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Selective leaching of low-grade phosphate ore using a mixture of organic acids

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ABSTRACT

In the present study, the reverse leaching method with the combination of acetic and lactic acid was used for the recovery of phosphate from carbonate phosphate ore, which contained about 10% P_2O_5. In the experiments carried out on the dissolution, leaching time, temperature, acid concentration, solid/liquid ratio, and particle size distribution were selected as important parameters, and their effects were evaluated. The results showed that the optimization of the leaching condition increased the grade of P_2O_5 to 29% with a recovery of 90%. The kinetic experiments (time-temperature) in optimal conditions revealed that activation energy for the leaching process was about 24.27 kJ/mol which is an indication of diffusion control processes and the rate of reaction was achieved $[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}] = k_0 e^{-24.27/RT}.t$. Results showed that the application of organic acid leaching would facilitate producing phosphate concentrate from low-grade calcareous phosphate ores.

Keywords : *Reverse leaching; Phosphate; Dissolution; Leaching Kinetic; Organic acid*

1. Introduction

Phosphates are essential resources for global agriculture, and phosphate deficiency would be one of the most important food supply problems in the future. Since the existing phosphate ores are of low grade, the need for ore concentration used in the industry is essential. Depending on the source of phosphate ore, various methods such as screening, scrubbing, dense medium separation, washing, roasting, calcination, leaching, and flotation methods are used [1, 2]. For example, crushing and screening are used to remove coarse, hard silicates, and attrition and scrubbing are applied to remove fine-grained clay minerals. When the primary gangue material is silica, flotation is utilized as a standard technique, and it is the best method for igneous phosphate ores [3-6]. Where many of the world's phosphate resources are sedimentary deposits, carbonate minerals are the main gangues, and consequently, the processing and profitability of these types of resources is difficult [7]. Calcareous phosphate flotation can be applied when carbonate minerals are well crystallized and phosphate particles are detached from other gangue minerals. When the phosphate ore contains soft and chalky carbonates, flotation is less applicable [8, 9]. In general, the separation of phosphate and carbonate gangue with flotation is highly challenging because of uniformity and similarity in physicochemical and surface chemical properties of the ingredients and complex solution chemistry of flotation produced by the dissolution of salts in the system [8, 10, 11]. However, carbonate-rich phosphate deposits can be processed by calcination and acid leaching methods. Calcination is used in areas having low-cost energy supply and limited water resources. However, this method has some general disadvantages, such as high energy costs, changing the products' surface properties and the reactivity of phosphate minerals, as well as decreasing the quality and reducing the products' solubility; therefore, the use of this method is limited [6, 12]. Regarding the problems that accompany sedimentary phosphate ores, acid leaching is a promising method that can be applied to treating the calcareous phosphate ores and more attention is being given to leaching methods. Leaching phosphate ores is possible using both inorganic acids (like sulfuric acid) and organic acids (like acetic acid, lactic acid, formic acid, etc.). Leaching calcareous phosphate ores with sulfuric acid have provided good results, but this acid is strong and significant amount of P_2O_5 is lost during the dissolution process. Leaching calcareous phosphates with weak organic acids is very selective and produces a better quality product. In this method, the produced wastes have fewer environmental hazards.

Weak organic acids show an appreciable degree of selective leaching of calcareous material in low-grade phosphate rocks and ores. However, given the high price of organic acids, it is essential to recover acids in the process to ensure an economical process. Thus, considering the reaction conditions and the nature and size of the particles, organic acids were introduced as promising agents in leaching calcareous phosphate rocks [13-17].

In this research, we studied the leaching feasibility of carbonate phosphate rocks from the Choram phosphate mine in Southern Iran with a combination of an equal ratio of acetic acid and lactic acid. To the best of our knowledge, this is the first study that uses mixed acid in phosphate leaching systems. In this study, after investigating the effective parameters such as temperature, stirring speed, solid to liquid ratio, acid dosage, and particle size, depending on the desirable grade and recovery as well as the process costs, the optimal amount of each parameter was identified.

