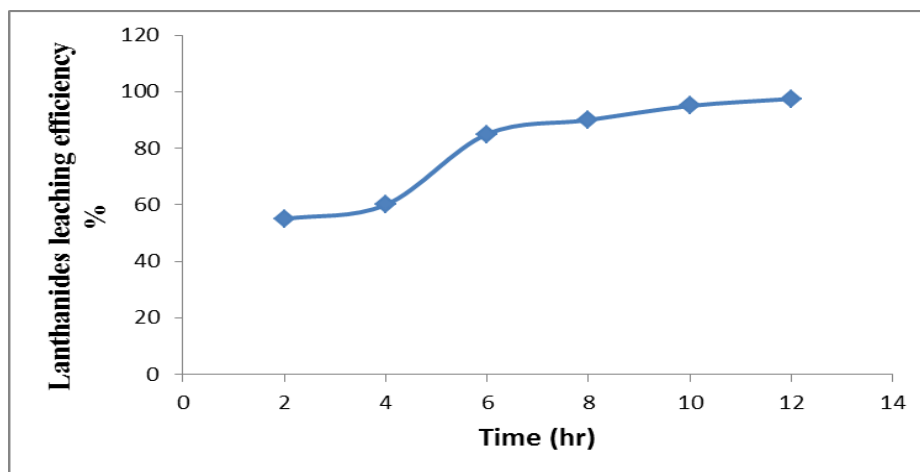
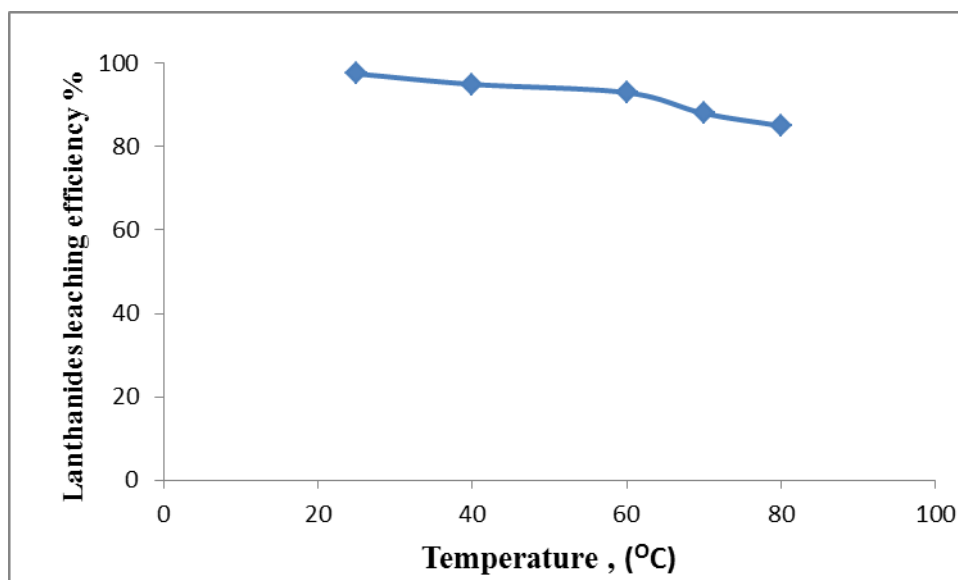


Fig. (6): Effect of contact time on lanthanides leaching from Gattar (GII) mineralized rocks

4. Effect of temperature

It was necessary to study its effect on lanthanides leaching. Different temperatures were studied from 25 °C, 40 °C, 60 °C, 70 °C and 80 °C. It was observed from data illustrated in Figure (7) was the highest leaching efficiency (97.5 %) was reached at 25 °C temperature. A slight decrease in the lanthanides leaching efficiency with increasing in temperature increase this is due to evaporation of some elements.



(Fig.7): Effect of temperature on lanthanides leaching from Gattar (GII) mineralized rocks

5. Effect of Solid / liquid ratio

A group of different ratios 1/2, 1/4 and 1/5 was performed between the study ore and the leaching acid. The obtained results revealed that a solid / liquid ratio of 1/2 was the effective ratio for optimum maximum lanthanides leaching efficiency (97.5 %) (Fig. 8). 40 g/l nitric acid, at room temperature (25 °C), - 60 mesh grain size, 12 hours contact time and 1/2 were the optimum conditions for maximum lanthanides leaching.

