



# Leaching of rare earths from Abu Tartur (Egypt) phosphate rock with phosphoric acid

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## Abstract

The leaching of rare earth elements (REEs) from Egyptian Abu Tartur phosphate rock using phosphoric acid has been examined and was subsequently optimized to better understand if such an approach could be industrially feasible. Preliminary experiments were performed to properly define the design of experiments. Afterward, 2<sup>4</sup> full factorial design was implemented to optimize the leaching process. Optimum REEs leaching efficiency ( $96.7 \pm 0.9\%$ ) was reached with the following conditions: phosphoric acid concentration of 30 wt.-% P<sub>2</sub>O<sub>5</sub>, liquid/solid ratio, mL/g, of 5:1, at 20 °C, and 120 min of leaching time. The apparent activation energy of the dissolution of REEs from phosphate rock using the phosphoric acid solution was -19.6 kJ/mol. D2EHPA was subsequently applied as an organic solvent for REEs separation from the acquired leach liquor. REEs stripping and precipitation were conducted, and finally, rare earth oxides with a purity of 88.4% were obtained. The leach liquor was further treated with concentrated sulfuric acid to recover the used phosphoric acid and produce gypsum with a purity of >95% at the same time. A flow diagram for this innovative cleaner production process was developed, and larger-scale experiments are proposed to further understand this promising approach to comprehensive phosphate rock processing.

**Keywords** Rare earth elements (REEs) · Separation optimization · Leaching · Abu Tartur phosphate rock · Egypt

## Introduction

Phosphate rock or pre-concentrated phosphate ore is an important raw material for the Egyptian economy with Egypt being the eighth largest phosphate rock producer in the world in 2020 [1]. Three main phosphate ore mining

zones can be differentiated in Egypt: (1) the area between El-Kharga and El-Dakhla Oases in the western desert, (2) the Nile valley near Idfu, and (3) the area along the red sea between Safaga and Quesir. The total phosphate ore reserves in Egypt are estimated to be as high as 2.8 billion t [2, 3], making Egypt the country with the third-largest phosphate rock reserves in the world, after Morocco (50 billion t) and China (3.2 billion t). The Abu Tartur phosphate deposit is the biggest of its kind in the Middle East [3]. Phosphate ore in this area is of sedimentary origin of which the most commonly encountered variants are Fluorapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F) and Francolite (Ca<sub>5</sub>(PO<sub>4</sub>,CO<sub>3</sub>)<sub>3</sub>F) [2].

Rare earth elements (REEs) play a critical role in civilization and human life. They are vastly utilized in most daily applications because of their unique chemical and physical properties [4, 5]. The tremendous dominance of Chinese producers, which supply > 90% of all REEs and register more REEs recovery and concentrations patents every year than all other producers combined [6–8], creates incentives to develop other REE resources currently considered unconventional. In this context, REEs recovered as a byproduct during phosphate ore processing may be a promising

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approach [9, 10]. Hakkar et al. [11] recently estimated that REEs co-recovered during phosphate ore processing in Morocco alone could have the potential to theoretically supply 7–15% of the global REEs demand. That is if all REEs could be recovered.

Sedimentary Abu Tartur phosphate ore from Egypt contains relatively high concentrations of up to 0.05–0.20 wt. % REEs [12–16], compared to those found in other sedimentary phosphate ores, which are roughly 0.05% [16, 17]. During wet phosphoric acid (WPA) production, the predominant process used to process phosphate ore to fertilizer, most of the REEs (>80%) in the phosphate ore are transferred to the solid phosphogypsum byproduct from where recovery is a challenge [14, 18–20]. Recovering REEs from the liquid phosphoric acid stream is possible, but only 20% of the REEs present in the phosphate ore transfer here so that the process is presently not economically feasible. Direct leaching of REEs from the phosphate ore or phosphate rock may be an attractive proposition since all REEs could theoretically be recovered and if done well the remaining ore matrix could simply be processed using present-day WPA production infrastructure. Besides, radioactive trace elements may also be extracted in this step so that the resulting phosphogypsum shows activity levels below regulatory control so that what is considered a low-level radioactive waste material in most countries today could be used as an inexpensive raw material in construction tomorrow [21–23].

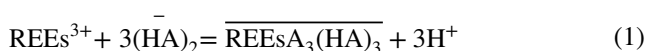
Although this is the first time that REEs are leached from Abu Tartur phosphate rock with phosphoric acid, the idea of directly leaching REEs from a raw material as a pre-processing step is not new and has been addressed in several studies: Al Khaledi et al. [24], for instance, proposed this for Abu Tartur phosphate rock from Egypt, Amine et al. [25] for Moroccan phosphate ore, Bandara and Senanayake [26, 27] as well as Stone et al. [28] for fluorapatite from Australia, Jin et al. [29] and Li et al. [30] for Zhijin phosphate rock from China, Jorjani et al. [31] and Soltani et al. [32] for apatite-concentrate from Iran, Kim et al. [33] for apatite-based ore from Mongolia, Ogata et al. [34] for Phalaborwa ore from South Africa, and Wu et al. [35] for Fanshan material from China.

REEs occur in phosphate rock through diadochic exchange for Ca in the apatite and francolite lattices. They can be released easily into a leaching solution through treatment with mineral acids. If phosphoric acid is chosen as a leaching agent, the process profits in a way that acid treatment initiates recrystallization to give calcium phosphate, while the predominant anion remains phosphate. This is to say that this process commences with destroying the apatite lattice which in turn reestablishes as calcium phosphate once the equilibrium concentration of the constituting ions in solution is reached and the solubility

product has been exceeded. All anions foreign to calcium phosphate accumulate in the solution. This is a strategy that is commonly and successfully applied in the WPA process for phosphoric acid production along the hemihydrate route, where  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  is recrystallized to give  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in the presence of a large excess of sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The approach is similar in both cases: releasing foreign ions into the solution while reforming a mostly “pure” lattice. In the case of apatite treatment with phosphoric acid, it is in the first place the extrusion of REEs. Secondly one profits from removing carbonate impurities that leave the system as  $\text{CO}_2$ .

Once the REEs are in solution, there are several options for their recovery from the WPA. Methods such as absorption, precipitation, crystallization, ion exchange, and solvent extraction have, for instance, been tested [36–40]. Though tested extensively, most of these methods face considerable techno-economic difficulties that have prevented large-scale industrial application. The precipitation approach, for instance, suffers from phosphorus (P) loss, high reagent consumption, and interactions with impurities [36, 41], while the high energy consumption is the main problem for the crystallization technique [16, 35]. Ion exchange, on the other hand, rarely exceeds metal recovery rates of 60% [38, 42]. The solvent extraction technique is considered the most promising approach for effective and industrial-scale recovery of REEs from WPA today [39, 40].

For this latter approach, various extractants such as TOPS-99, PC-88A, Cyanex 272, and 923, as well as the mixture of PC-88A + Cyanex 301 have been checked for their ability to remove REEs from phosphoric acid solutions [39, 43–46]. D2EHPA, DOPPA, and DNPPA are examples of acidic extractants, which were applied for REEs extraction from WPA [47–49]. Generally, the reaction between REEs and acidic extractants can be expressed as done in Eq. (1) [40].



where HA represents the acidic extractant.

The mixture of D2EHPA + TBP and D2EHPA + TOPO was applied for uranium (U) which is also naturally present in phosphate ore in relevant amounts [50–53] and REEs recovery into the green cake from WPA, and hydrofluoric acid was used as a stripping agent [54]. The organic mixture of DOPPA + TOPO does, however, exhibit a low synergistic effect on REEs and U extraction from WPA [48]. Wu et al. [40] reported that REEs could be extracted effectively from WPA by D2EHPA alone. Solvent mixtures (D2EHPA + TOPO/TBP) do decrease REEs extraction efficiency significantly though and increase the loss that is usually the most crucial element for the recovery operation. Although solvent extraction is a potentially effective method for REEs recovery from WPA, further systematic analysis is needed to better understand the potential use of this technology [16].

