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Selective leaching kinetics of calcareous phosphate rock in lactic acid

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Abstract

Lactic acid was used to investigate the selective leaching kinetics of calcareous phosphate rock. The influence of acid concentration, liquid/solid ratio, particle size and temperature was studied in order to expound the dissolution kinetics of calcareous material in the rock. 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. A semi-empirical model was suggested to illustrate the selective leaching of calcareous material analyzing the experimental data. The selective leaching curves were evaluated in order to test the validity of kinetic models for liquid–solid systems. The kinetic data were analyzed by graphical and statistical methods and it was found that the leaching of calcareous material in the rock was controlled by chemical reaction, i.e., $1-(1-\alpha)^{1/3}=19.1C^{1.753}(L/S)^{1.627}D^{-0.737}\mathrm{e}^{-42954.62/RT}t$. The apparent activation energy of the leaching process was 42954.62 J mol^{-1} over the reaction temperature range from 298 to 338 K.

Keywords: Selective dissolution; Calcareous material; Lactic acid; Leaching kinetics

1. Introduction

Phosphate rock is the only major source for phosphatic fertilizers and phosphorous-based chemicals. Commercial phosphate rocks should not contain more than 8–9% carbonates in order to be economical. These rocks are not generally recommended for direct use in acidulation plants unless their tricalcium phosphate content is increased to 70% or more [1]. The calcium carbonate content of low-grade phosphate rocks may be reduced by flotation and calcination methods. Flotation techniques may give good results with ores containing well-crystallized carbonates. The flotation results were found to be less satisfactory when the ore contained soft and chalky carbonates [2]. When the carbonate crystals were present in intergrown form in the ore matrix, the phosphate could not be separated by flotation without having been finely crushed [3,4]. Siliceous phosphate rocks were generally upgraded by a two-stage flotation technique; however, the beneficiation of phosphate ores containing carbonates was complicated due to the similarities in chemical behavior of the minerals present [5,6]. Beneficiation by calcination is based on the dissociation of calcareous material by thermal energy. In calcination a considerable amount of thermal energy is required to decompose the calcareous material and achieve the required degree of beneficiation [7].

The dissolution study of various ores in inorganic acids has been investigated in detail [8–11]. However, the studies regarding the dissolution of ores using organic acids are quite limited [12–19]. To study the leaching kinetics of magnesite ores, Demir et al. [20] and Oral et al. [21] used citric and acetic acids, respectively. The leaching process was claimed as surface reaction control using both of the organic acids. Ashraf et al. [19] used succinic acid to study the selective leaching of calcareous material in low-grade phosphate rock and the results were found to be consistent with a chemically controlled reaction. Economou and Vaimakis [14] used acetic acid to dissolve calcareous material in low-grade phosphate rock from Epirus area (Greece) and the results suggested that the dissolution process could take place in two steps. The first step was found to be relatively fast attributing to the dissolution of freely available calcite and/or spaces on the particles. While, in the second one the dissolution results were based on the presence of calcite in the interspaces between phosphopeloids. Using dilute acetic acid solutions, Economou et al. [15] studied the mechanism of the selective dissolution of calcite in low-grade phosphate ore, and the analysis of the results

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Nomenclature

C	acid concentration (%, v/v)
D	average diameter of particle (mm)
E_a	activation energy (J mol^{-1})
L/S	liquid/solid ratio (cm^3 g^{-1})
N	number of experimental data
SS	stirring speed (min^{-1})
t	reaction time (min)
T	reaction temperature (K)

Greek letters

α_{cxp}	dissolved fraction of Ca^{2+}
α_{cal}	predicted fraction of Ca^{2+}

suggested the model equation of a double exponential decay fitting the experimental data. The kinetic analysis results indicated that the controlling step of calcite dissolution in the low-grade phosphate rock was a chemical change. On the basis of some postulates suggested, the experimental results also concluded that the decomposition of carbonic acid (H_2CO_3) into carbon dioxide (CO_2) and water (H_2O) was most likely to be the rate-controlling step of the overall mechanism. In another similar work [16] based on the different pH regions, it was claimed that the mass transfer had a significant role in the rate-determining step of the overall reaction. Depending on the pH values, two different reaction mechanisms were suggested along with two different model equations fitting the corresponding experimental data. However, it was again concluded that the decomposition of carbonic acid (H_2CO_3) into carbon dioxide (CO_2) and water (H_2O) could be the rate-controlling step of at least two pH regions, 3.96–4.95 and 4.95–5.50. Fredd and Fogler [17] studied the kinetics of calcite leaching in acetic acid solutions. The analysis of the data indicated that, below about pH 2.9, the leaching of calcite was influenced by the transport of both reactants and products. However, above about pH 3.7, the rate of dissolution was controlled significantly by the kinetics of the surface reaction.

