Dissolution Kinetics of Phosphate Ore in SO2Saturated Water

4 AUTHORS, INCLUDING:

Mehmet Muhtar Kocakerim
Çankırı Karatekin Üniversitesi
66 PUBLICATIONS   **1,120** CITATIONS

SEE PROFILE

Cengiz Özmetin
Balikesir University
30 PUBLICATIONS   **302** CITATIONS

SEE PROFILE

Dissolution Kinetics of Phosphate Ore in SO$_2$-Saturated Water

Ahmet Yartaşı,* M. Muhtar Kocakerim, Sinan Yapıcı, and Cengiz Özmetin

Department of Chemical Engineering, Engineering Faculty, Atatürk University, Erzurum, Turkey

In this study, the dissolution of phosphate ore from Mazıdağı-Mardin, Turkey, the products formed, and the dissolution kinetics were investigated in SO$_2$-saturated water. In experiments, particle size, stirring speed, solid/liquid ratio, and temperature were chosen as parameters. It was determined by X-ray diffractometer that the final solid product contains $CaHPO_4 \cdot 2H_2O$, $Ca_3(SO_3)_2 \cdot SO_4 \cdot 12H_2O$, and $CaSO_4 \cdot 2H_2O$. It was observed that the dissolution rate increased with the increase in stirring speed and reaction temperature, and with the decrease in particle size and solid/liquid ratio. A semiempirical mathematical model in the following form, including the effect of the parameters was established to express the dissolution kinetics of phosphate ore: $-\ln(1 - X) = 35.874 D^{-0.512} w^{0.380} \cdot (S/L)^{-0.825} e^{-2575/T} t^{0.781}$, where X is the conversion fraction of the ore, w is stirring speed, D is particle size, and S/L is the solid/liquid ratio in weight. The activation energy for the process was found to be 21 408.55 J mol^{-1}.

1. Introduction

SO$_2$ gas produced with the roasting of sulfur minerals has substantially caused air pollution. SO$_2$ has been used only for the production of H$_2$SO$_4$ for a long time in the past. However, at present, this side product is being used for the extraction of ores and the production of some chemicals (Habashi, 1976).

Apatite is a widely distributed phosphate mineral with a hexagonal crystal structure and named according to the groups of F$^-$, Cl$^-$, OH$^-$, and CO$_3{}^{2-}$, in which it includes fluorapatite ($Ca_{10}(PO_4)_6 \cdot F_2$) and carbonate-apatite ($Ca_{10}(PO_4)_6 \cdot CO_3 \cdot H_2O$), with a hexagonal crystal structure. It exists in the colors of shades of green to gray-green and also white, brown, yellow, bluish, or reddish in nature. The name comes from a Greek word meaning "to deceive" because apatite is readily mistaken for other minerals (Hamilton et al., 1987).

Because of the fact that Turkey is an agriculturally dependent country, the fertilizer industry has vital importance. Phosphate fertilizers having an important place in the fertilizer industry are produced from phosphate rocks. The phosphate fertilizer consumption of the world has increased 8% on average per year. The fact that the population of the world is increasing continuously and that the fertilization of land with chemical fertilizers for the solution of the problem of food shortage has an important role shows that phosphate will protect its important place in the world economy as a much-needed material in the future (Calmonovici and Giuliette, 1990). Phosphorus is the basic material of phosphate fertilizers, and 76% of phosphorus production is consumed for fertilization. Chemical fertilizers, especially phosphate rocks, are of the most important imported materials of Turkey. For this reason, the efficient use of the phosphate rock sources of Turkey is very important.

The purpose of this study is to produce phosphate compounds and fertilizers from Mazıdağı-Mardin phosphate ores, which are the largest phosphate sources of Turkey, and to obtain the principal knowledge for fertilizer production with the use of SO$_2$. The use of SO$_2$ for the dissolution of phosphate ores has some advantages: (1) it is much cheaper than mineral acids due to direct use without any further chemical process, (2) it is very effective for the dissolution of phosphate rocks, and (3) the air pollution caused by SO$_2$ can be reduced. Thus it might be worthwhile to investigate the dissolution process in a stirred tank reactor to produce some phosphate products

and the effect of the parameters such as temperature, solid-to-liquid ratio, stirring speed, and particle size.

