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Dissolution Kinetics of Lanthanides from Abu Tartur Phosphate Rocks, with Tartaric acid

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Abstract

Phosphate rock is one of the most important REEs secondary resources. Accordingly, this work focuses on the selective leaching of REES from Abu-Tartur phosphate rock using Tartaric acid solution. The influence of various factors affecting the leaching process such as reaction time, acid concentration, liquid/solid mass ratio, reaction temperature and stirring speed were thoroughly studied to estimate the favor REEs dissolution in relation to P_2O_5. The leaching data shows that 90.5 and 26.8 % of REEs and P_2O_5 respectively could be leached from phosphate rock after 60 min using 1.0 M Tartaric acid and 5/ 1 liquid/ solid, mL/ g, ratio at room temperature with mechanical stirring of 300 rpm. The application of graphical and statistical approaches for the analysis of kinetic data revealed that the rate of REEs leaching from Abu-Tartur phosphate rock using Tartaric acid is determined by the ash layer diffusion step. The apparent activation energy for the dissolution process was calculated as 12.43 kJ/mol. The dissolution process could be expressed by the following semi-empirical kinetic equation:

$$\left[1 - 3(1-\alpha)^{\frac{2}{3}} + 2(1-\alpha)\right] = 0.22\, e^{-12431/RT} t$$

1. Introduction

Phosphate ore is an important economic deposit in Egypt. Three main mine areas are found in Egypt, namely; the western desert between El-Kharga and El-Dakhla Oases, the Nile valley near Idfu and along the red sea between Safaga and Quesir [1]. Abu Tartur phosphate deposit is one of the largest phosphates mining area (1000 million tons and 200 million tons proved) in the Middle East. This mining area is located in the western desert of Egypt, about 60 Km from El-Kharga City and 10 Km from the main road between El-Kharga and El-Dakhla Oases [2]. Phosphate ores in this area are of sedimentary origin and of the apatite group, of which the most commonly encountered, variants are; Fluorapatite $Ca_{10}(PO_4)_6(F,OH)_2$ and Francolite $Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}$ [3].

Recently, REEs years play a critical role in civilization and human life, since they are widely utilized in most everyday applications because of their unique chemical and physical properties. These elements have many applications such as reduction of energy consumption, increasing energy efficiency and advance lifestyle consumer and other medical applications [4-5]. Despite there are more than 200 minerals as a source of REEs, almost all their production has come from less than 10 minerals. The most economically

significant minerals known to contain essential or significant REEs are monazite, bastnasite, and xenotime [6].

Many studies have been reported on the leaching of rare earth from their ores [7- 9] described REEs leaching from the ore materials using $(NH_4)_2SO_4$. It was found that the leaching ratio of Neodymium (Nd) was 67.3 % at 1 % ammonium sulfide, 3 h leaching time, and 0.09 solid to liquid (S/L) ratio. Leaching of lanthanides from phosphogypsum was carried out using either free acids such as HCl and HNO_3 or these acids associated with Nonyl Phenol Ethoxylate [10]. The factors affecting the leaching process were optimized. Also, the kinetics of the leaching investigated as a function of temperature. The leaching of lanthanides by the associated system decrease the activation energy from 5.89 and 12.24 kJ mol^{-1} to 5.28 and 3.79kJmol^{-1} for HCl and HNO_3 respectively. Wang et al. [11] described the kinetics of leaching from phosphoric ore by HNO_3,; it was found that the leaching process was controlled by the chemical reaction. The apparent activation energy was calculated to be 70.6 kJmol^{-1}, and the apparent reaction order was 0.83.

Xingliang et al. [12] studied sulfuric acid as leaching agent to extracting REEs from the roasted ore of Dechang bastnaesite in Sichuan, China. It was found the apparent

activation energy is 9.24 kJ mol^{-1}, this proves that the leaching process is controlled by the diffusion of reactants and products through a porous layer. Chi *et al.* [13] studied the leaching kinetics of lanthanides from a manganese-removed weathered rare earth mud (MRW-RE mud) by HCl solutions. It was found that a shrinking-core model could be used to describe the leaching process, with the apparent activation energy about 10.17 kJ mol^{-1}.

Organic acids have been used for upgrading phosphate rocks containing calcareous materials, [14]. Formic acid was used to upgrade Abu Tartur calcareous phosphate from around 25% up to 28%, [15]. Other organic carboxylic acids used are, lactic acid, [16], acetic acid, [17] and succinic acid, [18] the mechanism of these reactions was found to be chemically controlled, with activation energy in the range 40-64 kJ/mol.

The purpose of this work is to investigate the effect of different factors on the kinetics of lanthanides dissolution from Abu-Tartur phosphate rock using Tartaric acid; in order to assess the dissolution mechanism and establish an empirical equation relating the rate constant of lanthanides leaching for the purpose of process design.

2. Experimental
2.1. Materials:

Tartaric acid (2, 3-Dihydroxybutanedioic acid), used in this research work was of reagent grade. The representative working sample was collected from the under study mine of Abu Tartur plateau located in the Western Desert of Egypt where the New Valley project is constructed. The sample was dried, crushed and sieved, and a particle size fraction of 150–63 μm was selected as a material for the subsequent experiment. The drying of sieved samples was done in an oven at 100 °C. These samples were brought to ambient temperature and were kept in well dried plastic jars. The chemical analysis of the representative working sample is shown in Table 1. The Mineralogical composition was obtained by powder X-ray diffraction (XRD, Rigaku model D/max-2500) to define the mineralogical structure, which illustrated in the X-ray diffraction pattern (Figure 1). XRD pattern clear that the main mineral phases of the phosphate rock sample is are Fluorapatite together with minor amounts of quartz, Dolomite, and Calcite.

