1934 © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 1934—1938 (1982) [Vol. 55, No. 6

Manufacture of High Pure Titanium(IV) Oxide by the Chloride Process. I. Kinetic Study on Leaching of Ilmenite Ore in Concentrated Hydrochloric Acid Solution

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(Received October 2, 1981)

Kinetic study of the leaching of powdered ilmenite ore was carried out in highly concentrated hydrochloric acid (11.3—11.6 mol dm^{-3}) at temperatures of 30 to 80 °C. The changes in shape and grain size of the ore particles with progress of the leaching was simultaneously observed with X-ray diffraction and electron microscope techniques. Titanium and iron were dissolved in a nearly stoichiometric ratio; the rate of the dissolution was significantly affected by the temperature of the acid solutions. From the analysis of the dissolution rates on the basis of the core-model, it was found that the dissolution rates at temperatures of 30 to 50 °C were well expressed by the rate equation based on the rate-determining step of the surface chemical reaction. The apparent activation energies were 81.2 kJ mol^{-1} for titanium and 73.2 kJ mol^{-1} for iron. The rate-determining step of the dissolution was changed at a temperature of about 50—60 °C; the dissolution rates at temperatures of 60 to 80 °C were limited by the diffusion of the dissolved metal ions through a residual layer of the ore. However, the rates after 2 or 3 h at high temperatures deviated from the rate equation because of the precipitation of hydrous titanium(IV) oxide on the surface of the ore by hydrolysis of the dissolved titanium(IV) ion.

Titanium(IV) oxide is used as a raw material of the white pigment which is utilized extensively in paints, paper, porcelain, and fibers. Some new uses based on being an n-type semiconductor, for example an electrode or a catalyst have recently been tried.

Titanium(IV) oxide is produced industrially by the sulfuric acid leaching of its minerals and the subsequent thermal hydrolysis of titanium(IV) sulfate solutions; this is commonly known as the sulfate process. It is also produced by the vapor phase oxidation of titanium(IV) tetrachloride.[1,2] Although the manufacture of titanium(IV) oxide by this latter process is gradually increasing, the former is still the most widely used.[2] The sulfate process, however, has serious disadvantages because the treatments of crude iron(II) sulfate and of the waste acid solution are difficult.[3] On the other hand, hydrochloric acid, which is very useful for decomposition of natural ores, allows comparatively easier recovery of the useful free acid from its waste solution than does sulfuric acid. In practice, the recovery of free hydrochloric acid from the waste solutions of steel cleansing is now feasible.[4–8] Accordingly, if it becomes possible to leach ilmenite ore in hydrochloric acid, the closed system of the manufacturing process of titanium(IV) oxide will be achieved. The pressurized leaching of ilmenite ore in hydrochloric acid solutions is now carried out to upgrade the ore, in which a large portion of iron is dissolved.[9–11] Titanium can also be dissolved in concentrated hydrochloric acid solutions by keeping the leaching solution at temperatures below about 90 °C.[12–14] In addition, the recovery of a number of metal ions by liquid-liquid extraction from hydrochloric acid solutions is considerably easier than that from sulfuric acid solutions.[15,16] The authors, therefore, intended to develop a new manufacturing process of high pure titanium(IV) oxide, which would be based on the leaching of ilmenite ore in concentrated hydrochloric acid solutions and the selective solvent extraction of titanium(IV) from the leaching solution by neutral organophosphorus compounds.

In this study, we investigated the leaching kinetics of powdered ilmenite ore in concentrated hydrochloric acid. Static leaching studies of ilmenite ore in hydrochloric acid solutions were performed by earlier workers[12–14] in order to obtain optimum conditions, but only a few reports on the kinetic study (using diluted hydrochloric acid solutions of 3 mol dm^{-3}) have been presented[17] and there is still a lack of the essential information in the kinetics of the dissolution behavior of titanium and iron in concentrated hydrochloric acid with respect to the leaching mechanism.

