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Successive Recovery of Uranium and Valuable Elements from Mineralized Dolostone, Gabal Alluga, Southwestern Sinai, Egypt

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ABSTRACT

The present work was conducted in two stages of leaching processes, stage one, an alkaline leaching of uranium and zinc from Alluga rock sample, Sinai area, using sodium hydroxide solution. The leaching conditions, including sodium hydroxide concentration, stirring time, temperature and liquid-solid ratio were studied. The optimum conditions were sodium hydroxide concentration (5mol/L), stirring time (180 min), liquid-solid ratio (4/1) and temperature (70°C), the leaching efficiency was about 91.2% for uranium and 93.5% for zinc.

The second stage took place on the spent residue left behind for leaching the rare earth elements using mixture of sulfuric acid and magnesium sulfate solution, the optimum conditions were achieved at sulfuric acid concentration (1mol/L), magnesium sulfate concentration (0.8 mol/L), temperature (200° C), stirring time (120 min), and liquid-solid ratio (3/1), under these conditions leaching efficiency of rare earth was 96.5%. The experimental leaching kinetic data of uranium, zinc and rare earth elements were well identified by a shrinking core model with diffusion control through a product layer, with apparent activation energies of 8.74 KJ/mol for uranium, 21.3 KJ/mol for zinc and 18.26 KJ/mol for rare earth elements.

Key Words: Recovery, Uranium, Zinc, REEs, Kinetic modeling, Shrinking core models

Introduction

Abu-Thor locality of west central Sinai is one of the most important areas that are related to carbonate- rich ores in Egypt [1]. It was first subdivided by Omara and Conil [2] into three regions, called: the Lower dolomitic, the Middle dolomitic limestone and the Upper dolomitic region. The latter varies in thickness from 18 m at W. Khaboba to 2 m at W. Alluga. This region is mainly consists of thickly to thinly bedded pinkish brown, hard compact crystalline dolostone which is cliff and step forming. These authors concluded that both Alluga and Abu Thor localities are of good uranium potentiality and in which some secondary uranium minerals and other minerals of Cu, V, REE are existed besides the Fe-Mn deposits in different concentrations. The main characteristic feature is the high trace element contents such as Zn ranges from 131 to 2192 ppm, Pb from 308 to 1764 ppm, Ni from 13 to 14674 ppm and Cu from 150 to 1432 ppm.

In the study area, the identified Zn, REEs and U-bearing minerals include mainly: Ankerite [Ca(Fe.Mg.Mn)(CO$_3$)$_2$], paratacamite (Cu.Zn)2(OH)3Cl, Rosasite [(Cu.Zn)$_2$(CO$_3$)(OH)$_2$],Monazite[(Ce.La)PO$_4$],ZippiteK$_4$(UO$_2$)(SO$_4$)$_3$(OH)$_{10}$.4H$_2$O, the uranium and REEs concentrations are mainly adsorbed upon some of the minerals in the host dolostone and which

essentially include; calcite CaCO$_3$, quartz SiO$_3$, hematite Fe$_2$O$_3$, besides variable amounts of rutile TiO$_2$, jarosite KFe(OH)$_6$(SO$_4$)$_2$ [3].

Hydrometallurgically, some studies have achieved to leach uranium, zinc and rare earth elements from a comparative Um Bogma ore materials, the kind of leaching whether be acidic   [4-8] or alkaline [9-10], depends upon the nature of the host rock, type of the gangues, availability and economic cost of reagent, and solubility of undesirable impurities, while, the host rock is acid consuming in nature because of the high carbonate content, the alkaline route is preferred for some features, that are high selective, low corrosive, avoid excessive acid consumption and insoluble of undesirable metals, such as iron and silica [11,17].

The aim of this work is to obtain the essential experimental data to improve a leaching process for uranium, zinc and rare earth elements from dolostone sample, Gabal Alluga, Southwestern Sinai, Egypt in a manner to keep away from the excessive acid consumption due to the existence of a relatively excessive carbonate content that attains 30%. Accordingly, a technological sample of dolostone assaying 1000 ppm U, 915 ppm Zn and 2000 ppm REEs has been collected. Then the study was directed to

explain the potentiality of recovery of the metals value successively, and in order to an improved understanding of the chemical reaction mechanism that is involved in the dissolution of these minerals that have an effect on the leaching process, kinetic studies have been achieve.

Materials and methods

Mineralogical characterization of the ore

Samples of the working dolostone ore were collected from different areas located in the upper member of Um Bogma formation, and the ore sample was firstly crushed then ground to –200 mesh size before quartering, then ,the ore was analyzed for the major element oxides besides the tenor of the economic metal values using the rapid silicate analytical procedure [18]. For the determination of the loss of ignition, special sample portions were used to estimate the weight loss at various temperatures.

Leaching procedure

Alkali leaching of uranium and zinc

The experimental dissolution processes were carried out to optimize the leaching relevant parameters for uranium and zinc by using sodium hydroxide, various sequences of leaching procedures were carried out. In these experiments, suitable volumes of sodium hydroxide

solutions with different concentrations were prepared as leaching agent and suitable weights of the working ore sample, were ground to -200 mesh size, then mixed according to the favored liquid to solid (L/S) ratio, with a certain speed rate at the favored temperature. The slurry was then stirred with different stirring times. The samples were filtered and the residue left behind was washed with distilled water the liquid phase were analyzed with the titration method against ammonium metavanadate for uranium content, while for the zinc, an atomic absorption spectrometer was used Mathew[19]. And the content of the rare earth elements, were determined spectrophotometrically. The leaching efficiencies of uranium, zinc, and rare earth elements were calculated according to the following equation:

$$R = \frac{C_M \text{ (g/L)} \times V \text{ (L)}}{C_o \text{ (g/L)} - M \text{ (g)}} \times 100 \qquad (1)$$

where: R is the leaching efficiency of uranium, zinc and REE(%), C_M is the concentration of the leached metal ion, V is the volume of the leach liquor, C_o is the original metal ion concentration , and M is the mass of the ore sample.

Acidic leaching of REEs

Several acidic leaching experiments were performed for recovering REEs from

the spent ore residue free from uranium and zinc by using sulfuric acid/magnesium sulfate mixture. Factors controlling leaching process such as; sulfuric acid/magnesium sulfate concentrations, effect of temperature, effect of S/L ratio and effect of stirring time were studied. At the end of each leaching experiment, the obtained aliquot filtrate was analyzed for REEs to calculate their leaching efficiency.

Analytical procedures

The collected working sample of dolostone has firstly been exposed to complete analysis for its major components using wet procedure [20]. In this procedure, an alkaline solution is prepared for SiO_2 and Al_2O_3 analysis and another acid solution for the determination of oxides MgO, CaO, K_2O, Na_2O , total iron, etc. However the analysis of metal ions, including Zn, V, Cu, Ni, Pb were performed by using an atomic absorption spectrometer (AAS) Unicam 969, England and the X-ray fluorescence technique. Uranium was determined by titration against ammonium meta vanadate, while for rare earth elements were determined spectrophotometerically, andEDX analysis was used for qualitatively determination of the purity of the final precipitates of the U , Zn and rare earth elements.

Results and Discussion

Chemical Composition

The collected sample of dolostone ore, was exposed to a complete chemical analysis, the results are shown in tables (1) and (2), that show clearly the content of SiO_2 is 25.42 %, Al_2O_3 is 3.62 %, and Fe_2O_3 is 4.16%, and also show the relatively high CaO and MgO contents attaining about 19.41 and 7.3 % respectively, which is a characteristic of the dolostone ore material. In practice, because of such high carbonate content that attained 33.95 %, the choice of alkaline leaching of both uranium and zinc in order to avoid high consumption of acid in traditional acidic leaching needed to be considered. While for the analysis of some trace elements, the working sample was subjected to X-ray fluorescence for the analysis of some trace elements. As shown in table (2), uranium, zinc, and rare earth elements, were existed in sensible concentrations, 0.1%, 0.0915 %, 0.20%, respectively.

Table (1): The chemical analysis of the working dolostone technological ore sample

Component	wt.%	Component	wt.%
SiO_2	25.42	K_2O	0.42
TiO_2	0.15	P_2O_5	0.16
Al_2O_3	3.62	SO_4	2.07
Fe_2O_3	4.16	*L.O.I .	33.95
MnO	3.33	Cl^-	0.70
MgO	7.30	**Total**	**100.7**
CaO	19.41		
Na_2O	0.04		

 *L.O.I. = loss on ignition at 1000°C

Table (2): XRF analytical results of the interesting trace elements in the working dolostone technological ore sample .

