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Kinetics of the dissolution of ilmenite in oxalic and sulfuric acid solutions

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Received 7 October 2012; Revised 5 April 2013; Accepted 17 April 2013

ABSTRACT: In this study, the effects of particle size, type and concentration of acid solution on dissolution kinetics of ilmenite are investigated. The results showed that both oxalic and sulfuric acid and their concentrations had relatively high effects on the dissolution rate of titanium, which increased with an increase in acid concentration. About 86.4% of titanium could be leached in 10 h when using 4 M oxalic acid, 1:20 solid/liquid ratio, 90 °C temperature and particle size less than 45 µm. Under similar experimental conditions with the exception of sulfuric acid concentrations of 4, 8 and 12 M, the titanium solubilization was 16.1%, 48.2% and 52.0%, respectively. The experimental data followed reaction kinetics and indicated that the shrinking particle model controlled the chemical reaction. The observed titanium dissolution rates could be expressed as $1 - (1 - x)^{1/3} = 0.0092C^{1.2022}t$ for oxalic acid for concentration varying between 1 and 4 M and $1 - (1 - x)^{1/3} = 0.0006C^{1.5977}t$ for sulfuric acid for concentration varying between 2 and 12 M, respectively. The fitted models for estimating the titanium dissolution rate from the experimental data indicated good accuracy with coefficient of determination (R^2) higher than 0.96. © 2013 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: tin tailing; ilmenite; sulfuric acid; hydrochloric acid; oxalic acid; citric acid

INTRODUCTION

Tin metallurgy continues to be commercially important in Thailand and Malaysia despite a sharp decrease in world's tin supply since 1983.^[1] The residue (namely, tin tailing) obtained from the process of mining and processing of tin is separated usually by means of gravitation techniques. The main components of tin tailing samples in Thailand are ilmenite (FeTiO_3), quartz (SiO_2), zircon (ZrSiO_4) and YPO_4 .^[2] It is desirable to recover a valuable resource and utilize these tin tailings. In this case, titanium is extracted rather than its disposal when feasible to contain the associated environment problems.

Titanium dioxide (TiO_2) is used as pigment and as filler in paper, plastic and rubber industries because of its whiteness and opacity.^[3] Unfortunately, high-grade titanium oxide is not available in nature, and titanium-rich ore is usually associated with iron most commonly as ilmenite (FeTiO_3).^[4] Many processes that have been commercially used to upgrade ilmenite to produce synthetic rutile involve a combination of the technologies of pyrometallurgy, hydrometallurgy and electrometallurgy.^[3]

The upgrading processes are generally expensive because of the involvement of multisteps of energy-sensitive thermoreductive conversions and leaching to remove iron impurities. Compared with the thermochemical and electrochemical processes, direct hydrometallurgical leach processes are advantageous in processing ilmenite ores because of low energy consumption and production of high quality of TiO_2 products.^[3] Examples of direct leaching processes are sulfuric acid leaching, hydrochloric acid leaching and sodium or potassium hydroxide leaching.

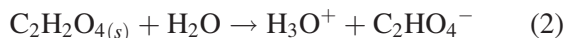
Ilmenite ore can be extracted by leaching using both strong inorganic acids and organic acids depending on study conditions. Leaching of alkaline-treated ilmenite paste at temperature of 150 °C resulted in high titanium releases of 89%, 92% and 93% when using sulfuric acid (6 M), hydrochloric acid (9 M) and oxalic acid (7.78 M), respectively.^[5] Zhang *et al.*^[6] also investigated hydrochloric acid (6.58 M) leaching of ilmenite at temperature of 105 °C. Nayl *et al.*^[7] studied kinetics of acid leaching of alkaline treated-ilmenite paste by sulfuric acid and oxalic acid. They showed that a high value of titanium dissolution of more than 90% at temperature of 150 °C could be achieved. These qualities make acid solvents suitable for mineral leaching under conditions of high temperature. Moreover, Janssen and Putnis^[4] carried out studies for oxidizing ilmenite at 700 °C in air for 12 h in order to make ilmenite more suitable for acid leaching.

