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Statistical Modeling of Leaching Low Grade Phosphate Ore with Hydrochloric Acid

Mohamed H. Taha, Hassan El-Shall and Ahmed M.Masoud,

1 Nuclear Materials Authority, P.O. Box 530, El-Maadi, Cairo 11381, Egypt
2University of Florida, PO Box 6135, Gainesville, FL 32611-6135, USA

Summary-The multivariate 2^3 full factorial methodologies is used to study the effect of leaching time, acid concentration, liquid/ solid ratio on the dissolutionof low grade phosphate ore using hydrochloric acid solutions in terms of the maximum P_2O_5 leaching efficiency and the minimum impurities (represented by Fe_2O_3) leaching efficiency. The obtained results were statistically analyzed by using analysis of variances (ANOVA) to measure the adequacy of the fitted model. Based on the design of the experiments, the first order regression model has been constructed to approximate the phosphate leaching efficiency. According to the optimum conditions, the validity of the model has been verified, and the results clear that there is an agreement between the predicted and experimental data which confirm the experimental adequacy of the models and the existence of the optimal conditions.

Introduction

Phosphorus is essential for food production. According to IFA, the world phosphate supply is expected to increase by 2.7% per annum between 2014 and 2018, whereas demand is projected to increase by 2.3% in the same period. The potential balance of phosphate is expected to rise from 2.7 Mt in 2014 to 3.7 Mt in 2018. The ratio of potential phosphate balance to global phosphate demand is likely to grow from about 6.4% in 2014 to 8.5% during the remaining period of the forecast period(1).

Phosphate deposits are classified into two main categories; igneous and sedimentary phosphate rocks. The phosphate minerals in both types of ore are of the apatite group, of which the most commonly encountered variants are; Fluorapatite $Ca_{10}(PO_4)_6$, $(F, OH)_2$ and Francolite $Ca_{10}(PO_4)_{6-x}$, $(CO_3)_x$ $(F, OH)_{2+x}$(2).

Phosphoric acid is mainly manufactured by the wet process, decomposing the phosphate rock either with sulfuric acid, hydrochloric acid or nitric acid. The sulfuric acid route is widely used but suffers from the fact that this process requires relatively high concentration phosphate rock (>28% P_2O_5) with low impurities; otherwise the reaction does not work effectively; this forces miners to produce higher quality rock, which both leads to inefficient exploitation of the limited natural resource and higher mining costs(3-4).

These problems can be solved by dissolving phosphate rock with hydrochloric acid with no gypsum by-product and the acidulation reaction is more rapid with hydrochloric acid than with sulfuric acid. Thus, there is neither need to heat the mixture to speed up the reaction, or any crystal formation problems requiring temperature stabilization (5-7).The reaction between phosphate rock and hydrochloric acid yields phosphoric acid and calcium chloride according to the following equation (8-9)

$$Ca_{10}(PO_4)_6F_2 + 20HCl \leftrightarrow 6H_3PO_4 + 10CaCl_2 + 2HF$$

The hydrochloric acid route is mainly used for the acidulation of high grade phosphate ores.After the acidulation process, the leach liquor is contacted with organic solvents such as Tri-butyl phosphate (TBP) and Methyl Isobutyl Ketone (MIBK) to extract phosphoric acid and leaves the $CaCl_2$ in the aqueous phase (10-11). Likewise, the obtained leach liquor could be directly precipitated as phosphate salts such as; treating the leach liquor with calcium salt to precipitate phosphoric acid in dicalcium phosphate form (DCP) (12).Precipitating sodium onohydrogen phosphates and sodium dihydrogen phosphate from the acidulate solution by usingsodium salt(13-14). Moreover, the hydrochloric acid was used for upgrading low grade phosphate ore to higher P_2O_5 grade by reducing the calcareous materials (6-15).

