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Leaching and Precipitation of Thorium Ions from Cataclastic Rocks, Abu Rusheid Area, South Eastern Desert, Egypt

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The leaching of thorium from representative samples collected from Abu Rusheid area, south Eastern Desert, Egypt using sulphuric acid has been studied. Factors affecting the leaching of thorium were investigated such as, acid type, S/L ratio, H_2SO_4 concentration, leaching time, temperature and grain size. The best conditions for leaching of thorium were, H_2SO_4 acid as the best acid, S/L ratio of 1:5, 3.0 M H_2SO_4, 2.0 hour of leaching time, -200 mesh size at 90°C. After leaching, the mixture was filtrated then divided into two parts the leach liquor and the residue. The leach liquor was adjusted at pH 1.0 by ammonia solution and addition 10 % oxalic acid. The precipitate obtained was filtrated and dried at 120°C for 1 hour. The obtained precipitate showed 91.60 % of thorium content when using 3.0 M H_2SO_4 acid. The quality of the precipitate was confirmed by XRF.

Keywords: Thorium / Leaching / Arsenazo III / XRF

Introduction

Abu Rusheid area lies in the southern part of the Eastern Desert of Egypt, along the lower reaches of Wadi Abu Rusheid. It is located about 45 Km southwest of Marsa Alam between latitude 24° 36' 43" and 24° 38' 26" N and longitude 34° 46' 0" and 34° 46' 35" E. The area could be reached from the Red Sea coast through Wadi Al Gemal and then Wadi Nugrus along a desert track about 40 Km long.

Thorium is a soft, paramagnetic, bright silvery radioactive actinide metal and its most important oxidation state is +4, represented in compounds such as ThO_2 and ThF_4 . It is found in several minerals, including thorianite (up to 90% ThO_2), monazite (1-15 % ThO_2) and thorite (up to 80% ThO_2). These minerals are less abundant compared to uranium because thorium does not form secondary minerals. They occur principally in granites and pegmatites, all thorium minerals contain some uranium, just as all primary uranium minerals contain some thorium. Thorium is a nuclear_element and is used as a source for nuclear power and as coating material for tungsten wire found in electronic equipment.

The Egyptian black sand beach deposits are the main thorium ore in Egypt due to the presence of monazite [1]. In Egypt, the thorium content in monazite can attain up to 30% and the Egyptian monazite assays 5.8% ThO_2. Large deposits of thorium are found in Australia, India, Norway and the United States and about 30,000 metric tons are extracted each year.

Abu Rusheid- Sikeit area has been studied by several authors [2-6] who reported that the exposed rocks in this area include ophiolitic rocks, ophiolitic melange, cataclstic rocks and intrusive

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rocks. The Abu Rusheid area is characterized by containing numerous mineralizations, so it can be called a poly mineralization area. The mineralization included: uranium minerals autunite, coeffinite, carnolite , uranophane and β uranophane. Thorium minerals were represented as uranothorite, thorite, cheralite and thorianite. Niobium minerals zinc, manganese minerals, base metals associated minerals such as zircon, monazite and xenotime are also present.

The leaching or dissolution of thorium is carried out through conventional or non-conventional techniques depending on the type of thorium minerals, the ore grade, the economy of the process and the environmental impact.

There is an economic technique for separation and purification of thorium from their hydrous oxide cake concentrate, which could be obtained by alkali treatment of Egyptian monazite sand [7]. The extraction from nitric acid medium used tributoxyethyl phosphate (TBEP) in *n*-paraffin [8] and trioctyl - phosphine oxide (TOPO) dissolved in cyclohexane and determination of thorium was by thoron [9]. The process of thorium extraction from sulphuric acid liquor generated from the chemical monazite treatment through a solvent extraction technique has been reported [10]. Thorium and uranium were separated from the nitrate medium using ion exchange Amberlite CG-400 and then determined using ICP-MS [11], or triphenylphosphine oxide (TPPO) [12].

The main objective of this paper is to study the optimum conditions for leaching thorium from cataclastic rocks and its precipitation as thorium oxalate.

Experimental

Chemicals and reagents

All the chemicals and reagents used in this work were of analytical reagent grade (AR). Double distilled water was used for preparation of all aqueous solutions and for dilution. Thorium stock solution was prepared by dissolving 2.38g of $Th(NO_3)_4.4H_2O$ in 1000 ml double distilled water to get a fixed concentration of 1000 ppm.

