# Leaching of non-treated ilmenite by HCl-CH$_3$OH-H$_2$O mixture and its kinetics

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The effect of the addition of methanol to leachant hydrochloric acid on the dissolution of non-treated ilmenite has been investigated. The kinetics of the dissolution processes have also been investigated. The dissolution of ilmenite is enhanced by the addition of little amount of methanol in hydrochloric acid. The leaching with 6 M HCl -0.5 M CH$_3$OH-H$_2$O mixture at 110°C and solid to liquid ratio (S/L) of 0.02 g/mL results in the dissolution of 91% Ti and 95% Fe compared to dissolutions of 53.5% Ti and 60% Fe in 6 M HCl alone. Decrease in leaching temperature and HCl concentration and increase in S/L ratio result in decrease in the extent of dissolution percentages. The kinetics of dissolution have been investigated by measuring the dependences of rate of dissolution on HCl concentration and temperature of leaching. The values of activation energy have been evaluated from the temperature dependence rate data. The kinetic data could be fitted to the Shrinking Core model of dissolution.

**Keywords**: Leaching, Kinetics, Ilmenite, HCl-CH$_3$OH-H$_2$O mixture, Dissolution
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A considerable amount of heavy mineral deposits containing ilmenite has been discovered in the southeastern coastal area of Bangladesh[1]. It is reported[1,2] that the coastal sand contains more than 10% heavy minerals, which in turn contains about 27% ilmenite.

Several attempts have been made to develop a suitable process to recover titanium from ilmenite sand. Ti(IV) has been separated effectively from Fe(III) present in a sulphuric acid leach liquor using solvent extraction, stripping and precipitation techniques[3-6]. The leach liquor was obtained by heating the powdered ilmenite sand in 18 M H$_2$SO$_4$ for long periods, usually >48 h. Past experience suggests that leaching with dilute mineral acid, such as HCl, HNO$_3$, H$_2$SO$_4$ and HClO$_4$, is not at all effective[7] for the dissolution of ilmenite. Only hydrofluoric acid was found to be effective[7,8]. However, this method suffers from some disadvantages such as the difficulties arising during handling of hydrofluoric acid, high leaching time and involvement of many steps to recover the desired product[9].

Recently, several authors have studied the leaching of ilmenite by HCl (refs 10-15), H$_2$SO$_4$ (refs 16, 17) and others[18,19]. Jana *et al*.[20] and Yorukoglu and Girgin[21] used HCl-CH$_3$OH-H$_2$O solution for leaching of deep sea nodules and La$_2$O$_3$, respectively.

Although, alcohol alone has no ability to leach the ilmenite, mixed leaching agents such as alcohol and mineral acids have been selected with an aim to improve the leaching quality of ilmenite to a leached product. Previously[22], it has been reported that hydrochloric acid-alcohol (ethanol) mixture shows a significant effect on the leaching of ilmenite. In another paper[23], the leaching of non-treated ilmenite by HCl-C$_2$H$_5$OH-H$_2$O and HCl-C$_6$H$_5$OH-H$_2$O mixtures and their kinetics have been reported. This paper discusses the leaching of ilmenite by HCl-CH$_3$OH-H$_2$O mixture. The kinetics of the leaching process have also been investigated and discussed.

## Experimental Procedure

### Reagents

Ilmenite sand was collected from the pilot plant of the Bangladesh Atomic Energy Commission (BAEC) at Cox's Bazar (about 160 km south of the port city of Chittagong). According to BAEC, the composition of the received sample was: TiO$_2$, 38.5; Fe$_2$O$_3$, 25.62; FeO, 29.75; SiO$_2$, 1.2; P$_2$O$_5$, 0.03; MnO$_2$, 1.3 and Cr$_2$O$_3$, 1.08%. The chemicals of the following specifications were used in this investigation: TiO$_2$ (E. Merck, 99%), FeNH$_4$(SO$_4$)$_2$.12H$_2$O (E. Merck, 99%), NH$_4$SCN (BDH, 98%), H$_3$PO$_4$ (BDH, 85%), HCl (BDH, 36%), HNO$_3$ (BDH, 69-72%), H$_2$SO$_4$ (BDH, 98%), H$_2$O$_2$ (BDH, 30%), CH$_3$OH (BDH, 95%).

