

KINETICS OF DISSOLUTION OF PHOSPHORITE IN ACID MIXTURES

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ABSTRACT. The kinetics of dissolution of a Nigerian phosphorite in mixed aqueous solutions of sulphuric and hydrochloric acids was investigated at temperatures of 60 to 90 °C. Some relevant operating variables affecting the rate of dissolution of phosphate value have been determined. Analysis of data with a familiar shrinking core model indicates that the diffusion through a permeable product layer is the rate controlling step of the dissolution process. The apparent activation energy for the phosphate dissolution was evaluated and results discussed.

INTRODUCTION

Heterogeneous reactions between solid inorganic minerals and aqueous solutions are of theoretical and practical interest. There are several reports [1-11] on the dissolution of phosphates in single aqueous acid solutions; hitherto only a few quantitative studies [12-14] have been conducted in acid mixtures. Hence, there is still a lack of essential information on the kinetics and mechanism of phosphate dissolution in aqueous solutions containing more than one acid.

Quite a number of wet chemical methods of processing phosphate ores into wet-process phosphoric acid and simple superphosphate fertilizer are known. Of the methods, the one involving the use of sulphuric acid as the acidulant is the most popular; various processes commonly employed are classified as anhydrite (CaSO_4), hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$), and dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), depending upon the nature of the calcium sulphate reaction product formed [15]. The slow reaction kinetics associated with the sulphuric acid method has been attributed [16] to the formation of calcium sulphate which blocks access of the acid to mineral grains.

Pretreatment enhances the efficiency of decomposition of phosphorites with mineral acids [17-20]. In these methods, the ore is subjected to physical treatments such as floatation, classification, wet disintegration, and roasting, prior to acidulation. The resulting decarbonated and enriched concentrates are suitable for the manufacture of highly concentrated wet-process phosphoric acid and phosphatic fertilizers [18,20].

This study investigates the kinetics of dissolution of phosphorite in aqueous solutions of sulphuric and hydrochloric acid mixtures. The particular phosphorite from the deposits near Ifo junction in Ogun state Nigeria constitutes a large part of the nation's phosphate resources. The kinetics of dissolution of the phosphorite in hydrochloric acid was previously [21,22] investigated.

Since it is important to understand the mechanism and to know the rate controlling step of the dissolution process, the kinetic model for the dissolution of fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) which is the major constituent mineral in the phosphorite has been investigated.

EXPERIMENTAL

Materials. The phosphorite sample used in this study was provided by the Geological Survey at Abeokuta Nigeria. The ore was finely pulverized in a ball mill and screened to produce the -53 μm particle size fraction of which the chemical analysis is given in Table 1. X-ray diffraction analysis of this fraction indicated fluorapatite ($\text{Ca}_5(\text{PO}_4)_3\text{F}$) as the major constituent mineral in it. Besides calcite (CaCO_3), dolomite ($\text{Ca.Mg}(\text{CO}_3)_2$) and quartz (SiO_2) were also detected as minor components.

Table 1. Chemical analysis of phosphorite sample.

Constituent	Content (w/w %)
P_2O_5	33.1
CaO	41.6
MgO	0.7
Al_2O_3	1.8
Fe_2O_3	1.6
SiO_2	6.2
MnO	0.3
K_2O	0.2
Na_2O	0.2
H_2O	3.9
F ⁻	4.4
CO_3^{2-}	3.8

Reagents. All chemicals used were of analytical grade. Deionized water was used for the preparation of all solutions. In this study, taking into consideration the strong exothermic reaction between sulphuric acid and phosphorite [23], the test solutions were 5.5 M H_2SO_4 and 2.4 M HCl solutions.

Equipment. A Pyrex flask (200 mL capacity with three necks) fitted with a condenser, a mechanical stirrer and a thermometer was used as the reaction vessel. The flask was heated with a thermostatically controlled isomantle.

An atomic absorption spectrophotometer (Buck Model 200) was used for the metal analyses. A powder X-ray diffractometer (Phillips model 12045 B4/3) was used for the mineralogical analysis.

Analytical methods. Chemical analysis of the sample and the products was carried out using standard procedures [24,25]. X-ray diffraction analysis of the sample and products was carried out according to the procedure of Klug and Alexander [26].

Measurement of dissolution kinetics. For each run, 100 mL of test solution was transferred into the reactor and brought to the required temperature (± 1 °C). Phosphorite (2 g) was added to the solution and the contents were well agitated. Samples of 2 mL were withdrawn at appropriate times during a run and analyzed colorimetrically for phosphate content by the vanado-molybdate method. This determination measures the extent of dissolution of the fluorapatite in the phosphorite.

