Characterization and Leaching Kinetics of Ilmenite in Hydrochloric Acid solution for Titanium Dioxide Production

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Abstract. A kinetic study of ilmenite in hydrochloric acid (HCl) leaching in the presence of reducing agent has been investigated. The effect of temperature ranging from 60 °C to 80 °C and HCl concentrations (4-9 M) on titanium and iron dissolution has been reported. The chemical and mineralogical studies of ilmenite samples was also performed using scanning electron microscopy with an energy disperse X-Ray (SEM-EDX), X-ray diffraction (XRD) and X-ray fluorescence techniques (XRF). From XRD analysis, ilmenite was found to be the main mineral phase in the presence of associated minerals such as rutile and hematite. SEM micrograph indicated that ilmenite before leaching has a homogenous and angular shape. After leaching for 3 hours, a few particles have reduced its particle sizes due to structural disruption during chemical attack by HCl, but some still retain their shapes. From chemical analysis of leached product, it is indicated that 85.6% of titanium dioxide with low iron content. The dissolution of ilmenite leaching in HCl is reasonably agreed well with a shrinking core kinetic model. The apparent activation energy for iron and titanium is 71.9 kJ mol⁻¹ and 90.1 kJ mol⁻¹ respectively.

1. Introduction

Ilmenite (FeTiO₃) has been one of the major sources of titanium dioxide (TiO₂) which is extensively used in paints, pigments, papers, porcelain, plastics and fibres [1]. The forms of high grade massive ilmenite minerals of greatest importance are relatively rare. Most deposits are often found in association with oxides such as hematite (Fe₂O₃) or magnetite (Fe₃O₄) and the more widely occurring titaniferous beach sand, which have resulted from natural erosion and concentration processes [2].

White titanium dioxide pigment is produced by two processes, namely the sulfate process and the chloride process. The two processes differ in both their chemistry and raw material requirement. The sulfate process, which utilizes ilmenite as a raw material, is well known and widely used but unfavorable. This is due to environmental concerns and the production of a large volume of by-products (ferrous sulfate) that require high capital cost for treatment. Alternatively, the chloride process, which utilizes rutile as a raw material, offers a more economical flowsheet and generates less waste materials. Nowadays, about 60% of the world’s TiO₂ pigments are manufactured using the chloride process, in
which natural or synthetic rutile (SR), or titanium-rich slag are used as feedstocks [3]-[4]. The shortage of rutile feedstock has prompted the upgrading of ilmenite to synthetic rutile. The use of ore with greater TiO₂ content allows a pigment producer to reduce the amount of iron sulfate by-product produced in the process [5]. In this work, characterization study of ilmenite has been done to really understand the composition and mineralogy of the sample and to study the effect of leaching parameters on ilmenite dissolution in hydrochloric acid.

2. Experimental study

2.1 Ore Characterization study
The chemical composition of samples was determined using X-ray fluorescence analysis (XRF). Their phase compositions were obtained using GBC EMMA (Enhanced Multi Materials Analyzer) diffractometer (CuKα) with subsequent match search by current Visual XRD EMMA software. The morphological studies of ilmenite and leached samples were done via Scanning Electron Microscopy (SEM) (Philips XL 20).

2.2 Leaching and Kinetic Study
2.2.1 Materials and Procedures. The ilmenite ore is heavy mineral sand originated from Western Australia, Australia which provided by School of Engineering, Murdoch University. They were mixed homogeneously, split and sampled to obtain a representative sample prior to the analyses. All samples were stored at room temperature. About 100 g of samples was ground in an iron-ring mill for 30 seconds. The crushed samples were then subjected for screening and sieving to achieve the required size fractions for leaching study. Hydrochloric acid (HCl) as leaching reagents with 32% purity and milipore water was used throughout the experiments. Batch leaching test was carried out using 500 cm³ glass reactor provided with a reflux condenser and a mechanical agitator. The desired volume of HCl of the required concentration was poured in the reactor and about 20 g of ilmenite ore was added. The reactor was heated to the desired temperature using a thermostatically controlled water bath. The leachate were taken from the reactor using syringe at various time intervals and filtered through Whatman Celulose Nitrate membrane filters with pore size of 0.45 µm. Leachate samples was analysed using Atomic Absoprtion Spectrometer (AAS) and UV/Visible Spectrophotometry to determine iron and titanium content respectively. After the leaching process completed, the slurry was filtered under vacuum and the residue was washed with 100 cm³ of 3% HCl. The washed residue was dried at 110 °C, calcined at 900 °C, and weighed. The iron and titanium contents were determined in the filtrate, wash liquor, and solid product.

