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Controlling calcium dissolution during lanthanides leaching operation from phosphogypsum waste

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ABSTRACT

This work developed a method for controlling calcium dissolution during leaching operation of lanthanides from phosphogypsum waste. The developed method was carried out in two steps, namely, A - leaching of the phosphogypsum by using mineral acids (HCl and HNO_3) with nonyl phenol ethoxylate (NPE) as a leaching solution. B- Addition of a soluble amino acid, e.g., glycine to the leaching solution to precipitate calcium glycinate. The obtained results showed dissolution of about 5 % of calcium content under the leaching conditions: 20 % acid, 25 °C, 0.5 g ml^{-} and 15 min. However, the presence of NPE in a concentration of 4 % decreases the calcium dissolution to about 2.5 %. Also, the kinetics of calcium leaching were investigated and it was found that, the data fitted the shrinking core model, in which both the interface transfer and diffusion through the product layer affected the reaction rate. Moreover, the addition of NPE to the acid leaching solution increases the apparent activation energy from 28 and 29 KJ/Mol to 36 and 50 KJ/Mol for HCl and HNO_3, respectively.

Key words: Controlling; Calcium; Dissolution Lanthanides; Leaching; Phosphogypsum

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INTRODUCTION

Phosphogypsum (PG) is a by-product derived from the production of phosphoric acid by wet process [1].

$$\mathbf{Ca_5\,(PO_4)_3F + 5H_2SO_4 + 10H_2O \rightarrow 3H_3PO_4 + 5CaSO_4{\cdot}2H_2O + HF} \qquad (1)$$

About 4.5-5 kg of phosphogypsum is produced for every kg of P_2O_5 manufactured. Although gypsum ($CaPO_4{\cdot}2H_2O$) is the major component of PG, it also contains metal impurities such as lanthanides and some radionuclide of potential health and environmental impact [2]. Moreover, the accumulation of PG waste from the fertilizer industries, which remain in regulating stacks occupying considerable land resources, is causing significant environmental problems worldwide. In this context, the scientific community is being pressured to find alternative ways for their disposal [3]. Among these ways HCl or HNO_3 acid solutions was used, for forming substantial amounts of calcium salts [4].

Previous study reported by Kouraim et al. showed that the leaching of lanthanides from phosphogypsum waste (PG) was successfully carried out using either HCl and HNO_3 acids or these acids associated with Nonyl Phenol Ethoxylate (NPE). Based on the experimental results NPE increased the leaching efficiency by 30 % relative to the corresponding unmixed acids. It was found that the leaching process could be described by a shrinking-core model. Also the leaching of lanthanides by the latter system decreased the activation energy from 5.89 and 12.24 KJ/M to 5.28 and 3.79 KJ/M for HCl and HNO_3 respectively [5].

Different methods are reported for combating calcium accumulation in the leaching circuit [6]. For example, commercially available water softeners can be used in the surface processing of the leach solution to physically and/or chemically remove calcium ions [7]. Although the complete removal of the calcium ions from the leach solution is most desirable, however, in many known leach operations the total removal of calcium ions from the leach solution with such equipment would be extremely expensive and would seriously affect the overall success of a commercial leach operation [8]. Actually, there are normally some calcium ions still present in the leach solution even after treatment with such equipment, and this calcium can foul the extraction means used for extracting the lanthanides from the leach solution [9]. In fact, certain chemicals commonly called "inhibitors" can be added to a solution to prevent scale accumulation due to calcium precipitation [10]. However, the normal amounts of inhibitors tend to stabilize the calcium species in the leach solution, causing the calcium to accumulate in the recycled leach solution to levels which may threaten the overall leach operation [11].

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 [12]. Their results showed that, the leaching process could be described by a shrinking-core model.

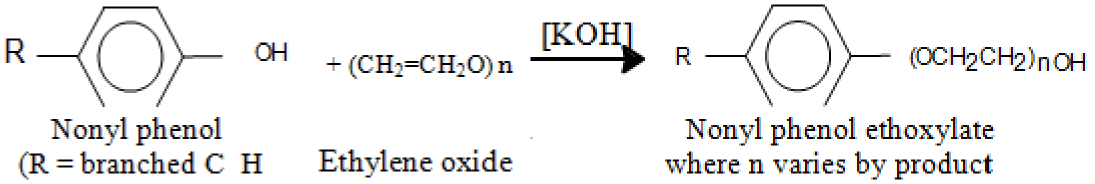
Jun et al. studied the kinetic of lanthanides leaching from the weathered crust elution-deposited lanthanide ores with ammonium sulfate solution. The results showed that the higher the leaching temperature or the smaller the ore particle size, the faster the leaching progress. The leaching mechanism was analyzed with different kinetics models [13].

