KINETICS OF ILMENITE DISSOLUTION BY HYDROFLUORIC ACID

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The leaching behaviours of titanium and iron values were examined in hydrofluoric acid solutions of various strengths at temperatures of 60 to 80°C. The rate was linearly dependent on the HF concentration but inversely proportional to the particle size of the ilmenite. Titanium leaching occurred at a much faster rate than iron leaching and the leaching rates of both were independent of the stirring speed over the range 0-400 rpm. The observed effects of the relevant operating variables on the dissolution rates were consistent with a kinetic model for chemical reaction control. The apparent activation energy for titanium dissolution was 51.08 kJ mol^{-1} and 53.90 kJ mol^{-1} for iron dissolution.

Key words: Hydrofluoric acid, Ilmenite dissolution, Kinetics

Introduction

Several million tonnes of heavy mineral deposits containing ilmenite, cassiterite, columbite, zircon, monazite, among others, have so far been discovered on the Jos plateau, in the middle Belt area of Nigeria. Of these minerals, only cassiterite had been fully exploited for commercial purposes, (Anon 1987), but certainly in the nearest future, all the minerals when fully exploited may become a potential source for the extraction of many valuable metals.

In the past we have carried out a number of studies on this ilmenite among which are: chemical beneficiation by hydrochloric acid leaching (Oderinde and Olanipekun 1992), extraction of titanium and iron values by hydrochloric-sulphuric acid mixture (Oderinde *et al* 1992) and by phosphoric acid solution (Olanipekun *et al* 1993). The predominant mineral of titanium is ilmenite found in commercial quantities in several parts of the world notably in United States of America, Canada, Australia, India, Finland, Norway and Spain (Mackey 1974). Most of the ilmenite mined is consumed to make pigments, via the sulphate process, for the paint, paper, and plastic industries, and metal.

Apart from the sulphate process, titania pigment has also been produced via the chloride process using rutile as the raw material. Compared to the sulphate process, only a small amount of waste is generated in the chloride process. A particular advantage of the chloride process is that it gives a very pure pigment; however, it is faced with a raw material supply problem (Mackey 1974; Narita *et al* 1983).

Among the different hydrometallurgical routes for extraction of titanium and iron from ilmenite, leaching under atmospheric pressure in mineral acids is considered to have some district advantages (Biswas and Mondal 1987; Hansen and Traut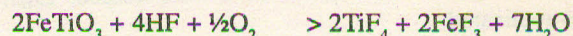 1989). Except for hydrochloric and sulphuric acids which have been widely used in this respect, there is, however, a very scanty information on the use of other mineral acids for metal extraction.

A process to manufacture pure titanium that would utilize lower grade, less costly and more readily available raw materials, such as ilmenite has long been sought. In this study, therefore, the dissolution of a Nigerian Ilmenite rock by hydrofluoric acid was investigated in order to obtain some essential data on the kinetics and mechanism of titanium and iron leaching.

The reaction under investigation may be written as:

$$FeTiO_3 + 4HF \longrightarrow TiOF_2 + FeF_2 + 2H_2O$$
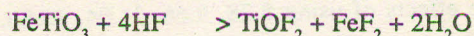
Alternatively, it may be written as

$$2FeTiO_3 + 4HF + \tfrac{1}{2}O_2 \longrightarrow 2TiF_4 + 2FeF_3 + 7H_2O$$

Both reactions above represent the leaching of titanium and iron values from ilmenite using hydrofluoric acid.

Experimental

The ilmenite ore used in this study was from the deposit on Jos Plateau around Bukuru area in Nigeria. The ore, supplied by the Kanari mill in Bukuru was dry-ground and sieved to collect three different particle size fractions: 25 to 37 μm, 45 to 53 μm and 88 to 105μm. The particle size analysis of the ilmenite showed no significant variations in chemical composition between the size fractions. The chemical analysis of the 88 to 105μm fraction is given in Table 1. The HF used was reagent grade (Aldrich Chemical Company, Inc USA).