Experimental

Unless otherwise stated, the ilmenite ore having a grain size range of 250 to 325 mesh was used in this study. The chemical composition after the sample was dried by heating at 110 °C is shown in Table 1. In one part of the experiments, the ilmenite ore having a grain size of 150—250 mesh, whose chemical composition was the same as that shown in Table 1 was also used. The leaching experiments of the powdered ilmenite ore were carried out in the highly concentrated HCl solutions of 11.3—11.6 mol dm^{-3} at temperatures of 30 to 80 °C. A 0.5 dm^3 three-necked flask equipped with a reflux condenser, a thermometer, and a stirrer was used as a reaction vessel. Five g of the ilmenite ore was suspended in 200 cm^3 of leaching solution, temperature-regulated at 30—80 °C; this

TABLE 1. CHEMICAL COMPOSITION OF THE ILMENITE ORE

Constituent	Content wt%
TiO_2	52.0
Fe[a)]	27.2
MnO	3.07
Al_2O_3	2.30
MgO	0.41
Cr_2O_3	0.04

a) $FeO+Fe_2O_3$.

was stirred continuously with a mechanical stirrer. The dissolution rates of titanium and iron were determined by pipetting about 5 cm^3 of the suspension from the flask as regular time intervals, filtering out the insoluble residue, and chemically analyzing the supernatant solution. Titanium and iron were determined by colorimetric methods.[18] The X-ray diffraction patterns were obtained by using a Rigaku Denki Geigerflex 2013 with Ni filtered Cu *Kα* radiation, with 30 kV and 10 mA. The surface observation was performed by using a Hitachi-Akashi Scanning Electron Microscope MSM 4C-102.

Results and Discussion

Analysis of Dissolution Rate. The electron micrographs of the ilmenite ore and the insoluble residues obtained from the suspension after the leaching experiment at 60 °C are shown in Fig. 1. Although the surface of the residues became rather porous during the leaching, no prominent changes were observed in the grain size and shape of the ores after the leaching. In this experiment, about 85% of the titanium and 90% of the iron in the ore were dissolved after 5 h. With these major constituents, most of the manganese and magnesium also dissolved. But the chemical analysis of the residue indicated that large amounts of aluminum, chromium, and silicon were still in it. However, the amounts of these residual minor constituents are not enough to maintain the grain size and shape of the ore particles. Therefore, a small portion of the dissolved titanium ion seemed to precipitate continuously by the hydrolysis at the ilmenite surface and to maintain the grain size and shape of the ore particles with other residual minor constituents during the leaching reaction. This assumption was supported experimentally by the result that the dissolution rate of titanium was slightly smaller than that of iron, although titanium and iron were dissolved in a near stoichiometric ratio. As described later, the X-ray diffraction patterns of the insoluble residues indicated the presence of rutile, anatase, and Ti_2O_3. On the other hand, at lower temperatures, the grain size of the ore particles was changed and gradually became smaller with the progress of the leaching, because of the absence of any precipitation of titanium oxides.

