REACTION KINETICS FOR THE LEACHING OF IMPURITIES FROM ROCK PHOSPHATE

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This paper presents a kinetic study of the leaching of iron and magnesium impurities from rock phosphate with hydrochloric acid. The effects of particle size, stirring speed, hydrochloric acid concentration and reaction temperature on the leaching rate were investigated. The data fitted a shrinking core model equation with reaction rate controlled by a diffusion mechanism. The rate was related to temperature by the Arrhenius relationship with the apparent activation energy being 18. 7kJ mol^{-1} for iron and 14.3kJ mol^{-1} for magnesium. The rate was linearly dependent on hydrochloric acid concentration and inversely proportional to the average diameter of the particles. The leaching rate of magnesium was relatively faster than that of iron but both exhibited similar leaching pattern under the same reaction conditions.

Key words: Impurities, Kinetics, Leaching, Rock phosphate.

Introduction

Phosphorous is the eleventh abundant element in the earth crust. All its known terrestrial minerals are orthophosphates though the reduced phosphide mineral schriebersite (Fe, Ni)$_3$P occurs in most iron meteorites. Some two hundred crystalline phosphate minerals have been described, but by far the major amount of phosphorus occurs in a single mineral family, the apatites and these are the only ones of industrial importance. Apatites have the idealized general formula Ca$_{10}$ (PO$_4$)$_6$×$_2$, and common members are fluorapatite, chlorapatite and hydroxylapatite. In addition, there are large deposits of amorphous phosphate rock phosphorite widely spread throughout the world and itsreserves are adequate for several centuries (Van Wazer 1961).

The phosphate rock deposit located near Ifo junction in Nigeria approximates in composition to fluorapatite, [C$_{a5}$ (PO$_4$)$_3$F], and in addition, there are occurrences of calcite, dolomite, magnesite, glauconite, as associated minerals. The deposit was estimated to contain several million tonnes of phosphate rock. Although commercial exploitation of the deposit is yet to commence, preliminary investigation, however, revealed the phosphate rock as a potential source of phosphorus, phosphoric acid and phosphatic fertilizers (Federal Ministry of Mines and power, 1987).

Phosphoric acid is manufactured on a large scale in a variety of concentrations and purities, and its production is still increasing steadily in most countries, especially for fertilizer manufacture, Thermal acid is about three times as expensive as wet acid and is being increasingly susbtitute by wet process acid in all but the applications most demanding (Van Wazer 1961).

The wet process of manufacturing phosphoric acid involves treating rock phosphate with sulphuric acid and the processes commonly employed are classified as dihydrate hemihydrate, and anhydrite, depending on the nature of calcium sulphate formed (Ishaque and Ahmad 1982). In addition to sulphuric acid, other mineral acids such as hydrochloric and nitric have also been used for decomposing rock phosphate (Parlea *et al* 1979; Nabiev *et al* 1987). In spite of the fact that the wet process is easy, simple and cheap to run, the method, however, has two major shortcomings i. e. (i) the product acid is usually coloured (yellow/green) and (ii) a defoamer is required to suppress the excessive foaming produced during acidulation. The former problem has been attributed to metallic impurities, especially iron while the latter is caused by carbonate minerals, notably magnesite and dolomite.
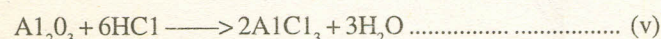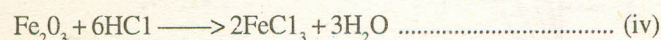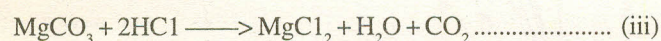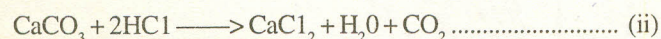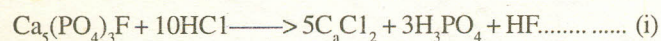
Although a number of publications (Ruiz *et al,* 1987; Nurugaiyan *et al* 1988; Kabbaj 1989) have appeared on the removal of metallic and non-metallic impurities from phosphoric acid by solvent extraction and ion-exchange techniques, the leaching mechanism of these impurities is yet to be reported. In fact, there is no information in literature on the kinetics of leaching of chemical elements other than phosphorus and calcium from phosphate minerals.