Instrumentation and equipment

All samples and reagents used in this work were weighed using a precise balance of precise type Schimadzu AY 220, with stability of sensitivity of 10^{-4} g and an accuracy of ±0.01%. A bench pH meter of Inolab digital pH meter, level 1.0 (England) was used for measuring all pH values of the different solutions in the pH range 0.00 – 14.00 with resolution of 0.01 pH and accuracy ±0.01. The scale of the pH meter was calibrated before each experiment using a standard buffer solution at ambient room temperature 22±1˚C. Double distilled water was used for preparing all standard solutions and reagents.

The absorbance of the investigated solution and Th , SiO_2, Al_2O_3, TiO_2, P_2O_5 was measured by using the Metertech Inc, model SP-8001, UV-visible spectrophotometer. This apparatus is a single beam recording spectrophotometer with a wavelength range from 200 to 1100 nm with an accuracy of ±1nm. 5.0 cm^3 quartz cells with a path length of 1.0 cm were used for the sample and blank. Sodium and potassium were determined by a Sherwood flame photometer model 410 (England), using a series of chemical solutions. The analysis of CaO, MgO and Fe_2O_3 were determined by titration [13].

Measurements

The unknown minerals were identified by using X-ray diffraction (XRD). The equipment used is the PHILIPS unit pw 3710/31 diffractometer with an automatic sample changer pw-1775, 21 position scintillation counter, Cu- target tube and Ni filter at 40 kV and 30 MA.

Trace elements such as V^{5+}, Cr^{3+},Ni^{2+}, Co^{2+} ,Zn^{2+} ,$Ga^{3+,}$ Rb^{+} , Sr^{2+} , Y^{3+}, Zr^{4+} , Nb^{5+} ,Pb^{2+} and Ba^{2} were measured using X-ray fluorescence (XRF). This equipment is a (PHILIPS) unit with automatic sample changer PW 1510, connected to a computer system using X-40 program for spectroscopy with the detection limit of 5.0 ppm. All measurements were performed at the Nuclear Materials Authority (NMA), Cairo, Egypt. Different concentrations of thorium were prepared by dilution. Thorium concentration was measured colorimetrically using Arsenazo III complex [14].

For determination of the concentration of thorium in the samples, the following procedure was carried out to reduce the effect of most interfering ions. One gram of the sample was put in a breaker and 10 ml of 4.0 N HNO_3 were added. The mixture was evaporated to near dryness on a hot plate. This was followed by the addition of 2.0 ml conc. H_2SO_4 and evaporation to dryness on a hot plate, then 50 ml water was added to the dried sample, and heated to a boiling point for five minutes. After cooling, the solution was filtered then the thorium was measured using Arsenazo III method.

Results and Discussion

Characterization

The studied samples were completely attacked using a mixture of acids HF, HNO_3, $HClO_4$ and HCl, [13] to determine the chemical composition of major oxides of the studied samples (cataclastic rock) which were collected from Abu Rusheid area, south Eastern Desert, Egypt (Table 1).

The thorium content in the sample was extracted at optimum conditions; 1.0 % DEHPA dissolved in cyclohexane, A:O ratio 1:1, pH 1.0 and shaking time 3.0 minutes at ambient room temperature (22 ±1^{o}C), while the stripping process was carried out on the loaded organic phase under optimum conditions; 2M sulfuric acid, A:O ratio 2:1, pH 1.0 and shaking time 3.0 minutes at ambient room temperature, the results are listed in (Table 2).

X- ray Fluorescence technique (XRF) was used to detect the trace elements present in the studied samples collected from Abu Rusheid area, south Eastern Desert, Egypt, (Table 3).

X-ray diffraction data of geologic samples collected from Abu Rusheid area, south Eastern Desert, Egypt indicated the presence of Xenotime (YPO_4), Zinnwaldite ($KLiFeAl(AlSi_3)O_{10}(OH,F)_2$) and Thorite ($(Th,U)SiO_4$), (Table 4).

Leaching investigations

The leaching process can be classified into two major methods, namely conventional or non-conventional techniques. The conventional method is the agitation technique for both acidic and alkaline leaching, while non-conventional one includes: pressure, bacterial, natural, chlorination and fluorination leaching.

The acid leaching method is characterized by its low cost, short leaching time, high extraction efficiency, availability and excellent impurities removal. A series of experiments were carried out to study the selective dissolution of thorium from the cataclastic rock. Different parameters that affect the leaching of thorium were studied such as; acid type, H_2SO_4 concentration, S/L ratio, leaching time, temperature and grain size.

