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Beneficiation of Mardin-Mazıdaği (Turkey) calcareous phosphate rock using dilute acetic acid solutions

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Abstract

The dissolution process of the carbonate-rich phosphate rocks from the Kasrik area (Mardin-Mazıdağı, Turkey) using dilute acetic acid has been investigated. The work involve to study the effect of the important variables such as reaction time, stirring speed, acetic acid concentration, temperature, particle size fraction, and stoichiometry. It has been found that the P_2O_5 content of the phosphate rock increases from 12.7 to about 29 wt.% following the dissolution. A mathematical model in the following form was applied to express the dissolution of calcareous material in the rock; $-\log(1-X)=kt^m$. The dissolution of calcareous material in the phosphate rock has been observed to take place in two steps, the first being fast and the second being slow.

Keywords: Phosphate rock; Acetic acid; Dissolution kinetics

1. Introduction

Phosphates are an essential element in the fertilizers used to supply food for mankind and animals. As world population continues to increase, so does the demand for phosphate. High-grade deposits of phosphate rock are being depleted day by day in the world, hence future sources will have to be derived from low-grade rocks containing various impurities. Low-grade phosphate rocks are not suitable for direct use in acidulation plants unless their tricalcium phosphate content is increased up to marketable and industrially acceptable levels.

The composition of these rocks varies from one deposit to another. Therefore, phosphate rocks from different sources are expected to behave differently in acidulation processes which are the heart of all phosphate fertilizers industries.

Most of the known world phosphate rock reserves are found in sedimentary marine deposits of the Upper Cretaceous and Eocene ages of the Mediterranean phosphogenic province in Morocco, Algeria, Tunisia, Egypt, Israel, Jordan, Syria, Saudi Arabia, Turkey and Iraq. Phosphate ores are divided to three groups according to their P_2O_5 content: low-grade ores (12–16% P_2O_5), intermediate-grade ores (17–25% P_2O_5), and high-grade ores (26–35% P_2O_5) Deposits that could be mined and processed economically to give about 28–38% P_2O_5 are considered commercial phosphate deposits [1].

Beneficiation can be achieved by various processes, depending upon the liberation size of phosphate from its associated gangue minerals. Different simple or complex combinations of the following processes may be used: crushing, grinding, screening, scrubbing, heavy media separation, washing, roasting, calcination and flotation [2].

Beneficiation by calcination is one of the well known processes. It is based on the dissociation of the calcium carbonate by thermal energy. Depending on the efficiency of the process, calcination may lead to almost complete disposal of the carbonates present in the phosphate rock [3–5]. Calcination is best carried out in fluidised beds from both technical and economic point of view. This is due to the numerous advantages of this technique especially the ease of material handling and the excellent thermal properties [6–9]. It has been observed that the calcination decreases the solubility and reactivity of the calcined phosphate rocks in the acidulent during the manufacture of phosphoric acid by the wet process [10].

The presence of free carbonates in the phosphate rocks usually requires additional acidulent (sulphuric acid) during the manufacture of phosphoric acid and super phosphates by the wet process. In addition, the carbon dioxide produced during acidulation causes more foaming and results in production of

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smaller size gypsum crystals, that may blind the downstream phosphgypsum filters, and a low quality phosphoric acid is produced [11]. The carbonate content in commercial phosphates should not exceed 8%.

The calcareous and/or dolomitic gangue material from a low-grade phosphate rock can be removed or reduced by the leaching process using organic acids such as acetic acid, citric acid, formic acid, etc., depending on the process parameters as well as nature and size of the raw material. For the selective leaching of the carbonate mineral both the nature of the acid and its concentration are significant factors so that the apatite present in the rock should not be lost due to chemical decomposition by reaction with the chosen acid. Many studies have been carried out for the beneficiation of calcareous phosphate using dilute acetic acid. Dilute acetic acid has been found to be one of the most promising leaching agents for this purpose [12–16].