6. Preparation of lanthanides from leach liquor stock solution

A leach liquor stock solution was prepared by applying the previously studied optimum leaching conditions, 40 g/l HNO₃ acid, 12 hours contact time, 1/2 S / L ratio, - 60 mesh grain size and room temperature (25 °C). A weight of 50 g ore was subjected to the above leaching conditions where 250 ml of the study Gattar (GII) mineralized rocks leach liquor was obtained.

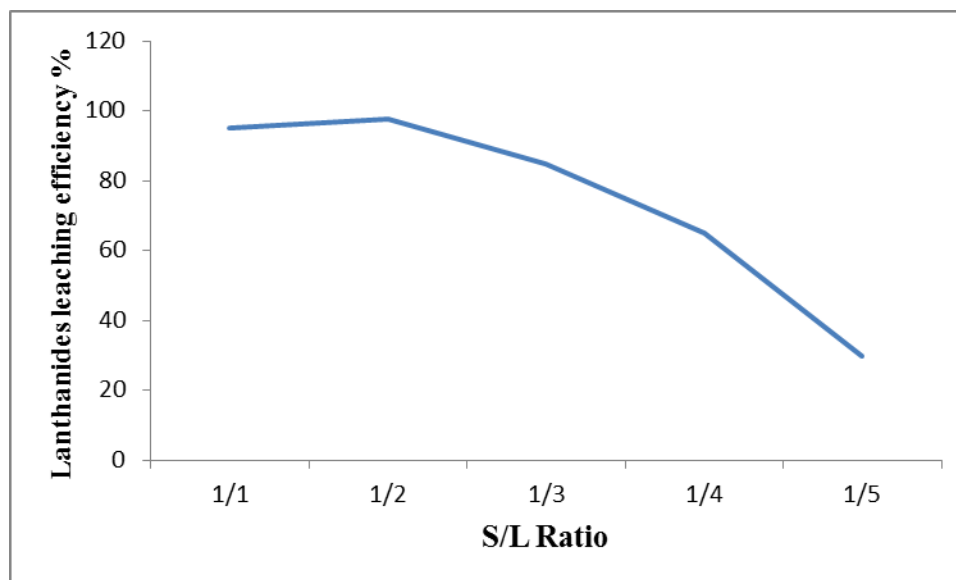


Fig. 8): Effect of solid/ liquid ratio on lanthanides leaching from Gattar (GII) mineralized rocks

7. Precipitation of lanthanides

Direct precipitation of the lanthanides precipitate was achieved by adjusting the pH value at 5 - 7 for the precipitation of the existed uranium rich in iron (XRF chart of the precipitated uranium, Fig.9). At pH value of 8.5 - 9.5 the valuable cake of REE hydroxide was obtained after filtration and drying. The obtained precipitate was analyzed by the Analytical Electron Scanning Microscope (AESM) model JSM 6510 LA

(JEOL) (3 different spots in the precipitate Fig. 10) showing the presence of some important REEs in different percentages, such as Pr, Nd, Sm, Eu, Y, Tm, Yb and Lu.

