



Leaching of Lanthanides from Phosphogypsum Waste using Nonyl Phenol Ethoxylate Associated with HNO₃ and HCl

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Abstract

Leaching of lanthanides from phosphogypsum (PG) was carried out using either free acids such as HCl and HNO₃ or these acids associated with Nonyl Phenol Ethoxylate (NPE). The factors affecting the leaching process were optimized. Also the kinetics of the leaching investigated as a function of temperature. Based on the experimental results NPE increased the leaching efficiency by 30 % relative to the corresponding free acids. It was found that the leaching process could be described by a shrinking-core model. Also the leaching of lanthanides by the associated system decrease the activation energy from 5.89 and 12.24 kJ/M to 5.28 and 3.79 kJ/M for HCl and HNO₃ respectively.

Keywords: Leaching; Lanthanides; Phosphogypsum Waste; Nitric Acid; Hydrochloric Acid; Nonyl Phenol Ethoxylate

1. Introduction

Although there are abundant supplies of lanthanide ores such as bastnasite, xenotime and monazite, the recovery of lanthanides from PG is a step towards the conservation of natural resources. The annual consumption of lanthanides is about 30.000 tones. They are used as deoxidizers; in alloys; in the production of cast iron and steel, as catalysts; in higher flints and flares; in the glass and ceramic industries; in the manufacture of control rods in nuclear reactors, and in many important industries [1-3].

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The phosphate deposit of the Abu-Tartur plateau, Western Desert, Egypt, is one of the largest phosphate deposits in the world. It is geo-morphologically localized in the southeastern portion of the Abu-Tartur plateau 600 km from Cairo [4]. One of the most important characteristics of the Abu-Tartur phosphate deposits is its relatively high content of lanthanides [5]. The most common method of producing phosphoric acid is the so-called (Wet Process) in which phosphate rock is reacted with sulfuric acid. This process produces commercial phosphoric acid and substantial quantities of hydrated calcium sulfate as a by-product, known as phosphogypsum (PG), according to the following reaction [1].



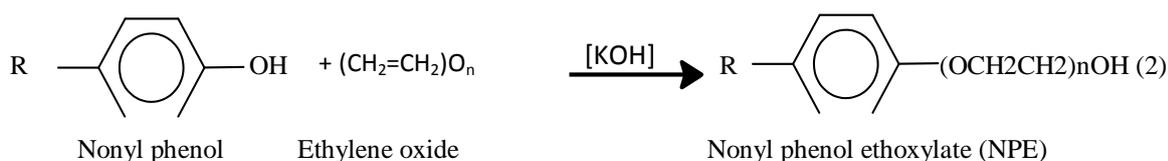
Wet-process phosphoric acid plants produce about 4.5 tons of phosphogypsum for each ton of P_2O_5 as phosphoric acid [6]. During production phosphoric acid by sulfuric acid treatment most of lanthanides (about 70 %) lost in PG residue. Phosphogypsum is composed mainly of gypsum ($CaSO_4 \cdot 2H_2O$) but also contains minor quantities of trace elements, lanthanides, P_2O_5 and F [7]. A significant benefit of Abu-Tartur phosphate rock processes for the recovery of the lanthanides lies in their relatively high content of lanthanides (averaging 0.2%., while the produced fertilizer would pollute the environment less with radioactive materials due to the low uranium content (averaging 25 mg/kg) [8].

For the pretreatment of PG waste to undergo leaching processes, Arocena et al. found that, the enrichment of trace and lanthanides in PG was concentrated in the fine size fraction ($< 20 \mu m$) compared to bulk PG [9]. The leaching of the lanthanides from phosphoric acid by-product has been studied in a number of works by different methods e.g. solvent extraction, ion exchange and acid leaching [10-13]. Zafar Iqbal Zafar and Mohammad Ashraf studied the selective leaching kinetics of calcareous phosphate rock by lactic acid. It was found that the leaching rate of calcareous material increased with increasing the acid concentration, liquid/solid ratio and temperature and decreasing particle size [14]. Chi et al. studied the leaching kinetics of lanthanides from a manganese-removed weathered rare earth mud (MRW-RE mud) by hydrochloric acid solutions. It was found that the leaching process can be described by a shrinking-core model, with the apparent activation energy about 10.17 kJ/M [15]. Ali and Mohammed studied a process for the treatment of Abu-Tartur phosphate rock using HNO_3 as a leaching agent for the recovery of lanthanides without interfering with the normal route proposed for fertilizer production. The results showed an assessment of complete dissolution of the lanthanides occurs in the phosphoric acid produced by sulfuric acid, they will be mostly lost in the co-produced PG [16]. On the other hand Kandil et al. studied the dynamic leaching of lanthanides from a Western Desert phosphate ore, Egypt (Abu Tartur) by hydrochloric acid, nitric acid and sulfuric acid solutions [17]. The results showed that, the leaching process could be described by a shrinking-core model. The present work was oriented to leaching the lanthanides using Nonyl phenol Ethoxylate (NPE) associated with nitric and hydrochloric acid from PG of Abu-Tartur phosphate ore. The parameters affect the leaching process were studied in terms of kinetic model to show the leaching mechanism of lanthanides from PG waste.