Table (1): Chemical analysis of Abu-Tartur phosphate concentrate

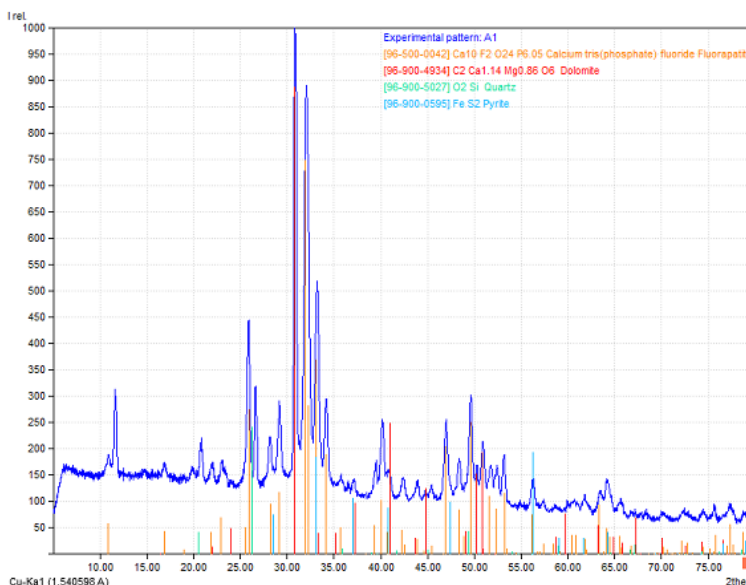| Constituent, %			
P$_2$O$_5$	30.1	SO$_3$	1.50
CaO	44.4	MgO	0.90
Fe$_2$O$_3$	3.8	Al$_2$O$_3$	0.46
F	2.8	Na$_2$O	0.28
SiO$_2$	2.3	L.O.I.*	5.1
Constituent, mg			
U	26	$\sum$ REEs	1440

L.O.I. = Loss of ignition

Fig (1): XRD pattern of Abu-Tartur phosphate working sample.

3.2. Procedure:

Leaching experiments were conducted at atmospheric pressure using a beaker set in thermostat water bath. In the leaching process, Tartaric acid solution was mixing with Abu-Tartur phosphate sample and leaching at a certain temperature for a certain period. Subsequently, the residue was removed by filtration. The amounts of REEs and P_2O_5 in the leaching filtrate were analyzed spectrometrically by the Arsenazo III [19] and (ammonium molybdate and ammonium metavanadate) [19] respectively. The leaching efficiency of REEs and P_2O_5 was determined as a function of leaching time, Tartaric acid concentration, liquid-solid ratio (mL/g), leaching temperature and stirring speed. The leaching efficiency, % was calculated by the following equations:

$$REEs\ leaching, \% = \frac{REEs\ concentration\ in\ the\ solution, g}{REEs\ concentration\ in\ the\ working\ sample, g} X\ 100$$

$$P_2O_5\ leaching, \% = \frac{P_2O_5\ concentration\ in\ the\ solution, g}{P_2O_5\ concentration\ in\ the\ working\ sample, g} X\ 100$$

The dissolution fraction (α) was calculated by the following equations.

$$\alpha(REEs)_{exp} = \frac{Amount\ of\ REEs\ in\ the\ solution, g}{Total\ amount\ of\ REEs\ in\ the\ working\ sample, g}$$

$$\alpha(P_2O_5)_{exp} = \frac{Amount\ of\ (P_2O_5)\ in\ the\ solution, g}{Total\ amount\ of\ (P_2O_5)\ in\ the\ working\ sample, g}$$

3. Results and discussion

This work consists of two parts: the first is an exhaustive study of the effect of variables that can affect the process rate (reaction time, Tartaric acid concentration, pulp density, temperature, and stirring speed), and the second is the evaluation of the phosphate dissolution kinetic by the application of several models.

3.1. Effect of parameters:

The following is a discussion of the obtained results for REEs and P_2O_5 leaching from Abu-Tartur phosphate rock with Tartaric acid solution. Here, the effects of reaction time, Tartaric acid concentration, liquid/ solid ratio, temperature and mechanical stirring speed on the dissolution process have been investigated.

3.1.1. Effect of reaction time

Fast leaching kinetics is beneficial for the industrial process. To study the effect of dissolution time, different durations ranging from 5 to 120 min were performed under the conditions of 0.4 M Tartaric acid, reaction temperature 20±1 °C, stirring speed 300rpm, liquid/solid ratio 3: 1, and ore sample particle size 150–63 μm. The experimental results are shown in Figure 2. In the initial stage of the reaction the concentration of Tartaric acid and phosphate rock is relatively high, so the reaction rate is relatively fast, the rock component is decomposed quickly, resulting that P2O5 and Σ REEs content in the leach liquor increased obviously. Numerically, as the reaction time increases from 5 to 60 min, the leaching percent of REEs and P2O5 increased from about 16.1 to 35.2 % for REEs, and from 3.6 to 8.2 % for P2O5. Further increase in stirring time more than 60 min has a slight effect on the REEs and P2O5 leaching efficiency. Therefore, in all proceeding experiments, the reaction dissolution time was kept at 60 min.
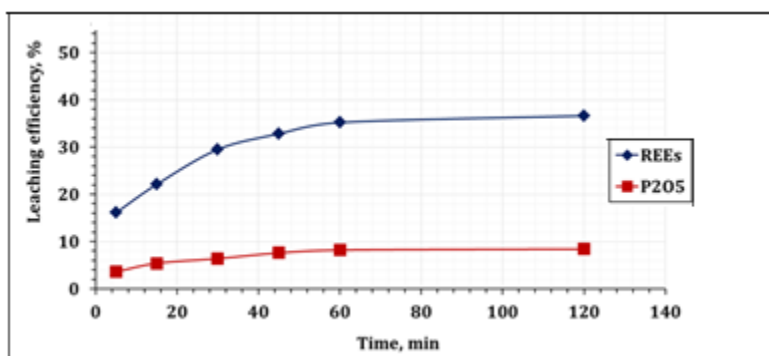

Fig (2): Effect of time on the REEs and P_2O_5 dissolution efficiency, % ([Tartaric acid]: 0.4 M; particle size: 150-63 μm; stirring speed: 300 rpm; L/S mass ratio: 30 ml/10 g; temperature: 20±1 ºC).