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For mining operations, it may be worthwhile to use lower temperature and avoid preheating to save energy. However, available published studies have shown that acid leaching is not efficient at lower temperatures. Zhang and Nicol^[8] studied the kinetics of the dissolution of ilmenite in sulfuric acid (4.5 M) solutions and reported that titanium dissolution reached a maximum value of 37% at temperature of 100 °C. Titanium dissolution in 6 M sulfuric acid solution was only 20% and 47% for leaching temperatures of 75 and 100 °C, respectively.^[7] Lasheen^[9] also stated that acid leaching of ilmenite by 12 M hydrochloric acid at temperature of 90 °C yielded only 1% titanium. The conventional acid leaching is carried out in strong acid at high concentration and temperature up to 12 M and 150 °C, respectively. However, the conventional leaching may not be very economical. Thus, this work proposed to use weak organic acid at low concentration and temperature of 90 °C. The objectives of this study were to examine the titanium and iron solubility during the acid leaching of ilmenite at 90 °C when using a weak acid and low concentration in comparison with strong acid and high concentration.

BACKGROUND

This investigation focuses on the kinetics of acid leaching of ilmenite at 90 °C by sulfuric and oxalic acid according to the following reactions:



TiOSO_4 and FeSO_4 are soluble when the sulfuric acid concentration is less than 14 M and temperature below 200 °C.^[8] The rate of dissolution of ilmenite has been found to be controlled by a chemical reaction at the ilmenite surface.^[7,8] Nayl *et al.*^[7] stated that the recovery of titanium increased with the increase of acid concentration at temperature of 150 °C, and therefore, the rate was not controlled by external diffusion. They proposed that reaction mechanism of liquid acid was transported through the boundary layer and the ilmenite solid to the reaction interface. At the same time, the titanium product diffused back from the reaction interface to the bulk solution. This can be related to the chemical reaction model (namely, shrinking particle model) that is represented by the following relation:^[8,10]

$$1 - (1 - x)^{1/3} = k_s t \quad (4)$$

in which x is the fraction dissolved at time t and k_s is the apparent first-order rate constant.

Zhang and Nicol^[8] stated that a combination of the shrinking particle rate expression, and the effects of particle size, acid concentration and temperature on the apparent rate constant, resulted in an overall expression for the extent of dissolution of titanium in sulfuric acid with time according to the Eqn (4) with

$$k_s = 1.97 \times 10^7 r_0^{-0.27} C_a^{0.75} \exp\left(-\frac{9026}{T}\right) \quad (5)$$

where k_s is the apparent rate constant in h^{-1} , r_0 is the initial particle radius in μm ($-38 + 25$, $-53 + 38$ and $-90 + 75 \mu\text{m}$), C_a is the concentration of sulfuric acid in g/L (450, 500 and 600 g/L) and T is the temperature in K (358, 365 and 373 K).

Luo *et al.*^[10] also demonstrated that in Eqn (4), the plot of $1 - (1 - x)^{1/3}$ vs time showed very good straight line fits both for the leaching of nickel and magnesium from saprolitic laterite material at temperatures of 70, 80 and 90 °C. Sulfuric acid is another parameter factor for the leaching process, resulting in little change and a very low reaction order for acid solutions. Jin *et al.*^[11] stated that the use of shrinking particle rate model accounted for the effect of acid concentration on the apparent rate constant, resulting in an overall expression for the dissolution of copper in sulfuric acid with time (Eqn 4) as follows:

$$\ln k_s = -5.23 + 0.12 \exp\left(\frac{-(\ln C - 3.8)^2}{0.022}\right) \quad (6)$$

where k_s is the apparent rate constant in min^{-1} and C is the concentration of sulfuric acid in g/L (33, 40, 47 and 54 g/L).

However, if the reaction rate is controlled by diffusion through an inert product layer, the metal extraction can be explained by a shrinking core model that is represented by the following relation^[12]:

$$1 - \left(\frac{2}{3}\right)x - (1 - x)^{2/3} = k_d t \quad (7)$$

Martínez-Luévanos *et al.*^[12] proved that Eqn (7) resulted in very good straight lines fits for the dissolution of iron from kaolin in oxalic acid solution of 0.05 and 0.5 M. They stated that iron dissolution from kaolin was controlled by diffusion through an inert product layer. These different study conditions and the small number of published papers do not allow researchers to draw a sound conclusion. Therefore, the present study is an attempt to contribute to fill this apparent gap in knowledge. The results obtained in this study were examined utilizing the well-known models for the dissolution of various particle sizes assuming the particles to be homogeneous and spherical. Subsequently, reaction

parameters of sulfuric and oxalic acid concentration were determined from the fitted relationships.