2. Experimental

2.1. Materials and Apparatus

Samples of PG (of density equals 2.29 g/cm³) were provided by the wet process phosphoric acid plant (from processing of Abu-Tartur phosphate ores, Egypt). Acid solutions were provided by El-Nasr Chemicals Company, Egypt. Metertech UV/VIS SP8001 Spectrophotometer, China, was used for measuring the concentrations of total lanthanides [18]. Holland Inolab pH meter, Germany, was used for pH determination. Barnstead water purifying system was used for supplying double distilled pure water for analysis. Nonyl phenol ethoxylate (NPE) are produced by reacting nonyl phenol and ethylene oxide with potassium hydroxide as a catalyst. The ratio of ethylene oxide to nonyl phenol determines the molecular weight of the product or the length of the molecule produced. The following reaction shows the preparation of nonyl phenol ethoxylate [19]:



(R = branched C₉H₁₉)

where n varies by product

The chemical analysis of phosphogypsum produced from processing of Abu-Tartur region is presented in Table 1.

Table 1. Chemical analysis of phosphogypsum

| Components | Conc. | Components | Conc. |
|--------------------------------|-------|-------------------|-------|
| Constituents (wt %) | | | |
| CaO | 25.3 | Na ₂ O | 0.09 |
| SO ₃ | 34.1 | K ₂ O | 0.04 |
| SiO ₂ | 9.82 | TiO ₂ | 0.4 |
| P ₂ O ₅ | 1.01 | F | 1.14 |
| Fe ₂ O ₃ | 5.80 | L. O. I.* | 21.2 |
| Trace concentrations (ppm) | | | |
| U | 14 | Th | 10 |
| ∑lanthanides | 1387 | | |

* L. O. I. Loss of ignition

2.3. Leaching procedure

In different 100 ml measuring beakers, a known amount of phosphogypsum (2.5g) was taken, with the addition of known volume of acid (5ml) at room temperature and mixed for a known time. Other processes were performed by using Nonyl phenol Ethoxylate (NPE) associated with nitric and hydrochloric acid, at the same studied conditions. The factors affect the desired leaching materials (such as contact time, acid concentration, liquid: solid ratio, temperature) were optimized.

2.4. Analysis procedure

Total lanthanides were determined by Arsenazo-III method. In weakly acidic solution, the reagent was violet, whereas their complex with lanthanides was green. To the acidic sample solution (pH \approx 1) 1 ml of 1% ascorbic acid solution was added. After few minutes, 1 ml of the format buffer and 2 ml of Arsenazo-III solution were added. The solution was diluted with distilled water to \approx 20 ml and the pH was adjusted to \approx 2.6 then up to 25 ml standard flask. The absorbance was measured at 650 nm against reagent blank solution [18].

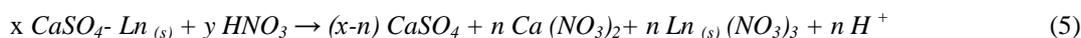
The leaching percent (L%) of lanthanides can be calculated as follow:

$$L \% = [(C_o - C_f)/C_o] \times 100 \quad (3)$$

Where, C_o is the initial lanthanides concentration of the received PG waste and C_f is the concentration of lanthanides after leaching.

3. Results and discussion

The possible chemical reactions that occur during leaching of phosphogypsum with hydrochloric and nitric acids can be described as follows:



Reactions 4 and 5 are of special interest for the leaching process.

3.1. Effect of acid concentration

The effect of acid concentration on the leaching efficiency of lanthanides from the phosphogypsum was studied at constant values of agitation speed 250 rpm, particle size -250 mesh, temperature 25 $^{\circ}$ C, and weight ratio of phosphogypsum and acid 0.5 g/ml. The leaching of lanthanides increases from 2 to 33 % using acids concentration ranged from 1 % to 20 % as shown in figure 1. This is probably due to the increase in viscosity with increasing the concentration of the leached lanthanides and calcium [17]. Thus, 20 % acid concentration is proposed as optimum for letter experiments. On the other hand, addition of NPE has significant effect on leaching of lanthanides either with hydrochloric acid or with nitric acid and is quantitative (30 %) even at 6 % acid.

3.2. Effect of solid mass to liquid volume (S/L)

The effect of ratio of phosphogypsum / added acid on the leaching efficiency of lanthanides was investigated by employing different stiochiometric amount of acid to leach 1 g of phosphogypsum. The leaching temperature remained at 25 $^{\circ}$ C, time of 15 min. and acids concentration of 20 % . Figure 2 illustrated the increase of acid amount is usually accompanied by an increase in the percent leaching, which tends to become independent at

ratios higher than 6. Thus, 0.5 g/ml is proposed as optimum for letter experiments.