The purpose of this work is to maximize the direct leaching efficiency of REEs from Abu Tartur phosphate rock using phosphoric acid as leachate and by systematically evaluating the relevant processing parameters to be able to propose a cleaner production route for Abu Tartur phosphate rock. Once the factors and the factor levels were properly defined, a  $2^4$  full factorial design was applied to optimize the process by obtaining the maximum REEs leaching efficiency. In addition, dissolution mechanisms were assessed to investigate the relevant parameters affecting the dissolution of lanthanides from Abu Tartur phosphate rock using phosphoric acid as a leachate to assess the dissolution mechanisms and establish empirical dissolution equations.

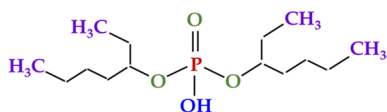
## Materials and methods

### Materials

A representative phosphate rock working sample was collected from the understudy mine of the Abu Tartur plateau in the Western Desert of Egypt, where the New Valley project is currently under development. The phosphate sample was crushed with a jaw crusher until the entire sample passed through a 150- $\mu\text{m}$  sieve. Afterward, the material was thoroughly mixed and dried for 24 h in an electric oven at 110 °C. Finally, the sample was cooled and stored for further use. Orthophosphoric acid (62 wt. %  $\text{P}_2\text{O}_5$ ) was supplied from Merck KGaA, Germany, and used to prepare leaching reagent solutions. Hydrochloric acid (37%) was purchased from Merck KGaA, Germany, and used to prepare stripping reagent solutions. Di-(2-ethyl hexyl) phosphoric acid (purity 95%) was provided by Merck KGaA, Germany, and utilized without purification. Kerosene (boiling point: 433–473 K) mostly aliphatic (96.2%) was supplied by Misr Petrol. Ltd., Egypt, and used as diluent. The structure formula of the utilized extractant is presented in Figure 1.

### Characterization of the abu tartur phosphate rock

X-ray powder diffraction (XD1180 model, Shimadzu, Japan) was applied to determine the mineralogical composition of the phosphate rock sample. The chemical analysis was conducted using X-ray fluorescence (XRF) spectroscopy (Axios, sequential WD-XRF spectrometer, PANalytical, UK). Inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 2100DV model, Perkin-Elmer, USA)



**Figure 1.** Structural formula of the D2EHPA organic solvent

was applied to determine the concentration of REEs in the solid sample after digestion treatment using a mixture of hydrofluoric acid, perchloric acid, and nitric acid as described by Li et al. [30].

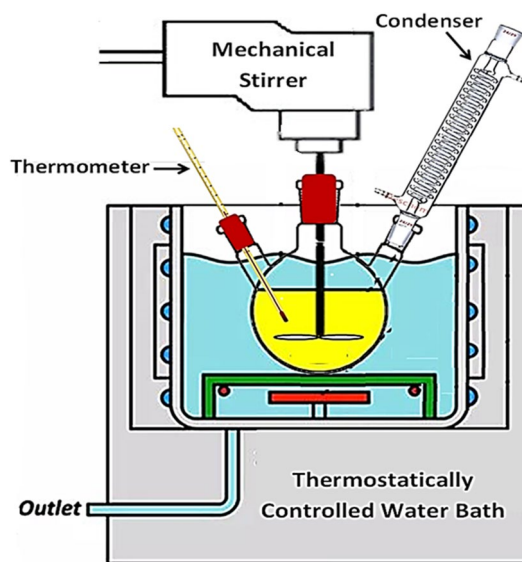
### Experimental set-up

The leaching experiments were conducted in a 500-mL glass reactor using a mechanical stirrer (DLH model, VELP, Italy). A thermostatically controlled water bath with an accuracy of  $\pm 1$  °C (TSSWB15 model, Thermo Scientific, USA) was employed to keep the reaction medium at a constant temperature. Figure 2 provides an overview of the experimental set-up.

### Optimization of the REE leaching efficiency

#### Preliminary tests

Preliminary leaching experiments were performed to investigate the effect of the main factors on the dissolution of phosphate rock using phosphoric acid as a solution agent. The investigated parameters were reaction time (15–900 min), phosphoric acid concentration (5–40 wt.-%  $\text{P}_2\text{O}_5$ ), liquid/solid ratio (2–7 mL/g), leaching temperature ( $25\text{--}60 \pm 1$  °C), and stirring speed (60–200 rpm). Leaching experiments were performed in duplicates. In the leaching process, a specific volume of phosphoric acid solution was heated and mixed with the desired amount of the ground phosphate rock sample with a particle size of 150  $\mu\text{m}$ . The solution was filtered once the residence time was achieved. The concentration of the REEs was determined using ICP-OES. The leaching efficiency % was calculated using Eq. (2):



**Figure 2.** Experimental set-up

$$\text{REEs leaching, \%} = \frac{\text{REEs concentration in the solution, g}}{\text{REEs initial concentration, g}} \times 100 \quad (2)$$

### Design of Experiments, model equation, and optimum

The design of experiment (DoE) methodology is a widely used approach to examine the overall main factor effects and interactions of different factors, which cannot be attended by the one-factor-at-a-time methodology. Accordingly, DoE is applied for obtaining better results with a minimum effort, time, resources, and costs [55, 56]. The full factorial design ( $2^p$ ) is the most widely used type of DoE, which is applied for screening and optimization studies. Based on this design, each parameter is investigated at two points, i.e., low (denoted as -1) and high (denoted as +1) [55–57]. The addition of center points (denoted as 0) to the design allows the researcher to check whether the effects' linearity is a reasonable assumption or whether quadratic terms should be added to the model [58]. In this study, the experiment order was random to avoid systematic errors. The results were analyzed with the Statgraphics v.16 (Statpoint Technologies, USA) software to determine the model equation as well as the global optimum. Modeling can be performed using the first-order model as defined in Eq. (3) [55, 56]:

$$y = b_0 + \sum_{i=1}^n b_i x_i + \sum_{i=1}^n \sum_{j>1}^n b_{ij} x_i x_j \quad (3)$$

or the second-order model, which is depicted in Eq. (4):

$$y = b'_0 + \sum_{i=1}^n b'_i x_i + \sum_{i=1}^n b''_i x_i^2 + \sum_{i=1}^n \sum_{j>1}^n b'_{ij} x_i x_j \quad (4)$$

where  $y$ : Target value: REEs efficiency [%];  $x_i$ : Factors;  $N$ : Number of factors: 4;  $b_0$ : Ordinate section;  $b_i$ ,  $b_{ij}$ ,  $b_{ji}$ : Regression parameters of linear, squared, and cross effects.

### Leaching kinetic analysis

The shrinking core model (SCM) is commonly applied to describe the fluid–solid heterogeneous reaction systems such as the leaching of REEs from phosphate rock using a phosphoric acid solution [59–61]. According to the SCM, one of the following steps could control the rate of the leaching reaction: (I) film diffusion control, (II) surface chemical reaction, and (III) ash layer diffusion control. In the present work, REEs leaching experiments were conducted at high stirring speed so that the film diffusion control step will not affect the rate of the reaction. Accordingly, the leaching reaction can be controlled only by ash layer diffusion control (Eq. 5) and surface chemical reaction (Eq. 6) [60, 61].

$$kt = 1 - 3(1 - \alpha)^{\frac{2}{3}} + 2(1 - \alpha) \quad (5)$$

$$kt = 1 - 3(1 - \alpha)^{\frac{1}{3}} \quad (6)$$

where  $k$  is the apparent reaction rate constant,  $t$  is the time, and  $\alpha$  is the leaching fraction.

### REEs separation investigation

REEs separation experiments (extraction and stripping) were conducted by liquid–liquid extraction technique using separatory funnels. Preliminary tests revealed that 15 min is sufficient to reach the reaction equilibrium for both extraction and stripping experiments. Accordingly, equal volumes of aqueous and organic phases ( $R_{aq/org} = 1$ ) were shaken for 15 min, at a stirring speed of 200 rpm/min at room temperature. After phase separation, the aqueous phase was filtered with Whatman phase separation (1 PS) paper to remove the traces of organic impurities. The REEs concentration in the aqueous phase was determined using ICP-OES and used to calculate the REEs extraction efficiency (%).