Trace element	ppm	Trace element	Ppm
Ba	1311	Pb	159
Cu	202	Cr	190
Ni	70	Sr	801
Nb	34	Ga	40
Zn	915	Zr	330
Rb	102	*U	1000
Cd	13	Co	24
Y	200	*∑ REEs	2011

 *∑ REEs analysis using spectrophotometer technique (Merczenko , 1986).

 *Uranium analysis using the oxidimetric titration method

Results of Uranium and Zinc Leaching

Effect of sodium hydroxide concentration

The effect of sodium hydroxide concentration upon the dissolution efficiencies of uranium and zinc were studied between 1.25 mol/L and 7.5 mol/L , the other dissolution factors were fixed at -200 mesh size ore for 3 hrs stirring time in a liquid-solid (L/S) ratio of 4/1 at 70°C. The obtained uranium and zinc dissolution efficiencies shown in figure (1) demonstrate

that the optimum sodium hydroxide concentration is 5 mol/L at which the uranium leaching dissolution has attained up to 91.2 % and the zinc leaching efficiency up to 93.5%, with further increase in sodium hydroxide concentration, has an adverse effect on the leaching efficiencies of uranium and zinc, this decrease is most probably due to the presence of more OH⁻ to a point at which diuranate would precipitate and also may be attributed to dissolution of many undesired impurities from the ore. Therefore, a 5 mol/L concentration of NaOH was thus considered as the optimum value.
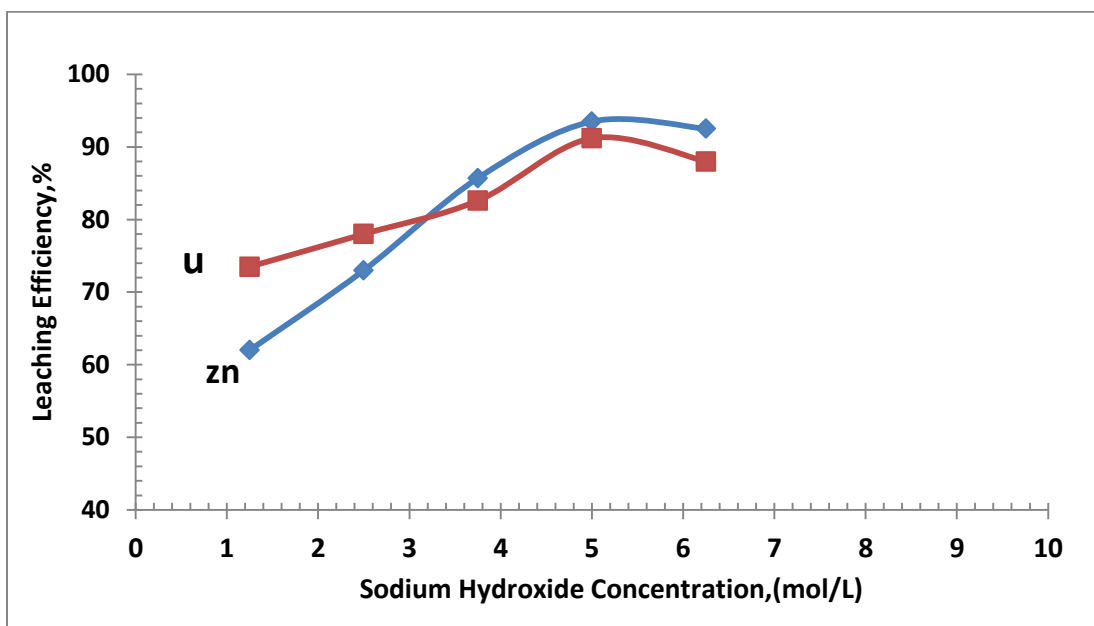
Figure (1): The effect of sodium hydroxide concentration upon the uranium and zinc dissolution efficiencies.

Effect of Leaching Time

The effect of the leaching time upon the uranium and zinc dissolution efficiencies by NaOH from the working sample was examined in a range varied from 30 to 240 min, the other dissolution conditions were fixed at NaOH concentration of 5 mol/L on an ore sample ground to -200 mesh size, at 70C temperature and using a L/S ratio of 4/1. From the results of dissolution efficiencies obtained in figure (2) it is revealed that a high uranium and zinc leaching efficiency exceeding 91.2 % and 93.5 % respectively occurs within 180 min. Therefore, it can be concluded that the preferred contact time for the highest uranium and zinc dissolution was 180 min.
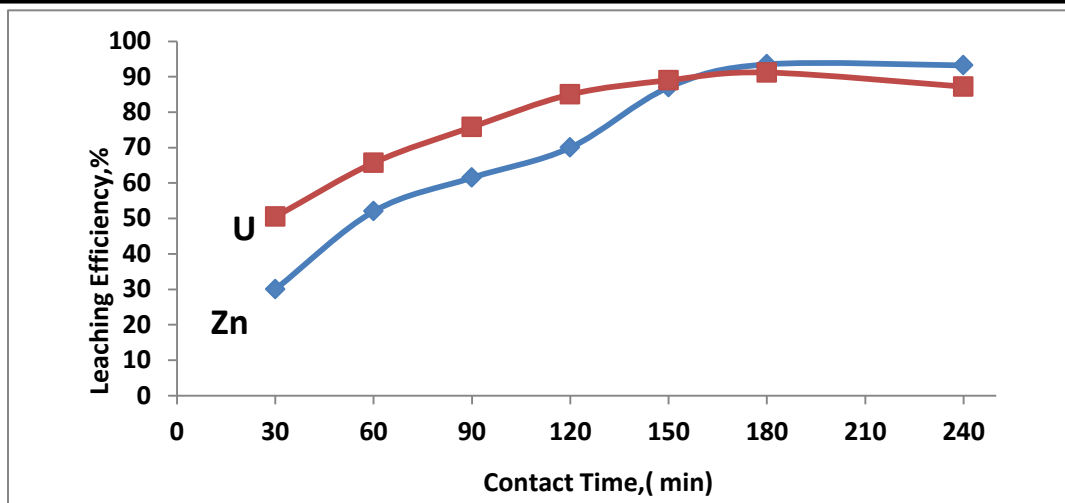
Figure (2): The effect of time upon the uranium and zinc dissolution efficiency.

Effect of Liquid/Solid Ratio

The effect of liquid/solid ratio upon the uranium and zinc leaching efficiencies were studied between 1/1 and down to 5/1. These experiments were conducted under fixed leaching conditions involving -200 mesh size ore material, 5 mol/L NaOH concentration for 180 min contact time at 70°C temperature. From figure.(3), it was found that beyond a L/S ratio of 4/1 no increase in the uranium or zinc leaching efficiencies were achieved. Therefore, a liquid/solid ratio of 4/1 could be considered as the best ratio at which the leaching efficiencies of uranium and zinc attained 91.2% and 93.5 % respectively under the previous   optimum   conditions.
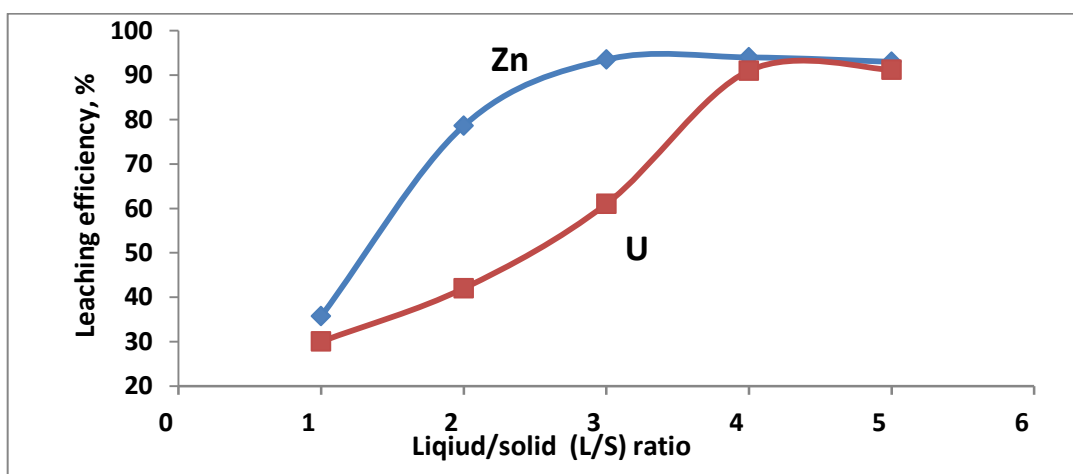
Figure (3): The effect of the L/S ratio upon the uranium and zinc dissolution efficiency