MATERIALS AND METHODS

Ilmenite

Ilmenite originating from the Department of Primary Industries and Mines, Ministry of Industry was ground in a ball mill and screened into size ranges of -45 , $-53+45$, $-63+53$ and $-106+63\ \mu\text{m}$. Titanium and total iron in the different particle size ranges of ilmenite were determined by the UV/visible spectrophotometer assays as described in ASTM E878-96 and ISO 6685 1982, respectively. Calibration curves for each metal were determined using standardized metal solutions. Surface area measurements were carried out using BET technique (Quanta Chrome ChemBET T-3000 TPR/TRD, USA). High purity N_2 was used as adsorbent. The adsorption–desorption isotherms were recorded at liquid N_2 temperature after degassing the sample. The adsorption data in the relative pressure was used to determine monolayer capacity using the BET equation.

Table 1 shows the percentage of titanium and total iron concentration in the ilmenite for the various particle sizes. Titanium dioxide and total iron concentration from ilmenite did not vary significantly with particle size, although different surface areas of 6.3 and $2.5\ \text{m}^2/\text{g}$ were determined for size ranges of -45 and $-53+45\ \mu\text{m}$, respectively.

EXPERIMENTAL PROCEDURE FOR LEACHING BY ACID SOLUTION

Effect of particle size

Ilmenite samples weighing $15\ \text{g}$ with different size ranges of -45 , $-53+45$, $-63+53$ and $-106+63\ \mu\text{m}$ were separately added to three-necked bottles ($1\ \text{L}$) containing $300\ \text{mL}$ of $1\ \text{M}$ citric acid. The bottle was set on a hot plate and stirred with a magnetic bar at $750\ \text{rpm}$. These experiments were carried out at $90\ ^\circ\text{C}$ and replicated two times. The leaching solution was filtered through a filter paper (Whatman No. 1) and

was subsequently diluted with sterile distilled water prior to the analysis of titanium and total iron.

Effect of type of acid solution and acid concentration

Experiments were conducted by preparing a series of bottles with the same composition described in previous section and using constant particle size range of $-45\ \mu\text{m}$. The acid solutions in this study included H_2SO_4 ($1\ \text{M}$); HCl ($1\ \text{M}$); lactic acid, $\text{C}_3\text{H}_6\text{O}_3$ ($1\ \text{M}$); citric acid, $\text{C}_6\text{H}_{10}\text{O}_8$ ($1\ \text{M}$) and oxalic acid, $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ($1\ \text{M}$), with different concentrations of H_2SO_4 acid (0.5 , 1 , 1.5 , 2 , 4 , 8 and $12\ \text{M}$) and oxalic acid (0.5 , 1 , 1.5 , 2 and $4\ \text{M}$).

RESULTS AND DISCUSSION

Effect of particle size

Particles of different sizes have different surface areas, and hence, the efficiency of metal dissolution can be expected to depend on the ilmenite particle size. Many published papers have indicated that leaching rates increase with a reduction in particle size, corresponding to an increase in surface area.^[13,14] However, the problems arise in handling of fine particle sizes during grinding and filtration.^[15] The iron leaching rate of ilmenite and its efficiency increased with a decrease in particle size as shown in Fig. 1. BET surface area was determined to be $6.3\ \text{m}^2/\text{g}$ for finer size range of $-45\ \mu\text{m}$ as compared with $2.5\ \text{m}^2/\text{g}$ for $-53+45\ \mu\text{m}$ size range. This increase was due to the finer particle size fraction, having more surface area and thus enhancing metal dissolution. However, the effect of particle size on the rate of titanium dissolution was smaller than in the case of iron dissolution. The percentage of iron dissolution was found to be 4.0% , 5.3% , 10.0% and 10.5% for size ranges of $-106+63$, $-63+53$, $-53+45$ and $-45\ \mu\text{m}$, respectively. On the contrary, the percentages of titanium dissolution were found to be only 0.26% , 0.27% , 0.27% and 0.28% in the corresponding particle size ranges. The results show a good agreement with the work of Zhang and Nicol,^[8] who stated that particle size had a low significant effect on metal dissolution. The iron dissolutions of the ilmenite in $450\ \text{g/L}$ sulfuric acid solution were about 20% , 19% and 17% for size ranges of $-38+25$, $-53+38$ and $-90+75\ \mu\text{m}$, respectively.^[8] However, copper dissolution of lead-containing copper matte in $40\ \text{g/L}$ sulfuric acid solution increased from 72% to 82% for size ranges of $-0.125+0.105$ and $-0.09+0.075\ \text{mm}$, respectively.^[11] In addition, iron extraction was 27% and 36% for kaolin particle sizes of $-300+150$ and $-75+45\ \mu\text{m}$, respectively.^[12]