Many studies have been carried out for the dissolution of phosphate minerals. However, few studies can be found on the dissolution of phosphate rocks with SO$_2$. Mc-Cullough et al. (1978) worked on the production of dicalcium phosphate from phosphate rock in a water containing SO$_2$ and carbonyl compounds. However, the purpose of their study was to prepare dicalcium phosphate from phosphate rock, not to investigate the kinetics of the process. It was recorded that this process has the economic advantage of recovering much of the SO$_2$ used and almost all of the carbonyl compounds after low-temperature thermal decomposition, and then recirculation of these substances to the system, in addition to the fact that SO$_2$ is much cheaper than mineral acids. Sardisco et al. (1984) studied the production of H$_3$PO$_4$, and some other phosphate compounds from low-grade phosphate ores were investigated, using H$_3$PO$_4$ as solvent reagent. In a study, H$_3$PO$_4$ was produced by wet method from a phosphate rock containing fluorapatite (Weston et al., 1984). The production of H$_3$PO$_4$ in high purity and of dicalcium phosphate with impurities was investigated using various grade phosphate rocks; it was emphasized that both products can be produced simultaneously (Bridger, 1979; Bridger et al. 1981). In another study, the dissolution kinetics of the crystals of fluorapatite in HCl solutions was investigated; the activation energy of the dissolution process was calculated as 10 kcal/mol^{-1} (Tarantsova et al., 1980). In addition to the above studies, the dissolution of phosphate rocks for H$_3$PO$_4$ and fertilizer production was investigated in different acidic solutions by some researchers: in HNO$_3$ (Parlea et al., 1978; Zhang and Muhammed, 1989), H$_3$PO$_4$ (Calmanovici and Giulietti, 1990), H$_2$SO$_4$ (Fitch et al., 1971; Treushcenko, 1987), and HCl (Tennakone et al., 1988; Konyukhova and Belekoskov, 1972) solutions.

2. Experimental Section

The phosphate ore used in the study was provided from the sources in Mazıdağı-Mardin in Turkey. The ore was crushed, ground, and then sieved to obtain fractions of 1700–1400, 1180–1000, 850–710, and 600–550 μm. The phosphate rock was analyzed, and the chemical analysis of the sample is given in Table 1. It was also determined, by X-ray diffractometer, that the ore contains carbonate-apatite, fluorapatite, and calcite (Figure 1).

Table 1. Chemical Analysis of the Phosphate Rock

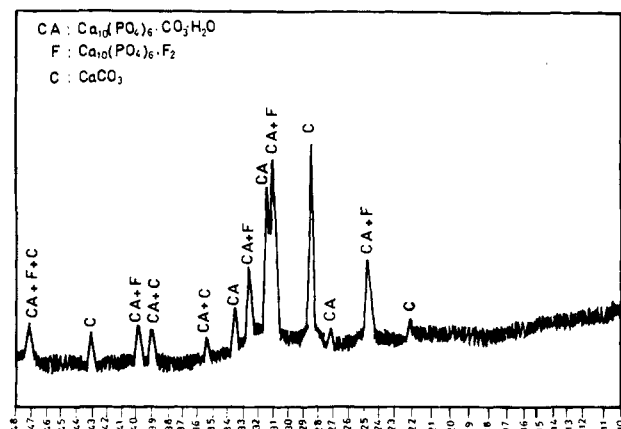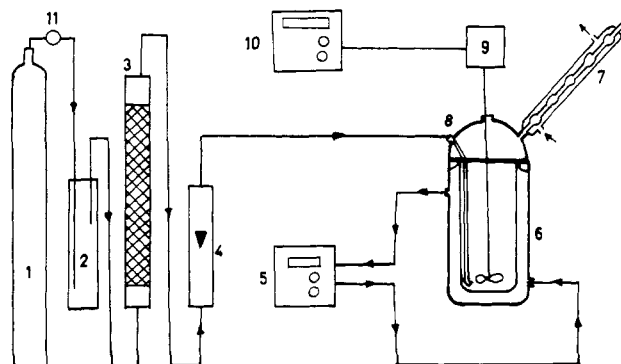| component	wt %
P₂O₅	24.560
CaO	55.040
SiO₂	1.700
SO₃	1.005
Al₂O₃	0.500
MgO	0.690
Fe₂O₃	1.090
moisture	1.090
heating loss	14.300
others	0.025

Figure 1. X-ray diffractogram of phosphate rock.

Figure 2. Schematic view of experimental test rig: (1) SO₂ cylinder; (2) dehydrator; (3) packed bed; (4) rotameter; (5) thermostat; (6) reactor; (7) condenser; (8) gas feeding and sampling; (9) mechanical stirrer; (10) stirrer control; (11) pressure gauge.

The dissolution process was carried out in a 250-mL glass reactor at atmospheric pressure. Reactor content was stirred by a mechanical stirrer, and a thermostat was used to control reaction temperature. During the leaching SO₂ gas was bubbled into the reaction vessel at a controlled rate in order to keep the solution saturated with SO₂ (Grimanelis et al., 1992; Kocakerim and Alkan, 1988; McCullough et al., 1978). The reactor was fitted with a cooler to prevent the reduction of reaction volume by the evaporation of the solution. An experimental test system is given in Figure 2. The parameters and their ranges used in the experiments are given in Table 2.