2. Materials and methods

2.1. Materials

- Sample Preparation

Acetic acid and lactic acid used in the tests are from Merck Co with a

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grade of ACS,ISO,Reag. Ph Eur and Ph Eur,BP,E 270, respectively. The samples were crushed using different crushers and mills to achieve different fractions. Then, they were dried in an oven at a drying temperature of 105ºC. Afterward, the fine-grained samples were sent for chemical analysis. Table 1 shows the results of the chemical analysis. The results of XRD analysis showed that the main constituents, in order of amount, are calcite, fluorapatite, quartz, clay minerals, and dolomite.

Table 1. The chemical analysis of the samples.

Components	P_2O_5	CaO	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	MnO	S	L.O.I	Others
Amount (%)	9.164	46.01	9.24	2.45	1.67	0.28	0.38	0.102	0.72	0.012	0.003	28.98	0.99

2.2. Methods

A crushed sample with a d80 value of 150 µ was added in a 500 ml batch leach reactor (first water and sample were mixed, and then acid was added) and agitated with a stirrer at 600 rpm. After leaching, the pulp was filtered, and the remaining solid of the filtering step was grinded under 70 µ to be prepared for analysis. In the analysis step, the powder was mixed with nitric acid. Perkin Elmer model for UV device was used for reading the amount of P_2O_5. Results f primary experiments showed that a further increase of the stirring speed would not affect the carbonate dissolution rate. In this study, the mixture of acetic acid and lactic acid with a volume ratio of 1:1 was used as the leaching agent, but it was not considered as an agent for experiments. Parameters in these tests were temperature, leaching time, acid concentration, solid to liquid ratio, and particle size. After batch leaching operation, the vessel was placed into the ice bath, and after filtration and drying the solid, a representative sample was prepared for chemical analysis.

After obtaining the grade and recovery of all leaching experiments, the results were investigated. For this purpose, the appropriate model and effective parameters were tried to be determined using the DX7 program. The method of experimental design in this software is fractional factorial design with four central points.

2.3. Process chemistry

The reactions between acids and carbonate materials are presented as follows [14, 18 and 19]:

$$CaCO_{3(s)} + 2CH_3COOH_{(aq)} \rightarrow Ca(CH_3COO)_{2(aq)} + CO_{2(g)} + H_2O_{(g)} \quad (1)$$

$$CaCO_3(s)+2CH3CH(OH)COOH(aq) \rightarrow Ca(CH_3CH(OH)COO)_2(aq)+ CO2(g)+H2O_{(g)} \quad (2)$$

The completion time for the above reactions could be different according to the concentration and type of the acid, solid to liquid ratio, temperature, stirring speed, and particle size. After the complete dissolution of carbonate materials, the acid begins to dissolve the phosphorus content of the ore. For example, by increasing the concentration of acid, the completion reaction time is decreased and due to the increase in project costs.

3. Results and discussion

In this research, after several initial tests, some parameters were considered as effective parameters, including leaching time, temperature, solid to liquid ratio, acid concentration, and particle size. The statistical design of experiments was used as well. Table 2 shows the conditions of the tests of the leaching experiments. An extreme decrease in recovery and grade was observed outside of the solid to liquid range. Therefore, for the sake of the process efficiency, acid recovery is necessary. After analyzing the experimental results, it was found that the interactions of these factors were more effective in the leaching process. Table 3 shows the tests' answers.

The ANOVA table was used for the detection of effective factors and the significance of the model. Table 4 shows the result of ANOVA.

According to Table 4, it is obvious that the results obtained from the proposed model are significant because the p-value is less than 0.05. On the other hand, parameters named A, B and C are considered as effective parameters, and they have the most effectivity among all factors.

Also, the normal distribution graph of the residuals is shown in Fig. 1.

Table 2. Test conditions for the leaching experiments.

Run	Time (minute)	Acid content (%)	Ratio of solid to liquid (g/g)	Temperature (°C)	Particle Size (µm)
1	70	25	0.2	45	300
2	40	35	0.3	70	-200
3	40	15	0.3	70	800
4	40	35	0.3	20	800
5	100	15	0.3	20	800
6	100	35	0.1	20	800
7	40	15	0.1	20	800
8	100	15	0.1	70	800
9	70	25	0.2	45	300
10	100	35	0.2	70	-200
11	100	35	0.3	70	800
12	40	35	0.1	70	800
13	40	15	0.3	20	-200
14	40	35	0.1	20	-200
15	100	15	0.1	20	-200
16	40	15	0.1	70	-200
17	100	15	0.3	70	-200
18	70	25	0.2	45	300
19	70	25	0.2	45	300
20	100	35	0.3	20	-200

Table 3. Results of leaching tests.