## Results and discussion

### Characterization of the phosphate rock

The chemical analysis of the phosphate rock is shown in Table 1. The phosphate rock sample contained 30.1%  $P_2O_5$  and 44.4% CaO with a CaO/ $P_2O_5$  ratio of 1.48. The value  $\geq 1$  indicates that Abu Tartur phosphate is a high-grade phosphate rock [2, 3]. The total REEs content of 1810 ppm (0.18%) is within typical ranges reported for sedimentary phosphate rocks. The XRD pattern (Fig. 3) of the sample indicates that the dominant mineral is fluorapatite, together with minor amounts of dolomite and calcite, quartz, pyrite, hematite, and limonite. This result is in accordance with the previously reported data for Abu Tartur phosphate rock [2, 3].

### Optimization of the REEs leaching efficiency

#### Preliminary test

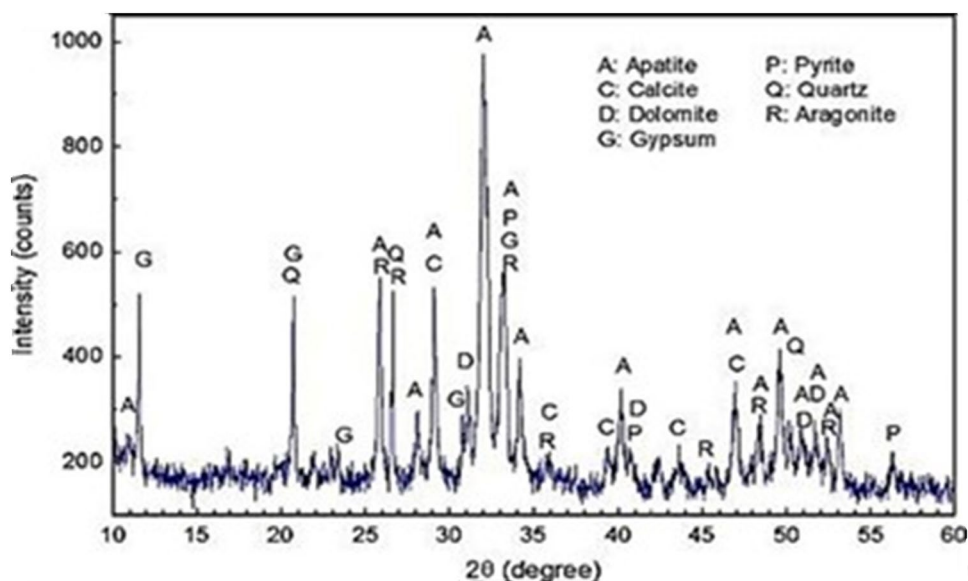
To properly design the DoE to optimize the leaching efficiency of REEs from Abu Tartur phosphate rock, preliminary leaching experiments were conducted. The effect of different parameters such as reaction time, phosphoric acid concentration, liquid/solid ratio, temperature, and mechanical stirring, on the target value, was evaluated (Fig. 4).

The effect of the reaction time on the dissolution rate of Abu Tartur phosphate rock was investigated within a range of 15 to 900 min. Fig. 4a shows that the leaching efficiency

**Table 1** Chemical characterization of Abu Tartur phosphate rock

Constituent, wt. %			
P <sub>2</sub> O <sub>5</sub>	30.1	SO <sub>3</sub>	1.50
CaO	44.4	MgO	0.90
Fe <sub>2</sub> O <sub>3</sub>	3.8	Al <sub>2</sub> O <sub>3</sub>	0.46
F	2.8	Na <sub>2</sub> O	0.28
SiO <sub>2</sub>	2.3	L.O.I.*	5.1
Constituent, mg/kg			
La	430.0	Dy	37.4
Ce	478.4	Ho	9.2
Pr	80.0	Er	30.1
Nd	440.0	Tm	4.1
Sm	68.0	Yb	19.6
Eu	18.5	Lu	3.8
Gd	52.3	Y	132.0
Tb	7.1	U	25.0
Σ REEs	1810.5		

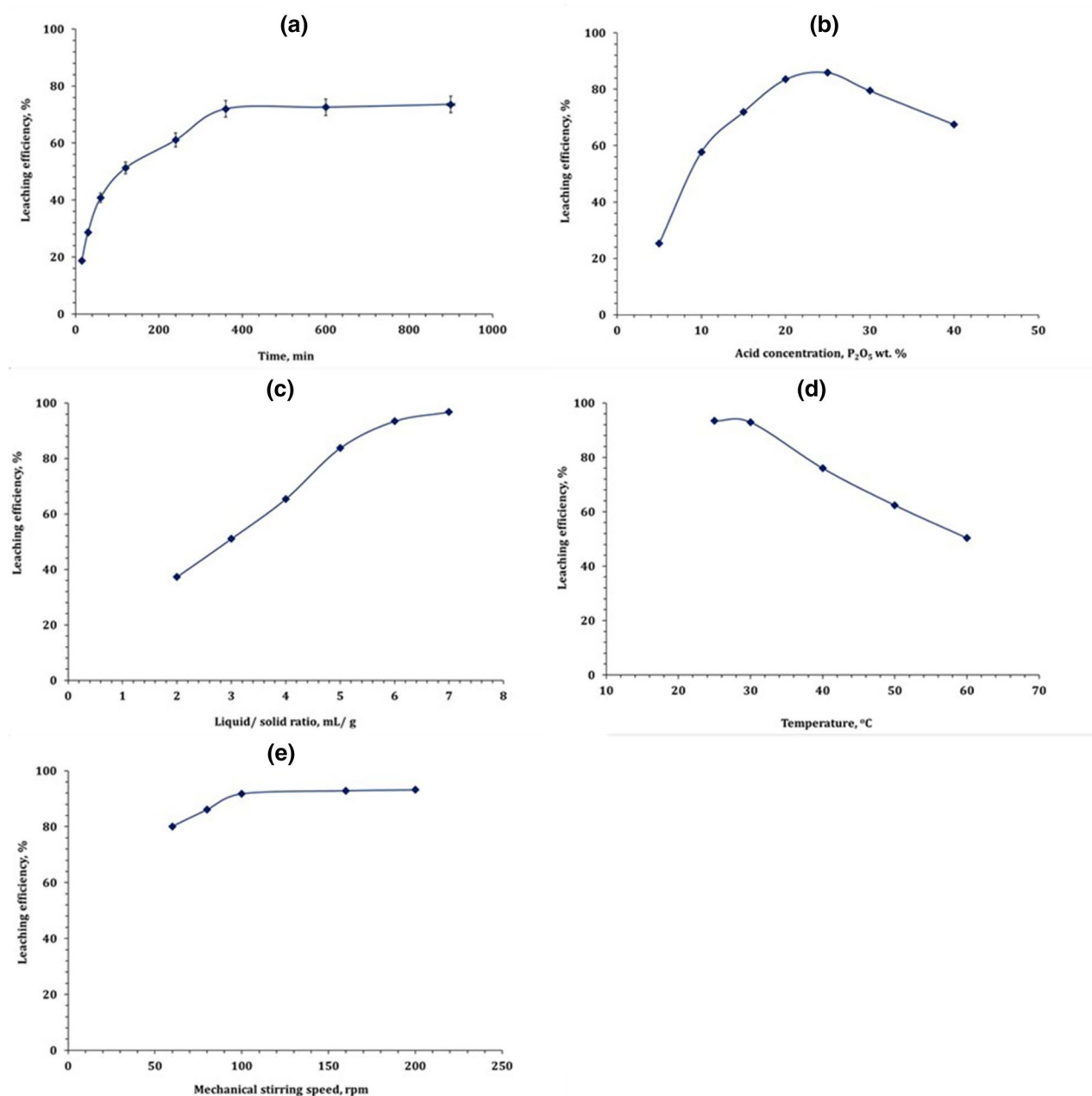
\*L.O.I. = loss of ignition

**Figure 3.** X-ray diffraction pattern of Abu Tartur phosphate rock

of REEs is increased as the reaction time increases from 15 to 360 min. A further increase in the leaching time has only a slight impact on the leaching efficiency. This indicates that the leaching rate of the reaction starts rapidly until ~360 min (equilibrium time), then the rate of reaction becomes very slow (Plateau shape). The same behavior has been reported for the leaching of P and REEs from an iron-rich fluorapatite concentrate [32], and phosphate ore from China [35, 62]. The reaction dissolution time was thus kept at 360 min in further experiments.

