DISSOLUTION OF PHOSPHORITE IN DILUTE HYDROCHLORIC ACID SOLUTION

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A powdered phosphorite ore was leached in dilute solutions (0.14 - 3.15 mol l^{-1}) of hydrochloric acid at temperature ranging from 50 to 70°. Both phosphorus and calcium were extracted in a nearly stoichiometric ratio. The rate of extraction of both elements was controlled by diffusion of the reagent through a residual layer of non-soluble components of the phosphorite, and not by surface chemical reaction. The apparent activation energies were evaluated for both elements and results given.

Key words: Dissolution, Phosphorite, Acid.

Introduction

The "wet process" is the more common of the two methods employed in the manufacture or phosphoric acid. The method involves the acidulation of the ore with mineral acids such as hydrochloric, sulphuric, and nitric. The rate at which a particular rock is decomposed by any of the acids varies with the origin of the rock [1]. However, the rate of decomposition is largest in both hydrochloric and nitric acids than in other acids [2].

The Kinetics of the leaching of phosphorite with acids other than hydrochloric acid has been reported [3-5]. There is, however, a report on the leaching of phosphorite with strong solutions of hydrochloric acid at temperatures below 50° [6]. It is well established that the rate controlling step of leaching reactions of ores is principally influenced by the leachant concentration and the reaction temperature. Other parameters such as agitation and particle size also affect the mechanism of the leaching reactions, but to a lesser extent.

The object of this paper, therefore, is to obtain essential information that are still lacking in the Kinetics of the dissolution behaviour of phosphorus and calcium from phosphorite in dilute hydrochloric acid. The two main reactions occurring between phosphorite and hydrochloric acid are given below:

$$Ca_5(PO_4)_3 F + 10HCl \longrightarrow 5CaCl_2 + 3H_3PO_4 + HF$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

Both reactions are quantitative. The effects of agitation and particle size on the reactions were also considered.

Experimental

Materials. The phosphorite ore used in this study was provided by the Geological Surveys of Nigeria. The ore was

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curshed, then ground in a ball mill, and screened to produce three different particle size fractions: 250 - 425, 100 - 250 and 61 - 100 µm. The chemical analysis of the fractions are given in Table 1.

Reagents. All the chemcials used were of analytical grade. Concentrated hydrochloric acid (36%, 1.18 g/ml at 20°) was diluted to the desired concentrations with distilled water.

Apparatus. A three-necked flask (250 ml capacity), fitted with a condenser, a water-sealed stirring rod, and a stopper, was used as the reactor for these studies. A water bath thermostated to ± 0.1° was used to control the reaction temperature.

Kinetics measurements. For each experiment, 2g of ore was dispersed in 200 ml of acid solution of a chosen strength and agitated at about 200 min^{-1}. 5 ml aliquots of sample were drawn from the reactor at regular intervals and analyzed for phosphours and calcium only.

Chemical analysis of the leachate. Phosphorus was determined photometrically by the vanado - molybdate method [7], and calcium with an atomic absorption spectrophotometer (Perkin-Elmer Model-403).

Results and Discussion

The extraction of phosphorus and calcium at various HCl concentration at 50° is illustrated in Fig. 1. The extraction of both elements in 2.10 and 3.15 mol l^{-1} rose initially with a faster rate up to 2 hr. after which it increased gradually but relatively slower. The extraction in 0.14 mol l^{-1}, however, was apparently very small and slow. Furthermore, it may be observed from Fig.1. that both elements followed nearly the same pattern of disssolution in all the acid solution. At any point in time, the amount of phosphours extracted in the HCl solution was slightly less than that of calcium, but the difference was not more than 2%. From the results, it was possible

to extract about 90% of either elements in 3.15 mol 1^{-1} HCl solution within 3 hr. at 50°.

The phosphorite was leached in 0.14 mol 1^{-1} HCl solution at temperatures of 50, 60 and 70° and the results are shown in Fig.2. The extraction of phosphorus and calcium, both, showed, a gradual but slow increase with increasing temperature.

The effect of agitation on leaching the ore in 0.14 mol 1^{-1} HCl solution at 50° is shown in Fig.3. Both phosphours and calcium extraction increased with increasing agitation.

