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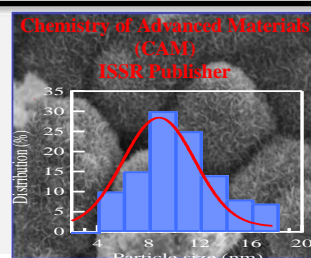
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## Leaching of Rare Earth Elements from Egyptian Western Desert Phosphate Rocks using HCl

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### Abstract

Rare Earth Elements from the western desert phosphate rocks (Abu-Tartur phosphate rocks, Egypt) were leached using hydrochloric acid. The effect of hydrochloric acid concentration, solid to liquid ratio, contact time and leaching temperature on leaching efficiency were investigated. Moreover, the kinetics of the leaching process was studied as a function of temperature. Under optimum leaching conditions, including hydrochloric acid concentration (1 M), solid to liquid ratio (1/3), kinetics analyses showed that the reaction rate of leaching is controlled by inner diffusion which can be described by the shrinking-core model. The diffusion-controlled process is characteristic by activation energy obtained value (11.76 kJ mol<sup>-1</sup>).

## 1. Introduction

According to the IUPAC, rare earth elements (REEs) are defined as a group of seventeen chemically similar metallic elements that comprise the fifteen lanthanide elements (atomic number 57 to 71) along with scandium and yttrium [1]. These two elements are tends to

occur in the same ore deposits as the lanthanides and exhibit similar chemical properties, therefore they considered as REEs. They originally obtained as earths or oxides from rare minerals, thus they were named rare earths [2]. REEs are classified into two categories; LREEs (lanthanum

through gadolinium, with atomic numbers 57–64) and HREEs (terbium through lutetium, atomic number 65 to 71), and also yttrium (atomic number 39). 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 of energy efficiency and advance lifestyle consumer and other medical applications [3-7]. 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 [8].

There are many sources of REEs in Egypt. Among of them, Abu-Tartur phosphate mine is the largest mine in Egypt and Middle East. The lanthanides content in phosphate Abu-Tartur is assaying 0.11 % [9, 10]. A lot of studies have been reported on the leaching of rare earth from their ores [11, 12] described REEs leaching from the ore materials using  $(\text{NH}_4)_2\text{SO}_4$ . It was found 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  $\text{HNO}_3$  or these acids associated with Nonyl Phenol Ethoxylate [13]. 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  $\text{kJ mol}^{-1}$  to 5.28 and 3.79  $\text{kJ mol}^{-1}$  for HCl and  $\text{HNO}_3$  respectively. Wang et al. [14] described the kinetics of leaching from

phosphoric ore by  $\text{HNO}_3$ , it was found that the leaching process was controlled by the chemical reaction. The apparent activation energy was calculated to be 70.6  $\text{kJ mol}^{-1}$ , and the apparent reaction order was 0.83. Xingliang et al. [15] studied sulfuric acid as leaching agent to extracting REEs from roasted ore of Dechang bastnaesite in Sichuan, China. It was found the optimum conditions including particle size (0.074–0.100 mm), sulfuric acid concentration of 1.50 M, S/L of 8 and stirring speed of 500 rpm. The apparent activation energy is 9.24  $\text{kJ mol}^{-1}$ , this proves that the leaching process is controlled by the diffusion of reactants and products through a porous layer. Chi et al. [16] 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  $\text{kJ mol}^{-1}$ .

One of the most important characteristics of the Abu-Tartur phosphate deposits is its relatively high content of lanthanides. The most common method of producing phosphoric acid is the so called (Wet Process) in which phosphate rock is reacted with sulfuric acid. This study aims to investigate and achieve the optimum conditions of REEs leaching from western desert phosphate rocks (Abu-Tartur phosphate rocks, Egypt) using HCl leaching.