Effect of leaching acid

To choose which acid type is the best for leaching thorium, several acid leaching experiments were tested using H_2SO_4, HCl, H_3PO_4 and HNO_3 acids as the leaching agent. The data given in Figure (1) indicate that sulphuric acid was the best leaching agent (91.95%) to leach thorium if compared with HCl (86.19%), H_3PO_4 (68.96%) and HNO_3 (83%) under the same experimental conditions.

Effect of H_2SO_4 concentration

The effect of sulphuric acid as the leaching agent was investigated using different concentrations ranging from 1.0 M to 6.0 M, while other leaching parameters were kept constant. The obtained results indicate that the best acid concentration of sulphuric acid is 3.0M which was found to give the highest leaching efficiency, 91.95%, (Fig.2).

Effect of solid/ liquid ratio (S/L).

The effect of S/L ratio on leaching of thorium was studied through the range between 1:4 to 1:20, while fixing the other parameters. The obtained results show that the leaching of thorium increased gradually from the ratio 1:4 to 1:5 after that it remained constant till the ratio 1:20; therefore, the best solid / liquid ratio which leached 91.95%, was found to be 1:5 (Fig.3).

Effect of leaching time

To study the effect of leaching time on thorium leaching, different leaching times in the range 1.0 hour to 3.5 hour were performed, while the other leaching conditions were kept fixed. The results show that the leaching efficiency increased from 1.0 hour till 2 hours (94.82%) and after 2.0 hours, it remained constant. Therefore, the best leaching time was found to be 2.0 hours, (Fig. 4).

Effect of temperature

Temperature plays a vital role which determines the reaction way, whether it is exothermic or endothermic and also may accelerate or slow-down the reaction. The effect of temperature on thorium leaching efficiency was studied by varying the temperature from room temperature, about

22±1°C, to 110°C. It was noticed that, the leaching efficiency (%) of thorium increased with increasing the temperatures and reached its maximum at 90 °C which dissolved 94.82% of thorium. At higher temperatures, the leaching efficiency decreased which can be related to evaporation, semi dryness of the matrix and breakdown for the material [15].

Effect of mineral grain size

In the present study, the samples were ground to particle size, -12 mesh (1.7mm) to -230 mesh (-0.063mm). To study the effect of grain size on thorium leaching efficiency, a series of experiments were carried out using different grades of the rock sample having grain size ranging from -12 mesh to -230 mesh, while the other leaching conditions were kept fixed. The results indicated that the highest thorium leaching efficiency reached was 94.82% with fine grain size -200 mesh, while lower size had much less thorium leaching efficiency, (Fig.6).

Proposed flow sheet

According to the obtained results, the following flow sheet was proposed for the recovery of thorium. In this case, 100g of the representative samples with particle size -200 mesh was subjected to acid leaching at the following optimum conditions: 3.0 M H_2SO_4 acid with ratio 1:5 (S/L) for 2.0 hours at 90^{o}C.

The solution was filtered and divided into two parts namely, the filtrate (leach liquor) and the residue. The thorium leach liquor was adjusted to pH 1.0 by ammonia solution then 10 % oxalic acid was added. The precipitate obtained was filtrated and dried at 120^{o}C for 1hour. The precipitate shows that 91.6% of thorium was formed by leaching with 3.0M H_2SO_4 acid, (Fig.7).

The final product of thorium was identified by X-ray fluorescence (XRF), [Philips experimental unit with automatic sample changer PW 1510, (JEOL-JSX-3222 Element Analyzer) connected to a computer system using X-40 program for spectroscopy with the detection limit 5.0 ppm, Atomic Energy Authority, Cairo, Egypt]. X-ray diffraction (XRD) showed that, the precipitate contains mainly 91.6 % thorium which confirms our investigation. The main impurities are Y, Ce, Yb, U, Ca and… (Fig.8).

Conclusion

The present study shows that thorium can be leached from cataclastic rocks using sulphuric acid under suitable leaching conditions. It was found that, the best leaching conditions for representative samples collected from Abu Rusheid area, south Eastern Desert, Egypt are 3.0 M H2SO4 acid, S/L ratio of 1:5, -200 mesh size and 2.0 hours of leaching time at 90oC. The obtained precipitate showed that 91.6% of thorium could be present under optimum conditions using 3.0M H2SO4 acid. The final precipitate was confirmed by XRF measurements.

