KINETICS OF THE SELECTIVE CHLORINATION OF ILMENITE

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ABSTRACT

Ilmenite ($FeO \cdot TiO_2$) may be beneficiated by selective chlorination in which the iron is selectively chlorinated as volatile iron chlorides, leaving behind an enriched residue of rutile (TiO_2). Relatively high partial pressures of chlorine and very low partial pressures of oxygen are required for the chlorination of either iron or titanium. Under equilibrium conditions at 1200 K and 1 atm., selective chlorination of ilmenite is not thermodynamically possible in the presence of carbon. The fact that this does occur in practice, however, indicates that non-equilibrium conditions should be maintained. Batch experiments conducted between 915 and 970 °C in a horizontal tube furnace showed that the kinetics of selective chlorination were limited by diffusion of iron through a product layer of TiO_2 which formed from the outside of a particle. This mechanism was supported by point analyses under a scanning electron microscope. The iron content of a sample was used to follow the kinetics of chlorination. It was shown that only about 4% of the titanium was lost as volatiles during chlorination. Calcium and manganese impurities to a lesser extent were removed easily during chlorination, whereas chromium, aluminium, niobium and magnesium were not removed. Vanadium and silicon could be removed only partially.

INTRODUCTION

Titanium finds commercial application in the form of titanium dioxide which has become the major white pigment material, and as the metal due to it low density and corrosion resistance [1,2]. Rutile with ideal formula TiO_2 and ilmenite with ideal formula $FeO \cdot TiO_2$ are the principal raw materials for both titanium metal and titanium dioxide. Whereas the world reserves of rutile are limited, ilmenite occurs extensively in Australia, Canada, India, Malaysia, Norway, Sweden, South Africa, the U.S.A. and the U.S.S.R. For economic reasons a raw material should contain more than 95% TiO_2 if it is to be used for production of $TiCl_4$, which is an intermediate in the production of metallic titanium and TiO_2.

Unwanted iron may be removed from ilmenite by one of the following four methods: preferential reduction of iron in the liquid [3,4] or solid [5–7] state; selective acid leaching [8]; preferential sulphidization of iron and its

separation by physical or chemical methods [9,10]; and selective chlorination with or without a reducing agent [4,11–14]. Only the first method has been utilized commercially.

Chlorination processes have also been suggested for the recovery of aluminium, iron, silicon and titanium from coal ash in fluidized beds [15,16]. Robinson et al. [17] described a process whereby the chromium to iron ratio of low grade chromite could be increased considerably by means of selective chlorination of the iron.

Chlorination processes for ilmenite fall into two groups: (a) direct chlorination in which all the components of the ilmenite are chlorinated and then separated while in the gaseous state leaving pure $TiCl_4$ which can then be oxidized with oxygen to high purity TiO_2 or reduced with magnesium to titanium metal; and (b) selective chlorination in which the iron in ilmenite is selectively chlorinated as volatile iron chlorides leaving behind an enriched TiO_2 residue.

Little work has been published on the kinetics of the latter process, and it is the objective of this paper to investigate the mechanism and kinetics of the selective chlorination of a domestic ilmenite.

THERMODYNAMICS OF CHLORINATION

Ilmenite is a compound consisting mainly of FeO and TiO_2 which are only loosely bound together, as shown by the small value of the standard free energy of formation, ΔG^0 [18]

$$TiO_2 + FeO = FeO \cdot TiO_2 \qquad \Delta G^0 = -5443 - 11.26T \text{ J mol}^{-1}$$

Therefore, from a thermodynamic point of view, ilmenite can be considered as a mixture of FeO and TiO_2, so that it is possible to examine the chlorination of FeO and TiO_2 separately and to compare the conditions required for each. This is done by means of the predominance area diagram (Kellogg diagram [19]) in Fig. 1 which shows the stable forms of iron and titanium compounds in the Fe–O–Cl and Ti–O–Cl systems under different conditions. At 1200 K, which is a typical chlorination temperature for ilmenite, the stable forms of iron and titanium compounds for given partial pressures of chlorine and oxygen are found by locating the gas composition on the figure and seeing which field it lies in.