In this paper, the kinetics of iron and magnesium leaching from rock phosphate by hydrochloric acid has been studied with a view to providing essential information on their reaction mechanism. Hydrochloric acid is chosen as the preferred

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leaching agent because of the large decomposition of rock phosphate in it. Moreover, the separation of metal chlorides through solvent extraction is easier from hydrochloric acid than from other acid medium (De *et al* 1970; Sekine and Hasegawa 1977).

The main reactions occuring between rock phosphate and hydrochloric acid include:

$$Ca_5(PO_4)_3F + 10HCl \longrightarrow 5C_aCl_2 + 3H_3PO_4 + HF \text{.............} \quad (i)$$

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \text{..................} \quad (ii)$$

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2 \text{................} \quad (iii)$$

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O \text{....................} \quad (iv)$$

$$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O \text{.................} \quad (v)$$

All the above reactions are quantitative and proceed rapidly. The kinetics of reactions (i) and (ii) have been studied in a previous paper (Olanipekun et al 1994). However, the kinetics of reactions (iii) and (iv) are of concern in this study.

Experimental

Materials. The rock phosphate used in this study was collected from the deposit near Ifo junction in Nigeria. It was ground and screened to produce three different size fractions: 61 to 100 μm, 100 to 180 μm, and 180 to 355 μm. The chemical composition of the rock phosphate is given in Table 1 while the initial amounts of iron and magnesium in the three fractions are presented in Table 2.

Table 1
Chemical composition of rock phosphate

Constituent	Content (%)
CaO	40.08
P_2O_5	33.26
SiO_2	5.68
F^-	3.84
CO_3^{2-}	3.19
H_2O	3.08
Fe_2O_3	1.83
MgO	1.62
Al_2O_3	1.55
SO_4^{2-}	1.25
Cl^-	1.14
K_2O	0.83
Mn O	0.51
Na_2O	0.30

Table 2
Initial amounts of iron and magnesium in rock phosphate fractions

Particle size Fraction (μm)	Fe (%)	Mg (%)
61 to 100	1.28	0.93
100 to 180	1.24	0.96
180 to 355	1.22	0.98

Reagents. All the chemicals used were reagent grade. Hydrochloric acid (36% purity, d. 1.18g ml^{-1} at 20°C) was diluted with distilled water to prepare the various hydrochloric acid concentrations.

Apparatus. The reaction vessel comprised a 500ml three-necked round-bottom flask with each neck fitted with a thermometer, a stirring rod (mechanically-driven), and a water-cooled reflux condenser. The reactor was placed on an electrical mantle with a thermostat and the reaction temperature was regulated to $\pm$ 1°C.

Measurement of Reaction Kinetics. For each run, 2g of the sample was suspended in 300ml hydrochloric acid solution of a particular strength and heated to the desired temperature, with continuous stirring. In all tests except one, stirring was done at 500 rpm. 2ml aliquots of the sample solution were pipetted out from the reactor at regular time intervals and analysed for iron and magnesium using an atomic absorption spectrophotometer (Perkin-Elmer Model 403).

