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Kinetics of the dissolution of ilmenite in sulfuric acid solutions under reducing conditions

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ABSTRACT

The kinetics of the dissolution of titanium and iron from an ilmenite sample has been studied in moderately strong sulfuric acid solutions in the absence and presence of reducing agents such as titanium(III) ions and sulfur dioxide. The effects of particle size, temperature, solid/liquid ratio, sulfuric acid concentration and titanium(III) concentration on the kinetics of dissolution have been investigated. The results have shown that both particle size and acid concentration have relatively minor effects on the rate of dissolution of titanium while temperature has a significant effect under the studied conditions.

The batch leach kinetics of ilmenite in acid solutions appears to fit a shrinking particle model, while in the presence of a decreasing titanium(III) concentration, the rate of dissolution of titanium can be fitted to a shrinking core model. Mathematical expressions for the batch leaching of the ilmenite have been established. The results suggest that the rate of dissolution of ilmenite in acid solutions is controlled by a slow chemical reaction on the surface of the mineral, while in the presence of a reducing agent such as titanous ions, the dissolution rate of ilmenite is significantly enhanced. The use of SO₂ as a reductant increases the dissolution of titanium only in the presence of ferrous ions. The role of Ti(III) ions and SO₂ during leaching is assumed to involve reduction of the iron(III) component in the mineral by a redox reaction on the surface.

Keywords: Ilmenite; Kinetics; Sulfur dioxide; Titanium(III); Sulfuric acid; Reductive leaching;

1. Introduction

Ilmenite (FeTiO₃) is one of the primary global sources of titanium dioxide which is extensively used in paints, paper, porcelain, plastics and fibres. The most important ilmenite minerals are those from the relatively rare massive deposits, which often occur in association with oxides such as hematite or magnetite, and the more widely occurring titaniferous beach sand deposits, which have resulted from natural erosion and concentration processes (Temple, 1966). One of the main commercial processes
for the production of titanium dioxide pigment from ilmenite minerals is the Sulfate Process (Barksdale, 1966; Mackey, 1994; Lasheen, 2009). It accounts for about 40% of world production for pigment titanium dioxide (Adams et al., 1997; Wang et al., 2009; Liang et al., 2005). In response to increasing environmental pressures, numerous investigations have been carried out and innovative techniques developed to improve the process (Kamala et al., 2006; Smith et al., 2006; Kretschmer and Derler, 2004; Welham and Llewellyn, 1998).

In the Chloride Process, a feedstock of high TiO$_2$ grade is required, as either natural rutile mineral (94-98% TiO$_2$), synthetic rutile (92-95% TiO$_2$), anatase (90-95% TiO$_2$), leucoxene (>68% TiO$_2$), or titanium slag (80-90% TiO$_2$). In this process, chlorine in a fluid bed reactor is reacted with the titanium feedstock at 925-1010 °C to give volatile titanium tetrachloride, which is then oxidised by combustion with pure oxygen at 985 °C to form anatase or rutile with the bulk of the chlorine recycled (Lasheen, 2005). The Chloride Process offers several advantages such as the yield of high quality product, a more eco-friendly process and the generation of smaller amount of waste products. However it requires high capital investment and high quality feedstock. Currently about 60% of the global pigment production of 4 million tpa is produced by the Chloride Process (Kamala et al., 2006; Mackey, 1994).

Despite the industrial importance of the sulfate process for ilmenite dissolution for producing pigment TiO$_2$ there has been surprisingly little published on the kinetics and mechanisms of the dissolution of ilmenite in strong sulfuric acid. It is now accepted that the species formed during the dissolution is TiO.SO$_4$·xH$_2$O (x = 0 or 1). Dissolution of ilmenite can be summarised by reaction (1) which implies that a high sulfuric concentration should aid dissolution, which is indeed the case. (Zhang and Nicol, 2009; Lasheen, 2009; Sasikumar et al., 2007; Liang et al., 2005; Welham and Llewellyn, 1998; Grey et al., 1996; Han et al., 1987; Barton and McConnel, 1979; Barksdale, 1966)

$$\text{FeTiO}_3 (s) + 2\text{H}_2\text{SO}_4 (aq) = \text{TiOSO}_4 (s) + \text{FeSO}_4 (s) + 2\text{H}_2\text{O} (l)$$  \hspace{1cm} (1)

When the sulfuric acid concentration is less than 14 M and the temperature is lower than 200 °C, the products, TiOSO$_4$ and FeSO$_4$ are soluble and thus the dissolution reaction of ilmenite can be expressed by reaction (2) (Liang et al., 2005; Han et al., 1987):

$$\text{FeTiO}_3 (s) + 4\text{H}^+ (aq) = \text{TiO}^{2+} (aq) + \text{Fe}^{2+} (aq) + 2\text{H}_2\text{O} (l)$$  \hspace{1cm} (2)

