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KINETICS OF HYDROCHLORIC ACID LEACHING OF LATERITE

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The kinetics of the leaching of powdered laterite was studied in aqueous solutions of hydrochloric acid at temperatures of 40, 50, and 60°. The dissolution of iron was largely affected by the acid concentration, while those of aluminium and silica were not significantly affected, aluminium and silica dissolved in a nearly stoichiometric ratio with aluminium slightly more dissolved than silica. The dissolution followed a first-order kinetics with specific rate constants ranging from (3.68-18.4) x 10^{-2} hr^{-1} for iron, (1.05-5.07) x 10^{-2} hr^{-1} for aluminium and (0.69-3.26) x 10^{-2} hr^{-1} for silica. The dissolution rates were well expressed by the rate equation based on the rate-determining step of the surface chemical reaction. The apparent activation energies were 56.7 KJ mol^{-1} for iron, 65.2 KJ mol^{-1} for aluminium, and 70.8 KJ mol^{-1} for silica.

Key words: Kinetics, Leaching, Laterite.

Introduction

The growing demand of aluminium has stimulated researches toward the exploitation of other sources of alumina, other than bauxite. One of these is laterite which occurs in large deposits in various part of the world. The extraction of alumina from laterite has been investigated [1], and one of the problems associated with this procedure is the formation of an insoluble slag. Moreover, the high contents of the iron and silica in laterite usually renders it unattractive for the production of alumina.

Some studies of the leaching of aluminous minerals have been reported [2-9] but only a few reports have been presented on the kinetics of acid leaching of laterite, except for the dissolution of nickel in H_2SO_4 [10].

In this study, we investigated the leaching kinetics of powdered laterite ore in dil. HCl solutions, in order to obtain essential information on the kinetics of the dissolution behaviour of iron, aluminium and silica in HCl solutions which is still lacking in literature.

Materials and Methods

Materials. The laterite sample used in this study was collected from Ilaro district, Nigeria. The ore was crushed in a steel Ellis mortar and powdered in an agate mortar. The fraction containing particles between 150 and 350 meshes was collected, washed with water and dried at 110° for about 3 hrs. The chemical composition of the laterite sample is given in Table 1.

Reagents. All the chemicals used were of analytical grade. Conc. HCl was diluted to the desired concentrations with distilled water.

Apparatus. The reaction vessel was a 100 ml three necked flask, equipped with a condenser, a water-sealed stirring rod, and a nitrogen- introducing tube. The container was placed in a water bath thermostated at 40-60° to 0.1°

Measurements reaction kinetics. About 1gm of the sample powder was suspended in 80 ml of acid solution in the reaction vessel, into which nitrogen gas had previously been introduced continuously. The mixture was then stirred at about 500 rpm; preliminary experiments over the stirring range 200-1400 rpm did not affect the rate of dissolution of the sample powder. 5ml aliquots of the supernatant solution was pipetted from the flask at regular time intervals, after the residual solids had settled down.

Chemical analysis of the reaction solution. The silica was determined photometrically by the yellow silicomolybdate method [11]. Both iron and aluminium were determined using Perkin-Elmer 403 atomic absorption spectrophotometer.

Results and Discussion

The amounts of iron, aluminium and silica, dissolved from the powdered laterite at different times are shown in Fig. 1. This figure shows that the dissolution of iron was strongly affected by the acid concentration, more than those of aluminium and silica in HCl solutions at the same molarity and temperature. However, the dissolution of aluminium and silica

Table 1. Chemical Composition of the Laterite.

Constituent	Content (%)
Al_2O_3	24.7
Fe_2O_3	42.5
SiO_2	19.6
TiO_2	1.3
CaO	0.5
MgO	0.9
Na_2O	0.07
K_2O	0.09
LOI	8.73

occurred in almost the same stoichiometric ratio, but that of aluminium was slightly higer. At any point in time, the amount of iron dissolved was more than five times as much as the amounts of aluminium and silica dissolved. Moreover, the total amount of these three components dissolved was lower than the weight loss of laterite. Thus, there are other components in the laterite that were also dissolved along with iron, aluminium and silica.

Three rate-determining steps have been studied in heterogeneous reactions, the diffusion in liquid film, the diffusion in residual layer, and the surface chemical reaction [12-15]. However, the diffusion in liquid film could not be rate-limiting since the dissolution rate of iron, aluminium and silica was apparently not zero-order, and was not affected by the stirring speed.

The first-order rate law is represented in logarithm terms by equation 1:

$$\log A = \log Ao - \frac{K1}{2.303} \cdot t \quad \text{.............................(1)}$$

where A is the amount of component remaining in laterite at time t, and was obtained from the difference in the amounts of components dissolved and their initial amounts Ao.

Plots of log A vs. t gave straight lines for the dissolution of iron, aluminium and silica (Fig. 2). The values of the specific rate constants as estimated from the slopes of the graphs are given in Table 2. From these values, it can be observed that the dissolution of iron occurred at a faster rate than those of aluminium and silica which did not seem to be much affected by the acid concentration as pointed out earlier. According to the studies of dissolution of titanium minerals in HCl and H_2SO_4 by Imahashi and Takamatsu [14], titanium and iron ions are transported to the solution when hydrated protons diffuse into the solid, as indicated by Sanemasa and Katsura [16].

