A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid

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Abstract

A kinetic study of the leaching of powdered ilmenite ore by hydrochloric acid has been investigated. The effects of (a) stirring speed ranging from 100 to 500 min⁻¹, (b) particle size ranging from 20 to 74 μm, (c) acid concentration ranging from 7.2 to 9.6 M and (d) temperature ranging from 70 to 90°C on titanium and iron dissolution are reported. The dissolution rates are significantly influenced by the temperature and concentration of the acid solutions. The experimental data for the dissolution rates of titanium and iron have been analyzed with the shrinking-core model for reaction control. The observed effects of the relevant operating variables on the dissolution rates are consistent with a kinetic model for diffusion control. The apparent activation energy for the dissolution of titanium and iron has been evaluated using the Arrhenius expression. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Ilmenite occurs associated with cassiterite, columbite, tantalite, wolframite, zircon and monazite in the Younger granites of Northern Nigeria. The ilmenite is mined principally from the alluvial deposits derived from these granites. More than 90% of the ilmenite produced in Nigeria is mined in the Jos Plateau and in outlying Younger granite masses in Bauchi, Zaria, Kano and Benue zones. Smaller quantities are also mined from the Older granite pegmatites in the Plateau, Kabba, Benue, Niger and Ondo zones [1].

The growing inability of the world’s natural rutile resources, now principally derived from Australia to meet the raw material needs of the ‘chloride’ pigment manufacturers, is one of the reasons for studying the upgrading of ilmenite into synthetic rutile.

For the past few decades, several articles [2–5] have appeared on the application of the leachant hydrochloric acid in many processes for upgrading ilmenite into synthetic...
rutile. The reactivity of ilmenite towards hydrochloric acid depends on the nature of the mineral, whether it has been altered or not. Indeed, a number of ilmenite deposits worldwide have been found to contain a mixture of both unaltered and altered ilmenites and in some cases rutile and leucoxene [6]. Generally, the unaltered ilmenite is more readily leached by hydrochloric acid than the altered ilmenite. A knowledge of the reactivity of a particular ilmenite towards hydrochloric acid is therefore essential for its upgrading by hydrometallurgical techniques.

Most leaching studies of ilmenite by hydrochloric acid were performed in order to obtain optimum conditions for upgrading the ilmenite into synthetic rutile. Addition of phosphate and fluoride to hydrochloric acid was found to enhance the leaching of ilmenite [7]. The leaching of ilmenite has also been reported to occur at a much faster rate in alcoholic hydrochloric acid solutions than in aqueous ones [8,9].

This work investigates the kinetics of the leaching of ilmenite by hydrochloric acid. As a leachant, hydrochloric acid is preferred to other acids because it allows comparatively easier recovery of the useful free acid from its waste solution. In addition, the recovery of a number of metal ions by liquid–liquid extraction from hydrochloric acid solutions is considerably easier than that from sulphuric acid solutions [10,11]. The particular type of hard rock ilmenite from the Jos Plateau was selected because it constitutes the major part of the Nigerian ilmenite resources. Although optimum conditions for upgrading the ilmenite into synthetic rutile by hydrochloric acid leaching were previously obtained [12], no attempt have been made to investigate the kinetics of the dissolution process, hence the reaction mechanism is not yet understood.

The leaching kinetics of some other ilmenite ores in dilute (0.03–1 M) and in highly concentrated (11.3–11.6 M) hydrochloric acid solutions has been investigated by earlier workers [13,14]. Since only a few kinetic studies have so far been carried out, there is still scanty data on the kinetics of the leaching of hard rock ilmenite by hydrochloric acid. The objective of the present investigation is to obtain essential information on the kinetics of the dissolution behaviour of titanium and iron in concentrated hydrochloric acid solutions with respect to the leaching mechanism.

2. Experimental

2.1. Material

A hard rock ilmenite from Jos Plateau (Nigeria) was used for all kinetic leaching tests. The ilmenite had the following chemical and mineralogical analyses:

Chemical analysis: 26.4% Ti, 35.2% Fe, 1.8% Mg.
Mineralogical analysis: 94.5% FeTiO, 2.5% spinel, 1.5% quartz, 1% garnet.

The particle size analysis of the ilmenite showed no significant variations in mineralogy between the size fractions: 20–37, 37–53 and 53–74 μm. The HCl used was reagent grade (Aldrich Chemical).

2.2. Equipment

A 200 ml three-necked round-bottomed Pyrex flask equipped with a thermometer, a mechanical stirrer and a reflux condenser was used as the batch reactor. The flask was
Fig. 1. Effect of stirring speed on the dissolution of Ti and Fe in 7.2 M HCl solution at 70°C.