Table (1): Chemical analysis of major oxides in (wt %)

	Oxides% \ Sample No.	A*	B*
	SiO_2	67.20	67.20
	Al_2O_3	13.21	14.10
	TiO_2	0.46	0.44
	$Fe_2O_3{}^T$	5.60	5.60
	CaO	1.40	2.80
	MgO	1.00	1.00
	Na_2O	5.55	5.06
	K_2O	1.54	1.94
	P_2O_5	0.38	0.31
L.O.I	110 °C	0.33	0.21
L.O.I	550 °C	0.66	0.45
L.O.I	1000 °C	1.64	1.05
	Total (%)	98.97	100.16

*** Average means of 10 samples**

Table (2): Determination of thorium after extraction and stripping process

Sample No.	Thorium content (ppm)		Extraction process		Stripping process			
					First cycle		Second cycle	
			Extraction (ppm)	Extraction (%)	Stripping (ppm)	Stripping (%)	Stripping (ppm)	Stripping (%)
A*	5505 5506 5508	5506	5158	93.67	4683	90.79	380	7.36
B*	5491 5493 5495	5493	5113	93.08	4715	92.21	316	6.18

*** Average means of 10 samples**

Table (3): Trace elements content (ppm) using XRF technique

Trace elements (ppm) / Sample No.	A**	B**
Cr	35	33
Ni	7	8
Cu	89	87
Zn	853	1183
Zr	475	752
Rb	4.33	487
Y	48	58
Ba	150	259
Pb	85	152
Sr	1892	2435
Ga	42	57
V	3	7
Nb	35	55
*Th	5506	5493
*U	2238	1928
*∑REEs	6791	7778

*** Determination by spectrophotometer**
**** Average means of 10 samples**

Table (4): X-ray diffraction data of the studied geologic samples (cataclastic rocks), Abu Rusheid area, south Eastern Desert, Egypt

Identified minerals / Sample		Xenotime YPO_4		Zinnwaldite $KLiFeAl(AlSi_3)O_{10}(OH,F)_2$		Thorite $(Th,U) SiO_4$	
dA°	**I/I°**	**dA°**	**I/I°**	**dA°**	**I/I°**	**dA°**	**I/I°**
9.87	9			9.90515	98		
4.71	10					4.72	85
4.54	11	4.55	25	4.51621	1		
3.44	100	3.45	100			3.55	100
3.34	23			3.34698	4		
3.30	25			3.30191	100		
2.87	3	2.75	9	2.89595	7	2.84	45
2.66	4			2.67656	4	2.67	75
2.56	15	2.56	50			2.52	30
2.43	5	2.44	13				
1.98	7			1.98151	2		
1.92	46	1.929	9				
1.82	6	1.824	13			1.83	65
1.76	12	1.768	50			1.76	25
1.72	15	1.925	18				
1.60	2	1.616	3				
1.54	3	1.543	9			1.54	20
1.44	2	1.432	9				
ASTM Card No.		**011-0254**		**041-1482**		**11-419**	

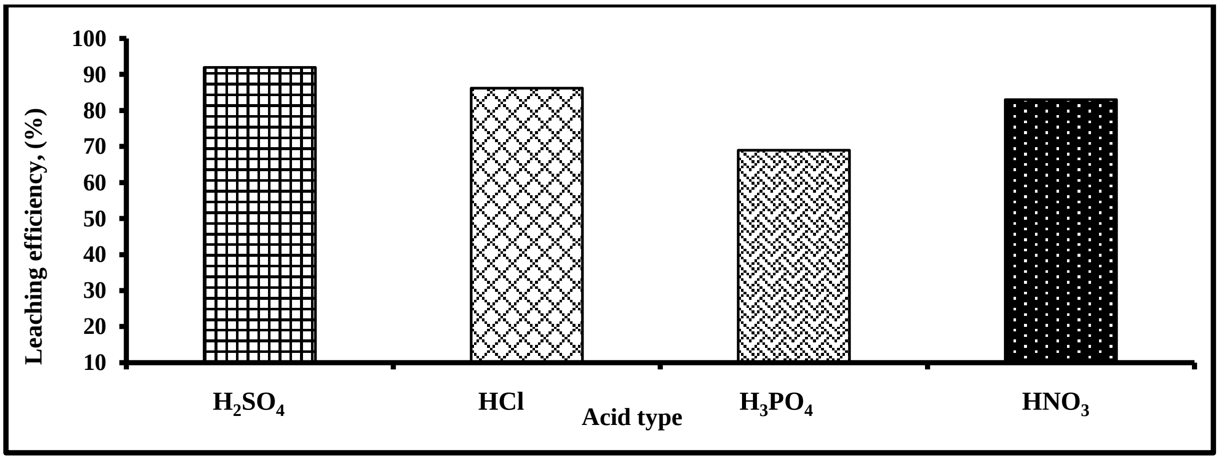

Fig. (1): Effect of different acid types on thorium leaching efficiency (%)

Leaching conditions for thorium: Temperature (90^{o}C), acid concentration (5.0 M), phase ratio S/L: 1/5 and leaching time 1.0 hour.

