

Study on the Effect of Mechanical Activation on the Kinetics of Hydrochloric Acid Leaching of Ilmenite

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The effect of mechanical activation on the particle size of a concentrated ilmenite and its effect on the kinetics of hydrochloric acid leaching have been investigated. It was observed that mechanical activation significantly enhances the dissolution of iron in hydrochloric acid, while it has a slight effect on dissolution of titanium. With the mechanically activated ilmenite, leaching conversion at 90 °C reached 80%. The enhanced dissolution was attributed to the increase of highly reactive crystal planes, defects formed in milling process and a dramatically decrease in the size of ilmenite crystals. The kinetic data of leaching of mechanically activated ilmenite was found to follow shrinking core model, i.e. $1-(1-\alpha)^{1/3} = K_A t$. Mechanically activating ilmenite decreased the activation energy of leaching from 43.69 (for samples leached without mechanically activating) to 18.23 kJ/mol.

Keywords: mechanical activation, ilmenite, kinetics of hydrochloric acid leaching

1. Introduction

The major use of titanium minerals is in the production of TiO₂, with relatively minor quantities used to produce the metal and titanium chemicals. Titanium dioxide is an important intermediate in the manufacture of paints, pigments, welding rod coating, ceramics, papers, and in other areas of chemical industry¹. The commonly used processes for the manufacture of white titanium dioxide pigment are the aqueous sulfate process and the anhydrous chlorination process. The sulfate process which utilizes ilmenite as a raw material is well known and widely applied, but it is time consuming, costly, and the byproduct ferrous sulfate is less marketable². In addition, the kinetics of dissolution of ilmenite in sulfuric acid is very slow.

The chlorination process involves dry chlorination of the enriched ilmenite or rutile at elevated temperatures, purification of TiCl₄ and then conversion to TiO₂. This route presently enjoys more favorable economics and generates less waste materials³. Shortage of natural rutile has encouraged research efforts to convert ilmenite into synthetic rutile for the chlorination process.

There are several processes for the production of synthetic rutile from ilmenite, most of which fall into one of the five following classifications:

- (1) Smelting processes, where the iron part of the ilmenite is reduced and melted to separate the iron from titanium. The titania slag is then leached with the sulfuric acid or with hydrochloric acid at elevated temperatures.
- (2) Reduction of ilmenite to convert ferric iron partially to the ferrous form or completely to the metallic iron form followed by acid leaching.
- (3) Reduction of the iron content of the ilmenite to the metallic iron followed by corrosion with oxygen and ammonium chloride.

(4) Oxidation and reduction of ilmenite followed by hydrochloric acid leaching, MURSO process.

(5) Roasting and magnetic separation followed by hydrochloric acid leaching, ERM. Process.

All these processes depend mainly on reductive and/or oxidative thermal pretreatment of ilmenite which is a severely energy consuming stage. Reductive pretreatment aims at converting the ferric iron in ilmenite into the ferrous state which is more soluble in hydrochloric acid.

Most leaching studies of ilmenite by hydrochloric acid were performed in order to obtain optimum conditions for upgrading the ilmenite into synthetic rutile.

Mechanical activation, usually carried out by high energy milling is reported to substantially accelerate the leaching kinetics of several sulfide and oxide minerals even at ambient pressures⁴. The enhanced effect is not only due to an increase in specific surface area of the milled powders, but also it has been attributed to structural disorder⁵, accumulating strain, amorphization of mineral particles, preferential dissolution of selective crystal planes, microtopography⁶ and formation of new phases more amenable to leaching⁴. However, to date no studies are found concerning the effect of mechanical activation on the leaching behavior of ilmenite in hydrochloric acid solution.

The purpose of the present study is to investigate the effect of mechanical activation on the kinetics of leaching of ilmenite concentrate in hydrochloric acid solution.

2. Experimental Procedure

2.1 Material

In the present work, ilmenite concentrate (powders with particle size in the range of 200-400 μm) was provided by Iluka Ltd in Australia. The chemical composition of the ilmenite sample is given in Table 1.

Table 1. Chemical composition of the ilmenite concentrate (wt%).

Compounds	TiO ₂	Fe (total)	MnO ₂	SiO ₂	Al ₂ O ₃	ZrO ₂
wt%	55	29.4	1.62	1.06	0.66	0.13

2.2 Mechanical Activation

An attrition mill was employed for the mechanical activation of the ilmenite samples. For each grinding experiment, a sample of about 150 g were subjected to dry milling using stainless steel balls of 8 mm in ambient atmosphere. The ore to ball weight ratio was maintained at 1:20 and milling was carried out at 350 rpm for all the experiments. The samples were activated in the attritor for 60, 120, 180, 300 and 600 min in separate experiments.

