
CHARACTERISTICS AND LEACHABILITY OF ZINC AND RARE EARTHS FROM ABU RUSHIED ORE MATERIAL, SOUTH EASTERN DESERT, EGYPT

*EL-HAZEK, N. T., *AMER, T. E., **BADR, M. H., **SHAWKY, N. M. and *ZAKY, D. I.

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

** *El-Azhar University, Faculty of Science (Girls), Chemistry Department.*

Corresponding author: E-mail tarikamer59@hotmail.com

Abstract

A rare earth (REEs) and Zn ore material belonging to a poly-metallic mineralization of Abu Rushied area, Southern Eastern Desert of Egypt is subjected to mineralogical analysis and acid leaching. The former proved that both Zn (assaying 5%) and REEs (assaying 3.1%) are found adsorbed upon the iron oxide mineral goethite (equivalent to 15 % Fe₂O₃). Acid leaching studies using sulphuric acid defined the optimum conditions for dissolving about 94% of Zn and 92.5% of REEs. Besides being a powerful oxidizing agent and can create chloric acid, NaClO₃ was incorporated in the leaching process to decrease the required input sulphuric acid. In addition, NaClO₃ adequate Na₂SO₄ that could be used in the early precipitation of the (light REEs)LREEs as their double sulphates.

Introduction

An interesting rare metal mineralization has recently been discovered by the Nuclear Materials Authority at Abu Rusheid area situated in Wadi El Gemal Basin at about 45 km south west of Marsa Alam. This mineralization is mainly associated with basic lamprophyre dykes that are intruded in some shear zones that cut through cataclastic quartzo – feldspathic rocks (gneisses and granites). The rare metals in the mineralized occurrences include mainly Zn, U, REEs, Sn beside Th, Nb and Ta. Different alteration processes have accompanied these mineralizations; namely silicification, argillization, carbonatization and ferrugination. In some places, several economic minerals are actually manifested. According to **Ibrahim et al. (2002⁽³⁾ and 2004⁽⁴⁾) and Rashed (2005) ⁽⁸⁾**, the U minerals are essentially represented by minor pitchblende, uranophane, kasolite, torbernite and autunite beside the U-bearing mineral astrocyanite which contains also Cu and REEs. While Nb and Ta minerals are represented by columbite, tapiolite, betafite and fergusonite, the principal Zn minerals involve franklinite, chalcophanite and woodruffite. In addition, xenotime, allanite and monazite are sporadically present in some places.

The present work has indeed been oriented towards the investigation of some physical and hydrometallurgical characteristics of one of the mineralized occurrences associated with a lamprophyre dyke. For this purpose, a technological sample was properly collected and was first subjected to the necessary analysis to define the nature of the studied mineralization. The sample was found to assay 5.0% Zn and 3.1% total REEs.

Experimental

Analytical Procedures

Chemical composition of Abu Rushied ore material

A representative sample portion of the collected technological sample was properly prepared for complete chemical analysis beside the tenor of the economic metal values. The major oxides were analyzed using the **Shapiro and Brannock (1962)**⁽⁹⁾ rapid silicate analytical procedure. Zn was analyzed by the atomic absorption technique using a Unicam instrument model 969 auto gas box at the wavelength 213.86 nm. With respect to REE, it was analyzed by using UV-Visible Recorder Spectrophotometer model Shimadzu UV-160A at 650 nm using 1% ascorbic acid, formate buffer, 0.05% arsenazo-III and then adjusting the pH at 2.6 (**Marczenko, 1986**)⁽⁷⁾.

Mineralogical composition of Abu Rusheid ore material

To investigate the mineralogical composition of Abu Rushied ore material, heavy liquid separation procedure was applied using bromoform (sp.gr.2.84). The obtained heavy mineral fractions were investigated under the binocular microscope and some picked mineral grains were analyzed by X-ray diffraction technique (XRD). A Philips X-ray generator model PW1140/90 fitted with a diffractometer model PW1050/80 was used. The X-ray tube used was a Cu- target model PW2233/30 fitted with a Ni-filter and was operated at 40 Kv and 20mA.