## 2. Experimental

### 2.1 Materials

The samples for this study were collected from the practical mine of Abu-Tartur plateau located in the western desert of Egypt. All the chemicals used were of laboratory grade reagent. Distilled water was used for the dilution and

preparation of solution of known concentration. The ore composition was analyzed using the Inductively Coupled Plasma-Optical Emission

Spectrometry (ICP-OES, Prodigy high dispersion ICP, Teledyne-Leeman Labs, USA) and the results are listed in Table 1.

**Table 1:** Chemical analysis of major and trace elements for Abu-Tartur phosphate rock sample

<i>Constituent</i>	<i>Concentration (%)</i>	<i>Constituent</i>	<i>Concentration (ppm)</i>	<i>Constituent</i>	<i>Concentration (ppm)</i>
<i>SiO<sub>2</sub></i>	5.00	<i>MnO</i>	0.09	Cu	15
<i>Al<sub>2</sub>O<sub>3</sub></i>	0.90	<i>F<sup>-</sup></i>	3.11	Cr	157
<i>Fe<sub>2</sub>O<sub>3</sub></i>	4.20	<i>Cl<sup>-</sup></i>	0.05	Cd	9
<i>CaO</i>	43.50	Zn	176	Ba	209
<i>MgO</i>	1.55	Zr	35	Ni	16
<i>P<sub>2</sub>O<sub>5</sub></i>	29.30	Th	5	Sr	1330
<i>TiO<sub>2</sub></i>	0.09	U	21	As	45
<i>Na<sub>2</sub>O</i>	1.42	V	182	* <i>L.O.I</i>	9.54
<i>K<sub>2</sub>O</i>	0.17	Pb	6	** $\Sigma$ REEs	2117

\*L.O.I: loss of ignition at 1000°C, \*\* $\Sigma$ REEs: Total Rare Earth Elements

## 2.2 Experimental Methods

The ore was crushed and screened to less than 200 mesh size. The leaching process of REEs from the ore was carried out at room temperature; stirring of leaching agent and phosphate sample was achieved using magnetic stirrer. HCl used as a leaching agent. In the present work the leaching is studied by batch technique, the concentration of HCl was varied between 0.1 and 2 M, the contact time was varied between 5 and 120 minute, S/L was varied between 1 and 0.166(gm/ml) and the temperature was varied between room temperature and 70 °C. At the end of each test, the leachate was analyzed for total REEs ions by using spectrophotometric method using Arsenazo-III in weakly acidic solution at pH 2.6 ,thus in such medium REEs react with Arsenazo-III to form a green complex which is the base of determination method[17]. The leaching percent (L, %) of total REEs can be calculated as this equation [18] :

$$L(\%) = \frac{C_{a,e}}{C_{s,i}} \times 100 \quad (1)$$

where;  $C_{a,e}$  (mg L<sup>-1</sup>) and  $C_{s,i}$  (mg g<sup>-1</sup>) are aqueous REEs concentrations at equilibrium and initial solid phases REEs concentrations, respectively.

