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KINETICS OF ILMENITE ORE DISSOLUTION IN ACID SOLUTIONS

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ABSTRACT. Kinetic study of the dissolution of ilmenite powder from Nigeria was investigated. The effects of (a) temperature ranging from 30 to 60°, (b) time ranging from 1 to 6 hrs, (c) hydrochloric acid concentration ranging from 2.3 to 6.0 M and (d) sulphuric acid concentration ranging from 0.5 to 3.0 M on titanium and iron dissolution are presented. From the analysis of the dissolution rates on the basis of the core model, it was found that the dissolution rates of both elements were well-expressed by the rate equation based on the rate-limiting step of the surface chemical reaction. The apparent activation energies were 64.02 kJ mol^{-1} for titanium and 60.76 kJ mol^{-1} for iron.

INTRODUCTION

A method of converting ilmenite to synthetic rutile is by acid leaching. Acid leaching is also very important for the recovery of titanium and iron from titaniferous ores. The chloride process, which involves pressurized leaching with hydrochloric acid, has been widely reported in literature [1-10]. Also the sulphate process involving sulphuric acid, has been used to dissolve titanium and iron from ilmenite [11-14]. There is also a report on the use of hydrofluoric acid for the leaching of ilmenite [15].

Most of the leaching studies of ilmenite in acid solutions were performed essentially to obtain optimum conditions but only a few reports on the kinetic study have been presented [15-18]. However there is no information in literature on the use of mixtures of acid solutions for the leaching of ilmenite.

This paper, therefore, reports the kinetics of the leaching of ilmenite powder in mixed solutions of hydrochloric and sulphuric acids. The generalized equations of the reactions are:

$$2FeTiO_3 + 14HCl + \frac{1}{2}O_2 \dashrightarrow 2TiCl_4 + 2FeCl_3 + 7H_2O \qquad (1)$$

$$2FeTiO_3 + 7H_2SO_4 + \frac{1}{2}O_2 \dashrightarrow 2Ti(SO_4)_2 + Fe_2(SO_4)_3 + 7H_2O \qquad (2)$$

It is important to note that the kinetics of both reactions were not studied independently because the effect of both acids on the dissolution rates was determined by the analysis of the reaction mixture.

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The effects of time, temperature, hydrochloric acid concentration, and sulphuric acid concentration on the dissolution of titanium and iron values have been investigated.

EXPERIMENTAL

Materials. The ilmenite ore in this study was obtained from Bukuru Mills, Nigeria. The ore was finely pulverized in a ball mill; the fraction containing particle sizes of 100-250 µm was collected by screening. This fraction was washed with water, and dried at 110° for about 3 hrs. The chemical composition of the ilmenite sample is given in Table 1.

Table 1. Chemical composition of the ilmenite.

Constituent	Content (%)
TiO_2	43.2
FeO	22.6
Fe_2O_3	16.8
Al_2O_3	2.3
SiO_2	3.8
MnO	2.5
Cr_2O_3	0.6
CaO	1.4
MgO	3.7
Na_2O	1.6
K_2O	0.8

Reagents. All the chemicals used were of analytical grade. Concentrated hydrochloric and sulphuric acids were diluted to the desired concentrations with distilled water.

Apparatus. The reaction vessel was a 100 ml three-necked flask; the centre neck was fitted with a water-sealed stirring rod, the two other necks were fitted with a condenser, and stopper, respectively. The container was placed in a water bath thermostated at 30 - 60°.

Measurements of reaction kinetics. The sample powder (1 g) was suspended in 80 ml of the acid solution in the reaction vessel. The mixture was then stirred at about 500 rpm; preliminary experiments over the stirring range 200-1400 rpm did not affect the dissolution rates [19]. 5 ml aliquots of the sample solution was withdrawn from the flask at regular time intervals and analyzed for titanium and iron.

Analytical methods. Titanium was determined colorimetrically by the peroxide method [20] and iron (II) with phenanthroline [21]. Total iron and other metals were determined using atomic absorption spectrophotometer (Perkin-Elmer Model 403).