During the last decade, there have been numerous published articles which indicate that phosphate deposits reserves are expected to be depleted in 50-100 years and peak phosphate is expected to be reached in 2033-2034 (16-17).Therefore, the direct utilization of low grade phosphate ores is necessary to face the increase in the extraction, processing and shipping cost of high grade phosphate. Although researchers have worked on the leaching of low grade phosphate ores using hydrochloric acid (6-15-18), Design of Experiments (DoE) methodology were not applied.

The design of experiments technique has been widely used in many scientific areas with several research aims. In this contribution, Design of Experiments was used in this work to study the leaching of P_2O_5 from low grade phosphate ore using hydrochloric acid. Statistical design and analysis of experiments were used in order to determine the main effects and interactions of hydrochloric acid concentration, solid-to-liquid ratio and reaction timein terms of the maximum P_2O_5leaching efficiency and the minimum impurities (represented by iron) leaching efficiency Therefore, full factorial design involving 8 treatment combinations and 3 replications of the central point are chosen to investigate the hydrometallurgical system.

Experimental

Materials

Hydrochloric acid (MERCK, Germany), was the chemical reagent grade. The representative working sample of Low grade phosphate ore was delivered from El-Nasr Mining Company. The ore sample was crushed with a jaw crusher until the whole sample passed through 150 µm sieve. Then the sample was thoroughly mixed and dried in an electric oven at 110 °C for 24 hours, then cooled and stored for further use. The chemical analysis of the ore sample is as shown in **Table 1**(19). The obtained results clear that the phosphate sample has low P_2O_5content

(19.3 %), and high CaOcontent (35.3 %) which showing the presence of other phases for calcium bearing minerals such as calcite and gypsum in addition to apatite.

Table 1. Chemical analysis of Low grade phosphate ore (19)

Constituent	%	Constituent	mg/kg
P_2O_5	19.3	**Mn**	190
CaO	35.3	**Zn**	149
Fe_2O_3	2.5	**Cd**	2.4
F	2.8	**Pb**	12.2
SiO_2	32.8	**As**	4.5

The obtained results clear that the phosphate sample has low P_2O_5content (19.3%), and high CaOcontent (35.3%) which showing the presence of other phases for calcium bearing minerals such as calcite and gypsum in addition to apatite.

The mineralogical composition of the phosphate working sample has been carried out using powder X-ray diffractometer (model XD1180, Schimadzu, Japan). The XRD analysis of the working sample presented in **Figure 1** indicating that the phosphate sample is dominated by Francolite$Ca_{10}(PO_4)_{6-x}$, $(CO_3)_x$ (F, OH)$_{2+x}$associated with calcium hydrogen phosphate hydrate $CaHPO_4$ $(H_2O)_2$, quartz, SiO_2 and calcite, $CaCO_3$.

