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Selective Leaching Kinetics of Calcareous Phosphate Rock in Phosphoric Acid

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Abstract: In the present study, reaction kinetics was carried out using low grade calcareous phosphate rock particles in dilute phosphoric solution. To study the reaction parameters a number of experiments were carried out in a glass reactor column. The results indicate that the selective leaching of the calcareous material in the rock is controlled by the fluid layer depending on the reaction conditions. The results also show that the value of reaction rate constant does not appear to be a strong function of the particle size while the value of mass transfer coefficient increases with an increase in particle size.

Key words: Selective leaching, beneficiation, calcareous material

INTRODUCTION

Phosphates are essential ingredients in the fertilisers used to supply food and feed for mankind and animals. There is no substitute for phosphate rock as a raw material in the production of phosphate fertilisers in the world at this time. As the world population continues to increase, so does the demand for phosphate. Phosphate rocks are complex raw materials and are mainly used in the manufacture of phosphate fertilisers. 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. Most of the world's phosphate rocks are of sedimentary origin and are primarily composed of the apatite group in association with a wide assortment of accessory minerals, fluorides, carbonates, clays, quartz, silicates, metal oxides, etc. Low grade phosphate rocks are not usually suitable for direct use in phosphate industries unless their tricalcium phosphate content is increased up to marketable and industrially acceptable levels. A number of techniques^[1,2] may also be applied for both the siliceous and high carbonate phosphate rocks.

Flotation of carbonate rich ore poses difficulties because the fatty acids and their derivatives used as flotation collectors have very poor selectivity for carbonates and phosphate minerals^[3]. It is possible that gangue minerals, such as quartz and pyrite, can easily be separated by flotation. However, the separation of calcite from collophane is not easy because both of these minerals have similar flotation characteristics^[4]. Research efforts to find details of the mechanism of interaction between ions in the liquid phase and the solid surfaces

involved are difficult due to the presence of impurities^[5]. Even a small level of some impurities in the ore have a marked effect on the surface properties of calcite and apatite as well as the ionic reactions in the liquid phase. It is recommended that the CaO: P₂O₅ ratio in the flotation product must be less than 1.6^[6].

The currently used commercial process of double flotation^[7] is not adequate for reducing the dolomitic impurity level to less than 1.0 weight percent MgO in the concentrate, as stipulated by the phosphate industry. Moudgil and Chanchani^[8] have carried out some fundamental studies in the development of two processes for the removal of dolomite from apatite. An extension of these fundamental studies to beneficiate the natural ores on a bench scale was also reported^[9]. However, a systematic optimization of the important variables was not attempted and no guidelines are yet available for processing such complex ores. Zhong *et al.*^[10] have reported an optimisation of some variables using a three stage flotation scheme with various chemicals and flotation reagents.

Beneficiation by calcination is one of the better known processes. But the high cost of energy required for calcination has always acted against the implementation of such proposals. However, in flash calcination less thermal energy may be required depending on the processing conditions, nature and type of the raw phosphate rock^[1]. Beneficiation by calcination is based on the dissociation of the calcium carbonate gangue materials by thermal energy. The process usually comprises crushing, sieving, washing (to reduce clay and chlorides); classification, calcination at about 950°C, hydration of the lime, separation of the lime and finally

further washing and drying^[11]. By hot quenching, the magnesium oxide is transformed into an insoluble magnesium hydroxide. Many problems in the fertiliser manufacture are caused by the Mg content^[12].

Phosphate beneficiation with electrostatic methods is gaining interest especially in those areas characterised by water shortage where many important ores are being mined. Results show that the concentrates can be obtained with fairly good recoveries especially for the ore having favourable liberation characteristics; unfortunately the electrostatic separation of pyrite from the phosphate phase is inefficient and the concentrate is polluted to a significant extent^[13]. A number of unit operations and a relatively higher cost of production of phosphate fertilisers in the phosphate industries has opened up a new and economical area of biotechnology. The microbiological production of acid solutions from sulphide minerals may be used as an equivalent technology to solubilize phosphate rock for the fertiliser industry. The metabolic activity of the micro-organisms is regulated by a series of factors that must be controlled to achieve maximum biological action. Control of temperature, pH and oxygen levels, is required for the maintenance of ideal leaching process conditions; otherwise the acid production is not enough to make the high phosphate content soluble and neutralize the carbonate material^[14].