Organic acids can be used for the selective leaching of carbonaceous material in low-grade phosphate rocks. The leaching capability of organic acids is relatively weak as compared to inorganic acids. However, the use of these weak acids shows an appreciable degree for selective leaching of calcareous material in low-grade phosphate rocks [19]. Apatite reserves are located in the North East of the country, e.g., Kakul, Lagarban, Oatkanala, Batkanala, East and South phosphorites [22,23]. The P_2O_5 content of the rock varies from deposit to deposit depending on the type and nature of the impurities. The rock of these areas contains an objectionable amount of calcareous material; therefore, it cannot be used directly for acidulation processes unless its P_2O_5 content is increased up to an industrially acceptable level. No guidelines are available in literature regarding the selective leaching kinetics of calcareous phosphate rock with lactic acid. The present work aimed to study the possibility for lactic acid to selectively dissolve calcareous material in the low-grade phosphate rock.

2. Lactic acid selectivity and chemistry of process

Strong organic acids cannot be used to selectively remove calcareous material in low-grade phosphate rocks. The strong acids may not react, for example, with pure calcium carbonate due to the large polarity of O–H bond present in these acids. However, in dilute solutions, water molecules tend to decrease the effect of polarity of the O–H bond resulting in selective leaching of calcareous material in the rock due to higher degree of ionization. The selected leaching agent should not attack the phosphate element. After the leaching process the liquid phase should be easily separable for regeneration and recycling. The dilute lactic acid is expected to be less destructive if some of the produced solution (wash of leached phosphate product) is added to the reaction solution, or recycled to the process. These characteristics allow the lactic acid molecules to leach the calcareous material rather than the tricalcium phosphate itself. Calcareous gangue material can be reduced by leaching low grade phosphate rocks by organic acids such as acetic acid, formic acid, succinic acid, lactic acid, etc., depending on the various parameters of the leaching process as well as nature and size of the sample particles. The succinic acid can be used to selectively dissolve the calcareous material in low-grade phosphate rock as it improves the P_2O_5 content up to industrially acceptable level. However, the use of this acid is limited by its solubility at lower temperatures, as it does not work below about 37 °C [19]. The formic and acetic acids give good results for selective leaching of calcareous material, but they may cause higher corrosion effects on the equipment along with greater tendency of attack on the phosphate element as well. Lactic acid, being relatively weak and having more organic character, can be expected to cause less corrosion effects on the equipment along with minimal risk of dissolution of the phosphate element itself as compared to formic and acetic acids. Therefore, the possibility of lactic acid to selectively dissolve the calcareous material in low-grade phosphate rock has been studied in the present work. The reaction between lactic acid and calcareous material can be written as follows:

$$\begin{aligned}&\mathrm{CaCO_3 + 2CH_3CH(OH)COOH}\\&\quad\rightarrow Ca[CH_3\mathrm{CH(OH)COO]_2 + CO_2 + H_2O}\end{aligned} \tag{1}$$

Reaction (1) may include the formation of carbonic acid and then decomposition into CO_2 and H_2O, and reaction for the other impurities depending on the nature and composition of the raw phosphate. This overall main reaction can represent, in fact, a lumping of a larger number of steps. However, the simplest mechanism necessary for the rational understanding of the selective leaching process can be simplified using the following general equations:

$$\mathrm{MCO_3(s) + 2HY(aq) \rightarrow MY_2(s/aq) + CO_2 + H_2O} \tag{2}$$

$$\mathrm{M_3(PO_4)_2 + 6HY \rightarrow 3MY_2(s/aq) + 2H_3PO_4} \tag{3}$$

where $M = Ca^{2+}$ and/or Mg^{2+}, $Y = CH_3CH(OH)COO^-$ (lactate).