3.1.2. Effect of Tartaric acid concentration:

Under the experimental condition of reaction temperature 20±1°C, liquid/solid ratio 3: 1, reaction time 60 min, and ore particle size 150-63 μm, the effect of Tartaric acid concentration on REEs and P_2O_5 leaching result was investigated in detail. The acid concentrations used in the experiments were ranging from 0.2 to 1.2M. Experimental results are shown in Figure 3. It can be seen that the dissolution of REEs and P_2O_5 increase from 19.4 to 67.2 and from 2.6 to 26.5% respectively with the increase in acid concentration while acid concentration varies from 0.2 to 1.0M. Further increase in Tartaric acid concentration has a slight effect on REEs and P_2O_5 leaching efficiency. This behavior may be attributed to that highly concentrated organic acid solution does not react with calcium carbonate because of the large polarity of the O–H bond

of the acid molecules and it is necessary to use dilute solution for an effective reaction. In dilute solutions, water molecules tend to decrease the effect of the polarity of the

organic acids O–H bond [16]. Therefore, 1.0 M Tartaric acid is the choice acid concentration used for the other experiments of the dissolution of Abu Tartur phosphate ore.
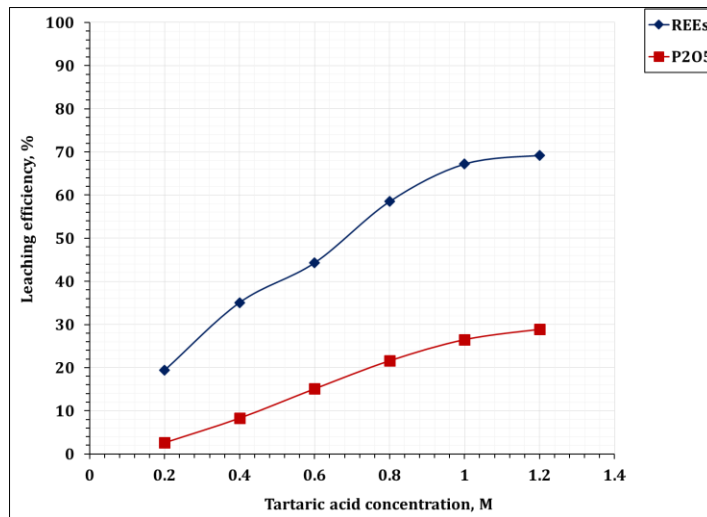

Fig (3): Effect of Tartaric acid concentration on the REEs and P_2O_5 dissolution efficiency, % (stirring speed: 300 rpm; particle size: 150-63 µm; L/S mass ratio: 30 ml/10 g; stirring time: 60 min; temperature: 20±1 ℃).

3.1.3. Effect of liquid/ solid ratio

With the condition: Tartaric acid 1.0 M, reaction time 60 min, reaction temperature 20°C, and ore sample particle size 150-63 µm, the effect of liquid/solid ratio on leaching result was investigated, using different liquid/solid ratio as 2: 1, 3: 1, 4: 1, 5: 1, 6: 1 and 7: 1. The experimental results are shown in Figure 4. It was found that the liquid/solid ratio is an important influence factor on the enrichment of phosphorus and REEs elements. Liquid/solid ratio affects the concentration of ore slurry and the chemical reaction between the Tartaric acid and phosphate rock, thus, it affects the grade and recovery rate of REEs and P_2O_5. Figure 6

shows that in the range of 2: 1 to 5: 1, the dissolution of REEs and P_2O_5 are increased with the increase liquid/solid ratio. At the liquid/solid ratio of 5: 1 the leaching efficiency of REEs and P_2O_5 reaches the maximum value, i.e., REEs, 90.5 % and that of P_2O_5 is 34.1%. That is may be due to the increase of solution bulk density which causes a decrease in the migration of different ions to the liquid medium. When the liquid/solid ratio further increases to 7: 1, there occur negligible changes in the efficiency of REEs and P_2O_5 leaching. Therefore, 50 ml/ 10 g, Tartaric acid/ phosphate rock mass ratio represents the preferred condition for the other dissolution experiments.
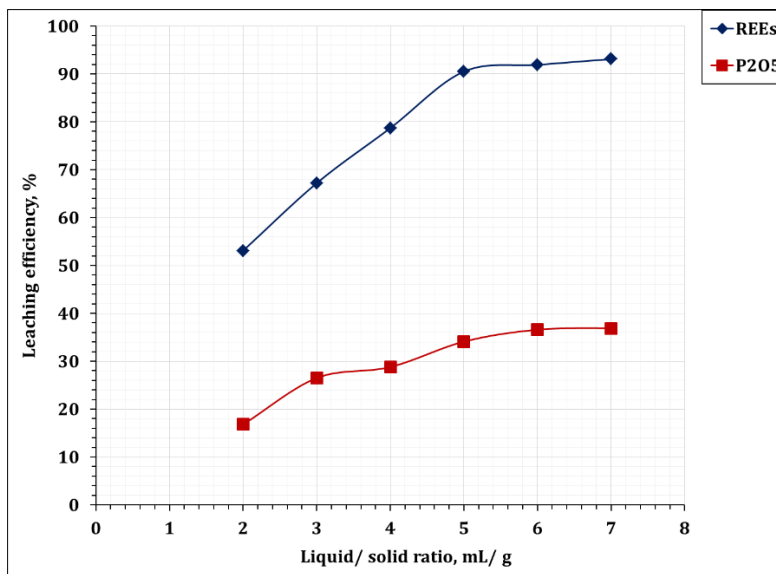

Fig (4): Effect of liquid/ solid ratio on REEs and P_2O_5 dissolution efficiency, % (stirring speed: 300 rpm; particle size: 150-63 µm; [Tartaric acid]: 1.0 M; stirring time: 60 min; temperature: 20±1 ℃).