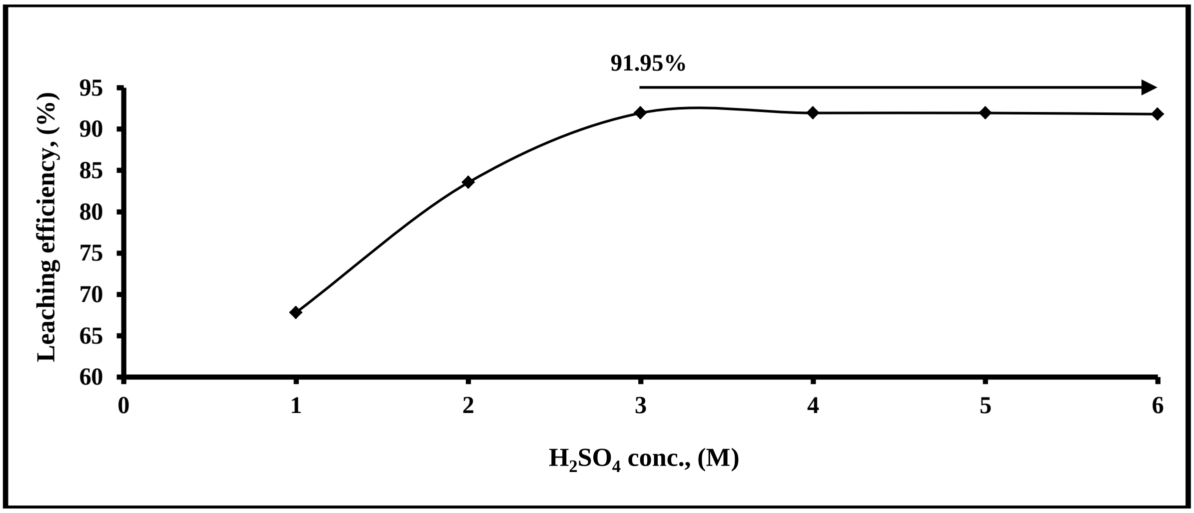

Fig. (2): Effect of H_2SO_4 concentration on thorium leaching efficiency (%)

Leaching conditions for thorium: H_2SO_4 acid, S/L: 1/5, temperature (90^{o}C) and leaching time 1.0 hour.

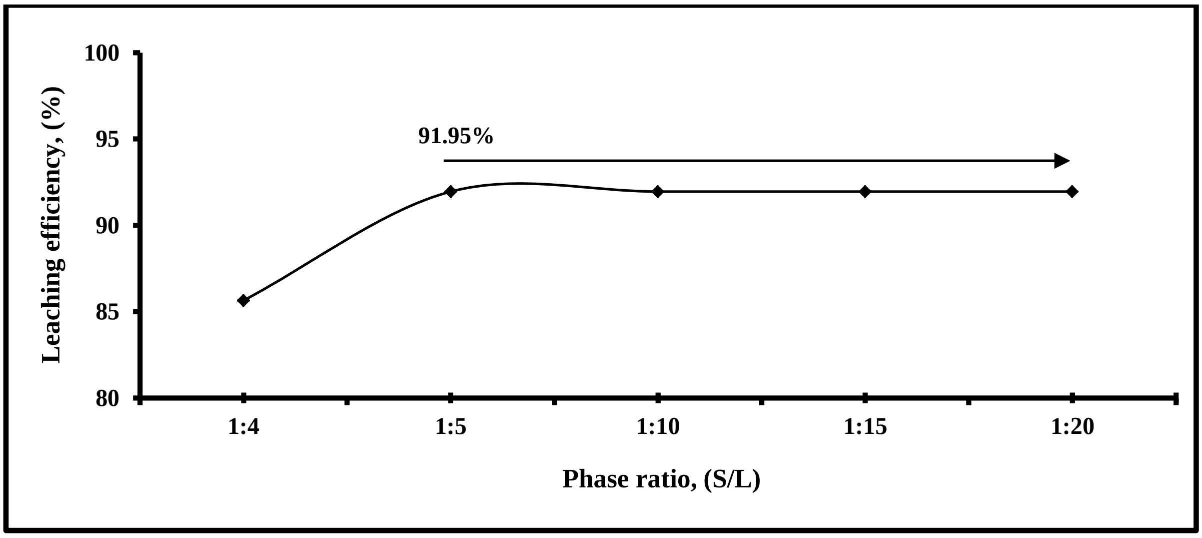

Fig. (3): Effect of phase ratio (S/L) on thorium leaching efficiency (%)

*Leaching conditions for thorium:*3.0 M H_2SO_4 acid, temperature (90^{o}C), and leaching time 1.0 hour.