The selectivity means that the leaching agent should not attack the phosphate element and thus the third reaction does not

Table 1
Analysis of the rock samples

Sample (mesh)	Size (mm)	P_2O_5%	AIR[a]%	LOI[b]%	CO_2%
−28 + 35	−0.589 + 0.417	15.89	2.13	30.74	28.29
−35 + 48	−0.417 + 0.295	16.23	2.29	30.12	27.75
−48 + 65	−0.295 + 0.208	17.32	2.63	29.11	26.87
−65 + 100	−0.208 + 0.147	19.67	2.83	26.83	24.67
−100 + 150	−0.147 + 0.104	22.39	2.97	22.13	20.13

[a] Acid insoluble residue (AIR) is defined as the amount of the residue that remained unreacted in the sample, after being treated with a standard HNO_3/HCl solution and ignited at 950 °C.

[b] Loss on ignition (LOI) is defined as the decrease in weight of the sample after being ignited from 550 to 950 °C. It refers to the amount of CO_2 in the sample, either before or after leaching.

take place, while the second one proceeds to completion or equilibrium depending on solubility products ($K_{sp} = 8.35$, 7.46 for $CaCO_3$ and $MgCO_3$, respectively) and acidity constants for lactic acid ($pK_a = 3.86$ at 25 °C) and CO_2 ($pK_1 = 6.35$, $pK_2 = 10.33$ for H_2CO_3). The values of the constants depend on the reaction temperature and the overall rate of selective leaching of calcareous material in the low-grade phosphate rock may be controlled by the kinetics of the dissolution process. The carbonic acid produced during the process is relatively weak and unstable; therefore, the CO_2 will be evolved after decomposition of the acid produced. Under normal conditions, the equilibrium for reaction (1) lies far to the right and it may be considered as an irreversible reaction due to the removal of CO_2 produced during the process by stirring the reaction mixture.

3. Methods and material

3.1. Sample preparation and analysis

After crushing and grinding the sample, U.S. Tyler standard sieves were used to sieve and collect different size fractions of low-grade calcareous phosphate rock. Using a mortar grinder, the +28 mesh (+0.589 mm) fraction was further crushed to get the required size fractions. Using an electric oven, these samples were dried at about 105 °C, cooled to room temperature and stored in closed desiccators for analysis. The analysis was carried out for each collected fraction to determine P_2O_5 content, acid insoluble residue (AIR), loss on ignition (LOI) and CO_2 content as shown in Table 1. Conventional methods [24] and instrumental analysis techniques were used for analysis. The calcination method was used to determine the calcareous material in the sample at 950 °C. Atomic Absorption Spectrophotometer (AAS) A-1800 Hitachi was used to measure the selective leaching rate of calcareous material in the rock. In the analysis, the dissolution fraction of calcareous material was calculated by Eq. (4):

$$\alpha_{\exp} = \frac{\text{Amount of calcium in the solution}}{\text{Total amount of calcium in original sample}} \tag{4}$$

and the recovery of P_2O_5 content was calculated by Eq. (5):

$$P_2O_5 \text{ recovery} = \left[\frac{\text{wt. of leached sample} \times P_2O_5\text{\% in leached sample}}{\text{wt. of original sample} \times P_2O_5\text{\% in original sample}}\right] \times 100 \tag{5}$$

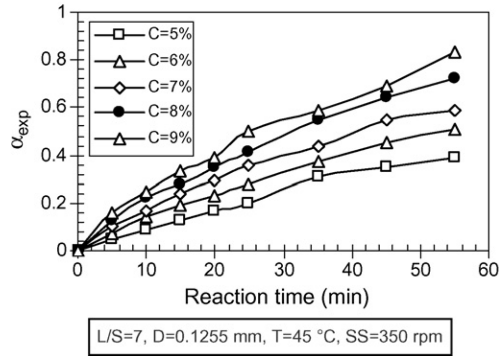

Fig. 1. Effect of reaction time on the conversion at different acid concentrations.

