

Kinetics of leaching process of REE from El-Missikat shear zone eastern Desert, Egypt

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ABSTRACT

The leaching process of uranium-REE ore from El-Missikat in a sulfuric acid solution using hydrogen peroxide as an oxidant was investigated. The leaching condition temperature, hydrogen peroxide concentration, sulfuric acid concentration, contact time, particle size, solid-liquid ratio and agitation rate were studied. The optimum process operating parameters were ore particle size 74 μm ; sulfuric acid concentration 2.5M; contact time 240 min; solid-liquid ratio 1:2; H_2O_2 concentration 0.5 M and agitation rate 600 rpm at temperature 25°C. The leaching efficiency of REE was about 70%, while the uranium leaching efficiency was about 95%. The experimental data were well interpreted with a shrinking core model with diffusion control through a porous product layer. The leaching process follows the kinetic model: $1-3(1-X)^{2/3} + 2(1-X) = k_1t$ with an apparent activation energy of 24kJ/mole.

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KEYWORDS

Leaching;
REE;
Shrinking core model;
Kinetics;
Diffusion.

INTRODUCTION

The study area of Gabal El-Missikat is one of the most important localities in the central Eastern Desert of Egypt for occurrence of uranium deposits; El-Missikat covers an area of about 80 km² and includes Gabal El-Garra and Gabal El-Gidami in addition to Gabal El-Missikat^[1]. El-Missikat uranium prospect area lies at about 3 km, midway between Safaga, on the red Sea coast and Qena in the Nile Valley. It is roughly bound by longitudes 33° 15' - 33° 28' E and latitudes 26° 24' - 26° 30' N where the mineralogical studies revealed the presence of uranium minerals such as uranophane, uraninite, soddyite and renadite^[2].

Gabal El-Missikat consists of rocks are essentially compound of quartz, potash feldspars, sodic

plagioclase and biotite. The main accessory minerals are sulfides, magnetite, zircon, apatite, fluorite, titanite, monazite, xenotime, uranothorite, rutile and uraninite. Hematite, epidote, muscovite and chlorite are present as secondary minerals^[3].

Recovery of metal values from the ores includes three main processes namely the physical upgrading, leaching and finally the metals recovery then purification with a great deal of chemical treatments through the extraction of metals from the obtained solution. This would be applied upon some minerals such as monazite heavy minerals from ores or residues either by gravitational differences or slight difference in magnetism ability. Leaching process is the dissolution of REE from the REE containing minerals in the ore. The selection of leaching procedure for dissolving REE minerals is dependant in part on

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the physical characteristics of the ore such as: type of mineralization, ease of liberation and the nature of other constituent minerals presents^[4]. During the past few decades, different types of leaching processes based on acid leaching and alkaline leaching methods were developed for processing uranium ore of different characteristics^[5].

Leaching (or solid extraction) is defined as the hydrometallurgical process which is used to dissolve valuable matter from its mixture with an insoluble solid by means of suitable reagent. In case of uranium ore material, uranium exists mainly in the hexavalent or tetravalent states. The hexavalent uranium oxide (UO_3) is the main constituent in secondary uranium minerals and may be considered as the amphoteric uranyl oxide [$(UO_2)O$] which is capable to form salts with both acid and alkaline reagents^[6].

Many precious metals have been leached from their ores such as batch leaching of uranium ore in Canada^[7], Oxidative leaching of molybdenum-uranium ore in wadi Sikait, Egypt^[8], Dissolution of nickel from lateritic nickel ore in Eskisehir region of Turkey^[9], Column leaching of lanthanides from Abu Tartur phosphate ore in Egypt^[10], leaching process of sella uranium ore in Egypt^[11], dissolution of total gold from Ijero-ekiti (Nigeria) gold ore deposit^[12], leaching of TiO_2 from Egyptian ilmenite^[13], leaching of nickel and cobalt from Chinese laterite ore^[14], leaching of Cobalt and copper have been leached successfully by HCl from Co-Cu ores in the Democratic Republic of Congo^[15] and phosphorus leaching from high phosphorus iron ores in China^[16].

Several leaching methods were studied and industrially applied for the breakdown of the principal REE minerals. There are two main breakdown methods worked out namely; the sulfuric acid and the caustic soda methods^[17]. The former was actually used most extensively in the USA. Depending on the acid/ore ratio, temperature and acid concentration, either Th or the REEs can be selectively solubilized or else both Th and REEs can be totally solubilized for later separation. The alkali method of monazite breakdown was mainly applied in Brazil and India^[18].

The aim of this work is to investigate a simple

leaching process of relatively low grade uranium-REE ore material from EL-Missikat, Eastern Desert, Egypt by using H_2SO_4 acid in the presence of H_2O_2 as an oxidant. This paper considers the kinetic aspects of uranium leaching. The effects of the main system variables on the leaching rate were examined, the kinetic model and the apparent activation energy were determined.

EXPERIMENTAL

Characterization of the REE ore

Samples were collected from El-Missikat which is located in the Eastern Desert, Egypt. The ore sample was firstly crushed to 297 μm and 149 μm then ground to 74 μm particle size. Sample characterization by XRF showed the presence of Ba, Pb, Fe, Mo, Nb, Zr, Y, Sr, U, Zn, Mn, Ca, K, S, Si and Al. The experimental work was performed upon the ore with sulfuric acid. The mineralization is considered mainly as uranium ore materials which is also associated with other economic minerals such as REE and other elements. Several experiments were carried out upon the ore to specify some of these economic minerals (REE). Series of experiments was carried out upon 10g sample portion of heavy concentrate ground to 74 μm size. After each experiment, the leach slurry was filtered, washed thoroughly with hot distilled water and then both filtrate and washing were made up to 100 ml. Uranium and REE leaching efficiency was calculated according to the following equation:

$$\text{Leaching efficiency of Uranium or REE, \%} = \frac{\text{Leached Metal ion conc.}}{\text{Original Metal ion conc.}} \times 100$$

Analytical procedures and instrumentation

The ore was analyzed for its major and minor elements using the reported methods and the results are shown in the TABLE (1).