2.2.2 Leaching Kinetic Study. The well-known kinetic models such as the shrinking sphere and the shrinking core models for the dissolution of sized particles under the assumption that the particles are homogeneous and spherical [6] is used to rationalise the kinetics of ilmenite dissolution in HCl solution. The models can be expressed as follows in the form of integrated rate equations for the reaction with H⁺ ions for the reaction A(aq) + bB(s) = products:

For the shrinking particle model:

\[ 1-\left(1-X\right)^{1/3} = b[H^+]_{\text{bulk}} r^3 t = k_{\text{app}} t \]  
(1)

For the shrinking core model:

\[ 1 - 3(1-X)^{2/3} + 2(1-X) = 6 b [H^+]_{\text{bulk}} D_H r^2 \rho^{-1} t = k_{\text{app}} t \]  
(2)

\[ 1 - 3(1-X)^{2/3} + 2(1-X) = 6 b [H^+]_{\text{bulk}} D_H r^2 \left(1-\varepsilon\right) \rho^{-1} t = k_{\text{app}} t \]  
(3)

where X = the fraction dissolved at time t, \( k_{\text{app}} \), \( k_{\text{app}} \) = apparent rate constant, [H⁺] = concentration of acid in bulk solution (mol cm⁻³), \( D_H \) = diffusion coefficient of H⁺ through the product layer (cm² s⁻¹), r = initial particle radius (cm), \( \rho \) = molar density of the dissolving metal in the initial particle (mol cm⁻³), \( \varepsilon \) = particle porosity, b = stoichiometric factor.
3. Results and discussion

3.1 Particles grain shape, mineral phase and chemical composition

The Capel area of south-west Western Australia has extensive buried beach sand deposits and this sample is a typical commercial concentrate from the region. The visual assessment of the samples showed that the sand is lighter in colour but still retains the submetallic lustre of ilmenite. From the surface morphology observation in Figure 1, it can be observed where some of the particles shapes have a rounded and angular shape but most of the particles have a very low and medium in sphericity. The chemical analysis indicated that this sample contained 53.9% TiO\(_2\) and showed some alteration, with 45.0% of the iron being in the ferric form. Examination of the XRD pattern of sample, ilmenite phase are the main minerals present in the sample followed by minor traces of hematite and rutile phase, as shown in Figure 2. The polished section of ilmenite sample is shown in Figure 3 showed the inclusion of other minerals by the patchy pattern with dark and grey appearance under high magnification. Further EDX analysis identified the presence of other elements such as vanadium, manganese and iron along with titanium. Further investigation can be seen by the optical micrograph in Figure 4 which also shows the weathering effect on the mineral.

![Figure 1. SEM micrograph of ilmenite particles grain.](image1)

![Figure 2. XRD patterns for ilmenite ore from Western Australia (K\(_\alpha\)Co, \(\lambda = 1.788965\)) (I: ilmenite; R: rutile; H: hematite)](image2)

![Figure 3 (a) Backscattered image of ilmenite polished section sample and (b) EDX analysis on selected area, at 200x magnification.](image3)
Figure 4. Optical micrograph showing the weathering effect on ilmenite sample (a) altered particles (b) particles with patchy pattern showed by red arrows.

3.2 Ilmenite leaching and kinetic study

3.2.1 Effect of HCl and leaching temperature. The degree of oxidation of the ferrous iron is expressed by the mole ratio $\frac{Fe^{3+}}{Fe}$ while the degree of leaching of iron during weathering is expressed by the mole ratio $\frac{Ti}{Fe}$. To express an overall degree of alteration of ilmenite, a quantitative method described by Equation 4 [7]:

$$M = \left(\frac{Fe^{3+}}{Fe}\right) \times \left(\frac{Ti}{Fe}\right)$$

(4)

where M is defined as the alteration factor. The value of M falls between the theoretical limits of zero, for unweathered ilmenite (i.e. theoretical FeTiO$_3$), to an infinitely large number, for completely weathered material containing little or no iron (e.g. leucoxene, TiO$_2$). Based on Equation 5, this ilmenite sample have alteration factor (M) of 1.2 which is moderately altered ilmenite.

During ilmenite leaching in HCl solution, Fe and Ti will dissolved in solution according to chemical reaction which can be represented by Equation 5 below:

$$FeTiO_3 + HCl \rightarrow Fe^{2+} + TiO^{2+} + 2H_2O$$

(5)

For the effect of different HCl concentration ([HCl] = 4 M-11 M; leaching temperature was remained constant at 70 °C for 5 hours) it shows that the initial leaching of Fe was greater than that of Ti but it did not remain so at longer times (Table 1). As the HCl concentration increased, the percentage dissolution of Ti became higher than that of Fe. This behaviour can be a result of the presence of hematite (Fe$_2$O$_3$) and rutile (TiO$_2$) in the sample which influence the initial and final dissolution behaviour. The alteration factor showed that this sample was slightly altered ilmenite, which contains rutile and fine grained hematite (in the altered region) as discussed in section 3.1. The results listed in Table 1 show that in 4 M HCl and 7 M HCl the iron dissolution predominated over that of titanium for up to 60 minutes. This was followed by a time at which some rates were similar. However, after 60 minutes Ti dissolution became greater than that of Fe, until it reached complete leaching at higher concentrations of HCl.