The amount of phosphorus and calcium extracted vs. time plots for different particle size fractions in 0.14 mol 1^{-1} HCl solution and at 50° is shown in Fig.4. As expected, extraction of both elements increased with decreasing particle size. It is evident from the results obtained that both agitation and particle size have some effect on the fraction reacted but neither of them is as important as the temperature and concentration effects.

There are two well-known equations that could be applied to study the rate of heterogeneous reactions [8]. For a chemically controlled reaction the rate equation for spherical partilces may be expressed as:

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

However, if the rate of chemical disssolution is very fast, the kinetics of leching usually obey a three dimensional diffusion equation of the following type:

$$1 + 2(1 - a) - 3(1 - a)^{2/3} = k_2 t \quad .... (2)$$

where 'a' is the fraction reacted at time t, k_1 and k_2 are the overall rate constants.

TABLE 1. CHEMICAL COMPOSITION OF PHOSPHORITE FRACTIONS.

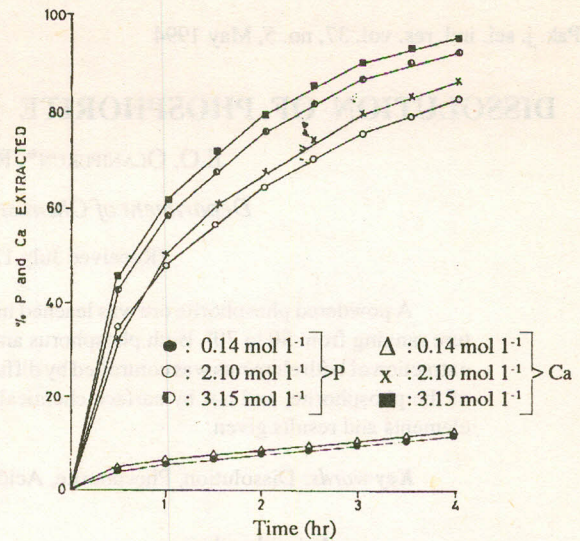| Content	Size fraction		
(%)	250-425 μm	100-250 μm	61 - 100 μm
P_2O_5	32.60	32.74	32.95
CaO	35.49	35.92	36.12
MgO	0.50	0.42	0.34
Al_2O_3	1.48	1.37	1.30
Fe_2O_3	1.50	1.43	1.54
SiO_2	5.89	6.12	6.36
MnO	0.20	0.24	0.29
K_2O	0.62	0.51	0.45
Na_2O	0.26	0.19	0.14
H_2O	3.89	3.72	3.60
F	4.08	4.23	4.42
CO_3	3.78	3.52	3.35
Cl	3.69	3.55	3.28
SO_4	2.10	2.25	2.17

Fig. 1. Change in the amounts of phosphorus and calcium dissolved at various HCl concentrations at 50°.
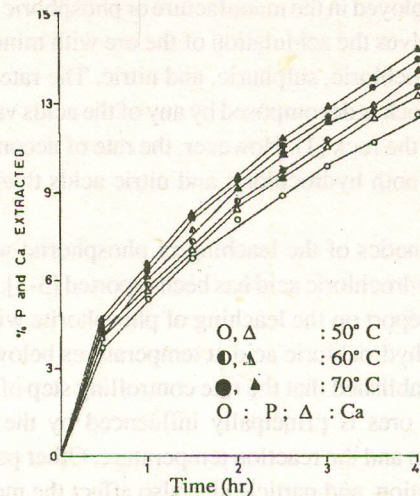

Fig.2. Change in the amounts of phosphorus and calcium dissolved at various temperatures in 0.14 mol. 1^{-1} HCl solution.
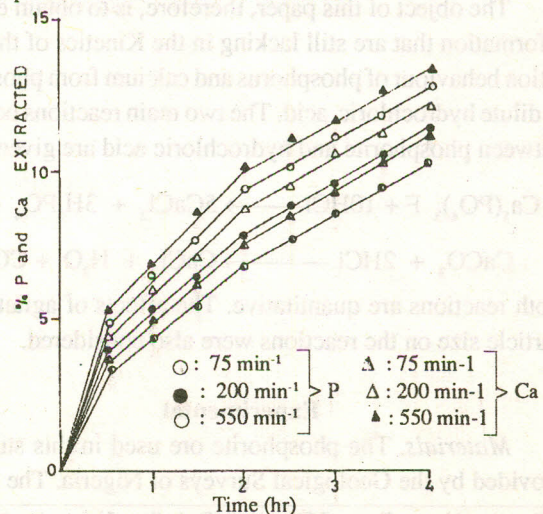

Fig.3. Change in the amounts of phosphorus and calcium dissolved in 0.14 mol. 1^{-1} HCl solution agitated at various speeds at 50°.