The effect of the phosphoric acid concentration was investigated for a range of 5 and 40 wt.-% P<sub>2</sub>O<sub>5</sub>, and the results are shown in Fig. 4b. It could be revealed that the increase in phosphoric acid concentration from 5 to 25 wt.-% P<sub>2</sub>O<sub>5</sub> drastically improves the leaching efficiency of REEs. The increase of the H<sup>+</sup> ions in the solution as the phosphoric acid concentration increases supports the results obtained [35, 62]. By increasing the phosphoric acid concentration to >25 wt.-%, the REEs leaching efficiency decreases sharply. This observation can be understood in terms of REEs precipitation as phosphate salts [32]. In addition, the presence





**Figure 4.** Effect of different parameters on REEs leaching efficiency from Abu Tartur phosphate rock with a particle size of 150  $\mu\text{m}$ . **a** reaction time: 5 mL/g; 100 rpm; 15 wt.-%  $P_2O_5$ ; 25 °C. **b** phosphoric acid concentration: 5 mL/g; 100 rpm; 360 min; 25 °C. **c** liquid/ solid

ratio (mL/g): 100 rpm; 20 wt.-%  $P_2O_5$ ; 360 min; 25 °C. **d** temperature: 6 mL/g; 100 rpm; 20 wt.-%  $P_2O_5$ ; 360 min. **e** stirring speed: 6 mL/g; 20 wt.-%  $P_2O_5$ ; 360 min; 25 °.

of fluoride ions in solution results in the precipitation of REE-fluorides [32, 63, 64]. 20 wt.-%  $P_2O_5$  was the acid concentration chosen to be used in the following experiments.

Fig. 4c shows the effect of liquid/solid ratio, mL/g, on the REEs leaching efficiency. The experimental results reveal the enhancement of REEs when the liquid/solid ratio is increased from 2 to 6 mL/g. This is due to the decrease in the solution bulk density, which causes an

increase in the migration of different ions to the liquid medium [32, 35]. The same trend has been observed during the dissolution of REEs and P from phosphate rock using phosphoric acid [35, 62]. Further increase in the liquid/solid ratio  $>6$  mL/g has only a slight impact on the REEs leaching efficiency. Thus, 6 mL/g represents the preferred condition for the subsequent dissolution experiments.

**Table 2** Factors levels of the 2<sup>4</sup> full factorial design

Factors	Coded variables	Low level (−1)	High level (+1)
Phosphoric acid concentration, P <sub>2</sub> O <sub>5</sub> wt.-%	A	10	30
Liquid/solid ratio, mL/g	B	3	5
Temperature, °C	C	20	40
Residence time, min	D	120	360

The effect of reaction temperature on the dissolution process was investigated for the following temperatures: 25, 30, 40, 50, and 60 ± 1 °C. As shown in Fig. 4d, by increasing the reaction temperature, the dissolution efficiency of REEs dramatically decreased. Therefore, room temperature (25 °C) was chosen to be used in subsequent experiments. This performance is mainly attributed to the idea that during the dissolution of REEs from phosphate rock, REEs solubility in a mixture solution of monocalcium phosphate–phosphoric acid is negatively impacted by the increase in reaction temperature due to the formation of insoluble REE phosphate salt, particularly at elevated temperature, as shown in the following equation [65].



Liang et al. [66], Wang et al. [39], and Wu et al. [16] also reported that the solubility of REEs in phosphoric acid solution is negatively correlated with the reaction temperature due to the formation of insoluble REE phosphates.

### Influences on the target values, model equation, and optimum

To optimize the dissolution of phosphate rock using a phosphoric acid solution, the following preconditions must be fulfilled: (I) selection of the target value, (II) choosing the appropriate parameters that impact the reaction yield, and (III) defining the suitable range for each of the variables that significantly influence the product yield [67]. In this work, the main target is to maximize the dissolution of REEs from phosphate rock. In accordance with the preliminary results, four factors namely, phosphoric acid concentration, P<sub>2</sub>O<sub>5</sub> wt.-% (A); liquid/solid ratio, mL/g (B); temperature, °C (C), and residence time, min (D), show a remarkable impact on the REEs leaching efficiency. The stirring speed was not selected for the optimization because it exhibits only a minor

effect on the leaching process (~7 %). Therefore, a 2<sup>4</sup> full factorial design was used for the REEs leaching efficiency optimization. According to the experimental plan, 16 runs (Nr. 1–16) and 4 replications (Nr. 17–20) of the center points were designed. The levels of the coded variables are displayed in Table 2.

The operating conditions, as well as the dissolution efficiency, are provided in Table 3. The displayed data show that the fourfold experiment conducted in the center point resulted in REE recovery rates of 80.75 ± 1.9%, while the average of the 16 runs for the base design was 78.78%. Since the recoveries obtained from the 16 runs and the fourfold experiments in the center point are close, it is assumed that there is no curvature present in the optimized model [55–57]. In this regard, the regression model equation with interaction terms (Eq. (4)) was used to describe the optimization process [55, 57].

An analysis of variance (ANOVA) has been performed to determine the parameters that contribute significantly to the REEs dissolution performance. The associated confidence interval was set to 95%. The model f-value of 98.9 denotes that the model was significant. Table 4 shows the influence of ten effects: four linear (A, B, C, D) and six binaries (AB, AC, AD, BC, BD, CD) on the yield of REEs. Insignificant terms were removed by the stepwise method.

The effect of the significant factors on the target values is shown in Fig. 5 as a Pareto diagram. Five effects namely (B, A, D, BD, and BC) are contributing significantly to the REEs leaching efficiency. The liquid/solid ratio has the highest positive impact due to a decrease in the systems bulk density, which increases the diffusion of the ions and therefore increases the leaching efficiency [32, 40]. This result is consistent with the obtained data from the preliminary experiments (Fig. 4C). The increase in the phosphoric acid concentration (up to 30 wt.-% P<sub>2</sub>O<sub>5</sub>) also enhances the REEs dissolution efficiency, which can be attributed to an increase of H<sup>+</sup> ion concentration as a result of the increase of the phosphoric acid concentration, which positively influences the leaching process [40, 62]. The least positive effect parameter on the leaching efficiency is the residence time, which can be due to the fast dissolution reaction. This fact is in accordance with the lowest yield variations obtained for the studied residence time range of 120–360 min (Table 2). The results from the preliminary experiments (Fig. 4A) as well as other reports show that the equilibrium of the leaching reaction is achieved after 360 min [32, 40, 62]. This result is inconsistent with the obtained data from the DoE methodology.

One of the main advantages of the DoE methodology is the ability to explore the effects of the interactions between the main variables on the leaching efficiency [32, 61]. The Pareto diagram demonstrated that the BD interaction (liquid/solid ratio and residence time, as well as BC (liquid/

**Table 3** Design matrix of the 2<sup>4</sup> full factorial design

Run	Factors				Levels				REEs Yield%
	(A) wt.%	(B) mL/g	(C) °C	D (min)	A	B	C	D	
1	10	3	20	120	−1	−1	−1	−1	47.6
2	30	3	20	120	1	−1	−1	−1	64.5
3	10	5	20	120	−1	1	−1	−1	75.8
4	30	5	20	120	1	1	−1	−1	96.6
5	10	3	40	120	−1	−1	1	−1	55.2
6	30	3	40	120	1	−1	1	−1	70.0
7	10	5	40	120	−1	1	1	−1	78.8
8	30	5	40	120	1	1	1	−1	92.0
9	10	3	20	360	−1	−1	−1	1	72.1
10	30	3	20	360	1	−1	−1	1	85.9
11	10	5	20	360	−1	1	−1	1	85.9
12	30	5	20	360	1	1	−1	1	97.8
13	10	3	40	360	−1	−1	1	1	76.4
14	30	3	40	360	1	−1	1	1	90.6
15	10	5	40	360	−1	1	1	1	78.4
16	30	5	40	360	1	1	1	1	92.8
17	<b>20</b>	<b>4</b>	<b>30</b>	<b>240</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>81.3</b>
18	<b>20</b>	<b>4</b>	<b>30</b>	<b>240</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>80.5</b>
19	<b>20</b>	<b>4</b>	<b>30</b>	<b>240</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>80.2</b>
20	<b>20</b>	<b>4</b>	<b>30</b>	<b>240</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>81.2</b>

Bold values are considered the most relevant values

The experiments correspond to the replicated center point

**Table 4** Analysis of variance for REEs leaching

Source	Sum of Squares	df	Mean Square	F-value	p-value
A: Phosphoric acid concentration	900.0	1	900.0	252.12	0.0000
B: Liquid/solid ratio	1152.6	1	1152.6	322.89	0.0000
C: Temperature	4.0	1	4.0	1.12	0.3174
D: Residence time	617.522	1	617.522	172.99	0.0000
AB	0.0225	1	0.0225	0.01	0.9385
AC	2.89	1	2.89	0.81	0.3917
AD	8.1225	1	8.1225	2.28	0.1657
BC	81.9025	1	81.9025	22.94	0.0010
BD	361.0	1	361.0	101.13	0.0000
CD	14.0625	1	14.0625	3.94	0.0785
Total error	32.127	9	3.56967		
Total (corr.)	3174.25	19			

solid ratio and temperature), negatively affects the REEs yield. This behavior is attributed to the formation of REEs phosphate precipitate as shown in Eq. 7 [62].