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3.1.4. Effect of temperature

To study the effect of temperature ranging from 20 to 50 ± 1 °C on the dissolution of REEs and P_2O_5 from Abu-Tartur phosphate rock has been investigated. The other parameters have been fixed at reaction time of 60 min, stirring speed of 300 rpm, Tartaric acid concentration of 1.0 M, particle size fraction of 150–63 μm, and liquid/ solid ration, 50 ml/ 10 g. The obtained results were presented graphically in Figure 5 as a relation between leaching efficiency and temperature. From the Figure, it is clear that REEs and P_2O_5 dissolution efficiency % was slightly increased by increasing the reaction temperature from 20 to 50 °C. Therefore, room temperature represents the preferred temperature for the other factors experiments.
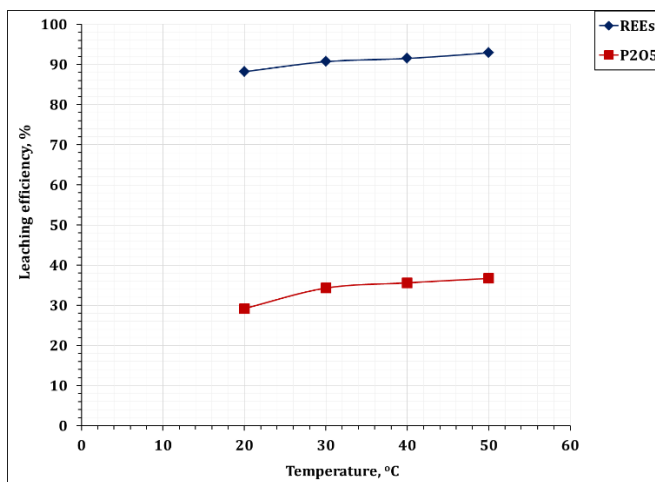

Fig (5): Effect of reaction temperature on REEs and P_2O_5 dissolution efficiency, % (stirring speed: 300 rpm; particle size: 150-63 μm; [Tartaric acid]: 3.0 M; stirring time: 60 min; L/S mass ratio: 50 ml/10 g).

3.1.5. Effect of Stirring Speed:

The experiment results of the effect of stirring speed range (200-500rpm) on REEs and P_2O_5 leaching efficiency are plotted in Figure 6. As can be seen from the Figure, under the same leaching conditions, as the stirring speed increased from 200 to 500 rpm, REEs and P_2O_5 leaching efficiency increased slightly from 89.1 to 91.8 and from 25.8 to 27.9 respectively. Thus, the change in stirring speed has no effect on REEs and P_2O_5 dissolution by the tartaric acid process. This indicates that the dissolution process does not seem to be controlled by mass transfer through the liquid film. This is mainly attributed to the fact that the phosphate ore particles are more dispersed in the acid solution as the stirring speed is increased, thereby increasing the contact area between them and the acid. However, the promotion effect is minimal as the fact that the leaching efficiency increases little with increasing stirring speed. From the viewpoint of improving leaching efficiency as well as saving energy, the stirring speed was fixed at 200 rpm in the subsequent experiments.
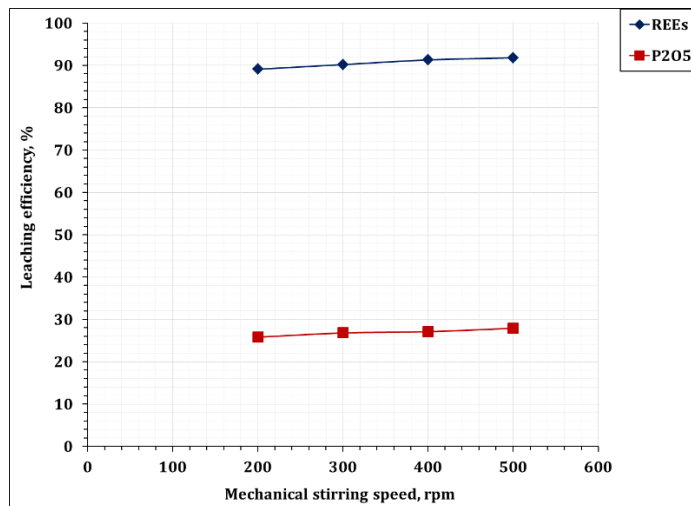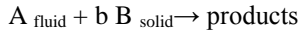

Fig (6): Effect of stirring speed on REEs and P_2O_5 dissolution efficiency, % (room temperature; particle size: 150-63 μm; [Tartaric acid]: 1.0 M; stirring time: 60 min; L/S mass ratio: 50 ml/10 g).