The regions of gas composition in which ilmenite is entirely chlorinated and in which only the iron is chlorinated are marked on Fig. 1. In both cases, relatively high partial pressures of chlorine (approaching 1 atm.) and very low partial pressures of oxygen are required. A lower partial pressure of oxygen is required for direct chlorination than for selective chlorination of iron. A substance such as carbon with a high affinity for oxygen is required in practice to obtain these conditions.
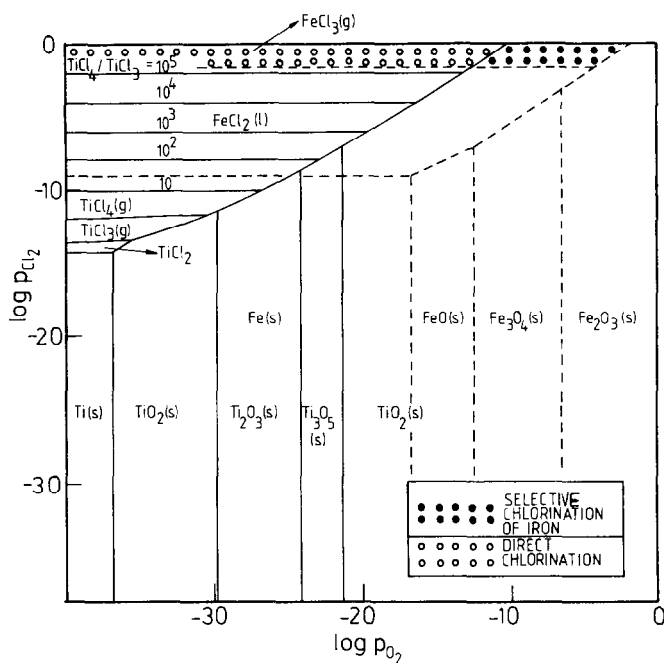
Fig. 1. Predominance area diagram of the Fe–O–Cl and Ti–O–Cl systems at 1200 K.

The partial pressure of oxygen in equilibrium with carbon, assuming CO is the gaseous product at 1200 K and 1 atm., can be calculated [18] as 1.28×10^{-19} atm. If the product is CO_2 under similar conditions, then the partial pressure of oxygen is calculated [18] as 6.17×10^{-18} atm. Therefore, under equilibrium conditions at 1200 K and 1 atm., chlorination of ilmenite in the presence of carbon should produce both iron and titanium chlorides.

Selective chlorination of ilmenite will thus occur if the partial pressure of oxygen is greater than about 10^{-12} atm. In the presence of carbon this is not theoretically possible, but may occur under non-equilibrium conditions, which can be promoted by limiting the amount of carbon and by using a form of carbon with a low reactivity.

EXPERIMENTAL

Figure 2 shows the horizontal tube-furnace of 50 mm internal diameter used for chlorination tests. The Pythagoras tube, a high temperature recrystallized alumina refractory, had an extended Pyrex glass tube on one side which acted as a condenser for the volatile chlorides, and was sealed at both sides by machined graphite stoppers. Chlorine and argon were fed to the furnace via glass tubing, the flow being monitored with a rotameter. Excess chlorine passed into a flask of sodium hydroxide solution where it was
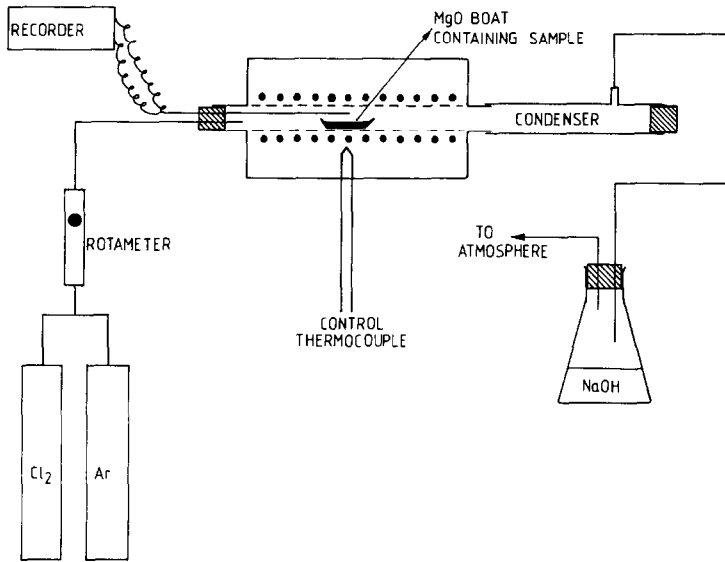
Fig. 2. Apparatus used for batch, laboratory scale chlorination tests.