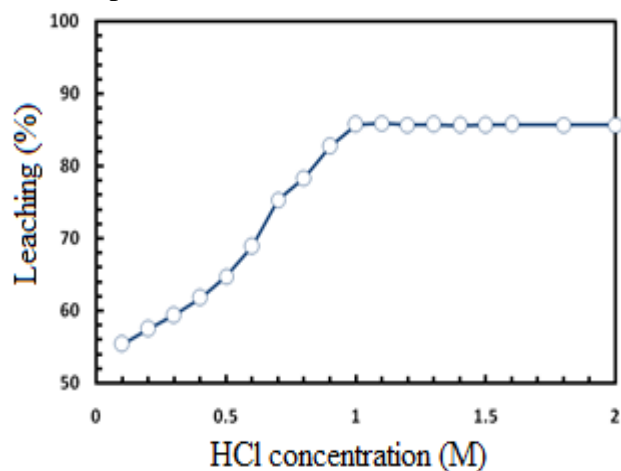
## 3. Results and Discussion

### 3.1 Leaching Results

#### 3.1.1 Effect of HCl Concentration

The effect of HCl concentration on the leaching efficiency of REEs from the ore was carried at constant values of agitation speed 200 rpm, particle size less than 200 mesh, 60 minute contact time, 1/3 S/L ratio at room temperature. The leaching of REEs increases from 55.35 to 85.66 % using acid concentration ranged from 0.1 to1 M as shown in Figure 1. These findings are very close to those obtained for waste phosphor [19]. It seems that the increase in acid concentration in the leaching medium caused the acid saturation near the solid particles .Thus, 1 M

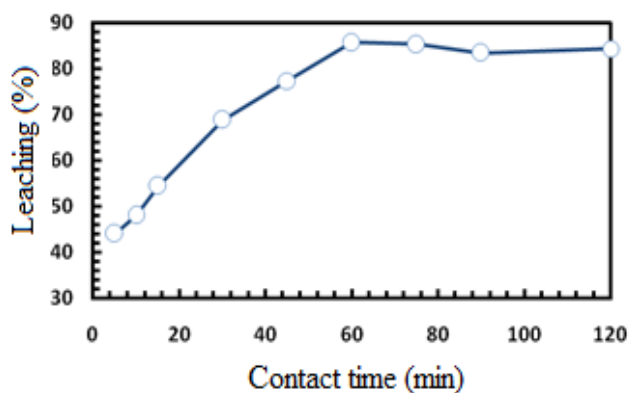
acid concentration is proposed as optimum for latter experiments.



**Figure 1:** Effect of HCl concentration on leaching efficiency of REEs.

### 3.1.2 Effect of Contact Time

Figure 2 shows the leaching ratio as a function of contact time. In these experiments, different leaching times (5 to 120 minutes) was tested. The other leaching conditions were kept fixed, 1 M HCl, 200 rpm stirring speed, S/L ratio of 1:3 at room temperature. The leaching of REEs increases from 44 to 85.66 % at 60 minutes.



**Figure 2:** Effect of contact time on leaching efficiency of REEs.

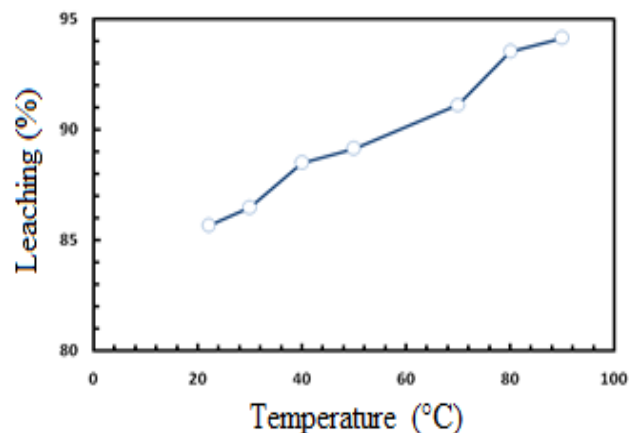
No further increasing in leaching of REEs after 60 minutes was observed. Therefore, 60 minute represents the preferred time for REEs leaching.

### 3.1.3 Effect of Solid to Liquid Ratio

The effect of the phosphate powder sample to hydrochloric acid ratio upon the leaching efficiency of REEs was investigated. A series of experiments were performed by varying S:L ratio from 1:1 to 1:6 while the other factors were kept constant at -200 mesh ore size, 1 M HCl, 200 rpm stirring speed and 60 minute contact time at room temperature. The leaching of REEs increased from 60.42 to 85.93 % by increasing the ratio from 1:1 to 1:3. Thus, the best S: L ratio is 1:3.