The present work aims to control the dissolution of calcium, in acid leach operation of lanthanides from PG by precipitating calcium ions from the leach solution at selected steps in the operation. However, when the operation not properly controlled, it will precipitate within the leaching circuit, thereby creating scaling and/or plugging problems throughout the operation [14]. The factors are optimized and kinetically determinate.

EXPERIMENTAL SECTION

2.1. Materials

Phosphogypsum sample was collected from the wet process phosphoric acid plant (from the processing of Abu-Tartur phosphate ores, Egypt). Table 1 presents its average of chemical composition of their constituents (on the dry basis). Hydrochloric and nitric acids were provided by El-Nasr Chemicals Company, Egypt. Nonyl phenol ethoxylate (NPE) was produced by reacting nonyl phenol with ethylene oxide in the presence of KOH 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 NPE [15]:



(2)

Table 1. Chemical analysis of phosphogypsum in weight %

Components	**Conc.**	**Components**	**Conc.**
CaO	25.3	Na_2O	0.09
SO_3	34.1	K_2O	0.04
SiO_2	9.82	TiO_2	0.4
P_2O_5	1.01	F	1.14
Fe_2O_3	5.80	L. O. I.	21.2
U	14	∑lanthanides	1387

2.2. Apparatus

Metertech UV/VIS SP8001 Spectrophotometer, China, was used for measuring the concentrations of total lanthanides, uranium ions, and other oxides [16, 17]. Holland Inolab pH meter, Germany, was used for pH determination.

2.3. Leaching procedure

In different 250 mL measuring beakers, a known amount of phosphogypsum (50 g) was taken, with the addition of a known volume of acid (100 mL) at room temperature and mixed for a known time. Other experiments were performed by using Nonyl phenol Ethoxylate (NPE) mixed with nitric and hydrochloric acids, at the same studied conditions. The factors affect the desired leaching conditions (such as contact time, acid concentration, solid: liquid ratio, temperature) were optimized. All experiments were performed using powder samples sized to 250 mesh at room temperature (25 ^{o}C)

2.4. Analysis procedure

Compleximetric titration method was used for determination of calcium content in different studied samples [16]. Na_2O and K_2O were determined using flame photometry, while total lanthanides and the other components were determined colorimetrically [17].

Calcium leaching % using in the kinetic studies was calculated by the following equation:

$$\mathbf{Ca\ \% = [(C_o - C_f)\,/\,C_f]\ X\ 100} \qquad (3)$$

Calcium dissolution control % (DC) calculated by the following equation:

$$\mathbf{DC\ \% = [\ (C_o - C_f)_{Ln} / (C_o - C_f)_{Ca}\ ]\ X\ 100} \qquad (4)$$

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

RESULTS AND DISCUSSION

The possible chemical reactions that occur during dissolution of phosphogypsum with hydrochloric as well as nitric acid can be described as follows:

$$\mathbf{x\ CaSO_4\text{-}\ Ln_{(s)} + y\ HCl \rightarrow (x\text{-}n)\ CaSO_4 + n\ CaCl_2 + n\ Ln_{(s)}\ Cl_3 + n\ H^+} \qquad (5)$$

$$\mathbf{x\ CaSO_4\text{-}\ Ln_{(s)} + y\ HNO_3 \rightarrow (x\text{-}n)\ CaSO_4 + n\ Ca\ (NO_3)_2 + n\ Ln_{(s)}\ (NO_3)_3 + n\ H^+} \qquad (6)$$

Reactions 5 and 6 are of special interest for the calcium dissolution process.

3.1. Effect of acid concentration

Calcium dissolution control (DC %) as a function of the acid concentration during the lanthanides leaching operation from PG was studied as shown in Fig. 1. In this respect two series experiments were carried out using HCl and HNO_3 only where others mixed with NPE under the following conditions, weight of PG to acid ratio 0.5 g mL^{-1} and contact time of 15 min. It was found that calcium DC decreases from 24 to ~ 8 % using acid concentration ranged from 1 % to 20 %. This means that, the calcium concentration increases 8 times while the lanthanides concentration increases only 2.75 times. On the other hand, the leaching operation by using the mixture acids with NPE has a significant effect on the calcium DC percentage, it increased quantitatively from 8.7 % to 17.9 and from 8.25 to 18.3 for HCl and HNO_3, respectively even at 20 % acid concentration compared to 8 % of acids without NPE. Table 2 showed a comparison between different leaching systems for calcium, lanthanide and the calcium controlling %. It is interested to mention here that 20 % acid percent was the optimum concentration for maximum lanthanides leaching [5]. Therefore, acid concentration of 20 % was used in other experiments.