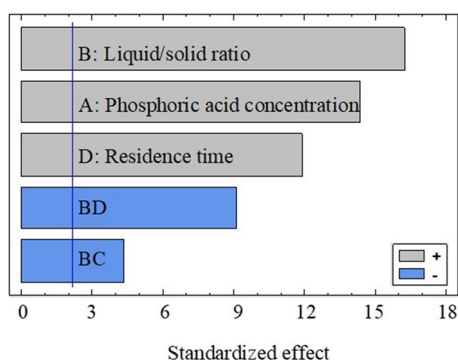
Modeling of the leaching reaction helps predict the REEs leaching efficiency at any point within the experimental factor boundary. Accordingly, the model equation of REEs dissolution from phosphate rock using phosphoric acid solution is displayed in Eq. (8).

$$\begin{aligned} \text{REEs efficiency (\%)} = & -47.345 + 0.75 \cdot (A) + 24.775 \cdot (B) \\ & + 0.905 \cdot (C) + 0.210104 \cdot (D) - 0.22625 \\ & \cdot (BC) - 0.0395833 \cdot (BD) \end{aligned} \quad (8)$$

where A: phosphoric acid concentration (P<sub>2</sub>O<sub>5</sub> wt.-%); B: liquid/solid ratio (mL/g); C: temperature (°C); and D: residence time (min).

In accordance with Eq. 8, about 96.6% of REEs can be successfully leached from phosphate rock using the following conditions: phosphoric acid concentration of 30 wt.-%





**Figure 5:** Pareto Diagram for REEs leaching process.

$P_2O_5$ , liquid/solid ratio of 5, room temperature (25 °C), and residence time of 120 min. The model was confirmed by conducting three experiments within the same operating conditions and obtaining a total REEs recovery rate of  $96.9 \pm 0.8\%$ .

The results of this work with regard to the REEs leaching yield from phosphate rock using phosphoric acid are compared with the accomplished yield of past studies from literature in Table 5. The four studies used very similar phosphoric acid concentrations ranging from 25 to 30 wt.-%  $P_2O_5$ , while the present work (DoE and OFAT methodologies) exhibits the lowest liquid/solid ratios of 5:1 and 6:1 or less than half the applied liquid/solid ratios reported in the literature. In addition, the DoE methodology shows a relatively low residence time (120 min) and a low reaction temperature (25 °C).

#### Specification of the leached acidulate solution

From the aforementioned investigation on the leaching behavior of REEs from Abu Tartur phosphate ore by phosphoric acid, a leaching experiment was carried out according to the

following optimum conditions: phosphate rock particle size  $\leq 150 \mu m$ , phosphoric acid concentration of 30 wt.-%  $P_2O_5$ , liquid/solid ratio of 5, and leaching time of 120 min at room temperature. The concentration of total REEs and main cations in the obtained acidic solution are shown in Table 6. The dissolution of the phosphate rock with phosphoric acid not only results in dissolving REEs but also results in the leaching of P, calcium, as well as other cationic impurities that are naturally found in the phosphate rock. In accordance with this finding, the present work aimed to recover both REEs and P (as valuable elements) from phosphate rock. The P yield of another phosphate rock dissolution cycle to reduce the cost of the proposed process was obtained. The yield leaching solution contained about 3.51 g/L  $\sum$  REEs, 56.6 g/L  $P_2O_5$ , 36.6 g/L calcium (as CaO), and 1.7 g/L iron (as  $Fe_2O_3$ ).

#### Leaching kinetic analysis

Two SCMs [Eqs. (5) and (6)] were examined at different temperatures, as shown in Fig. 6 and Fig. 7 to determine the kinetics of leaching REEs from Abu Tartur phosphate rock using a phosphoric acid solution. Fig. 6 depicts a perfectly straight line with an average correlation of 0.98. Therefore, Eq. (2) fits the experimental results well and it can be confirmed that the dissolution of REEs from Abu Tartur phosphate rock is in these experiments indeed controlled by an ash layer diffusion mechanism. The different values of the apparent rate constant,  $k$ , at different temperatures were obtained from the slopes of each line in Fig. 7 and are summarized in Table 7.

To further verify this proposal, the activation energy,  $E_a$  (J/mol), was determined using the following Arrhenius equation [59–61]:

$$k = A \exp^{-E_a/RT} \quad (9)$$

or

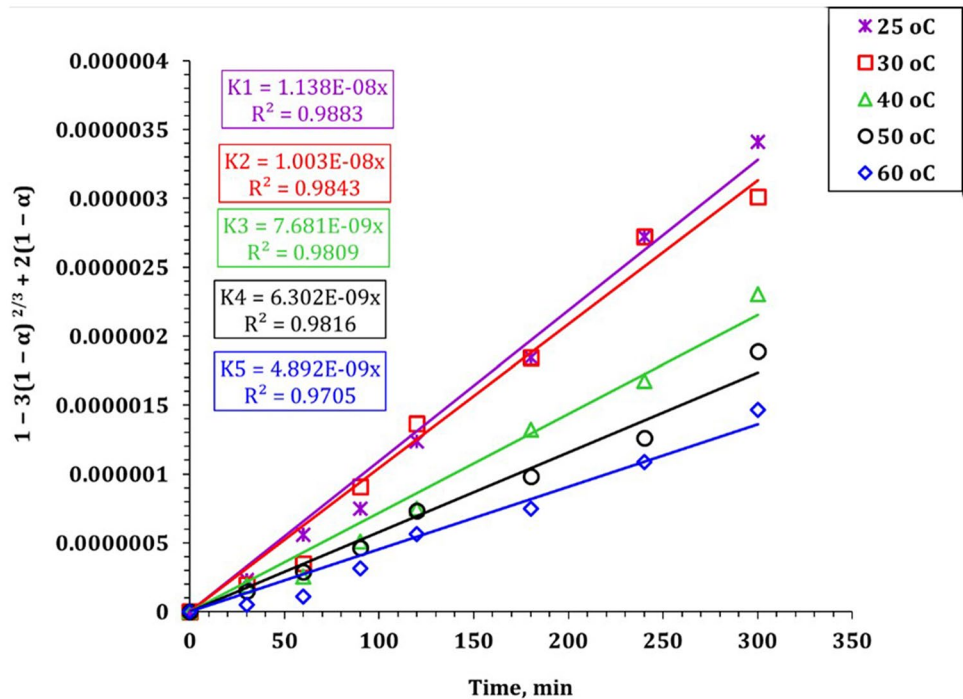
**Table 5** Comparison of the results from the present work with the REEs leaching from phosphate rock using phosphoric acid studies from the literature

		Location	Acid conc ( $P_2O_5$ wt.-%)	Liquid/solid ratio mL/g	Residence time min	Temp °C	Yield %
DOE	This work	Abu-Tartur, Egypt	30	5	120	25	96.6
			25	6	360	25	93.2
OFAT	Wang et al. [39]	Fanshan, China	30	10	240	25	94.1
	Li et al. [30]	Zhijin, China	25	12	120	60	97.8