The aim of present work was to study the enrichment of the low-grade natural phosphate ores from Mardin-Mazidagi Kasrik area (Turkey) by selective dissolution of calcite using dilute acetic acid.

2. Experimental

The low-grade phosphate rock sample was crushed with a jaw crusher and then sieved using ASTM standard sieves to collect various size fractions for analysis. All the sieved samples were dried in an electric oven at about 105 °C, cooled to room temperature and stored in closed desiccators. These sample fractions were analyzed for the main conditions, namely, P_2O_5 content, acid-insoluble residue (AIR), loss on ignition (LOI) and CO_2 content as shown in Table 1.

A sketch of the apparatus used for the dissolution process of phosphate rock is shown in Fig. 1. The dissolution process was carried out in a 500 ml jacketed cylinder glass reactor heated by a thermostat for keeping reactor contents at a constant temperature, equipped with a digital controlled mechanical stirrer, thermometer and a condenser to prevent losses by evaporation. For each run 10 g of phosphate sample was transferred with the proper amount of acetic acid solution into the reactor. At the end of each reaction, the reaction vessel was immediately placed in an ice bath to stop the reaction before the separation of the leach slurry by filtration. The remaining solids were dried and were weighed. In the filtrate the 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). Also P_2O_5 in the remaining solid was measured by the same colorimetric method in order to carry out an overall material balance on P_2O_5 to ensure no losses. The P_2O_5 material balance in all cases closed up correctly within 98.5–99.5%.

Table 1
Analysis of the phosphate rock samples

Sample (mesh)	Size (mm)	P_2O_5 (%)	AIR[a] (%)	LOI[b] (%)	CO_2 (%)
−25 + 35	500–710	10.01	2.26	34.12	32.55
−35 + 45	355–500	12.03	2.02	32.97	31.22
−45 + 60	250–355	12.70	2.15	32.15	30.51
−60 + 80	180–250	13.12	2.05	31.14	29.67

[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 when it is ignited from 105 to 950 °C. It refers to the amount of carbonates, organic matter and combined water that originally exists in the sample.

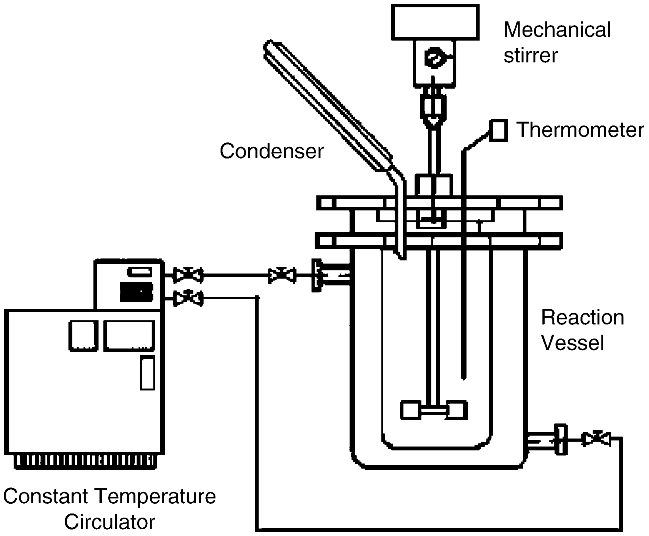

Fig. 1. Schematic view of experimental setup.

In the course of the analysis, it has been noticed that the combined water plus organic matter amounts to not more than 2% in all samples. The acid-insoluble residue (AIR) is approximately 2–2.5%.

The acid stoichiometry was the ration of the used acetic acid amount for each experiment and the required amount for the reaction:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca(CH_3COO)_2 + CO_2 + H_2O \qquad (1)$$

The acid stoichiometry was determined by using the following equation:

$$\text{acid stoichiometry} = \text{mol of } CH_3COOH/2\text{ mol of } CO_2 \qquad (2)$$

where mol of CH_3COOH is the amount of acetic acid of the used solution and mol of CO_2 is the amount carbon dioxide in the reacted sample of the phosphorite.