- 1- Generally, the samples used in this work were weighed using an analytical balance produced by Shimadzu (AY 220).
- 2- Mechanical stirrer model VELP Scientific.
- 3- Hot plate magnetic stirrer model Fisher Scientific.
- 4- The hydrogen ion concentration of the different

TABLE 1 : Chemical analysis of El-Missikat ore

M. Oxides	%	M. Oxides	%	T. Element	ppm	T. Element	ppm
SiO ₂	78	Na ₂ O	0.078	U	700	Ni	80
Al ₂ O ₃	10.2	K ₂ O	0.068	? REEs	500	Nb	87.5
Fe ₂ O ₃	4.4	MnO	0.1	Zn	400	Sr	201
P ₂ O ₅	0.75	TiO ₂	0.15	Pb	417	Zr	200
CaO	1.2	L.O.I**	1.7	Cd	92	Th	20.5
MgO	1.16	Total	98.506	Cu	100	Ba	200

L.O.I**Total loss in ignition

solutions was measured accurately using the pH-meter model (HAANA pH-mV-temp).

- 5- Total REE was determined by arsenazo III where the absorbance of its complex was measured at the wavelength 650nm^[19] by using UV-spectrophotometer "single beam multi-cells-positions model SP-8001", Metretech Inc., version 1.02.
- 4- ICP model (Prodigy Axial high dispersion ICP-OES-USA) used for determination individual REEs.
- 5- An atomic absorption model G.B.C.A.A, was used for measuring trace elements.
- 6- The X-ray fluorescence technique (XRF) was used to identify the unknown minerals using a PHILIPS X'UNIQUE II spectrometer Rh-target tube, 70KV, 15mA, LiF-220 analyzing crystal and Rh- target tube, 30 KV,60 mA, PE-001 analyzing crystal.
- 7- The X-ray fluorescence (XRF) element analyzer model JEol-JSX-3222.
- 8- Uranium was determined by titration against ammonium metavanadate^[20].

RESULTS AND DISCUSSION

Leaching results

Effect of H₂SO₄ concentration

A series of leaching experiments was carried out using different H₂SO₄ concentrations (0.5 to 3 M). The other leaching conditions were kept constant, where the ore particle size was 74 μm, a solid/liquid ratio of 1:3, contact time 300 min and a stirring rate of 700 rpm at 25°C. The leaching efficiencies are shown in Figure (1). From this Figure, it is clear that as the H₂SO₄ concentration increased from 0.5M to 3M, the uranium dissolution efficiency increased from 33% to 70% while the dissolution efficiency of REE increased from 23% to 54%. However, 2.5M H₂SO₄ was the H₂SO₄ concentration choice applied in the subsequent leaching experiments achieving the highest dissolution efficiencies.

Effect of contact time

In these experiments, different leaching times (30 to 300 min) was tested. The other leaching condi-

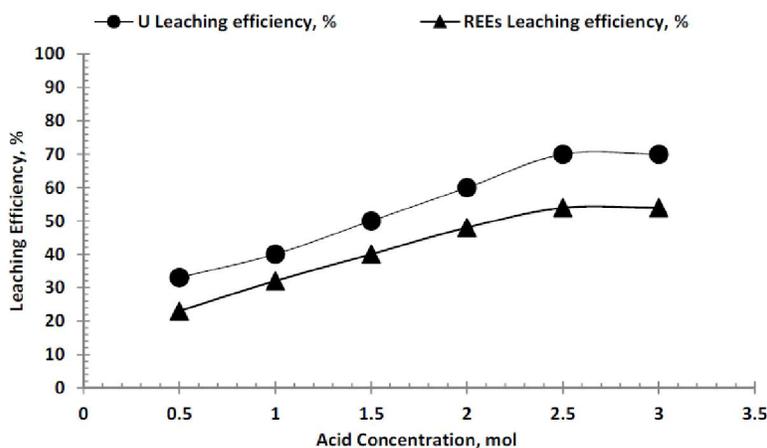


Figure 1 : Effect of H₂SO₄ concentration on the leaching efficiencies of uranium and REE (ore particle size 74μm, solid/liquid ratio 1:3, stirring speed 700 rpm, contact time 300 min at 25°C)

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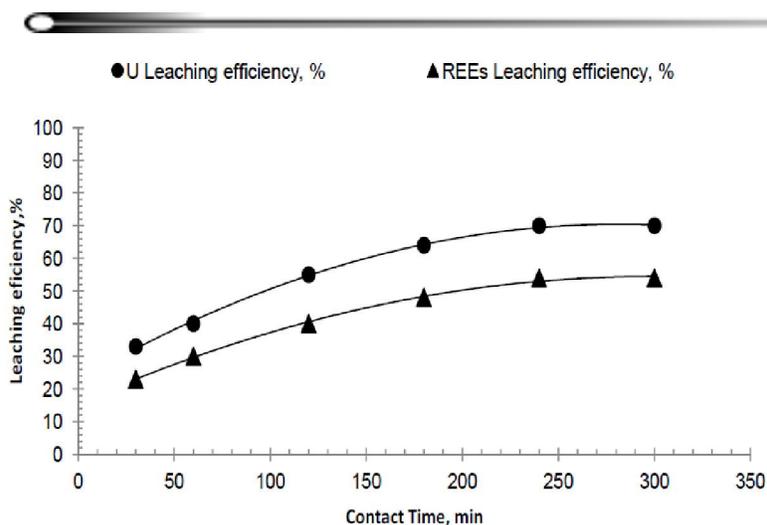


Figure 2 : Effect of contact time on the leaching efficiencies of uranium and REE (ore particle size $74\mu\text{m}$, $2.5\text{M H}_2\text{SO}_4$, solid/liquid ratio 1:3, stirring rate 700rpm at 25°C)