RESULTS AND DISCUSSION

The effect of hydrochloric acid on the dissolution of fluorapatite by sulphuric acid was studied at various H_2SO_4 :HCl volume ratios ranging from 100 to 0 volume % of the H_2SO_4 . The experiments were carried out for 30 min at 60°C and at 500 rpm of which the results are presented in Figure 1. It is clear from this figure that replacing part of the sulphuric acid with hydrochloric acid increases dissolution of the fluorapatite in the phosphorite ore up to a volume ratio of 50% of H_2SO_4 after which it tapers off. On the basis of the data, the 50:50 volume ratio was used for subsequent experiments.

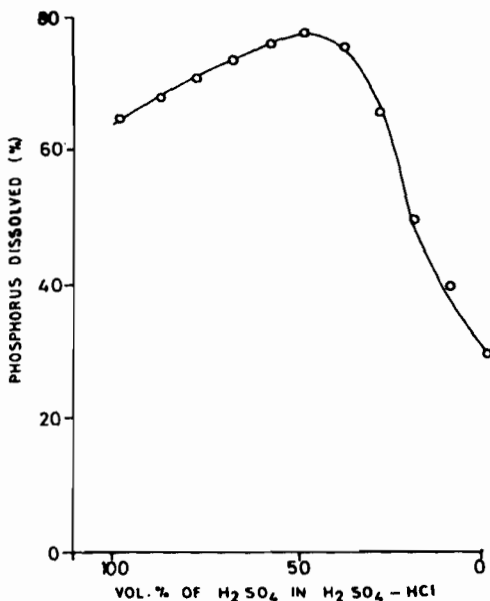


Figure 1. Effect of HCl on phosphate dissolution in H_2SO_4 solution (60°C , 30 min., 500 rpm).

The effect of stirring speed on the dissolution of fluorapatite was investigated in the acid mixture and in sulphuric acid alone at 60°C . The stirring speed was varied from 100 to 500 rpm and the results in Figure 2 indicate the dependence of the rate on stirring speed in both solution systems. This suggests that a single leaching mechanism is probably in operation in both. Indeed only diffusion controlled processes are affected by the stirring speed [27].

Figures 3a and 3b show the effect of temperature on the dissolution of fluorapatite in H_2SO_4 and in H_2SO_4 -HCl mixture, respectively. Still keeping the stirring speed at 500 rpm, the reaction temperature was varied from 60 to 90°C and the rate increased with increase in temperature. It is interesting to note that the dissolution pattern in both solution systems is identical. However, the heterogeneous reaction occurred at a relatively faster rate in the acid mixture than in the sulphuric acid alone. In both cases, best results were obtained at 90°C giving about 92% and 79% phosphate dissolution in the acid mixture and in the sulphuric acid alone, respectively.

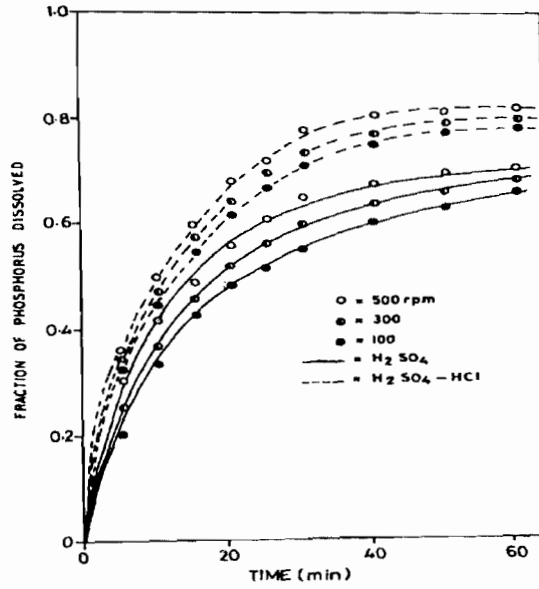


Figure 2. Effect of stirring speed on phosphate dissolution in H_2SO_4 and H_2SO_4-HCl solutions at $60^\circ C$.