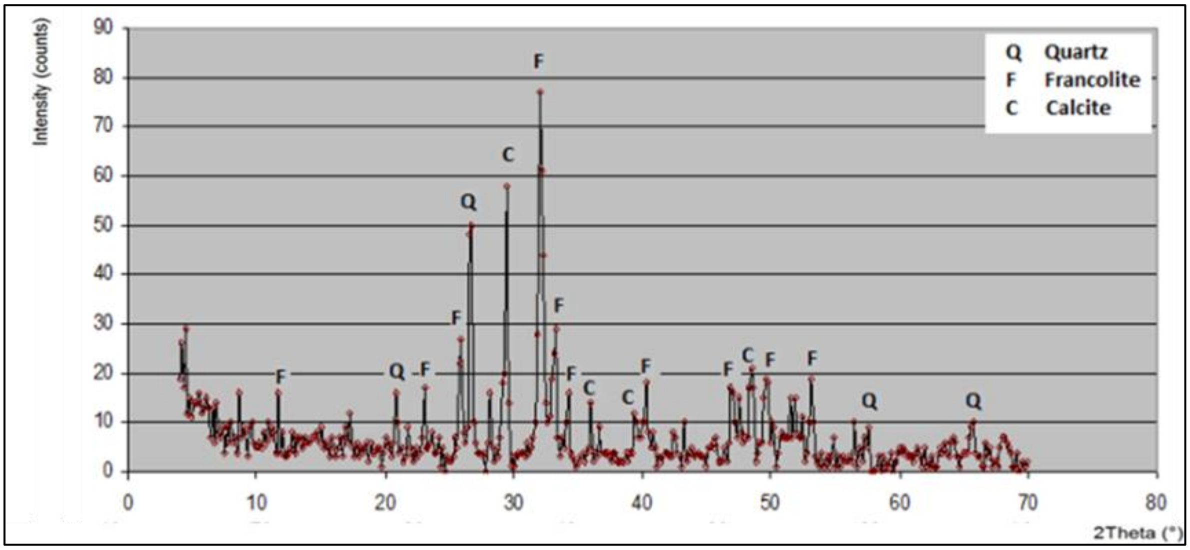

Fig.1.X-ray diffraction pattern of low grade phosphate ore sample.

Apparatus

The reaction was carried out in a cylindrical 1 L reactor of 10 cm diameter. It was fitted with Teflon-coated stirrer with 4 cm diameter and placed in thermostatically controlled water bath. The impeller tip speed was adjusted at 400 rpm. Filtration was performed using Buchner funnel of 4.6 in. diameter. Polypropylene filter cloth of 80 mesh aperture size was used. A vacuum pump was used for filtration.

Procedure

In leaching investigation, for each run 10 g of phosphate sample was transferred with the proper amount of hydrochloric acid solution into the reactor. Defoamer (oleic acid) was added when necessary. After the desired reaction time, the leach slurry was immediately separated by filtration. The remaining solids were dried and weighed. In the filtrate the, Fecontentwas determined by Atomic Absorption Spectrometer type GBC 932 AA (UK) while P_2O_5 content was determined by a colorimetric method (spectrophotometer type Shimadzu UV 1208, ammonium molybdate and ammonium metavanadate were used for P_2O_5 analysis)(20).The leaching efficiency, % was calculated by the following equations:

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

$$\mathrm{Fe_2O_3\ leaching,\%} = \frac{\mathrm{Fe_2O_3\ concentration\ in\ the\ solution,g}}{\mathrm{Fe_2O_3\ concentration\ in\ the\ working\ sample,g}}\ \mathrm{X\ 100}$$

Design of experiments

The statistical design of experiments (DoE) is an efficient procedure for planning to reduce the required experimentsfor optimizing the system. Generally, it was used to get better response with a minimum effort, time and resources (21). The design determines factors havingsignificant effects and the interaction effects of various factors on a response. Design of experiments includes three steps; statistical design of experiments, estimation of coefficients through a mathematical model with response prediction, and statistical analysis (22).

Today, the most widely used kind of experimental design, to estimate main effects as well as interaction effects, is the 2^p factorial design in which each variable is investigated at two levels (23). Based on analysis results, additional runs might be required. Among “2 level” methods, the “Central Composite Design” is favored by many scientists where several runs are performed at the midlevel of all factors (variables).

Results and Discussion

In the light of pre-experiments, three factors, namely, hydrochloric acidconcentration, solid-to-liquid ratio and reaction time were chosen as independent variables In order to optimizethe favor low grade phosphate ore dissolution in relation to impurity.

The experimental factorsare evaluated at two levels, low (denoted as −1), high (denoted as +1, and midlevel denoted as 0), and expressed as coded variablesas shown in **Table 2**. The experiment order was randomly to avoid systematic errors. The results are analyzed with the

Design Expert 10.0.4.0software (24), and the main effects and interactions between factors were determined.