Effect of Temperature

The effect of temperature upon uranium and zinc leaching efficiencies was examined under temperature range between 30° C and 70° C. These experiments were performed under fixed leaching conditions involve -200 mesh size ore material, 5 mol/L NaOH concentration for 180 min. contact time and liquid/solid ratio 4/1. From the obtained leaching efficiencies shown in

Figure (4), it is clearly shown that, when the temperature increased from 30◦C to 70◦C, the leached uranium increased from 87% to 91.2%. It is also was found that the zinc leaching efficiency increased from 59.5 % to 93.5 %. Thus, it can be concluded that a high temperature would be necessary for the acceleration of the reaction of hydroxyl ions with uranium and zinc in the alkaline dissolution.
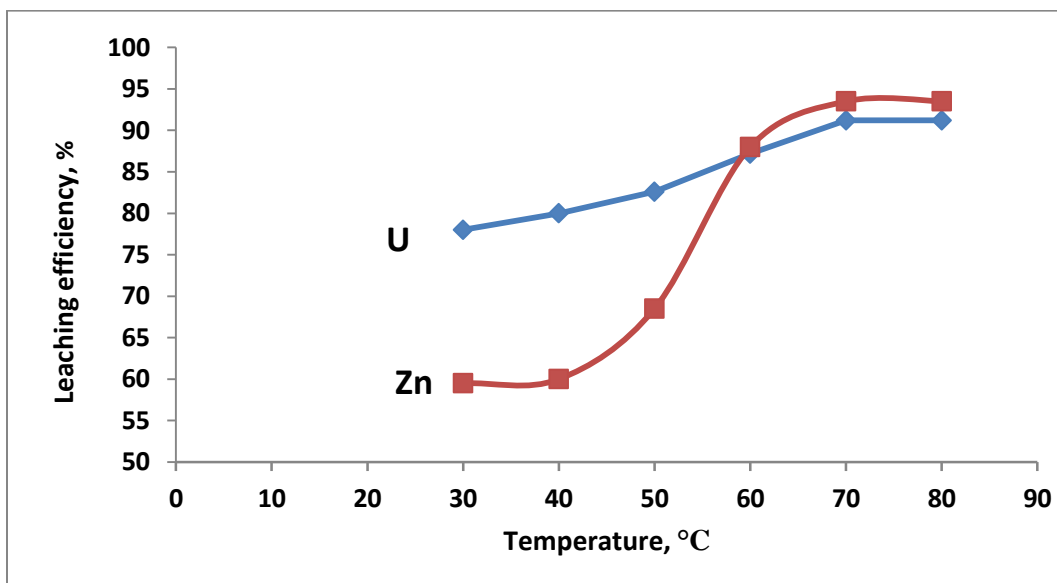

Figure (4): The effect of temperature upon the uranium and zinc dissolution efficiency

Leaching Kinetics Results of Uranium and Zinc

Leaching kinetics is of a great importance in the economics of the leaching processes of valuable and precious metals. Wang et al. [21], described the reaction process in sodium hydroxide solution as follows:

(i) Transfer of NaOH molecules from the bulk of solution to the surface of the solid

(ii) Diffusion of NaOH molecules through the solid layer to the reaction surface of the unreacted core,

(iii) Reaction between NaOH molecules and ore at the reaction surface of the unreacted core

(iv) Diffusion of the products from the surface of the unreacted core through the solid layer to the outer of the solid layer

(v) Transfer of the products from the surface of the solid to the solution bulk.

The leaching process is a typically solid-liquid heterogeneous reaction [22] and its corresponding kinetics follows the unreacted shrinking core model that was detailed by Lid- dell [23]. The leaching kinetics process could be described by the following equations:

When diffusion through the fluid film controls the process**:**

$$1 - (1 - x)^{2/3} = K_d\,T \qquad (2)$$

When diffusion through the solid product controls the process:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = K_d\,T \qquad (3)$$

When surface chemical reaction controls the process:

$$1 - (1 - x)^{1/3} = K_c\,T \qquad (4)$$

Where X, is the conversion fraction that reacted, T, is the time of reaction (min), K_d, is the rate constant for diffusion controlled process, (min^{-1}) and K_c, is the apparent rate constant for chemical reaction (min^{-1}).

By graphing the mentioned equations (2), (3) and (4) it was realized that the results did not match equations. (2,4). The best match for the results from 0 min to 180 min, at different temperatures was equation (3), a diffusion through the solid product controlled kinetic equation.The relationships between equation $1 - 3 (1 - X)^{2/3} + 2 (1 - X)$ and the time of leaching for both of uranium and zinc at different temperatures are plotted in Figures (7) and (8), it was showed that R^2 values for all the straight lines are greater than 0.9. This explains that the linear relationship is significant and suggests that the rate of leaching for uranium and zinc from dolostone working ore is diffusion through the solid product controlled.
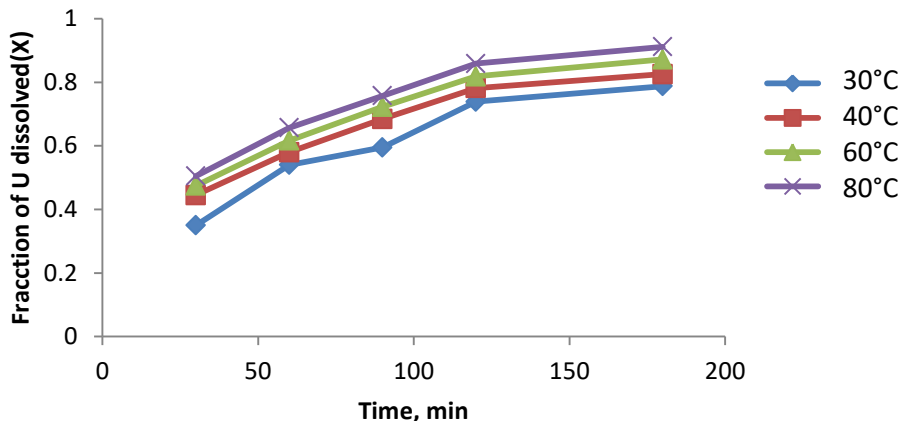
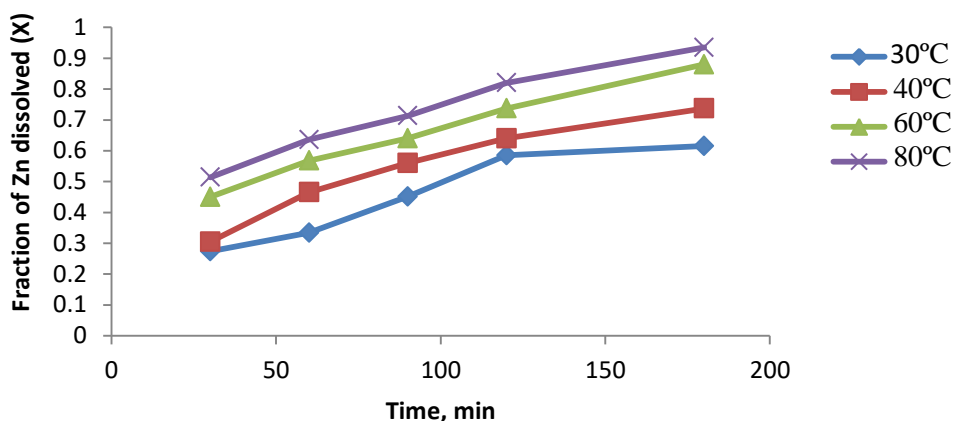**Figure (5): Effect of various temperatures on the uranium dissolution efficiency**