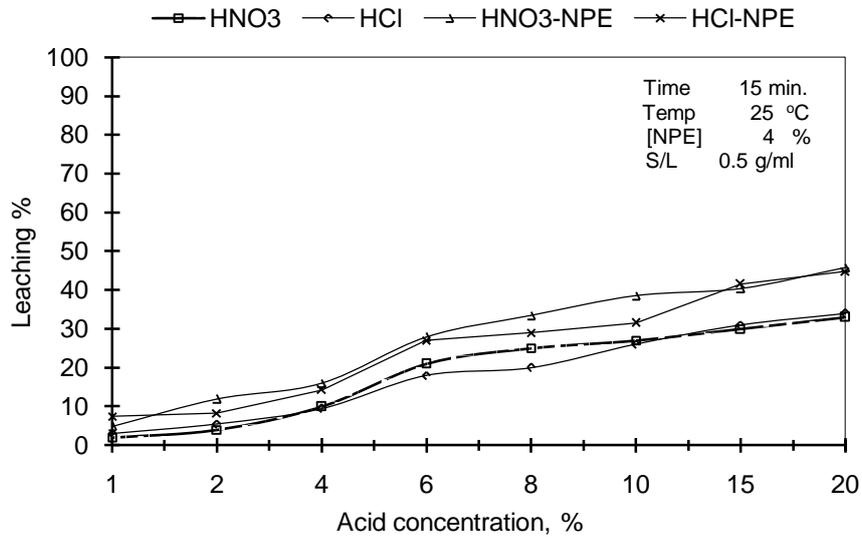


Fig. 1. Effect of acid concentration on the leaching efficiency of lanthanides

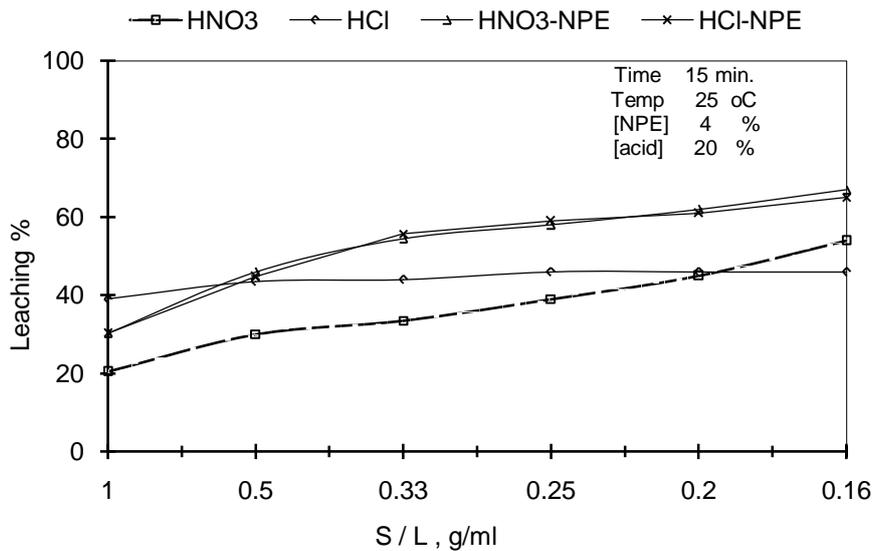


Fig. 2. Effect of solid to liquid (S/L), g/ml on the leaching efficiency of lanthanides

3.3. Effect of NPE concentration

The addition of NPE in the leaching of lanthanides from phosphogypsum either with HNO₃ or HCl based on its ability to form salts with this acids. The formed salts contains two parts , one is hydrophilic (acid) and the other is hydrophobic (NPE). To investigate the effect of NPE leaching was carried out at different NPE concentrations, the leaching temperature remained at 25 °C, S/L of 0.5 g/ml, time of 15 min. and acids

concentration of 20 %. The results are shown in figure 3 as expected; much leaching efficiency of lanthanides was achieved using even small concentrations of NPE.