Selective leaching of the carbonate mineral with careful control of pH (3.0) by H₂SO₄ may be used to purify high-grade sedimentary ores containing limited amounts of dolomite. The process is technically feasible, but any practical implementation would depend largely on economic considerations such as acid cost^[15]. For the selective leaching of calcareous material in low grade phosphate rocks, organic acids can be used^[16,17]. The dissolving ability of organic acids is relatively weak and these acids may cause a little corrosion effect in the industrial processes^[18]. Also, the use of organic acids at high temperature may be limited because of low boiling temperatures and their decomposition^[19,20].

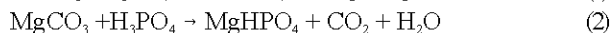
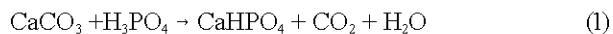
MATERIALS AND METHODS

The low grade phosphate rock is found in the northern area of Pakistan, district Abbottabad. These deposits contain silicious and calcareous impurities. The P₂O₅ content of the indigenous phosphate rock varies from 15 to 26%. The main deposits are Kakul, Lagarban, Batkanala, Oatkanala, Southern and Eastern Phosphorites. A number of samples of indigenous phosphate rock were collected for studying the leaching process and most of

the research facilities were available in the Department of Chemistry, Bahauddin Zakariya University, Multan. The calcareous material in low grade phosphate rock may be removed or reduced by using organic and inorganic acids such as citric acid, acetic acid and phosphoric acid, etc., depending on the process parameters as well as nature and size of the raw material particles. For the selection of an acid, the following important factors were taken into consideration:

1. The acid selected should not have tendency to dissolve the phosphate element itself.
2. Products must be collected separately.
3. The acid should be easily and economically recovered for reuse.
4. Selected acid should be cheaper.

In the present study, on terms of the above parameters dilute phosphoric acid was selected for the leaching process. During the reaction between strong acid and phosphate rock, the acid may react with the main constituents of the phosphate rock such as tri-calcium phosphate. In the case of dilute phosphoric acid results show that it is a promising leaching agent for the removal of calcareous material in the rock. Phosphoric acid is a relatively stronger acid and would be expected to have a faster diffusion rate than the organic acids in the leaching process. The small residence time of the particle in the continuous phase (having diluted acid) ensures that the solubility of phosphate elements is minimal. However, if water soluble mono-calcium phosphate (MCP) is formed, it can be simply separated by filtration or precipitated back into insoluble di-calcium (DCP) or tri-calcium (TCP) phosphate by using milk of lime. The reaction between phosphoric acid and calcareous materials can be written as follows:

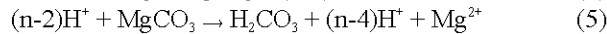
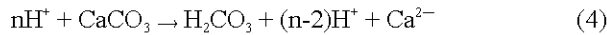


The by-products in the above reactions are insoluble, while the CO₂ is evolved as a gas. Reaction (1) and (2) may include the formation of unstable carbonic acid, which decomposes into CO₂ and H₂O; any reaction for the other impurities depends on the nature and composition of the raw phosphate. These two main reactions represent a lumping of a larger number of steps. The simplest detailed mechanism necessary for the rational understanding of this system may be given as follows:

- (a) Ionization of phosphoric acid, which is a relatively fast process described by the equation:

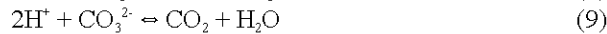
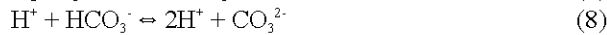


- (b) Diffusion of H^+ ions through the liquid to the exposed surface of the rock particle.
- (c) H^+ ions attack the particles of the calcareous and dolomitic gangue material in the rock.

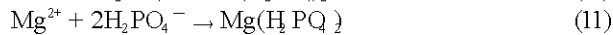
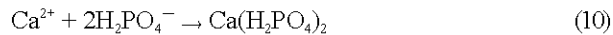


- (d) Ionization of H_2CO_3 :

When carbon dioxide dissolved in water, most of it was present as CO_2 molecules rather than H_2CO_3 molecules. However, if a small amount of carbonic acid is formed, the ionization which is a fast process may be described by the equations:



- (e) Diffusion products from the reaction sites to the bulk of the liquid.
- (f) Reaction between Ca^{2+} , Mg^{2+} and H_2PO_4^- may proceed as:



The formation of calcium and magnesium phosphate will depend on various parameters, such as the concentration of the acid, reaction time, temperature, nature and particle size of the raw phosphate rock used for the leaching process.