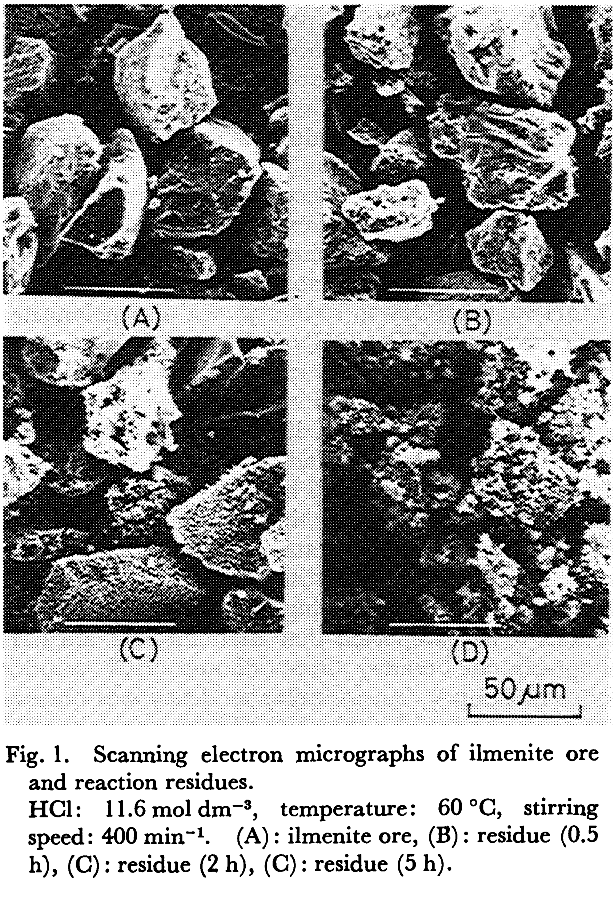

Fig. 1. Scanning electron micrographs of ilmenite ore and reaction residues.
HCl: 11.6 mol dm^{-3}, temperature: 60 °C, stirring speed: 400 min^{-1}. (A): ilmenite ore, (B): residue (0.5 h), (C): residue (2 h), (C): residue (5 h).

Accordingly, the dissolution rates of titanium and iron were analyzed on the basis of the extraction type core-model under the assumption that the ore is a homogeneous spherical solid phase.

The dissolution reaction of the ilmenite ore in hydrochloric acid solution is written as:

$$FeTiO_3 + 4HCl = TiOCl_2 + FeCl_2 + 2H_2O. \tag{1}$$

The reaction in Eq. 1 can be represented simply as Eq. 2:

$$A(l) + bB(s) = \nu P(l). \tag{2}$$

When the reaction percentage of component P was represented as x and the steady state of the reaction was assumed, the following Eq. 3 was obtained as the rate equation:

$$\frac{dx}{dt} = \frac{3\nu C_A}{\rho_P R} = \frac{1}{\frac{1}{k_L} + \frac{R}{D_e}\{(1-x)^{-1/3} - 1\} + \frac{1}{k_C}(1-x)^{-2/3}}. \tag{3}$$

Three rate-determining steps were studied: the diffusion in liquid film, the diffusion in residual layer, and the surface chemical reaction.[19] However, the diffusion in liquid film should not be the rate-determining step because the dissolution rate of titanium and iron was apparently not zero-order and was not affected by the stirring speed, as described in the next paragraph. Therefore, the following two equations were obtained

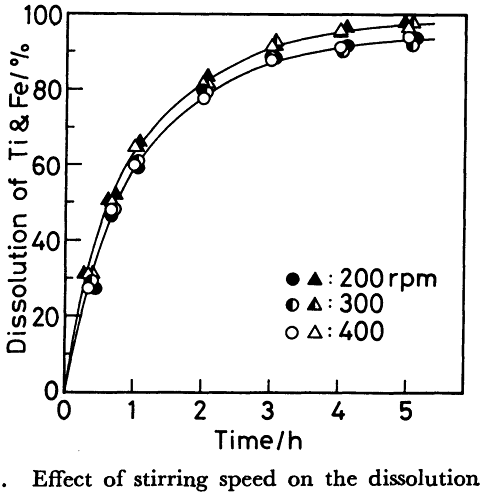

Fig. 2. Effect of stirring speed on the dissolution rates of Ti and Fe of ilmenite ore in concentrated HCl solution. HCl: 11.4 mol dm^{-3}, temperature: 70 °C. ○, ◐, ●: Ti, △, ▲, ▲: Fe.

for each rate-determining step by integration of Eq. 3.

i) For diffusion in residual layer (k_L, $k_C \gg D_e/R$)

$$1+2(1-x)-3(1-x)^{2/3}=\frac{6\nu C_A k_C}{\rho_P R^2}\,t, \qquad (4)$$

ii) for surface chemical reaction (k_L, $D_e/R \gg k_C$)

$$1-(1-x)^{1/3}=\frac{C_A k_C}{\rho_P R}\,t. \qquad (5)$$

Effect of Stirring Speed. Figure 2 shows the effect of stirring speed on the dissolution rate of titanium and iron in 11.4 mol dm^{-3} HCl solution at 70 °C. The diffusion in liquid film was not the rate-determining step of the reaction in Eq. 1. The dissolution rate of iron was slightly faster than that of titanium, but both were in a nearly stoichiometric ratio. On the basis of the data, subsequent experiments were carried out at the stirring speed of 400 min^{-1}.