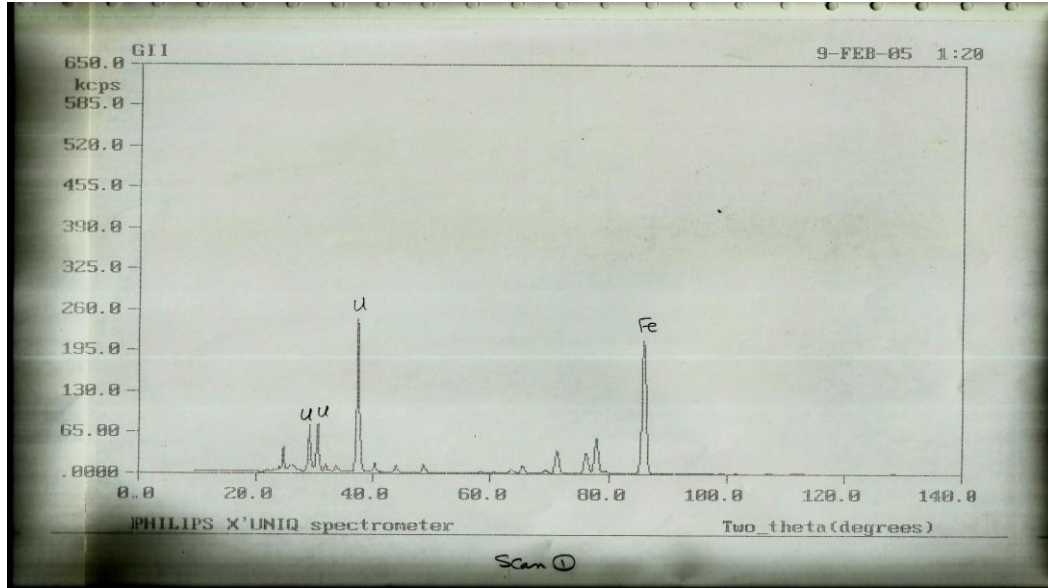
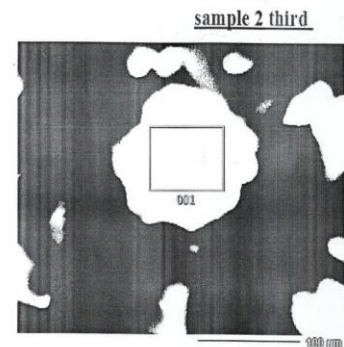
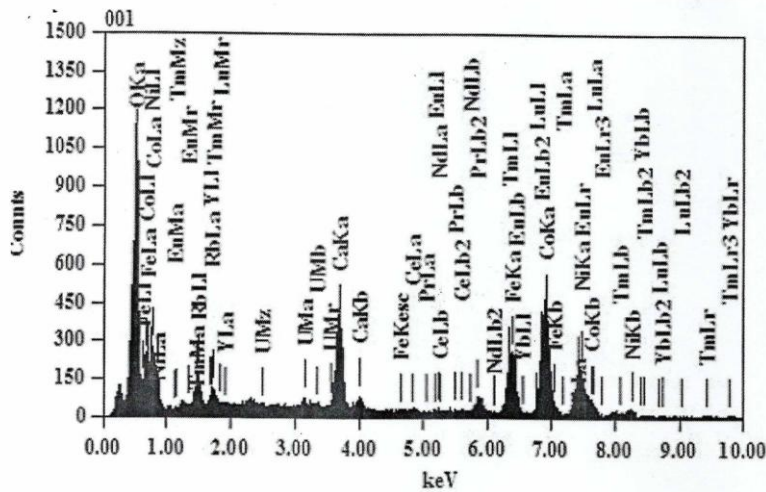
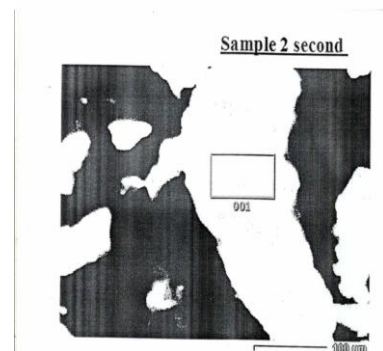
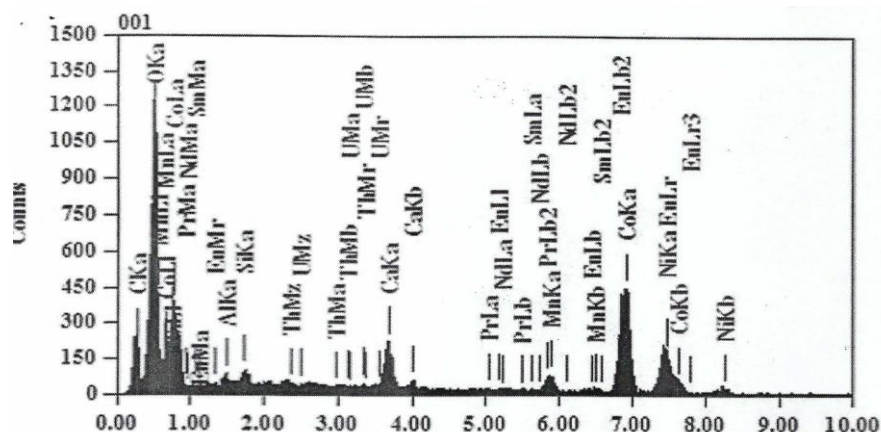