Run	P_2O_5 Grade in concentrate (%)	P_2O_5 Recovery (%)
1	26.06	89.92
2	25.31	89.47
3	16,55	93.33
4	14.77	94.00
5	17.54	91.50
6	25.07	78.2
7	27.29	86.74
8	27.62	80.45
9	25.83	85.6
10	23.83	73.1
11	25.77	82.20
12	25.32	79.4
13	16.77	90.6
14	27.06	78.4
15	25.3	80.94
16	30.97	84.80
17	25.77	86.06
18	27.02	86.72
19	27.57	86.05
20	21.53	83.30

Table 4. ANOVA data for the recovery of P_2O_5.

Source	Sum of Square	Mean Square	F Value	p-value Prob > F
Model	551.76	72.82	26.75	0.0001<
A	104.50	104.50	35.47	0.0001<
B	82.13	82.13	27.87	0.0002
C	123.99	123.99	42.08	0.0001<
D	14.01	14.01	4.75	0.0499
E	22.68	22.68	7.70	0.0168
DE	14.35	14.35	4.87	0.0476
Residual	35.36	2.95		
Lake of fit	23.91	2.66	0.70	0.7044
Pure Error	11.45	3.82		
Core Total	587.12			

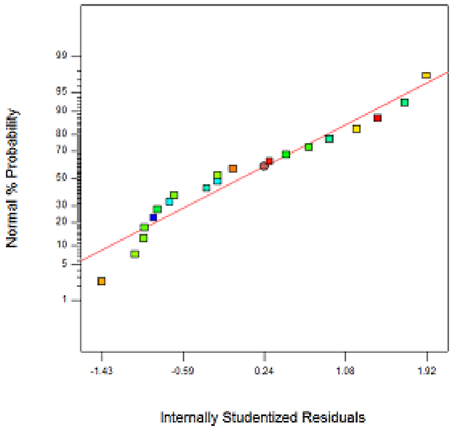

Fig. 1. Normal plot of residuals for the recovery of P_2O_5.

According to Fig. 1, it is clear that the residues are almost on a direct line with a normal distribution. Consequently, the model is acceptable.

3.1. Effect of reaction time and acid dosage

The effect of reaction time and acid dosage are shown in Fig. 2. According to the results, by decreasing the reaction time from 100 to 40 minutes, P_2O_5 grade increased. Results also showed that by increasing time over 60 minutes, the grade of P_2O_5 decreased. In order to complete the reaction between the acid and carbonate minerals, it is necessary to determine the optimal time. Afterward, the reaction between the acid and apatite begins and reduces the grade and recovery of P_2O_5.

According to the effect of acid concentration, as the acid concentration decreases from 35% to 15% (the combination of lactic acid and acetic acid), the amount P_2O_5 increases, and by enhancing the acid dosage from 15% to 35%, the P_2O_5 content reduces from 27.74% to 25.33%.

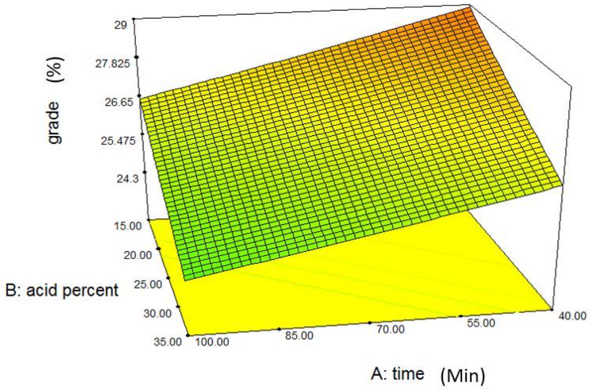

Fig. 2. The effect of time and acid dosage on phosphorus grades (Test Conditions: Temperature (45 °C), Time (minute)=60, Ratio of solid to liquid=0.2, Particle Size (μm)=300).