Table 2. Comparison between the leaching systems for Calcium, Lanthanides and Calcium DC %

Leaching systems	Lanthanides %	Calcium %	Calcium DC (La/Ca) %
20 % HCl	43.50	05.00	08.70
20 % HCl + 4 % NPE	44.80	02.50	17.92
20 % HNO_3	33.00	04.00	08.25
20 % HNO_3 + 4 % NPE	45.75	02.50	18.30

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

The effect of the ratio of phosphogypsum /acid on the calcium DC % was investigated by employing different stiochiometric amount of acid to leach 50 gram of phosphogypsum. The results illustrated in Fig. 2 showed that the higher calcium DC % of 8.7, 8.25, 17.9 and 18.4 was obtained at S/L equal 0.5 g/mL for leaching solutions of HCl, HNO_3, HCl-NPE and HNO_3-NPE, respectively, thus, 0.5 g/mL is proposed as optimum for latter experiments.

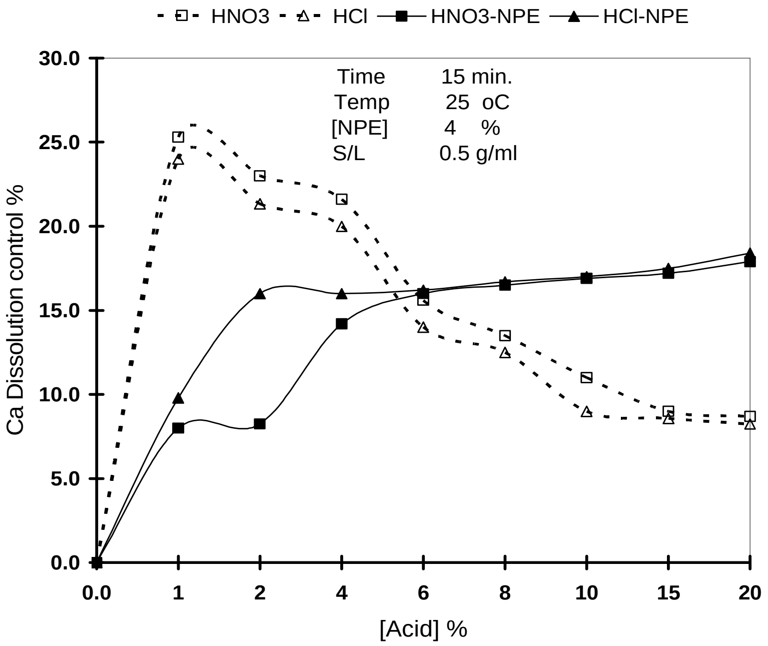


Fig. 1: Effect of acid concentration on the calcium dissolution control %

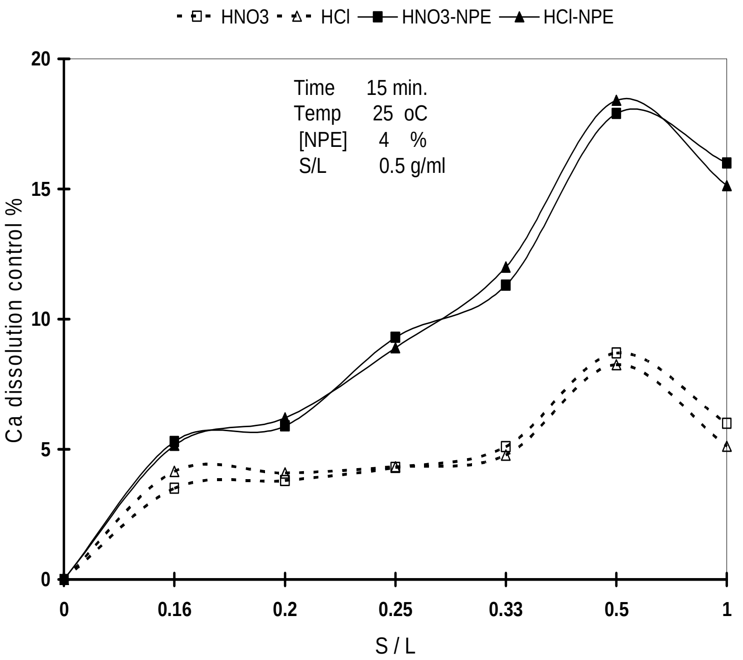


Fig. 2: Effect of solid to liquid (S/L), g/ml on the calcium dissolution control %

3.3. Effect of NPE concentration

To investigate the effect of NPE, the leaching process was carried out at different NPE concentrations; the other conditions remain constant as shown in Fig.3. The use of NPE based on its ability to form salts with these acids and the formed salts contains two parts, one is hydrophilic (acid) and the other is hydrophobic (NPE). The results showed high calcium DC % was achieved using even small NPE concentrations of 4 %. Table 3 showed the variation of calcium, lanthanides % as a function of NPE concentration, from this data we can conclude that, at the presence of 4 % NPE in the leaching solution of PG increases the leaching of lanthanides by about 9 % and decreases the calcium by about 60 % and increasing the ca dissolution control 8 times.