absorbed. The furnace temperature was controlled within $\pm 20\,^{\circ}$C by an on–off controller. A Pt/Pt–13% Rh thermocouple was used to measure the sample temperature independently. An MgO boat was used to hold the reaction mixture and was positioned at the centre of the furnace above the monitoring thermocouple. Temperatures of 915, 935, 950 and 970$\,^{\circ}$C were used.

Ilmenite was obtained from Richard's Bay Minerals (Pty.) Ltd., who beneficiate the heavy beach sands of St. Lucia at the Natal coast in South Africa. This ilmenite had a TiO_2 content of 49.7 mass% and an Fe content of 35.9 mass%. Powdered graphite with particle size 100% $< 106\ \mu$m was mixed intimately with 10.0 g of the 90–125 μm particle size fraction of the ilmenite before being placed in the previously heated furnace. At the start and at the end of a run the furnace was flushed with argon before and after the flow of chlorine was turned on and off respectively. Runs were carried out for 5, 10, 15, 25, 45, 50, 75, 100 and 110 minutes.

The reacted sample was washed with dilute HCl to remove all traces of chlorides and then dried and weighed. It was then subjected to heavy medium separation using di-iodomethane to remove the unreacted graphite from the sample and was then reweighed. A small amount of the sample was retained for EDAX (energy-dispersive analysis of X-rays) analyses in a scanning electron microscope. The remainder of the sample was finely ground for analysis by X-ray fluorescence. In order to overcome the effects of differences in mineralogical composition and particle size, fused glass discs were used instead of pressed pellets. Sodium tetraborate, $NaNO_3$ and Pb_3O_4 were used for fusion of the samples [20].

RESULTS AND DISCUSSION

A preliminary series of tests to determine the effect of chlorine flow rate on the rate of reaction showed that conversion of ilmenite was independent of flow rate at values higher than 1.4 l min^{-1}. A chlorine flow rate of 1.8 l min^{-1} was thus selected for all further tests.

The loss of titanium for each sample was calculated from a mass balance on the titanium in the original sample and that in the product. Owing to a small fraction of the TiO$_2$ being chlorinated, the loss of titanium increased with time and temperature, but this was never more than 6% and on the average only about 4% after 110 min. Thus selective chlorination of iron was taking place, as the loss of iron from a sample after 110 min was always higher than 78%. If the loss of titanium could be considered negligible, the fractional conversion X at time t is defined in terms of iron only

$$X = 1 - \frac{(\% \text{ Fe})(\text{mass of sample})_{t=t}}{(\% \text{ Fe})(\text{mass of sample})_{t=0}}$$

where the mass of the sample excludes any carbon.