A known amount of sample (about 2g) was heated in a Teflon (polytetrafluorethylene) cup with 250ml of hydrofluoric acid solution at a pre-determined temperature. The cup was partly covered by a Teflon watch-glass during the experiment. A

Table 1
Chemical composition of rock 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

magnetic hotplate was used for heating and stirring was done mechanically using a rod made from polypropylene. At intervals aliquots (2ml) of solution were removed using a transparent pipette made from polypropylene, diluted and analyzed for titanium and iron contents. Titanium was determined by a colorimetric method (Vogel 1961) and iron by atomic absorption spectrophotometry (Buck 200 Model).

Four test series were used to independently investigate the effects of the different variables.

One series investigated stirring speeds ranging from 50 to 400 rpm; another series investigated three different size fractions: 25 to 37, 45 to 53, and 88 to 105 ìm; the third series investigated the effects of using 8.28, 9.66, 11.04, 13.80, and 16.55M HF concentrations; in the fourth and the last series, temperatures of 60, 70, and 80°C were studied. Each test was replicated.

Results and Discussion

(a) *Agitation Effect*: If chemically controlled, the leaching rates should be independent of the stirring speed during the dissolution of the ilmenite by the acid. To verify this, a series of leaching experiments was run at 60°C in 11.04M HF solution for 1 hour using the 88 to 105ìm size fraction and at the various stirring speeds under investigation.The fractions of metals dissolved are plotted against the stirring speeds in Fig.1. The leaching of titanium and iron appears to be essentially independent of stirring speed between 0 and 400 rpm, and this apparently suggests that the rate is chemically controlled. These results are clearly in agreement with previous findings on ilmenite dissolution. Subsequent tests were performed at a stirring speed of 200 rpm.

(b) *Particle Size effect:* The particle size of an ore is an important factor in heterogeneous reactions. Consequently,

tests were conducted using three different particle sizes of the ilmenite ore, under the experimental conditions given above (11.04M HF, 200 rpm, 60°C). The results presented in Figs 2a and 2b show that the leaching rates of both metals are inversely proportional to the particle size of the ore. The fractions of titanium and iron dissolved increase with a decrease in the size of the ilmenite. However, the best results were obtained with the 25 to 37ìm fraction for both metals.

(c) *HF Concentration Effect*: The effect of HF concentration on the leaching rate of the ilmenite was studied at 60°C and at various HF concentrations. The fractions of titanium and iron dissolved in a period of time at the various concentrations of hydrofluoric acid are presented in Figs 3a and 3b respectively. The leaching rates of both metals increase steadily with increasing HF concentration but in no circumstance was titanium extraction greater than 70% and iron 46%, under the conditions of test.

(d) *Temperature Effect*: Fig 4 shows the type of dissolution curve obtained when the ilmenite was leached at various temperatures in 11.04M HF. The dissolution of titanium and iron increase with increase in the temperature of the reaction; however, titanium leaching occured at a much faster rate than iron leaching. At 80°C, titanium extraction was about 82% and iron about 56%, the latter was even less than the value obtained for titanium at 70°C. These results indicate that titanium was much more preferentially dissolved than iron under the conditions of test.

(e) *Elucidation of Leaching Kinetics and Mechanism:* To establish the rate-controlling mechanism of the dissolu-
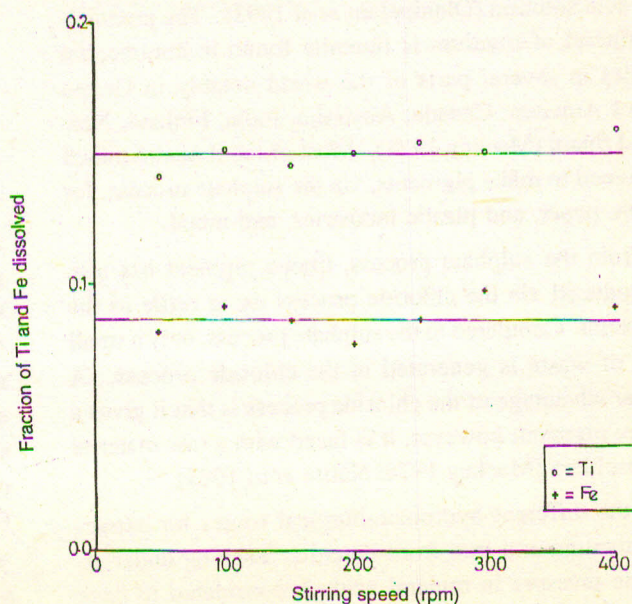