3.2. Dissolution Kinetic analysis

One of the major objectives of this study is the basic understanding of the mechanism of REEs dissolution kinetic from Abu-Tartur phosphate rocks in Tartaric acid solution. Leaching reactions are fluid–solid heterogeneous reactions which could be represented as the following:

$$A_{fluid} + b\,B_{solid} \rightarrow products$$

In order to establish the reaction kinetics and rate controlling step for the leaching of REEs in Tartaric acid solution, the experimental data were analyzed using the unreacted shrinking core model [20-21]. According to this model, the reaction is considered to take place first at the outer surface of the particle [22-23]. Based on this model, the leaching process REEs from phosphate rock can be divided into 5 steps as follows: (I) the leaching agent passes through the diffusion layer, spreads to the mineral particle surface, and reaches the mineral surface through the liquid and solid boundary mask. This is called the external diffusion process. (II) The leaching agent ions reaching the surface of mineral particles diffuse further into the particles; this is known as the internal diffusion process. (III) The leaching agent cations, which diffuse into the mineral particles, are exchanged with the adsorbed REEs ions. (IV) The insoluble substance produced by the leaching agent and mineral causes the solid film to thicken, and it exchanges with the desorbed REEs ions; at the same time, it diffuses from the solid film to the mineral surface. This is called the internal diffusion process. (V) The exchanged REEs ions diffuse from the surface of mineral particles to the leaching solution; this is known as the external diffusion process. The schematic of the leaching process [24] is shown in Figure 7.
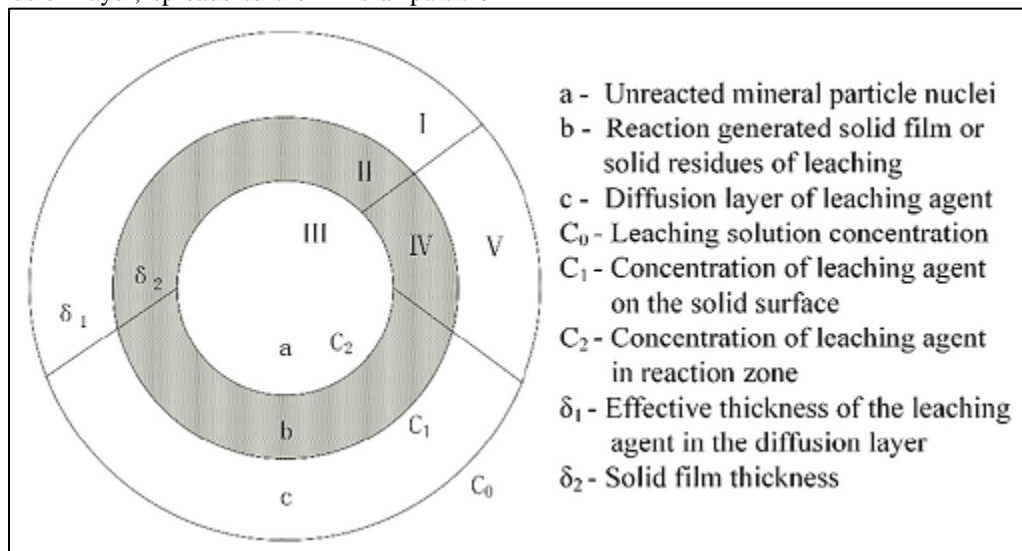

Fig (7): Schematic diagram of the leaching process of phosphate ore [24]).

The kinetics of the leaching reaction is controlled by the slowest rate step, which is called the rate-limiting step. There are three possible kinetic models [26-27] for REEs leaching process: kinetic model of film diffusion control, kinetic model of chemical reaction control, and kinetic model of ash layer diffusion control. The kinetic equations are given below:

$$[1 - (1 - \alpha)] = Kt \dots (1)$$

For film diffusion control step

$$\left[1 - (1 - \alpha)^{\frac{1}{3}}\right] = Kt \dots (2)$$

For a surface chemical reaction control step

$$\left[1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha)\right] = Kt \dots (3)$$

For ash layer diffusion control step

Where k is the reaction rate constants (min^{-1}) of the different steps in the leaching process, which are associated with the leaching conditions and ore properties. α is the fraction of S reacted (g), t is the leaching time (min).