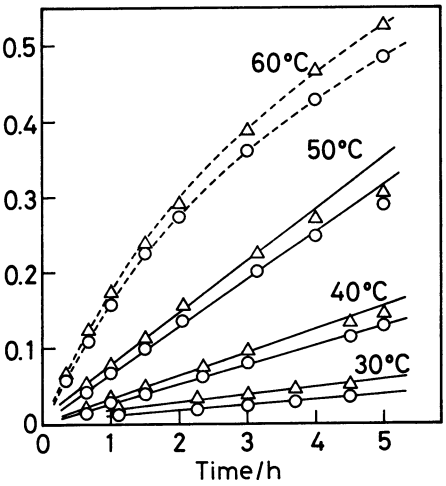

Fig. 3. Effect of temperature on the dissolution rates of Ti and Fe of ilmenite ore in concentrated HCl solution. $\{1-(1-x)^{1/3}\}$ *vs. t*.
HCl: 11.6 mol dm^{-3}, stirring speed: 400 min^{-1}. ○: Ti, △: Fe.

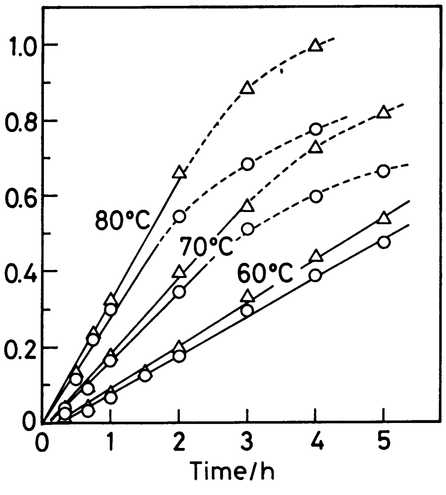

Fig. 4. Effect of temperature on the dissolution rates of Ti and Fe of ilmenite ore in concentrated HCl solution. $\{1+2(1-x)-3(1-x)^{2/3}\}$ *vs. t*.
HCl: 11.6 mol dm^{-3}, stirring speed: 400 min^{-1}. ○: Ti, △: Fe.

Effect of Temperature. Figures 3 and 4 show the effect of temperature on the dissolution rates of titanium and iron in 11.6 mol dm^{-3} HCl solution at temperatures of 30 to 80 °C. The dissolution rates at 30—50 °C shown in Fig. 3 were well expressed by Eq. 5, which is based on the rate-determining step of the surface chemical reaction; namely, there was a good linear relationship between $\{1-(1-x)^{1/3}\}$ and t. However, the linear relationship was no longer observable in the dissolution rate at 60 °C. This result indicates that the leaching reaction at temperatures above 60 °C was not limited by the surface chemical reaction. The rate constants, k_C, for the leaching reactions were calculated from the slopes of the straight lines in Fig. 3 and are given in Table 2. The apparent activation energies calculated from the Arrhenius plots of k_C were 81.2 kJ mol^{-1} for titanium and 73.2 kJ mol^{-1} for iron.