Fig. (9): XRF chart for uranium precipitated from the lanthanides stock solution



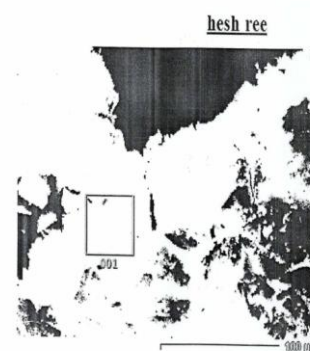
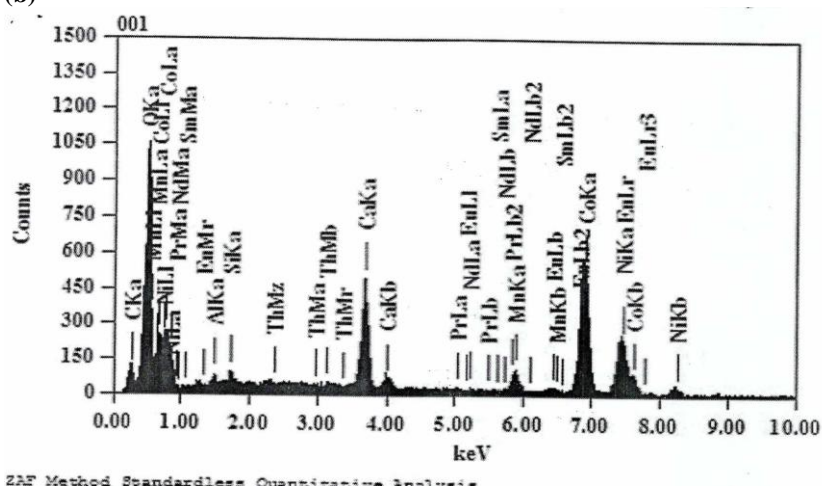
Element	C	O	Al	Si	Ca	Mn	Co	Ni	Pr	Nd	Sm	Eu	Th	U	Total
Mass	26.44	44.29	0.81	0.82	2.49	0.45	17.79	7.69	0.19	0.57	1.44	6.59	0.11	0.34	100

(a)



Element	O	Ca	Fe	Co	Ni	Rb	Y	Ce	Pr	Nd	Eu	Tm	Yb	Lu	U	Total
Mass	41.24	5.75	8.68	19.15	7.27	2.77	0.72	0.34	0.92	0.71	2.99	8.63	0.34	2.34	1.12	100

(b)



Element	C	O	Al	Si	Ca	Mn	Co	Ni	Pr	Nd	Sm	Eu	Th	Total
Mass	8.89	38.4	0.71	0.82	6.22	1.07	22.28	10.26	0.30	0.55	1.99	7.98	0.28	100

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Fig. (10 a,b,c): SEM micrograph and the corresponding EDX spectrum of the lanthanides oxalate precipitate

A proposed technical flowsheet was designed (Fig. 11) for the REE fractional crystallization from Gattar mineralized rocks (GII). This flowsheet shows the practical application of the present study. The ore was ground to – 60 mesh size, the optimized leaching conditions, filtration of the obtained leach liquor and precipitation of the final products (iron, uranium precipitates and REEs-hydroxide cake). According to this flowsheet, one kilogram ore when subjected to the above studied parameters gave about 4.3 grams of REE precipitate. The obtained final product REEs hydroxide can be subjected to a further purification process.

Conclusions

The present work revealed that the lanthanides recorded in the studied G. Gattar mineralized rocks (G II) ore were feasible to leaching. The acid agitation leaching technique was chosen according to the mineralogy of the ore. It was concluded that about 97 % of the lanthanides leaching efficiency and about 4.3 grams of REEs-OH precipitate per one kilogram ore can be obtained. Separation of iron, uranium and REEs was achieved through direct precipitation instead of using ion exchanger resin or liquid/liquid extraction techniques. The obtained

precipitate was analyzed by the Analytical Electron Scanning Microscope showing the presence of some important REEs in different percentages, such as Pr, Nd, Sm, Eu, Y, Tm, Yb and Lu.

Finally, it is very important to recommend that G. Gattar mineralized rocks (G II) ore is very promising ore, beside uranium, for REEs according to its feasibility to leaching process.