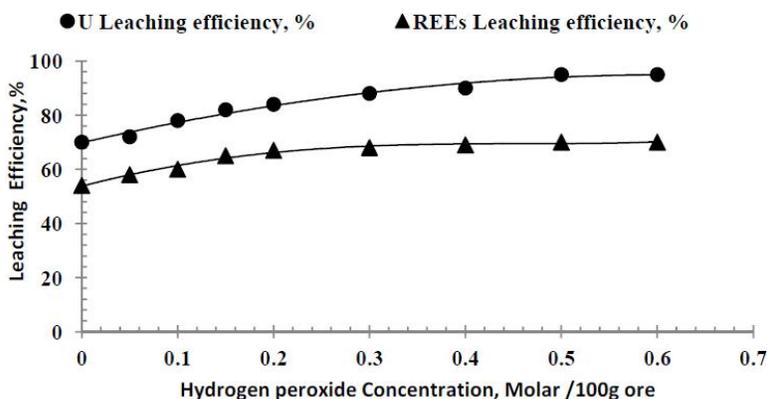


Figure 3 : Effect of the H_2O_2 concentration on the leaching efficiencies of uranium and REE (ore particle size $74\mu\text{m}$, $2.5\text{M H}_2\text{SO}_4$, solid/liquid ratio 1:3, stirring rate 700 rpm , contact time 240 min at 25°C)

tions were kept fixed, namely; $74\mu\text{m}$ ore grain size, $2.5\text{M H}_2\text{SO}_4$, 700 rpm stirring speed, solid/ liquid ratio of 1:3 at 25°C . For a leaching time of 300 min , the leaching efficiencies of uranium and REE reached 70% and 54% respectively. As the leaching time was extended, the leaching efficiency of uranium and REE did not increase. Therefore, it can be concluded that 240 min contact time represents the preferred condition for the subsequent uranium and REE ore dissolution experiments. The results are shown in Figure (2).

Effect of H_2O_2 concentration

The uranium and REE minerals present in the working ore need to be oxidized before dissolving because they are in oxidative states that cannot be dissolved under normal conditions. For this reason, H_2O_2 was chosen as a strong oxidizing agent^[21]. It has been shown that hydrogen peroxide under acidic

conditions can oxidize the low valence states of uranium and REE to high valence states which are readily soluble in the leaching solution.

In order to evaluate the effect of H_2O_2 , series of leaching experiments were carried out using $2.5\text{M H}_2\text{SO}_4$. These experiments were performed in the absence of and in the presence of different concentrations of H_2O_2 varying from 0.5M to 0.6M . The other leaching conditions were fixed at: a solid/liquid ratio of 1:3, contact time 240 min , stirring rate 700 rpm , $74\mu\text{m}$ ore grain size at 25°C . The results are shown in Figure (3). About 70% and 54% of uranium and REE respectively dissolved in the absence of H_2O_2 . As the milliliters H_2O_2 added increased the leaching efficiency of uranium and REE increased to 95% and 70% respectively. Therefore, $0.5\text{M H}_2\text{O}_2/100\text{g ore}$ represents the preferred condition for dissolution experiments.

Effect of stirring rate

The effect of the stirring rate was studied using conditions of: 74 μm particle size, 2.5M H_2SO_4 , 0.5 H_2O_2 , 1:3 solid/ liquid ratio at 25°C for 240 min. Stirring rate of 200 rpm, 300 rpm, 400 rpm, 500 rpm, 600 rpm and 700 rpm were examined. The leaching rates for uranium and REE increased as the stirring rate increased to 600 rpm reaching 95% and 70% leaching efficiencies respectively and then remained almost constant above 600 rpm. Therefore, the preferred speed was 600 rpm which was used for all the subsequent tests.

Effect of solid/liquid ratio

Working with fixed concentrations of 2.5M H_2SO_4 and 0.5M H_2O_2 , the effect of eight other solid/liquid ratios (1:1, 1:1.25, 1:1.5, 1:2, 1:3, 1:4 and 1:5) were tested under the same leaching conditions used for the solid/liquid ratio of 1:2. The re-

sults are shown in Figure (4). The leaching efficiencies of uranium and REE decreased at solid/liquid ratios of 1:1 and 1:75. Increasing the amount of acid by using a solid/liquid ratio of, 1:2 to 1:5 the extraction efficiency not increased. Therefore, a solid/liquid ratio of 1:2 was the preferred ratio.

Effect of particle size

The effect of particle size on the leaching of uranium and REE was studied using three different size fractions namely; 297 μm , 149 μm and 74 μm . It was found that, the leaching efficiencies of uranium and REE increased as the particle size of the working ore decreased. When a particle size of 297 μm was used, the leaching efficiency of uranium and REE sharply decreased to 57.14% and 36% respectively. As a result, the fraction with the smallest particle size 74 μm gave the highest dissolution result. This is due to the highest surface area of the small-

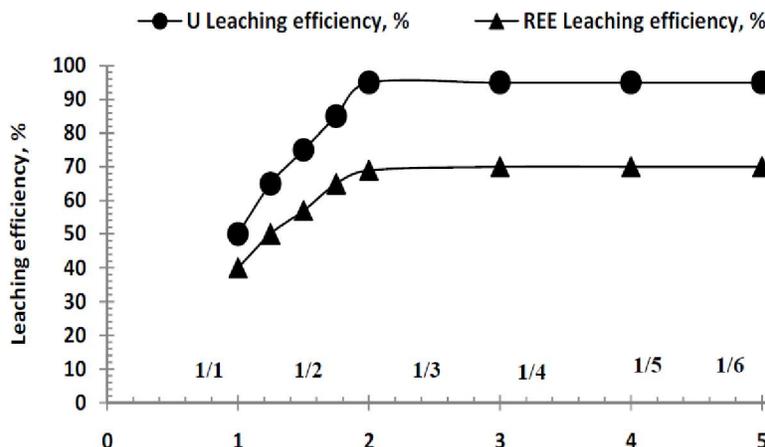


Figure 4 : Effect of solid/liquid ratio on the leaching efficiencies of uranium and REE (ore particle size 74 μm , 2.5M H_2SO_4 , 5ml H_2O_2 , contact time 240 min, stirring rate 600rpm at 25°C)