Fig 1. Effect of stirring speed on titanium and iron dissolution in 11.04M HF at 60°C (1 h, 88 to 105 μm).

tion reaction, the data obtained were analyzed with a familiar shrinking core model (Sohn and Wadsworth 1979). Fig 5 illustrates a plot of 1- (1-a) versus time, and the linear relationship observed on this basis seems to confirm that the ilmenite dissolution kinetics in the HF solution under the conditions of test are linear and surface-chemically controlled (Glassone *et al* 1941). Another criterion for determining the rate-controlling mechanism of such leaching reactions is the apparent activation energy Ea. Usually transport-controlled reactions have Ea values of 8 to 25 kJ

mol^{-1}, but for chemically controlled ones the values are considerably higher (Glassone *et al* 1941). The activation energies for titanium and iron leaching were evaluated from the Arrhenius relationship, Ink against T^{-1} (Fig 6) k's were obtained from the slopes of the curves in Fig 5 The data in Fig 6 show that Ink is inversely proportional the leaching
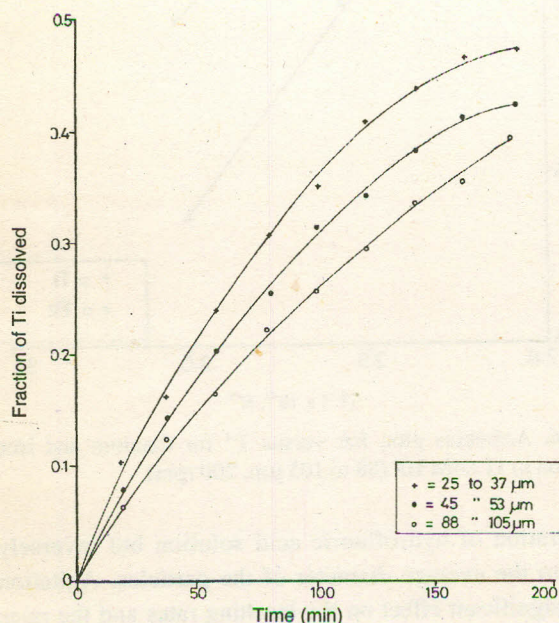

Fig 2a. Effect of particle size on titanium dissolution in 11.04M HF at 60°C (200 rpm, 1 h).
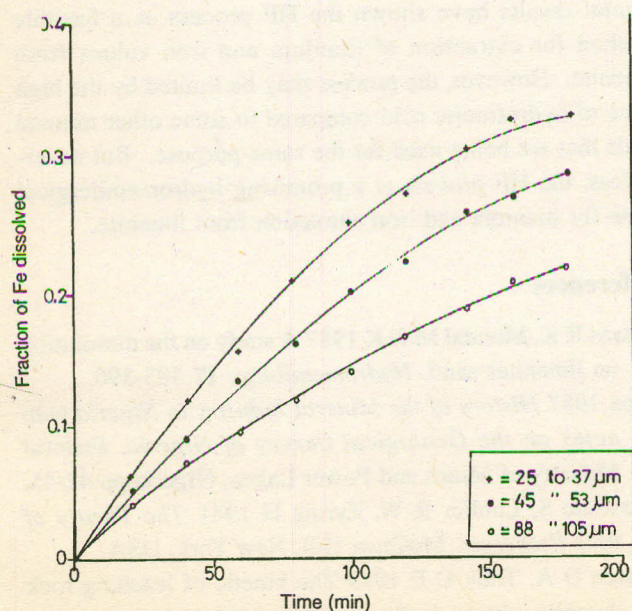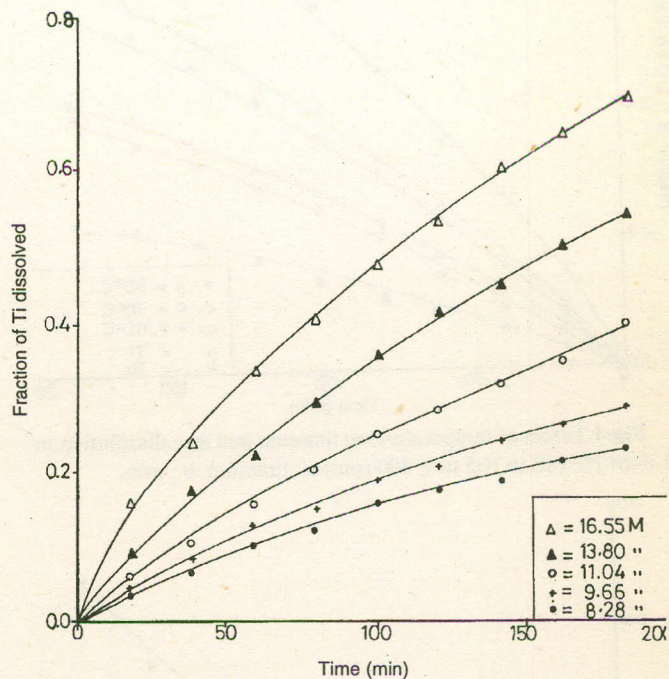