Table 1. Titanium dioxide and total iron concentration in the ilmenite size fractions.

Particle size (μm)	Total iron, Fe (%)	Titanium dioxide, TiO_2 (%)
$-106+63$	27.50	47.63
$-63+53$	26.36	47.19
$-53+45$	26.22	46.95
-45	26.37	47.20

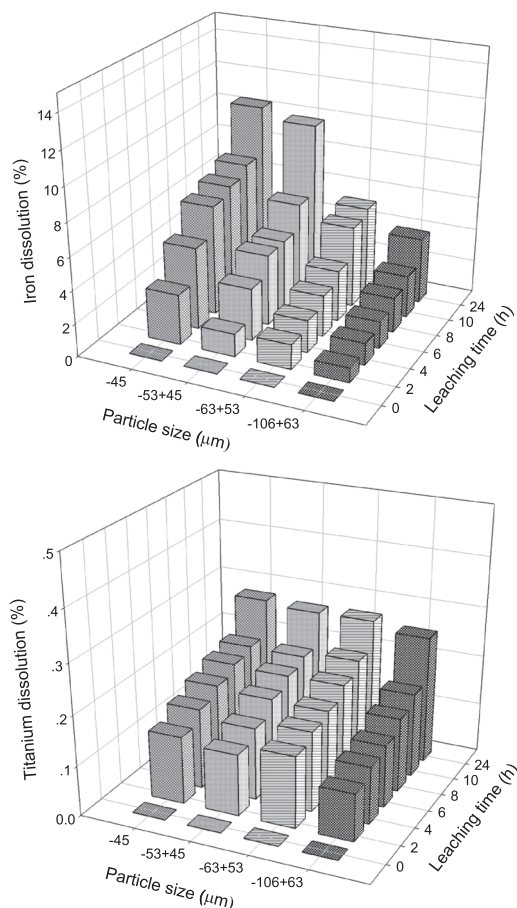


Figure 1. Percent iron and titanium dissolutions for 1 M citric acid leaching of ilmenite for different particle sizes.

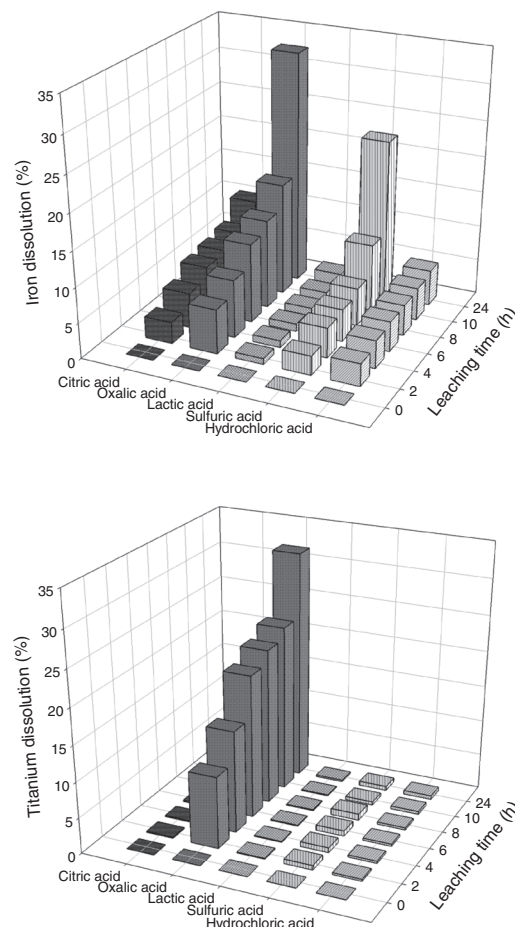


Figure 2. Percent iron and titanium dissolutions for 1 M acid leaching of ilmenite ($-45\ \mu\text{m}$).