Table2. The levels of experimental factors for the full factorial design

Factors	Coded variables	Low level (-)	High level (+)	Mid-level (0)
Hydrochloric acid concentration, %	A	2	10	6
liquid/ Solidratio, ml/ g	B	2	5	3.5
Time, min	C	2	10	6

The significant parameters

For 2^kfactorial designs, the addition of center points to design allows the researcher to check whether the linearity of the effects is a reasonable assumption or whether quadratic terms should be added to the model. In this regard, the experimental plan involved running 8 tests and 3 replications of the center points in random order to determine P_2O_5 and Fe_2O_3 leaching efficiency fromLow grade phosphate ore. The experiments matrix of this design and the low grade dissolution efficiency were performedin **Table 3**.

Table3. Design matrix of the 2^3 full factorial design

Design Run #	Run #	A		B		C		P_2O_5 %	Fe_2O_3 %
7	1	-1	2	1	5	1	10	21.5	5.7
5	2	-1	2	-1	2	1	10	5.4	1.1
1	3	-1	2	-1	2	-1	2	7.8	2.0
11	4	0	6	0	3.5	0	6	60.1	18.5
10	5	0	6	0	3.5	0	6	59.3	18.2
2	6	1	10	-1	2	-1	2	50.5	17.4
3	7	-1	2	1	5	-1	2	24.7	5.0
9	8	0	6	0	3.5	0	6	63.1	19.1
6	9	1	10	-1	2	1	10	50.7	21.2
8	10	1	10	1	5	1	10	90.4	43.1
4	11	1	10	1	5	-1	2	97.8	38.9

The results obtained from Table (3) show that 97.8% ofP_2O_5 was successfully leached from El-Sebeaya low grade phosphate ore(experiment number 4) according to the following conditions; 10% hydrochloric acid, liquid/ solid ration, ml/ g, of 5and reaction time 2 min. However, within the same conditions, 38.9% of the total iron content was leached. On the other hand, experiments number 1 and 5 are representing the lowest P_2O_5 leaching efficiency (7.8 and

5.4% respectively).The effects of the experimental factorsand their interactions influence the $P_2O_5$and Fe_2O_3leaching are summarized in **Table 4**. The positive values of these effects reveal thatthe increase of these parameters increased leaching efficiency. Conversely, negative values of the effects decreased the response (leaching%).

Table4. Estimated Effects and Coefficients for P_2O_5 and Fe_2O_3 leaching

		P_2O_5		Fe_2O_3	
	Term	**Coefficient Estimate**	**% Contribution**	**Coefficient Estimate**	**% Contribution**
	Constant	48.3		17.25	
Model	**A**-Acid conc.	28.75	69.84	13.35	73.72
Model	**B**-liquid/ solid ratio	15	19.01	6.38	16.81
Model	**C**-Contact time	-1.6	0.22	0.97	0.39
Model	AB	6.75	3.85	4.46	8.24
Model	AC	-0.2	0.004	1.01	0.42
Model	BC	-1.05	0.093	0.26	0.029
Model	ABC	-0.85	0.061	-0.15	0.009
Model	Curvature		6.84		0.36
Error	Lack of Fit		0		0
Error	Pure Error		0.085		0.022

The obtained results show that, the hydrochloric acid concentration had the greatest effect on $P_2O_5$and Fe_2O_3leaching % (69.8 and 73.7 respectively), followed by liquid/ solid ratio (19.0 for P_2O_5 and 16.8 for Fe_2O_3), and acid concentration-liquid/ solid ratio interaction(3.8 and 8.2) for $P_2O_5$and Fe_2O_3 respectively. On the other hand, acid concentration-time, liquid/ solid ratio-time, acid concentration-liquid/ solid ratio-time interactions have negative effect on P_2O_5leaching efficiency (-0.2, -1.05, and -0.8 respectively), while only acid concentration-liquid/ solid ratio-time interaction have negative effect on Fe_2O_3 leaching efficiency (-0.15).