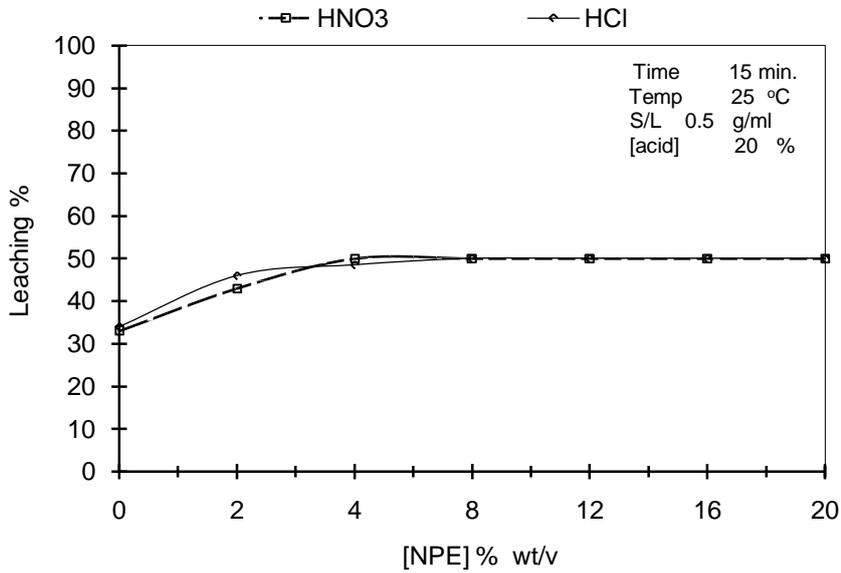


Fig. 3. Effect of NPE concentration on the leaching efficiency of lanthanides

3.4. Kinetic analysis

In order to establish the kinetic parameters and rate-controlling step for the leaching of lanthanides from phosphogypsum using hydrochloric, nitric acids and the associated NPE with these acids the experimental data can be analyzed according to the heterogeneous reaction models [20]: According to the model, the reaction between a fluid and a solid may be written as:



The rate of reaction between phosphogypsum particle and the acids may be controlled by one of the following steps: diffusion through the fluid film, diffusion through the ash/product layer or the chemical reaction at the surface. Let the time of completion of the leaching process be k^* , the fractional conversion of the ore α which equal:

$$\alpha = \frac{\text{Amount of lanthanide in the solution}}{\text{Total amount of lanthanide in original sample}}$$

and at any time t the integrated equations for fluid–solid heterogeneous reactions are:

for film diffusion control,

$$t = k^* [1 - (1 - \alpha)] \quad (7)$$

for chemical reaction control,

$$t = k^* [1 - (1 - \alpha)^{1/3}] \quad (8)$$

and for ash layer diffusion control,

$$t = k^* [1 - (2/3) \alpha - (1 - \alpha)^{2/3}] \quad (9)$$

The value of k^* depends on various reaction parameters according to the kinetic models. To determine the kinetic parameters and rate-controlling step for selective leaching of lanthanides from phosphogypsum, the experimental data were analyzed on the basis of fluid–solid heterogeneous reaction models. The validity of the experimental data into the integral rate was tested by statistical and graphical methods. The kinetic analysis results for the leaching process were found to be consistent with a ash layer diffusion control and the integral rate expression was determined to obey the following rate equation:

$$1 - (2/3) \alpha - (1 - \alpha)^{2/3} = kt \quad (10)$$

Using the conversion values for various reaction temperatures, the apparent rate constants, k , can be evaluated by plotting $1 - (2/3) \alpha - (1 - \alpha)^{2/3}$ versus t as shown in figures 4,5,6 and 7. The experimental results represented in this figures indicate no change in the leaching behavior of phosphogypsum after addition of NPE to either HNO_3 or HCl , a situation that may be attributed to the diffusion controlled nature of the reaction. Also, the stability of lanthanide leaching efficiency even with the increasing of the acid concentration, which is most clearly revealed by the curves for the largest particles, is a strong argument against a hydrogen ion diffusion limitation.

Using the Arrhenius equation, the activation energy can be evaluated from the plot of $\ln k$ versus $1/T$. After the evaluation of activation energy and pre-exponential factor the kinetic model for the leaching process may be expressed as:

$$1 - (2/3) \alpha - (1 - \alpha)^{2/3} = A^o e^{-Ea/RT} t \quad (11)$$

or

$$\ln k = \ln A - (E/RT) \quad (12)$$

Where A is a coefficient, R is the gas constant, T is leaching reaction temperature (Kelvin, K), and E is activation energy (kJ/M). The plot of $\ln k$ vs. $1/T$ shown in figures 8 and 9, gives straight line so the apparent activation energy E of the leaching process calculated from the slope of the straight line. Also the plot of $\ln k/T$ vs. $1/T$ as shown in figures 10 and 11 gives straight line with slope equal $-\Delta H/R$ and intercept equal $-\Delta S/R$. All the data of activation energy (kJ/M), enthalpy (kJ/M) and entropy (kJ/M) shown in table 2 this values falls within the activation energy conventionally found for inner diffusion-controlled leaching processes [21]. The results here suggested again that the leaching process in this study was indeed controlled by the diffusion of leaching chemical species into the solid particles. To enhance the leaching process, it is therefore desirable to create a suitable environment to accelerate the inner diffusion rate of leaching chemicals.