In the meantime, the environmental scanning electron microscope (ESEM-EXL30 Philips type) coupled with an energy dispersive X-ray analyzer (EDX unit system) was also used to define the elemental composition of the investigated grains. This technique has also been quite beneficial in identifying the individual composition of the REEs content of the working ore material.

Leaching Procedures

H₂SO₄ acid agitation leaching procedures, (**Especial Issue 2004**)⁽¹⁾ (**IAEA, 2001**)⁽⁶⁾, (**Novak and Cermakova, 2002**)⁽⁵⁾, were applied under different conditions

to study the dissolution efficiency of Zn and REEs. In each experiment, a ground ore sample portion was mixed with the acid solution of known concentration in a certain solid/ liquid (S/L) ratio and the pulp was agitated for a period of time at a fixed temperature.

At the end of each leaching experiment, the slurry was filtered and washed; both the filtrate and washings were made up to volume. Proper aliquots of the latter were then analyzed for the leached Zn and \sum RE metal values to calculate their leaching efficiencies.

Results and Discussion

Nature of the Working Abu Rushied Ore Material

Chemical composition

The working technological sample was provided from a mineralized basic lamprophyre dyke. The wall zone of the latter is essentially composed of a quartzo-feldspathic rock. The chemical analyses of a lamprophyre dyke sample and that of the wall rock are given in table (1), with an assay of 5% Zn and 3.1% \sum REE for the working technological sample.

Table (1): Chemical composition of the lamprophyre dyke and the quartzo-feldspathic wall rock of Abu Rusheid rare metal occurrence (wt. %).

Oxides	Lamprophyre dyke	Quartzo-feldspathic wall rock
SiO ₂	52.01	56.01
TiO ₂	3.01	3.16
Al ₂ O ₃	16.55	13.01
Fe ₂ O ₃	15.00	14.40
MgO	1.50	0.06
CaO	0.62	0.06
Na ₂ O	0.49	0.40
K ₂ O	4.51	4.04
P ₂ O ₅	0.67	0.73
L.O.I.	2.20	7.78
Total	96.56	99.65

From this table, it is evident that SiO₂ is low in Lamprophyre dyke than in Quartzo-feldspathic wall rock while TiO₂, Fe₂O₃ and P₂O₅ are almost similar. It is significant to refer to the K-metasomatism reflected in relatively high K₂O content

in both rocks samples while Na is markedly depleted. On the other hand, the lamprophyre dyke is characterized by a relatively high MgO attaining 1.5% while in the wall rock, it is quite low (0.06%).

Mineralogical investigation

In a trial to identify any economic minerals and to investigate the possible concentration of one mineral or another in certain size fractions, a representative portion of the working technological sample was properly subjected to a sieve analysis. For this purpose, the sample portion was soaked in water and the aggregates left behind were then crushed and grounded. The obtained whole grind was screened using a set of sieves ranging from 600 down to 80 μm (25 to 190 mesh sizes). From the obtained results showing in table (2), it is clearly evident that the component minerals are quite hard where a coarse fraction exceeding 0.6 mm (+25 mesh size) represents about 73 weight %. The less hard fractions ranging in size from -25 to +190 mesh size amounted to only about 20 weight %.

Table (2): Size fractions of the ground representative portion of Abu Rusheid technological sample.

Grain Size		Wt. ,g	Wt. %
μm	mesh number		
+600	+25	1744	72.97
-600 +400	-25 +41	160.6	6.72
-400 +300	-41 +52	80.8	3.38
-300 +200	-52 +75	102.4	4.28
-200 +80	-75 +190	143.6	6.01
-80	-190	0.15	0.01

For heavy liquid separation, each of the four obtained size fractions ranged from -25 to +190 meshes was deslimed by thorough water washing followed by drying at 110°C. The four deslimed and dried size fractions were then subjected to heavy liquid separation using bromoform (sp. gr. 2.84) to upgrade any possible metal values in the heavy fractions and to eliminate any associated gangue minerals before mineralogical analysis. The weight and proportion of the obtained heavy liquid fractions are given in table (3).