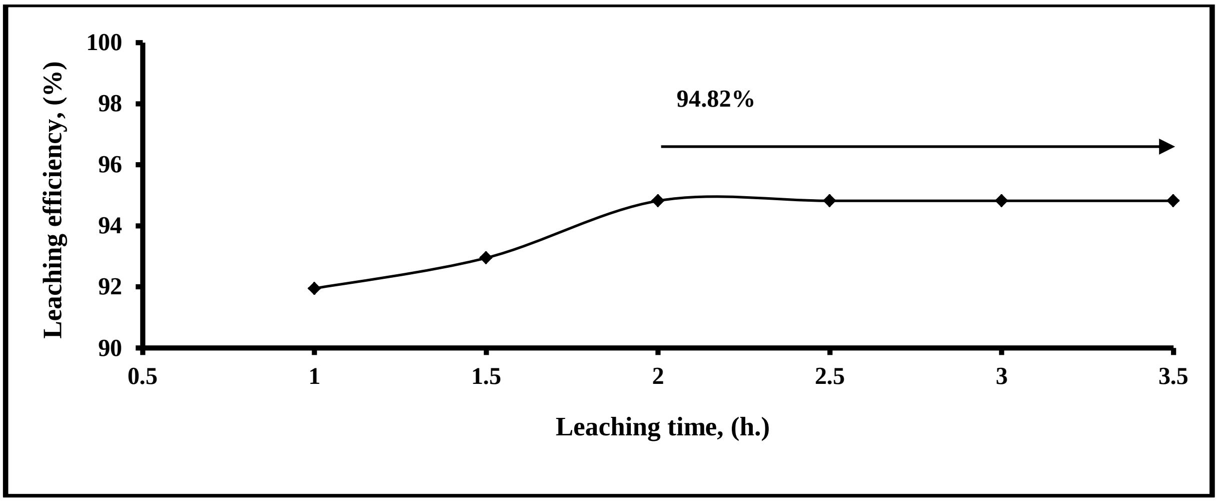

Fig. (4): Effect of leaching time on thorium leaching efficiency (%)

*Leaching conditions for thorium:*3.0 M H_2SO_4 acid, temperature (90^oC) and S/L: 1/5.

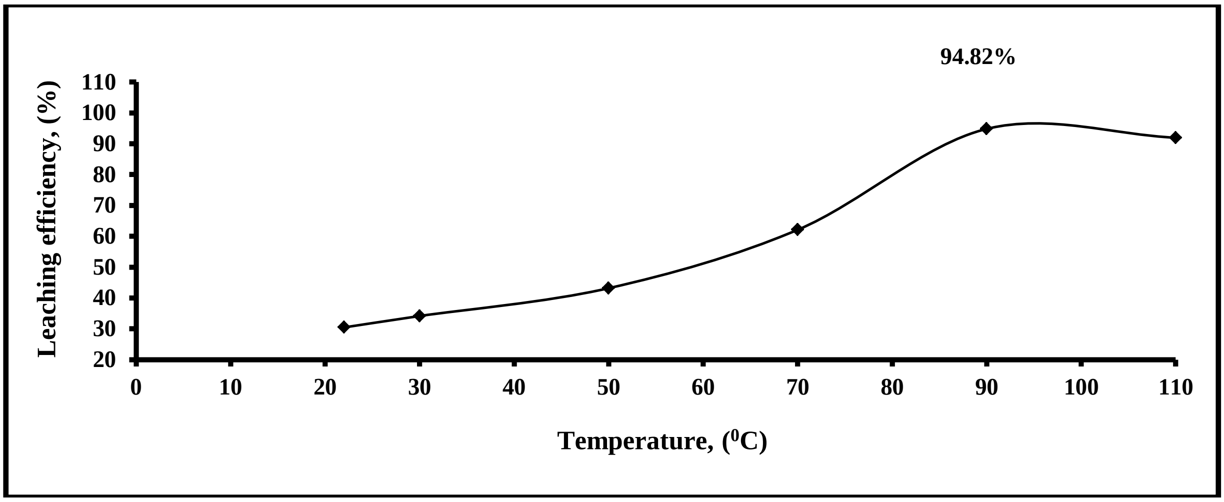

Fig. (5): Effect of temperature on thorium leaching efficiency (%)

Leaching conditions for thorium: 3.0 M H_2SO_4 acid, temperature (90^oC), S/L: 1/5 and leaching time 2.0 hour.