The rate of dissolution of ilmenite was found to be controlled by a chemical reaction at the ilmenite surface (Barton and McConnel, 1979; Han et al., 1987). It has been found that the dissolution of ilmenite can be enhanced under reducing conditions in solution by adding metals such as zinc, tin and iron (El-Khaliny, 1967; Rahm and Cole, 1981). Recently, a process has been described for reductive dissolution of
Ilmenite in sulfuric acid media (Roche et al., 2004; Stuart et al., 2007). It involves leaching of ilmenite minerals in relatively concentrated sulfuric acid of 400-700 g L\(^{-1}\) at temperatures of less than 110 °C in the presence of reductants such as scrap iron. It is also known that the dissolution of ilmenite can be enhanced by adding other metals such as zinc and tin (El-Khaliny, 1967). Mahmoud et al. (2004) and Lasheen (2005) have reported reductive leaching of ilmenite ores in hydrochloric acid using metallic iron. These authors indicated that addition of sufficient iron metal during leaching reduces the dissolved iron(III) to iron(II) and some of the dissolved titanium(IV) to titanium(III). The presence of a small quantity of titanium(III) ions in solution is assumed to have a role in reducing iron(III) in the ilmenite minerals and thus accelerates the rate of dissolution. A more recent electrochemical study on ilmenite (Zhang and Nicol, 2009) has suggested that reductive dissolution of ilmenite to form iron(II) and titanium(III) is possible and that the rate of dissolution of ilmenite is higher under reducing conditions.

The present study is part of a more extensive investigation into the kinetics of the dissolution of ilmenite in sulfuric acid solutions in the range of 400 to 600 g L\(^{-1}\) at temperatures below 110 °C and, in particular, the role of titanium(III) ions and other reductants in accelerating the kinetics.

2. Experimental

2.1 Materials

Powdered samples of ilmenite sand were provided by a local producer and used as received. The samples were also mineralogically and chemically analysed at the former BHP Billiton Technology Centre, Newcastle, NSW. The chemical assays of various size fractions are shown in Table 1, indicating that there is little variation in composition with particle size. The results of a mineralogical analysis of these ilmenite samples showed they contained about 95 % w/w ilmenite, 3.1 % leucoxene, 0.13 % rutile, 0.32 % hematite and other minor minerals. The estimated stoichiometry of this ilmenite is \(0.16\text{Fe}_2\text{O}_3\cdot0.65\text{FeO}\cdot\text{TiO}_2\) based on the chemical analysis. It is worth noting that about 1/3 of total iron exists as iron(III), although hematite is only a minor component in the sample.

Titanium(III) solutions were prepared by dissolving metallic titanium powder of 99.7 % purity (-100 mesh from Aldrich, USA) in hot sulfuric acid solutions and making up the solutions to 450 g L\(^{-1}\) sulfuric acid. Liquidified sulfur dioxide was supplied by BOC and nitrogen gas from Air Liquide was of high purity grade. Other chemicals were of analytical grade. Distilled water was used throughout the experiments.
2.2 Apparatus and procedure

Batch leach tests were conducted in a 500 mL cylindrical glass reactor, with the slurry being agitated by a glass bladed overhead stirrer. The stirrer was rotated at a speed of about 600 rpm such that the ilmenite particles were completely suspended. The reactor was heated using a hotplate equipped with a temperature control (±2 °C) system. A condenser with circulating ice-water was employed to minimise evaporation of the solutions from the reactor during the tests. The potential (Eh) of solution in the reactor was measured by a platinum wire against an external Ag/AgCl reference electrode and recorded using a Labview Data Acquisition System. All potentials are reported versus the standard hydrogen electrode.

Prior to each test, nitrogen gas was used to flush the reactor in order to expel oxygen and then 200 mL of the appropriate acid solution, without or with titanous ions (pre-analysed for total Ti and Ti(III)), was added and heated with nitrogen bubbling. Nitrogen bubbling during the leach tests was found to be unnecessary after the first few tests and was discontinued. When the set temperature was reached, samples of ilmenite were injected into the reactor and the leaching experiment started.

The rate of dissolution was monitored by taking aqueous samples of 2 mL at various times from the reactor which were filtered through 0.45 μm filter paper and analysing for the concentrations of iron and titanium. When the set sampling time was reached, the stirrer was temporarily stopped for 20 seconds to settle the ilmenite particles in order to retain the ilmenite particles in the reactor. After each aqueous sample was taken, the agitation was re-started and 2 mL of the fresh starting solution was added into the reactor to maintain an approximately constant volume. The cumulative rates of dissolution of titanium and iron were calculated at various times and expressed as a leaching fraction. Corrections were made for the solution removed for analysis and added after sampling.