2.3 Leaching Experiment

Acid leaching of ilmenite ore was carried out at solid/liquid weight/volume ratio of 1:5, using a 400 mL pyrex glass reactor and mechanical agitator with teflon stirring rod. The mixing rate speed was kept constant at 350 rpm throughout all the experiments. The leaching experiments were carried out isothermally at different temperatures (25, 60, 70, 80, 90 °C, which they could be controlled to within ± 2 °C), and for periods of up to 8 h in hydrochloric acid solutions with concentration in the range of 2-12 M. In each experiment, 200 ml of hydrochloric acid solution was preheated to the temperature required, before 40 g of ilmenite sample was added. After each experiment, the reaction slurry was filtered to determine the Fe content. To determine the percentage of ilmenite dissolved, the leached residue was dried in an oven at 110 °C for 24 h, weighed and the mass loss was determined.

2.4 Analysis and Characterization

The Fe content in the solution was determined using an atomic absorption spectrophotometer. An XRD instrument (Bruker Advance D8 X-ray diffractometer) was used to determine the effect of milling on the structure of the ilmenite samples, and scanning electron microscopy was applied to measure the size of the ilmenite particles after milling process.

3. Results and Discussion

3.1 Characteristics of Mechanically Activated Ilmenite

3.1.1 XRD

XRD patterns of the milled samples and the starting material are shown in Fig. 1. The XRD pattern of unmilled sample shows that the starting powder includes crystalline ilmenite and a small fraction of TiO₂ (rutile). The XRD patterns for milled samples indicate that no new diffraction peaks appeared during milling up to 10 h, and just small

broadening occurred in the main ilmenite peaks, which is an indication of reduction in ilmenite crystalline size due to mill process.

3.1.2 Particle Size

To estimate the average sizes of ilmenite particles, SEM micrographs were used. The variation of particle sizes with milling time is shown in Fig. 2. As it can be seen, ilmenite particle size decreases exponentially with time of activation, reaches to about 0.3 μm and remain nearly constant beyond 10 h of activation.

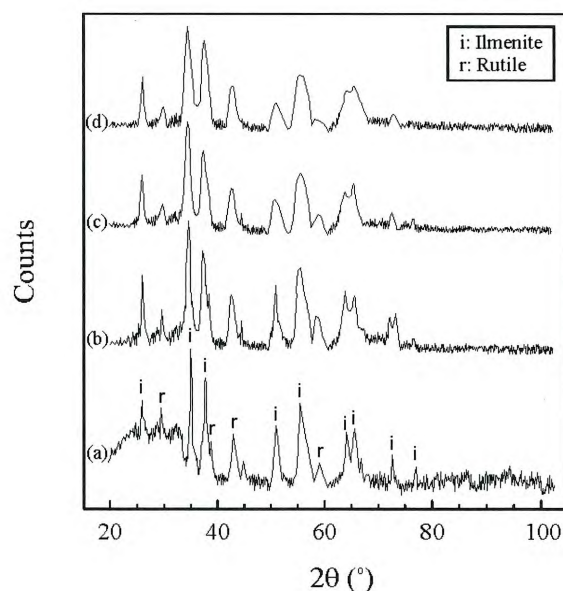


Figure 1. XRD patterns of ilmenite/carbon mixtures, a) just mixed, and attrition milled at 350 rev.min⁻¹ for b) 2, c) 5 and d) 10 h.

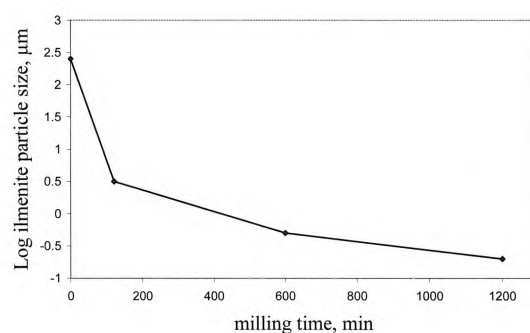


Figure 2. The effect of milling time on reduction ilmenite particle sizes.3.2. Leaching experiment.

3.2 Effect of the Studied Parameters on Leaching

3.2.1 Effect of Mechanical Activation

The extent of dissolution of Fe as a function of

activation time at 90 °C is shown in Fig. 3. The increasing time of activation up to 5 h, has a significant effect on the increasing solubility of iron in the acid solution, and beyond it, no important change can be detected. This observation is completely according to the change occurred in particle sizes (Fig. 2) and proportionally in particles free surface area. In the other words, reduction in particle size and of course in the crystalline size and the increase in surface area due to increasing milling time up to 5 h, increase the rate and extent of Fe dissolution during leaching process. Thereafter, change in the extent of iron dissolution became negligible, which is a direct result of decreasing the effect of milling process on size reduction beyond 5 h.