Table 3. Variation of Calcium, lanthanides % as a function of NPE concentration

[NPE] %	HCl			HNO_3		
	Ln %	Ca %	DC %	Ln %	Ca %	DC %
0	43.50	05.00	08.70	33.00	04.00	0.8.25
2	44.00	03.00	14.66	45.00	03.00	15.00
4	**44.80**	**02.50**	**17.92**	**45.75**	**02.50**	**18.30**
6	44.80	02.50	17.92	45.75	02.50	18.30

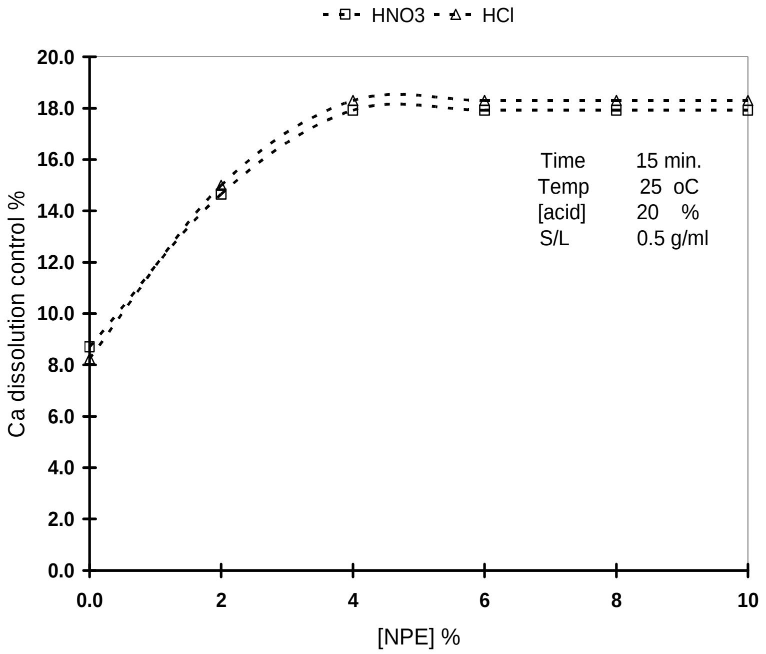


Fig. 3: Effect of NPE concentration on the calcium dissolution control %

3.4. Kinetic analysis of calcium leaching from phosphogypsum

In order to establish the kinetic parameters and rate-controlling step for the leaching of calcium from PG using hydrochloric, nitric acids and the associated NPE with these acids the experimental data can be analyzed according to the heterogeneous reaction models [18]: According to the model, the reaction between a fluid and a solid may be written as:

$$\textbf{F (fluid) + b S (solid)} \rightarrow \textbf{Products} \qquad \textbf{(7)}$$

The rate of reaction between PG particles 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 is k*, the fractional conversion of the ore α which equal:

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

and at any time t the integrated equations for fluid–solid heterogeneous reactions are as shown in table 4 :

Table 4. Fluid–solid heterogeneous reaction models

Model	Equation
film diffusion control	$t = k^{*}[1 - (1 - \alpha)]$
chemical reaction control	$t = k^{*}[1 - (1 - \alpha)^{1/3}]$
ash layer diffusion control	$t = k^{*}[1 - (2/3)\alpha - (1-\alpha)^{2/3}]$

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 calcium from PG, 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 [18]. The kinetic analysis results for the leaching process were found to be consistent with ash layer diffusion control and the integral rate expression was determined to obey the following rate equation:

$$1 - (2/3)\,\alpha - (1-\alpha)^{2/3} = kt \qquad (8)$$

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 4-7. The experimental results represented in these figures indicate no change in the leaching behavior of PG 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 calcium leaching efficiency even with the increasing of the acid concentration, which is most clearly revealed by the curves for larger 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:

$$1 - (2/3)\,\alpha - (1-\alpha)^{2/3} = A^{o}\, e^{-E/RT}\, t \qquad (9)$$

Or

$$\ln k = \ln A - (E/RT) \qquad (10)$$

Where A is a coefficient, R is the gas constant, T is leaching reaction temperature (Kelvin, K), and E is activation energy (KJ/M).