In experiments at controlled potential, a Metrom Dosimat 665 was utilized to inject a sulfuric acid solution of 450 g L$^{-1}$ containing titanous ions into the reactor in order to maintain the set potential. The volume of injected solution was recorded for calculation of the leaching rates at various times. In experiments using SO$_2$ as a reductant, a flowrate of 30 mL min$^{-1}$ was employed during the leach tests and SO$_2$ sparged for 30 minutes before addition of the ilmenite sample.

2.3 Chemical analyses

The titanium concentration in the aqueous samples was analysed using spectrophotometry of the titanium(IV)-H$_2$O$_2$ orange complex as described in a previous study (Zhang and Nicol, 2009). In the case of samples containing dissolved SO$_2$, adjustments were made to the above procedure in which residual SO$_2$ was first oxidised by chromium(VI).
Total iron in solution was measured using atomic absorption spectrometry. Titanium(III) concentrations were measured by titration against a 0.009 M Fe(III)-0.1 M H$_2$SO$_4$ solution using SCN$^-$ as indicator.

3. Results

3.1 Leaching with acid

It is well established that acid concentration has a great effect on the dissolution rate of ilmenite. Experimental results reported by Han et al. (1987) showed that the rate of dissolution increased up to about 14 M H$_2$SO$_4$ (1380 g.L$^{-1}$) in which maximum conversion was observed. In this study relatively dilute sulfuric acid solutions in the range of 400-600 g.L$^{-1}$ were utilized, aimed at a new process using low temperatures and relatively low concentrations of recycled acid. Thus, the standard leach conditions in this study involved the use of 10 g.L$^{-1}$ of the 38-53 µm size fraction of ilmenite in 450 g L$^{-1}$ H$_2$SO$_4$ solution at 85 °C. Other conditions were varied in order to establish the effects of the various parameters on the rate of dissolution.

3.1.1 Effect of temperature

The effect of temperature on the rate of ilmenite dissolution was studied in the range of 85-100 °C under otherwise standard conditions. The results obtained are shown in Figure 1. It is clear that, as expected, temperature has a significant effect on the rate of dissolution. The rates of dissolution of titanium and iron are similar at all temperatures, indicating the simultaneous dissolution of titanium and iron as expressed by the overall reaction (2). This reaction assumes that there is no solid product formed during leaching in low concentrations of sulfuric acid.

It can be seen that even at 100 °C the dissolution rate of ilmenite in low concentrations of sulfuric acid is low and it may take more than 24 hours to achieve 100 % dissolution of ilmenite under these conditions. Repeat experiments were conducted to check the accuracy of the kinetic measurements and the variation in the rate between duplicate experiments was less than 3%.

3.1.2 Effect of sulfuric acid concentration

Several experiments were carried out using sulfuric acid concentrations varying from 450 to 600 g L$^{-1}$ under otherwise standard conditions. From the results shown in Figure 2, it can be seen that the acid concentration has a little effect on the kinetics of leaching in this range of acidity, with the leach rate increasing only slightly with increasing acid concentration.
3.1.3 Effect of particle size

The effect of particle size on the rate of dissolution was examined with various size fractions under otherwise standard conditions. The results, given in Figure 3, are as expected with the rate increasing with decreasing particle size under standard conditions, although the effect is smaller than could be expected.

3.2 Leaching with SO$_2$

As outlined in the introduction, the kinetics of the dissolution of ilmenite can be enhanced in the presence of reducing agents. It is well known that SO$_2$ can reduce ferric iron in solution and therefore some experiments were performed with the sparging of gaseous SO$_2$ in the absence and presence of ferrous ions under otherwise standard conditions. The results of these experiments, given in Figure 4, also compare the results of an experiment conducted with addition of titanous sulfate solution to control the solution potential at 0.4 V in the presence of 20 g.L$^{-1}$ Fe(II). It also includes results of a test carried out in acid only, under standard conditions.