3. Results and discussion

The following is a discussion of the results obtained when phosphate rock was subjected to dissolution with acetic acid solutions. Here, the effects of reaction time, stirring speed, acetic acid concentration, stoichiometry and particle size on the dissolution process have been investigated.

3.1. Effect of reaction time

The effect of reaction time on the dissolution rate, using 200 rpm stirring rate, 1 M acetic acid concentration, 22 °C

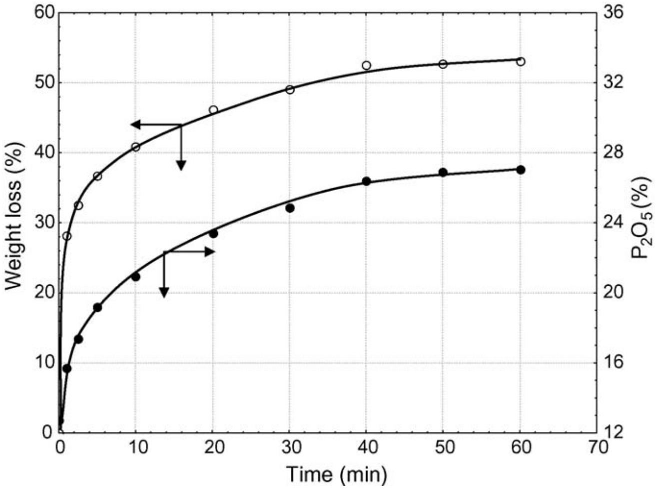

Fig. 2. Effect of reaction time on the dissolution process (stirring rate, 200 rpm; acid concentration, 1 M; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

(which was the temperature of the laboratory at this time), 250–355 μm particle size fractions, and 1 stoichiometry, is shown in Fig. 2. An increase in reaction time above 40 min has a minor effect on the amount of weight loss or on percent increase in P_2O_5 content.

3.2. Effect of stirring speed

The effect of stirring speed on the dissolution process, using 40 min reaction time of dissolution, 1 M acetic acid concentration, 22 °C, 250–355 μm particle size fractions, and 1 stoichiometry, is shown in Fig. 3. The mechanical stirring of the reactants has an important effect on the dissolution process. As can be seen from the figure, the weight loss and the P_2O_5 content of the remaining solids increased with an increase in the stirring speed to 200 rpm. This increase can be attributed to removal by stirring of the produced carbon dioxide gas film from the solid surface, which prevents the reaction of acid with calcite. Upon further increase of the stirring speed, no further increase of weight loss and P_2O_5 content was observed.

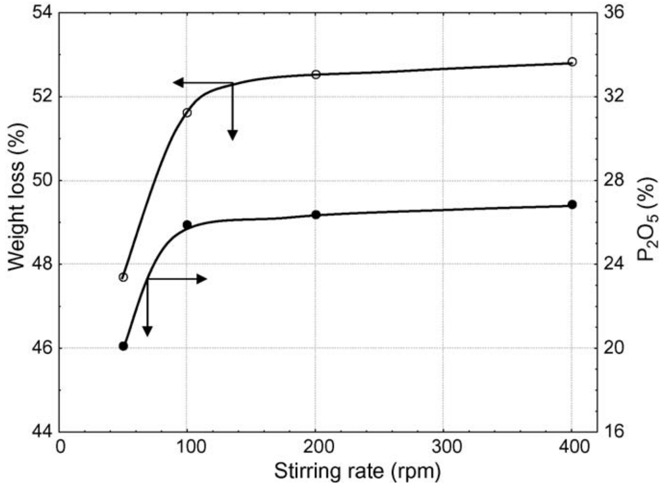

Fig. 3. Effect of stirring speed on the dissolution process (reaction time, 40 min; acid concentration, 1 M; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