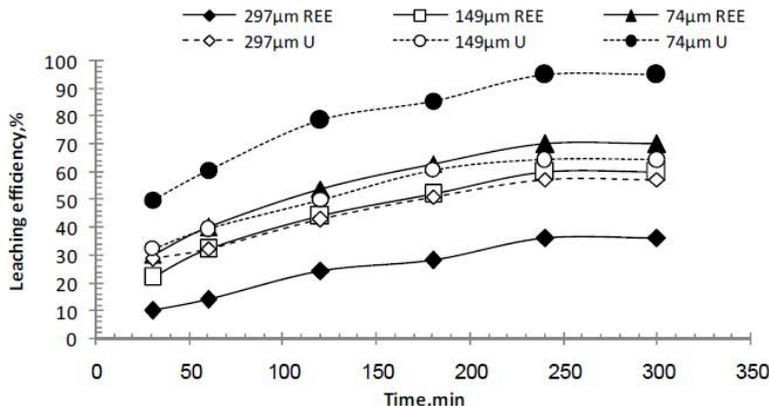


Figure 5 : Effect of particle size on the leaching efficiencies of uranium and REE (2.5M H_2SO_4 , 0.5M H_2O_2 , contact time 300 min, 1:2 solid/liquid, stirring rate 600 rpm at 25°C)

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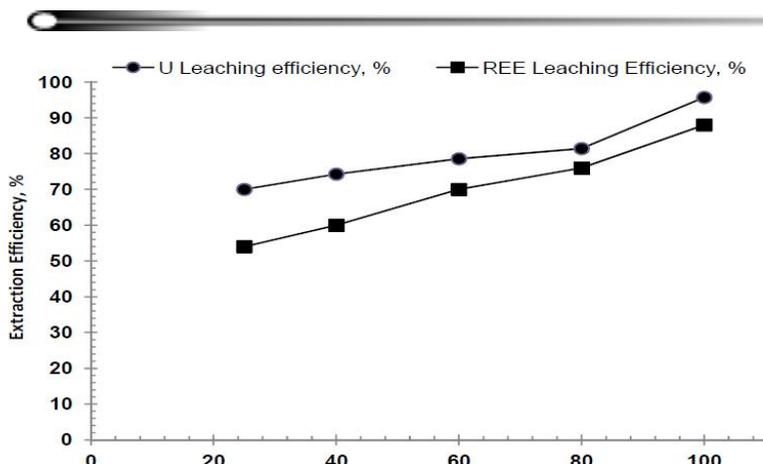


Figure 6 : Effect of temperature on the leaching efficiencies of uranium and REE (74 μ m, 2.5M H₂SO₄, S/L 1:2, 240 min, 600rpm)

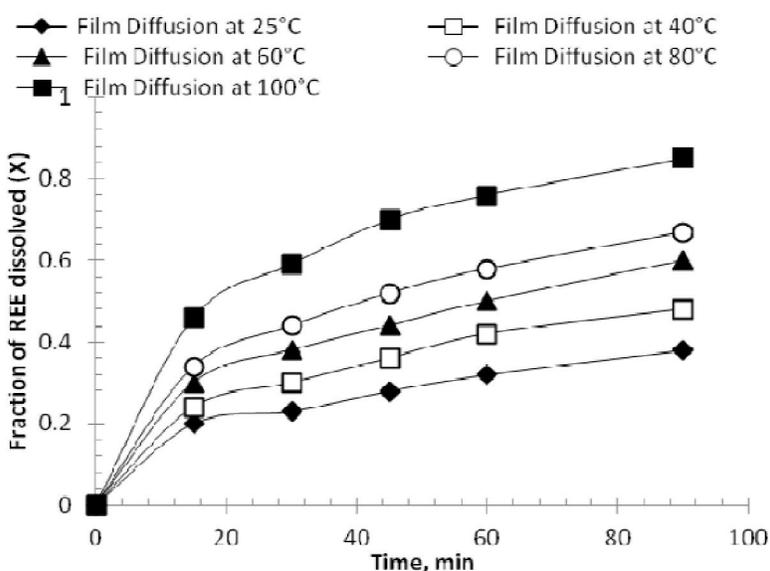


Figure 7 : Effect of different temperatures on the REE leaching efficiency (ore particle size 74 μ m, 2.5M H₂SO₄, 1:2 solid/liquid at stirring rate 600 rpm)

est particle size fraction; the conversion rates are inversely correlated with average initial diameter of the particles. The results are shown in Figure (5).

Effect of temperature

Leaching experiments were carried out at room temperature, 40°C, 60°C, 80°C and 100°C using the same conditions. The resulting leaching efficiencies are shown in Figure (6) and indicate that the temperature plays a critical role in the leaching of uranium and REE. For example, when working at room temperature, the obtained leaching efficiencies for uranium and REE were only 70% and 54% respectively. By increasing the temperature from 40°C to 80°C, the uranium and REE leaching efficiencies gradually increased from 74.28% to 81.42% and

from 60% to 76% respectively. A further increase in temperature to 100°C, gave uranium and REE leaching efficiencies of 95.7 % and 88 % respectively. Therefore, it can be concluded that higher leaching temperatures resulting higher leaching efficiencies.

Leaching kinetics of REE

Effect of temperature

Figure (7) presents the effect of the reaction temperature on the REE leaching rate in the range of 25°C–100°C under conditions of 74 μ m particles, 2.5M H₂SO₄ with a 1:2 solid/liquid ratio. The results show that the leaching rate of REE increases as the temperature increases. In order to obtain the kinetic equation and the apparent activation energy

for the dissolution of REE in the absence of H_2O_2 , the experimental data in Figure (7) were correlated to various kinetic models for solid-liquid reactions. Several equations were studied including^[22]:

$$1-3(1-X)^{2/3} + 2(1-X) = k_1 t, \quad (1)$$

$$1 - (1 - X)^{1/3} = k_2 t, \quad (2)$$

$$X = k_3 t, \quad (3)$$

Where k_1 , k_2 and k_3 are the apparent reaction rate constants (min^{-1}) for each case respectively and t is the leaching time (min) and X is the fraction reacted expressed as

$$X = \text{extraction}/100 \% \quad (4)$$

The data did not fit Eqs. (2,3). The best fit for the data from 0 min to 90 min was for Eq. (1), a diffusion controlled kinetic equation. The relationships between equation $1-3(1-X)^{2/3} + 2(1-X)$ and the leaching time for uranium at various temperature are plotted in Figure (8). The R squared values for all the lines are greater than 0.9. This indicates that the linear relationship between $1-3(1-X)^{2/3} + 2(1-X)$ and the leaching time (t) is significant and suggests that the leaching rate of uranium is diffusion controlled. The apparent activation energy was determined from the Arrhenius equation^[23,24]:

$$\ln k = \ln A - E_a/RT \quad (5)$$

Where k is the reaction rate constant, A is the frequency factor, E_a is the apparent activation energy and R is the ideal gas constant. The data for the four temperatures are plotted and given in Figure (9), and the regression analysis for these plots also shows that the linear relationship is significant. The apparent activation energy (E_a) was determined to be 24 kJ/mol.