RESULTS AND DISCUSSION

The time dependence of titanium and iron oxides dissolution was investigated at various temperatures between 30 and 60°. Fig. 1 shows the dissolution of Ti and Fe respectively, versus time (HCl 6M, H_2SO_4 1.2 M). There was an improvement in the dissolution of both metallic values with increase in temperature. The largest dissolution was, however, obtained at 60°, and was more than using either of the two acids. In earlier experiments not reported here, the dissolution of Ti and Fe in 6 M HCl alone, was 40% less, and in 6M H_2SO_4 alone, was 60% less than what was obtained for the mixed acid at the same reaction conditions [19]. Usually, such a dissolution as obtained for the mixed acid could only be achieved through harsher reaction conditions

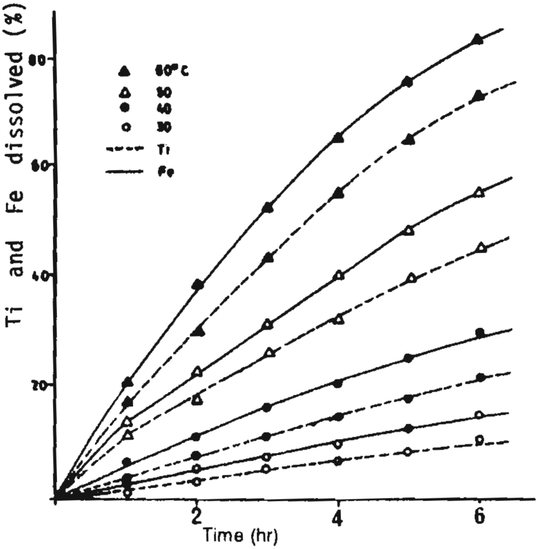

Fig. 1 Effect of temperature on Ti and Fe dissolution (HCl 6.0 M, H_2SO_4 1.2 M

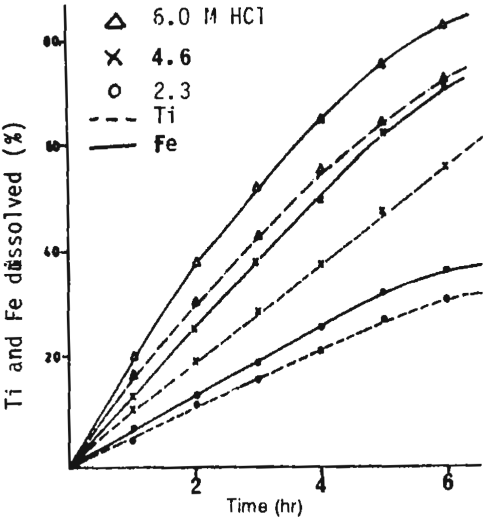

Fig. 2 Effect of HCl concentration on Ti and Fe dissolution (H_2SO_4 1.2 M, 60°C)

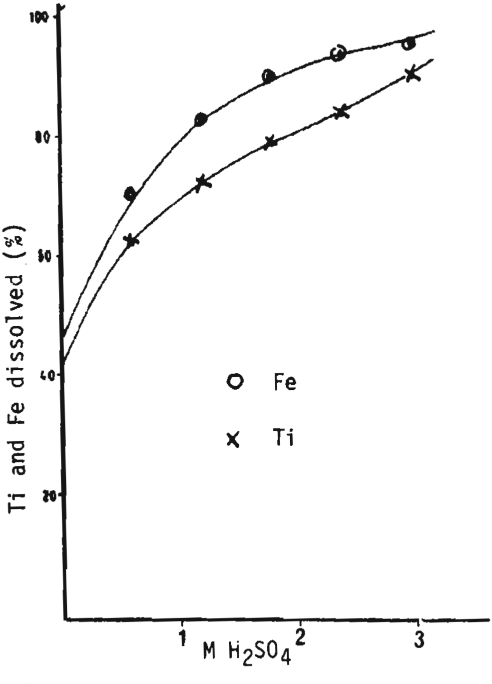

Fig. 3 Effect of H_2SO_4 concentration on Ti and Fe dissolution (HCl 6.0 M, 60°C, 6 hr)