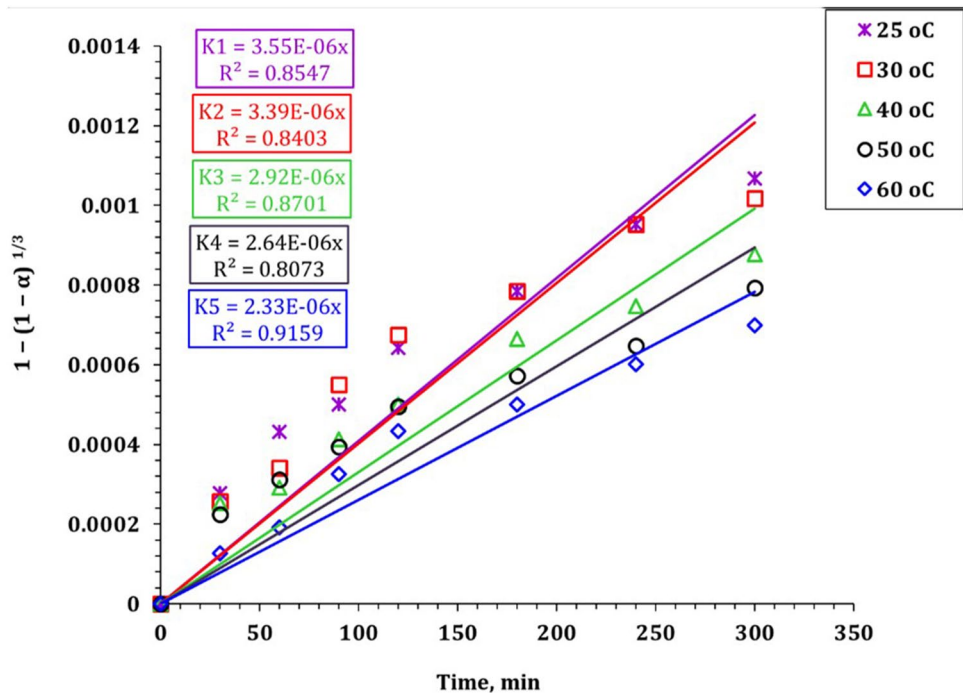
**Table 6** The chemical analysis of the obtained leach liquor

Oxides	$P_2O_5$	CaO	$Fe_2O_3$	$Al_2O_3$	$Na_2O$	MgO	$\sum$ REEs
Concentration, g/L	56.60	36.59	1.70	0.07	0.06	0.18	3.51

**Figure 6.** Effect of temperature on the function  $[1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)]$  (particle size: 150  $\mu\text{m}$ ;  $[\text{P}_2\text{O}_5]$ : 20 wt.-%; L/S mass ratio: 30 mL/5 g; mechanical stirring speed: 200 rpm).



**Figure 7.** Effect of temperature on the function  $[1 - (1 - \alpha)^{1/3}]$  (particle size: 150  $\mu\text{m}$ ;  $[\text{P}_2\text{O}_5]$ : 20 wt.-%; L/S mass ratio: 6 mL/g; mechanical stirring speed: 200 rpm).



$$\ln k = \ln A - (E_a/RT) \quad (10)$$

where  $k$  is the overall rate constant ( $\text{s}^{-1}$ ),  $A$  is the frequency factor ( $\text{s}^{-1}$ ),  $R$  is the universal gas constant (8.314 J/K $\cdot$ mol), and  $T$  is the reaction temperature (K).

The activation energy of the leaching reaction was evaluated from the plot of  $\ln k$  as a function of  $1/T$  (Fig. 8) and

found to be equal to  $-19.6$  kJ/mol, which again confirms that the leaching of REEs from Abu Tartur phosphate rock using a phosphoric acid solution in these experiments is controlled by ash layer diffusion [59–61]. Generally, a lower apparent activation energy of a chemical reaction is more favorable for the reaction. The same leaching controlling mechanism was reported for the dissolution of Guizhou Zhijin phosphate

**Table 7** The value of the rate constant,  $k$ ,  $\text{min}^{-1}$  for REEs, Fe, and  $\text{P}_2\text{O}_5$  at different temperature ranges

Temperature, °C	1000/T	$k$	$\ln k$
25	3.36	1.14E-08	-18.3
30	3.30	1.00E-08	-18.4
40	3.19	7.68E-09	-18.7
50	3.10	6.30E-09	-18.9
60	3.00	4.89E-09	-19.1

rock and Abu Tartur phosphate rock using phosphoric and hydrochloric acid earlier [30, 59].

### REEs separation investigation

REEs separation from the yield acidic leach liquor was performed using three steps: (I) REEs extraction using organic solvent, (II) REEs stripping from the loaded organic solvent, and (III) REEs precipitation.

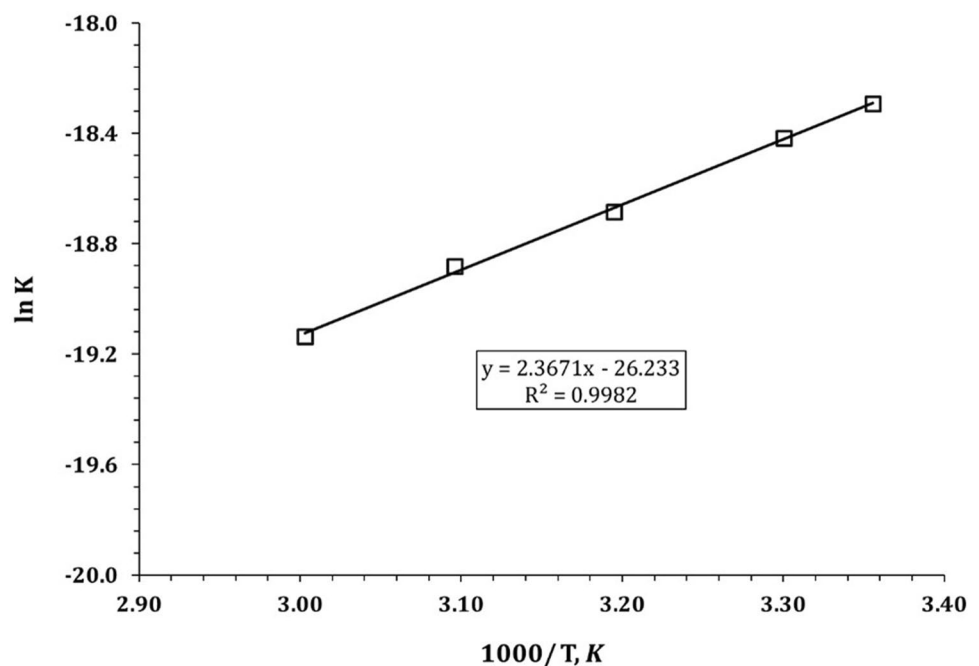
### REEs extraction studies

Figure 9 shows the impact of D2EHPA concentration (0.4–2.0 M dissolved in kerosene) on the REEs extraction from the phosphoric acid solution. The REEs extraction efficiency is enhanced with the increase of the D2EHPA concentration. This is in accordance with the findings in the literature [39, 40]. Although the increase in D2EHPA concentration increases the REEs extraction, it also decreases the mass transfer and increases the phase separation time