It can be seen that the dissolution rate of titanium in the presence of SO$_2$ is similar to that in the absence of SO$_2$. However, if ferrous ions are also present, the initial rate is higher - although it tends to the same value with SO$_2$ only at longer times. This higher rate in the presence of both 20 g.L$^{-1}$ Fe(II) and SO$_2$ could be related to the well known fact that SO$_2$ can react with Fe(III) thereby reducing the potential of the solution. Thus measurements showed that the solution potential in the presence of both 20 g.L$^{-1}$ Fe(II) and SO$_2$ reached a value of about 0.50 V and increased slightly to 0.52 V during the test, while the solution potential in the absence of Fe(II) was higher at about 0.56 V. This difference in the potentials could explain the observed differences in the leaching behaviour in the presence and absence of 20 g.L$^{-1}$ Fe(II). By comparison, the dissolution rate of titanium with addition of Ti(III) to control the potential at 0.4 V is higher than that with both 20 g.L$^{-1}$ Fe(II) and SO$_2$, which confirms the effect of the solution potential on the leaching kinetics as previously reported by Zhang and Nicol (2009).

3.3 Leaching with titanium(III) ions

The “standard” reductive leach conditions chosen for the study were 450 g L$^{-1}$ H$_2$SO$_4$, 85 °C, 2 g ilmenite (38-53 µm size fraction) in 200 mL of leach solution and a nominal initial concentration of about 4 g L$^{-1}$ Ti(III). Other conditions were varied in order to establish the effects of the various parameters on the rate of dissolution. These conditions were selected to investigate the kinetics of leaching ilmenite in
lower concentrations of sulfuric acid at lower temperatures which are used in the newly developed process (Roche et al., 2004; Stuart et al., 2007).

The significant effect of the addition of titanium(III) ions on the rate of dissolution of both titanium and iron in a 600 g L\(^{-1}\) \(\text{H}_2\text{SO}_4\) solution at 85°C is shown in Figure 5. Thus the extent of leaching of titanium increased from about 20% after 6 hours in the absence of Ti(III) to about 70% after 5 hours in the presence of 3.5 g L\(^{-1}\) Ti(III). The rate of dissolution of iron followed the same trends, so, although the rate of iron dissolution was measured in all experiments, several of the subsequent figures will show only the data for titanium. These data confirm that the dissolution of ilmenite can be accelerated under reducing conditions. Duplicate experiments conducted to check the accuracy of the kinetic measurements showed that difference was less than 5% in the extent of dissolution of both titanium and iron under these conditions.

### 3.3.1 Effect of solution potential

The effect of solution potential on the dissolution rate of ilmenite was investigated by conducting several experiments in which the Ti(IV)/Ti(III) ratio was initially adjusted to a set potential in the range of 0.1 to 0.4 V at an initial total concentration of 5 g.L\(^{-1}\)Ti. Other conditions were standard and the potential was maintained during the experiments by adding titanium(III) solution containing 450 g L\(^{-1}\) sulfuric acid as described above. The results of these experiments are shown in Figure 6 for the dissolution of titanium and Figure 7 for that of iron. These results clearly show that the dissolution rate of both titanium and iron increases with decreasing solution potential, consistent with the results obtained from a recent electrochemical study (Zhang and Nicol, 2009).

It is apparent that even under relatively mild reducing conditions at a potential of 0.4 V, significant increases in rate can be obtained. It also appears that the rate increases with decreasing potential but may attain a maximum at a potential of about 0.1 V. The rates of titanium and iron dissolution also appear to be the same at all potentials.

### 3.3.2 Effect of pulp density and particle size

Several experiments were performed under standard reducing conditions in which the amount of ilmenite was varied to give S/L ratios (gram mineral/mL solution) of 1/200, 1/100, and 1/20. From the results shown in Figure 8, it appears that the rates of dissolution of titanium are similar for the lower solids content, but the rate is lower at the highest solids content due to insufficient Ti(III) initially added to the solution to maintain a low potential. The calculated molar amount of Fe(III) in the 10 g. ilmenite sample was more than that of Ti(III) in solution. Thus, the potential after 12 hours was ~65 mV higher for the experiment at a S/L ratio of 1/20 than the potential with a
S/L ratio of 1/200. Therefore, in all subsequent experiments, a S/L ratio of 100 was selected to minimize the decrease in potential during an experiment.

The effect of the particle size of the ilmenite on the rate of leaching under reducing conditions is shown by the data for the dissolution of titanium in Figure 9. In these tests, the concentration of titanium(III) decreased by about 40% during the period of the experiment. As in the case of similar experiments in the absence of a reductant (Figure 3), the effect of the particle size does not appear to be significant.

3.3.3 Effect of concentration of sulfuric acid

Figure 10 shows the leaching rate of titanium in various concentrations of sulfuric acid under standard conditions with 3.5 g.L\(^{-1}\) Ti(III). There appears to be a small increase in rate with increasing acid concentration. As titanium(III) ions were found to be largely insoluble in 700 g.L\(^{-1}\) H\(_2\)SO\(_4\) at 85 °C and even at 100 °C, it was not possible to obtain data at this acid concentration. In addition, it has been reported (Han et al., 1987) that the solubility of titanium(IV) also decreases in high concentrations of sulfuric acid. The results in the absence of a reducing agent (Figure 2) showed that the rate of dissolution of the same ilmenite sample increased slightly with increasing acid concentration.