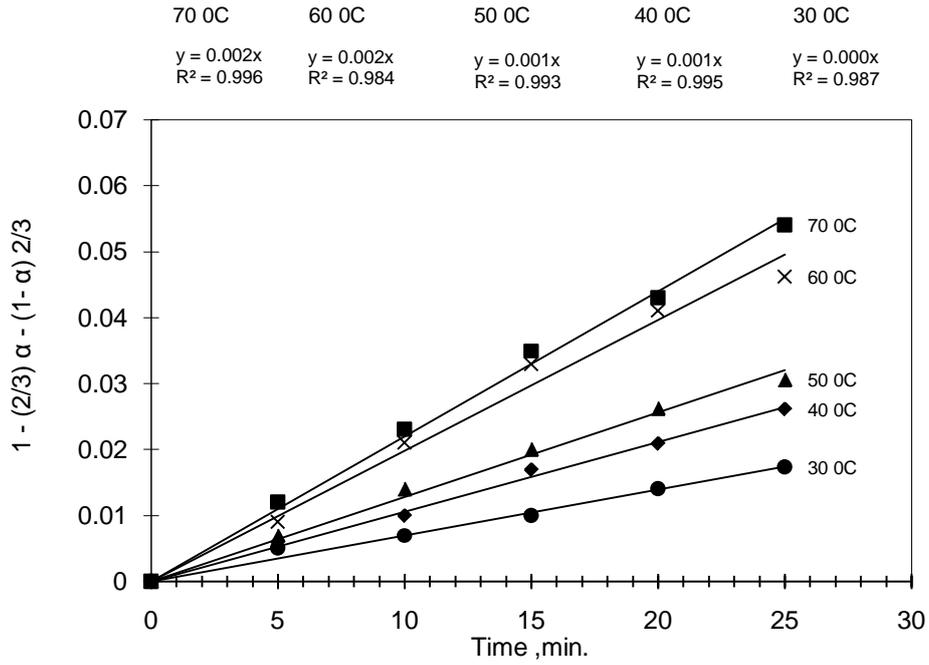


Fig. 4. Leaching kinetics of lanthanides from phosphogypsum by HNO₃

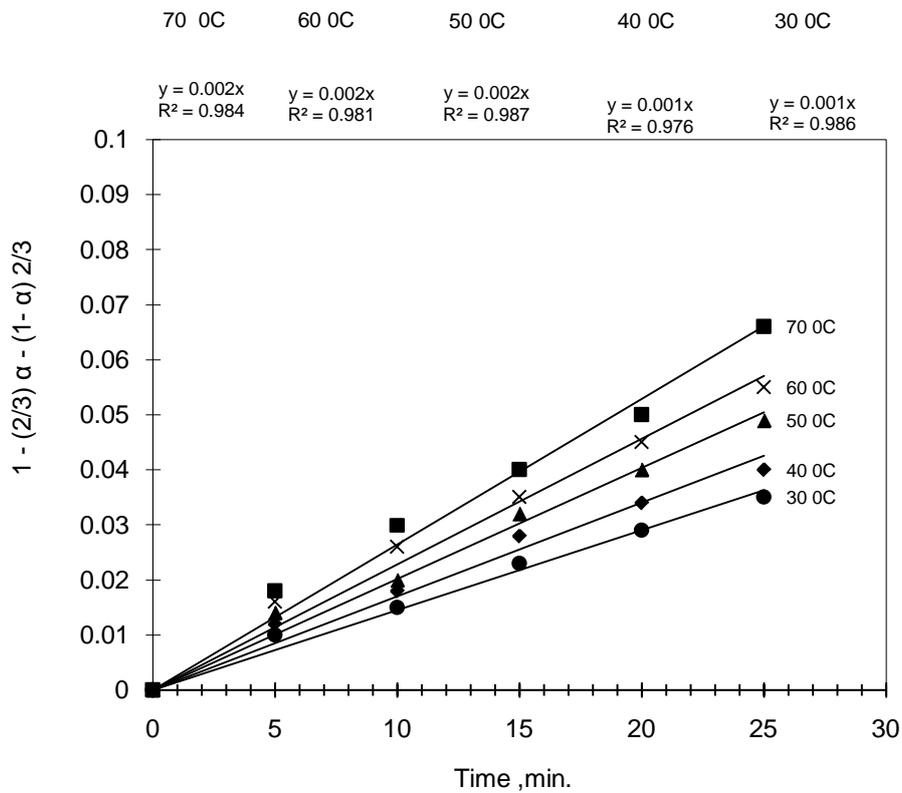


Fig. 5. Leaching kinetics of lanthanides from phosphogypsum by HCl

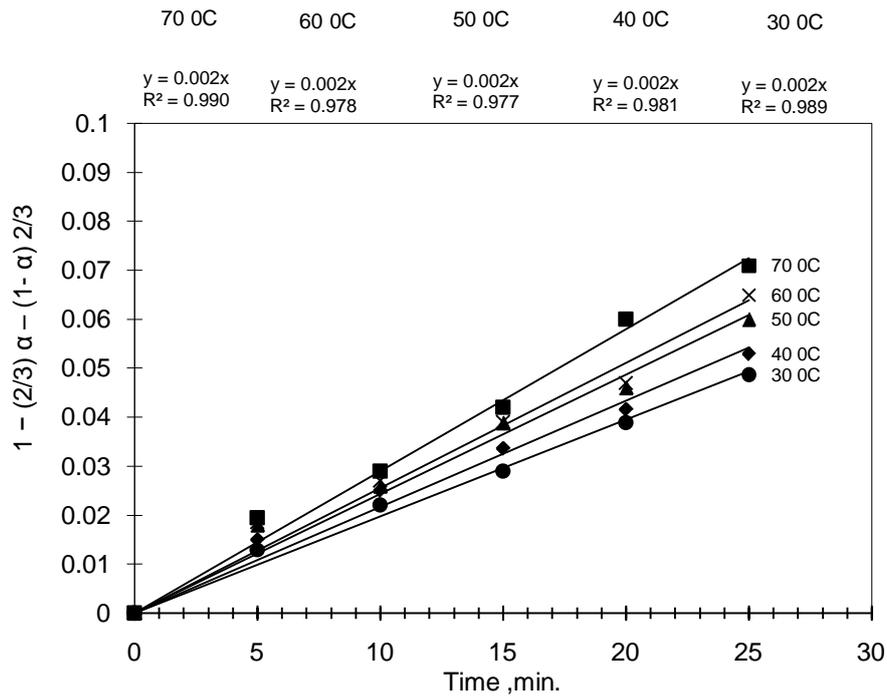