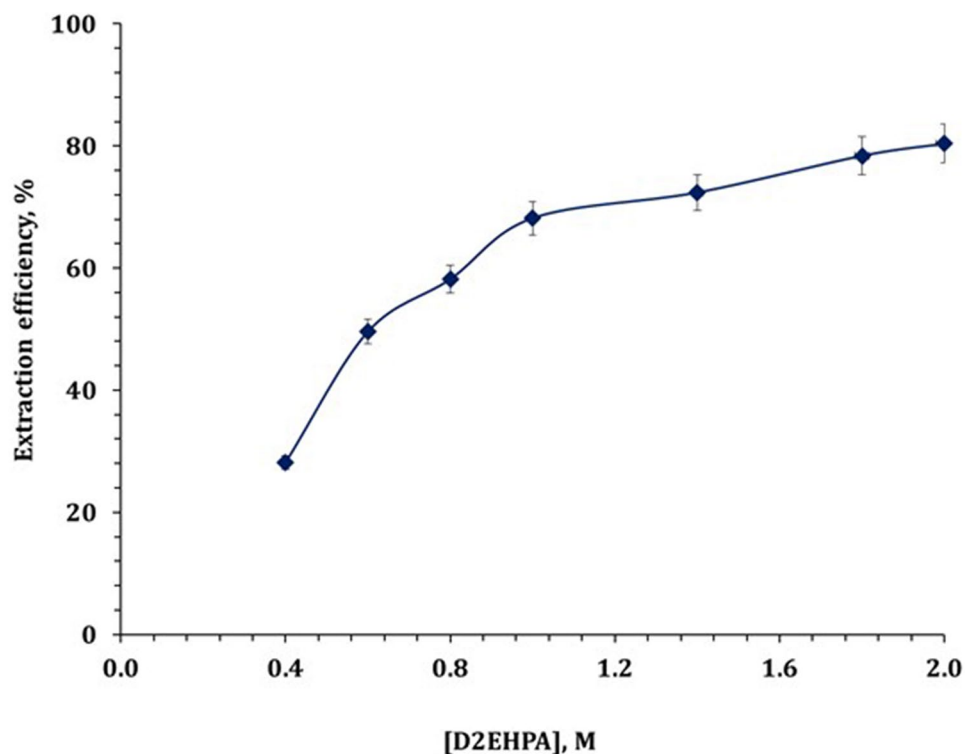
due to an increase in the organic phase viscosity. In addition, metal ions stripping from a metal ion-loaded concentrated D2EHPA in kerosene became more difficult [40]. 1.0 M D2EHPA was selected for further experiments. The isotherm of the REEs extraction process was investigated to develop a counter-current extraction process of REEs from the phosphoric acid solution. Accordingly, the number of stages for REEs extraction was evaluated based on the following conditions: 1.0 M D2EHPA, shaking time of 15 min at room temperature,  $R_{\text{aq/org}} = 1$ , and stirring speed of 200 rpm. Table 8 shows that 3 stages are sufficient for extracting approximately 95.4% of the total REEs.

### REEs stripping investigation

In a critical review on REEs stripping from loaded solvent, it was found that hydrochloric acid has a good tendency to strip REEs from D2EHPA [68, 69]. In this regard, the effect of the hydrochloric acid concentration ranging from 0.5 to 4.0 M on the stripping efficiency was investigated and the results are plotted in Fig. 10. The explored data make it obvious that as the hydrochloric acid increases to up to 3.0 M, the stripping efficiency increases to 70.5%. A further increase in the stripping agent has only a minor impact on the re-extraction process. Therefore, 2.0 M hydrochloric acid was selected to investigate the stripping isotherm and to evaluate the number of REEs stripping stages that are displayed in Table 9. Other parameters were fixed at 1.0 M loaded organic solvent, shaking time of 15 min, room temperature,  $R_{\text{aq/org}} = 1$ , and stirring speed of 200 rpm. 97.0%

**Figure 8.** Relation between  $\ln k$  and  $(1000/T)$ .

**Figure 9.** Impact of D2EHPA concentration on the REEs extraction efficiency.



**Table 8** REEs extraction isotherms

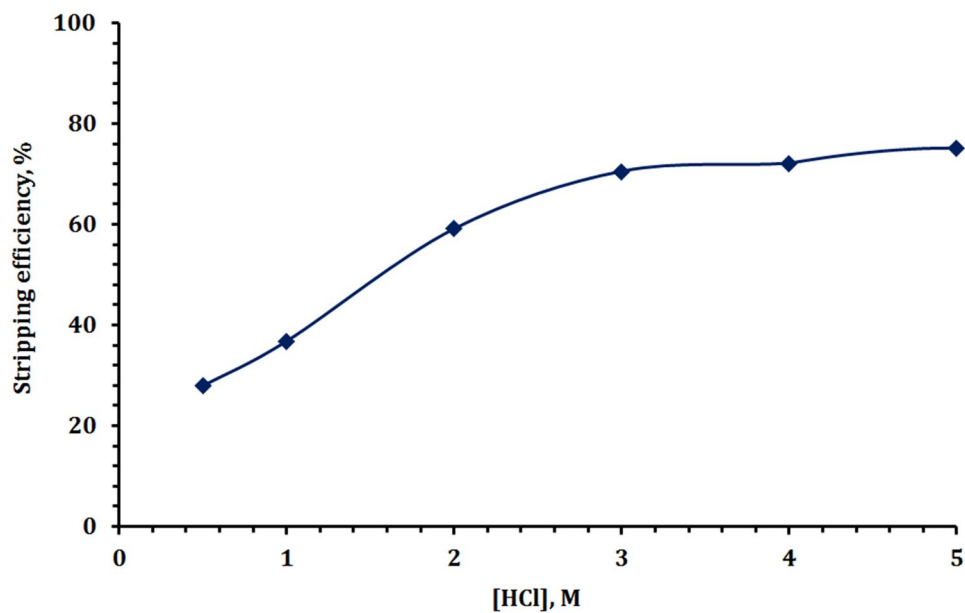
No. of stages	REEs concentration, ppm		E %
	Aqueous	Organic	
Zero	3507.8	zero	0
1	1094.4	2413.4	68.8
2	388.5	705.9	64.5
3	160.1	228.5	58.8

of the extracted REEs were successfully stripped using the 3 stages.

#### REEs precipitation process

The obtained REEs-loaded strip solution was introduced to a precipitation process. Oxalic acid has been used as it is

**Figure 10.** Impact of HCl concentration on the REEs stripping efficiency.



**Table 9** REEs stripping isotherms

No. of stages	REEs concentration, ppm		E %
	Organic	Aqueous	
Zero	2413.4	zero	0
1	711.9	1701.4	70.5
2	214.3	497.6	69.9
3	71.1	143.1	66.8

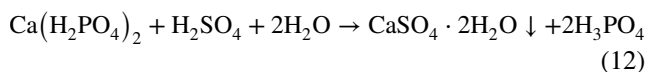
widely applied to precipitate REEs. The REEs oxalate can be expressed using the following equation [70, 71]:



REEs were precipitated from the obtained strip solution by the addition of excess oxalic acid under stirring for 1 h. The precipitated oxalate was filtered, washed with distilled water, and calcined in a muffle furnace at 850 °C for 2 h to obtain rare earth oxide ( $\Sigma\text{REO}$ ) [64]. The chemical analysis of the obtained rare earth oxide ( $\Sigma\text{REO}$ ) product was performed and is presented in Table 10. The percentage of total REOs in the produced precipitate was 88.4%. Individual REOs are shown in Table 11. The REOs precipitate was collected for further separation of individual REEs.

### Recovery of phosphoric acid and production of gypsum

As sulfuric acid is more common and less expensive than phosphoric acid, it could be added to the leaching solution after REEs separation to produce insoluble calcium sulfate and recover phosphoric acid according to the following equation:



The following parameters were applied for the recovery of phosphoric acid and to produce high-purity phosphogypsum: 98% sulfuric acid concentration, a stoichiometric ratio between sulfuric acid and calcium ions;  $30 \pm 1$  °C, for 4 hours [64]. After solid/liquid separation, the liquid phase (recovered phosphoric acid solution) could be recycled for a new cycle of the REEs dissolution process from phosphate rock. The solid phase (phosphogypsum) was rinsed with distilled water several times, dried, and then analyzed using XRD and XRF (Fig. 11 and Table 12). The

**Table 11** Individual REOs in the obtained rare earth oxide ( $\Sigma\text{REO}$ ) product

$\text{La}_2\text{O}_3$	17.05
$\text{Ce}_2\text{O}_3$	40.42
$\text{Nd}_2\text{O}_3$	24.26
$\text{Pr}_2\text{O}_3$	3.80
$\text{Sm}_2\text{O}_3$	1.48
$\text{Gd}_2\text{O}_3$	0.53
$\text{Y}_2\text{O}_3$	0.86
$\Sigma\text{REO}$	88.41

major composition of the phosphogypsum sample was analyzed by XRF. The data showed the produced phosphogypsum is clearly dominated by CaO (32.4%) and,  $\text{SO}_3$  (43.1%), together with some insignificant impurities so that the phosphogypsum obtained from this process could potentially (at least partly) substitute natural gypsum as a construction material [72]. These results are according to the mineralogical compositions estimated by XRD (Fig. 11) which showed two main strong peaks at diffraction angles of 25.7 ( $d = 3.47\text{\AA}$ ) and 31.75 ( $d = 3\text{\AA}$ ). These peaks indicate that the obtained precipitate is mainly composed of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ).