Figure 3 shows the conversion versus time curves for different experimental conditions. The results for 110 min at 970°C and an ilmenite/graphite ratio of 17 corresponded to a final TiO$_2$ content of 94%, which means that with proper process optimization an acceptable synthetic rutile can be produced.
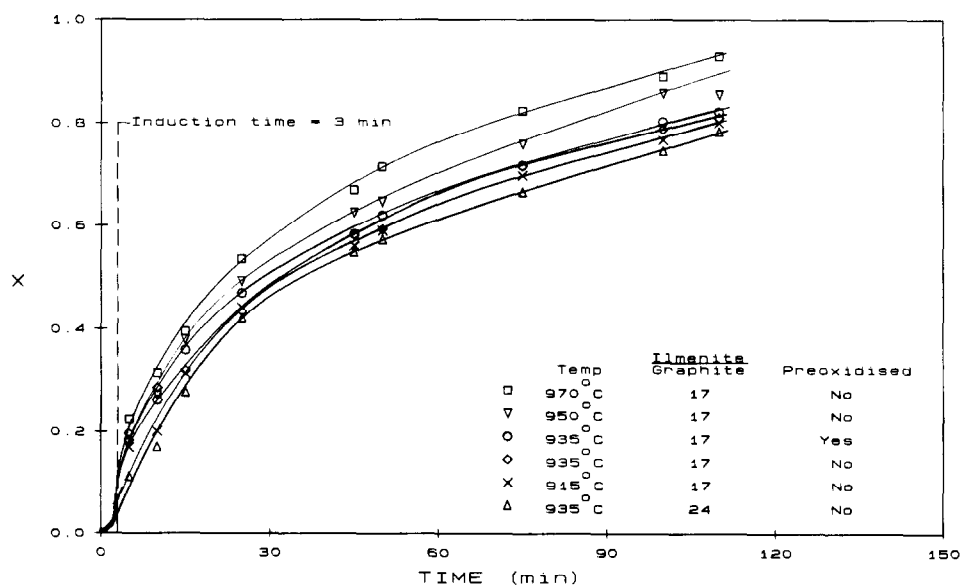

Fig. 3. Kinetics of selective chlorination of ilmenite for different experimental conditions.

Figure 3 presents results for two levels of ilmenite/graphite ratios at 935°C. Clearly, chlorination is more effective at the higher graphite content in the range 4–6 mass% graphite. The loss of TiO_2 of 3.5% was also better at the higher level of graphite. Fuwa et al. [14] observed similar results for a roasted ilmenite.

Pre-oxidized or roasted ilmenite ($Fe_2O_3 \cdot TiO_2$) in which the ferrous iron is oxidized to the ferric state, is often claimed to have superior chlorination characteristics [14]. This was tested by roasting some of the ilmenite in air at 1000°C for 4 h. Figure 3 shows that roasting yielded little or no benefit at a chlorination temperature of 935°C.

According to Fig. 3, the effect of temperature is relatively small between 915 and 970°C. Whereas Fuwa et al. [14] found that an increase in temperature caused an increase in the rate of chlorination of roasted ilmenite, Dunn [11] observed that when chlorinating ilmenite with phosgene, the effect of temperature on the rate of chlorination went through a maximum at 710°C and a minimum at 1110°C.

The presence of small concentrations of impurity elements in rutile may cause problems in the chloride process for producing pure TiO_2. These problems could be associated with fluxing or sintering in the bed during chlorination and in condensation of the volatile chlorides. Table 1 gives the analyses for impurity elements after 110 min of chlorination. It is clear that calcium is almost entirely removed, manganese is lowered considerably, vanadium is lowered reasonably, and silicon is lowered marginally, while magnesium, aluminium, chromium and niobium are present at the same or slightly higher levels than in the original ilmenite.

Figures 4–6 illustrate the change in composition of a grain of ilmenite after 5, 15 and 25 min of chlorination at 915°C. Conditions within the bed of ilmenite in the MgO boat in the tube furnace were not uniform. Grains

TABLE 1

Concentrations of impurity elements (in p.p.m.) in beneficiated ilmenite after 110 min of chlorination

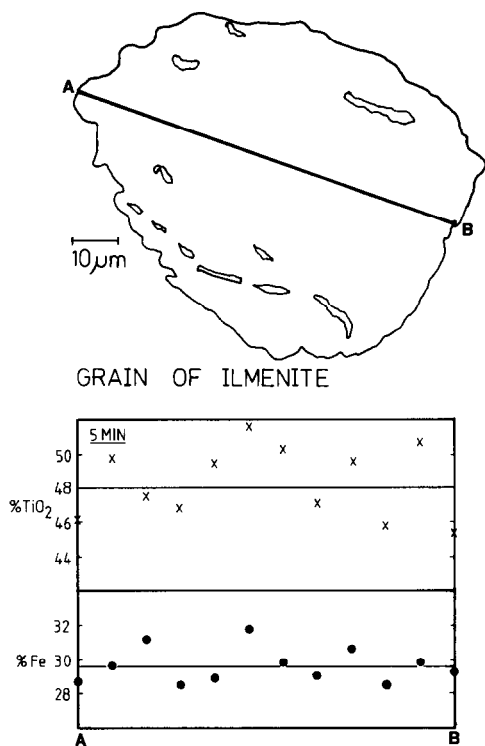| Tempe-rature (°C)	Ilmenite/ Graphite	Pre-oxida-tion	Mg	Al	Si	Ca	V	Cr	Mn	Nb
970	17	No	2030	1340	1840	0	360	720	980	760
950	17	No	2160	1270	1830	0	400	710	1160	730
935	17	Yes	1970	970	1020	0	850	680	1390	580
935	17	No	2270	1250	1950	10	390	640	1320	730
915	17	No	2340	1190	2100	20	460	690	1410	720
935	24	No	2280	1110	1640	0	630	660	1450	690
Natural ilmenite			2290	1160	2760	300	1200	510	6070	460