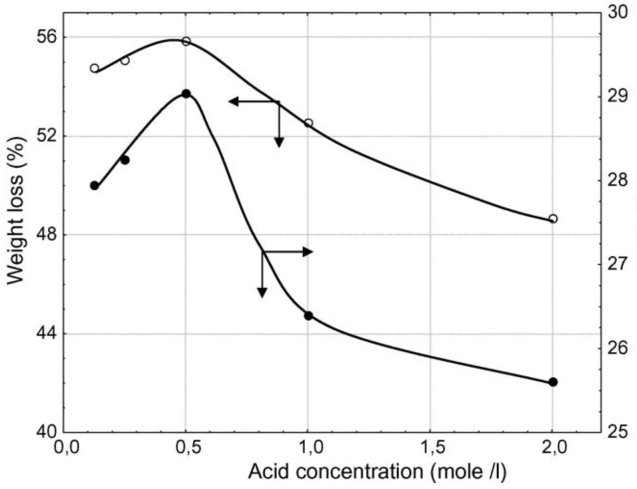

Fig. 4. Effect of acetic acid concentration on the dissolution process (reaction time, 40 min; stirring rate, 200 rpm; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

3.3. Effect of acid concentration

The effect of acid concentration in the acetic acid solution on the dissolution process at a dissolution time of 40 min, a stirring speed of 200 rpm, a temperature of 22 °C, a particle size fraction of 250–355 μm, and a stoichiometry of 1 was investigated. As seen from the experimental results given Fig. 4, the weight loss and P_2O_5 content were increased by increasing acid concentration from 0.125 to 0.5 mol/l and then they decreased slightly with an increase of the acid concentration. This fact probably indicates that, at the range of 40 min residence time, the controlling step of the dissolution process was the diffusion of calcium hydrate ion into the bulk solution. More concentrated solutions offer more resistance to diffusion. Similar behavior has been observed by Economou and Vaimakis [16] for beneficiation of Greek calcareous phosphate ore by using acetic acid.

3.4. Effect of temperature

The effect of reaction temperature on the dissolution process was investigated for the temperatures of 15, 22, 30, 40 and 50 °C at a reaction time of 40 min, a stirring speed of 200 rpm, an acid concentration of 0.5 M, a particle size fraction of 250–355 μm, and a stoichiometry of 1. As can be seen in Fig. 5, the weight loss and P_2O_5 content were increased by increasing the reaction temperature from 15 to 22 °C and then they remain almost constant at a level of 55–56% weight loss and 28.5–29% P_2O_5.

3.5. Effect of particle size

Fig. 6 shows the effect of particle size on the dissolution process at a reaction time of 40 min, a stirring speed a stirring

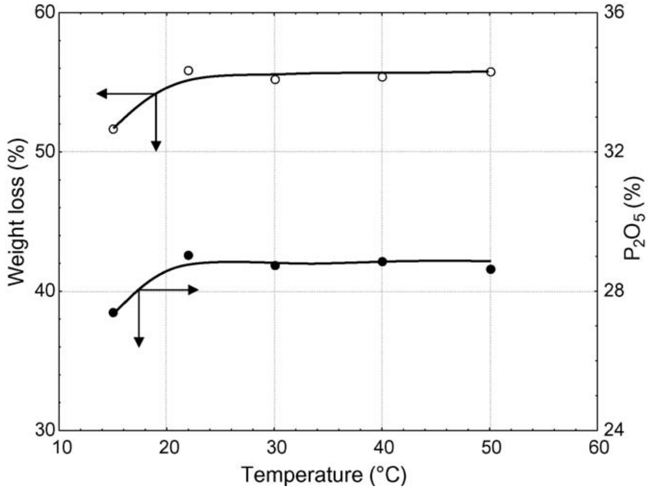

Fig. 5. Effect of reaction temperature on the dissolution process (reaction time, 40 min; stirring rate, 200 rpm; acid concentration, 1 M; particle size, 250–355 μm; stoichiometry, 1).

speed of 200 rpm, an acid concentration of 0.5 M, a temperature of 22 °C and a stoichiometry of 1. The experimental results showed a continuous increase of the weight loss with a decrease of the particle size.