**Method**

The sand was dry-ground and sieved to collect particles of >63 μm-<125 μm in size. A known amount of sand (usually 1 g) was heated in a pyrex flux under reflux with a known volume of leaching agent (usually 50 mL) at a predetermined temperature. A magnetic hot plate was used for heating and agitation (300 rpm). At intervals, duplicate aliquots (0.5 mL) of solution were removed, diluted and analyzed colorimetrically; one for titanium content[24] and the other for iron content after oxidising with nitric acid[25].

In stage-wise leaching, the residue was filtered off and heated with 50 mL fresh leachant. To study the effect of solid to liquid phase ratio on leaching, the amount of ilmenite was kept constant and the volume of leaching agent was varied. A plastic coated stirrer bar was used for magnetic stirring. During temperature dependence study, the leaching flask was placed inside a thermostated water bath.

**Theoretical analysis**

At a constant temperature, phase mixing rate and solid to liquid phase ratio, the rate of dissolution of a solid by a liquid reagent may be expressed as[26]:

$$-\frac{dW}{dt} = k.A.C^a \qquad \qquad \ldots(1)$$

where $W$ is the weight of the unreacted solid at a time $t$, $A$ its surface area, $C$ the reagent concentration, $a$ the reaction order with respect to the reagent concentration and $k$ is the rate constant. If $W$ is expressed in g, $A$ in $dm^2$, $C$ in mol $dm^{-3}$ and $t$ in s, then $k$ will be in g dm $s^{-1}$ $mol^{-1}$ provided a is unity.

In order to get an integrated form of rate equation from Eq. (1), the variation of $A$ with $t$ must be taken into consideration. This requires the consideration of using uniform spherical particles in the experiment. If a very closely sieved fraction is used in experiment, then a definite amount of powder will contain approximately the same number of particles. Let 1 g sample of particle size between 63 and 125 μm contains n number of particles on an average, then, the area occupied by 1 g powder ($A$), is approximately given by:

$$A = n \, 4 \, \pi \, r^2 \qquad \qquad \ldots(2)$$

where, $r$ is the radius of each particle. As the radius of each particle ($r$) decreases with time of leaching, the weight at any instant can be calculated from the following relation:

$$W = n \, (4/3)\pi \, r^3 \rho \qquad \qquad \ldots(3)$$

where, $\rho$ is the density of the material. From Eqs (1-3), the following equation is obtained:

$$-\frac{dr}{dt} = \frac{kC^a}{\rho} \qquad \qquad \ldots(4)$$

Now on integration within the limits $r = r_o$ when $t = 0$ and $r = r$ when $t = t$, Eq. (4) gives ($C$ is assumed constant in this interval of time):

$$r_o - r = \frac{kC^a t}{\rho} \qquad \qquad \ldots(5)$$

The fraction reacted, $R$ at any time is defined as:

$$R = \frac{W_o - W}{W} \qquad \qquad \ldots(6)$$

where $W_o$ and $W$ are the initial weight and weight after certain time, respectively Then for spherical particles, $R$ may be presented as follows:

$$R = \frac{(4/3)\pi \, r_o^3 \rho - (4/3)\pi \, r^3 \rho}{(4/3)\pi \, r_o^3 \rho} \qquad \qquad \ldots(7)$$

Eq. (7) gives: $r = r_o \left(1-R\right)^{\frac{1}{3}} \qquad \qquad \ldots(8)$

With the help of Eq. (8), the Eq. (5) takes the form:
$$r_o - r_o (1-R)^{1/3} = kC^a t/\rho$$

or, $1 - \left(1-R\right)^{1/3} = qt \qquad \qquad \ldots(9)$

where, $q$ = pseudo rate constant = $kC^a/\rho \, r_o$. It is important to note here that the final rate equation is independent of number of particles but dependent on the radius of each particle on which the rate is varied inversely. Equation (9) is based on the Shrinking Core model of particles during leaching.

Equation (9) states that the plot of $1-\left(1-R\right)^{1/3}$ versus $t$ at a certain reagent concentration yields straight line with slope equalling to $q$. For a powder of closely related mesh number, the terms $\rho$ and $r_o$ in $q$ are constant; so that the value of $q$ will vary apparently on the reagent concentration, $C$. If the values of $q_{HCl}$ are determined from the slopes of $1-\left(1-R\right)^{1/3}$ versus $t$ plots at various reagent concentrations (HCl), then the following relationship will hold:

$$\log q_{HCl} = \log (k/\rho r_o) + a \log [HCl] \qquad \ldots(10)$$

Equation (10) indicates that the plot of $\log q_{HCl}$ versus $\log[HCl]$ will give straight lines with slope equalling to $a$ and the intercept ($I$) equalling to $\log\left(k/\rho\, r_o\right)$. It is, therefore, apparent that the value of the dissolution rate constant, $k$ can be evaluated from the value of $I$ provided $\rho$ and $r_o$ are known for the powder under investigation.