KINETIC ANALYSIS

A number of models are available in literature^[21-23], regarding mass transfer and reaction kinetics of dissolution of solid particles with surrounding fluid. For noncatalytic reaction of particles with surrounding fluid, the progressive conversion and the unreacted core models may be considered. The progressive conversion model may be used when a liquid reacts throughout the solid particle at all times, most likely at different rates at different locations within the particle. However, the unreacted core model seems to reasonably represent reality in a wide variety of situations and approximates real particles more closely in most cases than does the progressive conversion model^[21].

Phosphoric acid has been used to selectively remove calcareous material from the matrix of the low grade phosphate rock. The calcareous rock particle is reacted with the leaching agent and, as a result, the final particle is hard, firm and unchanged in size. Therefore, the shrinking core model with changing size may not properly work in the present case. Keeping in view the dissolution behaviour of calcareous rock particle in the continuous phase, the unreacted core model^[21] may be considered to appropriately work regarding reaction kinetics in the selective leaching of calcareous material in low grade phosphate rock.

Figure 1 indicates that $R_0 - r_c$ is the thickness of the apatite film around the unreacted core of the rock particle. If the apatite film thickness is small the reaction will progressively proceed with higher molar flux shrinking the rock particle inwardly. The shrinking of the rock particle will cause an increase in the film thickness around the unreacted core of the rock particle. However, if the reaction is slow the chemical reaction will control the leaching process. Thus the presence of any liquid or apatite layer becomes immaterial and the quantity of material reacting will be proportional to the available surface of the unreacted core of the rock particle. If on the interface $C_{A_0} = C_{A_s}$ there will be no concentration gradient over the fluid and apatite film. Thus the molar flux will depend on the amount of disappearance of the component $bB_{(s)}$ per unit surface of the particle rather than the concentration gradient over the fluid and apatite film. The amount of disappearance of the component $bB_{(s)}$ will depend on the concentration of component $A_{(s)}$ at the interface, reaction rate constant and the stoichiometry of the reaction between the acid and rock particle. Calcareous material in the rock particle reacts with phosphoric acid. As a result of the reaction, the acid concentration at the liquid-solid interface decreases and at the steady state the rate of dissolution of calcareous material from the apatite is equal to the rate of

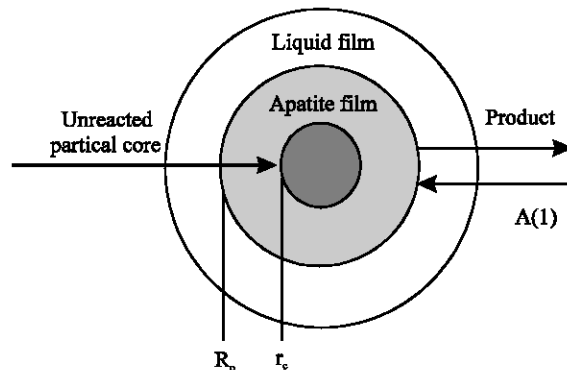


Fig. 1: The shrinking core of the rock particle

consumption of the leaching agent. The reaction between phosphoric acid and calcareous materials may be written in a more general form:



The reactant $A_{(l)}$ diffuses from the main bulk to the exterior surface of the rock particle with radius R_0 and then progressively to the radius r_c where it reacts with the calcareous material, $bB_{(s)}$ to form $F_{(l)}$, $G_{(g)}$ and $W_{(l)}$. The compounds, $F_{(l)}$ and $W_{(l)}$ then diffuse out of the porous matrix along with the evolution of CO_2 gas, $G_{(g)}$. If the reaction at the surface of the rock particle is slow, the reaction kinetics will be of great significance in controlling the rate of consumption of $bB_{(s)}$ from the core of the rock particle rather than the diffusion of component $A_{(l)}$ to the surface of the particle. The hard particle of apatite matrix is not shrinking with time and it may be assumed that the concentration profile at any instant to be the steady-state profile over the particle apatite film (R_0-r_c). The concentration driving force, given by $C_{A_0} - C_{A_s}$ is constant at all times during reaction between the leaching agent and the phosphate rock particle. However, in a fluid–solid reaction system, the reaction rate is generally controlled by one of the following steps^[21]:

for film diffusion control

$$\frac{t}{k^*} = [X_B] \quad (13)$$

for a chemically controlled process

$$\frac{t}{k^*} = \left[1 - (1 - X_B)^{1/3} \right] \quad (14)$$

for product-layer-diffusion control

$$\frac{t}{k^*} = \left[1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) \right] \quad (15)$$

where, $t/k^* = kt$ and k stands for reaction rate constant or mass transfer coefficients depending on the above integral rate expressions. X_B = conversion of calcareous material after time, t . These integral rate expressions were used to test the validity and best fit of the experimental data.