3.6. *Effect of stoichiometry*

The effect of stoichiometry on the dissolution process is shown in Fig. 7. The other experimental conditions were 40 min reaction time of dissolution, a stirring speed of 200 rpm, 0.5 M acetic acid concentration, 22 °C, and 250–355 μm particle size fraction. It can clearly be seen from figure that the weight loss and the P_2O_5 content of the remaining solids increased sharply with an increase of the stoichiometry up to (mol of CH_3COOH)/(2 mol of CO_2) = 1. After that, a very slight increase was observed.

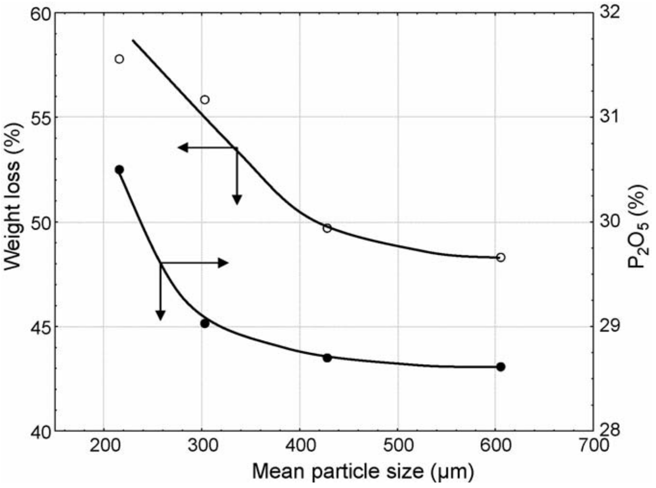

Fig. 6. Effect of particle size on the dissolution process (reaction time, 40 min; stirring rate, 200 rpm; acid concentration, 1 M; temperature, 22 °C; stoichiometry, 1).

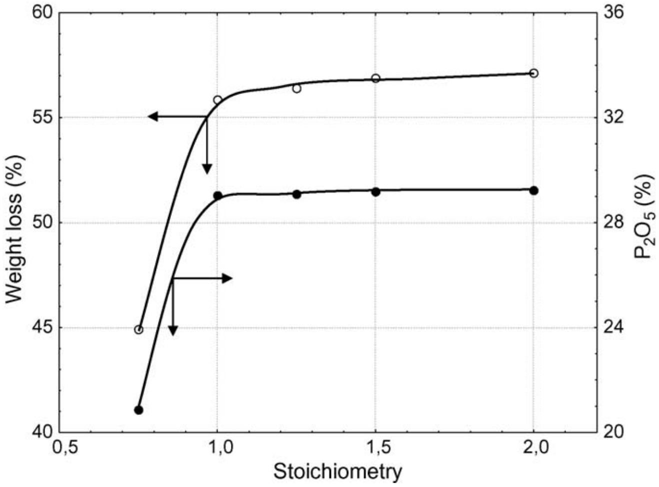

Fig. 7. Effect of stoichiometry on the dissolution process (reaction time, 40 min; stirring rate, 200 rpm; acid concentration, 1 M; temperature, 22 °C; particle size, 250–355 μm).

3.7. *Dissolution kinetics*

A detailed study of the kinetics of calcite dissolution is shown in Figs. 8 and 9. The experimental conditions used were a stirring speed of 200 rpm, a temperature of 22 °C, 250–355 μm particle size fraction, a stoichiometry of 1 and acetic acid concentrations of 0.5 and 1.

The percentage of weight loss and P_2O_5 content in the remaining solids, as well as the percentage amount of P_2O_5 loss in the solution, at various fixed periods of time for acetic acid concentrations of 0.5 and 1 are shown in Figs. 8 and 9, respectively. It can clearly be seen from Figs. 8 and 9 that the dissolution process was almost finished after a time of 40 min.