3.2. Experimental procedure

The leaching process was carried out in a 500-ml open glass reactor with a spherical bottom at a rate of 350 rpm. A known amount of the acid with specific liquid/solid ratio was slowly added into the reactor vessel containing the fixed amount of the sample −100 + 150 mesh (−0.147 + 0.104 mm) fraction for each run. The reaction mixture was heated by a constant temperature bath and equipped with a mechanical stirrer having a digital controller unit. A number of experiments were carried out with varying acid concentration, liquid/solid ratio and calcareous rock particle size at different reaction temperatures with a constant stirring rate of 350 rpm. The reaction was stopped placing the reactor in an ice bath at the end of each reaction. The solid phase was separated from the solution by filtration and dried at 105 °C before weighing and analysis. The leach solution was analyzed by AAS to determine the Ca^{2+} content for the leaching kinetics. The CO_2 content of the solid phase was also determined by calcination method to find the degree of beneficiation after the dissolution of calcareous material in the rock.

4. Results and discussion

4.1. Effect of parameters

A number of experiments were carried out to see the effect of leaching reaction time on the dissolution of calcareous material at varying acid concentration, liquid/solid ratio, particle size and reaction temperature as shown in Figs. 1–4, respectively. Depending on the leaching conditions, the results indicated that the leaching rate of calcareous material increased with increasing the acid concentration, liquid/solid ratio and temperature and decreasing particle size. In the selective leaching of calcareous material the acid concentration could be increased up to a certain limit as shown in Fig. 1. After a certain value of the acid concentration the leaching rate of calcareous material was not much higher, a situation that could be attributed to the increase in the polarity of the acid O–H bond decreasing the number of hydrogen ions due to the decrease in water amount more and more in the medium.

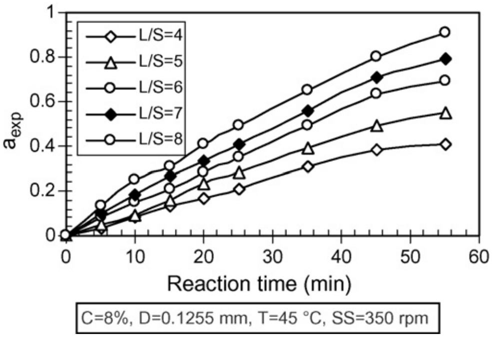

Fig. 2. Effect of reaction time on the conversion at various liquid/solid ratios.

Ozmetin et al. [25] used acetic acid for the leaching of colemanite ore and the results indicated that the rate of formation of a sparingly soluble solid layer around the particle increased resulting in a decrease in the dissolution process when the acid concentration was increased after a certain value in the medium. However, in the present case of selective leaching of calcareous material in the rock the acid concentration should not be increased more than the required level to avoid the acid attack on phosphate element during the leaching process.

Under the specific reaction conditions, the degree of selective leaching increased with an increase in liquid/solid ratio as shown in Fig. 2. It was found in a separate experiment that with lower acid concentration (<3%) the value of liquid/solid ratio considerably increased to achieve the required degree of dissolution. However, higher liquid/solid ratio is resulted in a relatively lengthy process including handling, filtration and regeneration of the consumed acid. It was also found in a separate experiment that higher acid concentration (>9–10%) did not show a significant increase in the dissolution of calcareous material in the rock due to an increased effect of polarity of the O–H bond present in the acid.

The leaching rate of calcareous material increased with a decrease in particle size as shown in Fig. 3. The efficiency of the leaching process is increased with a decrease in the particle size, a situation that can be attributed to the increasing surface area per unit weight of sample as well as the liberation of more calcareous material from the apatite matrix due to an increase in the degree of size reduction more and more. The efficiency of the leaching process can be increased by further size reduction and fine grinding of the phosphate feed but the problems related to handling, filtration and marketing of fine phosphates, may not allow grinding to exceed a certain limit. On the other hand, higher amount of energy for grinding and size reduction would cause an extra cost to the process.