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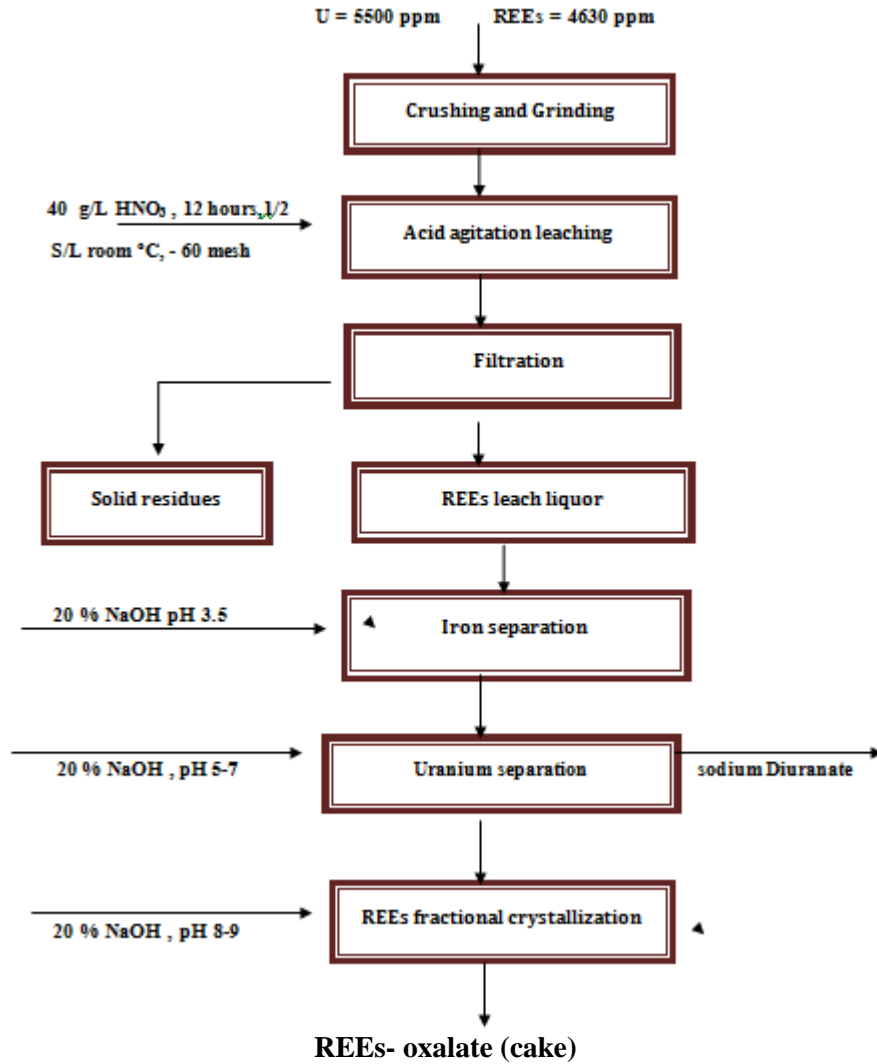


Fig. (11): Flow sheet for REEs fractional crystallization from Gattar mineralized rocks GII)

"دراسة ذوبانية اللانثانيدات من صخورها المتمعدنة بجبل جتار ، الصحراء الشرقية - مصر"

هشام محمد كمال

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الخلاصة

تعتبر منطقة جبل جتار من أكثر مواقع تمعدنات اليورانيوم الواعدة ، وتقع شمال الصحراء الشرقية لمصر عند تقاطع خط عرض $27^{\circ} 30' / 7^{\circ} 27'$ شمالاً مع خط طول $33^{\circ} 17' / 5^{\circ} 17'$ شرقاً، وتغطي مساحة حوالي 2 كيلومتر مربع.

إن التغيرات الحرمانية لكثلة جبل جتار الجرانيتية عند GII التواجد أوضحت زيادة في عناصر Ni, Cu, Zn, Pb, Mo, Nb, Rb, HREEs ونقص في عناصر Ba, Co, Sr, V.

وفي هذا البحث تم دراسة استخلاص العناصر الأرضية النادرة من عينة تكنولوجية للتواجد G II من خلال عمليتي الإذابة والترسيب ، وكانت الظروف المثلى لإذابة تصل إلى 97 % هي: 40 جرام/ لتر تركيز حامض النيتريك ، 12 ساعة تقليب ، ونسبة خام / حامض 2/1 ، ودرجة حرارة الغرفة وحجم حبيبات - 60 ميش. وتمت عملية الترسيب المباشر بدلاً من طرق الفصل الأخرى مثل الاستخلاص بالمذيبات العضوية أو الراتجات الأيونية وغيرها . فتم ترسيب اليورانيوم أولاً عند الأس الهيدروجيني 6 تقريباً ثم العناصر الأرضية النادرة عند الأس الهيدروجيني 8-9.5 . وباختبار الراسب الذي تم الحصول عليه بجهاز الميكروسكوب الإلكتروني الماسح تأكد وجود العناصر الأرضية النادرة التالية (Pr, Nd, Sm, Eu, Y, Tm, Yb and Lu).