For the study of effect of different temperature ([HCl] = 7 M was kept constant for 5 hours), it can be seen that as the leaching time progressed up to 1 hour, the extractions of Fe and Ti increased with increasing temperatures from 80 °C to 110 °C. After 4 hours of leaching at 90 °C, 95% of Fe and Ti was dissolved in solution and less than 2 hours at 100 °C and 110 °C.
Table 1. Effect of HCl concentration and temperature on the leaching efficiency (%) of Fe and Ti for ilmenite leaching in HCl solution at various parameters shown in the table.

| Leaching conditions | 1 h       | 2 h       | 3 h       | 4 h       |
|---------------------|-----------|-----------|-----------|-----------|
|                     | Fe | Ti | Fe | Ti | Fe | Ti | Fe | Ti |
| [HCl]/(M)           |    |    |    |    |    |    |    |    |
| 4                   | 35 | 29 | 45 | 46 | 63 | 65 | 67 | 79 |
| 7                   | 40 | 43 | 55 | 60 | 67 | 74 | 79 | 83 |
| 9                   | 86 | 95 | 97 | 98 | 97 | 98 | 97 | 98 |
| 10                  | 90 | 98 | 97 | 98 | 97 | 98 | 97 | 98 |
| 11                  | 94 | 100| 97 | 100| 97 | 100| 97 | 100|
| T/°C                |    |    |    |    |    |    |    |    |
| 80                  | 35 | 43 | 55 | 60 | 67 | 74 | 67 | 83 |
| 90                  | 64 | 69 | 81 | 88 | 94 | 90 | 95 | 91 |
| 100                 | 85 | 95 | 93 | 98 | 96 | 99 | 97 | 100|
| 110                 | 92 | 99 | 99 | 99 | 100| 100| 100| 100|

3.2.2 Evaluation of Activation energy. The activation energy can be derived from the Arrhenius plot of Ln dX/dt as a function of -1000/RT. The activation energy for ilmenite reaction in HCl obtained in this study is 90.0 kJ mol\(^{-1}\) for Fe and 71.9 kJ mol\(^{-1}\) for Ti. A high values of activation energy of ilmenite ranging from 62 to 92 kJ mol\(^{-1}\) in HCl or H\(_2\)SO\(_4\) was also reported suggesting that the mixed chemical-diffusion controlled reaction [8]–[11].

![Arrhenius plot for Fe and Ti dissolution on ilmenite samples](image1)

**Figure 5.** Arrhenius plot for Fe and Ti dissolution on ilmenite samples ([HCl] = 7 M, pulp density = 4 g/L, T = 80 °C, 90 °C, 100 °C, 110 °C, time = 5 h, size fraction = +53-63 µm).

3.2.3 Kinetic reactions. The reaction scheme of ilmenite leaching in HCl solutions is complex because of the high acid concentration used and the complex mineralogy of ilmenite samples. The reactions between ilmenite and HCl change the concentration of reagents with time and affect the kinetics of ilmenite dissolution. Examination of plots based on the equations and the two expressions on the left hand side of Equations 1 and 2 as a function of time for ilmenite sample showed that only Equation 2 (shrinking core model) gave a straight line (for the time period of 0 to 30 min) with a higher correlation (R\(^2\)=1) compared to Equation 1 (shrinking particles) as shown in Figure 6, both for Fe and Ti dissolution. Thus, the reaction kinetics of ilmenite is controlled by diffusion of the mass transport through a thickening product or solid layer on the surface. This assumptions also can be validated with SEM analysis on leaching residue after 5 hours of leaching as shown in Figure 7 below. The observation on surface of leaching ilmenite residue showed that the solid layer forms on the surface of particles after 5 hours of leaching and this solid layer inhibit further dissolution of ilmenite. Further investigation should be done on solid layer that form around the ilmenite grains.
4. Conclusion
The direct leaching of ilmenite in HCl to obtain synthetic rutile can be achieved without the pre-treatment of the raw materials which consume large energy and cost. However, it is still depend on the mineralogical nature of ilmenite samples. The more altered ilmenite become more difficult to directly leach ilmenite in acid without oxidation or reduction process. Further investigation on using reducing agent should be done to enhance the leaching rate of ilmenite. In this work, ilmenite samples obtained can be categorized as moderately altered ilmenite had resulted high leaching efficiency of Fe and Ti in HCl solution. Therefore, direct leaching method could be new potential methods for production of titanium dioxide from synthetic rutile.

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