RESULTS AND DISCUSSION

Low grade phosphate rock sample was crushed in a mechanical crusher. The crushed material was sieved using different sieves to collect -4+12, -12+30, -30+40 and -40+60#(mesh). These fractions were dried in a drying oven and then stored in polyethylene bottles for further analysis. A glass column reactor was used to note the

Table 1: Effect of particle size on residence time, terminal velocity and conversion of calcareous material in the leaching process using 0.4312 g Mol cm^{-3} phosphoric acid

Average radius, R_0 , (cm)	Residence time, (Sec)	Terminal Velocity, ($cm\ s^{-1}$)	Conversion, X_B
0.01675	11.32	6.36	0.053313
0.02525	7.52	9.57	0.022031
0.05675	4.22	17.06	0.00536
0.161	3.68	19.57	0.001734

residence (reaction) time of the particle in the continuous phase. The reactor was washed with distilled water and then filled with 2.5% H_3PO_4 up to a certain mark for each run. Low grade phosphate rock particle was added to the continuous phase (2.5% H_3PO_4) from the top of the column reactor with the help of a spatula. The residence time of the particle in the reactor column was noted using a stopwatch. After each run, a sample of the continuous phase (H_3PO_4) was taken and analyzed. A number of particles were used to generate data for the leaching process. Conventional^[24] as well as instrumental analysis techniques such as Atomic Absorption Spectrophotometer (A-1800 Hitachi) were used for analyses.

In this study, the reaction parameters such as terminal velocity, reaction rate constant and mass transfer coefficients were studied on the basis of conversion of calcareous material in the leaching process. Results show that the residence time of the particle in continuous phase decreases with the increase of particle size. Therefore, depending on residence time, the terminal velocity of the particle increases with an increase in its size as shown in Fig. 2. On the other hand, the fractional conversion decreases with an increase in the particle size as shown in Table 1. The effect of residence time on X_B , $1-(1-X_B)^{1/3}$ and $[1-3(1-X_B)^{2/3}+2(1-X_B)]$ is given in Fig. 3. The effect of particle size on the reaction rate constant and mass transfer coefficients in the selective leaching of calcareous material is shown in Fig. 4. The results indicated that the value of mass transfer coefficient for fluid layer control appreciably increased with an increase in particle size. However, the value of reaction rate constant did not appear to be a strong function of the particle size which agreed with the previous study concerning the dissolution of calcareous material in formic acid^[25]. The statistical analysis was carried out to test the validity of the experimental data using Eq. 13, 14 and 15. The regression coefficients obtained for the integral rate expressions were calculated. The values of coefficient of determination for these integral rate expressions (film diffusion, chemical reaction and product-layer-diffusion control) were compared.

In the calculations, it was found that the best value of regression coefficient promising the rate expression was for fluid layer control and its value was calculated as 0.9936. From the results of the statistical

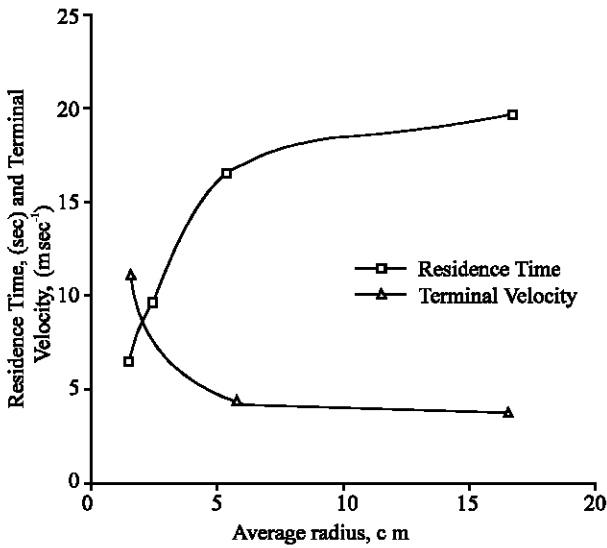


Fig. 2: Effect of particle size on residence time and terminal velocity in the leaching process