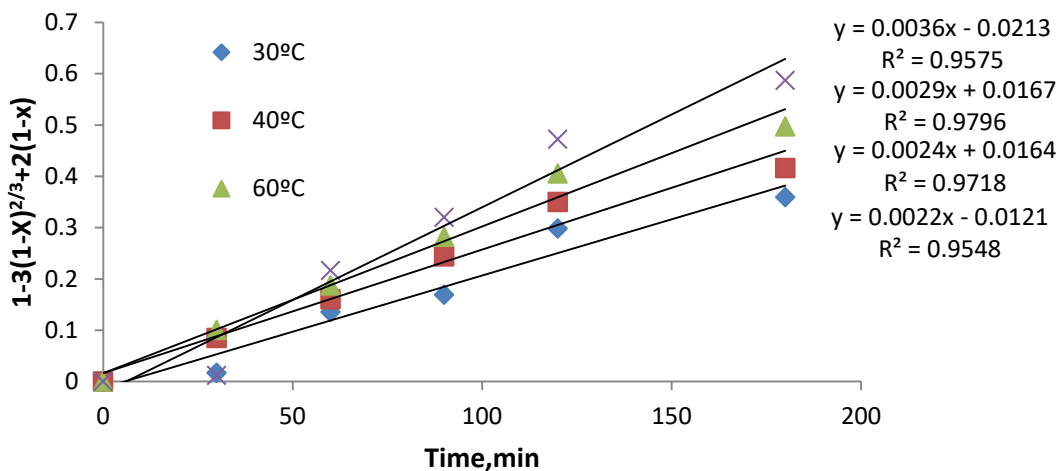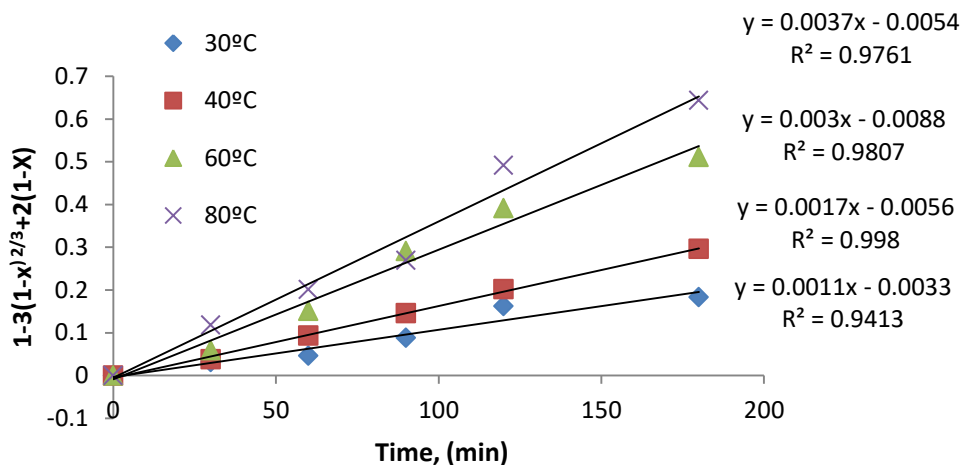**Figure (6): Effect of various temperatures on the zinc dissolution efficiency**

Figure (7): Realationship between 1-3(1-X) $^{2/3}$ +2(1-X) and dissolution time for uranium at various temperature

y = 0.0037x - 0.0054
R² = 0.9761

y = 0.003x - 0.0088
R² = 0.9807

y = 0.0017x - 0.0056
R² = 0.998

y = 0.0011x - 0.0033
R² = 0.9413

Figure(8): Realationship between 1-3(1-X) 2/3 +2(1-X) and dissolution time for zinc at various temperatures

The apparent activation energy can be determined from the Arrhenius equation:

$$Ln\ K = -E_a / RT + ln\ A \qquad (5)$$

Where k, is the reaction rate constant, E_a is the apparent activation energy, R, is the ideal gas constant, and A, is the frequency factor. The results of the four different temperatures are graphed and showed in Figures (9) and (10), these graphs indicates that the linear relationship is significant. The apparent activation energy Ea was determined from the slopes of the straight line where the slope is $-E_a/R$. The values of the activation energies were calculated to be 8.74 KJ/ mol for uranium dissolution and 21.3KJ/ mol for zinc dissolution.

y = 1.051x + 2.6669
R² = 0.9932

Ea=1.051x 8.314=8.74
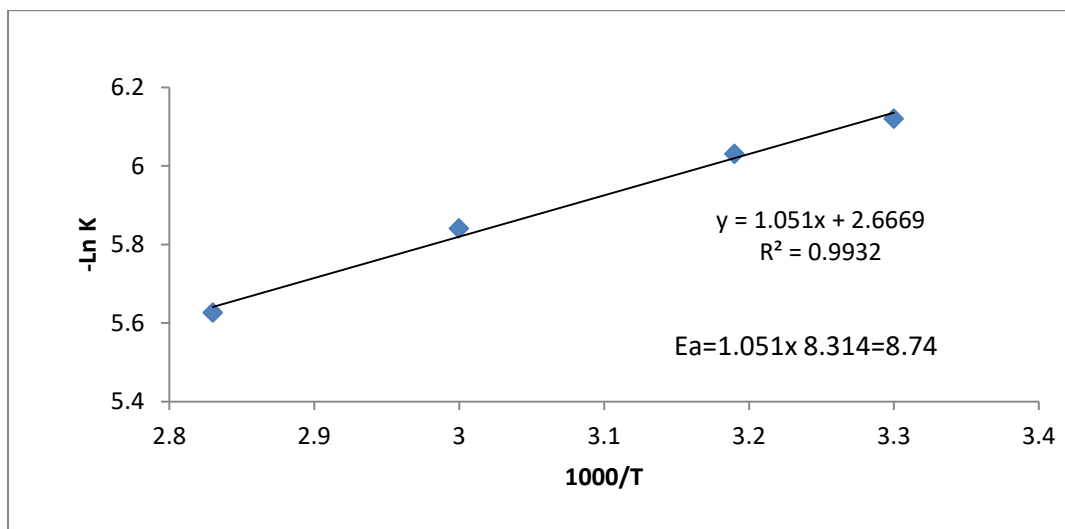
Figure(9): Arrhenius plot for uranium dissolution at different temperatures

y = 2.5663x - 1.7614
R² = 0.9533
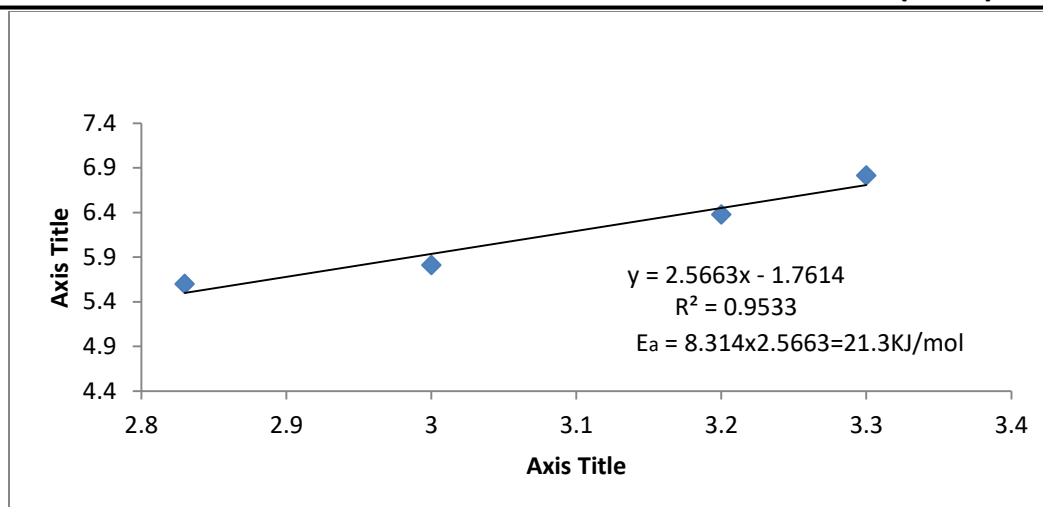Ea = 8.314x2.5663=21.3KJ/mol

Figure (10): Arrhenius plot for zinc dissolution at various temperatures,

From the calculated activation energy, it is it is clear that the dissolution reaction of uranium and zinc from dolostone ore material is controlled by a diffuson through the outer layer product process at different temperatures 30ºC, 40ºC, 60ºC, 80ºC. The various values of the apparent rate constants K at different temperatures and the corresponding correlation coefficient rates R^2 are summarized in Table (3).

Table (3): The values of the apparent rate constant K, min^{-1} with the correlation coefficient R^2 at different temperature range.

	Uranium		Zinc	
T, °C	K (min^{-1})	R^2	K (min^{-1})	R^2
30	0.0022	0.9548	0.0011	0.9413
40	0.0024	0.9718	0.0017	0.998
60	0.0029	0.9796	0.0030	0.9807
80	0.0036	0.9575	0.0037	0.9761

Recovery of Uranium and Zinc from Hydroxide Leaching Solution

Uranium and zinc were recovered from the hydroxide leaching solution of the dolostone working sample, 4 L of leaching solution was prepared from leaching of 1 kg of the ore sample using the previous optimum dissolution conditions (5 mol/L sodium hydroxide solution, 180 min, 70°C, and S/L ratio 1:4). The concentrations of U and Zn in this solution was found to reach 0.229 g/L uranium and 0.214 g/L zinc, and

leaching efficiency of 91.8 % for uranium and 93.5 % for zinc.