Fig 3a. Effect of HF concentration on titanium dissolution at 60°C (88 to 105 µm, 200 rpm).

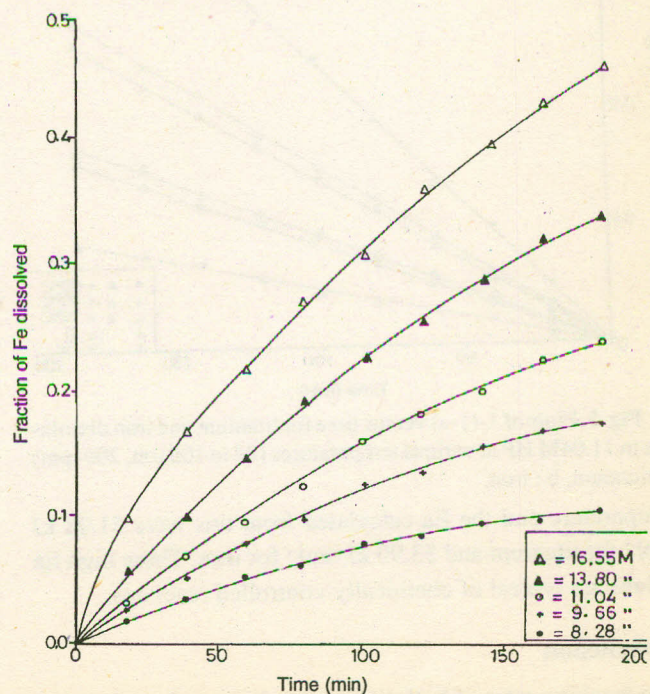**Fig 2b.** Effect of particle size on iron dissolution in 11.04M HF at 60°C (200 rpm, 1 h).

Fig 3b. Effect of HF concentration on iron dissolution at 60°C (88 to 105 µm, 200 rpm).
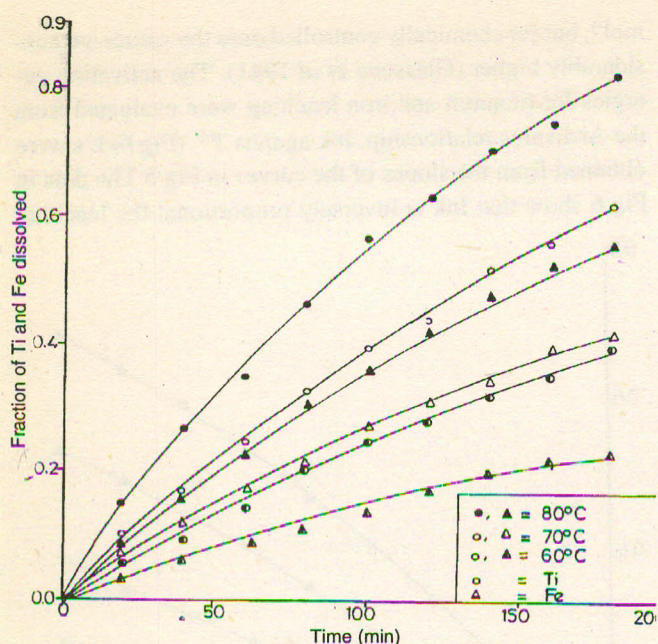
Fig 4. Effect of temperature on titanium and iron dissolution in 11.04M HF (88 to 105 μm, 200 rpm) a : titanium, b : iron.
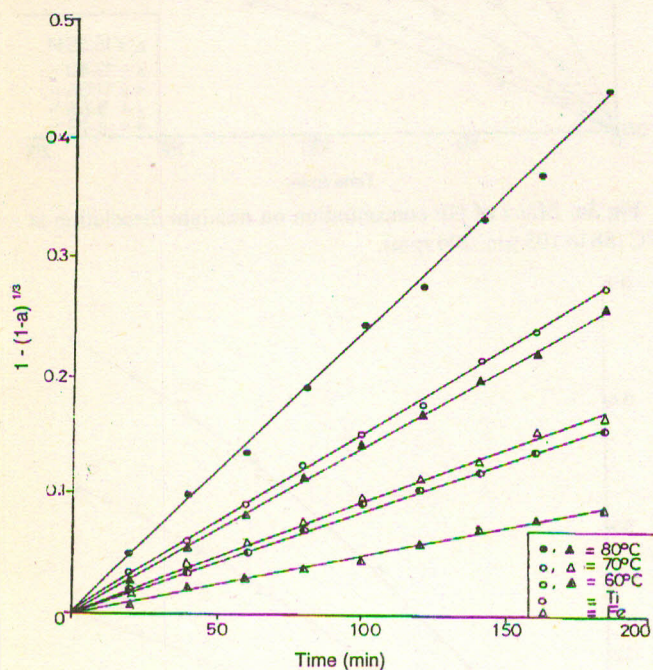