To make a study on the effect of temperature on the rate of dissolution, $q_T$ values are to be determined at different temperatures, $T$ (K) and the data should be plotted according to the Arrhenius equation:

$$\log q_T = \text{ constant } - (E_a/2.303RT) \qquad \ldots(11)$$

where, the symbols have their usual significances. The slope of the plot of $\log q_T$ versus $(1/T)$ is equal to $-E_a/2.303R$, so that the value of the apparent activation energy, $E_a$ could be easily calculated.

**Results and Discussion**

One gram non-treated ilmenite sand having particle size of 63-130 μm was leached with 50 mL of mineral acids (HCl, HNO$_3$ and H$_2$SO$_4$) and methyl alcohol (0.5 M) mixtures at their boiling temperatures. Fig. 1 shows the effect of leaching time on the weight percentages of titanium and iron dissolved. It is found that the wt% metal dissolved (percentages of titanium and iron dissolved from the sand) is increased with increasing the leaching time up to about 7 h. Within this time about 91% Ti and 95% Fe are dissolved in 6 M HCl-0.5 M CH$_3$OH-H$_2$O mixture. Under similar condition ~34% Ti and 47% Fe, and 10% Ti and 25% Fe are dissolved in 3 M H$_2$SO$_4$-0.5 M CH$_3$OH-H$_2$O and 6 M HNO$_3$-0.5 M CH$_3$OH-H$_2$O mixtures, respectively. It is reported earlier[27], that, the leaching of non-treated ilmenite by 6 M HCl alone yields 53.5% Ti and 60% Fe dissolutions. Therefore, it is concluded that a mixture of 6 M HCl-0.5 M CH$_3$OH-H$_2$O is a better leaching agent than 6 M HCl alone, 3 M H$_2$SO$_4$-0.5 M CH$_3$OH-H$_2$O and 6 M HNO$_3$-0.5 M CH$_3$OH-H$_2$O mixtures for leaching of non-treated ilmenite sand. It is concluded that increased leaching in HCl mixed with alcohol might be due to a certain change in the interfacial property of ilmenite/leachant interface. Since alcohol is less polar than HCl and H$_2$O, it possibly penetrates the pores of ilmenite. This wetting facilitates the diffusion of HCl in the infrastructure of ilmenite and consequently, enhanced leaching is observed.

The effect of HCl concentrations in the leachant containing 0.5 M CH$_3$OH on the maximum wt% of Ti and Fe dissolved from ilmenite is shown in Fig. 2. It indicates that the dissolution of the maximum wt% of Ti and Fe increases extensively with increasing HCl concentration in the leachant. However, over 6 M HCl concentration, the variation in the extent of leaching is almost negligible and hence 6 M HCl mixed with CH$_3$OH is suggested to be used as a leachant for non-treated ilmenite.

The effect of methyl alcohol concentration in 6 M HCl on the dissolution of ilmenite is shown in Fig. 3.
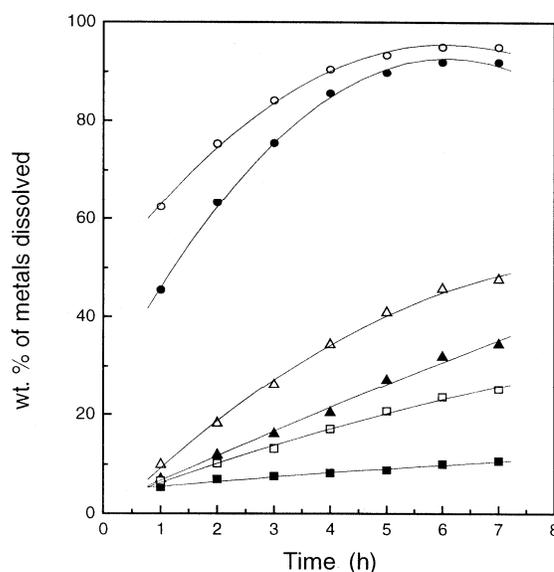