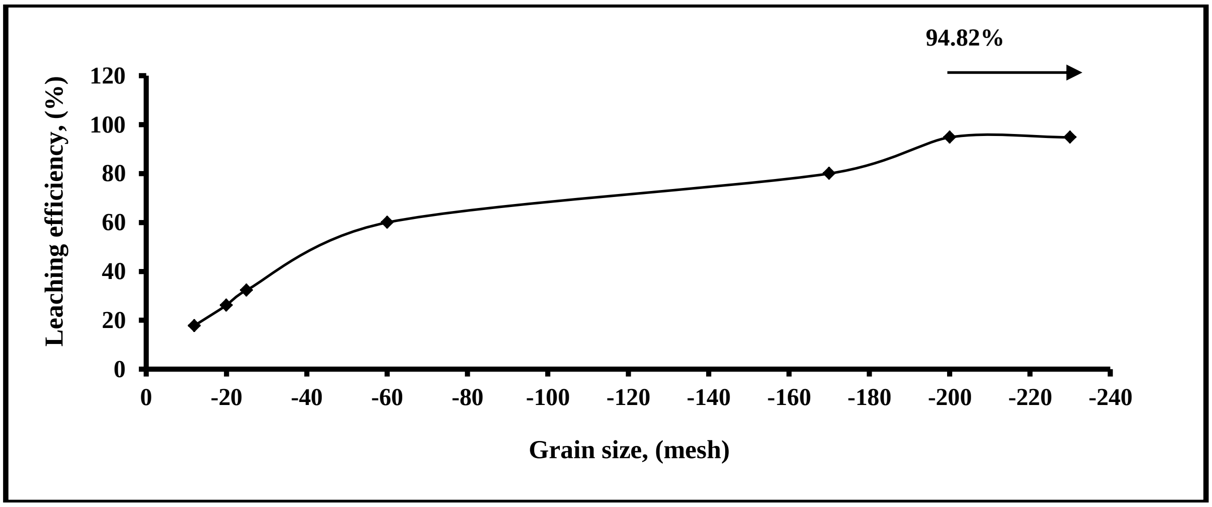

Fig. (6): Effect of grain size on thorium leaching efficiency (%)

Leaching conditions for thorium: 3.0 M H_2SO_4 acid, temperature (90^oC), S/L: 1/5 and leaching time 2.0 hour.