### 3.1.4 Effect of Temperature

The effect of temperature on leaching efficiency of REEs was carried out in the temperature range from 22 to 90 °C at a stirring rate of 200 rpm, for 60 minute and 1:3 solid to liquid ratio. The resulting leaching efficiencies are shown in Fig. 3 and indicate that the temperature plays a critical role in the leaching of REEs.



**Figure 3:** Effect of temperature on leaching efficiency of REEs.

At room temperature, the obtained leaching efficiencies for REEs were found to be around 85.65 %. By increasing the temperature to 90 °C, the leaching efficiency is gradually increased to 94.12 %. Thus, high temperature is favorable to leaching efficiency of REEs.

### 3.1.5 Obtained Leach Liquor

Under the above optimum conditions, 1 kg of properly ground sample (-200 mesh size) of Abu-Tartur phosphate sample was treated with 3 liters of 1 M HCl solution and 200 rpm agitating speed for 60 min. at room temperature. The insoluble gangue residue is then filtered and the obtained leach liquor is found to assay 665 mg L<sup>-1</sup> of total REE. Indicating a leaching efficiency of 94.5 % using a spectrophotometric technique. The chemical analysis of the individual rare earth elements (Table 2) in the leached liquor obtained from phosphate sample were determined using an ICP-OES technique.

**Table 2:** Chemical analysis of REEs for phosphate leach liquor using ICP-OES

REEs	Conc. (mg L <sup>-1</sup> )	REEs	Conc. (mg L <sup>-1</sup> )
La	85.4	Dy	18.6
Ce	141.3	Ho	11.0
Pr	18.5	Er	5.0
Nd	97.5	Tm	31.5
Sm	28.1	Yb	6.3
Eu	4.6	Lu	9.1
Gd	44.9	Y	90.2
Tb	9.4	Sc	63.3

### 3.2 Kinetic Analysis

The data obtained in the leaching of REEs at the varying temperature were analyzed with the shrinking-core model, in order to establish the kinetic parameters and rate-controlling step for the leaching of REEs using HCl [20]. Detailed explanation of the model is shown elsewhere [21]. The leaching kinetics can be subdivided into outer/inner diffusion and chemical control model. When more than one step limits the leaching kinetics, this process is considered to be mixed controlled [22].

i. Chemical reaction controls:

$$[1 - (1 - \alpha)^{1/3}] = k_1 t$$

(2)

ii. Outer diffusion controls:

$$[1 - (1 - \alpha)] = k_2 t \quad (3)$$

iii. Inner diffusion controls

$$[1 - (2/3)\alpha - (1 - \alpha)^{2/3}] = k_3 t \quad (4)$$

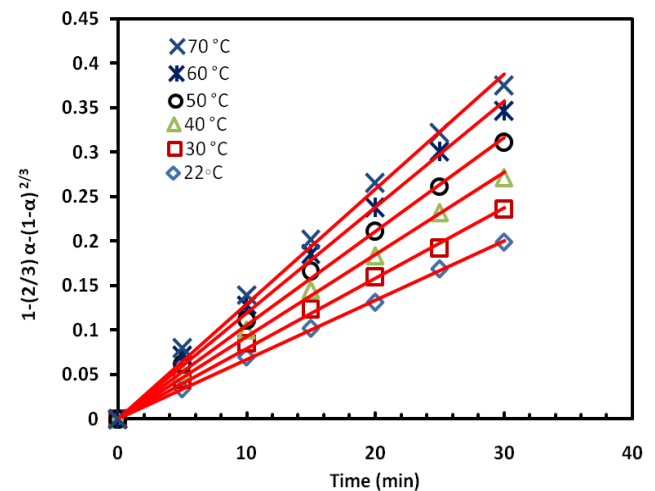
iv. Mixed controls:

$$[1 - (1 - \alpha)^{1/3}] = (k_4 C_0 M / r_0 p) t \quad (5)$$

where;  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are rate constant (min.<sup>-1</sup>) for different control steps, respectively;  $t$  is leaching time (min);  $C_0$  is the initial concentration of leaching reagent;  $r_0$  is the initial radius of the ore sample particle;  $p$  is molar density of the sample particle;  $m$  is the mass in gm of the sample particle;  $\alpha$  is the rare earth leached fraction where  $\alpha$  expressed as:

$$\alpha = \frac{\text{Amount of REEs in the solution}}{\text{Total amount of REEs in original sample}} \quad (6)$$