Fig. 4. Composition of a grain of ilmenite after chlorinating for 5 min at 915°C.
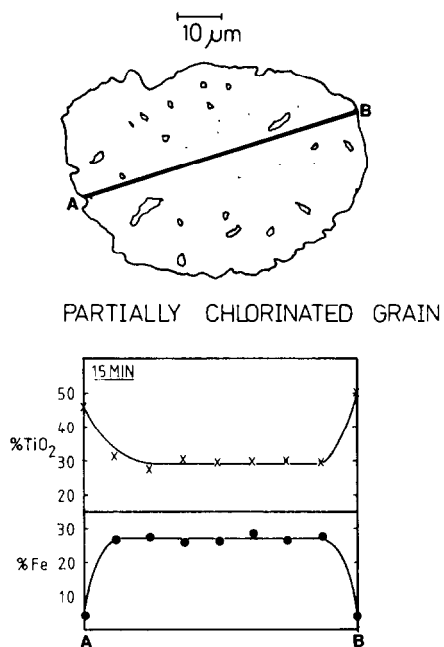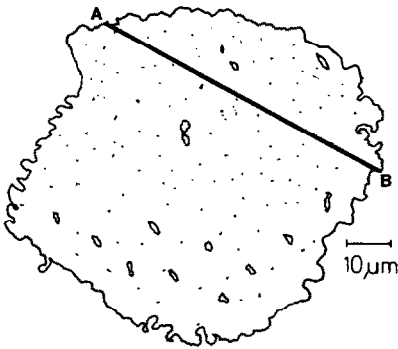

Fig. 5. Composition of a grain of ilmenite after chlorinating for 15 min at 915°C.

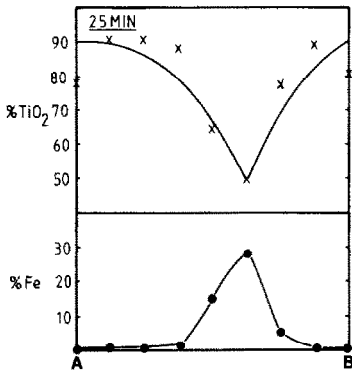PARTIALLY CHLORINATED GRAIN
CONTAINING SMALL PORES

Fig. 6. Composition of a grain of ilmenite after chlorinating for 25 min at 915° C.

on the surface were more accessible to chlorine and could be expected to be converted to a greater extent than those below the surface. However, the grains shown in these figures were fairly representative of each run. The size, shape and general appearance of the grains did not change greatly during chlorination.