In the present work, it was decided to recover U and zinc from the prepared pregnant hydroxide leach liquor of Alluga ore material by using direct precipitation technique. Firstly uranium was precipitated from the hydroxide leach liquor by decreasing its pH value down to the range of 12-13 using HCl solution where uranyl chloride product was obtained. After the filtration, drying and calcination, the obtained product was subjected to EDX qualitative analysis which reflected a high purity product with about 68.78% of uranium content as shown in Figure (11).
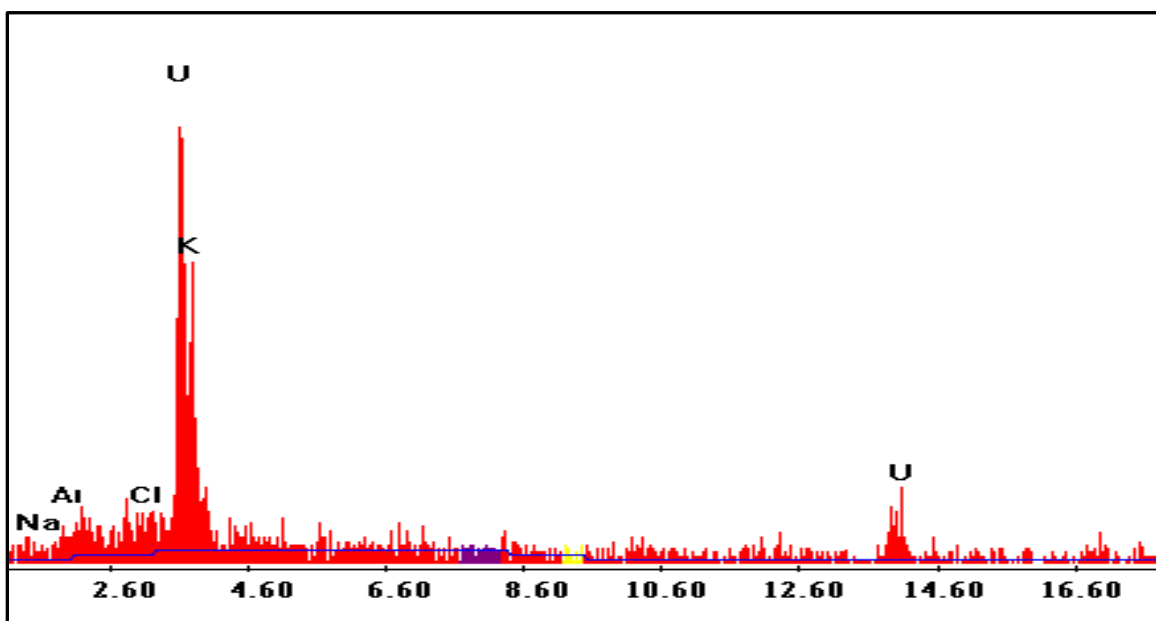

Figure (11): EDX analysis of the prepared uranyl chloride product.

Finally the pH the of collected leach liquor was decreased down to 10 - 9.5 using sulfuric acid solution followed by proper crystallization of the formed zinc sulfate.

The obtained product was subjected to ESEM-EDX qualitative analysis which reflected a high purity product with 60.89% of zinc content, Figure (12).
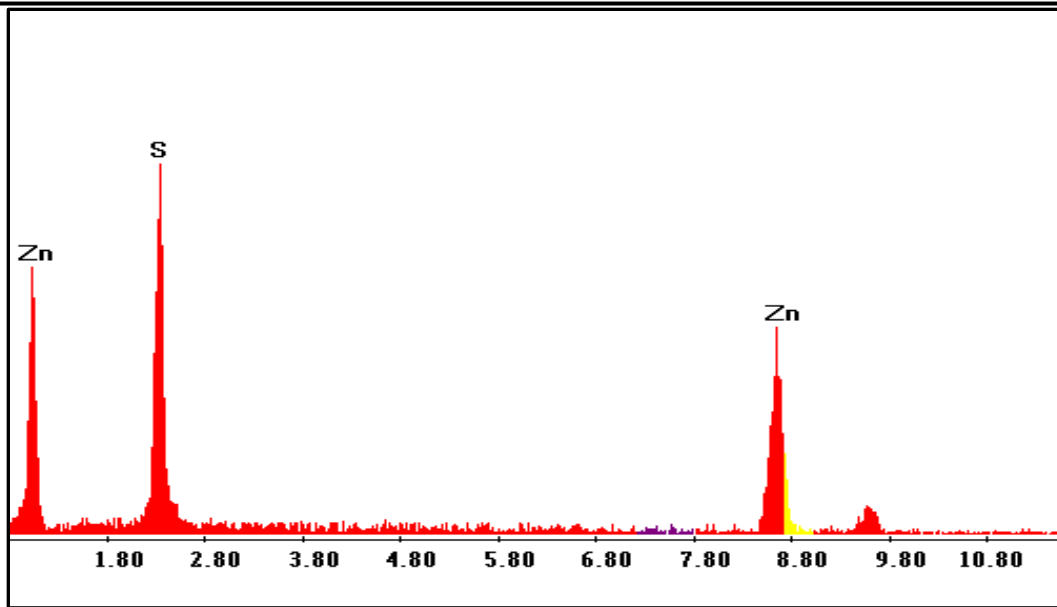
Figure (12): EDX analysis of the prepared zinc sulfate product.

Results of REEs Leaching

After recovery of uranium and zinc from the working ore, acidic conditions are used additionally to the ion exchange reaction with active cations like NH_4^+ or Mg^{2+} to liberate the adsorptive ligated as well as the more strongly bound REEs from the ore residue at which the content of REEs was 1900 ppm, acidic agitation leaching process by using sulfuric acid was performed to leach the included REEs content [24]. To optimize the leaching conditions of REEs, the following leaching factors were studied.

Effect of Reagent Type

The effect of reagent type upon the leaching efficiency of REEs from ore residue was studied, and the other leaching conditions as stirring time (3 h) and solid / liquid ratio (1/3) at 70°C temperature were fixed. Comparing single sulfate salt solution (1M) and single sulfuric acid (1M) with mixed leaching agents, Figure (13) indicates an increasing REEs leaching efficiency of about 10 to 25 % absolute. This is attributed to the intended co-liberation of REEs from the exchangeable phase as well as the colloid phase. Apart from this, impurities are liberated increasingly with use of H_2SO_4 due to the more acidic conditions. The results show that the rare earth leaching efficiency by $MgSO_4$ (96%) are comparable to the rare earth leaching efficiency by $(NH_4)_2SO_4$ (90%). In comparison with $(NH_4)_2SO_4$, the usage of $MgSO_4$ could reduce the leaching of impurities,[25,26] **.**
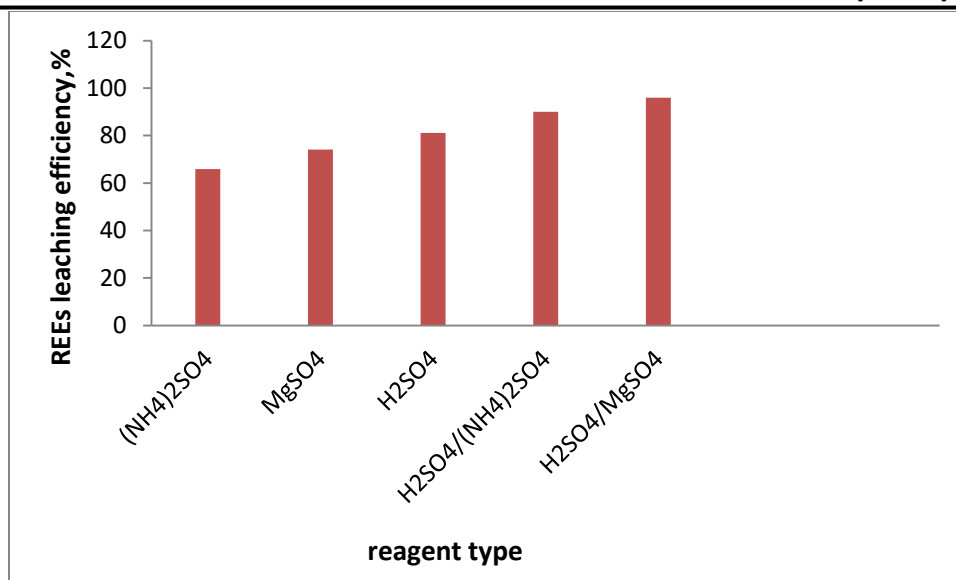
Figure (13): Effect of reagent type upon the REEs leaching efficiency