The kinetic data of the present study were analyzed using graphical and statistical methods. As the experimental results were analyzed using fluid-solid heterogeneous reaction models

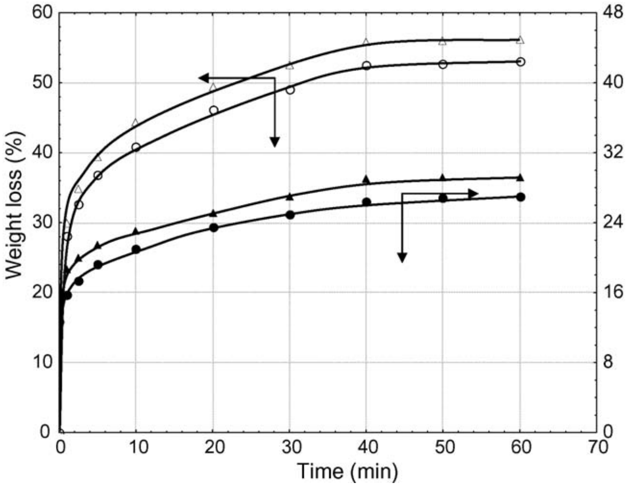

Fig. 8. Kinetics of the calcite dissolution process. The percent weight loss (white points) and the percent P_2O_5 loss (black points) in the remaining solids vs. time for acid concentrations of 0.5 (triangular points) and 1 M (circular points) (stirring rate, 200 rpm; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

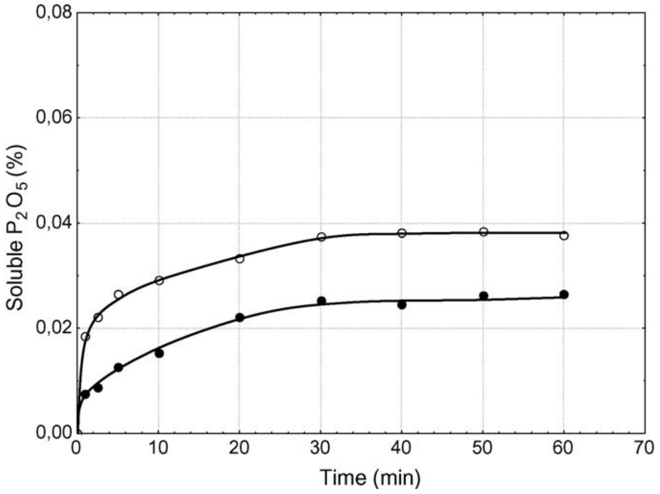

Fig. 9. During calcite dissolution P_2O_5 % loss vs. time for acid concentrations of 0.5 (white points) and 1 M (black points) (stirring rate, 200 rpm; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

by graphical and statistical methods, it was found that the data fit none of these kinetic models. However, further attempts to fit the results to a kinetic model led to the following expression which is called the pseudohomogeneous first-order reaction model [16]:

$$-\log(1-X)=kt^m \tag{3}$$

where X is the conversion fraction, k the rate constant and m is the constant.

Fig. 10 shows the plot of Eq. (3) in a log–log diagram for acetic acid concentrations of 0.5 and 1. It can be clearly seen from the figure that the dissolution process took place in two steps; the first step was fast and the second slow. The fast step dissolution is a situation which may be attributed to freely available calcite material and/or spaces on the particle. On the other hand, the slow one indicates the dissolution of calcite present in the pockets of the apatite matrix of low-grade phosphate rock. Employing regression analysis, the pseudohomogeneous first-order reaction kinetics models were obtained for the two different acid concentrations (0.5 and 1) and two steps. The models and the correction coefficients of linear fitting are shown in Table 2. It can clearly be seen from the models that the first steps had very close rate constants (k) and constant m. The rate constants of the second steps were 5–6 times more than those of the first steps. The correction coefficients were more marked for the first steps.