It is worthy to mention that the calculated activation energy suggests a diffusion controlled process for EL-Missikat low grade REE ore material

at temperatures 25°C, 40°C, 60°C, 80°C and 100°C. The different values of the apparent rate constants k_1 and k_2 at different temperatures and their corresponding correlation coefficient rate are summarized in TABLE (2).

Effect of H_2SO_4 concentration

The effect of the H_2SO_4 concentration was studied from 0.5 to 2.5 M on the REE leaching rate in the absence of H_2O_2 with a 1:3 solid/liquid ratio at 25°C. There is a general increase in the leaching rate as the H_2SO_4 concentration increases. The corresponding plots of $1-3(1-X)^{2/3} + 2(1-X)$ versus time at various concentrations are graphed in Figure (10). It can be seen that an initial H_2SO_4 concentration of 2.5M is necessary to obtain a high dissolution rate of REE. In order to obtain the reaction order for the total H_2SO_4 concentration, log-log plots of the rate constants versus the total H_2SO_4 concentration are plotted and given in Figure (11). The slope of the line, or the reaction order of the total H_2SO_4 concentration, is 1.19. Hence, the leaching rate of REE strongly depends on the acid concentration.

Effect of particle size

The effect of particle size (74 μm , 149 μm and 297 μm) on the rate of the REE leaching reaction in the presence of 2.5M H_2SO_4 , 0.5 M H_2O_2 and a 1:2 solid/liquid ratio is illustrated in Figure (5). There is a general increase in the leaching rate as the particle size decreases. One reason for this is that for smaller particle sizes, there is an increase in the reaction surface area which enhances the mass transfer process of leaching. Another reason is that the solid particles were activated during grinding. The plots of $1-3(1-X)^{2/3} + 2(1-X)$ against time for the various particle sizes are graphed in Figure (12).

TABLE 2 : The value of the apparent rate constants, k_1 and k_2 , min^{-1} with the correlation coefficient at different temperature range

Temp., °C	Apparent k_2 , min^{-1}	R^2	Apparent k_1 , min^{-1}	R^2
25	0.001461	0.729	0.00063	0.977
40	0.002	0.767	0.00111	0.993
60	0.002646	0.799	0.00185	0.991
80	0.003155	0.793	0.00251	0.997
100	0.004847	0.821	0.00504	0.996

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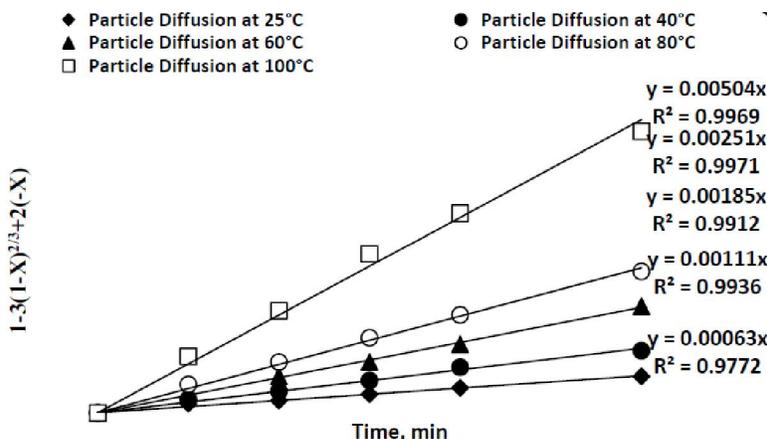


Figure 8 : Relationship between $1-3(1-X)^{2/3} + 2(1-X)$ and leaching time for REE at various temperatures (ore particle size $74\mu\text{m}$, $2.5\text{M H}_2\text{SO}_4$, 1:2 solid/liquid, at stirring rate 600 rpm)

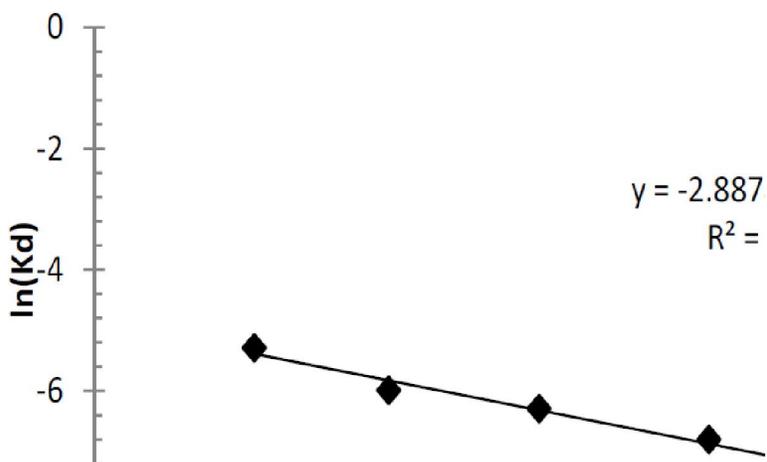


Figure 9 : Arrhenius plot for REE leaching (ore particle size $74\mu\text{m}$, $2.5\text{M H}_2\text{SO}_4$, 1:2 solid/liquid, at stirring rate 600 rpm)