At a given condition, each experiment was repeated three times, and the arithmetic average was used in kinetic analysis. These experiments could be repeated with a maximum deviation of ∓2%. It was determined that the accuracy of chemical analysis shows a maximum deviation of ∓1.5% compared with the results of X-ray analysis of the ore. The number of the experiments is enough to be able to investigate kinetically the behavior of this sort of process.
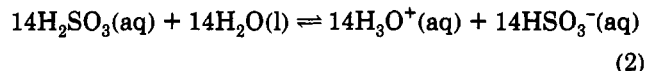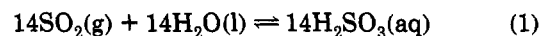
Table 2. Parameters and Their Ranges Used in the Experiments

| parameters	values
particle size (μm)	1550, 1090, 780, 575
stirring speed (s⁻¹)	31.42, 52.358, 73.303, 94.245
temperature (°C)	5, 10, 15, 20, 25, 30
solid/liquid ratio (in wt)	0.015, 0.03, 0.06, 0.10
time (s)	180, 300, 600, 900, 1500, 1800

The reaction vessel and its contents were heated to the reaction temperature, after 100 mL of distilled water was placed into the reaction vessel, and the solution was saturated with SO₂. A certain amount of the ore was added into the reactor, and the contents of the reaction vessel were stirred at a certain stirring speed for a desired period while SO₂ introduction was continuing. As soon as the process finished, the contents of reaction vessel were filtered, and P₂O₅ in solution was analyzed by gravimetric method (Scott, 1963).

3. Results and Discussion

3.1. Dissolution Reactions. The dissolution process was carried out using the solutions of water saturated with SO₂. For this process, pH measurements were taken at the beginning and at the end of the experiments at the temperature of 15 °C, and it was determined that pH values varied in the ranges of 0.60–0.62 and 1.20–1.70, respectively. It is obvious that H₂SO₃ produced by the dissolution of SO₂ in water makes the acidity of the reaction system quite high. For the process the following reactions can be written. When SO₂ gas is in contact with water the following equilibrium is established (Prausnitz, 1969):

$$14SO_2(g) + 14H_2O(l) \rightleftharpoons 14H_2SO_3(aq) \tag{1}$$

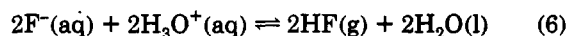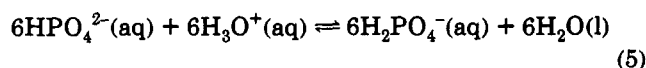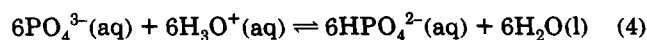$$14H_2SO_3(aq) + 14H_2O(l) \rightleftharpoons 14H_3O^+(aq) + 14HSO_3^-(aq) \tag{2}$$

The solubility of H₂SO₃ depends upon temperature and pressure. The dissolution reaction of phosphate ore in water can be written as follows:
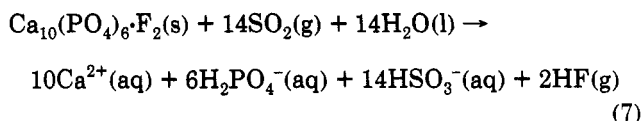
$$Ca_{10}(PO_4)_6 \cdot F_2(s) \rightarrow 10Ca^{2+}(aq) + 6PO_4^{3-}(aq) + 2F^-(aq) \tag{3}$$
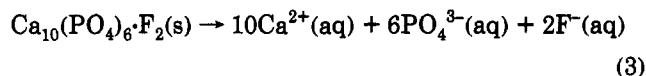
At moderate temperatures, for the solutions in the pH range of 1–2, since the ratio of [HPO₄²⁻]/[H₂PO₄⁻] is approximately on the order of 10⁻⁶, [HPO₄²⁻] is available in trace amounts in the system. Only the first dissociation of H₃PO₄, H₃PO₄ ⇌ H⁺ + H₂PO₄²⁻, is important (Mortimer, 1979). And at these conditions the quantity of SO₃²⁻ is also almost neglibile in comparison with HSO₃⁻.
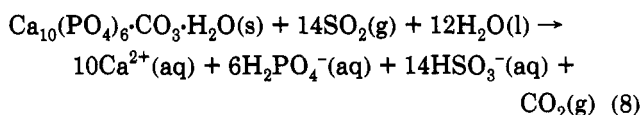
The presence of H₃O⁺ ions from the dissolved SO₂ in the solution results in the following equilibria (Mortimer, 1979), increasing the dissolution of the ore:

$$6PO_4^{3-}(aq) + 6H_3O^+(aq) \rightleftharpoons 6HPO_4^{2-}(aq) + 6H_2O(l) \tag{4}$$

$$6HPO_4^{2-}(aq) + 6H_3O^+(aq) \rightleftharpoons 6H_2PO_4^-(aq) + 6H_2O(l) \tag{5}$$