Effect of type of acid solution

Percent iron and titanium dissolutions depend on the interactions of many of the same parameters affecting the leaching of ilmenite. Among these acid solutions, dependent factors play an important role. The iron and titanium solubility were examined during the acid leaching of ilmenite when different types of acid solution were used (lactic, hydrochloric, citric, sulfuric and oxalic acid). The increase of lactic acid concentration to more than 1.2 M had no effect on the dissolution of calcareous phosphate material because the number of hydrogen ions decreased with decreasing amount of water in the medium.^[15] Therefore, the ionic strength for all types of acid solution in this experiment was set at 1 M. Figure 2 shows that 1 M oxalic acid resulted in greater metal ion dissolutions among the acid solutions considered, especially in case of titanium dissolution. Titanium dissolution after 24 h was found to be about 32% in oxalic acid solution, whereas the dissolutions in lactic acid, hydrochloric acid, citric acid and sulfuric acid appeared to be lower than 1%. Iron dissolution (% extraction) after 24 h appeared to be

1.9%, 5.0%, 10.5%, 22.4% and 32.7% in lactic acid, hydrochloric acid, citric acid, sulfuric acid and oxalic acid solutions, respectively. The percentage of iron dissolution was higher than that of titanium dissolution, which agrees with the findings of Lasheen.^[9] The differential dissolution behavior of titanium and iron in sulfuric acid has been explained in terms of their microtopographic features and solvation mechanisms in the work of Sasikumar *et al.*^[16,17]

Nayl and Aly^[5] stated that leaching of alkaline-treated ilmenite paste at temperature of $150\ ^\circ\text{C}$ by oxalic acid (6.35 M) resulted in higher titanium dissolution compared when using sulfuric acid (6 M) and hydrochloric acid (9 M). Nayl *et al.*^[7] also showed that extraction of the alkaline-treated ilmenite paste in the 2.4 M oxalic acid and 2 M sulfuric acid solutions at $150\ ^\circ\text{C}$ was similar and close to about 10%. Their results proved that titanium dissolution occurred in both oxalic acid and sulfuric acid, but it was more effective in the case of sulfuric acid at the lower concentration. These findings are different than the results obtained in this work. This variation is likely due to many parameters such as the type of ores and

the use of lower ionic strength of 1 M. In order to investigate the effectiveness of oxalic acid and sulfuric acid on titanium dissolution, the next experiment was set up using various acid concentrations.

Effect of acid concentration

Acid concentration is an important factor during acid leaching. The effect varying concentration of oxalic acid from 0.5 to 4 M and sulfuric acid from 0.5 to 12 M was studied. The other experimental parameters were fixed at solid/liquid ratio of 1:20, temperature of 90 °C and size range of $-45\ \mu\text{m}$. The results presented in Figs 3 and 4 show titanium dissolution of ilmenite for different oxalic acid and sulfuric acid concentrations, respectively. The effect of increasing acid concentration for both oxalic acid and sulfuric acid was obvious. This happened because the dissolution rate perhaps was proportional to the concentration of the reducing species on the surface of the dissolving solid.^[12] The titanium dissolutions after 10-h leaching in 0.5, 1, 1.5, 2 and 4 M oxalic acid were found to be about 4.9%, 23.2%, 31.8%, 48.5% and 86.4%, respectively. The titanium solubilized in different concentrations of

sulfuric acid after leaching for 10 h was significantly lower than in the oxalic acid. The results from this work were in reasonable agreement with the findings of Nayl and Aly.^[5] They reported that leaching of alkaline-treated ilmenite paste with 6.35 M oxalic acid resulted in higher titanium dissolution compared with leaching with 6 M sulfuric acid at 150 °C. The ilmenite is less soluble in sulfuric acid, which also agrees with the findings of Zhang and Nicol^[8] who observed that titanium dissolution in 4.5 M sulfuric acid at 100 °C was only about 37%. The low dissolution of titanium in sulfuric acid or hydrochloric acid may be due to hydrolysis,^[5,18] polymerization^[19–21] and precipitation of titanium species.^[5,19] Martínez-Luévanos *et al.*^[12] also stated that oxalic acid was used as the leaching agent because of its properties of higher acidity, complexing power and possibly reducing ability when compared with other organic acids such as citric, malonic and acetic acids.