Results and Discussion

The effect of particle size on the leaching rate of iron and magnesium from rock phosphate was examined by running a series of experiments using the three different particle size fractions at 70°C in 3. 12M HCl solution. The results are illustrated in Fig. 1 from which an obvious relation between the reaction rate and the particle sizes can be observed. The leaching rate increased with decreasing particle size, were implies that the rate is inversely proportional to the average diameter of the particle. However, magnesium dissolution occurred at a relatively faster rate than iron dissolution in all cases, and was highest using the 61 to 100 μm fraction. On the basis of these data, subsequent experiments were performed using the 61 to 100 μm fraction. Fig 2 illustrates the effect of stirring speed on the leaching rate of iron and magnesium at 70°C in 3.12M HCl at various speeds ranging from 100 to 500rpm. The result shows an increase in reaction rate with increasing speed of rotation thus suggesting the diffusion process as the rate-controlling step of the leaching reaction.
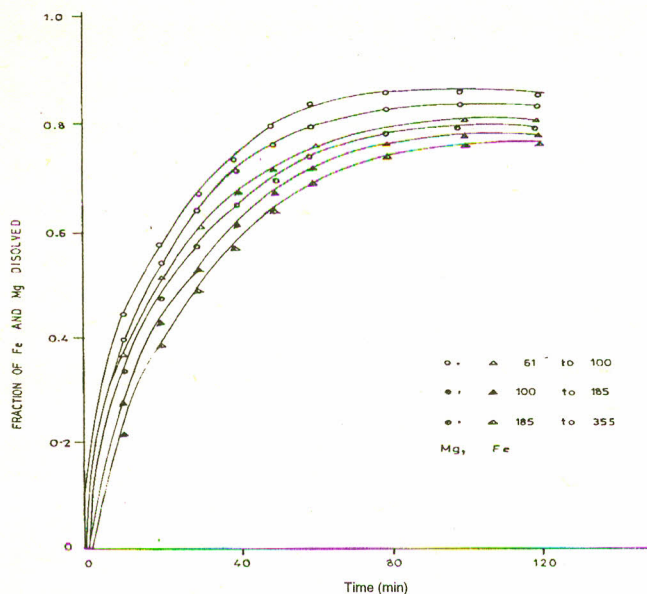
Fig 1.Effect of particle size on iron and magnesium leaching (500 rpm, 70°C, 3.12M HCl).
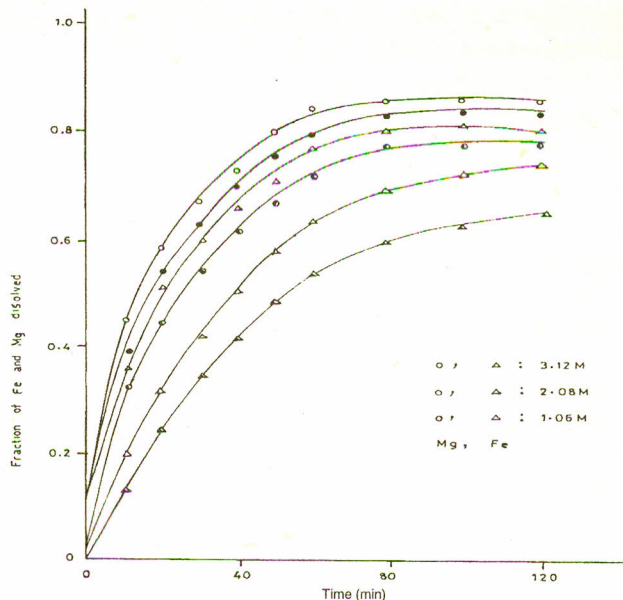

Fig. 3. Effect of HCL concentration on iron and magnesium leaching (61 to 100um, 500 rpm, 70°C).
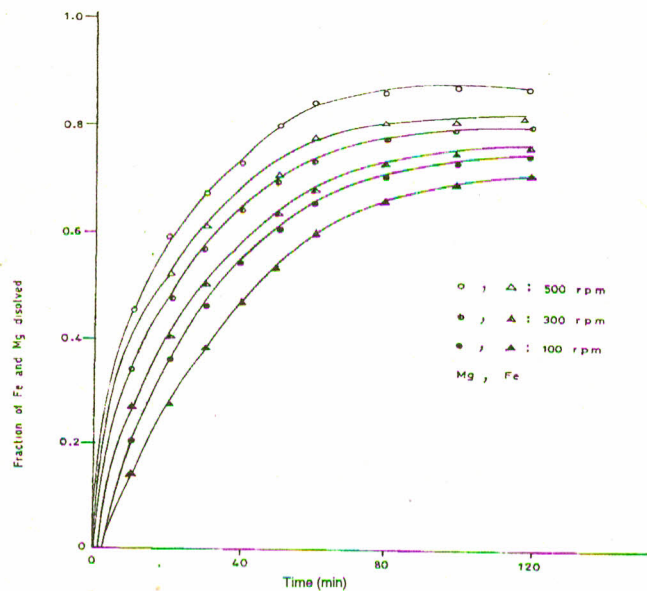