Effect of H_2SO_4 / $MgSO_4$ concentration

The effect of addition of $MgSO_4$ salt to H_2SO_4 acid solution (1 M) upon the leaching efficiency of REEs from spent ore residue was studied between 0.4 M and 1 M, and the other dissolution optimum conditions as stirring time (3 h) and solid / liquid ratio (1/3) at temperature 70°C were fixed. The obtained results, Figure (14), indicated that, the best $MgSO_4$ concentration was 0.8 M for leaching about 96.5 % of REEs content. At higher concentration of 120 g/L, REEs leaching efficiency was slightly decreased to about 96%.
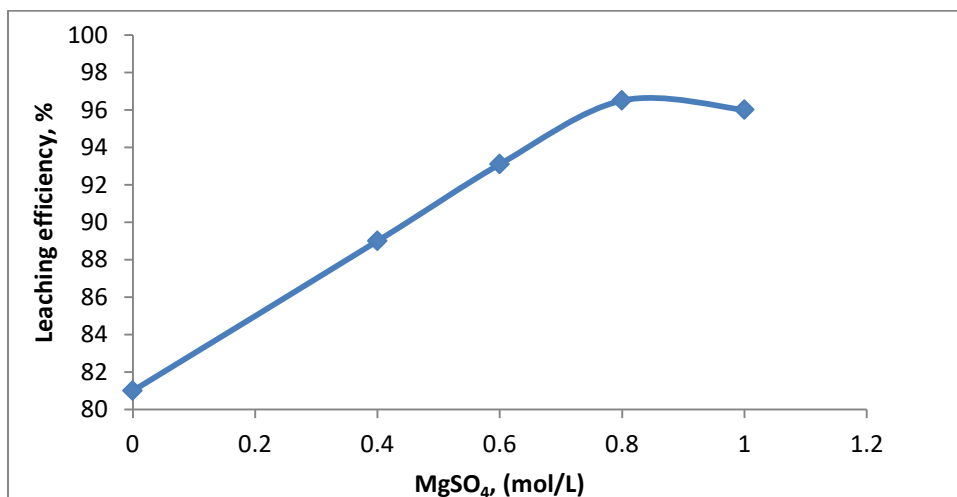

Figure (14): The effect of $MgSO_4$ concentration upon the REEs leaching efficiency

Effect of Stirring Time

For studying the influence of time upon REEs dissolution efficiency, several dissolution experiments have been examined by varying the stirring time between 60 and 150 min. The other dissolution optimum conditions were fixed at sulfuric acid conc of (1M), solid / liquid ratio of (1:3), at temperature 70°C. From the results illustrated in Figure (15), it was noticed that by increasing the stirring time, the leaching efficiency of REEs increases and reaches its maximum value 96.5 % at 120 min. By increasing the leaching time to 150 min., there was no marked increase in the dissolution efficiency of rare earth elements.
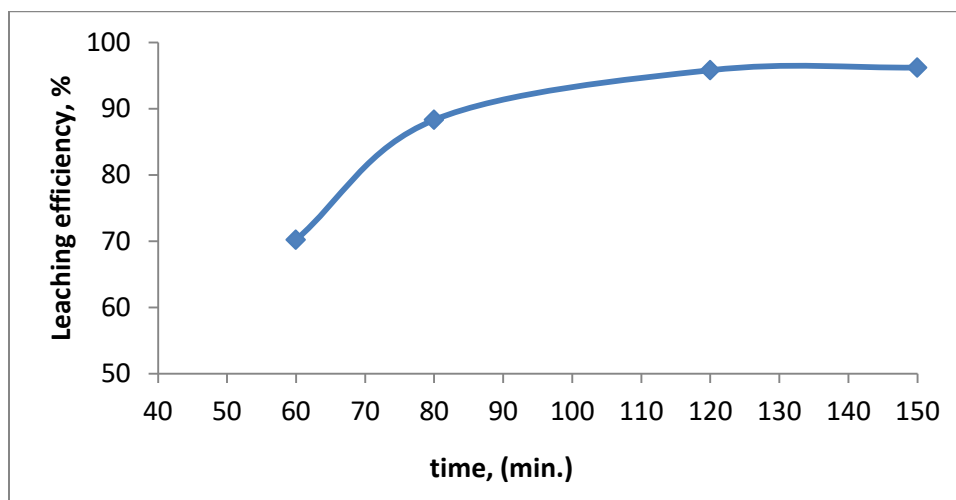

Figure (15): The effect time upon the REEs leaching efficiency

Effect of Temperature

The influence of leaching temperature was performed at 25°, 40°C, 60°C, and 80°C and using the above fixed optimum conditions. The results of dissolution efficiencies were shown in Figure (16) and clarified that the temperature causes highly improvement in the dissolution efficiency of rare earth. As an example, the obtained dissolution efficiencies for rare earth was only 70.2% at the room temperature. And when temperature increased from 60°C to 70°C, the rare earth dissolution efficiencies sharply increased from 76.48% to 96.5%. An incremental increase in temperature to 80°C, gave a slightly increase in REE leaching efficiency. Therefore, it can be considered that temperature of 70°C is the optimum temperature.
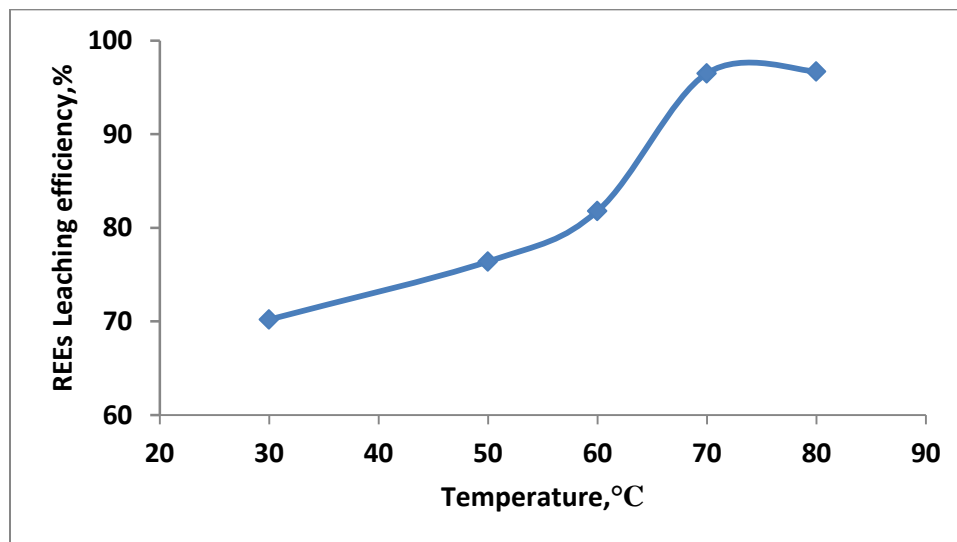
Figure (16): The effect temperature upon the REEs leaching efficiency

Effect of the Liquid/ Solid Ratio

For studying the influence of L/S ratio upon dissolution efficiency of REEs, several leaching experiments were examined at various liquid/solid ratios (L/S) from 1:1 to 5:1 at the fixed conditions of (1M) H_2SO_4, stirring time of 120 min. at temperature 70°C. The obtained results, Figure (17) indicated that, at the L/S ratio of 3/1 to 5/1, only slight decrease in the leaching efficiencies of REEs takes place. Thus, 3/1 would be considered as the optimum Liquid/Solid ratio.
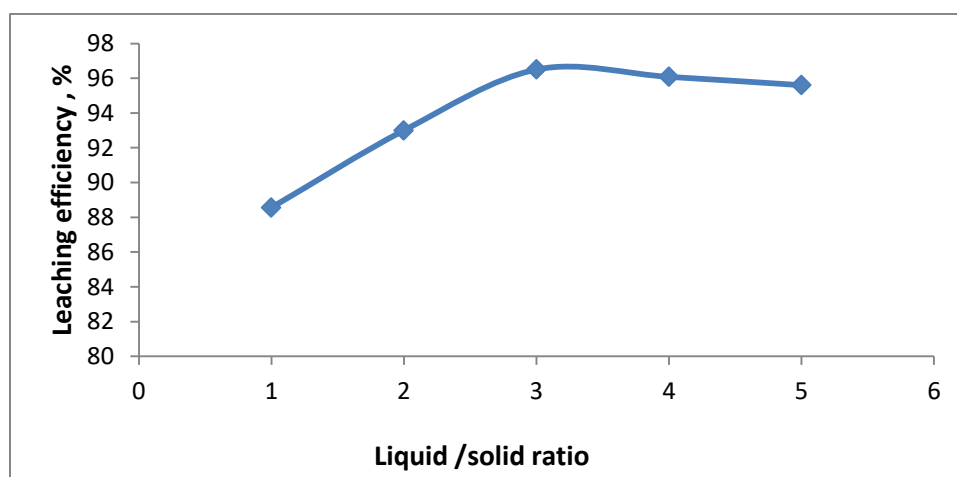