Table (3): Bromoform heavy fractions of the sieved ground representative portion of Abu Rusheid technological sample.

Size fraction, μm		mesh number		Wt, g	Heavy Fractions	
					g	Wt. %
-600	+400	-25	+41	151.2	19.6	12.96
-400	+300	-41	+52	73.4	25.9	35.29
-300	+200	-41	+52	91.5	7.8	8.52
-200	+80	-75	+190	122.2	13.1	10.72

From this table, it was found that the heavy fraction recovered from the size range of -41 to +52 mesh exceeded about 35 % while those recovered from the other sizes were ranged from 8.5 to 12.9 %. Investigation of the obtained heavy mineral fractions of Abu Rusheid technological sample under the binocular microscope revealed that goethite or hematite is the main mineral constituent. The mineral ranges in color from brown to dark brown and is mainly found as massive aggregates with some surficial scattered mineralized spots of light colors. To a much lesser extent, some pyrite mineral grains have also been observed.

X-ray diffraction analysis

Some of the picked mineral grains from the present heavy fractions were subjected to X-ray diffraction analysis. Unfortunately, no economic mineral species corresponding to Zn and/or rare earth elements has been defined. The obtained diffraction data revealed the goethite pattern (FeO OH) as the principal mineral beside that of quartz and minor kaolinite (Table 4). The presence of the latter as a minor constituent is essentially due to prior desliming.

ESEM analysis

Failure to identify any economic Zn or REE mineral components, the present mineralogical study was directed towards elemental analysis using ESEM-EDX technique to determine the possible source for such valuable constituents. This technique is indeed a powerful tool in studying minute particle surfaces and their admixtures; a matter which deciphers important mineralogical characteristics.

Accordingly, some of the light and grey colored spots upon the goethite and some pyrite picked grains were subjected to EDX analysis. The bright and grey spots upon goethite revealed the chemical composition, summarized in table (5). The latter indicates enrichment in the REEs where they assay 53.37 and 42.47 %

respectively. In the meantime, the analyzed bright and grey spots were found to assay 2.02 and 6.49 % Zn respectively.

Table (4): X-ray diffraction data of goethite and the associated minerals in the heavy fractions separated from Abu Rusheid technological sample.

Sample		Goethite FeOOH ASTM # 17-536		Quartz SiO ₂ ASTM # 50490		Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ ASTM #60221	
d A°	I/I _o	d A°	I/I _o	d A°	I/I _o	d A°	I/I _o
4.18	30	4.18	100	--	--	--	--
3.55	12	--	--	--	--	3.58	100
3.34	100	3.38	10	3.34	100	--	--
2.70	10	2.69	30	--	--	--	--
2.45	30	2.452	25	2.458	12	2.50	80
1.82	24	1.799	8	1.817	4	1.78	40
1.72	22	1.721	20	1.67	7	1.67	50
1.56	12	1.564	16	--	--	--	--
1.54	14	--	--	1.541	15	1.54	10
1.50	6	1.509	10	--	--	1.49	100

Table (5): ESEM analysis of the REEs in the bright and grey spots upon the separated goethite mineral grain.

REE	Wt. %			REE, Distribution %
	Bright	Grey	Average	
La	12.11	9.46	10.79	22.4
Ce	2.82	1.92	2.37	4.9
Pr	4.93	3.77	4.35	9.04
Nd	13.34	10.80	12.07	25.1
Sm	1.51	1.12	1.32	2.7
Er	1.12	0.30	0.71	1.5
Yb	3.04	2.20	2.62	5.4
Y	14.86	12.90	13.88	28.9
Total wt.%	53.73*	42.47*	48.11	99.9

*Balance is represented by some major rock constituents including mainly Na, Ca, Al, Fe, and Si.