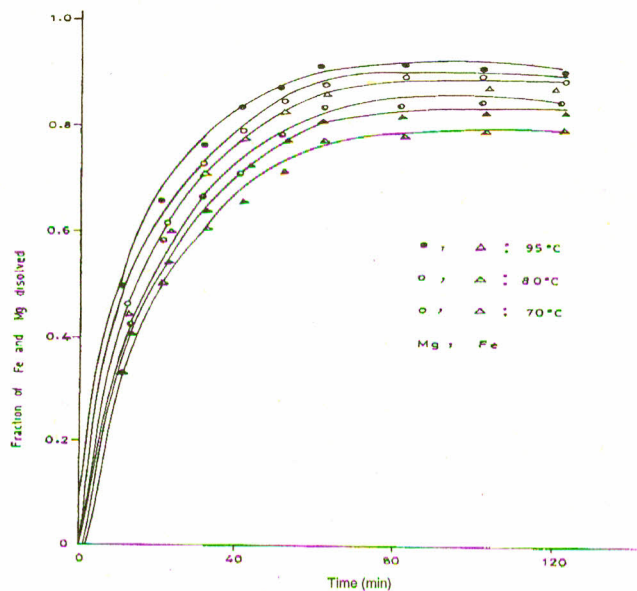Fig 2. Effect of stirring speed on iron and magnesium leaching (61 to 100 um, 70°C, 3. 12M HCl).

Fig 4.Effect of temprature on iron and magnesium leaching (61 to 100 um, 500 rpm, 3. 12M HCl).

The effect of hydrochloric acid concentration on the reaction rate was studied by leaching the rock at 70°C and the acid concentration was varied from 1.06 to 3.12M. The results in Fig. 3 show that the data followed a smooth and consistent curve over the concentration range suggesting that a single leaching mechanism was possibly operative over this range. In all cases the rate increased with increasing acid concentration and highest extraction was obtained in 3.12M solution of hydrochloric acid, which was 79.8% for iron and 86.2% for magnesium.