$$2F^-(aq) + 2H_3O^+(aq) \rightleftharpoons 2HF(g) + 2H_2O(l) \tag{6}$$

Thus the overall reaction can be written as

$$Ca_{10}(PO_4)_6 \cdot F_2(s) + 14SO_2(g) + 14H_2O(l) \rightarrow$$

$$10Ca^{2+}(aq) + 6H_2PO_4^-(aq) + 14HSO_3^-(aq) + 2HF(g) \tag{7}$$

In the case of carbonate-apatite, the same reactions take place in the system except that $2F^-$ is replaced by CO_3^{2-} in reaction 3 and 2HF by CO_2 in reactions 6 and 7. The overall reaction for carbonate-apatite can be writted as follows:

$$Ca_{10}(PO_4)_6 \cdot CO_3 \cdot H_2O(s) + 14SO_2(g) + 12H_2O(l) \rightarrow$$

$$10Ca^{2+}(aq) + 6H_2PO_4^-(aq) + 14HSO_3^-(aq) +$$
$$CO_2(g) \tag{8}$$

In the range of pH = 1.2–1.7 in the present experimental conditions, therefore, $H_2PO_4^{2-}$ is produced in addition to other main species available in the reaction medium such as HSO_3^- and Ca^{2+}. After dissolving the ore, the solution obtained at the end of the reaction was separated from the undissolved solid, and SO_2 was then completely removed by heating the solution. It was reported that monocalcium phosphate was dissociated by heating according to the following reaction (McCullough *et al.*, 1978; Grover *et al.*, 1981):

$$Ca(H_2PO_4)_2 \rightarrow H_3PO_4 + CaHPO_4 \tag{9}$$
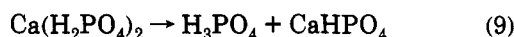
The precipitation formed during this heating was separated from the solution and analzyed by an X-ray diffractometer. It was found that the precipitate contains $CaHPO_4 \cdot 2H_2O$, $CaSO_4 \cdot 2H_2O$, and $Ca_3(SO_3)_2 \cdot SO_4 \cdot 12H_2O$ (Figure 3). The formation of sulfate compounds of calcium, seen in Figure 3, is a result of the oxidation of SO_3^{2-} to SO_4^{2-} due to the catalytic effect of metal mineral ions available in the system such as Fe(II) and Mn(II) (Moore and Moore, 1976).

3.2. Conversion Kinetics. The experimental results were examined using the conversion fraction of P_2O_5 in solid, $X_{P_2O_5} = (C_{0,P_2O_5} - C_{P_2O_5})/C_{0,P_2O_5}$, versus time, where C_{0,P_2O_5} is the initial concentration of P_2O_5 and $C_{P_2O_5}$ is the unreacted concentration in the system. Results were submitted in the form of graphs plotted $X_{P_2O_5}$ vs t.

3.2.1. Effect of Particle Size. The effect of the particle size on the dissolution rate of the phosphate ore was investigated for the fractions of 1700–1400, 1180–1000, 850–710, and 600–550 μm at the temperature of 15 °C, solid/liquid ratio of 0.03, and stirring speed of 31.42 s^{-1}. The results obtained from the experiments are given in Figure 4. As seen from the figure, the particle number per weight of the ore, in other words the surface area, increases when the particle size decreases. This also means an increase in the exposure of value mineral to the reactive. For this reason, the conversion rate increases with decreasing particle size.

3.2.2. Effect of Stirring Speed. The effect of the stirring speed on the dissolution rate was investigated at the stirring speeds of 31.42, 52.36, 73.30, and 94.25 s^{-1} at the temperature of 15 °C, solid/liquid ratio of 0.03, and particle size of 1700–1400 μm. The experimental results are exhibited in Figure 5. It can clearly be seen from the figure that the dissolution rate increases with increasing stirring speed, which can be attributed to the reduction of the liquid film thickness around the solid particle due to the increase of the velocity of the solid relative to the liquid velocity.

3.2.3. Effect of Solid/Liquid Ratio. The effect of the solid/liquid ratio on the conversion rate was studied for the ratios of 0.015, 0.03, 0.06, and 0.10 at the
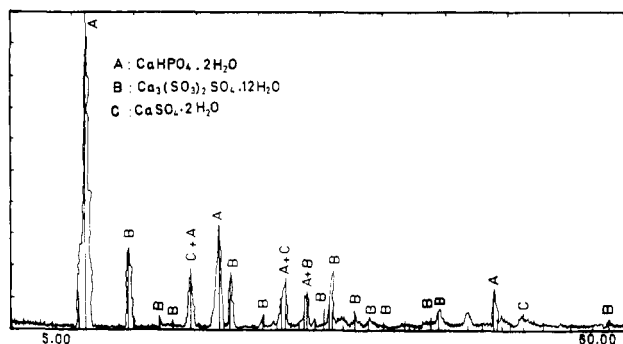