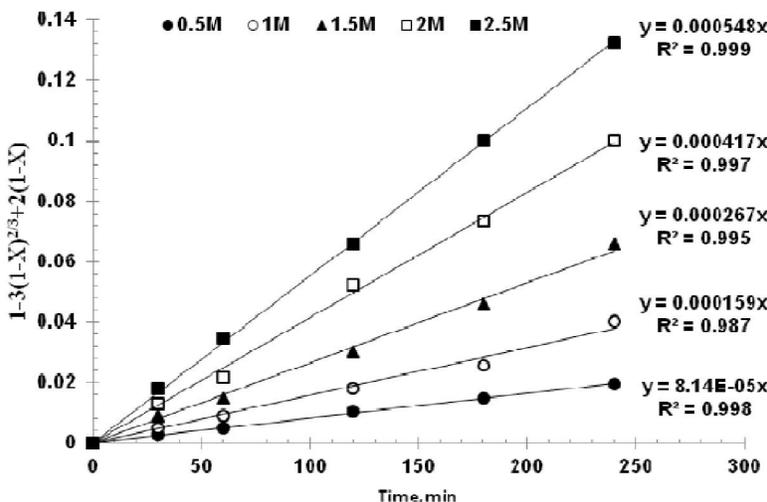


Figure 10 : Relationship between $1-3(1-X)^{2/3} + 2(1-X)$ and leaching time for REE leaching at various H_2SO_4 concentration (ore particle size $74\mu\text{m}$, contact time 300 min, 1:3 solid/liquid, stirring rate 700rpm at 25°C)

The apparent rate constant was determined and plotted versus the inverse of the initial average particle diameter d and the results are shown in Figure (13). The linear relationship between the rate constant k ,

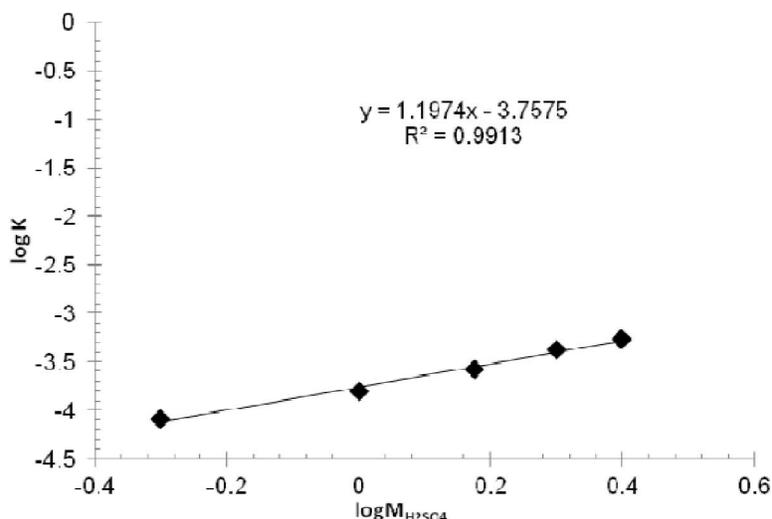


Figure 11 : Log-log plot of the rate constant versus H_2SO_4 concentration (ore particle size $74\mu m$, contact time 300 min, 1:2 solid/liquid, stirring rate 600 rpm at $25^\circ C$)

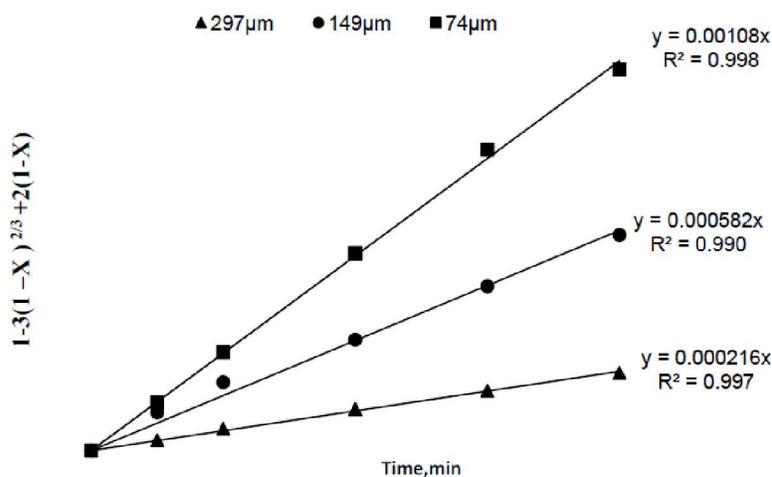


Figure 12 : Relationship between $1-3(1-X)^{2/3} + 2(1-X)$ and leaching time for REE leaching with different particle sizes ($2.5M H_2SO_4$, $0.5M H_2O_2$, contact time 240 min, 1:2 solid/liquid ratio, stirring rate: 600rpm at $25^\circ C$)

and the inverse of (d) indicates that the ash layer diffusion reaction on the particle surface is the rate-limiting step of the dissolution process.

The application of diffusion model for different particle size fractions is shown in Figure (13). From the corresponding k_d and particle size values, plots of $\log k$ versus $\log d^{-1}$ were obtained. As seen from Figure (11), the order of the reaction was found inversely proportional to power 1.155 of particle size ($[d_0]^{-1.155}$).

Determination of empirical kinetic model equation of REE

Equation 6 can describe the leaching of REE in El-Missikat rock by diluted sulfuric acid. However, its applicability is limited by the specific values used

for different reaction parameters (particle size fraction of $74\mu m$ and sulfuric acid concentration of $2.5 M$) at various temperatures.

$$k_{REE} = 10.53 e^{(-24.003/RT)} \quad (6)$$

The application for the other different reaction parameters (sulfuric acid concentration and particle size fraction) could be achieved by considering the effect of these parameters on the rate constant of El-Missikat rock leaching reaction. Therefore, equation 7 could be used to describe the effect of the different reaction parameters on the empirical kinetic model which representing the leaching process of REE by diluted sulfuric acid.

$$K_{REE} = \text{REE} P^b C^c e^{-Ea/RT} \quad (7)$$

Where P is the particle size, C is the acid concen-

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tration, R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the reaction temperature (in Kelvin). E_a are the activation energy (J mol^{-1}) for REE, k_{REE} , b , c are constants related to the different variable investigated. These constants are obtained in the next section.