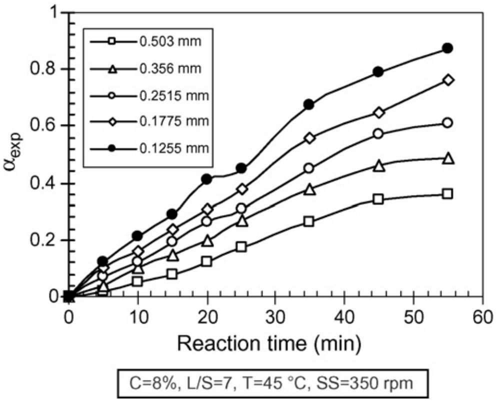

Fig. 3. Effect of reaction time on the conversion at varying particle size.

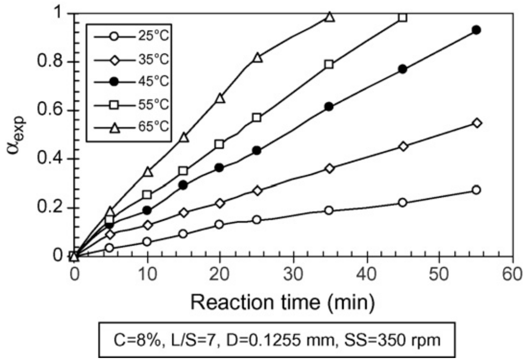

Fig. 4. Effect of reaction time on the conversion at various temperatures.

At various reaction temperatures, a number of experiments were carried out to see the effect of reaction time on the dissolution of calcareous material at specific reaction conditions as shown in Fig. 4. The typical rate curves indicate that, by increasing the temperature, the leaching rate of calcareous material in low-grade phosphate rock increases with a decrease in reaction time required to reach the equilibrium. After about 45–50 °C the leaching rate of calcareous material is not appreciable, a situation which can be attributed to the fact that higher temperatures may tend to decrease the solubility of lactate along with the contamination of CO_2 gas with water and lactic acid vapors.

The effect of reaction time on P_2O_5 and CO_2 contents was studied depending on acid concentration, liquid/solid ratio, reaction temperature and particle size used in the leaching process as shown in Fig. 5. The results indicate that lactic acid can be used to reduce calcium carbonate in low-grade calcareous phosphate rock as it improves the degree of beneficiation and makes it viable as a feed to an acidulation plant. For example, at 45 min the P_2O_5 content raised up to about 35% along with corresponding reduction in CO_2 content up to 70% of the sample at a phosphate weight recovery of more than 75%. The economics of the leaching process also depends on the price of the acid and

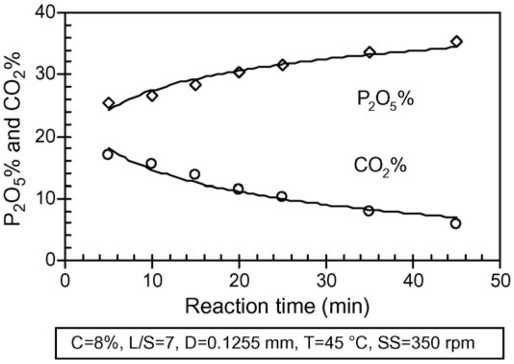

Fig. 5. Effect of reaction time on P_2O_5 and CO_2 contents.

the cost of its recovery from the leach solution. Depending on the type and nature of raw phosphate rock, the suggested process is relatively economical than the import of high-grade rock from other countries. Lactic acid may be recovered from the leach solution by various methods. However, the use of sulfuric acid is potentially the most attractive method for recovering the organic acid from the leach solution [19].

4.2. Kinetic analysis

Fluid–solid heterogeneous reactions are of great industrial importance and have a number of applications in different chemical and hydrometallurgical processes. A successful reactor design phenomena for these processes is based on kinetic data. In order to establish the kinetic parameters and rate-controlling step for the dissolution of calcareous material in low-grade phosphate rock using lactic acid, the experimental data can be analyzed according to the heterogeneous reaction models [26]. According to the model, the reaction between a fluid and a solid may be written as:

$$\mathrm{F_{(fluid)}} + \mathrm{bS_{(solid)}} \rightarrow \text{Products} \tag{6}$$