Figure 3. X-ray diffractogram of solid obtained by SO_2 removal from phosphate solution.
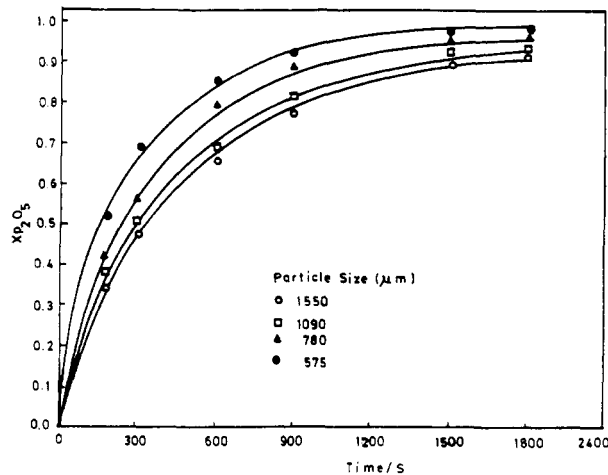

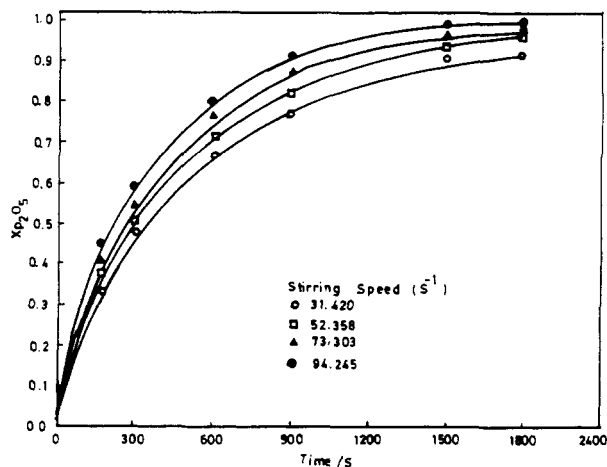**Figure 4.** Effect of particle size on dissolution of phosphate rock.

Figure 5. Effect of stirring speed on dissolution of phosphate rock.

temperature of 15 °C, stirring speed of 31.42 s^{-1}, and particle size of 1700–1400 μm. As can be seen in Figure 6, which the experimental results are shown, the conversion rate decreases with increasing solid/liquid ratio. As the amount of the solid in the reaction medium increases with increasing solid/liquid ratio, the amount of the liquid per amount of the solid decreases due to constant solubility of SO_2 gas in water at a certain temperature.

3.2.4. Effect of Reaction Temperature. The effect of the reaction temperature on the conversion rate was investigated at the temperatures of 5, 10, 15, 20, 25, and 30 °C, solid/liquid ratio of 0.03, stirring speed of 31.42 s^{-1}, and particle size of 1700–1400 μm. The experiments
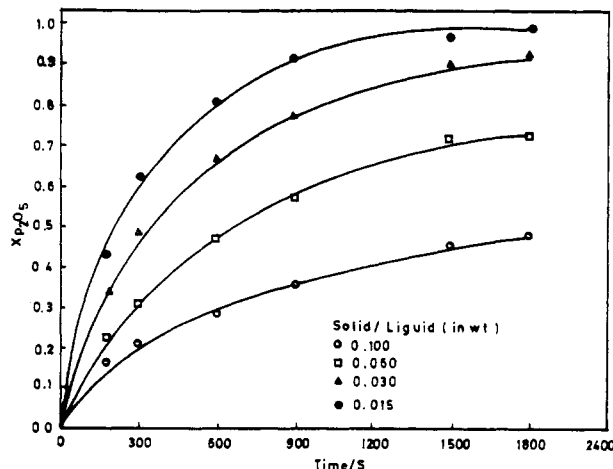
Figure 6. Effect of solid/liquid ratio on dissolution of phosphate rock.
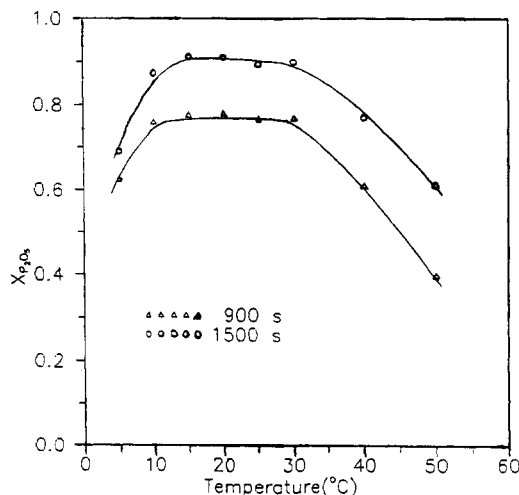

Figure 7. Conversion of phosphate rock with temperature for two reaction periods.

showed that the temperature has an increasing effect on the dissolution process up to 15 °C, reaching a maximum there; the dissolution remains almost constant up to 30 °C, and then the temperature has a decreasing effect after this temperature, as shown in Figure 7. This behavior of the dissolution process can be explained by the change in the solubility of SO_2 with temperature since the solubility of gases decreases with temperature. The decrease in the conversion rate with the decrease in the amount of SO_2 in the solution counterbalances the increase in the rate with temperature, giving unchanged dissolution kinetics between 15 and 30 °C, and a further increase in temperature cannot counterbalance the decrease in reaction rate due to the decrease in the solubility of SO_2. When the effect of the reaction temperature on the kinetics of the process is investigated, the data from the runs up to 15 °C were employed since they show a regular behavior, as shown in Figure 8.