Fig. 6. Leaching kinetics of lanthanides from phosphogypsum by HNO₃-NPE

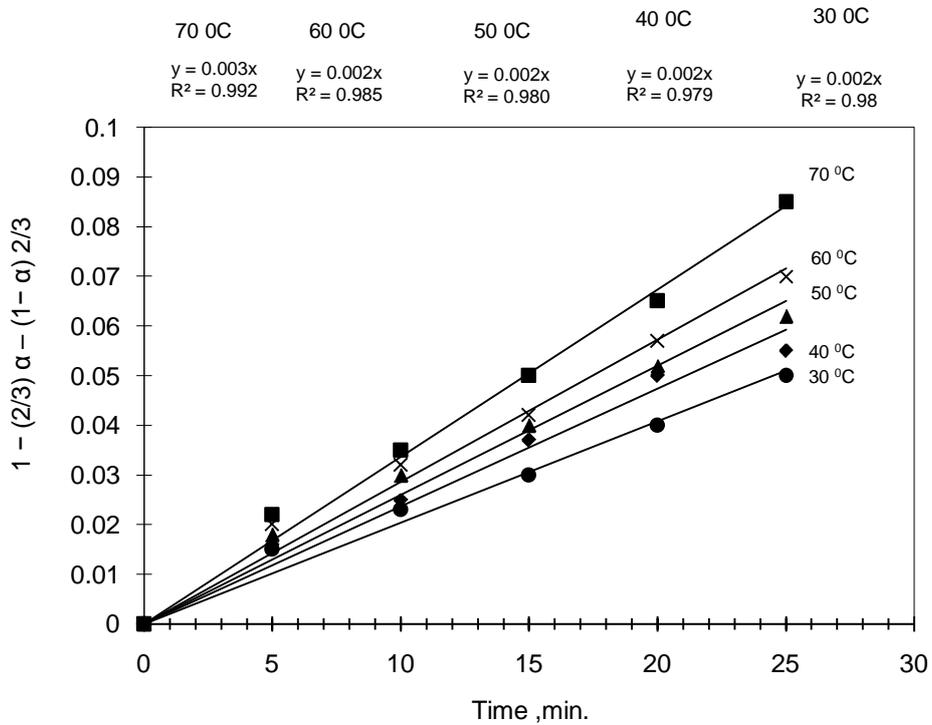


Fig. 7. Leaching kinetics of lanthanides from phosphogypsum by HCl-NPE

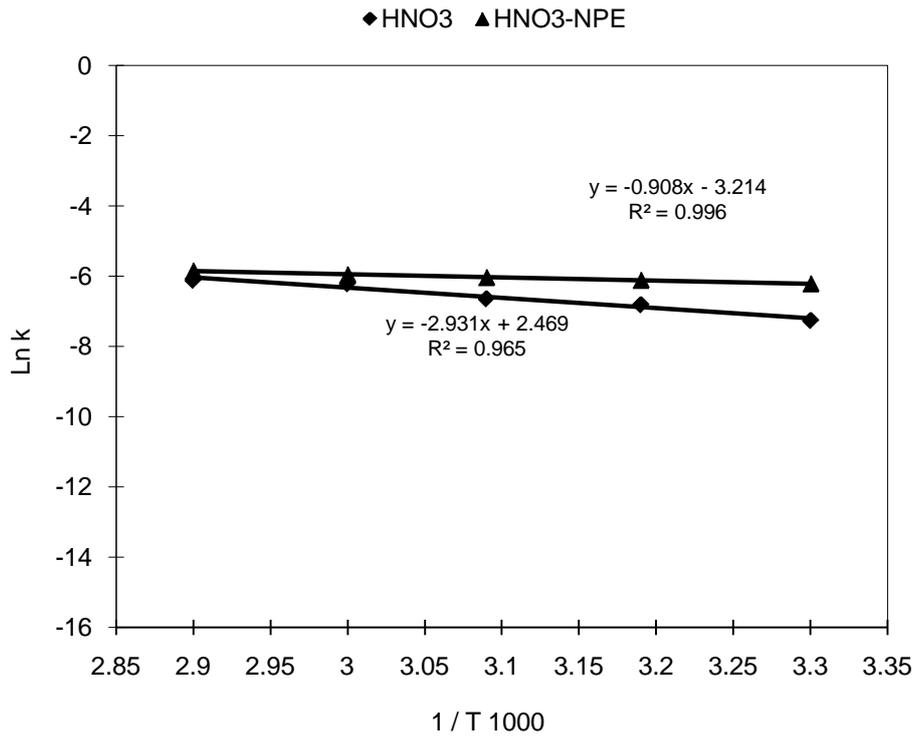


Fig. 8. Activation energy of lanthanides leaching from phosphogypsum by HNO₃ and HNO₃-NPE