Arrhenius plots of ln (K) vs. T^{-1} for calcium leaching data are shown in figures 8 & 9. Also, the plot of ln k/T vs. T^{-1} was shown in figures 10 & 11 gives straight line with slope equal - ΔH/R and intercept equal - ΔS/R. All the data of activation energy (KJ/M), enthalpy (KJ/M) and entropy (KJ/M) were shown in table 5. This value falls within the activation energy conventionally found for inner diffusion-controlled leaching processes [19]. Increasing of activation energy in the presence of NPE might be probably to increase of the viscosity of the leaching mixture. In comparison, Li et al. [20] obtained activation energy of 40.14 KJ/Mol for the dissolution of vanadium from black shale in acid leaching and proposed that the dissolution process was controlled by the interface transfer and diffusion across the product layer. While Dehghan et al. [21] reported activation energy of 49.2 KJ/Mol for the low-grade calcareous sphalerite in acidic ferric chloride solution and proposed that the leaching process was controlled by the same model.

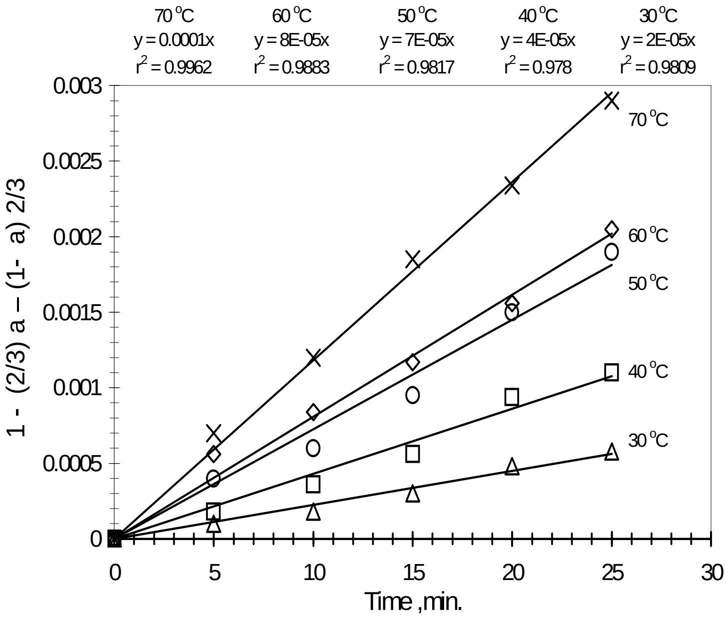


Fig. 4: Leaching kinetics of calcium from phosphogypsum by HNO_3

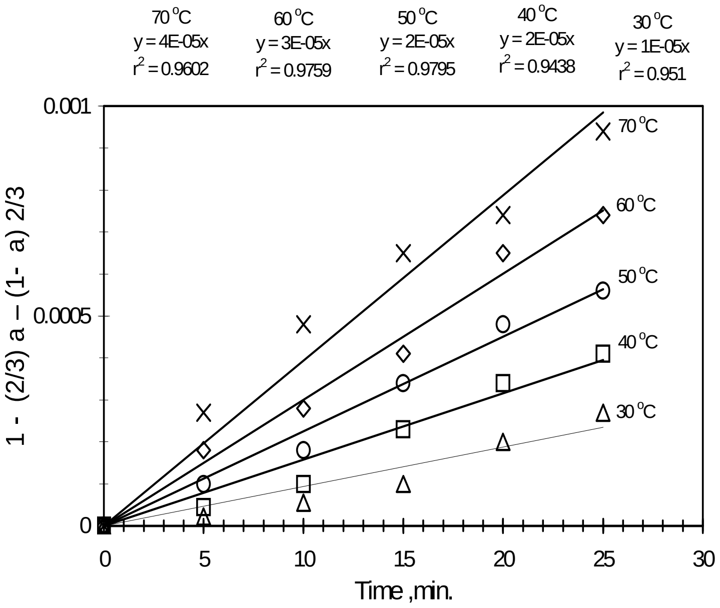


Fig. 5: Leaching kinetics of calcium from phosphogypsum by HCl

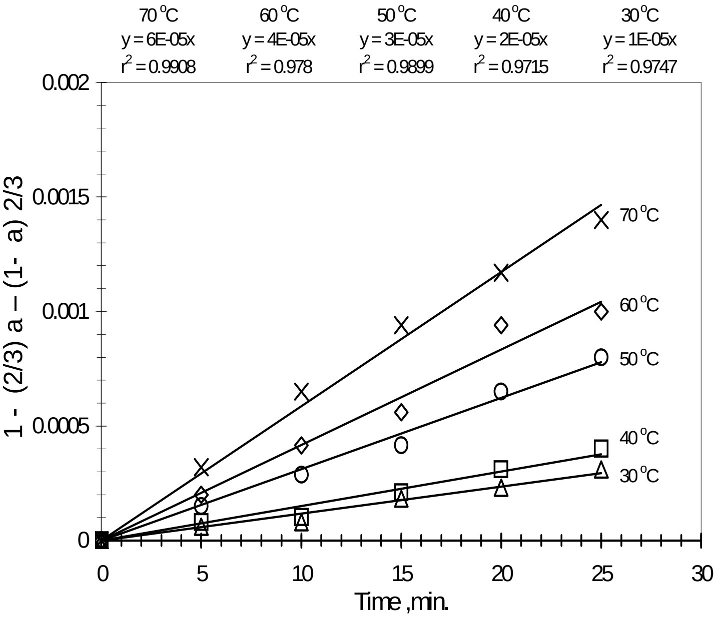


Fig. 6: Leaching kinetics of calcium from phosphogypsum by HNO_3-NPE

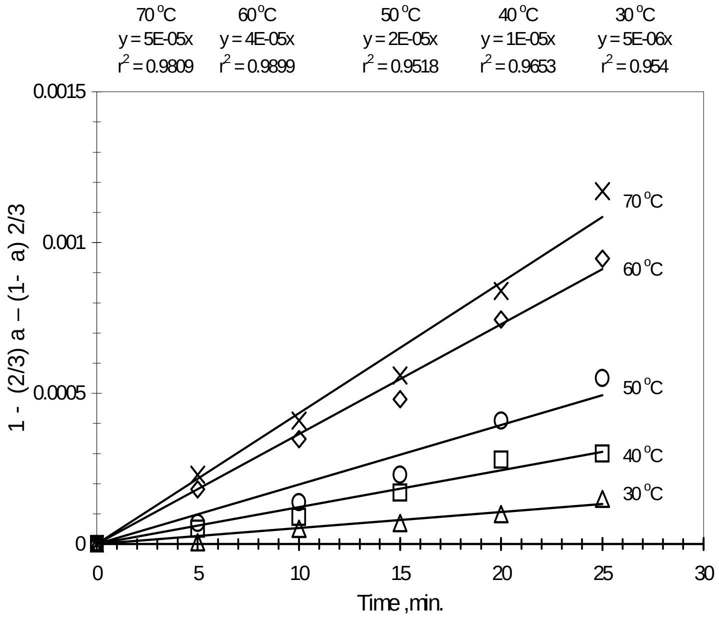


Fig. 7: Leaching kinetics of calcium from phosphogypsum by HCl-NPE

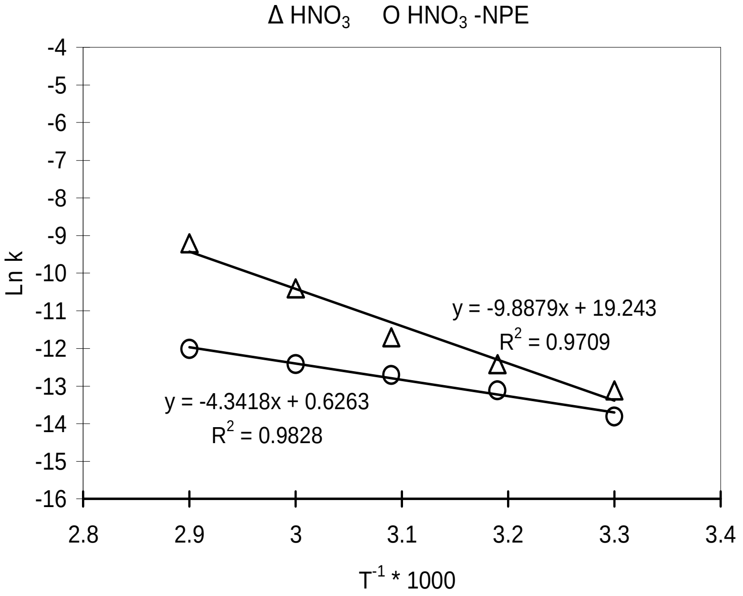


Fig. 8: Activation energy of calcium leaching from phosphogypsum by HNO_3 and HNO_3-NPE