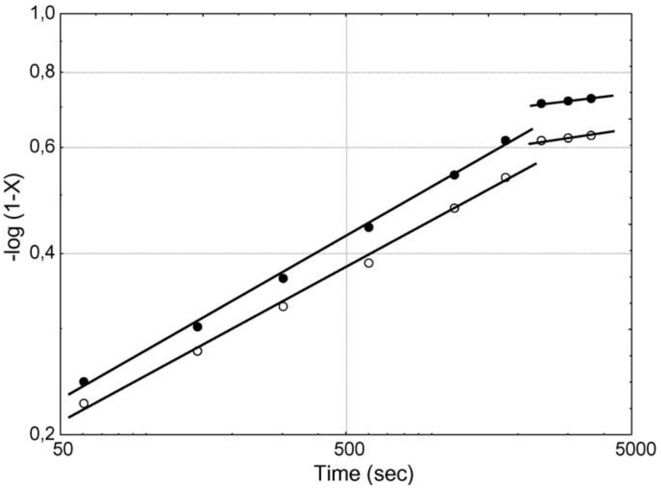

Fig. 10. Analysis of the pseudohomogenous first-order reaction kinetics models for the two different acid concentrations of 0.5 (black points) and 1 (white points) (stirring rate, 200 rpm; temperature, 22 °C; particle size, 250–355 μm; stoichiometry, 1).

Table 2
Pseudohomogeneous first-order reaction kinetics models

Acid concentration	Step	Kinetic model	Correction. coefficient
0.5	1st (fast)	$-\log(1-X)=0.0780t^{0.254}$	0.9961
	2nd (slow)	$-\log(1-X)=0.409t^{0.053}$	0.9869
1	1st (fast)	$-\log(1-X)=0.0784t^{0.273}$	0.9974
	2nd (slow)	$-\log(1-X)=0.504t^{0.044}$	0.9894

The economy of the dissolution process depends on the price of acetic acid and the cost of its recovery. Acetic acid may be recovered from the calcium acetate solution by possible routes as reported in a similar work [14].

4. Conclusions

In this experimental investigation the factors that might affect the increase of P_2O_5 % upon treatment with dilute acetic acid solution of low-grade calcareous phosphate rock in Turkey have been studied. The factors that have been considered are reaction time, stirring speed, concentration of acetic acid, stoichiometry, and particle size. The response of the phosphate mineral to the acid was tested by analyzing the filtrate solution. The following conclusions can be drawn:

(1) Acetic acid can be used to reduce the calcareous material in low-grade phosphate rock as it improves the P_2O_5 content up to marketable and industrially acceptable level. We found that the more effective conditions of the dissolution by using diluted acetic acid were 40 min of reaction time of dissolution, a stirring speed of 200 rpm, 0.5 M acetic acid concentration, 22 °C, 250–355 μm particle size fraction, and 1 stoichiometry. The dissolution process took place mainly by dissolving the calcite spaces, while almost of the P_2O_5 remained in the solid phase. The more effective experimental conditions led to a phosphate concentration of about 29–30% of P_2O_5.
(2) The kinetics analysis indicated that the dissolution of calcite spaces took place in two steps, the first one fast and the second slow. Kinetics data for the two above steps can be represented by a rate equation of $-\log(1-X)=kt^m$ where k varies between 0.0780 and 0.0784 for the fast step and 0.409 and 0.504 for the slow step and m varies between 0.254 and 0.273 for the fast step and 0.044 and 0.053 for the slow step, depending on the acid concentration.
(3) The economics of the dissolution process mainly depends on the price of acetic acid and the cost of its recovery. Acetic acid may be recovered from solution by a number of routes.

Depending on the type and nature of raw phosphate rock, the suggested process of beneficiation is relatively economical than the import of high-grade rock from other countries.

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