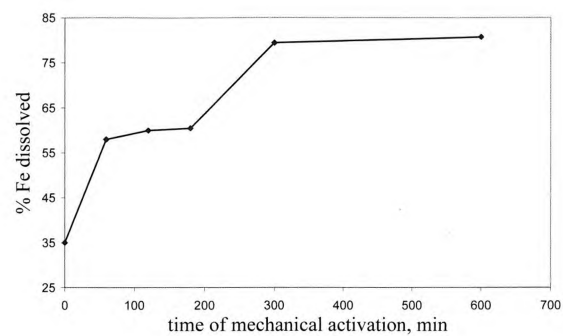


Figure 3. Effect of mechanical activation time on the Fe dissolution.

3.2.2 Effect of Acid Concentration

The effect of hydrochloric acid concentration on the extent of Fe dissolution at 90 °C and for 4 h agitation, is shown in Fig. 4. From the results it is clearly evident that, with increasing acid molarity up to 6 M, the total iron leaching efficiency increased steadily from 21.8% for 2 M HCl to 80%. Thereafter, the increase of iron dissolution became negligible, while ilmenite dissolution increased with acid concentration up to 12 M, continuously. Because the high acid concentration has a pronounced retarding effect on the hydrolysis reaction, and hence higher amounts of titanium remain soluble in HCl solution. For this reason the optimum acid concentration was determined in the range of 6 to 8 M.

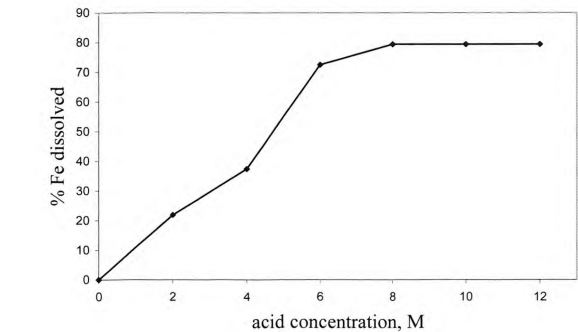


Figure 4. Effect of acid concentration on the Fe dissolution.

3.2.3 Effect of Leaching Temperature

The effect of the leaching temperature upon Fe dissolution was studied in the range of 25 to 90 °C, while the other leaching conditions were fixed at 8 M acid in 1:5 (w/v) ratio for 4 h agitation. The results obtained are shown in Fig. 5. The amount of leached iron is directly correlated with temperature up to 90 °C. Although the increase of the temperature below the boiling point has been reported to have very little effect on the Fe dissolution. However the hydrolysis reaction of TiOCl_2 is known to be much enhanced at higher temperature, and it is thought to be the main reason for such a sudden improvement in Fe removal and rutile recovery.

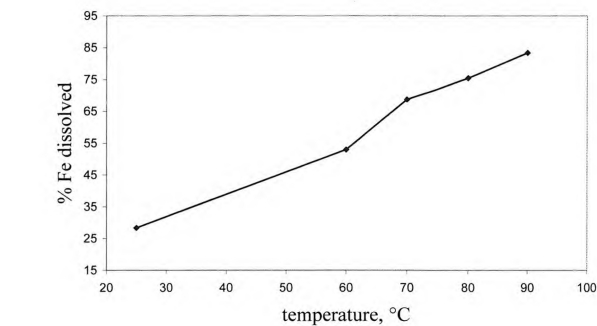


Figure 5. Effect of leaching temperature on the Fe dissolution.

3.2.4 Effect of Leaching Time

The effect of time on the leaching efficiency of ilmenite is shown in Fig. 6. Most of the iron fraction amenable to leaching from the ilmenite mineral grains is solubilized within 4 h. Thereafter, the additional iron dissolution became negligible.

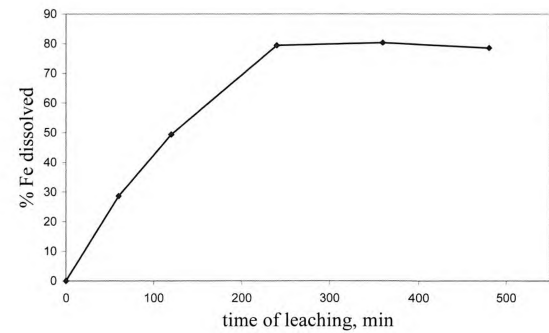
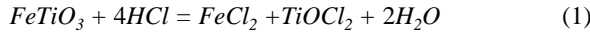


Figure 6. Effect of leaching time on the Fe dissolution.