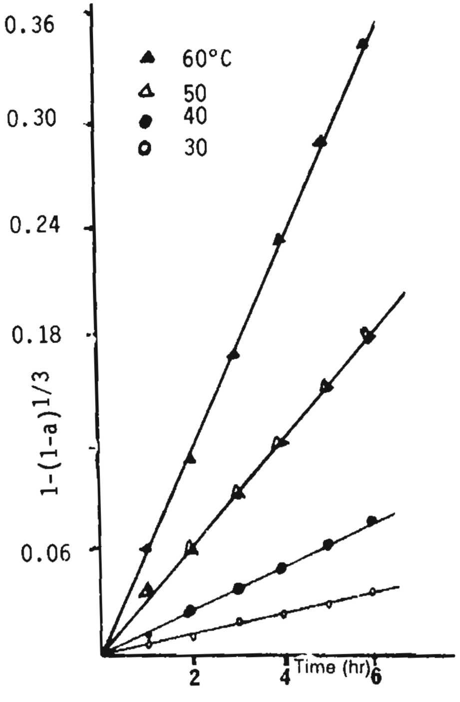

Fig. 4 Dissolution of Ti, plot of $1-(1-a)^{1/3}$ *vs* time at various temperatures (HCl, 6.0 M, H_2SO_4 1.2 M)

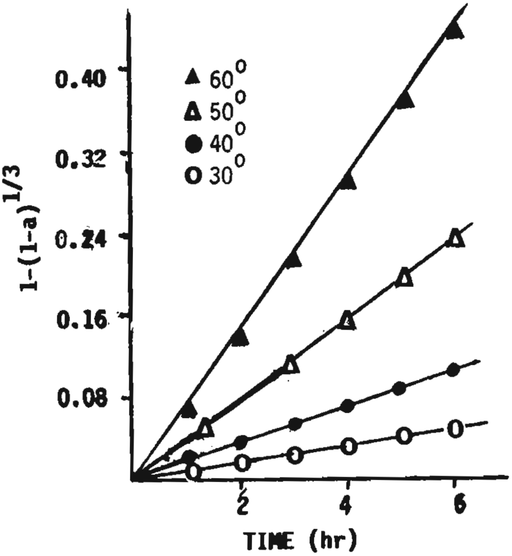

Fig. 5 Dissolution of Fe, plot of $1\text{-}(1\text{-a})^{1/3}$ *vs* time for various temperatures (HCl 6.0 M, H_2SO_4 1.2 M)

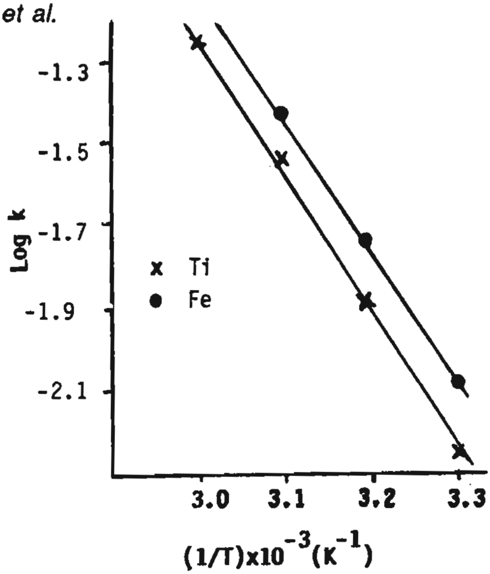

Fig. 6 Arrhenius plot, log K *vs* 1/T, for Ti and Fe dissolution (HCl 6.0 M, H_2SO_4 1.2 M)

[16,18]. These results obviously indicate that the addition of H_2 SO_4 to HCl caused better dissolution of Ti and Fe values. This implies that both acids have a complimentary effect on the dissolution of ilmenite in the acid solutions. However, under the experimental conditions, the highest levels of titanium and iron extracted were 72 and 83%, respectively.