3.3.4 Effect of temperature

Figure 11 shows the leaching rate of titanium at various temperatures under otherwise standard conditions in the presence of titanium(III) ions. As expected, temperature has a significant effect on the rate of leaching of ilmenite.

4. Discussion of kinetics and kinetic models

The experimental results obtained in this study were examined utilizing the well known models for the dissolution of sized particles such as the shrinking particle and the shrinking core models under the assumption that the particles are homogeneous and spherical (Levenspiel, 1972). In the shrinking particle model, the rate is governed by a chemical reaction on the surface of the reacting particles, while in the shrinking core model the rate is governed by mass transport through a thickening product layer on the surface. These models can be expressed as follows in the form of integrated rate equations:

For the shrinking particle model:

\[
1-(1-X)^{1/3} = k_s t = bkVC_a^n t / r_0
\]
For the shrinking core model,

\[1-3(1-X)^{2/3} + 2(1-X) = k_D t = 6VbD_e C_a t / r_o^2\]  

(4)

In which \(X\) is the fraction dissolved at time \(t\); \(k_S\), \(k_D\) are apparent first-order rate constants; \(b\) is stoichiometric coefficient; \(k\) is an intrinsic rate constant; \(V\) is the molar volume of reacted substance; \(C_a\) is the bulk concentration of acid; \(D_e\) is effective diffusivity in the product layer; \(r_o\) is initial particle radius; \(n\) is reaction order in the terms of acid concentration.

Note that, in the case of the shrinking particle model, \(k_S\) will be inversely proportional to the initial particle radius while \(k_D\) is inversely proportional to the square of the initial particle radius for the shrinking core model.

4.1 Kinetic model for dissolution with acid alone

As could be expected from a dissolution reaction that produces only soluble products, it was found that all of the experimental data obtained with acid alone can be fitted to the expression for the shrinking particle model. Figure 12 show an example of the fits for both the shrinking particle model and shrinking core model for results of a typical experiment carried out in 450 g.L\(^{-1}\) H\(_2\)SO\(_4\) at 85 \(^\circ\)C in the absence of reductants.

Figures 13-15 show the plots of the shrinking particle model as applied to the data in Figures 1-3 for the dissolution of titanium. The slopes of these plots provide a value for \(k_S\) that is proportional to the rate constant for the dissolution process.

The values of \(k_S\) at different temperatures can be used in an Arrhenius plot to derive an apparent activation energy of 75.0 kJ mol\(^{-1}\) for the dissolution of titanium as shown in Figure 16. This relatively high activation energy is indicative of a rate-controlling slow chemical reaction. Liang et al. (2005) reported an activation energy of 72.6 kJ mol\(^{-1}\) for the dissolution rate of ilmenite in 15.4 M H\(_2\)SO\(_4\) (~1 H\(_2\)SO\(_4\)500 g.L\(^{-1}\)) at temperatures from 100 to 198 \(^\circ\)C. Whilst Han et al. (1987) reported an activation energy of 64.4 kJ mol\(^{-1}\) 18 M H\(_2\)SO\(_4\) (~1800 g.L\(^{-1}\)) over the temperature range of 88-115 \(^\circ\)C; and Barton and McConnel (1979) obtained a value of 90 kJ mol\(^{-1}\) in 4.7 M to 12.5 M H\(_2\)SO\(_4\) (460 to 1230 g.L\(^{-1}\)) between 65-85 \(^\circ\)C.

The \(k_S\) values obtained from the lines in Figure 14, were found to be approximately proportional to \(C_a^{0.75}\) in which \(C_a\) is the acid concentration in g L\(^{-1}\). Similarly, the effect of the initial particle size on the values of \(k_S\) for the dissolution of titanium at 85 \(^\circ\)C is obtained from the slopes of the lines in Figure 15 and can be used to derive an empirical relationship whereby \(k_S\) is proportional to \(r_o^{-0.27}\). Note the \(r_o\) is initial particle radius in \(\mu m\), which is calculated as the mean of the upper and lower sizes in the size fraction.
A combination of the shrinking particle rate expression, and the effects of particle size, acid concentration and temperature on the apparent rate constant, gives an overall expression for the extent of dissolution of titanium in acid with time of the form:

\[ 1-(1-X)^{1/3} = k_S t \]  
(3)

in which \( k_S = 1.97 \times 10^7 r_o^{-0.27} C_a^{0.75} \exp(-9026/T) \)  
(4)

where \( k_S \) is the apparent rate constant in h\(^{-1}\), \( r_o \) is the initial particle radius in µm, \( C_a \) is the concentration of sulfuric acid in g L\(^{-1}\), and \( T \) is the temperature in °K.