Fluid/solid reaction models were used for the analysis of the data to evaluate the slowest step and the kinetic parameters for the leaching of REEs leaching from Abu-Tartur phosphate rock using Tartaric acid solution. The reliability and validity of the data were examined by statistical as well as by graphical approaches. Under the conditions used in this work, external diffusion has been found not to apply to the experimental fact that rate of stirring does not affect the fraction of the dissolved material and its effect, therefore, will not be analyzed [28]. Accordingly, equations 2 and 3 will be applied to figure out the kinetic of Abu-Tartur phosphate rock leaching process. In this regard, the results obtained from the reaction temperature investigation has been used to plot the relation between $[1 - (1 - \alpha)^{1/3}]$, and $[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)]$ against time t as shown in Figures 8 and 9 respectively. The fit model should give a straight line which passes through the origin.
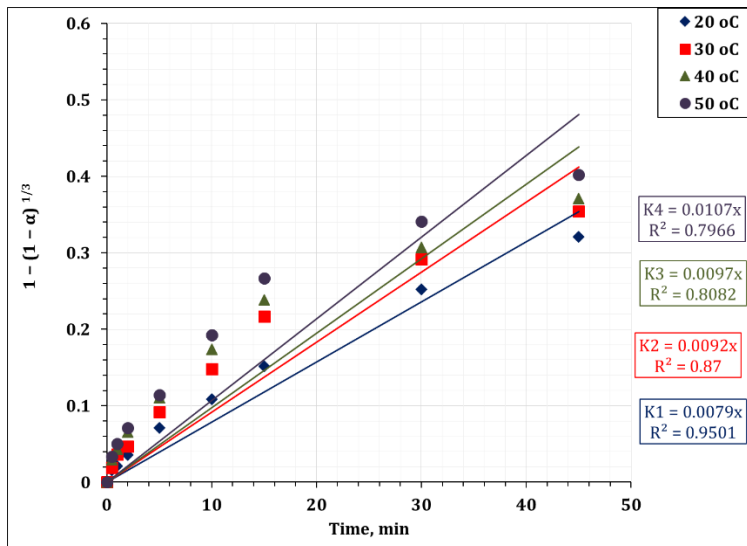
Fig (8): Effect of temperature on the function $[1 − (1 − α)^{1/3}]$ (particle size: 150-63 μm; [Tartaric acid]: 1.0 M; L/S mass ratio: 50 ml/10 g; mechanical stirring speed: 300 rpm).
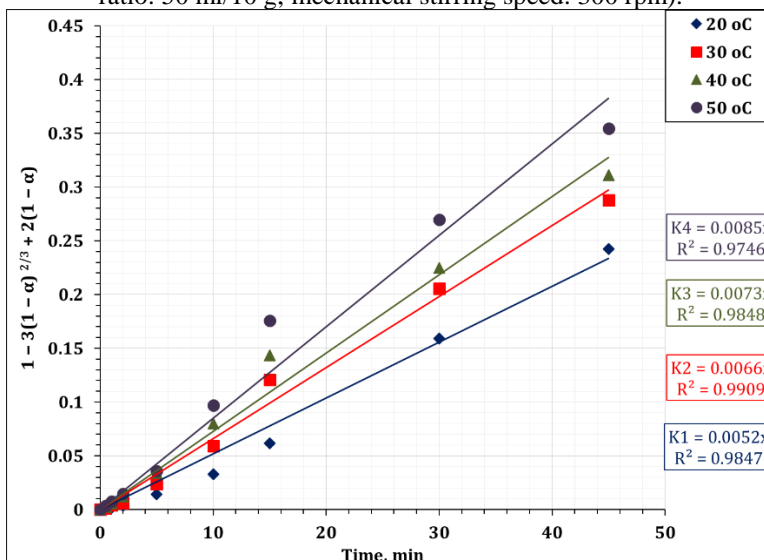

Fig (9): Effect of temperature on the function $[1 − 3(1 − α)^{2/3} +2(1 − α)]$ (particle size: 150-63 μm; [Tartaric acid]: 1.0 M; L/S mass ratio: 5/ 1; stirring speed: 300 rpm).

From the Figures, it was perceived that the rate determining step of the dissolution reaction is ash layer diffusion controlled. The rate expression for leaching reaction of REEs was found to follow the rate equation 3.

The values of the regression coefficients and the apparent rate constants calculated at different reaction temperature are shown in Table 2.

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

Temperature, ℃	Apparent K, min^{-1}	ln K	Correlation coefficient
20	0.0052	-5.26	0.98
30	0.0066	-5.02	0.99
40	0.0073	-4.92	0.98
50	0.0085	-4.77	0.97

The activation energy (Ea) of REEs dissolution reaction was calculated from the Arrhenius equation:

$$K = k_o \, e^{-Ea/RT} \dots (4)$$

Where k is the overall rate constant (min^{-1}), k_o is the frequency factor (min^{-1}), Ea is the activation energy (J mol^{-1}), R is the universal gas constant (8.314 J $K^{-1}mol^{-1}$), and T is the reaction temperature (Kelvin).

From Equations 3 and 4, Arrhenius equation could be written as the following:

$$\left[1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha)\right] = k_o \, e^{-Ea/RT}t \dots (5)$$

According to Arrhenius equation, the relation between ln k and 1/T will give a straight line with a slope of –Ea/R and an intercept of ln k_o (Figure 10). From the Figure, it is clear that the relation is found to be linear with a correlation coefficient of 0.98. From the Figure, the activation energy and frequency factor k_o of REEs dissolution reaction have been calculated and found to be equals 12.43 kJ/mol and 0.22 min^{-1}. The activation energy value is below 20 kJ/mol, which proves that REEs leaching process form Abu-Tartur

phosphate rock using Tartaric acid solution is controlled by internal diffusion kinetics [20, 29]. Generally, a lower apparent activation energy of a chemical reaction is more favorable for the reaction. The apparent activation energy of the leaching system of the combined leaching agent is lower than that of ammonium sulfate, indicating less resistance in the leaching process and resulting in a higher leaching efficiency, which is consistent with the results of the leaching test [25].

Using the values of k_o and activation energy, Equation (5), can be written as,

$$\left[1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha)\right] = 0.22 \, e^{-12431/RT}t \dots (6)$$

The magnitude of energy of activation calculated for REEs leaching shows that the reaction of REEs with Tartaric acid is ash layer diffusion. Moreover, this value is in agreement with the value of activation energy found in a similar study [26].
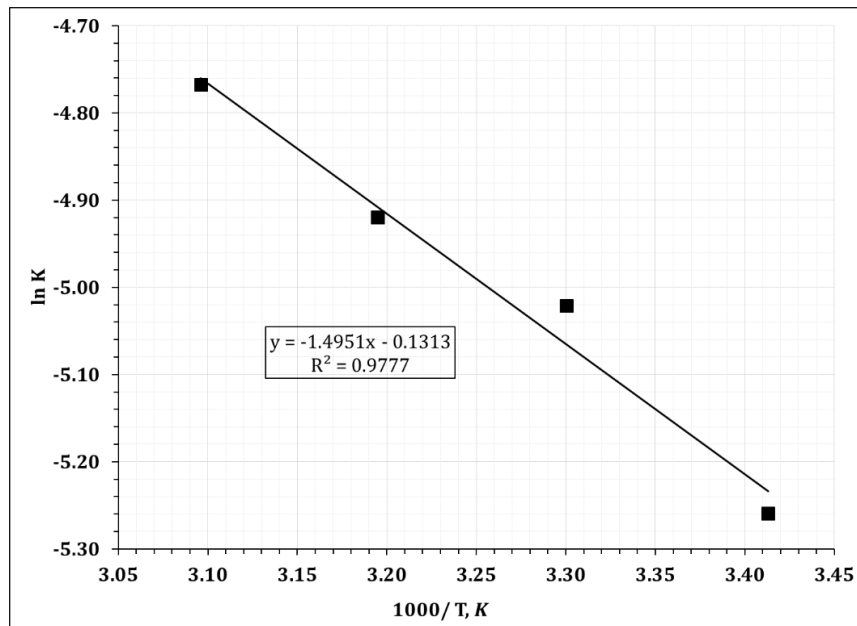