3.2. Interaction effect of leaching time and solid to liquid ratio

The effect of this interaction is shown in Fig. 3A. Reducing the solid to liquid ratio and increasing reaction time up to 100 minutes reduce the P_2O_5 grade drastically. However, by increasing the solid content and increasing the reaction time to 100 minutes, the reaction was not completed, and the process needed more time to remove carbonate materials. In other words, by increasing the solid to liquid ratio, more time would be needed to complete the process.

3.3. Interaction effect of time and particle size

Fig. 3B shows the effect of the *interaction effect of time and particle size.* By decreasing particle size below 200 micrometers and increasing reaction time to 100 minutes, the grade of P_2O_5 decreased sharply, and by increasing particle size to 800 micrometers, more time was needed to complete the process to remove all carbonates. Size reduction increased surface area, and therefore more carbonates were exposed to acid.

3.4. Interaction effect of acid concentration and solid to liquid ratio

By increasing the solid to liquid ratio, acid concentration had more effect on increasing P_2O_5. In other words, increasing the feed amount required more acid and more time. This was because the carbonate amount in the pulp increased and required more acid to dissolve the minerals (Fig. 3C).

3.5. Interaction effect of temperature and solid to liquid ratio

Increasing the temperature and enhancing the solid to liquid ratio increased the grade of P_2O_5 in the concentrate, and conversely, decreasing the temperature and increasing the solid to liquid ratio reduced the P_2O_5 grade. Increasing the temperature enhanced the reaction rate in the boundary layer, and led to the further dissolution of the feed. On the other hand, at low temperatures, by increasing the feed amount, due to the lack of sufficient acid to react with carbonates, the grade of the product reduced (Fig. 3D.).

3.6. Interaction effect of particle size and solid to liquid ratio

By increasing the solid to liquid ratio, the grade of the product decreased, as shown in Fig. 3E. Also, the use of a feed with a finer size distribution increased the grade indicating the effect of size on the leaching performance. In this condition, using finer particles increased acid contact with carbonate minerals, which increased the reaction rate.

3.7. Interaction effect of time and acid dosage and the ratio of solid to liquid

Fig. 4 shows the effects of three parameters simultaneously on the P_2O_5 grade. By increasing all three parameters from their low levels to their high levels, the P_2O_5 grade is reduced about 2.8%.

Fig. 4. Effect of interaction between time and acid dosage and the amount of solid to 1-liter liquid on the grade of phosphorus (Tests Conditions: Temperature (°C)=45, Time(minute)=60, Acid content (%)=25, Ratio of solid to liquid=0.2, Particle Size (μm)=300).

3.8. Optimization

By optimizing the leaching parameters summarized in Table 5, the final test was performed, and its results showed that it was possible to produce a marketable phosphate concentrate with 90% recovery and 29% P_2O_5 grade.

Table 5. Optimized conditions for leaching experiments.

Temperature (°C)	Time (minute)	Acid content (%)	Ratio of solid to liquid	Particle Size (μm)
20	40	15	0.2	300

3.9. Kinetics analysis

In heterogeneous solid-liquid reactions, the reaction rate is controlled either by the diffusion of reactant through the solution boundary layer, or through a solid product layer, or by the rate of the chemical reaction at the surface of the core of unreacted particles [20]. The shrinking core model considers that the leaching process is controlled by fluid film diffusion or chemical reaction control. The simplified equations of the shrinking core model, when either diffusion or the surface chemical reactions are the slowest steps, can be expressed as follows, respectively [20]:

If the produced layer controls the kinetics of dissolution, the shrinking core model is presented by the following equation:

$$1-3(1-\alpha)^{\frac{2}{3}}+2(1-\alpha) = k_d t = k\exp(-E_a/RT).t \qquad (1)$$

Assuming that the chemical reaction control is the slower step, the shrinking can be used through the following equation to describe the leaching kinetics:

$$1-(1-\alpha)^{\frac{1}{3}}=\frac{KM_B C_A}{\rho_B a r_0} t=k_r t=k\exp(-E_a/RT).t \qquad (2)$$

Similarly, when the controlling step is diffusion in the boundary layer, the shrinking core model is as follow:

$$[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]=\frac{2M_B D C_A}{\rho_B a r_0^2} t=k_d t=k\exp(-E_a/RT).t \qquad (3)$$

Where α= reacted fraction; k=kinetic constant; M_B=MW solid; C_A=acid conc. (%, w/w); ρ_B = solid density; a=stoichiometric coefficient of reagent in reaction; r_0=initial radius of particle; t=reaction time; D=diffusion coeff. in porous product layer, T= absolute temperature, R= universal constant of gas, E_a=activation energy and k_d and k_r=rate constants, which are calculated from Eqs. (2) and (3), respectively.