The investigation of phosphate ore leaching using hydrochloric acid by One-factor-at-a-time procedures show that, the reaction time has positive effect on the phosphate dissolution efficiency (10-18). However, the application of full factorial design for the phosphate leaching using hydrochloric acid clear that the reaction time has negative effect on P_2O_5 leaching efficiency. This behavior could be explained as a result of the reaction between the leached phosphoric acid and calcium chloride to produce insoluble calcium hydrogen phosphate according to the following equations;

$$\mathrm{Ca_3(PO_4)_2 + 6\,HCl \rightarrow 2H_3PO_4 + 3\,CaCl_2}(1)$$

$$H_3PO_4 + CaCl_2 \rightarrow CaHPO_4 \downarrow (2)$$

The obtained results confirm the main advantage of the 2^k factorial design compared to the One-factor-at-a-time approach, where it show the effects of main variables and also the effect of variables interactions.

After performing the experiments, the analysis and model fitting of the experimental data come into nature (25). In this regards, the normal first order model (fitted model) between significant factors and the response was developed to illustrate the dependence of the response on the significant factors for P_2O_5 and Fe_2O_3 leaching investigation. The model is expressed below as:

$$Y = b_o + b_1A + b_2B + b_3C + b_{12}AB + b_{13}AC + b_{23}BC + b_{123}ABC \qquad (3)$$

Where Y = the leaching percentage; b = regression model coefficients of all corresponding main and interaction factors; and A, B, and C = dimensionless coded factors for hydrochloric acid concentration, aqueous/ solid ratio, and time respectively. The coefficients of Equation (3) are presented in Table 4. Based on the results obtained in Table4, the regression model equation with interaction terms could be expressed in Terms of Coded Factors as the following equation:

$$Y_{P2O5} = 48.30 + 28.75A + 15.00B - 1.60C + 6.75AB - 0.02AC - 1.05BC - 0.85ABC \qquad (4)$$

$$Y_{Fe2O3} = 17.25 + 13.35A + 6.38B + 0.97C + 4.46AB + 1.01AC + 0.26BC - 0.15ABC \qquad (5)$$

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients. According to equations 4 and 5, it is indicated that in order to maximize the low grade phosphate ore dissolution process, the effects with positive sign have to kept at high level, while the effects with negative sign have to kept at low level.

The Statistical Analysis for the Proposed Model

The statistical analysis of the model was performed in the form of analysis of variance (ANOVA) as shown in **Tables 5 and 6**. This analysis included the Fisher's F-test (overall model significance), and its associated probability P (F). The analysis also includes the Student's t-value for the estimated coefficients and associated probabilities P(t). The obtained results show that, at 95% confidence intervals, hydrochloric acid concentration, liquid/ solid ratio and acid concentration-liquid/ solid ratio interaction are statistically significant to P_2O_5 leaching process whilereaction time has been found insignificant.Values of "Prob> F" less than 0.0500 indicate model terms are significant. Therefore A, B, and AB are significant model terms for P_2O_5 and Fe_2O_3 leaching process.

Table 5. Analysis of variance for P_2O_5 leaching

ANOVA for selected factorial model						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	8797.48	7	1258.91	313.68	0.0032	significant
A-Acid concentration	6612.5	1	6612.5	1647.63	0.0003	significant
B-Liquid/ solid ratio	1800	1	1800	448.5	0.0022	significant
C-Time	20.48	1	20.48	5.1	0.1527	not significant
AB	364.5	1	364.5	90.82	0.0108	significant
AC	0.32	1	0.32	0.08	0.8042	not significant
BC	8.82	1	8.82	2.2	0.2764	not significant
ABC	5.78	1	5.78	1.44	0.353	not significant
Curvature	647.97	1	647.97	161.46	0.0061	significant
Pure Error	8.03	2	4.01			
Cor Total	9468.4	10				

Table 6. Analysis of variance for Fe_2O_3leaching

ANOVA for selected factorial model						
Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	1926.75	7	275.25	1310.72	0.0008	significant
A-Acid concentration	1425.78	1	1425.78	6789.43	0.0001	significant
B-Liquid/ solid ratio	325.13	1	325.13	1548.21	0.0006	significant
C-Time	7.6	1	7.6	36.21	0.0265	significant
AB	159.31	1	159.31	758.62	0.0013	significant
AC	8.2	1	8.2	39.05	0.0247	significant
BC	0.55	1	0.55	2.62	0.2466	not significant
ABC	0.18	1	0.18	0.86	0.4523	not significant
Curvature	6.97	1	6.97	33.2	0.0288	significant
Pure Error	0.42	2	0.21			
Cor Total	1934.15	10				