Semi-quantitative point analyses for titanium and iron were obtained by means of an EDAX, as shown in Figs. 4–6. Unreacted ilmenite was not uniform in composition throughout a grain, which is also reflected in the scattered composition after 5 min. After 15 min some iron was removed from the outer zone of a grain and this had the effect of raising the TiO_2 content in this zone. After 25 min the unreacted core shrank inwards as iron diffused through the grain to the surface where it reacted with chlorine. These results suggest that a shrinking core mechanism is operative. Since the TiO_2 product layer which forms from the outside inwards was impermeable, it is possible that diffusion of iron through this layer was the rate-controlling step. Fuwa et al. [14] observed a similar shrinking core pattern during the selective chlorination of roasted ilmenite, but assumed that a first-order irreversible reaction controlled kinetics. It was found that such an approach [21] could not be used to describe the results in Fig. 3.
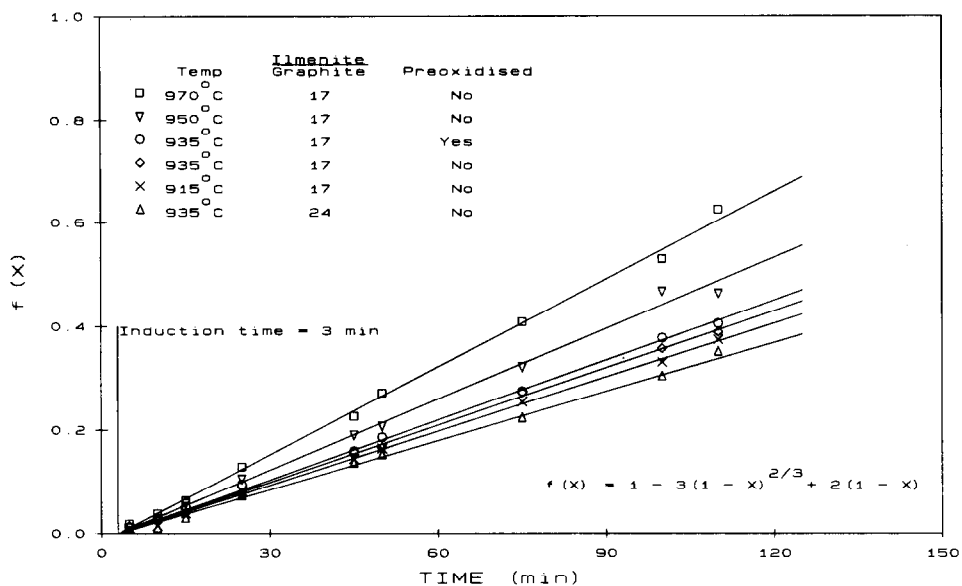
Fig. 7. Isothermal reaction kinetic data plotted according to a model for diffusion through a product layer as the rate-limiting step.
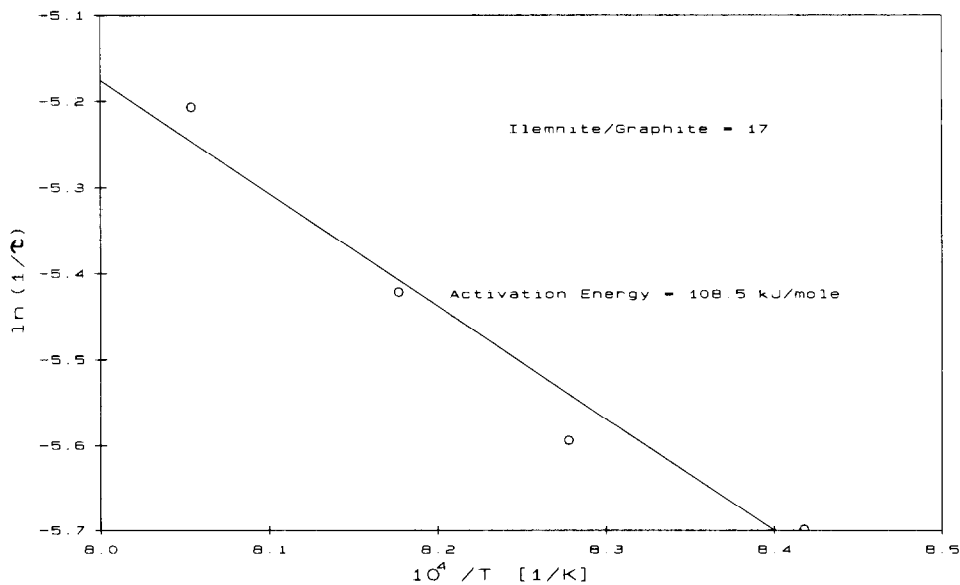

Fig. 8. Arrhenius plot for the selective chlorination of ilmenite in the temperature range 915–970 °C.