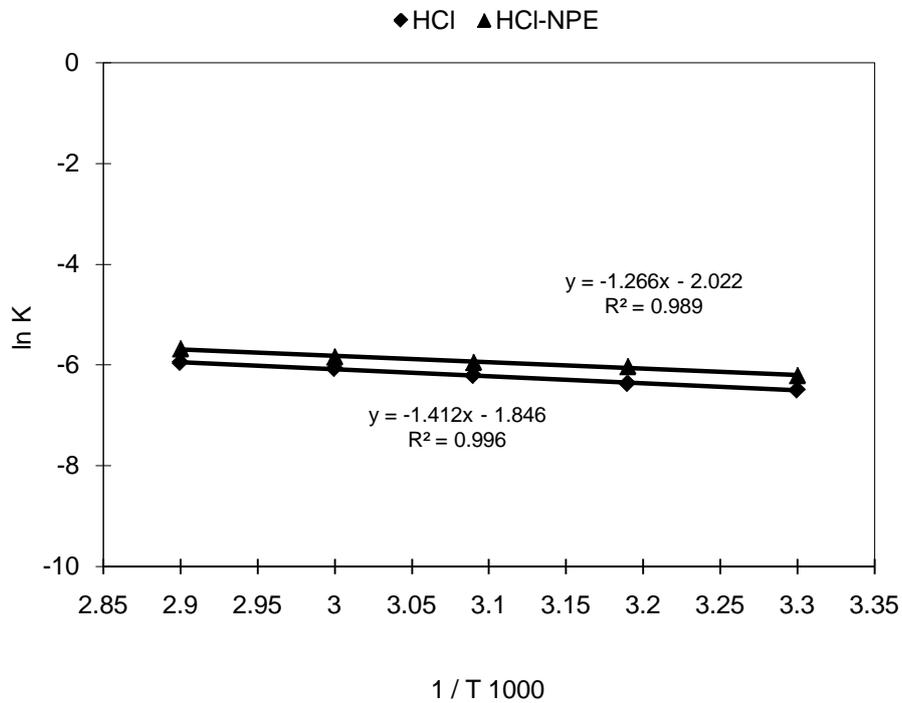


Fig. 9. Activation energy of lanthanides leaching from phosphogypsum by HCl and HCl-NPE

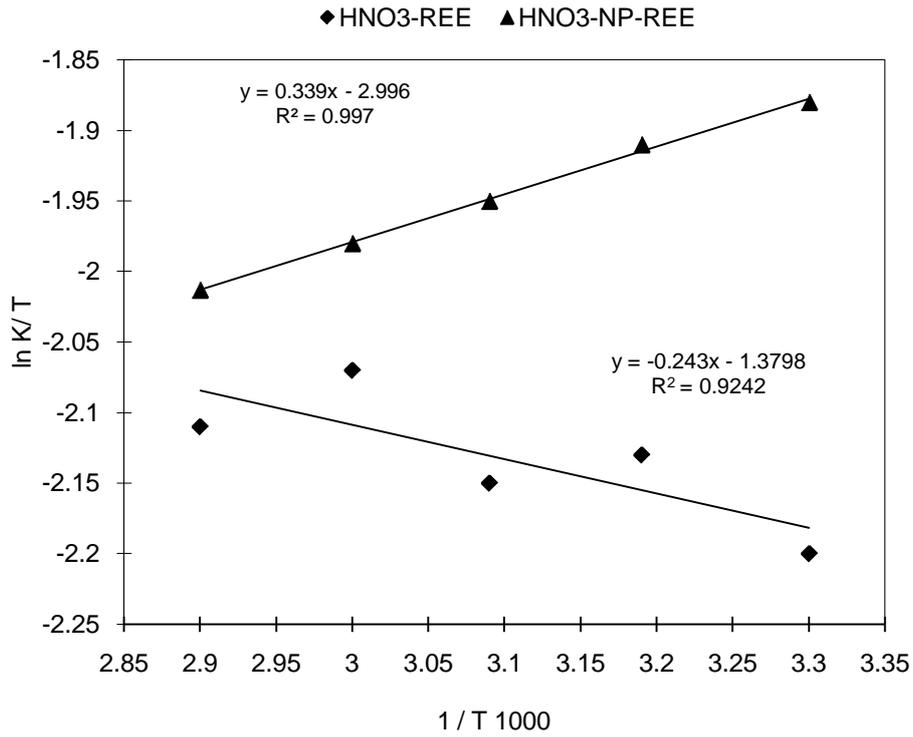


Fig. 10. Enthalpy and entropy of lanthanides leaching from phosphogypsum by HNO₃ and HNO₃-NPE