Sulfuric acid concentration

Sulfuric acid concentration effect on the leaching reaction kinetic model equation for REE was analyzed to evaluate the constant c in equation 7. According to equation the following relation express the relation between rate constant, k , obtained from Figure (10) for REE at different sulfuric acid concentration be expressed by the following relation:

$$K_{\text{REE}} = k_4 C^c \quad (8)$$

Where k_4 is constant equal $k_{\text{REE}} P^b e^{-E_a/RT}$. The relation between $\log K_{\text{REE}}$ values obtained at different sulfuric acid concentration against $\log M_{\text{H}_2\text{SO}_4}$ for El-Missikat ore leaching reaction should give a straight line with a slope of (c for REEs) and intercept of $\log k_4$. Figure (11) represents the relation between the logarithmic values of leaching rate constant $\log K_{\text{REE}}$ of the leaching process as a function of logarithmic values of sulfuric acid concentration $\log M_{\text{H}_2\text{SO}_4}$.

From Figure (11), it is clear that a straight line was obtained with For REEs a straight line with slope of 1.197, correlation coefficient of 0.991 and intercept of -3.757. According to equation 8 and Fig-

ure (11), c was found to be equal 1.197 also k_4 was found to equal 1.747×10^{-4} . Therefore, equation 8 could be expressed as the following:

$$K_{\text{REE}} = 1.7478 \times 10^{-4} C^{1.197} \quad (9)$$

Ore particle size

The effect of ore particle size on the leaching reaction kinetic model equation for REE was analyzed to evaluate the constants b in equation 7. According to equation 7 the relation between the rate constant, k , obtained from Figure (12) for REE at different particle size can be expressed by the following relation:

$$K_{\text{REE}} = k_5 P^{b2} \quad (10)$$

Where k_5 is constant equal $k_{\text{REE}} C^c e^{-E_a/RT}$. Based on equation 10, the relation between $\log K_{\text{REE}}$ values obtained at different ore particle size against $\log P$ for the ore leaching reaction should give a straight line with slope b for REE and the intercept equal $\log k_5$. Figure (13) represent the relation between the logarithmic values of leaching rate constant $\log k_{\text{REE}}$ of the leaching process as a function of logarithmic values of mean radius of particle size fraction $\log P$.

From Figure (13), it is clear that a straight line was obtained with a slope of -1.155, correlation coefficient of 0.981 and intercept of -0.778 for REE. The slope of the straight lines of REE indicates that the leaching process by diluted sulfuric acid is controlled by the layer diffusion model. According to equation 10 and Figure (13), b was found to be equal

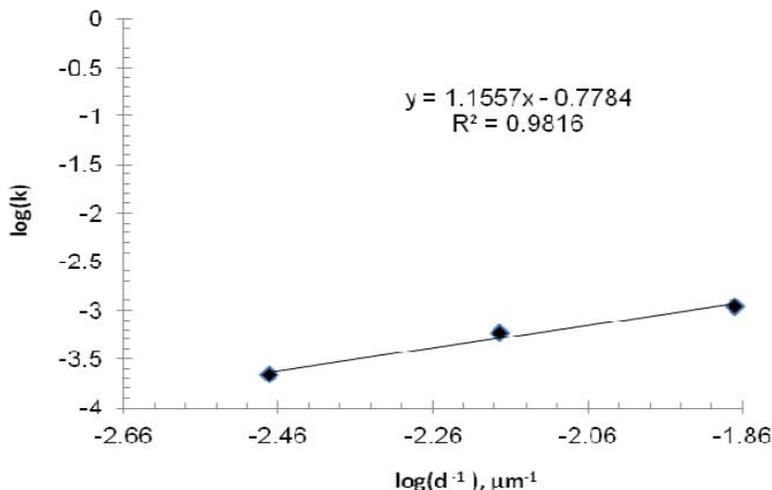


Figure 13 : Plot of the rate constant versus the inverse of the particle diameter ($2.5\text{M H}_2\text{SO}_4$, $0.5\text{M H}_2\text{O}_2$, contact time 240 min, 1:2 solid/liquid ratio, stirring rate 600rpm at 25°C)

-1.155 also k_3 was found to equal 0.1665. Therefore, equation 10 could be expressed as the following:

$$K_{\text{REES}} = 16.6 \times 10^{-2} P^{-1.155} \quad (11)$$

From the previous data analysis for different factors affecting the leaching of REE, equation 7 is given as the following:

$$K_{\text{REES}} = \frac{C^{1.197} P^{-1.155} e^{-(24.0/RT)}}{\text{REES}} \quad (12)$$

In El-Missikat ore leaching process by diluted sulfuric acid, unless otherwise stated, the following conditions were taken in the leaching process. The ore leaching experiments were carried out from 10 g ore with particle size of 74 μm by using 2.5 M sulfuric acid temperature of 25°C were used in all experiments unless otherwise given. Under these conditions, \dot{K}_{REE} could be evaluated from equations 6, 9, 11 and 12 as the following:

$$\dot{K}_{\text{REE}} (0.074)^{-1.155} (2.5)^{1.197} = 10.53$$

$$\text{So } \dot{K}_{\text{REE}} = 17.3 \times 10^{-2}$$

$$\dot{K}_{\text{REE}} (2.5)^{1.197} e^{-(24.0/8.314 \times 298)} = 16.6 \times 10^{-2}$$

$$\text{So } \dot{K}_{\text{REE}} = 5.6 \times 10^{-2}$$

$$\dot{K}_{\text{REE}} (0.074)^{-1.155} e^{-(24.0/8.314 \times 298)} = 1.747 \times 10^{-4}$$

$$\text{So } \dot{K}_{\text{REE}} = 8.7 \times 10^{-6}$$

Therefore, relative mean \dot{K}_{REE} equals 7.7×10^{-2} .