Calculation of the percent distribution of the REEs in the two analyzed spots revealed that La, Nd, and Y represent 22.4, 25.1 and 28.9 % i.e. over 75 % of the total REEs. However, Ce which is the most abundant REE in the earth's crust was found to assay only 4.9 %. Such a distribution of REEs is difficult to be present in one mineral species. So, these elements would most probably represent the products of chemical weathering of some REE mineral species and were later adsorbed to varying degrees upon available iron oxides. In this regard, the deficiency in Ce might be due to its oxidation in the prevailing weathering conditions and thereby was early deposited elsewhere.

Early, the studied area proved the presence of some important REEs, Zn and U-bearing minerals. Thus, **Ibrahim et al. (2002⁽¹⁾ and 2004⁽²⁾) and Rashed (2005)⁽³⁾** have reported the presence of the following minerals:

-Zn- Mn oxide minerals;

- i. Franklinite (Zn, Mn²⁺, Fe²⁺) (Fe³⁺, Mn³⁺) O₄.
- ii. Woodruffite (Zn, Mn²⁺) Mn₃⁴⁺ O₇. 12 H₂O.

-REE-U- bearing minerals;

- i. Astrocyanite [(Ce Cu₂ (RE)₂ UO₂ (CO₃)₅ OH₂ 1.5 H₂O)].
- ii. Fergusonite (Nb, Y, Ta, U, Al, Mg, REE) O₄, beside minor pitchblende and some secondary U minerals (uranophane, kasolite, torbernite and autunite).

-REE minerals;

- i. Xenotime YPO₄.
- ii. Monazite (Ce, La, Th) PO₄.
- iii. Allanite (Ce, Ca, Y) (Al, Fe)₃ (SiO₄)₃. OH.

The difficulty to identify such minerals in the technological sample used in the present work might be due to their extremely minute nature. Alternatively, the corresponding elements have been leached from these minerals elsewhere and were then adsorbed on the goethite surface.

Chemical testing

To reveal the association of the present economic metal values with goethite, a selective dissolution test for goethite was performed. Conditions of this test involved the following leaching conditions:

Acid	:	Conc. HCl
S/L Ratio	:	1/2

Leaching time : 2 hrs
Leaching temp. : 100°C

The obtained leaching results indicated that goethite was completely dissolved together with the associated economic metal values; namely REEs and Zn constituents.

From the foregoing mineralogical investigation, it could be stated that a physical upgrading process should be applied before chemical processing. In this regard, simple tabling would separate apart the heavy goethite fraction (economic) and the light fraction (gangue) in a manner to enrich the economic metal values in the former.

Results of Acid Leaching of Abu Rushied Ore Material

The relatively high content of SiO₂, Al₂O₃ and Fe₂O₃ (Table1) suggest acidic leaching. In general, acidic leaching process depends largely on a number of factors which have to be carefully studied in order to obtain the optimum recovery. These factors include mainly acid concentration, agitation time, leaching temperature, solid / liquid ratio and oxidation state. In the present work, acid agitation leaching tests were performed using H₂SO₄ acid upon 25 g ore fractions ground to -200 mesh size.

Effect of H₂SO₄ concentration

It was studied between 100 and 400 g/l H₂SO₄, while fixing the other factors at -200 mesh size ore finesses, 6 hours (hrs) agitation time, 100°C leaching temperature and 1:2 solid-liquid (S/L) ratio. The leaching efficiencies of REEs and Zn, Fig. (1), indicated that Zn is relatively more easily leached than the REEs where at 100 and 200 g/l acid concentration, the leaching efficiency of the former attained 52.4 and 80.3 % respectively, while for the latter it reached only 11.6 and 33.1% respectively. Increasing the acid concentration to 300 and 400 g/l improved greatly the REEs leaching efficiency to 84.8 and 94.8 % respectively. At these acid concentrations, 87.1 and 98.2% Zn leaching efficiencies have been realized. Using 400 g/l acid concentration at a solid/liquid ratio of 1:2 would be equivalent to 800 kg acid / Ton ore which is relatively high. This can indeed be due to the intimate association of the studied metal values (REEs and Zn) with goethite and the relatively weak solubility of Fe³⁺ in sulfuric acid solutions.