It should be emphasized that the above derived rate equation is only really applicable to the rate of dissolution of titanium in solutions containing only sulfuric acid within the ranges of particle size, acid concentration and temperature used in this investigation.

### 4.2 Kinetic model for dissolution in the presence of titanium(III)

The experimental results obtained in the presence of titanium(III) were also analysed utilizing the above two kinetic models for the reaction of spherical particles. In this case, it was not possible to maintain a constant Ti(III) concentration during an experimental run and the concentration decreased with time due to both oxidation by the iron(III) in the ilmenite and also to some extent by oxidation by dissolved oxygen. A comparison of the data for dissolution of titanium as fitted to these two models is shown in Figure 17 for the data in Figure 8.

It is apparent from Figure 17 that approximately straight lines are obtained when data are fitted to the shrinking core model, while the shrinking particle model results in curved lines. It was also found that the mathematical form of the shrinking core model provided a better fit to the data in the presence of titanium(III) ions. This is not expected, as the products of ilmenite leaching are soluble under the conditions in this study and the residue is a small fraction of acid insoluble material.

One possible reason for this result is that the concentration of titanium(III) in the leaching solution decreases and thus the potential increases during the course of any one experiment, resulting in a decreasing slope with extent of reaction in the plots of the shrinking particle model. Thus, one cannot expect the data to fit the expected shrinking particle model unless correction could be made for the varying titanium(III) concentration. Another possible reason is the formation of a “purple-black” mixed oxidation state Ti(IV)-Ti(III) sulfate complex in sulfuric acid solutions (Cservenyak et al., 1996a and 1996b), but its effect on the kinetics and mechanism of leaching ilmenite needs to be further understood.
In many dissolution processes, however, the fact that a particular model best fits the data does not necessarily imply that the rate-determining step is appropriate. In this case, the rate determining step is mass transport through a product layer on the surface of the mineral, although the high value of apparent activation energy calculated below for the reaction indicates that mass transport is unlikely to be rate-determining. Hence, we will simply use the shrinking core model as a mathematical method of deriving an apparent rate constant \( k_D \) for a particular experiment that can be used to quantitatively establish the effects of other experimental parameters on the rate.

Figure 18 shows the plots of the shrinking core model as applied to the data in Figure 11 for the effect of temperature on the dissolution of titanium in the presence of titanium(III). The values of \( k_D \) obtained from the slopes at different temperatures can be used to derive an apparent activation energy of 90 kJ mol\(^{-1}\) for the dissolution of titanium under reducing conditions according the Arrhenius equation, as shown in Figure 19. This activation energy value is comparable to the value of 75 kJ mol\(^{-1}\) obtained with acid alone (Section 3.4.1) and to the value of 90 kJ.mol\(^{-1}\) obtained by Barton and McConnel (1979) over the temperature range of 65-85 °C in 4.7 M to 12.5 M H\(_2\)SO\(_4\) solutions.

Similarly, the values of \( k_D \) obtained from the data in Figures 9 and 10 can be used to derive empirical expressions for the effects of particle size and acid concentration on the rates of dissolution in the presence of titanium(III). A combination of the shrinking core rate expression and the effects of particle size, acid concentration and temperature on the rate of ilmenite dissolution will result in an overall expression for the extent of dissolution of titanium with time of the form

\[
 k_D t = 1 - 3(1-X)^{2/3} + 2(1-X) \quad (5)
\]

in which

\[
 k_D = 2.5 \times 10^{10} \ r_0^{-0.30} \ C_a^{0.70} \ \exp(-10811/T) \quad (6)
\]

where \( k_D \) is apparent rate constant in h\(^{-1}\), \( r_0 \) is the initial particle radius in \( \mu m \), \( C_a \) is the concentration of acid in g L\(^{-1}\) and \( T \) is the temperature in °K.

A comparison of the calculated values for \( k_D \) in terms of equation (6) with the observed \( k_D \) values for individual experiments carried out in the presence of Ti(III) ions is shown in Figure 20. The correlation is reasonably satisfactory and suggests that the overall rate equation (6) can be used to predict the rate of dissolution of titanium in the presence of adequate titanous ions within the ranges of particle size, acid concentration and temperature used in this investigation.