The empirical kinetic model equation for REE is evaluated as the following

$$K_{\text{REE}} = 7.7 \times 10^{-2} C^{1.197} P^{-1.155} e^{-(24.0/RT)} \quad (13)$$

CONCLUSIONS

Uranium and REE can be easily leached from Uranium/ REE ore by using H_2SO_4 acid in the presence of H_2O_2 as the oxidant. Using conditions of: 2.5 M H_2SO_4 ; 0.5 M H_2O_2 ; a stirring rate of 600 rpm, a solid/liquid ratio of 1 : 2, 240 min and a particle size of 74 μm , gave leaching efficiencies of about 95% for uranium and 70% for REE. The reaction order of the total H_2SO_4 concentration is 1.19. Hence, the leaching rate of REE strongly depends on the acid concentration. The order of the reaction was found inversely proportional to power 1.155 of particle size ($[d_p]^{-1.155}$).

The leaching kinetics of REE showed that the

rate of REE leaching using H_2SO_4 acid in the presence of H_2O_2 as an oxidant is diffusion controlled and follows the shrinking core model 1-3 $(1-X)^{2/3} + 2(1-X) = k_1 t$ with an apparent activation energy of 24 kJ/mol. The kinetics study also showed that the leaching reaction has a strong dependence on the concentrations of acid and hydrogen peroxide. The linear relationship between the rate constant, k , and the inverse of the initial particle diameter indicates that the rate of REE leaching is diffusion controlled.

REFERENCES

- [1] N.A.Mohamed; Distribution and extraction of uranium and some trace elements from the mineralized zones of El-Missikat- El-Eredya area, Eastern Desert, Egypt, ph.D, Cairo Univ., 184 (1995).
- [2] T.E.Amer, T.M.Ibrahim, S.A.Omar; Micro-probe studies and some rare metals recovery from El Missikat mineralized shear zone. Eastern Desert, Egypt, Assiut-Egypt, (2) 225-238 (2005).
- [3] T.M.Ibrahim; Geologic and radioactive studies of the basement-sedimentary contact in the area west Gabal El Missikat, Eastern Desert, Egypt, PhD.Thesis, Mansoura University, El Mansoura, Egypt, 214 (2002).
- [4] R.C.Merritt; In the extractive metallurgy of uranium, Colorado, School of Mines Res.Inst., Golden, Colorado, 83 (1971).
- [5] C.K.Gupta, T.K.Mukherjee; Hydrometallurgy in extraction processes, CRC Press, Boca Raton, 1, 70 (1990).
- [6] International atomic energy agency, Significance of mineralogy in the development of flowsheets for processing uranium ores, Technical Report Series, IAEA No. 196, Vienna, (1980).
- [7] K.E.Haque, J.J.9Laliberté; Batch and counter-current acid leaching of uranium ore, Hydrometallurgy, 17(2), 229–238 (1987).
- [8] T.A.Lasheen, M.E.El-Ahmady, H.B.Hassib, A.S.Helal; Oxidative leaching kinetics of molybdenum-uranium ore in H_2SO_4 using H_2O_2 as an oxidizing agent, Chem.Sci.Eng., 7(1), 95–102 (2013).
- [9] Tevfik Agacayak1, Veysel Zedef; Dissolution kinetics of a lateritic nickel ore in sulfuric acid medium, Acta Montanistica Slovaca Ročník 17, číslo, 1, 33-41 (2012).
- [10] A.T.Kandil, M.M.Aly, E.M.Moussa, A.M.Kamel, M.M.Gouda, M.N.Kouraim; Column leaching of

Full Paper

- lanthanides from Abu Tartur phosphate ore with kinetic study journal of rare earths, **28(4)**, 576 (2010).
- [11] Y.M.Khawassek, M.H.Taha; Kinetic Leaching of sella uranium ore with hydrochloric acid solution, 45th international october confrence on mining and metallurgy 16-19 october, Bor Lake, Bor (Serbia), ISBN 978-86-6305-012-9, (2013).
- [12] A.A.Baba, F.A.Adekola, D.O.Ojutemieden, F.K.Dada; Solvent extraction of gold from hydrochloric acid-leached Nigerian gold ore by tributylphosphate, Chem.Bull., "POLITEHNICA" Univ.(Timisoara), **56(70)**, 1 (2011).
- [13] N.El-Hazek, T.A.Lasheen, R.El-Sheikh, S.A.Zaki; Hydrometallurgical criteria for TiO₂ leaching from Rosetta ilmenite by hydrochloric acid, Hydrometallurgy, **87(1-2)**, 45-50 (2007).
- [14] L.Jinhui, X.Daoling, C.Hao, W.Ruixiang, L.Yong; Physicochemical factors affecting leaching of laterite ore in hydrochloric acid, Hydrometallurgy, **129-130**, 14-18 (2012).
- [15] A.M.Clotilde, B.A.F.Mulaba; Dissolution of oxidised Co-Cu ores using hydrochloric acid in the presence of ferrous chloride, Hydrometallurgy, **108(3-4)**, 233-236 (2011).
- [16] V.Wen-Tang X.Author, R.Zheng-De, G.Yi-Feng; Removal of phosphorus from high phosphorus iron ores by selective HCl leaching method, Journal of Iron and Steel Research, International, **18(5)**, 1-4 (2011).
- [17] L.Eyring; Progress in the science and technology of rare earths, Pergamon, Oxford, **1**, (1964).
- [18] Rare earth elements; The Global Supply Chain Marc Humphries Specialist in Energy Policy, Congressional Research Service, 7-5700 (2012).
- [19] Z.Marczenko; Spectrophotometric determination of elements, John Wiley & Sons, Inc., New York, (1986).
- [20] A.R.Eberle, M.W.Lerner, C.G.Cold beck, C.J.Rodden; Titrimetric determination of uranium in product, Fuel and Scrap Materials after Ferrous Iron Reduction in Phosphoric Acid, New Brunswick Laboratory, USAEC, (1964).
- [21] F.A.Cotton, G.Wilkinson; Advanced inorganic chemistry, 5th Edition, New York: Wiley, 456-458 (1988).
- [22] F.Habashi; Principles of extractive metallurgy, General Principles, New York: Gordon and Breach, **1**, 111-252 (1980).
- [23] H.S.Ray; Kinetics of metallurgical reactions. New Delhi: Oxford & IBHC, 1-75 (1993).
- [24] O.Levenspiel; Chemical reaction engineering, 3rd Edition, Wiley: New York (1999).