TABLE 2. KINETIC PARAMETERS OF THE LEACHING OF ILMENITE ORE IN CONCENTRATED HCl SOLUTION AT LOW TEMPERATURE

Temp/°C	$k_C \times 10^6$/m h^{-1}	
	Ti	Fe
30	1.23	1.72
40	3.83	4.29
50	9.20	10.4
Activation energy/kJ mol^{-1}	81.2	73.2

On the other hand, the dissolution rates at 60—80 °C shown in Fig. 4 were also well expressed by Eq. 4, which is based on the rate-determining step of the diffusion in the residual solid layer. That is to say, the surface chemical reaction at temperatures above 60 °C became so fast that the dissolution rates were limited by the diffusion in the residual layer. In this case, the diffusion rate of H_3O^+ was presumed to be quite fast because we used highly concentrated hydrochloric acid solution in the leaching experiments. Accordingly, the diffusion of Ti^{4+} (titanium ions present in aqueous solutions were not only mononuclear species such as $Ti(OH)^{3+}$, $TiO(OH)^+$, $Ti(OH)_3^+$ but also polynuclear species such as $(TiO)_8(OH)_{12}^{4+}$ [20]) and Fe^{2+} produced by the surface chemical reaction of the unreacted core was the rate-determining step. However, as shown in Fig. 4, there was not a linear relationship between $\{1+2(1-x)-3(1-x)^{2/3}\}$ and t in the dissolution curves after 4 h at 70 °C or after 3 h at 80 °C. This deviation from the rate equation was thought to be dependent on the precipitation of the titanium(IV) oxide on the ore particles by hydrolysis of the titanium ion present in the leaching solution at high temperatures. Earlier workers[17] have reported that titanium ions are liable to precipitate readily from diluted HCl solutions ($<$0.3 mol dm^{-3}), but a similar tendency was observed to happen frequently even in highly concentrated HCl solutions.The X-ray diffraction patterns and the electron micrographs of the reaction residues obtained after the leaching experiment at 70 °C were shown in Figs. 5 and

$$TiOCl_2 + H_2O = TiO_2 + 2HCl$$

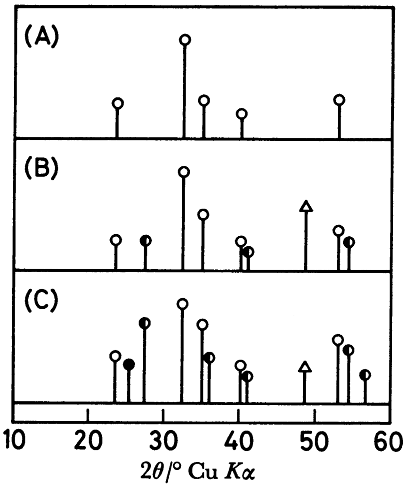

Fig. 5. X-Ray diffraction patterns of ilmenite ore and reaction residues.
HCl: 11.6 mol dm^{-3}, temperature: 70 °C, stirring speed: 400 min^{-1}. (A): ilmenite ore, (B): residue (2 h), (C): residue (4 h). ○: ilmenite, ◐: rutile, ●: anatase, △: Ti_2O_3.

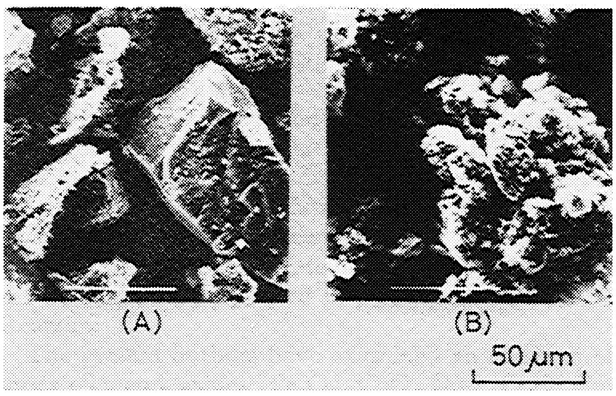

Fig. 6. Scanning electron micrographs of reaction residues.
HCl: 11.6 mol dm^{-3}, temperature: 70 °C, stirring speed: 400 min^{-1}. (A): residue (2 h), (B): residue (4 h).