Regards to the statistical modeling performed by Design Expert 10.0.4.0software, the optimal conditions for low grade phosphate oreusing hydrochloric acid solution were: 10% hydrochloric acid concentration, liquid/ solid ratio, ml/ g, 5/1, and reaction time of 2 min.

According to these optimal conditions, about 97.8% oftheP$_2$O$_5$was successfully leached from low grade phosphate oreusing hydrochloric acid. The same optimal conditions yield about 38.8% leaching percent for Fe$_2$O$_3$.

Validation of the model

The scattered diagram for the experimental results of low grade phosphate oredissolution using hydrochloric acid and the predicted results obtained using the re-fitted models for each level of the central composite design matrix are given in Figures 2 and 3 for P$_2$O$_5$ and Fe$_2$O$_3$ respectively. The predicted results are calculated using Equations 4 and 5. The correlation of the linear regression is found to be about $R^2 = 0.95$ for both of P$_2$O$_5$ and Fe$_2$O$_3$. Statistically, this means that 95.0% of the sample variation can be explained by the independent variables. This indicates that the first-order polynomial equations (4 and 5) are satisfactory for identifying the optimum level of the investigated factors for low grade phosphate ore dissolution process.

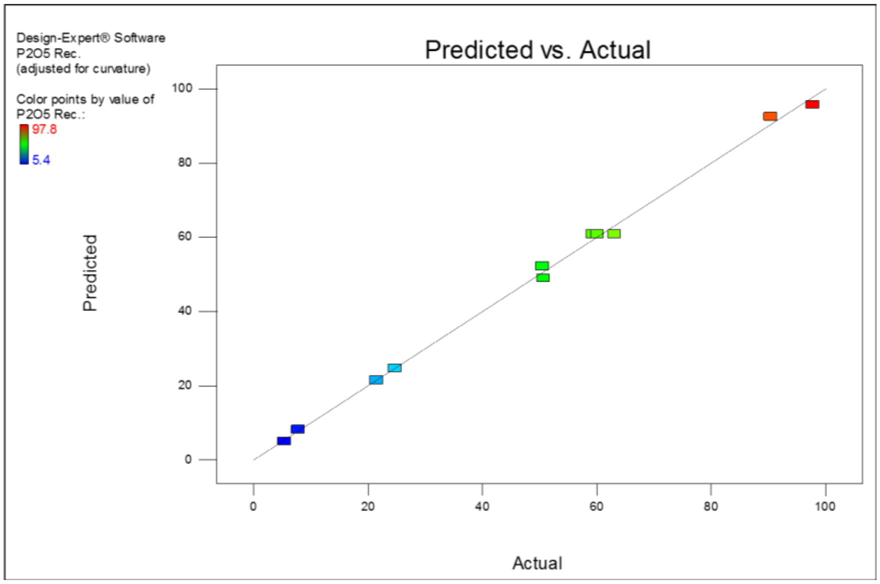

Fig.2. Scatter diagram of experimental values versus predicted values by Equations (4).