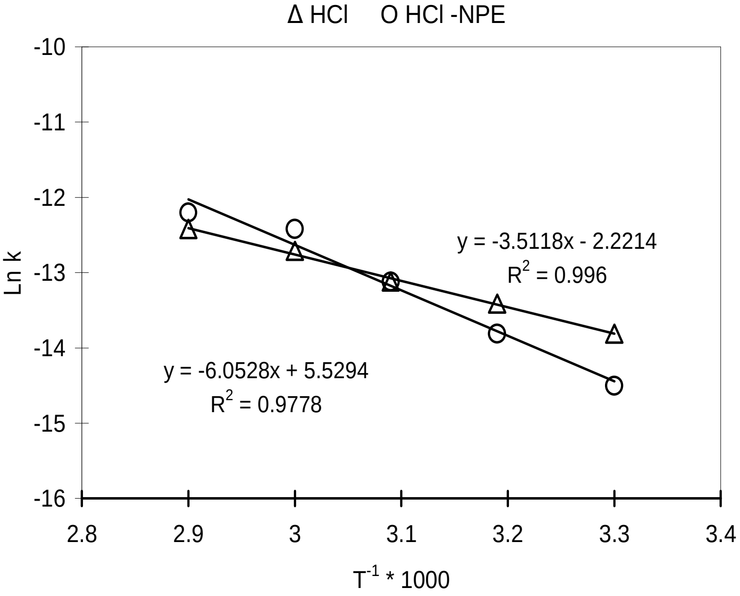


Fig. 9: Activation energy of calcium leaching from phosphogypsum by HCl and HCl-NPE

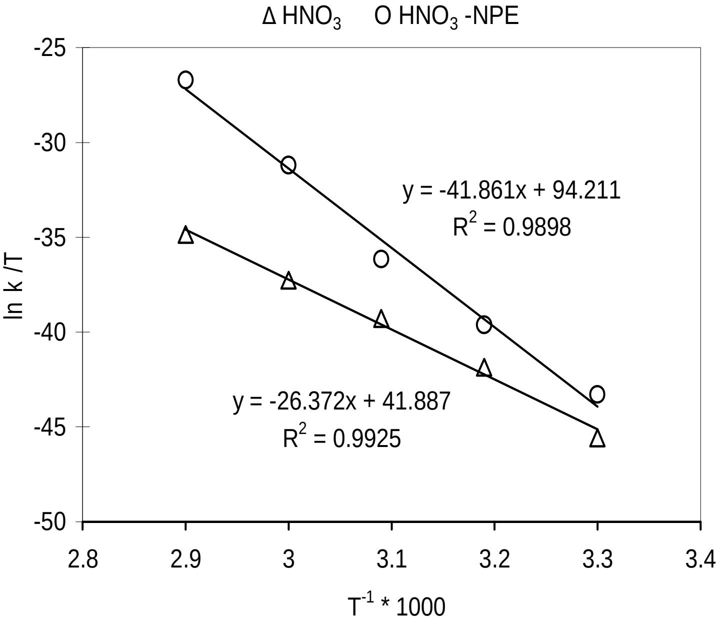


Fig. 10: Enthalpy and entropy of calcium leaching from phosphogypsum by HNO_3 and HNO_3-NPE

Table 5: Thermodynamic data for leaching of calcium

Leaching agent	**ΔH°**	**ΔS°**	**E** (kJ/M)
HNO_3	**219**	**- 347**	**28**
HNO_3-NPE	347	- 780	36
HCl	**199**	**- 280**	**29**
HCl-NPE	265	- 481	50

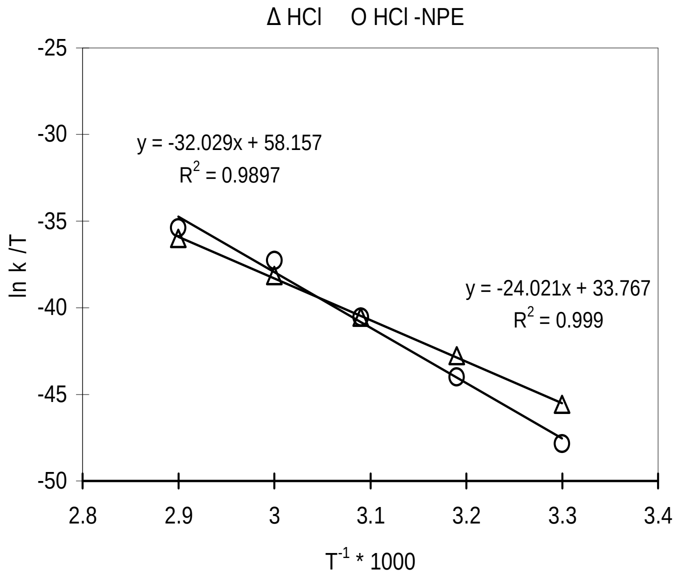


Fig. 11: Enthalpy and entropy of calcium leaching from phosphogypsum by HCl and HCl-NPE