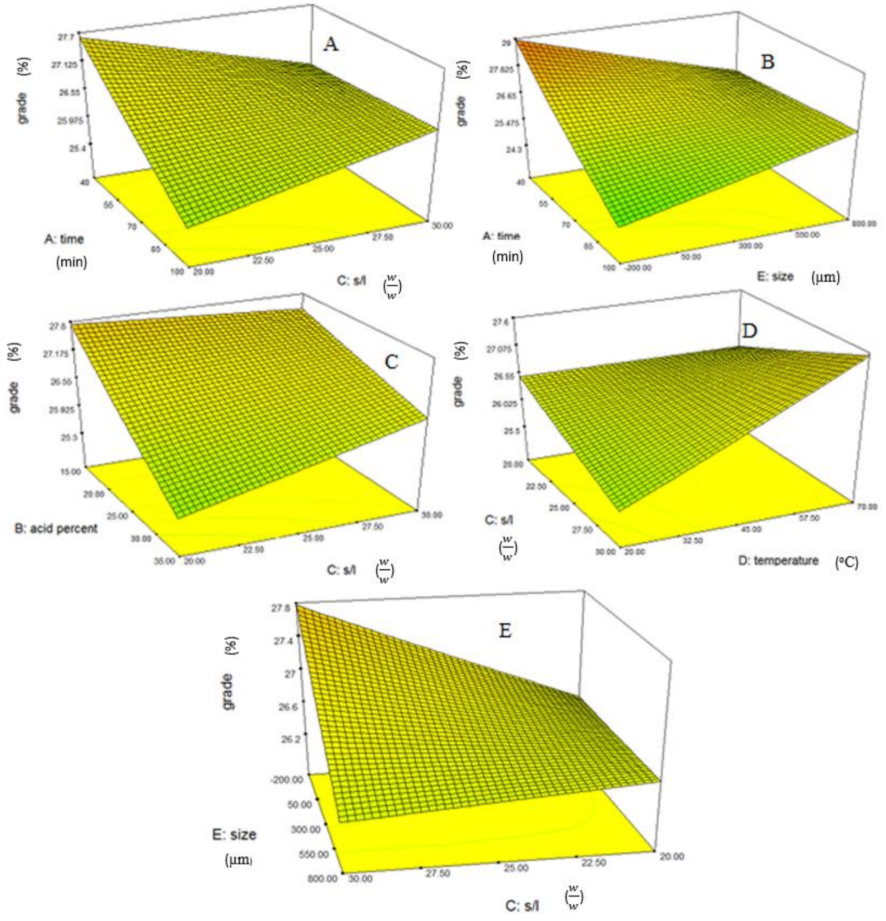

Fig. 3. Interaction effect on phosphorus grade, A: time and solid to liquid ratio, B: time and particle size, C: acid dosage and solid to liquid ratio, D: temperature and ratio of solid to liquid, D: particle size and solid to liquid ratio, E (Tests Conditions: Temperature (°C) =45, Time (minute) =60, Acid content (%) =25, Ratio of solid to liquid=0.2, Particle Size (µm) =300).