Fig. 1 — Effect of leaching time on the dissolution of metals from non-treated ilmenite by different acid alcohol-water mixture. Leachant composition: (○●), 6 M HCl-0.5 M CH$_3$OH-H$_2$O; (Δ▲), 3.0 M H$_2$SO$_4$-0.5 M CH$_3$OH-H$_2$O; (□■), 6 M HNO$_3$-0.5 M CH$_3$OH-H$_2$O. S/L = 0.02 g/mL; temp. = 110°C; stirring speed = 300 rpm. Solid symbols are for Ti and open for Fe.
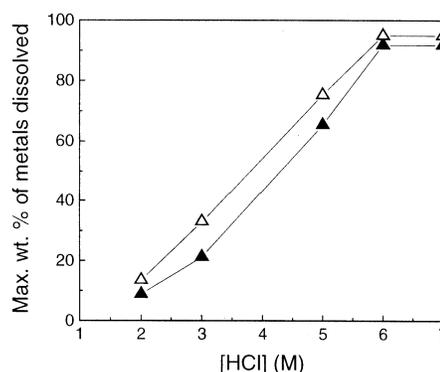


Fig. 2 — Effect of HCl concentrations in the leachant on the maximum wt% of Ti and Fe dissolved from ilmenite. [CH$_3$OH] = 0.50 M; S/L = 0.02 g/mL; temp. = 110°C; leaching time = 6 h; stirring speed = 300 rpm.
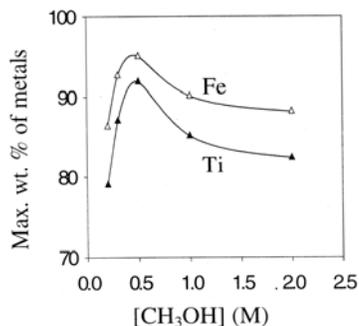
Fig. 3 — Effect of methyl alcohol concentration in 6 M HCl on the dissolution of ilmenite. S/L = 0.02 g/mL; temp. = 110 $^o$C; leaching time = 6 h; stirring speed = 300 rpm.

It is seen from Fig. 3 that the maximum dissolution weight percentages of both Ti and Fe increase with increasing methanol concentration in the leachant up to 0.5 M. On further increasing the methanol concentration in the leachant, the maximum dissolution wt% of both Ti and Fe decrease. Therefore, it is concluded that the effective concentration of methanol in the leachant is 0.5 M.

The effect of temperature on leaching of non-treated ilmenite by 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture is shown in Fig. 4. Figure 4 indicates that the dissolution percentage of titanium and iron increases extensively with increasing leachant temperature. At 45 °C, the dissolution percentages of Ti and Fe are 9.6 and 12%, respectively. However, at 110°C, these values are 91 and 95% for Ti and Fe, respectively. From the above study, it is concluded that temperature has a significant effect on the leaching of non-treated ilmenite by HCl-$CH_3OH$-$H_2O$ mixture.

The effect of solid to liquid phase ratio on the dissolution of ilmenite by HCl-$CH_3OH$-$H_2O$ mixture has been investigated. Figure 5 shows the percentage of metals dissolved on leaching at various solid to liquid (S/L) phase ratios (g/mL). In these experiments, L is always taken as 50 mL of 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture and S is varied from 1 to 4 g ilmenite. It is observed from figure that the leachable percentages of both Ti and Fe decrease considerably on increasing the S/L ratio. At S/L ratio of 0.02 g/mL, the dissolution of titanium and iron are 91 and 95%, respectively; and the respective values decreases to only about 37 and 53% at S/L ratio of 0.08 g/mL. This result shows that the leaching of the non-treated ilmenite sand by HCl-$CH_3OH$-$H_2O$ mixture is very much dependent on S/L ratio.