Levenspiel [21] showed that if diffusion through a product layer is rate-controlling, then for a spherical particle

$$\frac{t}{\tau} = f(X) = 1 - 3(1-X)^{2/3} + 2(1-X)$$

where τ is the total time required for full conversion $X = 1.0$. Figure 7 shows plots of $f(X)$ vs. time for the data of Fig. 3. Satisfactory fits to straight lines are obtained. Therefore it is reasonable to assume that diffusion of iron through a product layer of TiO_2 was the rate-controlling step. The reaction constant $(1/\tau)$ shows a dependence on temperature, which is illustrated as an Arrhenius plot in Fig. 8. The activation energy of 108.5 kJ mol^{-1} could be calculated from the slope of this plot.

CONCLUSIONS

Under equilibrium conditions at 1200 K and 1 atm. selective chlorination of ilmenite is not thermodynamically possible in the presence of carbon. However, the fact that this did occur and that only about 4% of the titanium was lost as volatiles indicated that non-equilibrium conditions were maintained. Besides iron, calcium and manganese were the only impurities that were removed effectively by chlorination. Pre-oxidation of the ilmenite did not enhance its selective chlorination significantly. The rate-controlling step was identified as diffusion of iron through a product layer of TiO_2 which formed from the outside of an ilmenite particle. An activation energy of 108.5 kJ mol^{-1} was calculated for the process.

ACKNOWLEDGEMENTS

REFERENCES

1 E.M. Considine (Ed.), Chemical and Process Technology Encyclopedia, McGraw-Hill, New York, 1974, p. 1102.
2 Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Wiley, New York, 1969, Vol. 20, p. 349.
3 A.W. Knoerr, Engng. Min. J., 153 (1952) 72.
4 S.D. Hill and R.R. Wells, Light Metals, Metall. Soc., A.I.M.E., New York, Vol. 1, 1976, p. 541.

5 M.K. Hussein and S.Z. El-Tawil, Indian J. Technol., 5 (1967) 97.

6 M.I. El-Guindy and W.G. Davenport, Metall. Trans., 1 (1970) 1729.

7 I.E. Grey and A.F. Reid, Trans. Inst. Min. Metall., 83 (1974) C39.

8 S. Kataoka and S. Yamada, Chem. Eng., 80 (1973) 92.

9 S. Prasad and J.B.P. Tripathi, Indian J. Appl. Chem., 21 (1958) 162; Chem. Abstr. 16486e, Vol. 53, 1959.

10 N.K. Hiester, E.M. Liston and D. Goerz, in H. Forberg (Ed.), Light Metals, Proc. 103rd AIME Annual Meeting, Vol. 2, Metall. Soc. AIME, New York, 1974, p. 401; Chem. Abstr., 123718v, Vol. 81.

11 W.E. Dunn, Trans. A.I.M.E., 218 (1960) 6.

12 C. Sankaran, R.N. Misra and P.P. Bhatnagar, Advances in Extractive Metallurgy, Inst. Min. Metall., London, 1967, p. 480.

13 A.A. Rabie, M.Y. Saada and S.Y. Ezz, Advances in Extractive Metallurgy, Inst. Min. Metall., London, 1967, p. 501.

14 A. Fuwa, E. Kimura and S. Fukushima, Metall. Trans. B., 9 (1978) 643.

15 A.K. Mehrotra, L.A. Behie, P.R. Bishnoi and W.Y Svrcek, Ind. Eng. Chem. Process. Des. Develop., 21 (1982) 37.

16 A.K. Mehrotra, L.A. Behie, P.R. Bishnoi and W.Y Svrcek, Ind. Eng. Chem. Process. Des. Develop., 21 (1982) 44.

17 M. Robinson, H.B. Wilson, A.D. Crosby and K.J. Talati, Extraction Metallurgy '81, Inst. Min. Metall., London, 1981, p. 393.

18 JANAF Thermochemical Tables, U.S. Bureau of Standards (1971).

19 T. Rosenquist, Principles of Extractive Metallurgy, McGraw-Hill, Tokyo, 1974, p. 245.

20 C.E. Austen and B.G. Russel, Report No. 1599, National Institute for Metallurgy, Johannesburg (1974).

21 O. Levenspiel, Chemical Reaction Engineering, 2nd edn., Wiley, New York, 1972.