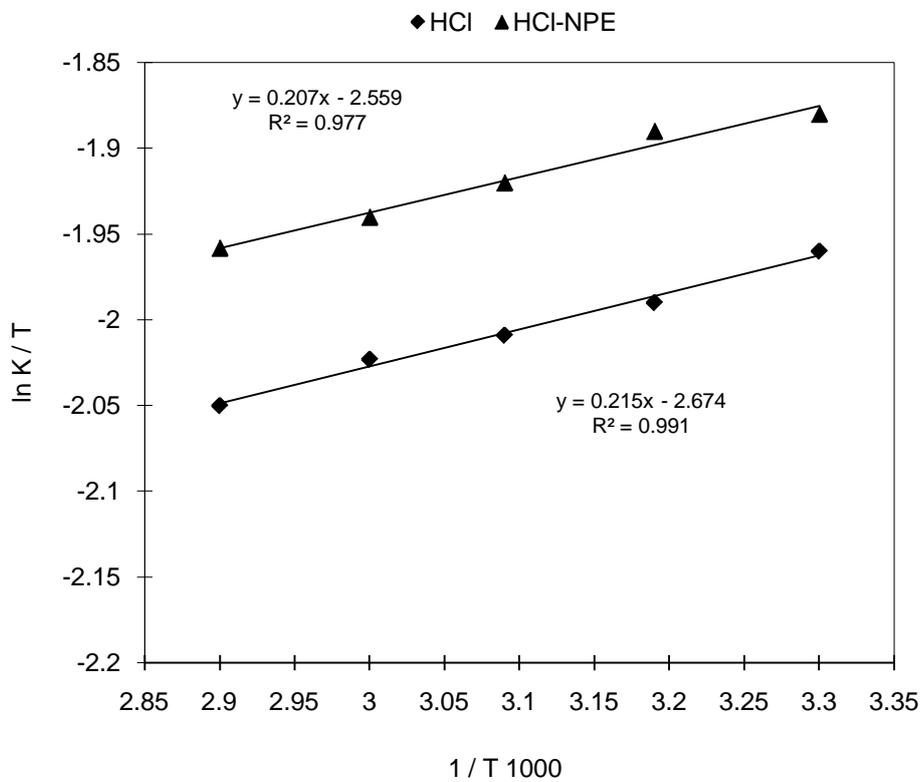


Fig. 11. Enthalpy and entropy of lanthanides leaching from phosphogypsum by HCl and HCl-NPE

Table 2. Thermodynamic data for leaching of lanthanides

| Leaching agent | ΔH° | ΔS° | E |
|-----------------------|------------------|------------------|-------|
| HNO ₃ | 01.43 | - 04.46 | 12.24 |
| HNO ₃ -NPE | - 01.41 | - 12.49 | 03.79 |
| HCl | 00.90 | - 11.15 | 05.89 |
| HCl-NPE | 00.86 | - 01.06 | 05.28 |

3.5. Chemical analysis of the phosphogypsum leach liquor

The chemical analysis of the leach liquor resulted from phosphogypsum leaching operation shown in table 3 showing the high values of calcium in the leach liquor therefore it was recommended that the leach liquor required further purification to obtain high grade of lanthanides.

Table 3. Chemical analysis of the phosphogypsum leach liquor

| Components | HCl | HCl - NPE | HNO ₃ | HNO ₃ - NPE |
|--------------------------------|-------|-----------|------------------|------------------------|
| CaO | 7500 | 5000 | 12500 | 5250 |
| SO ₄ | 6500 | 4000 | 15000 | 6500 |
| Fe ₂ O ₃ | 1200 | 920.0 | 1270 | 790.0 |
| ∑lanthanides | 1110 | 1115 | 1112 | 1120 |
| F | 230.0 | 110.0 | 245.0 | 90.00 |
| K ₂ O | 40.00 | 32.00 | 50.00 | 43.00 |
| TiO ₂ | 21.00 | 06.00 | 17.00 | 05.00 |
| Th | 06.00 | 04.00 | 08.00 | 05.00 |
| U | 14.00 | 14.00 | 14.00 | 14.00 |
| Total (ppm) | 16621 | 11201 | 30212 | 13817 |
| Lanthanides in leach liquor, % | | | | |
| ∑lanthanides % | 06.67 | 09.95 | 03.60 | 08.10 |

4. Conclusion

The leaching behavior of lanthanides from phosphogypsum has been investigated using hydrochloric acid , nitric acid and the association of those acids with NPE . The results demonstrate that lanthanides was leached more better in the presence of NPE. Also the leaching of lanthanides by the associated system decrease the

activation energy from 5.89 and 12.24 kJ/M to 5.28 and 3.79 kJ/M for HCl and HNO₃ respectively. So this study clearly highlights that the association of NPE with HCl or HNO₃ can be used as a potential leaching system for the leaching of lanthanides from phosphogypsum waste.

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