Nonisothermal Behavior of the Oxidation of Natural Ilmenite Pellet

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The kinetics of the oxidation of a cement-bonded pellet made of natural ilmenite was studied with an unsteady nonisothermal kinetic model derived by assuming pseudo-steady state mass transfer through the product layer and unsteady state heat transfer within the pellet. The derived model agreed well with the experiments. It was further found that the amount of the heat accumulated inside the pellet during oxidation was too great to be negligible in comparison with that lost to its surroundings, especially, in the initial period. During the oxidation of an ilmenite pellet with pure oxygen, the overall reaction rate was mainly controlled by the intrapellet diffusion of oxygen and the total heat transfer rate was principally limited by the poor heat conduction through the product shell. In the case of the oxidation of the ilmenite pellet with diluted oxygen, it is reasonable to analyze the reacting pellet as an isothermal system provided the oxygen concentration being less than 10 mol%.

KEY WORDS: ilmenite; cement-bonded pellet; oxidation; nonisothermal kinetics; unreacted core shrinking model; unsteady heat conduction; rate-controlling step; intrapellet diffusion.

1. Introduction

For efficient making use of the abundant ilmenite deposits, a great number of processes have been proposed to produce the substitute of natural rutile.¹⁾ As an intermediate step, preoxidation of ilmenite is beneficial for the subsequent treatment, such as reduction and selective chlorination in upgrading ilmenite especially for the poorly weathered ores. Isothermal kinetics on the oxidation of natural ilmenite with diluted oxygen was reported previously.²⁾ In this paper, special attention will focus on the nonisothermal behavior of the oxidation of an ilmenite pellet with pure oxygen and the deviation of the kinetic parameters caused by this nonisothermal effect.

As pointed out previously,²⁾ the oxidation of a natural ilmenite pellet with pure oxygen could hardly be analyzed as an isothermal reaction system because an appreciable temperature rise inside the pellet was observed during the reaction. In order to clarify its nonisothermal behavior, the oxidation kinetics of the natural ilmenite pellet was quantitatively studied with a nonisothermal kinetic model derived by taking simultaneously mass and heat balance into account and by analyzing them as pseudo-steady state and unsteady state processes respectively.

2. Experimental

The reaction rate of the oxidation of a cement-bonded ilmenite pellet with pure oxygen was measured thermogravimetrically from 1073 to 1173 K with 50 K temperature interval. Inner diameter of the reactor was 50 mm

and gas flow rate was controlled at $1.67 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$ (NTP). Over 150 K temperature rise was found inside the pellet during the oxidation with pure oxygen by inserting a sheathed CA thermocouple (1 mm ϕ in outer diameter) into the pellet center. In order to avoid the influence of the reaction heat, the rate constant of the intrinsic chemical reaction and the effective diffusivity of oxygen through product layer and their temperature dependence were measured with the same kind of ilmenite pellet by using diluted oxygen (9.8 mol% O_2 - N_2) in the temperature range from 1073 to 1273 K and other experimental condition being similar to that for the oxidation with pure oxygen. As will be proved later, the oxidation of the ilmenite pellet with such a gas mixture can be analyzed as isothermal reaction.

The natural ilmenite used in the experiment was from Australia, of which chemical composition and particle size distribution were given in **Tables 1** and **2**. According to the X-ray diffraction (XRD) analysis, it mainly consisted of ferrous titanate (FeTiO_3) and small amount of pseudobrookite (Fe_2TiO_5). The size of the pellet containing 8.0 mass% of Portland cement as binder was from 12.5 to 13.0 mm in diameter. Chemical composition of the cement was presented in **Table 3**. After curing at 323 K under saturated water vapor atmosphere for one week and then dehydration at 1173 K under deoxygenated nitrogen stream for one hour, the strength of the pellet was greater than 100 kg per pellet and the combined water contained originally in the pellet was completely removed. Details about the experimental apparatus and operation procedure, which were reported previously,²⁾ will not be repeated here.

According to the XRD results before and after

Table 1. Chemical composition of Australian ilmenite used. (mass%)

Component	TiO ₂	T·Fe	FeO	Fe ₂ O ₃	MnO	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Cr ₂ O ₃	V ₂ O ₅	MgO	CaO
Amount	52.21	31.95	26.14	16.71	1.73	1.52	1.00	0.005	0.02	0.12	0.40	0.14

Table 2. Particle size distribution of the natural ilmenite used.

Size range (μm)	Mass ratio (mass%)
$d_p < 44$	67.18
$44 < d_p < 74$	18.63
$74 < d_p < 149$	13.21
$149 < d_p < 250$	0.72
$250 < d_p < 500$	0.26

Table 3. Chemical composition of the Portland cement. (mass%)

Component	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO
Amount	65.6	20.9	4.7	2.7	1.75

Table 4. Main physical properties of solid reactant and products.