Kinetic analysis

The acid leaching of a given type of ore from different sources also requires further kinetic studies, despite the

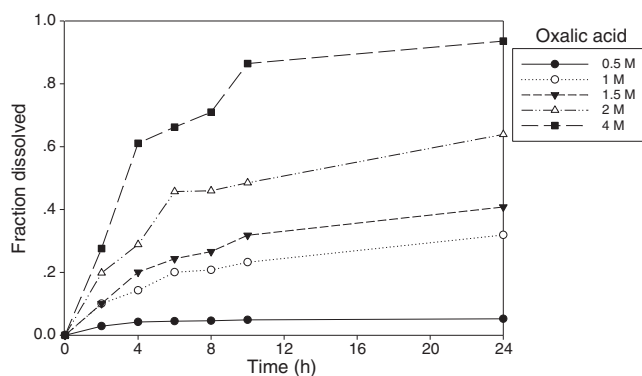


Figure 3. Titanium dissolution for oxalic acid leaching of ilmenite at different acid concentrations.

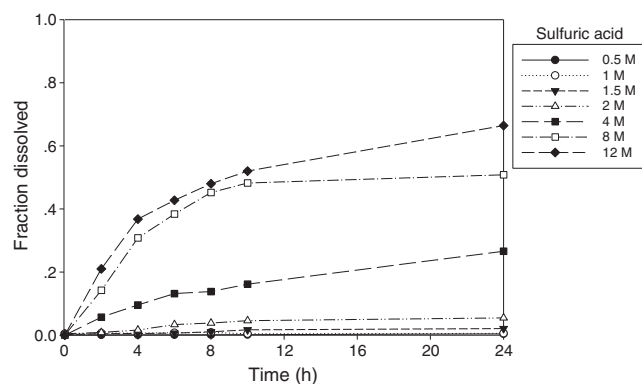


Figure 4. Titanium dissolution for sulfuric acid leaching of ilmenite at different acid concentrations.

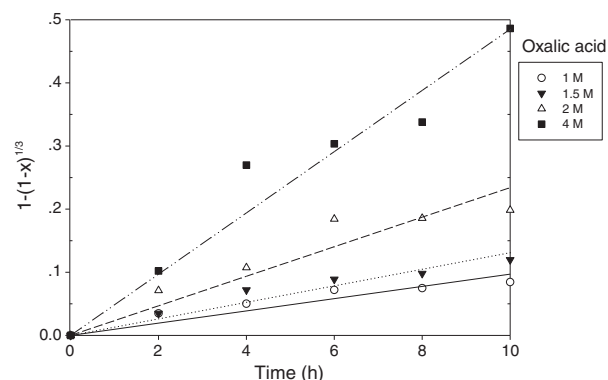


Figure 5. Plots of $1 - (1 - x)^{1/3}$ vs time for various oxalic acid concentrations.

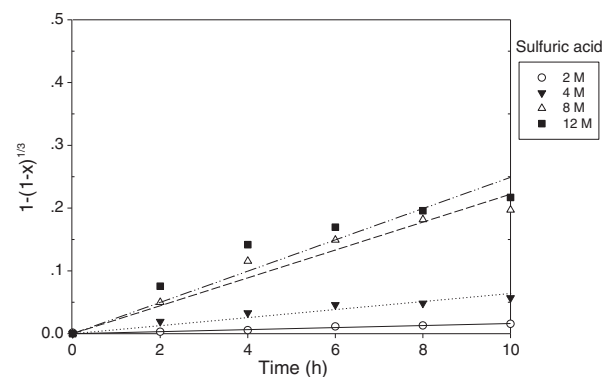


Figure 6. Plots of $1 - (1 - x)^{1/3}$ vs time for various sulfuric acid concentrations.

Table 2. Results of regression analysis between $1 - (1 - X)^{1/3}$ and t for different concentrations of acid solutions.