Table (17): Effect of Liquid/Solid ratio upon REEs leaching efficiency

Kinetic Leaching Results of REES

The leaching of rare earth is a typical heterogeneous reaction, that can be described by the shrinking core model in which there are three methods to identify the rate of reaction: diffusion through a fluid, diffusion through the solid product layer and chemical reaction at the core surface of the particle [27,28]. The rate of rare earth leaching was identified by Tian and Li [29,30] using the diffusion through the solid product layer method. Accordingly, the equation for this product layer diffusion can be expressed as:

$$1 - 2/3\ X - (1 - X)^{2/3} = K\ T \qquad (5)$$

Figure (18) shows the relationship between $1 - 2/3\ X - (1 - X)^{2/3}$ and dissolution times, the plots show straight lines at different temperatures. The apparent rate constant K can be obtained from the slopes of the straight lines. The activation energy of the dissolution reaction (E_a) is calculated using the Arrhenius equation, which can be expressed as:

$$ln\ K = ln\ A - Ea\ /\ (RT)$$

Figure (19) shows a plot of $ln\ K$ against $1/\ T$, from the slope of the straight line which represents the value of $-E/R$, the activation energy of rare earth was determined to be 18.26 KJ/mol.
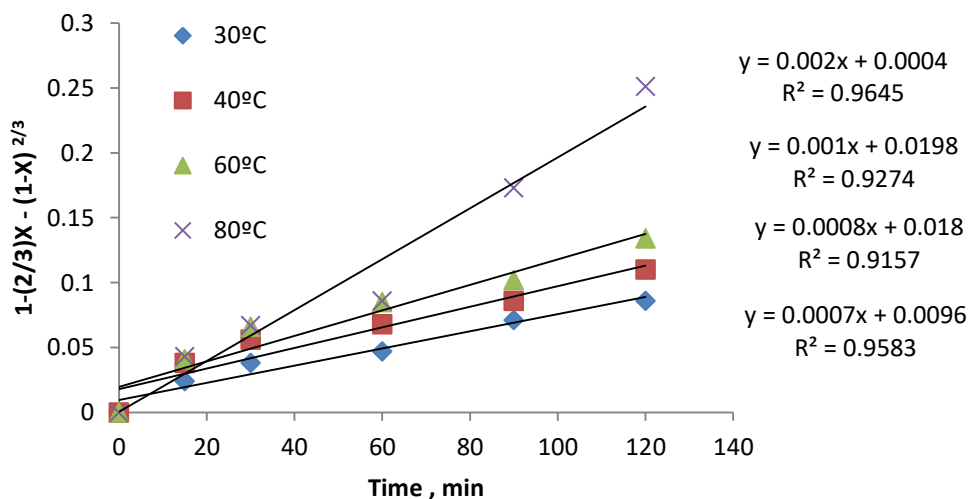

y = 0.002x + 0.0004
R² = 0.9645

y = 0.001x + 0.0198
R² = 0.9274

y = 0.0008x + 0.018
R² = 0.9157

y = 0.0007x + 0.0096
R² = 0.9583

Figure (18): The relationships between 1 - 2/3 X - (1 - X) $^{2/3}$ and time upon REE dissolution at different temperatures

$$y = 2.1972x + 0.0743$$
$$R^2 = 0.9644$$

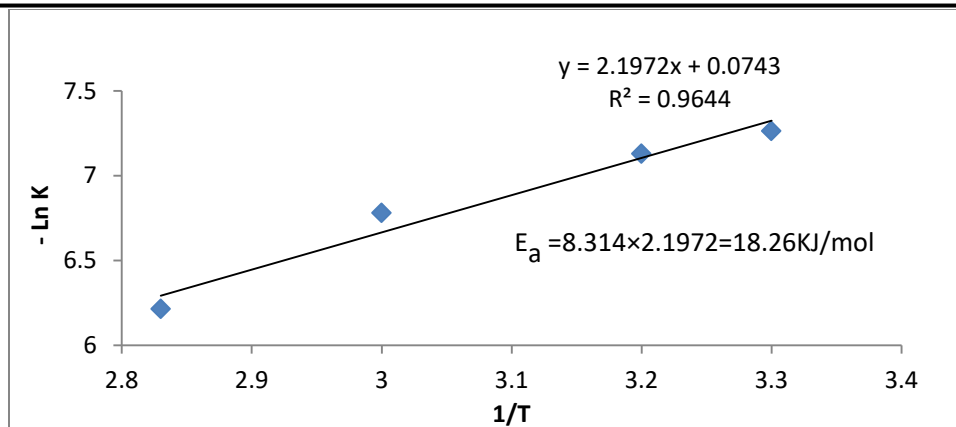$$E_a = 8.314 \times 2.1972 = 18.26 KJ/mol$$

Figure (19): Arrhenius plot for REEs dissolution at different temperatures *Recovery of REEs*

To prepare a rich rare earth leaching solution, 1000 g of the spent ore residue was subjected to $H_2SO_4/MgSO_4$ agitation leaching under the obtained leaching conditions. A volume of 3litter was obtained assaying 626.7 mg/L REEs. To increase the concentration of REEs, this leach liquor was then subjected to evaporation process to reduce the volume to 500 ml in order to obtain a REEs- oxalate concentrate [31, 32]. The latter was accomplished by adjusting the pH of the solution to 4.5, then by the addition of 10% oxalic acid, REEs oxalate was precipitated at pH 1. The obtained REEs oxalate precipitate was then calcined at 800 °C for 3 h and analyzed by using EDX technique Figure (20).
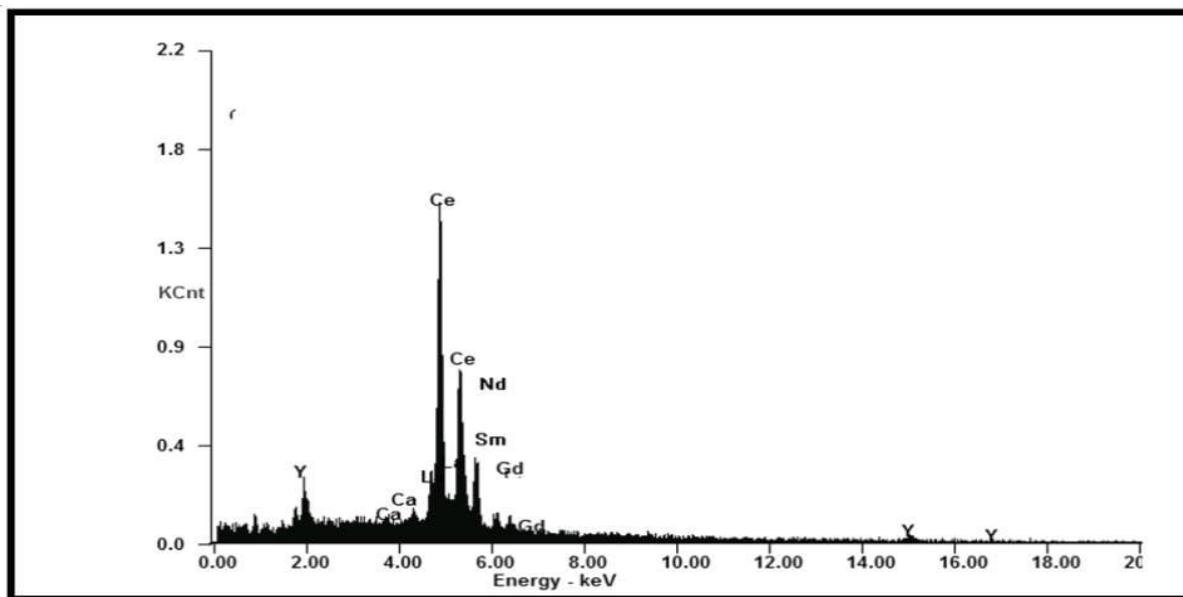

Figure (20): EDX analysis of the prepared REEs oxide .