Fig. 2. Effect of particle size on the dissolution of Ti and Fe in 7.2 M HCl solution at 70°C.
heated by a thermostatically controlled isomantle to reach and maintain the desired temperature within ±1°C.

2.3. Procedure

For each run, 150 ml of HCl solution of predetermined molarity was charged into the reactor and heated to the required temperature. Thereafter, ilmenite (0.5 g) was added to the reactor and the contents were well agitated. Solution samples of 2 ml were withdrawn at appropriate times during a run and analyzed for titanium by colorimetry [15] and for iron by atomic absorption spectrophotometry.

3. Results

3.1. Agitation effect

The effect of agitation on the dissolution of titanium and iron was investigated in 7.2 M HCl solution with the 53–74 μm size fraction of the ilmenite at 70°C, using stirring

![Graph showing the effect of HCl concentration on the dissolution of Ti and Fe at 70°C.](image)

Fig. 3. Effect of HCl concentration on the dissolution of Ti and Fe at 70°C.
speeds of 100–500 min\(^{-1}\). The results in Fig. 1 show that the dissolution rates are independent of the stirring speed. The diffusion in the liquid film is not the rate-determining step of the dissolution reaction in Eq. (1). On the basis of the data, subsequent experiments were carried out at a stirring speed of 500 min\(^{-1}\) to ensure that the contribution to mass transfer by natural convection was negligible.

3.2. Particle size effect

The effect of particle size on the dissolution of titanium and iron was investigated in 7.2 M HCl solution at 70°C, using the three particle size fractions: 20–37, 37–53, and 53–74 μm. As expected, the results presented in Fig. 2 show that the dissolution rates are inversely proportional to the average initial diameter of the particles.

![Figure 4](image)

Fig. 4. Effect of temperature on the dissolution of Ti and Fe in 7.2 M HCl solution.
3.3. Concentration effect

The effect of HCl concentration on the dissolution of titanium and iron was investigated at 70°C using the 53–74 µm size fraction of the ilmenite. The HCl concentrations used are 7.2, 8.4 and 9.6 M. The fraction of titanium and iron extracted vs. time plots for the different HCl concentrations can be derived from Fig. 3. Concentration of the leachant has a significant effect on the leaching of the ilmenite but in no case was the fraction of titanium and iron extracted more than 80 and 85%, respectively.

3.4. Temperature effect

The effect of temperature on the dissolution of titanium and iron was investigated in 7.2 M HCl solution using the 53–74 µm size fraction at temperatures of 70, 80 and 90°C. From the results shown in Fig. 4, it can be observed that both metals were largely dissolved at 90°C. Tests at higher temperatures would be less suitable due to increased corrosion rates and loss of HCl vapour.

4. Discussion

4.1. Analysis of dissolution rates

The dissolution rates of titanium and iron were analyzed with the shrinking core model for reaction control under the assumption that the ore is a homogeneous spherical solid phase [16].

The overall reaction for the dissolution of ilmenite by hydrochloric acid may be written as:

$$\text{FeTiO}_3 + 4\text{HCl} \rightarrow \text{TiOCl}_4 + \text{FeCl}_2 + 2\text{H}_2\text{O}. \quad (1)$$

For the titanium and iron dissolution kinetics, two established kinetic models were used, expressed by the following equations:

$$1 - (1 - a)^{1/3} = \frac{Mk_1C_A t}{dr} = k_1 t, \quad (2)$$

$$1 + 2(1 - a) - 3(1 - a)^{2/3} = \frac{6uMDCA t}{dr^2} = k_2 t, \quad (3)$$

where $k_1$ is the first-order rate constant (m min$^{-1}$), $M$ is the molecular weight of the solid reactant (kg mol$^{-1}$), $C_A$ is the acid concentration (mol m$^{-3}$), $D$ is the diffusion coefficient (m$^2$ min$^{-1}$), $d$ is the density of the particle (kg m$^{-3}$), $r$ is the initial radius of the particle (m), $a$ is the fraction reacted at time $t$ (min), $k_1$ (m min$^{-1}$) and $k_2$ (m$^2$ min$^{-1}$) are the overall rate constants, and $u$ is the stoichiometric coefficient (−). Eq. (2) is applicable to chemically controlled processes and Eq. (3) to diffusion controlled processes through the porous product layer.
Examination of plots of the above kinetic equations as functions of time showed that only Eq. (3) gives perfectly straight lines (from 0 to 120 min) but Eq. (2) does not, meaning that the dissolution reaction was not controlled by the chemical reaction taking place on the surface of the mineral. Plots of the function \(1 + 2(1 - a) - 3(1 - a)^{2/3}\) vs. time at the leaching temperatures shown in Fig. 5 indicated that the dissolution rates of titanium and iron at 70 to 90°C give a good correlation with the diffusion kinetic Eq. (3). In this case, two diffusion processes compete in determining the reaction rate: (i) diffusion of \(H^+\) (from HCl) and (ii) diffusion of Ti\(^{4+}\) and Fe\(^{2+}\) produced by the surface chemical reaction of the unreacted core. The diffusion rate of \(H^+\) was presumed to be fast due to its relatively small size compared to Ti\(^{4+}\) and Fe\(^{2+}\). The comparatively large size of Ti\(^{4+}\) is further supported by the fact that titanium ions present in aqueous solutions are not only mononuclear species such as \([Ti(OH)]^{4+}\), \([TiO(OH)]^{4+}\), \([Ti(OH)]_2^{5+}\) but also polynuclear species such as \([(TiO)_n(OH)_{12}]^{4+}\) [17]. Accordingly, the diffusion of Ti\(^{4+}\) and Fe\(^{2+}\) which was presumed to exhibit slower kinetics than \(H^+\), is the rate-controlling step of the dissolution reaction.