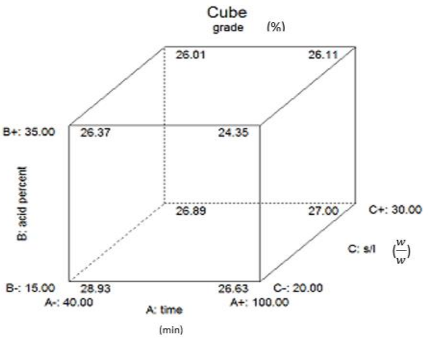

Fig. 4. Effect of interaction between time and acid dosage and the amount of solid to 1-liter liquid on the grade of phosphorus (Tests Conditions: Temperature (°C)=45, Time(minute)=60, Acid content (%)=25, Ratio of solid to liquid=0.2, Particle Size (µm)=300)

In the kinetics studies, activation energy is calculated using the Arrhenius equation, $k=k_0 e^{-Ea/RT}$, in which Lnk graph vs 1/T is a straight line with a slope of -Ea / R and provides an intercept Lnk_0. In the diffusion control process, activation energy would be less than 25 kJ/mol and in the chemical control, it would be more than 40 kJ/mol [20].

- Kinetics experiments

Some researchers studied carbonate leaching with an organic acid. Results from leaching Greek Epirus phosphate rocks in acetic acid suggested that the dissolution process was a two-step procedure. The first step involving the dissolution of available free carbonate minerals was found to be relatively fast, but in the second step, the dissolution was controlled by the presence of carbonate in the spaces between phospho-lipids [19].

In the optimal conditions, several experiments were performed at different temperatures and times to determine leaching kinetics of the Choram phosphate. After doing the tests at optimal conditions, a sample of the obtained solid (product) was sent to the chemical laboratory for chemical analysis to obtain α (extraction percentage) in each test. Experimental results and equations of the shrinking core model are given in Table 6.

Variation in the calcite content in the phosphate sample according to the reaction time at different temperatures is shown in Fig. 5.

As shown in Fig. 5, by increasing the time and temperature, carbonate solubility increased and the reaction was completed faster. k_r and k_d are the graph slopes obtained from the equations of the shrinking core model versus time as below:

$$1-(1-\alpha)^{\frac{1}{3}}=k_r t \xrightarrow{\qquad\qquad} k_r=\frac{1-(1-\alpha)^{\frac{1}{3}}}{t} \quad (4)$$

$$[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]=k_d t \xrightarrow{\qquad\qquad} k_d=\frac{[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]}{t} \quad (5)$$

The constant values of reaction rate, k_d and k_r, which are calculated from equations 4 and 5, for various temperatures are given in Table 7.

Table 6. Characteristics of experiments and equations of the shrinking core model.

Time (min)	α				$1-(1-\alpha)^{\frac{1}{3}}=k_r t$				$[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]=k_d t$			
	Temperature (°C)											
	20	35	50	65	20	35	50	65	20	35	50	65
1	0.67	0.70	0.71	0.70	0.31	0.33	0.34	0.33	0.08	0.08	0.09	0.09
3	0.71	0.73	0.75	0.75	0.34	0.35	0.37	0.37	0.09	0.09	0.10	0.10
5	0.76	0.76	0.83	0.87	0.38	0.38	0.45	0.49	0.11	0.10	0.14	0.16
10	0.79	0.80	0.93	0.94	0.41	0.42	0.59	0.61	0.12	0.12	0.21	0.22
15	0.81	0.86	0.94	1	0.43	0.48	0.61	1	0.13	0.15	0.22	0.33
20	0.84	0.91	0.98	1	0.46	0.55	0.73	1	0.15	0.19	0.27	0.33
40	0.92	0.99	1	1	0.57	0.78	1	1	0.20	0.29	0.33	0.33
60	0.98	1	1	1	0.73	1	1	1	0.27	0.33	0.33	0.33
80	1	1	1	1	1	1	1	1	0.33	0.33	0.33	0.33

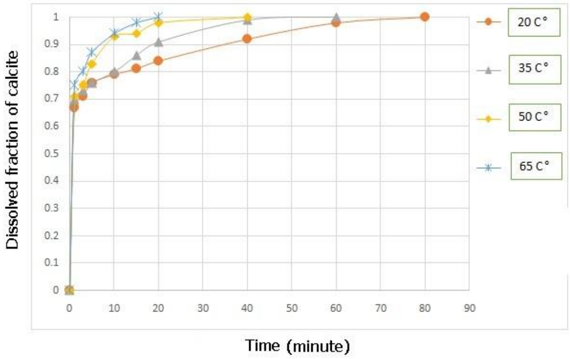

Fig. 5. The effect of time and temperature on carbonate mineral removal (Tests Conditions: Temperature (°C)=45, Time(minute)=60, Acid content (%)=25, Ratio of solid to liquid=0.2, Particle Size (μm)=300).