3.3 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 phase⁷⁾. The overall reaction for the dissolution of ilmenite by hydrochloric acid may be written as:



For the iron dissolution kinetics, two established kinetic models were used [7], expressed by the following equations:

$$1 - (1 - \alpha)^{1/3} = \frac{MK_c C_A t}{dr} = k_A t \quad (2)$$

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

where k_c is the first-order rate constant ($\text{m} \cdot \text{min}^{-1}$), M is the molecular weight of the solid reactant ($\text{kg} \cdot \text{mol}^{-1}$), C_A is the acid concentration ($\text{mol} \cdot \text{m}^{-3}$), D is the diffusion coefficient ($\text{m}^2 \cdot \text{min}^{-1}$), d is the density of the particle ($\text{kg} \cdot \text{m}^{-3}$), r is the initial radius of the particle (m), α is the fraction reacted at time t (min), k_1 ($\text{m} \cdot \text{min}^{-1}$) and k_2 ($\text{m}^2 \cdot \text{min}^{-1}$) 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 produced porous layer. Examination of plots of the above kinetic equations as functions of time, for the data obtained in the present study, showed that Eq. (2) gives perfect straight lines from 0 to 240 min but Eq. (3) does not, meaning that the dissolution reaction was controlled by the chemical reaction takes place on the surface of the mineral. Plots of the function

$[1 - (1 - \alpha)^{1/3}]$ vs. time at different leaching temperatures is shown in Fig. 7. It indicates that the dissolution rates of iron at 70 to 90°C have a good agreement with the chemical reaction Eq. (2) in this range of temperature.

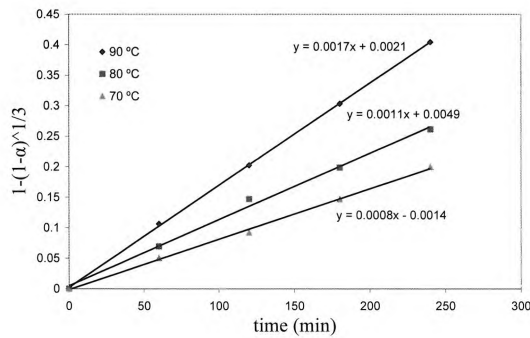


Figure 7. Plots of $1 - (1 - \alpha)^{1/3}$ vs. time for Fe dissolution at various temperatures.

The relation between the overall rate constant from Eq. (2) and temperature may be expressed by the Arrhenius equation:

$$k = A \exp(-E_a / RT) \quad (4)$$

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

Rate constants for different temperatures were calculated from the plots in Fig. 7, and the Arrhenius plot

of $-\ln k$ vs. $1000/T$ plotted correspondingly in Fig. 8. From the Arrhenius plot, the activation energy for iron dissolution was estimated to be 18.29 kJ/mol. The same way applied for unmilled sample, resulted in activation energy of about 43.69 kJ/mol.

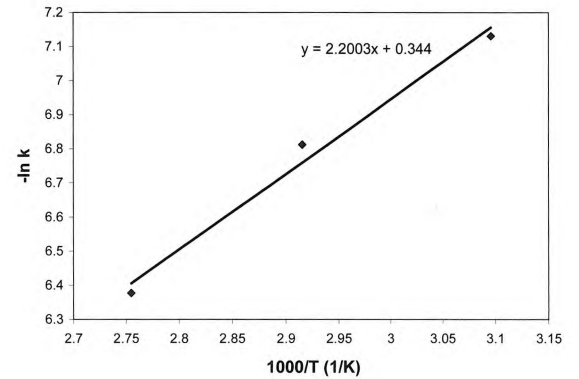


Figure 8. Arrhenius type plot for kinetic data of Fig. 7.

4. Conclusions

Mechanical activation of ilmenite resulted in substantial increase in structural disorder added the enhancement of surface area because of milling to submicron particle sizes. Leaching of activated ilmenite was found to be an efficient process. The extent of removal of iron was found to increase with time, temperature and acid concentration in the leaching solution. The maximum dissolution of Fe was more than 79% for ilmenite sample activated for 300 min and leached at 90 °C, 8 M and 4 h. The apparent activation energy for leaching found to be about 18.29 kJ/mol for sample activated for 5 h, and 43.69 kJ/mol for unmilled ones. Leaching of activated ilmenite was found to a higher efficiency than of unmilled.

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