Effect of leaching time

It was studied in the range of time from 2 to 8 hrs. The other leaching conditions were fixed at H₂SO₄ concentration of 300 g/l, -200 mesh size ore, at 100°C leaching

temperature and using 1:2 S/L ratio. The leaching efficiencies, Fig. (1), revealed that extending the leaching time to 8 hrs at 300 g acid/l was able to almost leach the same REEs amount obtained at 400 g/l for 6 hrs, while the Zn leaching efficiency was only 90.4%. Complete Zn leaching with about 95% REEs leaching requires an acid concentration of 400 g/l when time is 6h.

Effect of leaching temperature

It has a great effect upon the acid leaching efficiency for both REEs and Zn, within the range from 25 up to 100 °C. The other leaching conditions were fixed at -200 mesh size ore material, 300 g/l H₂SO₄ acid concentration for 6 hrs agitation time and at 1/2 S/L ratio. The obtained data, Fig. (1), revealed actually the importance of high temperature to obtain reasonable leaching efficiencies of the REEs. Working at room temperature under the mentioned conditions did not leach more than 28.7% only of REEs while that of Zn amounted up to 68.2%. Increasing the leaching temperature to 50°C has increased the leaching efficiencies of the REEs to only 32.3%. Further increasing the leaching temperature to 60 and 100°C increased the leaching efficiency of the REEs up to 62.4 and 84.8% respectively, while that of Zn has only steadily increased to 81.6 and 87.1% respectively. It can thus be mentioned that while acid concentration is important for Zn leaching, the leaching temperature is quite important for leaching the REEs.

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

The effect of the solid /liquid ratio upon REEs and Zn leaching efficiencies was studied between 1/2 and 1/5. In these experiments, the fixed leaching conditions involved -200 mesh size ore material, 300 g/l H₂SO₄ concentration for 6 hrs agitation time at 100 °C as leaching temperature. Under these conditions, the acid input would be varied between 600 and 1500 kg/t ore. From the obtained leaching efficiencies, Fig. (1), it was found that beyond 1/2 S/L ratio, only slight steady increase in the leaching efficiencies of both REEs and Zn has been achieved. Accordingly, a solid ratio of 1/2 would be considered as optimum at which the leaching efficiency of REEs and Zn attained 84.8 and 87.1% respectively. Improving the latter could be realized by extending the leaching time beyond 6 hrs.

Effect of sodium chlorate addition

From the foregoing leaching results involving high H₂SO₄ acid concentration, it was thought that the addition of NaClO₃ would improve the leaching efficiencies of the metal values. NaClO₃ which besides being powerful oxidizing agent might reduce H₂SO₄ consumption through creating chloric acid (HClO₃). The effect of

NaClO_3 /ore amount ratio upon REEs and Zn dissolution was thus studied over a range from 5% to 25% at the following conditions: -200 mesh size ore material, 300 g/l H_2SO_4 concentration, 100°C leaching temperature, 6 hrs agitation time and 1/2 S/L ratio.