The effect of the HCl concentration ranging from 2.3 to 6.0 M, on the dissolution was kept at 1.2 M. The results are shown in Fig. 2. Increasing the concentration of HCl improved the dissolution of Ti and Fe.

In order to study the effect of H_2SO_4 concentration ranging from 0.6 to 3.0 M on the Ti and Fe dissolution, the ilmenite powder was leached at 60°, while keeping the HCl concentration at 6.0 M and the time at 6 hrs. From the results shown in Fig. 3, concentration of H_2SO_4 had a more pronounced effect on Ti and Fe dissolution, than HCl concentration. With 3 M H_2SO_4, the amount of titanium remaining in the residue was less than 11%, and that of iron was less than 6%.

The leaching of Nigerian ilmenite powder in the acid mixtures, a heterogenous reaction, was found to follow the shrinking core model [22]. This model assumes that the reaction rate is controlled by one of these three steps: diffusion of acid through a film surrounding the particle, chemical reaction on the surface of the particle, and diffusion of the products back through the film.

The fact that the degree of stirring did not affect the dissolution rate [19] eliminated the diffusion steps as the rate-limiting step. Moreover, the dissolution rates were not zero-order. Thus, the dissolution rate was most likely to be controlled by surface chemical reaction. The relevant rate equation is:

$$1 - (1-a)^{1/3} = kt \qquad (3)$$

Where a is the fractional amount of component leached, k is the overall rate constant, and t is the time (hr). The rates of titanium and iron dissolution are shown in Figs. 4 and 5. The results show that the dissolution rates of both elements were well-expressed by Eqn. (3), which is based on the rate-limiting step of the surface chemical reaction; namely, there was a good linear relationship between $1\text{-}(1\text{-a})^{1/3}$ and t. The slope of each of the straight lines in Figs. 4 and 5 is k (the overall rate constant).

These k values are plotted in Fig. 6 in accordance with the Arrhenius relationship:

$$\log k = \log A - \frac{Ea}{2.303R} \cdot \frac{1}{T} \qquad (4)$$

Where k is the overall rate constant, A is the pre-exponential factor, Ea is the activation energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K). The plots show that log k is inversely proportional to temperature. The apparent activation energies were 64.02 kJ mol^{-1} for titanium and 60.76 kJ mol^{-1} for iron, as calculated from the slopes of the Arrhenius plots. These values of the activation energy were less than what were obtained in either HCl or H_2SO_4 alone. For instance, Ea for Ti in HCl was 75.46 and for Fe was 70.49 kJ mol^{-1} [19]. The Ea values indicate that the rate of dissolution of Ti was affected by the temperature change more intensively than that of iron. This is similar to what was observed in either HCl or H_2SO_4 alone [19]. The faster rate of dissolution of iron, however corresponds to increase in the pre-exponential factor, A.

Activation energy, Ea, is an important parameter for determining the mechanism of heterogenous reactions. According to Glasstone *et. al* [23], transport-controlled reactions have activation energies ranging from 8 to 25 kJ mol^{-1}, whereas that the chemical process is considerably higher. It therefore, follows from the Ea values that the rate of dissolution of Ti and Fe in HCl-H_2SO_4 mixtures, was controlled by chemical reaction on the surface of the particle.

CONCLUSIONS

From the experimental study it may be concluded:

1. Temperature has a significant effect on the rate of dissolution of titanium and iron from the ilmenite powder.
2. The concentration of sulphuric acid has a more pronounced effect on titanium and iron dissolution, than hydrochloric acid concentration. However, the dissolution of both elements was larger in the acid mixtures, than either of the acids alone.
3. The results indicated that the reaction was controlled by chemical reaction on the surface of the particle.
4. The apparent activation energy for titanium was about 64 kJ mol^{-1} and for iron about 61 kJ mol^{-1}. These values are by far higher than those of diffusion processes, and are only evident of chemically-controlled processes.

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