The conversion kinetics was investigated using the conversion fraction data versus time by taking into consideration the fluid–solid reaction models (Levenspiel, 1972; Wen, 1968), but it was statistically determined that the data do not fit any of these models. The kinetics was also tested using pseudohomogeneous reaction models, and it seems that the reaction rate does fit a pseudohomo-
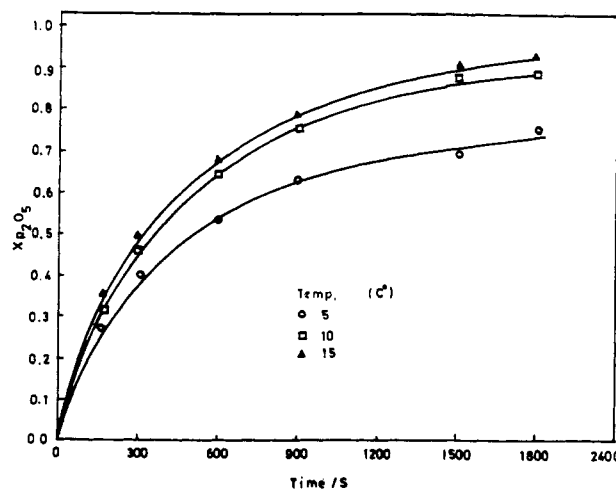

Figure 8. Effect of temperature on dissolution of phosphate rock.

geneous first-order reaction model in the following form.

$$dX/dt = k(1 - X) \tag{10}$$

When the experimental results were then examined using the following model (Hulbert and Huff, 1970),

$$-\ln(1 - X) = kt^m \tag{11}$$

it was determined that the reaction is represented best by this model. To establish a semiempirical model representing the system, it was accepted that the dissolution process can be written as follows:

$$-\ln(1 - X) = k_o D^a w^b (S/L)^c e^{-E/RT} t^m \tag{12}$$

Employing multiple regression, using a computer package program, the following values for constants were obtained: $k_o = 35.874$ $a = -0.512$ $b = 0.380$ $c = -0.825$ $m = 0.781$ $E = 21\,408.55$ J mol^{-1} Thus eq 12 can be written as follows:

$$-\ln(1 - X) = 35.874 D^{-0.512} w^{0.380} (S/L)^{-0.825} e^{-2575/T} t^{0.781} \tag{13}$$

To test the agreement between the experimental conversion values and the values calculated from the empirical equation, the plot of X^{exp} vs X^{prd} was drawn. As seen in Figure 9, the agreement between the experimental and calculated values are very good with a relative mean square of errors of 0.0595 calculated by the equation

$$ER = \left[\frac{1}{N} \sum_{i=1}^{N} \frac{(X^{prd} - X^{exp})^2}{(X^{prd})^2} \right]^{1/2} \tag{14}$$

where X^{prd} is the calculated value, X^{exp} is the experimental value, and N is the number of experimental data. Figure 10 also shows the comparison between experimental conversion values and those calculated from the pseudohomogeneous first-order reaction model established in the same way as eq 13. The relative mean square of errors between experimental and calculated conversion values for this model is 0.1371. When one compares Figures 9 and 10, it can be clearly seen that the deviation between the experimental and theoretical values is higher in the pseudohomogeneous first-order model, while the agreement between the experimental and calculated conversion values is very good for the model $-\ln(1 - X) = kt^m$. This empirical model can be applicable for the
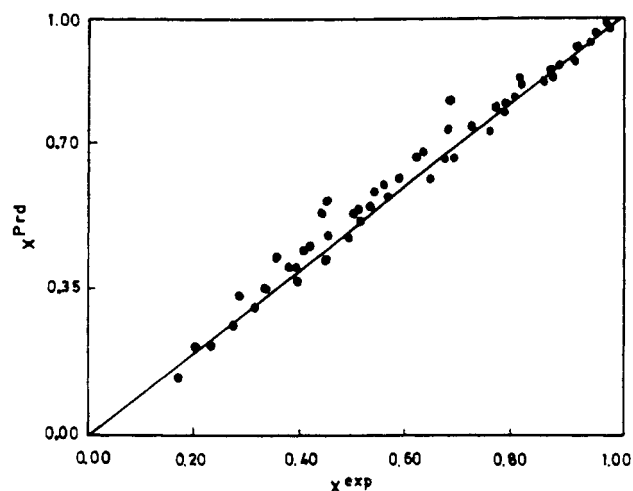
Figure 9. Comparison of experimental and theoretical conversion values from semiempirical model in eq 16.
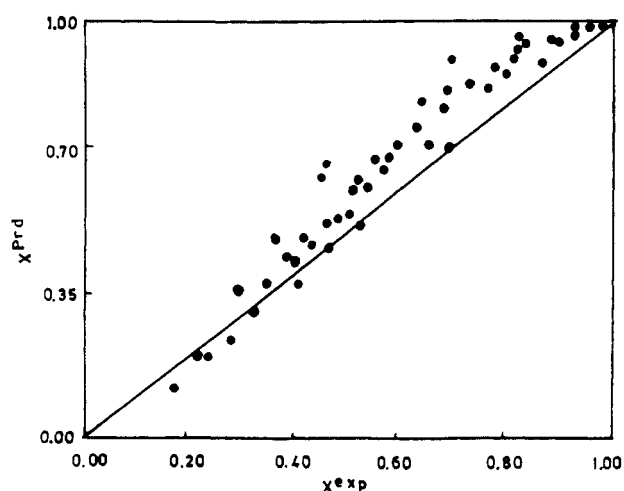