In order to study the effect of temperature on the reaction rate, tests were carried out in 3.12M hydrochloric acid solution at various temperatures. The data shown in Fig. 4 varied systematically with temperature ranging from 70 to 95°C and which implies that just a single mechanism was controlling the reaction rate over this temperature range. The fraction of magnesium leached at 80 and 95°C do not differ widely after 40min of leaching. However, the highest dissolution was observed at 95°C and fraction extracted was about 92% for magnesium and 88% for iron.
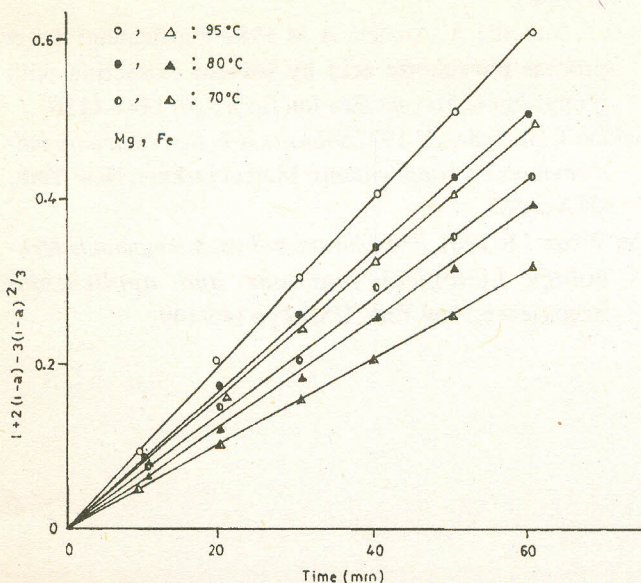
Fig 5. Plot of $1+2 (1-a)-3(1-a)^{2/3}$ versus time for iron and magnesium leaching (61 to 100um, 500 rpm, 3.12M HC1).
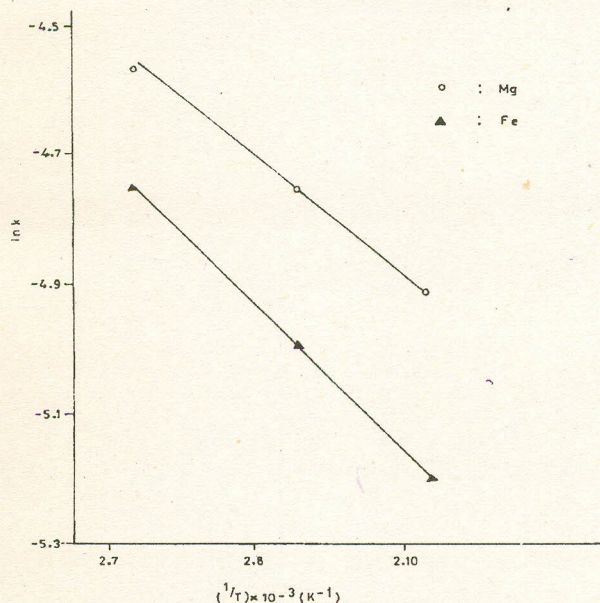

Fig 6. Arrhenius Plot, Ink Versus T^{-1} for iron and magnesium leaching (61 to 100um, 500 rpm, 3.12M HCL).

The observed effect of stirring speed on the leaching rate suggests that the rate of reactions (iii) and (iv) was perhaps diffusion - and not surface - chemically controlled mechanism. Diffusion controlled reactions usually follow the rate equation below which is based on the shrinking core model (Habashi 1979).

$$1 + 2(1 - a) - 3(1 - a)2/3 = kt \dots\dots (vi)$$

where a is the fraction of metal dissolved at time t, and k is the overall rate constant. In applying this model, the particles are assumed to be spherical in shape and the results obtained on fitting data to eqn. (vi) are shown in Fig. 5. It can be observed that there is a good linear relationship between {1 + 2 (1 - a) - 3 (1 -a) 2/3} and t which indicates the diffusion process as both possible operating mechanism for both leaching reactions in 3.12M HC1 solution at temperatures of 70 to 95°C for the first 60min of leaching.

The overall rate constant k, was calculated from the slope of the lines in Fig. 5 and plotted against the leaching temperatures according to the Arrhenius relationship. The results presented in Fig. 6 show that Ink is inversely proportional to temperature, and from this plot the apparent activation energies calculated were 18.7 kj mol^{-1} for iron and 14.2 kj mol^{-1} for magnesium. The observed high leaching rate together with the relatively low values of the activation energy (< 20 kj mol^{-1}) are indicative of a diffusion and not a chemically-controlled mechanim (Glasstone *et al*, 1941).

Conclusions

The following may be concluded from this study:

1. Over the temperature interval 70 to 95°C, the leaching of iron and magnesium occurred according to a linear rate law with associated apparent activation energies of 18.7 kj mol^{-1} and 14.2 kj mol^{-1} respectively.

2. The leaching rate was affected by the stirring speed and followed the shrinking core model rate equation for diffusion controlled reactions.

3. The rate increased with increasing temperature and hydrochloric acid concentration but decreased with increasing average diameter of the particles.

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