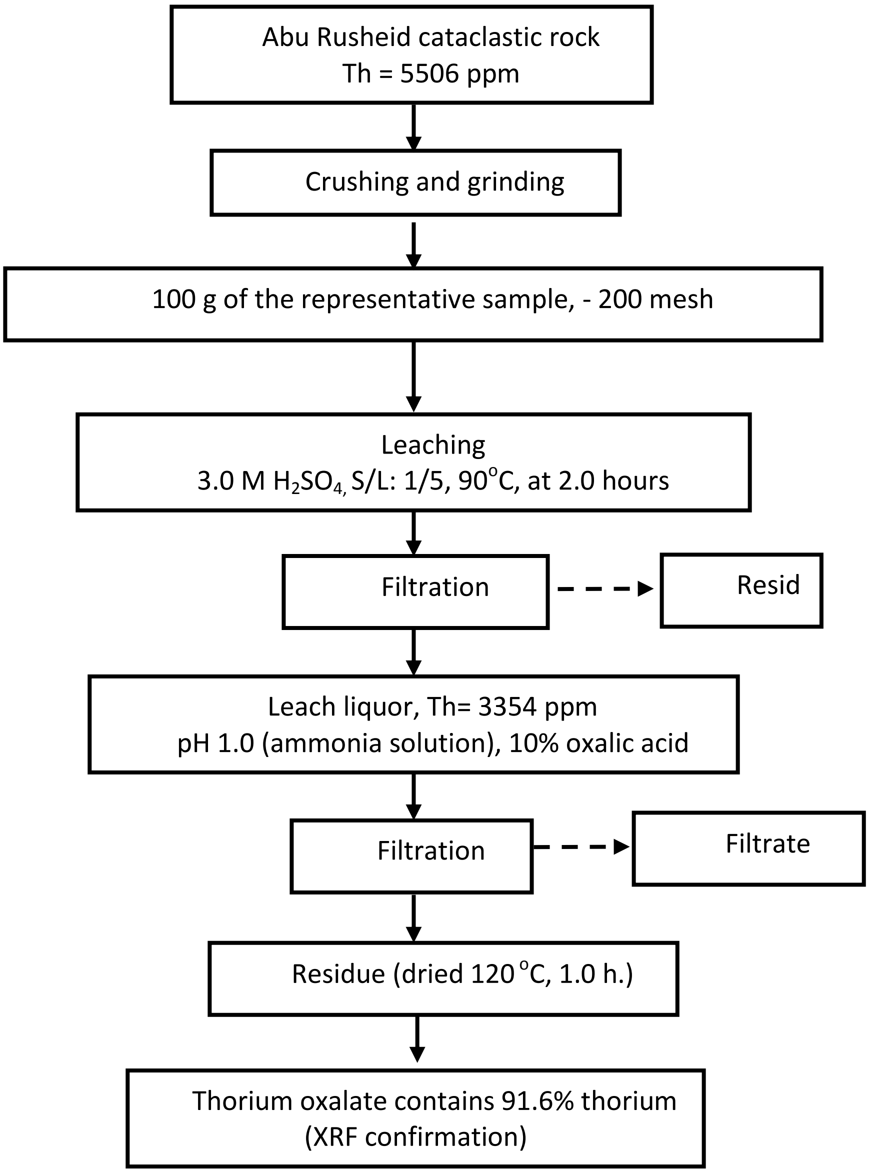

Fig. (7): Proposed flow sheet for leaching thorium with 3.0 M H_2SO_4 from the representative samples (cataclastic rocks), Abu Rusheid area, south Eastern Desert, Egypt

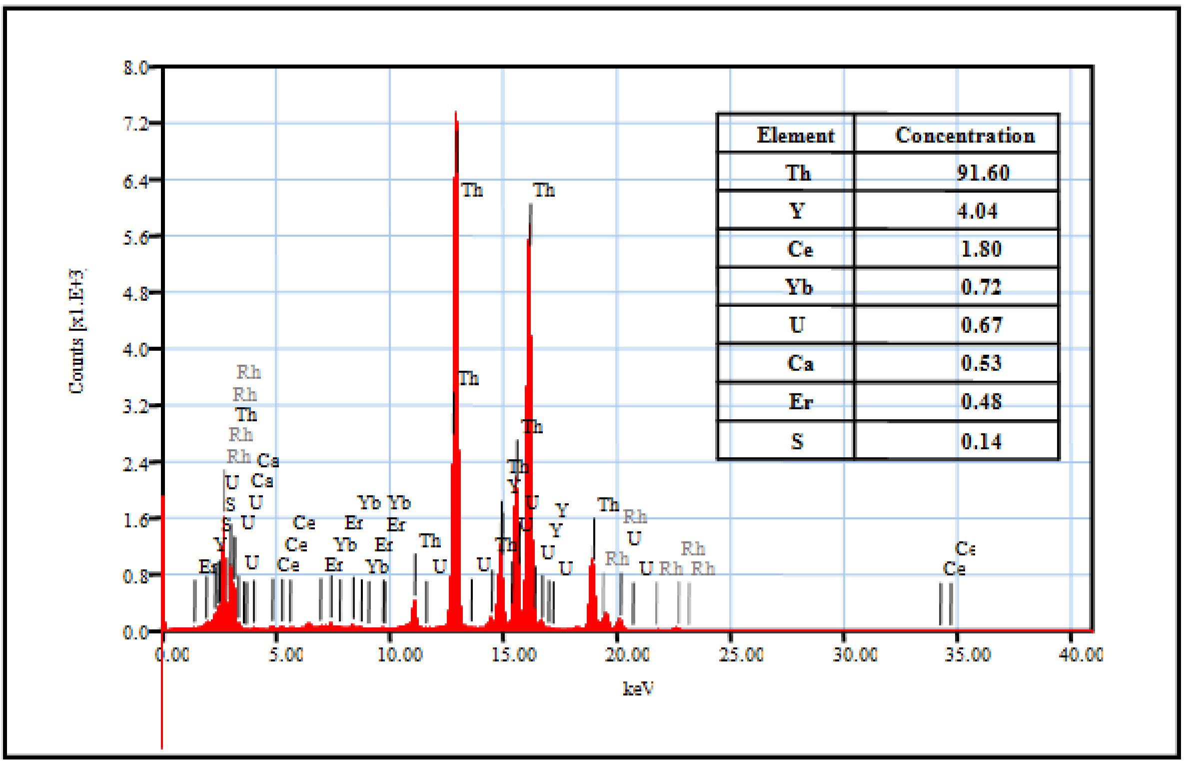

Fig. (8): XRF analysis of separated thorium from geological samples (cataclastic rocks), Abu Rusheid area, south Eastern Desert, Egypt

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