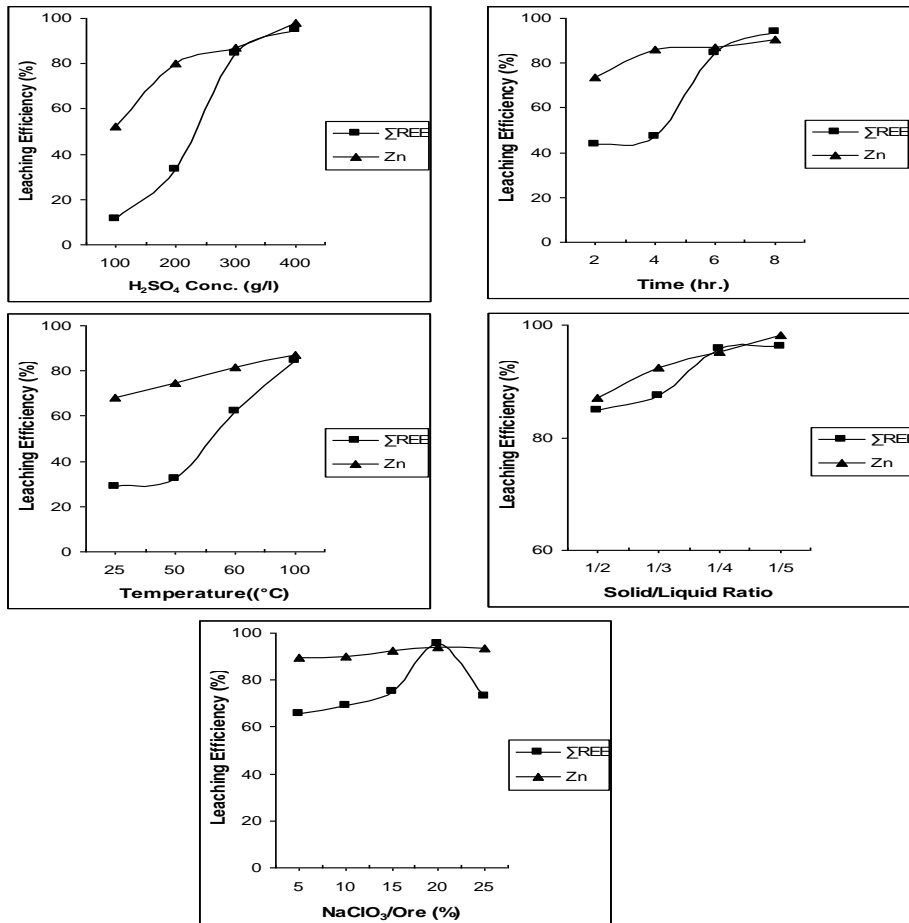


Fig. (1): Results of agitation leaching of Abu Rushied ore material under various conditions.

From the leaching efficiencies, Fig.(1), it is clear that increasing the amount of NaClO_3 addition results in increasing the leaching efficiencies of the valuable metals. The highest REEs (95.4 %) and Zn (94.1 %) leaching efficiencies were obtained when adding 20% NaClO_3 . Comparing these results with the corresponding leaching efficiencies obtained by 300 g H_2SO_4 /l in absence of NaClO_3 , gave that the REEs and Zn dissolution have increased from 84.8 and 87.1 % to 95.4 and 94.1 %

respectively. Further increasing the latter to 25 % of the input ore has seriously decreased the leaching efficiency of the REEs to 73.2 %. This might be due to excessive H_2SO_4 consumption in creating the $HClO_3$. However, this acid should have dissolved more iron and in turn REEs. Accordingly, it can be concluded that partial formation of insoluble double RE sulfates due to increased Na_2SO_4 would interpret the decreased soluble REEs.

In this regard, trials to decrease the used acid concentration (300 g/l) in presence of the same amount of $NaClO_3$ were attempted. Two leaching experiments were conducted at acid concentrations of 100 and 200 g/l H_2SO_4 and using 20 % $NaClO_3$ under the above mentioned leaching conditions at 6hrs.

From the obtained results given in table (6), it is clear that the leaching efficiencies of REEs and Zn at 100 g H_2SO_4 /l have been greatly decreased to 70.6 and 76.1 % respectively. Increasing the acid concentration to 200 g/l has however increased the leaching efficiencies of REEs and Zn to 92.5 and 93.9 % respectively. So the, presence of $NaClO_3$ has resulted in saving the input sulfuric acid from 400 to 200 g/l.