Table 7. Values for k_r and k_d and correlation coefficients at various temperatures.

Temperature (°C)	Constant rate of reaction (min^{-1})		Correlation coefficients (R^2)	
	k_r	k_d	k_r	k_d
20	0.0089	0.0034	0.8605	0.9326
35	0.0131	0.0049	0.8765	0.9114
50	0.0202	0.0073	0.8281	0.8223
65	0.0375	0.0142	0.7502	0.9165

Table 5 revealed that the dissolution of carbonate in the Choram phosphate ore is controlled by the diffusion reaction. The application of kinetics model of the diffusion reaction controlled by $[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}]$, as shown in Fig. 6.

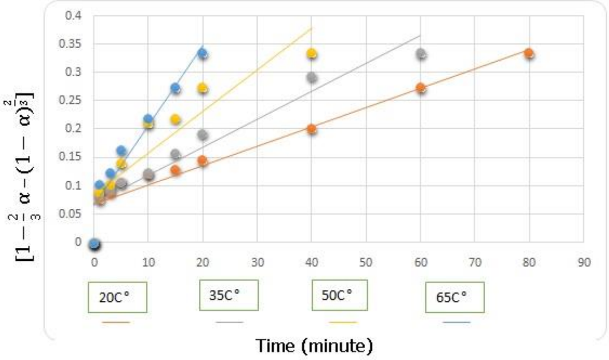

Fig .6. Application of kinetics model of diffusion reaction to the Choram phosphate ore (Tests Conditions: Temperature (oC) =45, Time (minute) =60, Acid content (%) =25, Ratio of solid to liquid=0.2, Particle Size (μm) =300)

Using the Arrhenius equation, $k=k_0\ e^{-Ea/RT}$, a graph of Lnk versus 1000/T resulted in a straight line with a slope of −Ea/RT and a width of the origin of Lnk_0 (Fig. 7).

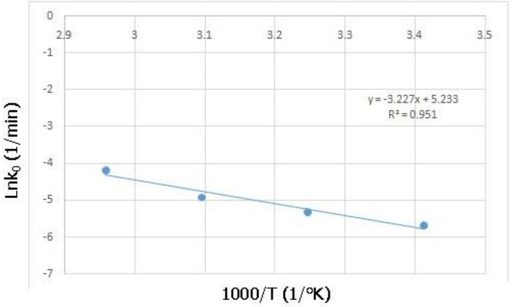

Fig. 7. Logarithmic graph of Arrhenius equation.

Using the Arrhenius equation and Fig. 7, the following values were calculated:

$$-\frac{Ea}{R}=-3.23 \xrightarrow{\qquad\qquad} E_a = 26.27\frac{kj}{mol} \quad (6)$$

$$\text{Ln}(K_o) = 5.23\frac{1}{min} \xrightarrow{\qquad\qquad} K_o= e5.23 = 186.8\times103\frac{1}{min} = 3.11\times103 \quad (7)$$

After calculating the activation energy (E_a), the leaching kinetics model for this study can be described by equation 7:

$$[1-\frac{2}{3}\alpha-(1-\alpha)^{\frac{2}{3}}] = 3.11\times10^3 e^{-26.27/RT}.t \quad (8)$$

4. Conclusions

The combination of acetic acid and lactic acid in equal proportions reduced the carbonates in the Choram phosphate ore, decreased the phosphorus corrosion, and resulted in a high grade (29%) and recovery (about 90%) of P_2O_5. This combination provides the optimum grade of phosphate for industries. The results indicated that the leaching of calcareous material and the P_2O_5 content increased as the reaction time, acid concentration, and liquid/solid ratio increased. Optimum selective leaching was achieved after 60 min reaction with 25% w/w acid, 30% w/v solids, and a particle size of 300 μm at 45 °C.

The dissolution kinetics of the calcareous material with the combination of acetic and lactic acids proved to fit the shrinking core model for a diffusion reaction process. The activation energy was determined to be 24.27 kJ/mol.

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