Most natural ilmenites contain some iron(III) in the lattice and, as outlined in Section 2.1, the sample used in this study has an approximate composition 0.16 Fe\(_2\)O\(_3\)•0.65 FeO•TiO\(_2\). In a previous electrochemical study, it was found that cathodic reduction of this ilmenite at potentials below about 0.3 V results in selective dissolution of iron and that the rate of iron dissolution is almost identical to that calculated from the charge passed for a process involving reduction with one electron per iron, such as
\[
\{\text{Fe}^{2+} \cdot y\text{Fe}^{3+} \cdot \text{Ti}^{4+} \cdot (3+1.5y)\text{O}^{2-}\} + 3y\text{H}^+ + ye = y\text{Fe}^{2+} + \text{FeTiO}_3 + 1.5y\text{H}_2\text{O} \quad (7)
\]

On the basis of this, it is not unreasonable to suggest that dissolution of ilmenite in the presence of titanium(III) ions occurs as a result of this reaction coupled to that for the oxidation of titanium(III) (Kelsall and Robbins, 1990; Zhang and Nicol, 2009).

\[
\text{TiO}^{2+} + 2\text{H}^+ + e = \text{Ti}^{3+} + \text{H}_2\text{O} \quad E^0 = 0.10 \text{ V at } 25 \degree \text{C}; 0.046 \text{ V at } 60 \degree \text{C} \quad (8)
\]

to give

\[
\{\text{Fe}^{2+}y\text{Fe}^{3+}\text{Ti}^{4+}(3+1.5y)\text{O}^{2-}\} + 3y\text{H}^+ + y\text{Ti}^{3+} = y\text{Fe}^{2+} + \text{FeTiO}_3 + 1.5y\text{H}_2\text{O} + y\text{Ti}^{4+} \quad (9)
\]

This electrochemical step is then followed by

\[
\text{FeTiO}_3 + 4\text{H}^+ = \text{TiO}^{2+} + \text{Fe}^{2+} + 2\text{H}_2\text{O} \quad (2)
\]
in which the rate of dissolution of stoichiometric ilmenite in acid (reaction 2) is significantly greater than that of the iron-rich natural sample. The dependence of the rate of leaching on the potential could be expected to follow from the potential-dependence of the half-reactions (7) and (8).

### 5. Conclusions

1). The kinetics of dissolution of ilmenite have been investigated at relatively low temperatures in the presence and absence of Ti(III). In solutions containing only sulfuric acid, the effects of particle size (25 to 90 µm) and acid concentration (450 to 600 g L\(^{-1}\)) are minor whilst the effect of temperature (85 to 100 °C) is significant. The batch leach kinetics in acid solutions appear to fit a shrinking particle model with the rate of dissolution controlled by a slow chemical reaction with an activation energy of 75.0 kJ mol\(^{-1}\). The following rate equation has been established that includes the effects of these variables on the fraction (X) leached after a time (t),

\[
1-(1-X)^{1/3} = k_S t \quad \text{in which} \quad k_S = 1.97 \cdot 10^7 r_0^{-0.27} C_a^{0.75} \exp(-9026/T)
\]

2). The dissolution of ilmenite in moderately strong sulfuric acid solutions in the presence of titanium(III) ions significantly accelerates the leaching of ilmenite by reducing the iron(III) component of the mineral lattice. Again, the kinetic data obtained for the dissolution of titanium and iron in the presence of titanium(III) ions have been analysed in terms of the effects of temperature, S/L ratio, particle size and sulfuric acid concentration. A suitable mathematical expression for the leaching of ilmenite in the presence of titanium(III) ions has been found to be that used to describe the shrinking core model.
\[ k_{D} t = 1 - 3(1-X)^{2/3} + 2(1-X) \quad \text{in which} \quad k_{D} = 2.5 \times 10^{10} r_{o}^{-0.30} C_{a}^{0.70} \exp(-10811/T) \]

The apparent activation energy was found to be 90 kJ per mole which suggests that the rate-controlling step in the dissolution of ilmenite involves slow chemical and/or electrochemical reactions on the mineral surface.

3). Use of SO\(_2\) as a reductant improves the rate of dissolution of titanium only in the presence of ferrous ions in solution, but the effect is significantly less than that of titanium(III) ions due to the lower potentials attainable with Ti(III).

Acknowledgements

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References


Figure Captions

Figure 1. Effect of temperature (100 °C (■), 92 °C (♦), 85 °C (▲)) on the dissolution rate of 38-53 µm ilmenite in 450 g L⁻¹ sulfuric acid solution. Solid lines are for Ti and broken lines for Fe.

Figure 2. Effect of sulfuric acid concentration (■ 450, ▲ 500, ♦ 600 g L⁻¹) on the rate of dissolution of 38-53 µm ilmenite at 85 °C. Solid lines are for Ti and broken lines for Fe.