4.2. Composition of the product layer formed

The fact that the reaction rate was independent of the stirring speed suggests that an insoluble layer was formed at the interface. In order to verify this assumption experimentally, the reaction residue obtained after leaching the ilmenite in 9.6 M HCl solution
at 90°C for 5 h was subjected to X-ray diffraction analysis. The X-ray diffraction pattern of the insoluble residue indicated the presence of TiO$_2$, Ti$_2$O$_3$, SiO$_2$ and unleached FeTiO$_3$. Ti$_2$O$_3$ was presumed to be produced by hydrolysis of Ti (III) ion formed by the reduction of Ti (IV) ion with chloride ion during the leaching according to the reactions:

$$\text{Ti}^{4+} + \text{Cl}^- \rightarrow \text{Ti}^{3+} + 1/2\text{Cl}_2.$$  \hspace{1cm} (4)

$$2\text{Ti}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Ti}_2\text{O}_3 + 6\text{H}^+.$$  \hspace{1cm} (5)

Titanium (IV) oxide was precipitated by the hydrolysis of titanium (IV) ion present in the aqueous solution according to the reaction:

$$\text{TiOCl}_2 + \text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{HCl}.$$  \hspace{1cm} (6)

The foregoing observations are in good agreement with what has been reported by others [14].

**4.3. Estimation of activation energy**

The relation between the overall rate constant from Eq. (3) and temperature may be expressed by the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right),$$ \hspace{1cm} (7)

where $k$ is the overall rate constant (m$^2$ min$^{-1}$), $A$ is the frequency factor (min$^{-1}$), $E_a$ is the activation energy (J mol$^{-1}$), $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), and $T$ is the reaction temperature (K).

![Fig. 6. Arrhenius plot for Ti and Fe dissolution in 7.2 M HCl solution.](image)
Rate constants for different temperatures were calculated from the plots in Fig. 5 and the Arrhenius plot of \( \ln k \) vs. \( T^{-1} \) is shown in Fig. 6. From the Arrhenius plot is calculated the activation energy of 67.1 kJ mol\(^{-1}\) for titanium and 62.4 kJ mol\(^{-1}\) for iron. Although both values seem to suggest a chemical reaction control, recent studies showed that some diffusion controlled reactions have unusually high activation energy. For instance, the activation energy for the diffusion controlled dissolution of titanium and iron from ilmenite in hydrochloric acid solution was reported [14] as 48.9 and 53.7 kJ mol\(^{-1}\), respectively. Similarly, the activation energy for the diffusion controlled hydrochloric acid leaching of iron from bauxite varied from 62 to 79 kJ mol\(^{-1}\) for different particle size fractions [18]. On closer examination, it appears that the rate controlling mechanism of heterogeneous dissolution reactions is sometimes better predicted from plots of the kinetic equations rather than from the activation energy value. In some instances, the same mechanistic information is derivable from both variables.

5. Conclusions

The following conclusions can be drawn from this study.

1. Both temperature and concentration of hydrochloric acid have a significant effect on the rate of dissolution of titanium and iron from the ilmenite ore. In all tests, not more than 80% of titanium and 85% of iron dissolved. Apparently, this is due to the reaction conditions used which were not too vigorous. The actual amount of element leached depends on ilmenite mineralogy and reaction variables.

2. X-ray diffraction confirmed that during leaching a product layer consisting mainly of TiO\(_2\), Ti\(_2\)O\(_3\), SiO\(_2\) and unleached FeTiO\(_3\) is formed around the shrinking core of the unreacted material.

3. The results indicated that the shrinking core model for spherical particles is applicable and that the reaction is controlled by diffusion of titanium (IV) and iron (II) through the porous product layer.

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References