Acid solution	Fitted equation	Coefficient of determination, R^2	Rate constant, k_s
1 M oxalic acid	$1 - (1 - X)^{1/3} = 0.0097 t$	0.8556	0.0097
1.5 M oxalic acid	$1 - (1 - X)^{1/3} = 0.0131 t$	0.9250	0.0131
2 M oxalic acid	$1 - (1 - X)^{1/3} = 0.0234 t$	0.8736	0.0234
4 M oxalic acid	$1 - (1 - X)^{1/3} = 0.0485 t$	0.9442	0.0485
2 M sulfuric acid	$1 - (1 - X)^{1/3} = 0.0016 t$	0.9618	0.0016
4 M sulfuric acid	$1 - (1 - X)^{1/3} = 0.0064 t$	0.9071	0.0064
8 M sulfuric acid	$1 - (1 - X)^{1/3} = 0.0222 t$	0.9450	0.0222
12 M sulfuric acid	$1 - (1 - X)^{1/3} = 0.0249 t$	0.8837	0.0249

success of metal extraction by the same type of acid on other ores. Consequently, it is desirable to find a kinetic model for a particular ore sample. The shrinking particle model (Eqn 4) was used to fit the experimental data presented in Figs 3 and 4 for titanium dissolution in oxalic acid and sulfuric acid, respectively. The apparent rate constants k_s obtained from Eqn (4) and the regression coefficients were determined from the plots at each acid concentration in Figs 5 and 6. Results presented in Table 2 that show that titanium dissolution from ilmenite in different acid concentrations indicated a good fit with coefficient of determination (R^2) higher than 0.86. Plots of $1 - (1 - x)^{1/3}$ vs time of data from Fig. 5 yielded straight lines with the R^2 values ranging from 0.86 to 0.94 for oxalic acid concentrations between 1 and 4 M. Results obtained from the leaching by sulfuric acid also showed linear relationships with R^2 values of 0.88, 0.95, 0.91 and 0.96 for 12, 8, 4 and 2 M sulfuric acid concentrations, respectively. These high values of R^2 show that titanium dissolutions from ilmenite by oxalic and sulfuric acid are controlled by chemical reaction model (Eqn 4).

The relationships for the combined chemical reaction model that accounts for the effect of acid concentration on the apparent rate constants k_s for the titanium dissolution in oxalic and sulfuric acids with time in Eqn (4) are presented as follows:

$$k_s = 0.0092 C_A^{1.2022} \quad (R^2 = 0.9796) \quad (8)$$

$$k_s = 0.0006 C_B^{1.5977} \quad (R^2 = 0.9634) \quad (9)$$

where k_s is the apparent rate constant in h^{-1} and C_A and C_B are molar concentrations of oxalic acid and sulfuric acid, respectively.

The developed models are reasonably good and could be used to predict the rate of dissolution of titanium within the experimental ranges of particle size, acid concentration, type of acid solution and temperature used in this investigation. Moreover, the chemical reaction model of this study follows the findings of Zhang and Nicol^[8] who reported that the experimental data for leaching of ilmenite with sulfuric acid alone could be represented by the shrinking particle model.

Nayl *et al.*^[7] also confirmed that their acid leaching rates of alkaline-treated ilmenite paste by oxalic and sulfuric acid were consistent with a kinetic model for chemical control.

CONCLUSION

This study examined the kinetics of acid leaching of ilmenite with oxalic and sulfuric acid solutions. Particle size was found to have a low significant effect on titanium dissolution. However, the type of acid solution and concentration had a large effect on the titanium dissolution. Results showed higher levels of titanium dissolutions when using oxalic acid solution among all acid solutions considered. The dissolution also increased with increasing acid concentration. Leaching of ilmenite in the experimental conditions of 4 M oxalic acid, solid/liquid ratio of 1 : 20, 90 °C temperature and size range of $-45 \mu\text{m}$ resulted in 86.4% titanium within 10 h. The dissolution kinetics of ilmenite with oxalic and sulfuric acid solutions could be adequately represented by the shrinking particle model indicating a reaction controlled process.

Acknowledgements

The ilmenite samples used in the experiments were supplied by the Department of Primary Industries and Mines, Ministry of Industry. The authors gratefully acknowledge the support of the Department of Chemical Engineering, Faculty of Engineering, Mahidol University for the use of the laboratory and other facilities.

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