The rate of reaction between calcareous material particle and the leaching agent 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 calcareous material be α and at any time t the integrated equations for fluid–solid heterogeneous reactions are:

for film diffusion control,

$$t = k^*[1-(1-\alpha)] \tag{7}$$

for chemical reaction control,

$$t = k^*\left\lfloor 1-(1-\alpha)^{1/3}\right\rfloor \tag{8}$$

and for ash layer diffusion control,

$$t = k^*\left\lfloor 1-3(1-\alpha)^{2/3}+2(1-\alpha)\right\rfloor \tag{9}$$

The value of k^* depends on various reaction parameters according to the kinetic models. For example, according to the chemical reaction controlled model, Eq. (8) k^* is:

$$k^* = \frac{\rho_\mathrm{B} R_\mathrm{o}}{b K_\mathrm{s} C_\mathrm{A}} \tag{10}$$

where k^* is the time for complete dissolution (min), ρ_B the molar density of the solid reactant (mol m^{-3}), R_o the radius of the solid particle (m), b the stoichiometric coefficient of the solid, k_s the surface reaction rate constant (m min^{-1}) and C_A is the leaching agent concentration (mol m^{-3}). To determine the kinetic parameters and rate-controlling step for selective dissolution of calcareous material in low-grade phosphate rock, 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 chemically controlled reaction and the integral rate expression was determined to obey the following rate equation:

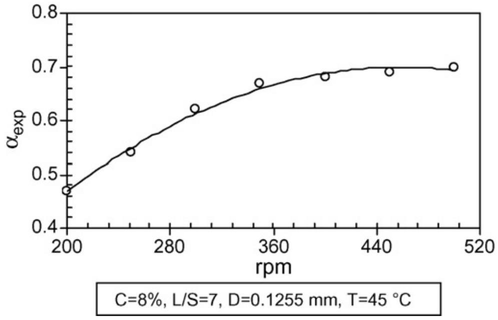

Fig. 6. Effect of rpm on the conversion at specific reaction conditions.

$$1-(1-\alpha)^{1/3} = kt \tag{11}$$

Using the conversion values for various reaction temperatures, the apparent rate constants, k, can be evaluated by plotting $1-(1-\alpha)^{1/3}$ versus t. 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:

$$1-(1-\alpha)^{1/3} = A_\mathrm{o}\mathrm{e}^{-E_\mathrm{a}/RT}t \tag{12}$$

The above kinetic model may be used to describe the selective leaching of calcareous material in the rock. However, its applicability is limited by the specific values used for different reaction parameters (acid concentration, liquid/solid ratio, particle size) at various temperatures. To test the applicability of this model, the reaction parameters may be included as they also affect the rate of leaching of calcareous material in low-grade phosphate rock. Therefore, to include the effect of the reaction parameters on the kinetic model, a semi empirical model was developed by statistical multiple regression. To establish this model representing the selective leaching process, it was accepted that the reaction rate constant k could be written as follows:

$$k = k_\mathrm{o}C^a(L/S)^b D^c \mathrm{e}^{-E_\mathrm{a}/RT} \tag{13}$$

Combining Eqs. (11) and (13) it follows that:

$$1-(1-\alpha)^{1/3} = k_\mathrm{o}C^a(L/S)^b D^c \mathrm{e}^{-E_\mathrm{a}/RT}t \tag{14}$$

where α is the conversion fraction, C the acid concentration, L/S the liquid/solid ratio, D the particle size, R, k_o, a, b, c constants, T the reaction temperature, E_a the activation energy, t the reaction time for the leaching process. The stirring speed was omitted from multiple regression analysis as the results in Fig. 6 showed that the dissolution of calcareous material in the sample increased slowly with an increase up to 350 rpm. Further increase in the stirring rate did not show a significant effect on the leaching fraction, which indicates that the diffusion through the fluid film does not act as a rate-controlling step. For statistical calculations by simultaneous multiple regression a computer program gave the following values for the constants:

$$k_o = 19.1, \quad a = 1.753, \quad b = 1.627,$$

$$c = -0.737, \quad E_a = 42954.62\,\mathrm{J\,mol^{-1}}$$

The value of activation energy for the selective leaching of calcareous material indicates that the process is a chemically controlled reaction, which is consistent with the values obtained in the fluid–solid reaction systems [19–21]. The experimental results indicate a change in the dissolution behaviour of calcareous material after about 318 K, a situation that may be attributed to the mixed chemically-diffusion controlled nature of the reaction. However, at lower temperatures the selective leaching of calcite appears to be chemically controlled process, which agrees with the similar findings reported in the literature [27]. Depending on the type and nature of the solid materials as well as strength of the leaching agents, a number of calcite dissolution mechanism studies are reported in literature [15–17,28–34]. Depending on the parameter conditions and nature of the material, different reaction mechanisms have been suggested. However, at moderate pH values, most of the studies have resulted into the conclusion that the overall rate of dissolution is controlled by a chemical change. For the dissolution of calcareous material in the rock with acetic acid, Economou et al. [16] found that in the pH range from 2.37 to ∼4 a chemical change was rate-controlling for the overall process. Considering the strength of the acid used in the selective leaching, the results of the present study were also supported by the similar work [17], which claimed that the calcite dissolution above about pH 3.7 was significantly controlled by the kinetics of the surface reaction. On the other hand, kinetic analysis for the rate production of calcium material in the leach solution reveals that the diffusion-controlled mechanism is not the predominant mechanism in the leaching process. The mechanism of calcite dissolution for the rate-determining slowest step needs further investigations; however, the results indicate that the controlling step of the overall process of the heterogeneous reaction is a chemical change. Thus, using the values obtained by simultaneous multiple regression analysis the Eq. (14) may be given as:

$$1-(1-\alpha)^{1/3} = 19.1C^{1.753}(L/S)^{1.627}D^{-0.737}\mathrm{e}^{-42954.62/RT}t \tag{15}$$

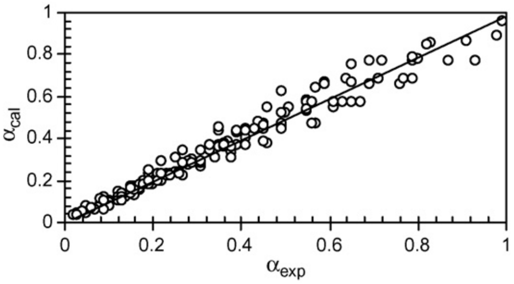

Fig. 7. Agreement between experimental and calculated conversion values.

To test the agreement between the experimental conversion and the values calculated from the semi empirical model, the graph of α_{exp} versus α_{cal} was plotted as shown in Fig. 7. It is observed that the agreement between the experimental and calculated values is very good with a correlation coefficient of 0.983 and standard deviation of ±0.04156. The data in the scatter diagram show a positive tendency to cluster around the regression line, which can be attributed to the existence of a good relationship between the variables. The value of the standard deviation of regression or standard error of estimate of α_{cal} on α_{exp} indicates that the degree of scatter of the observed values about the regression line is small. Using the statistical analysis with 157 number of experimental data, a relative mean square of errors of 0.1296 was calculated by Eq. (16):

$$\mathrm{ER} = \left[\frac{1}{N}\sum_{i=1}^{N}\frac{(\alpha_{cal}-\alpha_{exp})^2}{(\alpha_{cal})^2}\right]^{1/2} \tag{16}$$

The value of relative mean square of errors indicates that, in probabilistic models, such a value of the random errors is not significant. It is necessary to check the reproducibility and applicability of the semi-empirical model by using the different adjustable parameter conditions for the leaching of calcareous material in low-grade phosphate rock. Therefore, using the different parameter values in the semi-empirical model, the reaction periods for 70% dissolution of calcareous material were calculated as shown in Table 2. The comparison between case 1 and 2 as shown in Table 2 indicated that when the acid concentration decreased from 8 to 7%, the reaction period increased from 46.94 to 59.32 min. Although the reaction period increased about 1.26-fold, about 26.4% more amount of sample could be handled. For the cases 1 and 3 in Table 2, when the acid concen-

Table 2
The values of chosen parameters and the reaction periods calculated from Eq. (15) for these parameters

Case	C (%, v/v)	L/S ($\mathrm{cm^3\,g^{-1}}$)	D (mm)	T (K)	Dissolution (%)	t (min)
1	8	7	0.1255	318	70	46.94
2	7	7	0.1255	318	70	59.32
3	9	7	0.1255	318	70	38.18
4	8	6	0.1255	318	70	60.32
5	8	8	0.1255	318	70	37.77
6	7	8	0.1255	318	70	47.74
7	8	7	0.1775	318	70	60.61
8	8	7	0.1255	328	70	28.61
9	8	7	0.1255	308	70	79.55

tration decreased from 9 to 8%, the reaction period increased only about 8.76 min, indicating relatively poor efficiency of the leaching process as compared to the above case.