Fig (10): Relation between ln K and (1/T) K X 1000

To test the workability and reproducibility of the suggested model, the experimental data were compared with the calculated ones. The comparison of the two sets of data has been shown in Figure 11. The scatter diagram (Figure 11) represents that the arrangement between α_{exp} and α_{cal} is good. The value of correlation coefficient (0.98) indicates that the relationship between the two variables is good.

For 24 experimental observations, the relative mean square of errors was determined using the following equation:

$$ER = \left[\frac{1}{N} \sum_{i=1}^{N} \frac{(\alpha_{cal} - \alpha_{exp})^2}{(\alpha_{cal})^2}\right]^{1/2}$$

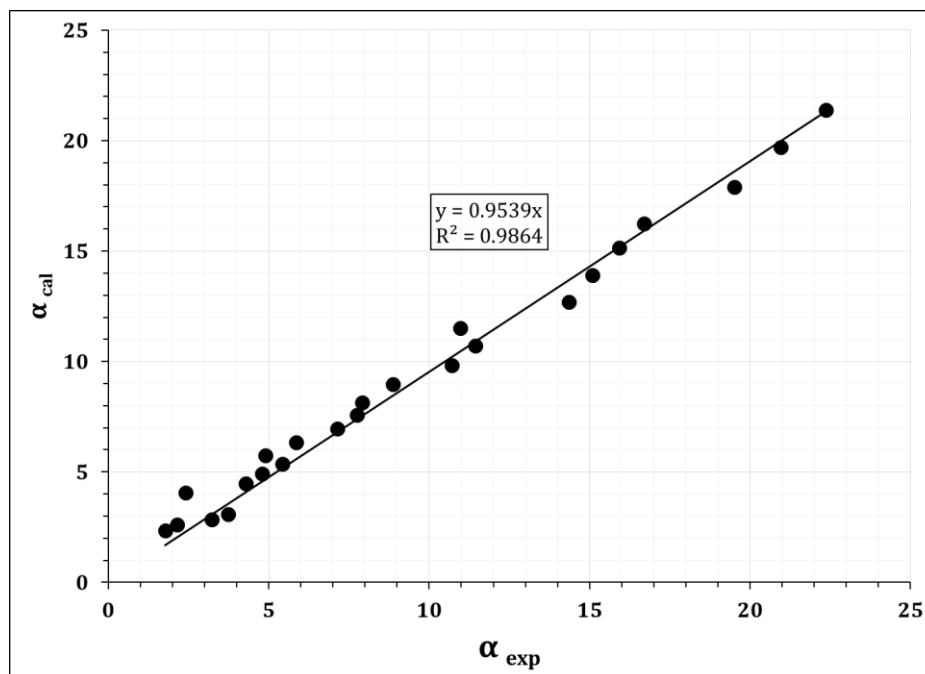The relative mean square of errors (0.024) also reasonably supports the applicability of the model.

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Fig (11): Agreement between experimental and calculated dissolution fractions

4. Conclusion:

The leaching of REEs from Abu Tartur phosphate rock using Tartaric acid solution has been investigated in terms of the highest REEs leaching efficiency with the minimum P_2O_5 leaching efficiency. The influence of different variables on the leaching process such as; leaching time, Tartaric acid concentration, reaction temperature, stirring speed, and liquid/ solid ratio has been studied. The preferred leaching conditions have been determined as, reaction time of 60 min; Tartaric acid concentration of 1.0 M, room temperature, and liquid/ solid ratio, mL/ g of 5: 1. Within these conditions,

the REEs and P_2O_5 leaching efficiency performance are 90.5 and 26.8 % respectively. Fluid/solid reaction models were used for the analysis of the data to evaluate the slowest step and the kinetic parameters for REEs leaching process. From the obtained results, it is clear that REEs leaching from phosphate rock with Tartaric acid is an ash layer diffusion-controlled process. The activation energy of the leaching process has been calculated and found to be equal to 12.43 kJ/mol.

References

[1] M. Khalil, and M. L. Denchi: Basins geometry and tectonic origin of the western Desert of Egypt, relevance to economic resources. In: El Sayed A.A., Youssef Eds., Proceedings of the 5th International Conference on the Geology of the Arab World, Cairo University II, (2000), 523–542.

[2] A. El-Kammar, Phosphorites: Visible target for optimistic prosperity, "National Workshop on Development of phosphate industries in Egypt" Nuclear Materials Authority, Cairo, Egypt, 7 - 8 September (2014).

[3] European Fertilizer Manufacturers Association, Booklet No. 4 of 8 Production of phosphoric acid. Belgium, (2000).

[4] C. R. Hammond, The Elements, CRC Handbook of Chemistry and Physics, Section 4, 89 th Ed, Boca Raton: CRC Press/ Taylor and Francis (2009).

[5] R. Eggert, C. Wadia, C. Anderson, D. Bauer, F. Fields, L. Meinert, P. Taylor, Rare earths: market disruption,

innovation, and global supply chains, Annu. Rev. Environ. Resour. 41 (2016).