TABLE 2. SPECIFIC RATE CONSTANTS OF THE LEACHING OF IRON, ALUMINIUM AND SILICA IN DIL. HCl SOLUTIONS AT 60°.

Concentration mol/l	$K_1 \times 10^{-2}$ Hr^{-1} Fe	Al	SiO_2
0.6	3.68	1.05	0.69
0.9	7.83	1.97	1.28
3.0	18.4	5.07	3.26

Therefore, it follows from our results that both aluminium and silica were little transported to the acid solution probably because the hydrated protons could not diffuse well into the solid. However, the large dissolution of iron in HCl has been attributed to the high complexing affinity of the chloride anion for the ferric iron [17,18].

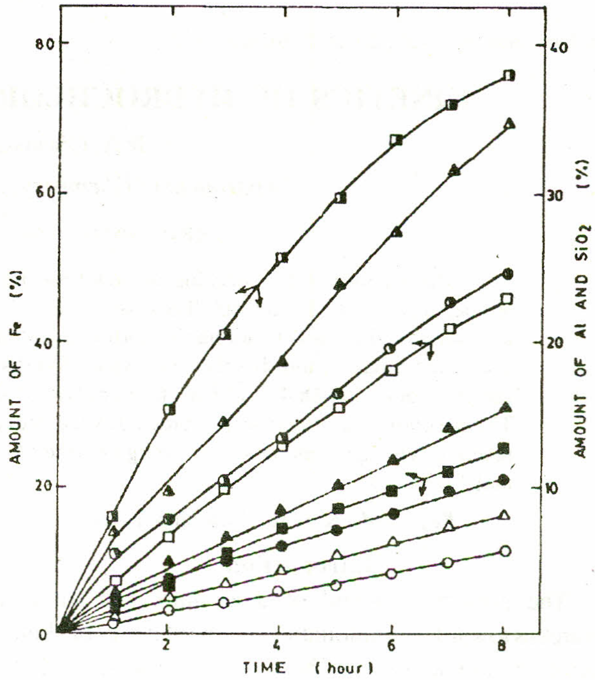

Fig. 1. Change in the amounts of aluminium, iron, and silica dissolved in HCl solution at 60°.

Al : Δ
Fe: ■ 0.6 mol/l
SiO_2: O

Al : ▲
Fe: □ 0.9 mol/l
SiO_2 : ●

Al: ◭
Fe: ◧ 3.0 mol/l
SiO_2: ◐

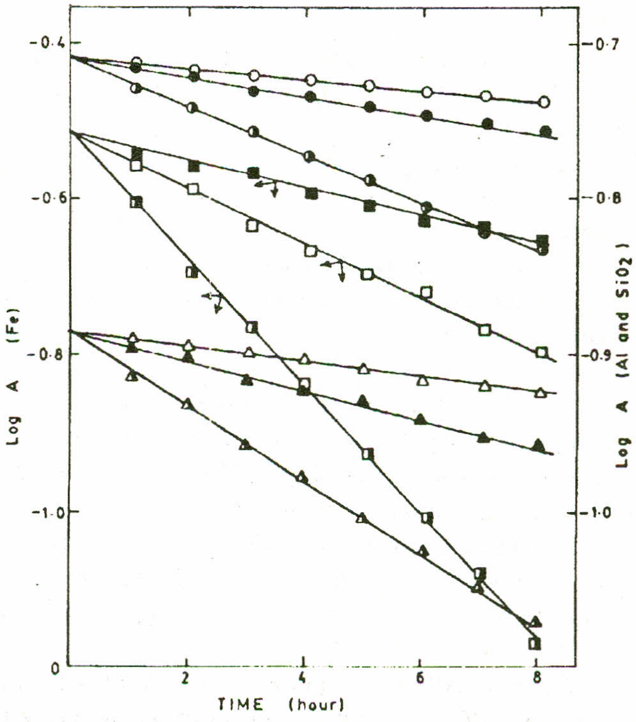

Fig. 2. First order plots of aluminium, iron and silica dissolutions in HCl solutions at 60°.