Figure 3. Effect of particle size (▲ 25-38, ■ 38-53, ♦ 75-90 µm) on the rate of dissolution of the ilmenite in 450 g L⁻¹ H₂SO₄ at 85 °C. Solid lines are for Ti and broken lines for Fe.

Figure 4. The dissolution rate of titanium from 38-53 µm ilmenite in 450 g L⁻¹ acid at 85 °C in the presence and absence of reductants. (x) acid only; (■) SO₂; (♦) 20 g L⁻¹ Fe(II) and SO₂; (▲) 20 g L⁻¹ Fe(II) and Ti(III) added to control potential at 0.40 V.

Figure 5. Effect of Ti(III) on the leaching of ilmenite (38-53 µm) in 600 g L⁻¹ H₂SO₄ with (closed symbols) or without (open symbols) 3.5 g L⁻¹ Ti(III) at 85 °C. Solid line for Ti and dashed line for Fe.

Figure 6. Effect of potential on the rate of dissolution of titanium under standard conditions with initially 5 g L⁻¹ Ti(IV). (■ 0.11 V, ♦ 0.16 V, ▲ 0.3 V, (x) 0.4 V) Also shown is the data for the dissolution of titanium in the absence of Ti(III) ions (o).

Figure 7. Effect of potential on the rate of dissolution of iron under standard conditions with initially 5 g L⁻¹ Ti(IV). (■ 0.11 V, ♦ 0.16 V, ▲ 0.3 V, (x) 0.4 V) Also shown is the data for the dissolution of iron in the absence of Ti(III) ions (o).

Figure 8. Effect of solid /liquid ratio on the rate of dissolution of titanium under standard conditions with 4.5 g L⁻¹ Ti(III). S/L ratios 1:200 (■), 1:100 (♦) and 1:20 (▲).

Figure 9. Effect of particle size on the rate of dissolution of titanium under standard conditions with 4.2 g L⁻¹ Ti(III). Particle size 25-38 µm (♦), 38-53 µm (●), 53-75 µm (■) and 75-90 µm (▲).
Figure 10. Effect of sulfuric acid concentration on the rate of dissolution of titanium under otherwise standard conditions with 3.5 g L\(^{-1}\) Ti(III).
Acid concentration 400 (●), 450 (▲), 500 (■) and 600 g L\(^{-1}\) (♦).

Figure 11. Effect of temperature on the rate of dissolution of titanium under otherwise standard conditions in the presence of 3.5 g L\(^{-1}\) Ti(III).
Temperature 80 (●), 90 (♦), 100 (■) and 110 (▲) °C.

Figure 12. Application of results of an experiment to both shrinking particle model and shrinking core model. Square symbols are for titanium and triangles for iron.

Figure 13. The effect of temperature on the rate of dissolution of titanium in acid (data from Fig.1).
(▲) 85 °C, (♦) 92 °C, (■) 100 °C.

Figure 14. The effect of acid concentration on the rate of dissolution of titanium in acid (data from Fig.2).
(▲) 450, (■) 500, (♦) 600 g L\(^{-1}\) acid.

Figure 15. The effect of particle size on the rate of dissolution of titanium in acid (data from Fig.3).
(■) 25-38, (▲) 38-53, (♦) 75-90 µm.

Figure 16. Arrhenius plot of the data from Fig.13.

Figure 17. Data from Fig.8 fitted to shrinking core model (■) and shrinking particle model (▲).
S/L ratios of 1/100 (solid lines) and 1/20 (dashed lines).

Figure 18. Shrinking core model plots for the effect of temperature on the rate of dissolution of titanium in the presence of Ti(III).
80 °C (■), 90 °C (●), 100 °C (▲) and 110 °C (♦). (Data from Fig.11)

Figure 19. Arrhenius plot of the data from Fig.18.

Figure 20. Comparison of observed k\(_D\) (in h\(^{-1}\)) for individual experiments carried out in the presence of Ti(III) with that calculated using the overall rate equation (6).
Table 1. Chemical Analyses of the Ilmenite Samples

<table>
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<tr>
<th>Size µm</th>
<th>TiO₂</th>
<th>Ti</th>
<th>Fe</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Cr₂O₃</th>
<th>MgO</th>
<th>MnO</th>
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<tr>
<td>53-75</td>
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<td>16.10</td>
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<td>0.39</td>
<td>0.23</td>
<td>0.92</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Figure 13

Figure 14
Figure 15

![Graph showing time in hours on the x-axis and \(1-(1-X)^{1/3}\) on the y-axis.]

Figure 16

![Graph showing \(\ln k_s\) on the y-axis and \(T^{-1}, K^{-1}\) on the x-axis.]

\[\text{ACCEPTED MANUSCRIPT}\]