TABLE 3. KINETIC PARAMETERS OF THE LEACHING OF ILMENITE ORE IN CONCENTRATED HCl SOLUTION AT HIGH TEMPERATURE

Temp °C	$D_e \times 10^{10}$/m^2 h^{-1}	
	Ti	Fe
60	1.84	2.03
70	3.14	3.51
80	4.98	6.09
Activation energy/kJ mol^{-1}	48.9	53.7

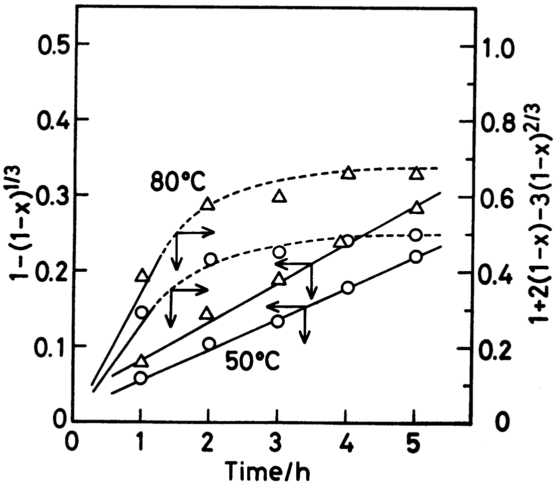

Fig. 7. Effect of ore grain size on the dissolution rates of Ti and Fe of ilmenite ore in concentrated HCl solution.
$\{1-(1-x)^{1/3}\}$ and $\{1+2(1-x)-3(1-x)^{2/3}\}$ vs. t.
HCl: 11.6 mol dm^{-3}, stirring speed: 400 min^{-1}, ore grain size: 150—250 mesh. ○: Ti, △: Fe.

6, respectively. The intensity of the diffraction peaks based on ilmenite decreased as the leaching continued, while the peaks of rutile gradually appeared. The peaks based on anatase and Ti_2O_3[21] were also observed in the X-ray diffraction patterns of the residues, though they were minor peaks. Ti_2O_3 was presumed to be produced by hydrolysis of Ti(III) ion formed by the reduction of Ti(IV) ion with chloride ion during the leaching. The times of formation of rutile as an insoluble matter were consistent with that of the deviation of titanium dissolution curves from the rate equation shown in Fig. 4. It can therefore be said that the hydrolysis of a part of dissolved titanium ion and the change in thickness of the residual layer have caused the deviation of the titanium dissolution curves. The deviation of the iron dissolution curves from the rate equation was also observed to follow that of titanium. This tendency was considered to depend upon the adsorption of dissolved iron ion and the change in thickness of the residual layer by the precipitation of titanium(IV) oxide. The effective diffusion coefficient, D_e, was calculated from the slopes of the straight lines in Fig. 4 and is given in Table 3. The apparent activation energies calculated from the Arrhenius plots of D_e were 48.9 kJ mol^{-1} for titanium and 53.7 kJ mol^{-1} for iron.

Effect of Ore Grain Size. Figure 7 shows the result obtained by using the powdered ilmenite ore of 150—250 mesh in 11.6 mol dm^{-3} HCl solution at 50 and 80 °C. The dissolution rate at 50 °C was well expressed by Eq. 5, while the initial dissolution rate at 80 °C was expressed by Eq. 4. On the basis of the data, the following reaction constant, k_C, and effective diffusion coefficient, D_e, for titanium were calculated: k_C(50 °C) $=9.38\times10^{-6}$ and D_e(80 °C) $=6.03\times10^{-10}$. These values agreed approximately with the results obtained by using the ilmenite ore of 250—325 mesh, as shown in Tables 2 and 3. It can therefore be said that the rate analysis used in this study was reasonable.

Nomenclature

b = Stoichiometrical coefficient (—).
C_A = Hydrochloric acid concentration in the solution (kg mol m^{-3}).
D_e = Effective diffusion coefficient in the residual layer of the particle (m^2 h^{-1}).

k_C = Rate constant for the reaction Eq. 2 (m h^{-1}).
k_L = Mass transfer coefficient (m h^{-1}).
R = Particle radius (m).
t = Time (h).
x = Reaction percentage (—).
ρ_P = Mole density (kg mol m^{-3}).
ν = Stoichiometrical coefficient (—).

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