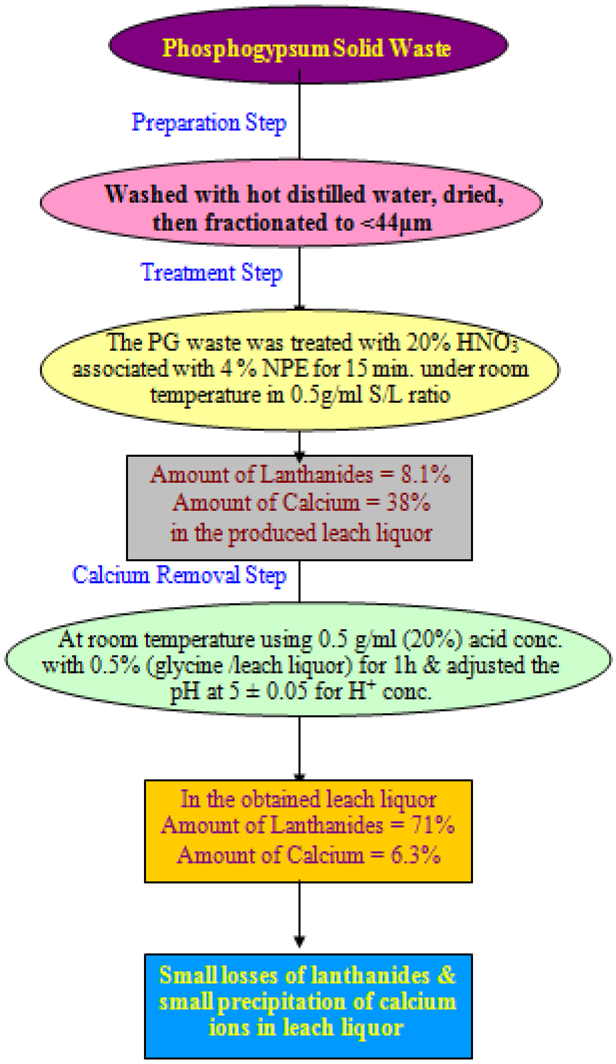


Fig.12. Flow Sheet of calcium dissolution controlling process

3.5. Removal of Calcium

The precipitation experiments of calcium were carried out under the conditions of 0.5 mL g^{-1} (20%) acid, and 0.5 % glycine (mass ratio of glycine to PG leach liquor) at 25 °C for 1h,. The concentrations of hydrogen ion were adjusted to the pH of 5 ± 0.05. The chemical analysis of the leach liquor before and after addition of glycine to the PG was illustrated in table 6. The results show the high values of calcium in the leach liquor before the addition of glycine, while, the calcium removal can be remarkably improved when glycine was added as precipitant reagent. Meanwhile, glycine can combine with other ions like, iron ion to generate acid-insoluble iron glycinate hydrate and consume all ferric ions and a portion of ferrous ions. Massive impurities are decreased to form glycinate salt by adjusting of pH value. Complete flow sheet of the calcium dissolution controlling processes showed in Fig.12.

Table 6. Chemical analysis of some ions in the prepared leach liquor before & after addition of glycine (µg/mL)

Components	**HCl**		**HCl-NPE**		**HNO_3**		**HNO_3-NPE**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
Ca^{2+}	7500	220	5000	145.0	12500	300	5250	95.0
SO_4^{2-}	6500	390	4000	245.0	15000	420	6500	270
Fe^{3+}	1200	70.0	920	32.0	1270	85.0	790.0	40.0
∑lanthanides	1110	1050	1115	1070	1112	1020	1120	1065
F^-	230.0	25.0	110	15.0	245	30.0	90.0	14.0
K^+	40.0	10.0	32.0	5.00	50.0	10.0	43.0	5.00
Ti^{4+}	21.0	12.0	6.00	6.00	17.0	5.00	5.00	2.00
Th^{4+}	6.00	4.00	4.00	2.00	8.00	3.00	5.00	2.00
U^{6+}	14.0	7.00	14.0	4.00	14.0	8.00	14.0	3.00
Total	16621	1788	11201	1524	30212	1881	13817	1496
Lanthanides in leach liquor, %								
Ln (s) %	6.67	59.0	9.95	70.0	3.60	54.0	8.10	71.0
Calcium in leach liquor, %								
CaO %	45.00	12.00	44.50	9.50	41.30	15.90	38.00	6.35

CONCLUSION

The calcium dissolution behavior during the lanthanides recovery process from PG waste has been investigated using hydrochloric, nitric acids and the latter acids with NPE. The experimental results reveal that the calcium concentration was decreased about 8 times in the presence of NPE. Also, the kinetic results clearly highlights that the association of NPE with HCl or HNO_3 acid solutions can be used as a potential leaching system for the decreasing of calcium dissolution in the leach liquor during the lanthanides leaching and recovery operations from PG waste. The leaching by the associated system increases the energy required for calcium dissolution from 28, 29 KJ/M to 36 and 50 KJ/M in case of HNO_3 and HCl, respectively. In addition, glycine can be quantitatively precipitated the calcium ions and more other impurity ions present in the leach liquor at a cretin condition with small loss of lanthanides.

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