The kinetics equation is obtained by try and error method [23]. Only equation (4) has been found to give a perfect straight line with plotting  $1 - (2/3)\alpha - (1 - \alpha)^{2/3}$  vs. time (t). Figure 4 shows the different leaching temperatures with a good correlation  $R^2 > 0.99$ . It follows the inner diffusion control model [24].



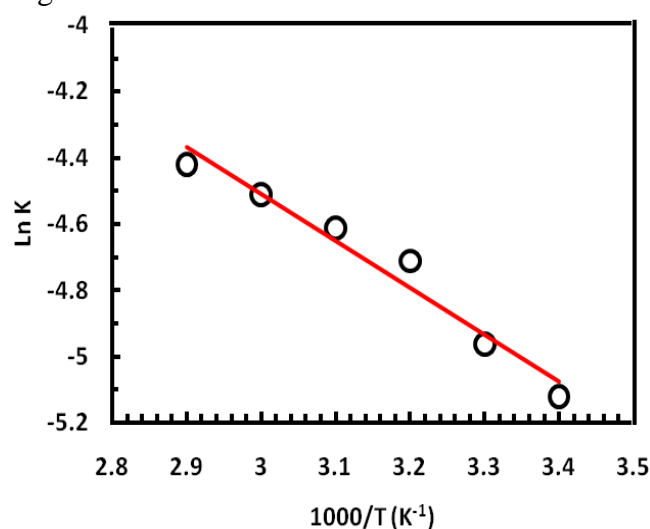
**Figure 4:** Plot of  $1-(2/3)\alpha-(1-\alpha)^{2/3}$  vs. time at various temperatures.

### 3.3 Calculation of Activation Energy

To further verify this proposal, the activation energy ( $E_a$ ) was determined using the following Arrhenius equation [25]:

$$\ln k = \ln A - (E_a/RT) \quad (7)$$

Where,  $k$  is the overall rate constant,  $A$  is the frequency factor,  $E$  is the activation energy ( $\text{kJ mol}^{-1}$ ),  $R$  is the universal gas constant ( $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) and  $T$  is the reaction temperature (Kelvin). From the slopes of these plots in Figure 5, the rate constants were determined and plotted against  $1/T \times 10^{-3}$  (Arrhenius plot) as presented in Fig. 5.



**Figure 5:** Arrhenius plot for REEs leaching from phosphate ore, the solid line is the linear fit.

To calculate the activation energy, a plot of  $\ln k$  vs.  $1/T$  should be a straight line with a slope of  $-E_a/R$  and an intercept of  $\ln A$ . The activation energy of the overall reaction was calculated as  $11.76 \text{ kJmol}^{-1}$ . The value of the activation energy also proves that the leaching of REEs from phosphate ore in hydrochloric acid liquid system is controlled by diffusion through

the product/ash layer. As its activation energy is between  $4$  and  $12 \text{ kJ mol}^{-1}$  [26].

## 4. Conclusions

To sum up, hydrochloric acid used to leach REEs from Abu-Tarture phosphate ore, the parameters effect on the leaching efficiency as acid concentration, solid to liquid ratio, contact time and temperature, were investigated at a constant stirring speed of 200 rpm. The results showed that on high ratio of REEs could be leached at the optimum conditions. Kinetic studies in the temperature range  $22-90^\circ \text{C}$  indicates that the REEs leaching process with hydrochloric acid is controlled by diffusion through the product/ash layer. The activation energy was found to be  $11.76 \text{ kJ mol}^{-1}$ .

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