[6] L. Wang, X. Huang, Y. Yu, L. Zhao, C. Wang, Z. Feng, D. Cui, Z. Long, Towards cleaner production of rare earth elements from bastnaesite in China, J. Clean. Prod. 165 (2017) 231–242.

[7] N. Krishnamurthy, C.K. Gupta, Extractive Metallurgy of Rare Earths, CRC Press, 2004.

[8] Y. Xiao, Z. Feng, X. Huang, L. Huang, Y. Chen, X. Liu, L. Wang, Z. Long, Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching, Hydrometallurgy 163 (2016) 83–90.

[9] A. Kumari, R. Panda, M.K. Jha, Y.L. Jin, J.R. Kumar, V. Kumar, Thermal treatment for the separation of phosphate and recovery of rare earth metals (REMs) from Korean monazite, J. Ind. Eng. Chem. 21 (2015) 696–703.

[10] M. N. Kouraim, M. M. Fawzy, O. S. Helaly, Leaching of Lanthanides from Phosphogypsum Waste using Nonyl Phenol Ethoxylate Associated with HNO_3 and HCl,

International Journal of Sciences: Basic and Applied Research, 16(2) (2014) 31-44.

[11] W. Shengdong, J. Kaixi, J. Xunxiong F. Lingyong, F. Yanqing, J. Wei, Z. Denggao, Kinetic study on leaching of RE in phosphorite, Nonferrous Metals (Extractive Metallurgy) 10 (2011) 9.

[12] F. Xingliang, L. Zhiqi, C. Dali, W. Liangshi, W. Liangshi, H. Xiaowei, H. Xiaowei, Kinetics of rare earth leaching from roasted ore of bastnaesite with sulfuric acid, Transactions of Nonferrous Metals Society of China 23 (2013).

[13] R. Chi, J. Tian, G. Zhu, Y. Wu, S. Li, C. Wang, Z. A. Zhou, Kinetics of Rare Earth Leaching from a Manganese-Removed Weathered Rare Earth Mud in Hydrochloric Acid Solutions, Separation Science and Technology 41 (2006), 1099 -1113.

[14] Z.I. Zafar, M. M. Anwar and D. W. Pritchard, Innovations in beneficiation technology for low grade phosphate rocks, Nutrient Cycling in Agroeco systems 46: (1996), 135-151.

[15] G. F. Malash, S. M. Khodair, Beneficiation of Abu Tartur phosphate rock by partial acidulation with formic acid, Alexandria Engineering Journal 44: (2005), 487–492.

[16] Z.I. Zafar and M. Ashraf, Selective leaching kinetics of calcareous phosphate rock in lactic acid, Chemical Engineering Journal 131: (2007), 41-48.

[17] M. Gharabaghi, M. Noaparast, M. Irannajad, Selective leaching kinetics of low-grade calcareous phosphate ore in acetic acid, Hydrometallurgy 95: (2009), 341–345.

[18] M. Ashraf, Z.I. Zafar and T. M. Ansari, Selective leaching kinetics and upgrading of low-grade calcareous phosphate rock in succinic acid, Hydrometallurgy 80: (2007), 286–292.

[19] Marczenko, Z., Balcerzak, M., and Kloczko, E. Separation, preconcentration and spectrophotometry in inorganic analysis. Amsterdam, The Netherlands: Elsevier Science (2000).

[20] O., Levenspiel, Chemical Reaction Engineering, 3rd ed. John Wiley, New York, (2003).

[21] H. Y. Sohn, Chemical Reaction Engineering in the Chemical Processing of Metals and Inorganic Materials Part I. Advances in Fluid-Solid Reaction Analysis, Korean Journal of Chemical Engineering, 20 (2), (2003), 185.

[22] Gao W C, Wen J K, Li Z B. Dissolution kinetics of magnesium from calcined serpentine in NH_4Cl solution [J]. Industrial &Engineering Chemistry Research, 53: (2014), 7947−7955．

[23] Ma, J., Du, X., Qin, Y., Wu, Z., Chi, R., & Wang, C. Kinetics on leaching of potassium from phosphorus–potassium associated ore in HCl– H_3PO_4 media. Transactions of Nonferrous Metals Society of China, 27(8), (2017), 1870–1877.

[24] Aracena A, Jerez O, Antonucci C. Senarmontite volatilization kinetics in nitrogen atmosphere at roasting/melting temperatures [J]. Transactions of Nonferrous Metals Society of China, 26: (2016), 294−300．

[25] Yan, H., Liang, T., Liu, Q., Qiu, T., & Ai, G. Compound leaching behavior and regularity of ionic rare earth ore. Powder Technology, 333, (2018),106–114.

[26] H.F. Aly, M.M. Ali, M.H. Taha. Dissolution Kinetics of Western Desert Phosphate Rocks, Abu Tartur, with Hydrochloric Acid. Arab Journal of Nuclear Science and Applications, 46(5), (2013), 1-16.

[27] Y. M. Khawassek, M.H. Taha, A.A. Eliwa, "Kinetics of Leaching Process using Sulfuric Acid for Sella Uranium Ore material, South Eastern Desert, Egypt", International Journal of Nuclear Energy Science and Engineering, 6, (2016), 62-73.

[28] Y. M. Khawassek, and M. H. Taha, Kinetic Leaching of Sella Uranium Ore with Hydrochloric Acid Solution, 45th International October Conference on Mining and Metallurgy 16-19 October, Bor Lake, Bor (Serbia), (2013), ISBN 978-86-6305-012-9.

[29] M. Ashraf, Z.I. Zafar and T. M. Ansari, Selective leaching kinetics and upgrading of low-grade calcareous phosphate rock in succinic acid, Hydrometallurgy 80 (2007) 286-292.