Figure 6 represents the effects of the solid to liquid phase ratio on the concentrations of Ti and Fe in
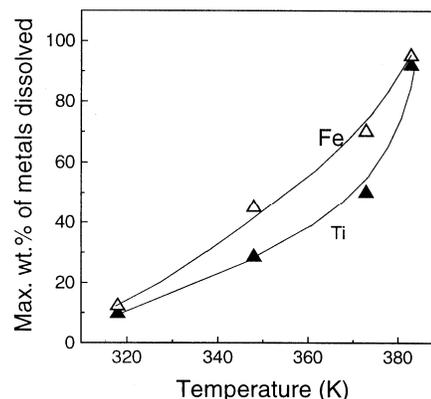


Fig. 4 — Effect of temperature on the leaching of non-treated ilmenite by 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture. S/L = 0.02 g/mL; temp. = 110°C; leaching time = 6 h; stirring speed = 300 rpm.
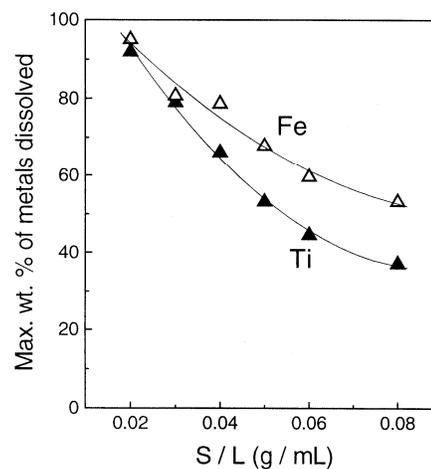


Fig. 5 — Effect of solid to liquid phase ratio (S/L) on the dissolution of ilmenite by 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture. Leaching time = 6 h; stirring speed = 300 rpm; temp. = 110$^o$C.
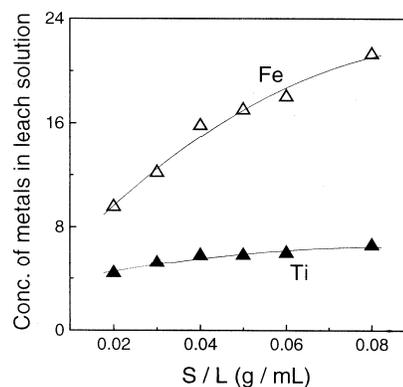


Fig. 6 — Effect of solid to liquid phase ratio on the concentration of Ti and Fe in the leached solution. Leaching agent, 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture; time = 6 h; stirring speed = 300 rpm and temp. = 110$^o$C.

leached solution. It is seen from Fig. 6 that the concentration of both metals in the leached solution increases with increasing S/L ratio in the system. However, the increase of titanium concentration in the leached solution with the increase of S/L ratio is very low as compared with the concentration of iron. At higher S/L ratio, Fe is preferentially dissolved in HCl medium, whereas, $TiO^{2+}$ is thermohydrolysed to form insoluble $H_2TiO_3$ (metatitanic acid) according to the following reaction:

$$TiO^{2+} + 2H_2O \longrightarrow H_2TiO_3 + 2H^+ \qquad \ldots(12)$$
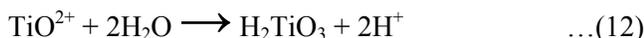
which happens possibly when the aqueous titanium concentration reaches to the value of about 6 g/L. This result indicates that the leaching at higher solid to liquid ratio cannot be suggested to get higher concentration of Ti and Fe in the leachant. However, the stage-wise leaching is recommended for higher recovery percentages of Ti and Fe in the higher S/L ratio.

The kinetics of the dissolutions of non-treated ilmenite by HCl-CH₃OH-H₂O mixture has been investigated at various acid concentrations and the data are found to be fitted by the Shrinking Core model of leaching. For the Shrinking Core model, the initial dissolution data give $1-(1-R)^{1/3}$ versus $t$ plots as straight lines, where $R$ represents the ratio of the amount of titanium or iron leached to the amount of titanium or iron present initially in the sample, respectively. Fig. 7 shows the typical $1-(1-R)^{1/3}$ versus $t$ plots for dissolutions of both Ti and Fe by HCl-0.5 M CH₃OH-H₂O mixture at its boiling temperature and at S/L ratio of 0.02 g/mL. Since straight lines are obtained for both metals, the slope of the lines will be equal to $q$, the pseudo rate constant in Eq. (9). The values of $q_{HCl}$, min⁻¹ at various hydrochloric acid concentrations have been calculated from the slope of the lines.