4 - Conclusion

From the foregoing study, the general conclusions can be summarized:

1– A procedure for recovering uranium and zinc can be achieved by an alkali leaching by using NaOH solution of 5 (mol/L) concentration at the optimum conditions of ore / NaOH ratio: 1/4, 3 h. stirring time at 70 °C temperature .The dissolution percentages were 91.2 and 93.5 for both uranium and zinc respectively. The kinetic data using the unreacted shrinking core model showed that leaching process is controlled by diffusion through the outer product layer, the activation energy was found to be 8.74 KJ/mol for uranium and 21.3 KJ/mol for zinc.

2- A procedure for recovering REEs from the spent ore residue can be achieved by $H_2SO_4/MgSO_4$ leaching solution at the optimium conditions of H_2SO_4(1 mol/L) /$MgSO_4$(0.8 (mol/L) concentration , 120 min. Stirring time , and S/L ratio of 1/3 at 70°C temperature. The leaching efficiency was 96.5%. From the kinetic studies of the rare earth dissolution, the reaction rate was found to be controlled by the diffusion through the outer product layer process, and the activation energy was calculated to be 18.26KJ/mol.

References

1. El Aassy, I., Botros, N. H., Abdel Razik, A., El Shamy, A. S., Ibrahim, S. K., Sherif, H. Y., Moufei A.A. Report on proving of some radioactive occurrences in west central Sinai (International Report). Cairo, Egypt: N.M.A.(1986) .

2. Omara, S. and Conil, R. : Lower Carboniferous foraminifera from southwestern Sinai, Egypt. Annals Soc. Geol. Belgique, 88,221-240 (1965).

3. Mira, H. I., Aita, S. K., Remobilization of uranium and copper through karstification processes; A case study in Abu Thor locality, Um Bogma region, West Central Sinai, Egypt. Annals of the Geological Survey of Egypt, Retrieved from, 31,21–42, (2009).

4. Abdel Fattah, N. A., Uranium extraction from gibbsite- bearing sediments and other economic elements by using solvents and

organic compounds (Abu Zeneima Area, Sinai, Egypt), (M. Sc. Thesis). Fac. Sc., Zagazig Univ., Egypt (2003).

5. Abdel Moneim A., Uranium extraction from Abu Zeneima Sedimentary Ore Material, Sinai, Egypt (Ph.D. Thesis). Fac. Sc., El-Mansoura Univ., Egypt.(2005).

6. Amer, T. E., Geochemistry and extraction of U, Cu and Mn from the ore materials of the uraniferous Paleozoic sedimentary rock, West Central Sinai, Egypt (Ph. D. Thesis) Fac. Sc., Cairo Univ., (1997).

7. Amer, T. E., Mahdy, M. A., El Hazek, N. T., El Bayoumi, R., & Hassanein, S., Application of acid pugging and ferric salts leaching on West Central Sinai uraniferous siltstone. 30th Annual Hydrometallurgical Conference, Proceedings of an International Symposium Processing Metallurgy of Uranium, Saskatchewan, Canada,(2000).

8. El Hazek, M. N., Ahmed, F. Y., El Kasaby, M. A., & Attia, R. M., A sulfuric acid leaching of polymetallic Abu Zeneima gibbsite-shale. Hydrometallurgy, 90, 34–39,(2008).

9. Gillman, A., Developing uranium projects three continents, Australia Uranium Summit, Perth, Australia,(2010).

10. Lunt, D., Boshoff, P., Boylett, M., & E1-Ansary, Z., Uranium extraction: The key process drivers. The Journal of Southern African Institute of Mining and Metallurgy, (2007).

11. Sole, K. C., Cole, P. M., Feather, A. M., & Kotze, M. H., Solvent extraction and ion exchange applications in Africa's resurging uranium industry. A review. Solvent Extraction and Ion Exchange, 29, 868–869.(2011).

12. El-Nadi, Y.A., Daoud, J.A., Aly, H.F., Modified leaching and extraction of uranium from hydrous oxide cake of Egyptian monazite. Int J Miner Process 76:101-110, (2005).

13. Frackiewicz, K., Kiegiel, K., Herdzik-Konecko, I., Chajduk, E., Zakrzewska-Trznadel, G., Wolkowicz, S., Bartosiewicz, I., Extraction of uranium from low-grade Polish ores:

dictyonemicshales and sandstones. Nukleonika, 58, 451–459.(2012).

14. Chung, DY., Seo, HS., Lee, JW., Yang, HB., Lee, RH., & Kim, KW., Oxidative leaching of uranium from SIMFUEL using Na_2CO_3–H_2O_2 solution. Journal of Radioanalytical and Nuclear Chemistry, 284, 123–129.(2010).

15. Abdel-Aal EA. Kinetics of sulfuric acid leaching of low-grade zinc silicate ore. Hydrometallurgy;55:247–254.(2000).

16. Santos FMF, Peina PS, Porcaro A, Oliviera VA, Silva CA, LeãoVA. The kinetics of zinc silicate leaching in sodiumhydroxide. Hydrometallurgy; 102:43–9.(2010).

17. Zhang Y, Deng J, Chen J, Yu R, Xing X. Leaching of zinc fromcalcined smithsonite using sodium hydroxide.Hydrometallurgy ;131–132:89–92.(2013).

18. L. Shapiro, N.W. Brannock, Rapid analysis of silicate, carbonate and phosphate rocks. United States Geological Survey Bulletin, 114, 65 (1962).

19. Mathew, K.J., Bürger S, Ogt S. V, Mason P.M.E.M. and Narayanan U. I., :Uranium assay determination using Davies and Gray titration Proceedings of The Eighth International Conference on Methods and Applications of Radioanalytical Chemistry (Marc Viii) Kailua- Kona, Hawaii, 5.(2009).

20. Marczenko,Z.;Spectrophotometric determination of elements. New York: John Wiley and Sons(1986).

21. Wang R, Tang M, Yang S, Zhagn W, Tang C, He J, et al. ; Leaching kinetics of low grade zinc oxide ore inNH_3–NH_4Cl–H_2O system. J Cent South Univ Technol ;15,679–83.(2008).

22. Levenspiel O., Chemical reaction engineering, Ind. Eng. Chem. Res. 38,11,4140-4143 (1999).

23. Lid-dell KC., Shrinking core models in hydrometallurgy: whatstudents are not being told about the pseudo-steadyapproximation. Hydrometallurgy. **79**, 62–8, (2005).

24. X. Feng, Z. Long, D. Cui, L. Wang, X. Hwang, G. Zhang, Kinetics of rare earth leaching

from roasted ore of bastnaesite with sulfuric acid. Trans Nonfarrous Metals Soc China 23(3): 849-854, (2013).

25. Xiao, Y.; Chen, Y.; Feng, Z.; Huang, X.; Huang, L.; Long, Z.; Cui, D. Leaching characteristics of ion-adsorption type rare earths ore with magnesium sulfate. Nonferrous Met. Soc. China , 25, 3784–3790.(2015).

26. Xiao, Y.; Feng, Z.; Hu, G.; Huang, L.; Huang, X.; Chen, Y.; Long, Z. Reduction leaching of rare earth from ion-adsorption type rare earths ore with ferrous sulfate. J. Rare Earths , 34, 917–923.(2016).

27. Qiu, T.; Zhu, D.; Fang, X.; Zeng, Q.; Gao, G.; Zhu, H. Leaching kinetics of ionic rare-earth in ammonia-nitrogen wastewater system added with impurity inhibitors. J. Rare Earths, 32, 1175–1183.(2014).

28. Xiuchuan Ran, Zijie Ren, Huimin Gao, Renji Zheng, Junxun Jin: Kinetics of Rare Earth and Aluminum Leaching from Kaolin. Minerals.7 (9), 152 (2017).

29. J. Tian, J.Q. Yin, R. Chi, G.H. Rao, M.T. Jiang, K.X. Quyang, Kinetics on leaching rare earth from the weathered crust elution-deposited rare earth ores with ammonium sulfate solution.; Hydrometallurgy, 101, 166–170, (2010).

30. T. Li, A. Tu, Y. Zhang, M. Zhang, R. Chi, Kinetic study on leaching of rare earth from weathered crust Leaching Rare Earth Ore with mixed ammonium salts. Ind. Miner. Process, 38, 19–24 (2009).

31. Eyring L. (1964): Progress in the science and technology of the rare earths, Vol.1,P. 310. Pergamon Press, Oxford.

32. Moldoveanu,G.A.; Papangelakis, V.G.; Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism; Hydrometallurgy ;V. 117-118,P. 71–78,(2012).