Table (6): Effect of H_2SO_4 concentration in presence of 20 % $NaClO_3$ on the leaching efficiencies of REEs and Zn

H_2SO_4 Conc.(g/l)	Leaching Efficiency (%)	
	REEs	Zn
100	70.6	76.1
200	92.5	93.9

From the above studied leaching factors, it can be concluded that the optimum leaching conditions for dissolving the metal values of Abu Rusheid ore material (REEs and Zn) can be summarized as follows:

Grain size	: -200 mesh
Acid concentration	: 200 g/l
Leaching time	: 6 hrs.
Leaching temperature	: 100 °C
Solid/liquid ratio	: 1/2
$NaClO_3$ /ore wt%	: 20

Conclusions

The obtained mineralogical results of Abu Rushied Zn-REE mineralized locality suggested its similarity with the Chinese REE- ion adsorption ore (Jiangxi clay). (CAEA, 2003)²In both types, Ce content is quite low while La, Nd and Y are relatively enriched. Due to excessive sulphuric acid consumption for leaching these metal values, $NaClO_3$ as a powerful oxidizing agent was incorporated. Besides

creating chloric acid, to help the leaching process, it was used for precipitating the LREEs as their double sulphate. Study of the various relevant leaching factors indicated that for dissolving about 94%Zn and 92.5% REEs, the optimum conditions upon an ore grind to -200 mesh size should involve a sulphuric acid concentration of 200 g/l in a solid/ liquid ratio of 1/2 for 6 hrs at 100°C and using 20% ore weight of NaClO₃.

Finally, in the light of the present study it could be recommended that, a physical beneficiation process should be applied before chemical processing. Simple tabling would separate apart the heavy goethite fraction (economic) and the light fraction (gangue) to enrich the economic value of Abu Rusheid ore material.

Acknowledgments

The authors would like to express their deep gratitude to Prof. M. E. Ibrahim for providing the technological sample and helping in ESEM analyses.

References

1. Acta Metallurgica Slovaca, 10, (2004), Special Issue,(96-106)
2. AEA (2003), Chinese Atomic Energy Agency, Personal communication.
3. IBRAHIM, M. E., SALEH, G. M., ABD EL NABY, H. H., AMER, T. E., MAHMOUD, F.O., ABU EL HASSAN, A. A., IBRAHIM, I. H., ALI, M. A., AZAB, M.S., RASHED, M. A., KHALEL, F. M. AND MAHMOUD, M. A.,(2002): Uranium and Associated Rare Metals Potentialities of Abu Rusheid Brecciated Shear Zone I, south Eastern Desert, Egypt. (Internal Report).
4. IBRAHIM, M. E., SALEH, G. M., ABD EL NABY, H. H., AMER, T.E., MAHMOUD, F. O., ABU EL HASSAN, A. A. IBRAHIM, I. H., ALI, M. A., AZAB, M. S., RASHED, M. A., KHALEL, F. M. AND MAHMOUD, M. A.,(2004): Uranium and Associated Rare Metals Potentialities of Abu Rusheid Brecciated Shear Zone I, south Eastern Desert, Egypt. (Internal Report).
5. J. NOVAK and H. CERMAKOVA, proceedings of Algoritmy, (2002), Conference on Scientific computing pp. 207-214.
6. Manual of acid in situ leach uranium mining technology International Atomic Energy Agency(IAEA)August (2001)
7. MACZENKO, Z., (1986): "Separation and spectrophotometric determination of elements" Eills Hrwood, Ltd. Pupl., New York,
8. RASHED, M. A., (2005): "Geologic Studies on a New Occurrence of Nuclear Materials in Abu Rusheid Area, SE. Desert, Egypt", Ph.D. Thesis, Fac.Sc. Damietta, El Mansoura Univ., Egypt.
9. SHAPIRO, I. and BRANNOCK, W. W. (1962): Rapid Analysis of Silicate, Carbonate and Phosphate Rocks, USGS Bull. 1144- A.