The calculated $\log q_{HCl}$ values for the dissolution of both the metals at various acid concentrations are plotted in Fig. 8 as $\log q_{HCl}$ versus $\log[HCl]$ plots at constant CH₃OH concentration of 0.5 M, boiling temperature and S/L ratio of 0.02 g/mL. In both cases straight lines are obtained. Slopes of the plots for Ti and Fe are 2.0 and 2.5, respectively. It is, therefore, concluded that the exponent $a$ on the reagent concentration for the dissolution of Ti and Fe from ilmenite are 2 and 2.5, respectively. Intercepts of the plots for Ti and Fe are –3.95 and –3.90, respectively.
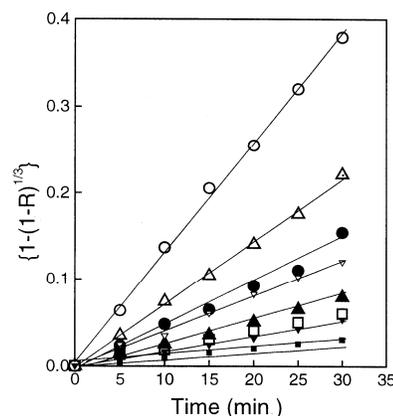


Fig. 7 — Typical $[1-(1-R)^{1/3}]$ versus time plots for the dissolutions of Fe and Ti by HCl-0.50 M CH₃OH mixture at boiling temperature and S/L of 0.02 g/mL. [HCl]: (●○), 6 M HCl; (▲△), 5 M HCl; (▼,▽), 4 M HCl and (■□), 3 M HCl. Solid symbols are for Ti and open for Fe; stirring speed = 300 rpm.
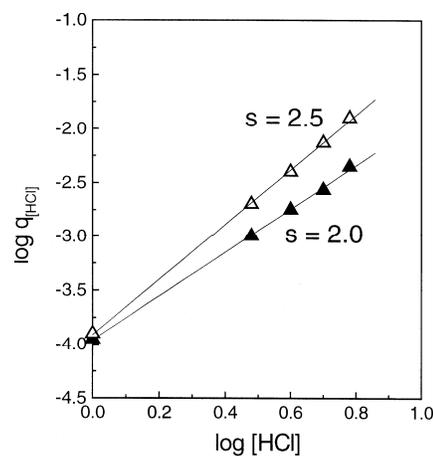


Fig. 8 — $\log q_{HCl}$ versus $\log[HCl]$ plots for the dissolutions of Fe and Ti by HCl-0.50 M CH₃OH mixture at boiling temperature, S/L of 0.02 g/mL and stirring speed = 300 rpm.

Temperature dependences of rates of titanium and iron dissolutions from ilmenite by 6 M HCl-0.5 M CH₃OH – H₂O mixture are given in Fig. 10, where $\log q_T$ has been plotted against $10^3/T(K^{-1})$. The values of $q_T$, min⁻¹ at various temperature have been calculated from the slope of the lines of $[1-(1-R)^{1/3}]$ versus $t$ in min plots (Fig. 9) for the dissolution of both Ti and Fe by 6 M HCl-0.5 M CH₃OH-H₂O mixture at various temperatures and at S/L ratio of 0.02 g/mL. The experimental points in both cases in Fig. 10 do not fall on straight lines. Curves are obtained with limiting higher negative slope in the higher temperature region and vice versa. From the values of the limiting slopes, apparent activation energies have been calculated. In the lower
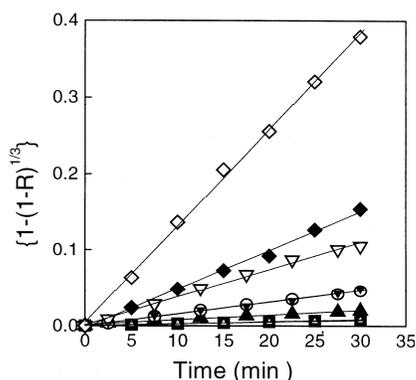
Fig. 9 — Typical $[1-(1-R)^{1/3}]$ versus time plots for the dissolution of both Fe and Ti by 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture at different temperatures. S/L = 0.02 g/mL; stirring speed = 300 rpm. Leaching temperature: (♦◊), 383 K; (▼,▽), 368 K; (▲,○), 348 K and (■,△), 318 K. Solid symbols are for Ti and open for Fe.
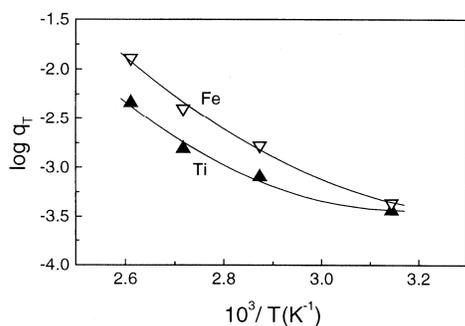