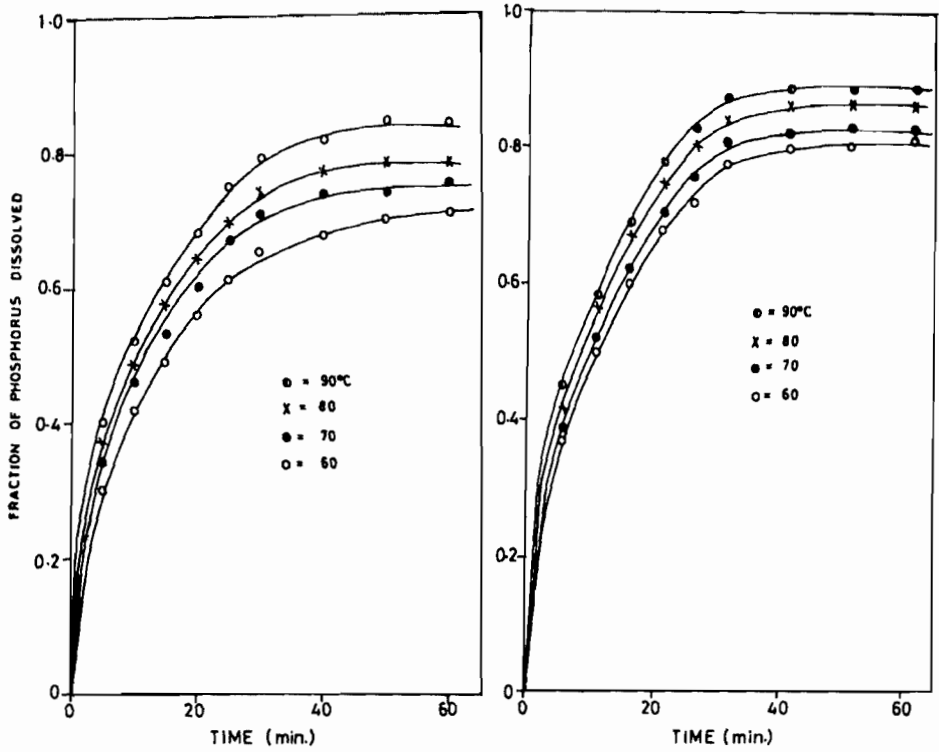
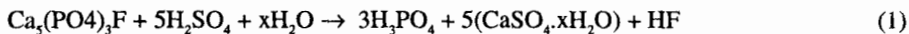


Figure 3. Effect of temperature on phosphate dissolution ($60^\circ C$, 500 rpm). (a) H_2SO_4 solution (b) H_2SO_4-HCl solution.

The reaction between fluorapatite and sulphuric acid can be represented by equation (1) and with the sulphuric-hydrochloric acid mixture by equation (2):



It can be seen that a feature common to both reactions above is the formation of calcium sulphate which tends to coat the mineral surface. This product has been found [16,28] to impede access of the mineral to further acid attack thus reducing the reaction rate. The extent to which the rate is affected depends on the nature of the calcium sulphate formed of which three types have been identified [15]: anhydrite, hemihydrate, and dihydrate. The effect of calcium sulphate on the reaction rate is in the order: anhydrite > hemihydrate > dihydrate [4]. However, in this study, X-ray diffraction confirmed that only the dihydrate was formed in both reactions (1) and (2). This probably is because the dissolution was carried out with dilute sulphuric acid solution and at temperatures below 100 °C. If the temperature is higher than 100 °C, hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and anhydrite (CaSO_4) are formed which are difficult to filter [23]. Also in concentrated sulphuric acid solution (>80%) recrystallization of the hemihydrate to the anhydrite occurs [29] according to the reaction:



But since the same type of calcium sulphate was formed in both reactions (1) and (2), therefore the variation in the reaction rates cannot be attributed to the type/nature of the calcium sulphate formed.

An important factor that influences the rate of heterogeneous reactions is the exposed surface area of the dissolving mineral [30], in this case fluorapatite. The more the exposed surface area, the more rapidly will the reaction occur. It therefore follows that the exposed area on the fluorapatite surface will depend largely on the amount of calcium sulphate formed. It can be observed from equations (1) and (2) which involve sulphuric acid alone and sulphuric-hydrochloric acid mixture, respectively, that the number of moles of calcium sulphate formed are different. In other words, reaction (2) should occur at a relatively faster rate than (1) because the mineral surface is more exposed in the former. In order to confirm this, the solid reaction products obtained in H_2SO_4 and H_2SO_4 -HCl solutions were analyzed for sulphate which indirectly quantifies the calcium sulphate formed. Results of the chemical analysis showed that the sulphate content of the solid reaction product of the acid mixture is about 76% that of the sulphuric acid alone. This probably explains the observed variation in phosphate dissolution rate in both solution systems.