### Proposed flow diagram for REEs recovery from phosphate rock

A flow diagram (Fig. 12) is suggested for the recovery of REEs from Abu Tartur phosphate rock according to the following stages: (I) dissolution of REEs using phosphoric acid solution, (II) REEs extraction from the leaching solution using D2EHPA organic solvent, (III) REEs stripping from the loaded organic solvent using hydrochloric acid solution, (IV) precipitation of REEs using oxalic acid, (V) precipitation of high-purity phosphogypsum from the leaching solution after solvent extraction using concentrated sulfuric acid, and finally (VI) recycling the recovered phosphoric acid after phosphogypsum precipitation for the REEs dissolution stage.

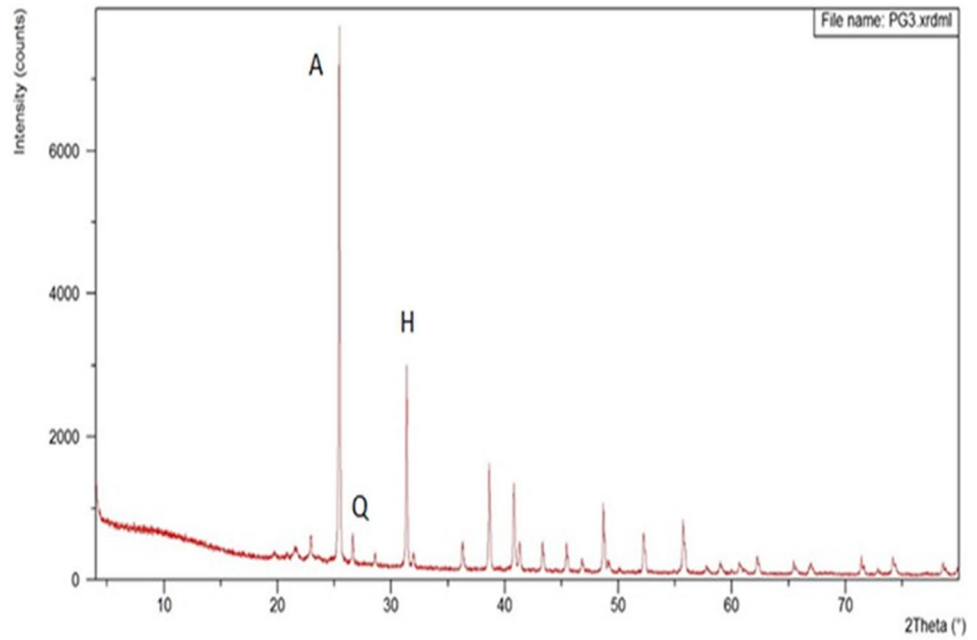
The proposed process has reached a level of maturity that allows for larger-scale experiments. The benefits are obvious: (1) an integral process which allows for generating phosphoric acid and recovering REEs, (2) the enrichment of REEs in one phase (liquid phase), (3) very limited anion impurities introduced to the leaching solution, and (4) the production of highly pure phosphogypsum.

**Table 10** Analysis of the obtained rare earth oxide ( $\Sigma\text{REO}$ ) product

Component	CaO	$\text{Fe}_2\text{O}_3$	MgO	NaO	$\text{P}_2\text{O}_5$	$\Sigma\text{REO}$
Assay (%)	9.37	1.06	0.96	0.40	0.16	88.4



**Figure 11:** X-ray diffraction pattern of phosphogypsum sample.

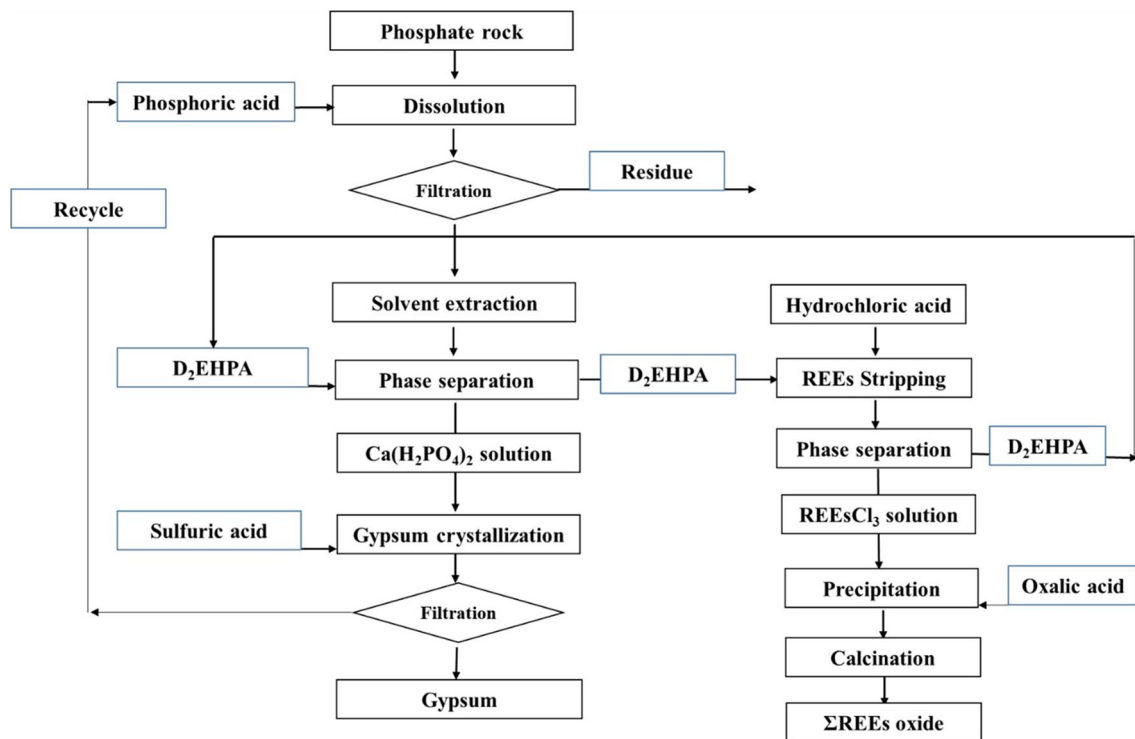


**Table 12** XRF analysis for the produced phosphogypsum

Oxides	CaO	SO <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
Content, wt. %	32.4	43.1	0.2	2.5

## Conclusion

The leaching of REEs from Abu Tartur phosphate rock using a phosphoric acid solution has been investigated. The results



**Figure 12:** A proposed flow diagram for REEs and P recovery from phosphate rock.

showed that the reaction rate increases with time while the hydrogen ion  $[H^+]$  concentration, the liquid/solid ratio, and the leaching temperature negatively affect the leaching efficiency. The leaching of REEs from phosphate rock was optimized using a  $2^4$  full factorial design. The studied factors were phosphoric acid concentration, liquid/solid ratio, residence time, and temperature. After optimization,  $96.7 \pm 0.9\%$  of the REEs successfully leached out under the following optimum conditions: phosphoric acid concentration of 30 wt.-%  $P_2O_5$ , 120 min residence time, at a temperature of 20 °C, and a liquid/solid ratio of 5 mL phosphoric acid per g phosphate rock. The kinetics of the REEs leaching process was found to be governed by the shrinking core model as the chemical control process. The mathematical treatment for the obtained data showed that the apparent activation energy of the dissolution of REEs was  $-19.6$  kJ/mol. REEs separation from the attained leach liquor was achieved using solvent extraction and subsequent precipitation of the REEs was performed with oxalic acid. REOs with a purity of 88.4% could be recovered. Phosphoric acid as well as gypsum with high purity ( $>95\%$   $CaSO_4 \cdot 2H_2O$ ) could be produced using concentrated sulfuric acid. The cleaner production process is promising and is ready to be tested on a larger scale (TRL 6). A flow diagram for REEs recovery from Abu Tartur phosphate rock has been developed.

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**Data availability** All data used that was not obtained through own measurements by the authors is openly accessible and has been referenced.

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