Fig 5. Plots of 1-(1-a) versus time for titanium and iron dissolution in 11.04M HF at various temperatures (88 to 105 μm, 200 rpm) a : titanium, b : iron.

temperature and the Ea calculated from this were 51.08 kJ mol^{-1} for titanium and 53.90 kJ mol^{-1} for iron. These high Ea values are typical of chemically-controlled reactions.

Conclusion

The leaching rates of both titanium and iron values from the ilmenite ore are linearly dependent on the temperature and
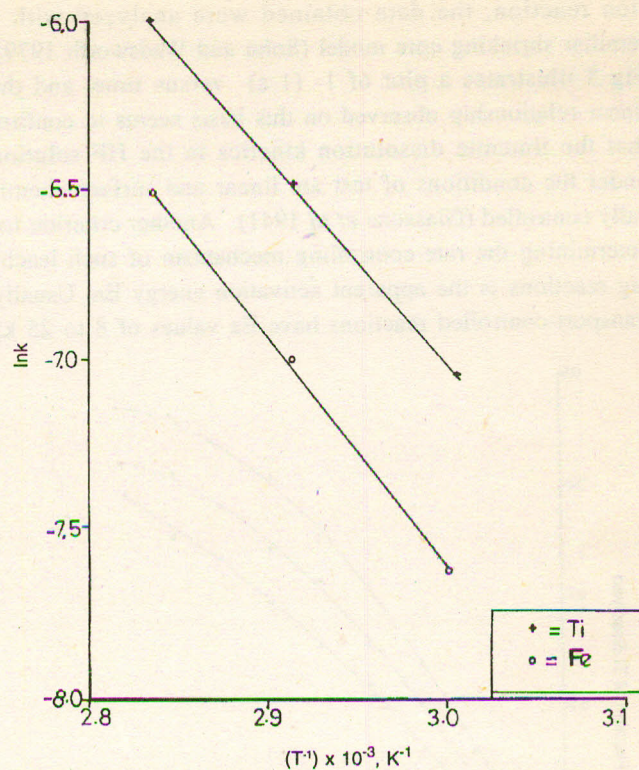

Fig 6. Arrhenius plot, Ink versus T^{-1} for titanium and iron dissolution in 11.04M HF (88 to 105 μm, 200 rpm).

concentration of hydrofluoric acid solution but inversely related to the average diameter of the particles. Agitation had no significant effect on the leaching rates and the rates were surface chemically-controlled on the basis of the observed relevant operating kinetic parameters. The experimental results have shown the HF process as a feasible method for extraction of titanium and iron values from ilmenite. However, the process may be limited by the high price of hydrofluoric acid compared to some other mineral acids that are being used for the same purpose. But nevertheless, the HF process is a promising hydrometallurgical route for titanium and iron extraction from ilmenite.

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