In order to see whether reactions (1) and (2) proceed by the same or different mechanism, two previously established shrinking ore models were used, expressed by equations (4) and (5) [31,32]:

$$1 - 2/3a(1-a)^{2/3} = k_1 t \quad (4)$$

$$1 - (1-a)^{1/3} = k_2 t \quad (5)$$

where a is the fraction of phosphate dissolved at time t , k_1 and k_2 are the overall rate constants. Equation (4) is based on the assumption that the rate-controlling step is the diffusion through a permeable product layer and (5) is based on the surface chemical reaction step as the rate

controlling step. Fitting of the experimental data to both kinetic equations indicated that only equation (4) gave the best straight lines as presented in Figures 4a and 4b for dissolution in sulphuric acid alone and in the acid mixture, respectively. This confirms the initial assertion from the stirring speed experiments that a single reaction mechanism is possibly operating in both solution systems. Moreover, the results show that addition of hydrochloric acid to sulphuric acid only alters the rate but not the mechanism of the dissolution process.

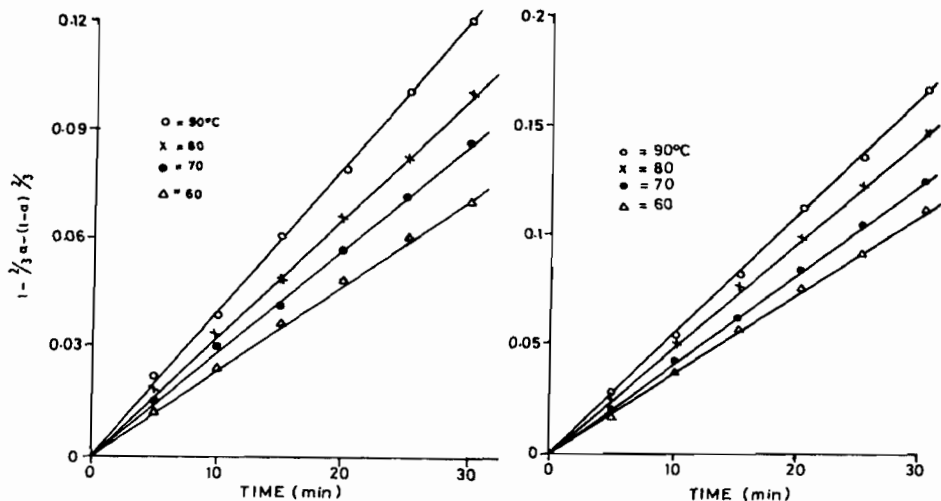


Figure 4. Plot of $1 - \frac{2}{3}a - (1-a)^{2/3}$ vs. time at various temperatures for phosphate dissolution (a) H_2SO_4 solution (b) H_2SO_4 - HCl solution.

Figure 5 shows the Arrhenius plot for fluorapatite dissolution, the rate constant k_1 being calculated from the slopes of the lines in Figures 4a and 4b. The apparent activation energy for the dissolution of fluorapatite in sulphuric acid alone was 17.60 kJmol^{-1} and 13.25 kJmol^{-1} in the acid mixture. Both values are typical of diffusion-controlled dissolution processes [33]. However, the different values further account for the observed variation in reaction rates in both solution systems.

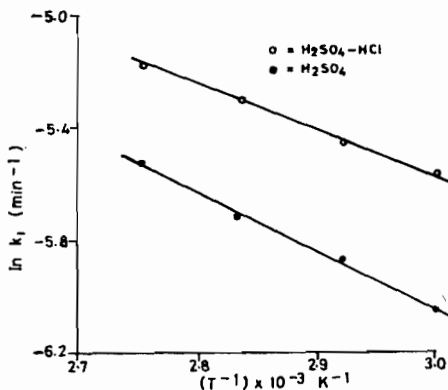


Figure 5. Arrhenius plot for phosphate dissolution in H_2SO_4 and H_2SO_4 - HCl solutions.

CONCLUSION

It has been established in this study that addition of hydrochloric acid enhances the dissolution of fluorapatite by sulphuric acid. The added acid only influences the rate but does not alter the mechanism of dissolution which is the diffusion through a permeable product layer. Besides, it has been found that the consumption of sulphuric acid used as an acidulant in the industrial production of wet-process phosphoric acid and simple superphosphate fertilizer from phosphorite can be substantially reduced by replacing a portion of the acid with hydrochloric acid. Although, the economic details of the "sulphuric acid-hydrochloric acid process" have not been worked out, since this is beyond the scope of the present study, however, the results of the various physico-chemical parameters of commercial significance obtained in this study indicate that the "mixed acid process" apparently has greater economic and industrial potentials than the usual industrial operation (the "sulphuric acid process") which is still widely used for the manufacture of both agro-industrial products. In a related investigation [12], it has been shown that the decomposition of phosphorite ore by hydrochloric acid was enhanced by partially replacing the acid with sulphuric acid.

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