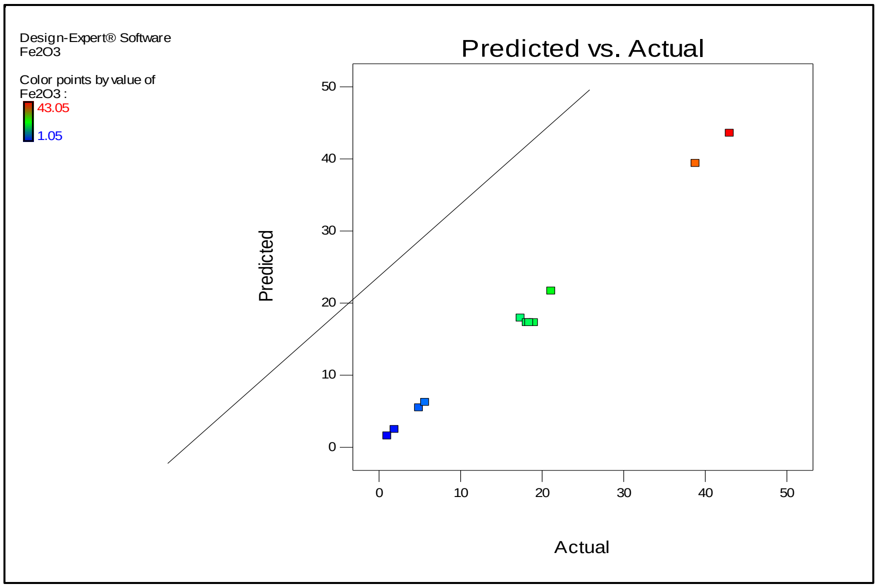

Fig.3. Scatter diagram of experimental values versus predicted values by Equations (5).

The validation of the model was achieved by performing additional experiments under the predicted optimal conditions; 10% hydrochloric acid concentration, liquid/ solid ratio, ml/ g, 5/1, and reaction time of 2 min. The two experiments yielded an average P_2O_5 leaching efficiency of 98.1% and 39.0% for Fe_2O_3 leaching %, which clear that there is an agreement between the predicted and experimental results confirmed the experimental adequacy of the models and the existence of the optimal conditions. This means that, the models developed was considered to be accurate and reliable for low grade phosphate ore leaching with hydrochloric acid in terms of the highest P_2O_5 leaching efficiency with the possible lowest Fe_2O_3 leaching %.

Leaching Process Investigation

Based on the aforementioned investigations, a leaching experiment was carried out for the low grade phosphate ore using hydrochloric acid solution regarding to the optimal dissolution conditions. After filtration, phosphoric acid is generally precipitatedfrom acidulate leach liquor as phosphate salts which are used as fertilizers. For example, calcium salt is used to precipitate phosphoric acid in dicalcium phosphate form (DCP), (12-26). After the phosphate salt precipitation process, for the economic viability of the leaching process, the recovery of hydrochloric acid from the precipitation raffinate calcium chloride solution is important because it will significantly reduce the requirement for fresh leaching agent. Hydrochloric acid could be regenerated from the calcium chloride filtrate for recycle by treating the precipitation solution with sulfuric acid Sulfuric acid is more common and less expensive than hydrochloric acid, in order to neutralize calcium chloride and producing relatively pure calcium sulfate di-hydrate, and to recover hydrochloric acid for reuse in leaching process according to the following equation (26).

$$CaCl_2 + H_2SO_4 + 2H_2O \rightarrow CaSO_4 . 2H_2O \downarrow + 2HCl$$

Conclusion

The leaching of P_2O_5 from low grade phosphate ore has been investigated using hydrochloric acid solution under various experimental conditions in order to optimize the leaching process. Full factorial design was chosen to investigate the hydrometallurgical system. Three factors (acid concentration, liquid/ solid ml/ g, ratio, andleaching time) and two value levels were studied. The factorial design analysis was performed in order to identify the main and the interaction effects of the various factors. The obtained results show that, at 95% confidence intervals, hydrochloric acid concentration, liquid/ solid ratio and acid concentration-liquid/ solid ratio interaction are statistically significant to P_2O_5 leaching process while reaction time has been found insignificant. The optimum conditions have been determined as, hydrochloric acid concentration of 10%, reaction time of 2 min and liquid/ solid ratio, ml/ g of 5:1. Under these optimum conditions, the overall P_2O_5leaching efficiency performance is 97.8% while Fe_2O_3 leaching percent was 38.8%.

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