Fig.10 — $\log q_T$ versus $10/T$ (K$^{-1}$) plots for dissolutions of Fe and Ti from ilmenite. Leaching agent, 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture; time = 6 h; stirring speed = 300 rpm and S/L = 0.02 g/mL.

temperature regions ($\sim$ 50°C), the activation energies are 16.5 and 21.76 KJ mol$^{-1}$ for titanium and iron dissolutions, respectively, whereas the respective values in the higher temperature region are 66 and 90 KJ mol$^{-1}$, respectively.

Density, $\rho$ of the powdered ilmenite sample was estimated to be 4.72 g cm$^{-3}$, picnometrically. The average radius of the particle used in leaching may be considered to be 0.005 cm, since it varied from 0.00315 to 0.0063 cm. So the value of $\rho r_0$ becomes equal to 0.0236 g/cm$^2$. The intercepts of the straight lines in Fig. 8 are –3.95 and –3.90 for the dissolutions of Ti and Fe, respectively. Since $I = \log(k/\rho r_0)$ from Eq. (10), the magnitude of the dissolution rate constant, $k$ comes out as 10$^{-5.577}$ and 10$^{-5.527}$ for Ti and Fe, respectively. However, the unit of $k$ apparently depends on the value of $a$ in Eq. (1) or (10). It is virtually g (cm$^3$/mmol)$^a$ min$^{-1}$ cm$^{-2}$ (since dm$^3$/mol $\equiv$

cm$^3$/mmol) from Eq. (1). The values of $a$ are 2 and 2.5 for Ti and Fe dissolutions, respectively. So the dissolution rate constant, $k$ equals to 10$^{-5.577}$ g cm$^4$ min$^{-1}$ mmol$^{-2}$ and 10$^{-5.527}$ g cm$^{5.5}$ min$^{-1}$ mmol$^{-2.5}$ for titanium and iron dissolutions, respectively.

The value of $a$ equalling to 2 for titanium dissolution indicates that the following chemical reaction is rate determining:

$$TiFeO_3 + 2HCl \rightarrow TiOCl_2 + H_2O + FeO \qquad …(13)$$
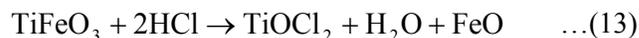
On the other hand, the value of $a$ equalling to 2.5 for iron dissolution indicates the following two chemical reactions are rate determining:

$$FeO + 2HCl \rightarrow FeCl_2 + H_2O \qquad …(14)$$

$$\tfrac{1}{2}Fe_2O_3 + 3HCl \rightarrow FeCl_3 + \tfrac{3}{2}H_2O \qquad …(15)$$
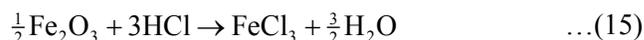
When both reactions represented by Eqs (14) and (15) contribute equal to rate, then the exponent of the hydrochloric acid concentration term in the rate equation will be 2.5.

The above statement is valid only at higher temperature of leaching since the activation energies of very high values are obtained in the higher temperature region. However, as the temperature of leaching decreases (say at around 325 K), very low activation energies ($\sim$16.5 KJ mol$^{-1}$) are obtained. The low activation energies in the lower temperature region indicate that the diffusion of HCl to the ilmenite matrix is the rate determining in lieu by the chemical reactions given above.

### Conclusions

The following conclusions can be drawn from the present investigation:

Hydrochloric acid-methanol mixture is found to be a good leachant than that of nitric acid-methanol-water, sulphuric acid-methanol-water or HCl alone for the dissolution of ilmenite. The effective concentrations of HCl and $CH_3OH$ for the maximum wt % dissolution of both metals from ilmenite are 6 M and 0.5 M, respectively. Optimum condition for leaching with 6 M HCl-0.5 M $CH_3OH$-$H_2O$ mixture is at boiling temperature and S/L ratio of 0.02 g/mL. Under this condition 91% Ti and 95% Fe are dissolved from ilmenite in comparison to the dissolution of 53.5% Ti and 60% Fe by 6 M HCl alone. The high values of activation energies in the higher temperature region indicate the rate of the dissolution reaction is chemically controlled.

However, the rate of the process is diffusion controlled in the lower temperature region.

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