Figure 10. Comparison of experimental and theoretical values from pseudohomogeneous first-order model.

experimental condition ranges and reactor geometry of the present study.

Finally, it can be said that the most effective parameter is the solid/liquid ratio, with a power of −0.825. Stirring speed and particle size have less effect on the dissolution, but particle size affects inversely the process and it is more effective than the stirring speed. The activation energy for the process was found to be 21 408.55 J mol^{-1}. The dissolution kinetics can be expressed very well by this semiempirical mathematical model. Further investigation can be carried out to see the effect of the pressure, since the solubility of SO_2 increases with increasing pressure. Increasing the solubility of SO_2 can shorten the dissolution period, so giving the facility of studying in high solid/liquid ratios effectively. A more detailed pilot scale work is suggested to be able to carry the investigation to the industrial application.

4. Conclusions

In this study in which the dissolution of phosphate rock was investigated in a semibatch reactor, it was observed that SO_2-saturated water can dissolve the ore efficiently. For the experimental conditions of the present study, it was found that the main dissolution products are $H_2PO_4^-$ and HSO_3^- in the solution. After SO_2 dissolved in the solution was removed by heating, the main solid products were determined to be $CaHPO_4 \cdot 2H_2O$, $Ca_3(SO_3)_2SO_4 \cdot$

$12H_2O$, and $Ca(H_2PO_4)_2 \cdot H_2O$ in the solution and $CaSO_4 \cdot 2H_2O$ in solid phase. It was determined that the reaction fits a model in the form of $-\ln(1 - X) = kt^m$. The dissolution rate increases with increasing stirring speed and decreasing solid/liquid ratio and particle size. The most effective parameter is the solid/liquid ratio, with a power of −0.825. Stirring speed and particle size have less effect than particle size on the dissolution, but particle size affects inversely the process and it is more effective than stirring speed.

It was observed that the temperature has an increasing effect on the dissolution process up to 15 °C, reaching a maximum there; the dissolution remains almost constant up to 30 °C, and then the temperature has a decreasing effect after this temperature. This behavior of the dissolution process can be explained by the change in the solubility of SO_2 with temperature; the solubility of gases decreases with temperature. The decrease in the conversion rate with the decrease in the amount of SO_2 in the solution counterbalances the increase in the rate with temperature, giving unchanged dissolution kinetics between 15 and 30 °C, and a further increase in temperature cannot counterbalance the decrease in reaction rate due to the decrease in the solubility of SO_2. To extend this investigation to higher pressure conditions can be interesting. A semiempirical mathematical model, which expresses the process very well, was established. Since no study on the kinetics of phosphate rocks in water with SO_2 was detected in the literature, no comparison of the kinetic data was made.

Nomenclature

a = constant in eq 12
b = constant in eq 12
c = constant in eq 12
C_{0,P_2O_5} = initial concentration of phosphate rock [kmol m^{-3}]
$C_{P_2O_5}$ unreacted concentration of phosphate rock [kmol m^{-3}]
D = particle size [μm]
E_A = activation energy [J mol^{-1}]
k = rate constant in eq 10
k_o = rate constant in eq 12
L = amount of liquid [kg]
m = constant in eq 11
R = universal gas constant [J K^{-1} mol^{-1}]
S = amount of solid [kg]
T = temperature [K]
t = time [s]
X = conversion fraction
w = stirring speed [s^{-1}]

Literature Cited

The Bank of Industrial Development of Turkey. Kimya Sektör Araştırması: Fosfat. **1979**, *17*, 1–157.

Bridger, G. L. Process for Producing Phosphoric Acid and Dicalcium Phosphate. U.S. Pat. 4,141,958, 1979.