For the cases 1 and 4 in Table 2, when the liquid–solid ratio increased from 6:1 to 7:1, the decrease in the reaction period was about 13.38 min. While, for the cases 1 and 5 in Table 2, when the liquid–solid ratio increased from 7:1 to 8:1, the reaction period decreased only about 9.17 min, which indicated that the liquid–solid ratio of 7:1 could be more beneficial. On the other hand, for the cases 1 and 6 in Table 2, the interchange of concentration and liquid–solid ratio does not show any significant effect on the reaction period, a situation that indicates that these two parameters equally compete for the selective dissolution of calcareous material in the rock. For the cases 1 and 7 in Table 2, when the particle size decreased from 0.1775 to 0.1255 mm, the reaction period also decreased from 60.61 to 46.94 min, a situation which could be attributed to the fact that the size reduction lead to easier liberation of the calcareous material from the apatite matrix.

For the cases 1 and 8 in Table 2, when the reaction temperature increased from 318 to 328 K, the reaction period decreased from 46.94 to 28.61 min with an increase in the amount of handled material about 39%. On the other hand, for the cases 1 and 9 in Table 2, when the reaction temperature increased from 308 to 318 K, the reaction period decreased from 79.55 to 46.94 min with an increase in the amount of handled material about 41%. Comparing these two cases, the results indicated that to study with 318 K reaction temperature was more advantageous than the other temperatures. As a result, 8% (v/v) acid concentration, 7:1 liquid–solid ratio $cm^3\,g^{-1}$, 0.1255 mm particle size, $350\,min^{-1}$ stirring speed and 318 K reaction temperature can be recommended as the parameter values giving the optimum selective leaching rate (case 1).

To increase the rate of leaching of calcareous material in the rock with lactic acid, the results for the semi empirical model indicate that the reaction period may be reduced by increasing the acid concentration and/or liquid–solid ratio as long as the dissolution of phosphate element is not significant. Further reduction in particle size can be expected to improve the efficiency of the leaching process depending on the type and nature of low-grade calcareous phosphate rock. According to the required degree of selective leaching, the study can be extended to a pilot scale work to beneficiate low-grade calcareous phosphate rock. Although the design parameters may need some further studies at an industrial scale, however, the method may be of value to others confronted with the need to use typical indigenous rock phosphates of various countries in the world.

5. Conclusions

Lactic acid can be used to selectively dissolve the calcareous material in low-grade phosphate rock as it improves the P_2O_5 content of the rock and makes it viable as a feed to an acidulation plant. The effective parameters on the dissolution rate are reaction temperature, particle size, acid concentration and liquid–solid ratio with a constant stirring speed of 350 rpm. Selective leaching is a complicated process; therefore, for dissolution of calcareous material according to the required degree of beneficiation, the acid concentration and liquid–solid ratio should be optimized depending on the stoichiometric requirements along with the process conditions.

Analysis of the kinetic data by different kinetic models indicates that the selective leaching of calcareous material in low-grade phosphate rock with lactic acid is a chemically controlled process. The value of activation energy is found to be $42954.62\,J\,mol^{-1}$, which agrees with a chemically controlled reaction. A semi-empirical kinetic expression including the parameters used in the selective leaching process was developed, and this expression can estimate the calcareous fraction reacted with a relative mean square of errors of 0.1296. The analysis of the results given in Table 2 reveals that applicability of the suggested model is good and it can work within a certain range for the choice of adjustable parameter values depending on the degree of selective leaching. According to the analysis results it can be recommended that the parameter values for the optimum selective leaching rate are $C = 8\%$ (v/v), $L/S = 7\,cm^3\,g^{-1}$, $T = 318\,K$, $SS = 350\,min^{-1}$ and $D = 0.1255\,mm$.

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