Plots of the above Kinetic equations as functions of time were examined for leaching the ore in 0.14 mol 1⁻¹ HCl solution at temperatures of 50, 60 and 70°. Plots of the function 1 - (1 a)^{1/3} vs. time are shown in Fig.5. The dissolution of both phosphorus and calcium did not fit well to eq. 1, as the plots gave no perfectly straight lines. This shows that the leaching of phosphours and calcium in the acid solution at the reaction

temperatures was not by a chemically controlled reaction mechanism. Similarly, leaching data from these studies were treated and it could be observed from Fig. 6 that the dissolution rate of both elements was well expressed by eq. 2, which is based on a diffusional controlled mechanism.

The slope of each of the lines in Fig. 6 is k_2 and these k_2 were plotted against 1/T in Fig. 7 (Arrhenius relationship).
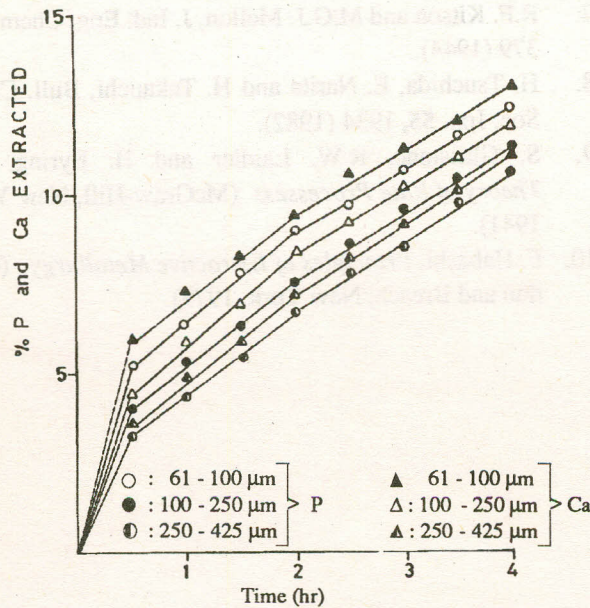

Fig.4.Change in the amounts of phosphorus and calcium dissolved in 0.14 mol. 1⁻¹ HCl solution at 50° using fractions of different particle sizes.
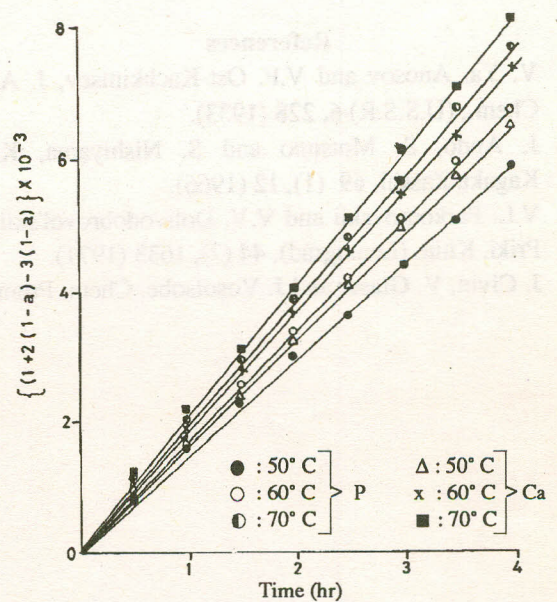