Al : Δ
Fe: ■ 0.6 mol/l
SiO_2: O

Al: ▲
Fe: □ 0.9 mol/l
SiO_2 : ●

Al: ◭
Fe: ◧ 3.0 mol/l
SiO_2: ◐

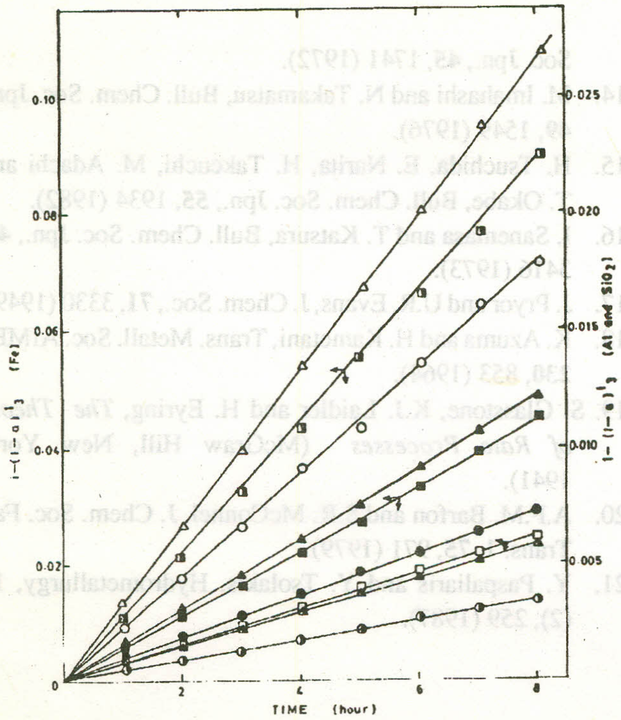

Fig. 3. Dissolution of aluminium, iron and silica in 0.6 mol/l HCl solution at 40, 50 and 60°. Plots of $1\text{-}(1\text{-}a)^{1/3}$ versus time

Al: △		Al: ▲		Al: △	
Fe: □	40°	Fe: ■	50°	Fe: ◧	60°
SiO_2: ◐		SiO_2: ●		SiO_2 : O	

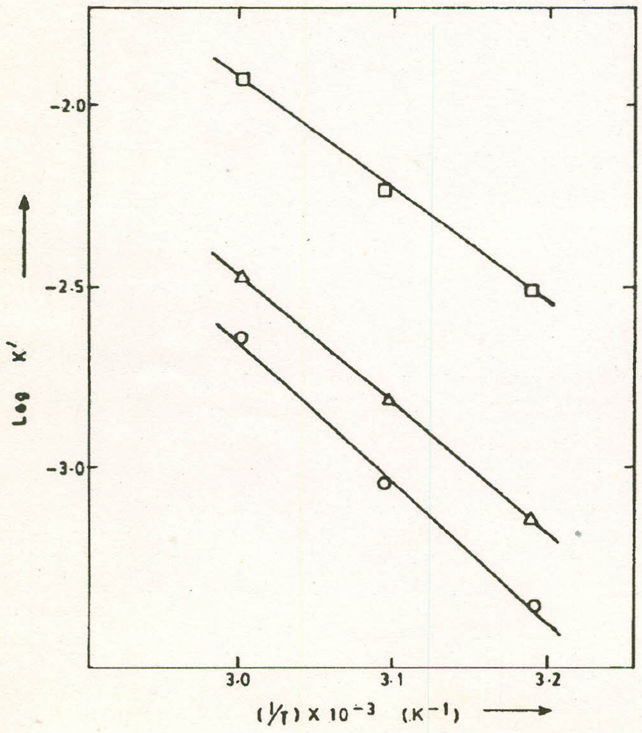

Fig. 4. Arrhenius plots for the dissolution of aluminium and silica in 0.6mol/l HCl solution. □: Fe; △: Al ;O: SiO_2.

Since the dissolution rate of the components was not dependent on the rotational speed of the stirrer, it therefore implies that the dissolution processes were not likely to be transport controlled. The following equation for the rate-determining step based on surface chemical reaction has been given by various workers [12-15].

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

where a is the ratio of the amounts of components dissolved, to their initial amounts, and K^1 is a constant. The initial amounts of components in the laterite sample can be calculated from Table 1, while the amounts of components dissolved were estimated experimentally.

The plots of $1\text{-}(1\text{-}a)^{1/3}$ against t in 0.6 mol/l HCl solution at 40, 50 and 60°, are shown in Fig. 3, which gave straight lines. These linear relationships indicate that the leaching reactions between 40 and 60° were limited by the surface chemical reaction. The apparent activation energies calculated from the Arrhenius plots of log K^1 vs. 1/T (Fig. 4) were 56.7 KJ mol^{-1}, 65.2 KJ mol^{-1} and 70.8 KJ mol^{-1} for iron, aluminium and silica, respectively. These values suggest that the rate of dissolution of iron was affected by the temperature change less intensively than those of aluminium and silica. Moreover, these values also account for the differences in the dissolution rates of the three components, i.e. iron, aluminium and silica.

In general, the high values of the apparent activation energies are further evidence that surface chemical processes control the rate of dissolution of iron, aluminium and silica from laterite in the HCl solution [19,20]. Paspaliaris and Tsolakis [21] reported values of 62-79 KJ mol^{-1} for the leaching of iron oxides from diasporic bauxite in HCl, however, no value for the apparent activation energies of the dissolution of iron, aluminium and silica from laterite in HCl has been reported.

In conclusion, dissolution reactions of iron, aluminium and silica from laterite in dil. HCl solutions (0.6 - 3.0 mol/1), at 40-60°, have been found to be controlled by surface chemical processes. Under the same reaction conditions, the dissolution rate of iron was much faster than those of aluminium and silica and reasons for these have been given.

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