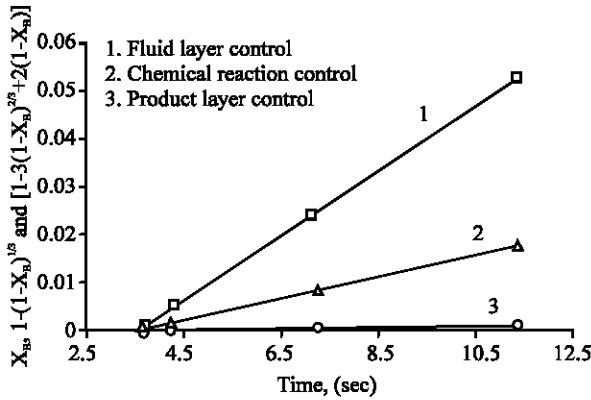


Fig. 3: Effect of reaction time on X_B , $1-(1-X_B)^{1/3}$ and $[1-3(1-X_B)^{2/3}+2(1-X_B)]$

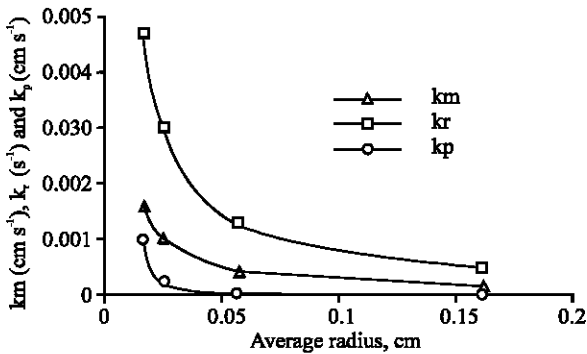


Fig. 4: Effect of particle size on mass transfer coefficients and reaction rate constant in the selective leaching of calcareous material

analyses, it was found that the selective leaching of calcareous material in low grade phosphate rock in phosphoric acid was controlled by the fluid layer around the unreacted shrinking core of the particle and the integral rate expression was determined to obey the following rate equation:

$$[X_B] = kt \quad (16)$$

CONCLUSIONS

- The selective leaching of calcareous material from a low grade calcareous phosphate rock depends on the kinetics of the chemical reaction involved in the leaching process. The results indicate that the residence time of the calcareous material in the continuous phase decreases as the particle size is increased. Depending on the residence time, the terminal velocity of the particle is increased as the particle size increases (Fig. 2). On the other hand, the fractional conversion decreases with an increase in the particle size (Table 1).
- The statistical analysis results indicate that the selective leaching of calcareous material in low grade phosphate rock is controlled by the fluid layer around the shrinking core of the particle. The results also show that the value of mass transfer coefficient for the fluid layer control appreciably increases with an increase in particle size. However, the value of reaction rate constant does not appear to be a strong function of the particle size as the change has been found very small. However, in the present case a very small change in the reaction rate constant may be due to the porous matrix of the rock particles. The efficiency of the leaching process is naturally expected to increase with a decrease in the particle size as this may tend to liberate more calcareous material from the apatite matrix.
- The economy of the leaching process mainly lies with the regeneration of the used acid in the process. But in the present study, a considerable amount of apatite may be dissolved during the complete dissolution of calcareous material; however, there would be no need to regenerate the leaching agent (phosphoric acid) as the resulting solution is expected to have mono-calcium Phosphate (MCP) which is important fertiliser along with the unreacted apatite relatively in a pure form. On the other hand, depending on the concentration of the leaching agent some of the amount of calcareous material and apatite may be resulted in the form of insoluble di-calcium phosphate (DCP) along with the unreacted

apatite. Regarding these integral rate expressions complete spherical particles of calcareous sample may be used to get more promising values of parameters in the leaching process

- The type and nature of phosphate rock particle will have its direct effect on the speed of attack of the carbonates by the leaching acid. Hard phosphate rocks may tend to be more rigid and less porous than the soft phosphates and if the calcareous material is not free in the apatite matrix, the diffusion of ionic species through the aqueous phase to the reaction sites may not favour the efficiency of the leaching process.

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