Fig.6. A plot for the function $1 + 2 (1 - a) - 3(1 - a)^{2/3}$ vs. time for different temperatures.
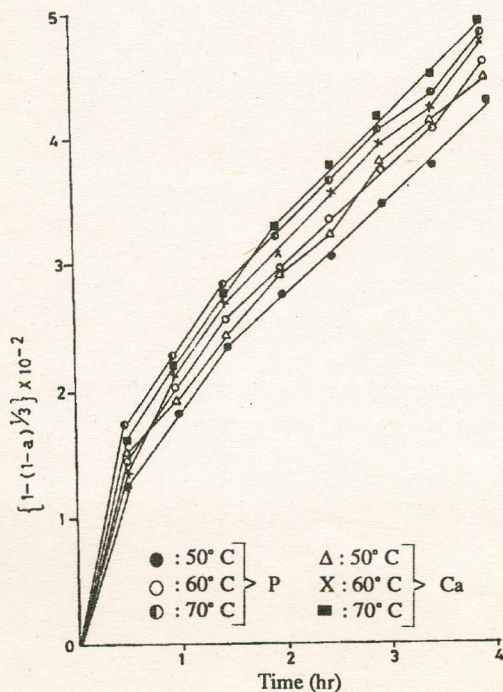

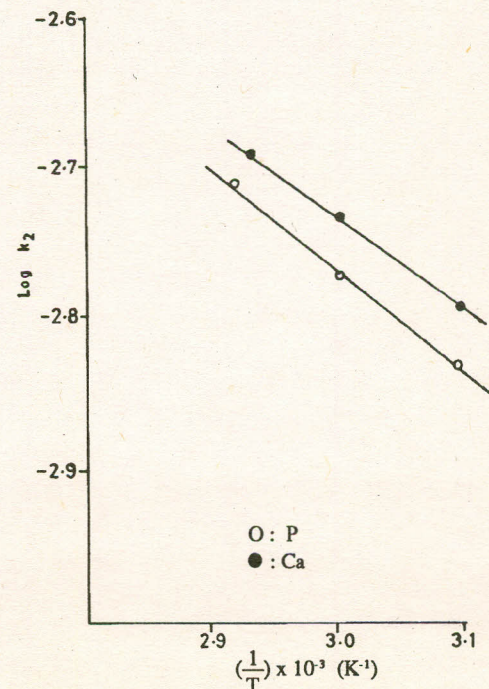Fig.5. A plot for the function 1- (1 - a)^{1/3} vs. time for different temperatures.

Fig.7.A plot of log k_2 vs. 1/T.

The apparent activation energies were calculated from the plots and are 12.69 kJ mol^{-1} for phosphorus and 10.58 kJ mol.$^{-1}$ for calcium. These values are evident of a diffusional controlled-mechanism, since they fall within the range for transport controlled mechanisms [9]. The rate controlling step may, however, change from diffusion control at low acid concentrations to chemical control at high acid concentrations [10].

References

1. V. Ya. Anosov and V.F. Ost-Kachkintsev, J. Appld. Chem., (U.S.S.R) 6, 228 (1933).

2. J. Ando, S. Motsuno and S. Nishiyama, Kogyo Kagaku Zasshi, 69 (1), 12 (1966).

3. V.L. Parkomovskii and V.V. Dolivodobrovol'skii, Zh. Priki. Khin. (Leningrad), 44 (7), 1633 (1971).

4. J. Civin, V. Glaser and J. Vosolsobe, Chem. Prum., 28 (6), 289 (1978).

5. G. Parlea, M. Parlea and A. Iovi, Bul. Stiint. Tech. Inst. Politekh. Traian Vuia Timisoara, Ser. Chem., 24 (1), 73 (1979).

6. M. N. Nabiev, S.B. Mamadzhanov, V.T. Akbarova, A. M. Amirova and M.R. Adylova, Uzb. Khim. Zh., 6, 3 (1987).

7. R.F. Kitson and M.G.J. Mellon, J. Ind. Eng. Chem., 16, 379 (1944).

8. H. Tsuchida, E. Narita and H. Takauchi, Bull. Chem. Soc. Jpn. 55, 1934 (1982).

9. S. Glasstone, R.W. Laidler and H. Eyring, The Theory of Rate Processess (McGraw-Hill, New York, 1941).

10. F. Habashi, Principles of Extractive Metallurgy (Gordon and Breach, New York, 1979).