Bridger, G. L.; Drees, C. B.; Roy, A. H. A New Process for Production of Purified Phosphoric Acid and/or Fertilizer Grade Dicalcium Phosphate from Various Grades of Phosphatic Materials. *Ind. Eng. Chem. Process Des. Dev.* **1981**, *20* (3), 416–424.

Calmanovici, C. E.; Giulietti, M. Technological Optitude of Some Brazilian Phosphate Rocks for Acid Decomposition. *Ind. Eng. Chem. Res.* **1990**, *29* (3), 482–488.

Fitch, E. B.; Roberts, E. J.; Weber, W. C. Phosphoric Acid by the acidulation of Phosphate Rock with Sulphuric Acid. U.S. Pat. 3,552,918, 1971.

Grimanelis, D.; Neou-Syngouna, P.; Vazarlis, H. Leaching of a Rich Greek Manganese Ore by Aqueous Solutions of SO_2. *Hydrometallurgy* **1992**, *31*, 139–146.

Habashi, F. Sulphur Dioxide in Metallurgy. *Sulfur Inst. J.* **1976**, *12*, 3–4.

Hamilton, W. R.; Wooley, A. R.; Bishop, A. C. *Minerals, Rocks and Fossils*, 4th ed.; Country Life Books: Twickenham, Middlesex, England, 1987; p 86.

Hulbert, S. F.; Huff, D. E. Kinetics of Alumina Removal from a Calcined Kaolin with Nitric, Sulphuric and Hydrochloric Acid. *Clay Miner.* **1970**, *8* (337), 340–345.

Kocakerim, M. M.; Alkan, M. Dissolution Kinetics of Colemanite in SO_2-Saturated Water. *Hydrometallurgy* **1988**, *19*, 385–392.

Konyukhova, L. I.; Belokoskov, V. I. Recovery of Phosphoric Acid from an Apatite Concentrate by Extraction with 1-Butanol. *Khim. Tecknol. Pererab. Redkomet. Syr'ya Kol'sk. Poluostrava* **1972**, 3–11.

Levenspiel, O. *Chemical Reaction Engineering*, 2nd ed.; John Wiley and Sons: New York, 1972; pp 357–377.

McCullough, J.; Phillips, J. F.; Tate, L. R. Preparation of Dicalcium Phosphate Rock by the use of Sulphur Dioxide, Water, and Carbonyl Compounds. U.S. Pat. 4,113,842, 1978.

Moore, J. W.; Moore, E. A. *Environmental Chemistry*; Academic Press, Inc.: London; 1976; pp 210–211.

Mortimer, C. E. *Chemsitry; A Conceptual Approach*, 4th ed.; Van Nostrand Co.: New York, 1979; pp 593–596, 796–798.

Parlea, G.; Lovi, A.; Parlea, M. Studies on the Decomposition Process of Phosphate Rocks with Nitric Acids. *Timisoara, Ser. Chim.* **1978**, *23* (1), 22–24.

Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1969; pp 380–383.

Sardisco, J. B.; Holcomb, D. E.; Drechsel, E. K. Phosphoric Acid and Additional Products from Phosphate Ore. U.S. Pat. 4,479,923, 1984.

Scott, W. W. *Standard Methods of Chemical Analysis*, 6th ed.; Van Nostrand Co.: New York, 1963; Vol. 1, pp 798–865.

Tarantsova, M. I.; Kulikov, B. A.; Chaikina, M. V.; Kolasov, A. S.; Boldyre, V. V. Kinetics of Dissolution of Fluoroapatite Crystals in Solutions of Hydrochloric Acid. *Ser. Khim. Nauk.* **1980**, *4*, 55–61.

Tennakone, K.; Weerasooriya, S. V. R.; Jayatissa, D. L.; Domayanthi, M. L. W. D.; Silva, L. H. K. Nonhygroscopic Superphosphate Fertilizer from Apatite and Hydrochloric Acid. *Inst. Fundam. Stud. Fertilizer Res.*, **1988**, *16* (1), 87–96.

Treuschenko, N. N.; Belyakov, V. A.; Pozin, M. E. Interaction of Components of Phosphate Raw Material with Dilute Sulphuric Acid Solutions. *Zh. Prikl. Khim.* **1987**, *60* (8), 1681–1685.

Wen, C. Noncatalytic Heterogeneous Solid-Fluid Reaction Models. *Ind. Eng. Chem.* **1968**, *60* (9), 34–17.

Weston, W. C.; Wen, J. W.; Mandel, F. S. Process for Producing Wet Process Phosphoric Acid from Phosphate Rocks Containing Fluochlorapatite and Related Minerals. U.S. Pat. 4,485,078, 1984.

Zhang, Y.; Muhammed, M. An Integrated Process for the Treatment of Apatite Obtained from Dephosphorization of Iron Ore. *J. Chem. Technol. Biotechnol.* **1990**, *47*, 47–60.