Properties	Reactant	Product
Apparent density ρ_a (kg·m ⁻³)	3 120	3 230
True density ρ_s (kg·m ⁻³)	4 260	4 320
Porosity ε (—)	0.268	0.252
Effective thermal conductivity k_e (W·m ⁻¹ ·K ⁻¹)	0.938	1.07
Thermal diffusivity $\alpha \times 10^7$ (m ² ·s ⁻¹)	3.47	4.11
Specific heat capacity c_p (J·kg ⁻¹ ·K ⁻¹)	850	804

oxidation, the reaction within the experimental temperature range for both the oxidation of the pellet with pure oxygen and that with diluted oxygen can be expressed as follows:

The thermal diffusivity of the solid reactant and products were measured at 1 173 K with THERMAL PARAMETER MEASUREMENT EQUIPMENT (TC-3000) by means of laser flash and their corresponding density and porosity were measured according to JIS M 8716-1971 and JIS M 8717-1971, respectively. Some main physical properties of the pellet were summarized in **Table 4**.

In order to determine the emissivity of the oxidized pellet, the pellet surface temperature was directly measured with an optical pyrometer in the course of the oxidation with pure oxygen. The value which made the calculated pellet surface temperature and the measured ones fit best was selected as the emissivity.

3. Theoretical Analysis

3.1. Nonisothermal Kinetic Model

From the macroscopic point of view, the oxidation of

Fig. 1. Schematic diagram of the reacting pellet as a non-isothermal reaction system.

the ilmenite pellet proceeded topochemically,²⁾ and the validity of the pseudo-steady state assumption for mass transfer during gas-solid reaction has been theoretically proved by Bischoff.³⁾ It is, however, more reasonable to analyze the heat conduction through the solid medium as an unsteady state process, because the rate of heat accumulation caused by the heat capacity of the solid material is usually comparable in magnitude with that of heat loss.^{4,5)} The unsteady-state nonisothermal kinetic model was derived on the basis of the unreacted core shrinking model⁶⁾ and by analyzing the mass transfer and heat transfer within the pellet as pseudo-steady state process and unsteady state process, respectively. The reacting system was schematically depicted in **Fig. 1**.

Based on the aforementioned assumption, the shrinking rate of the reaction front can be expressed as Eq. (2).

$$\frac{d\eta_i}{dt^*} = -\frac{1}{\frac{k\eta_i^2\kappa(1-y_o)}{k_f} + \left[\frac{r_o k}{(D_o)_{eff}}\right]\eta_i(1-\eta_i) + 1} \quad \text{.....(2)}$$

According to the first law of thermodynamics, the following local energy conservation must be maintained at the reaction front.

$$\begin{aligned} &\text{heat accumulation rate} = \\ &\text{heat generation rate} - \text{heat loss rate} \end{aligned}$$

or written mathematically as Eq. (3). Details of the derivation of Eq. (3) are given in the Appendix.

$$\eta_i^2 \frac{\partial \Psi_i}{\partial \theta_i} = \frac{\partial}{\partial \eta} \left(\eta^2 \frac{\partial \Psi}{\partial \eta} \right) \bigg|_{\eta_i} + \frac{\partial \gamma}{\partial \eta} \bigg|_{\eta_i} \quad \text{.....(3)}$$

Within the unreacted core and product layer, there is no

heat generation source, and the energy conservation can be expressed as Eqs. (4).

$$\eta_r^2 \frac{\partial \Psi_r}{\partial \theta_r} = \frac{\partial}{\partial \eta_r} \left(\eta_r^2 \frac{\partial \Psi_r}{\partial \eta_r} \right) \quad (4-a)$$

$$\eta_p^2 \frac{\partial \Psi_p}{\partial \theta_p} = \frac{\partial}{\partial \eta_p} \left(\eta_p^2 \frac{\partial \Psi_p}{\partial \eta_p} \right) \quad (4-b)$$

The parameters appearing in Eqs. (2) through (4) are defined by Eqs. (5). Dimensionless position of the reaction front,

$$\eta_i = r_i/r_o \quad (5-a)$$

Dimensionless reaction time,

$$t^* = bkM_s(c_b - c^*)t/(r_o \rho_a x_s) \quad (5-b)$$

Dimensionless temperature,

$$\Psi_k = T_k/T_b, \quad (k=i, r, \text{ or } p) \quad (5-c)$$

Dimensionless time,

$$\theta_k = \alpha_k t/r_o^2, \quad (k=i, r, \text{ or } p) \quad (5-d)$$

Dimensionless position, of which η_i is the same as that defined in Eq. (5-a),

$$\eta_k = r_k/r_o, \quad (k=i, r, \text{ or } p) \quad (5-e)$$

Dimensionless rate of heat generation,

$$\gamma = bv_g(-\Delta H^0)/(T_b k_e r_o) \quad (5-f)$$

where,

$$v_g = (c_b - c^*)S_o / \{ \kappa(1 - y_o)/k_f + [r_o/(D_o)_{eff}](1 - \eta_i)/\eta_i + 1/(k\eta_i^2) \} / (4\pi) \quad (5-g)$$

The initial and boundary conditions are given by Eqs. (6) to (8).

$$\eta_i = 1, \Psi_k = 1, \text{ when } t^* = 0 \text{ and } \theta_k = 0, \quad (k=i, r, \text{ or } p) \quad (6)$$

At the pellet center, because of its symmetry,

$$\frac{\partial \Psi_r}{\partial \eta_r} = 0, \quad (0 < t^* < t_{x=1}^*) \quad (7)$$

and at the external surface,

$$\frac{\partial \Psi_p}{\partial \eta_p} = B_i(1 - \Psi_s)/2, \quad (0 < t^* < t_{x=1}^*) \quad (8)$$

where, B_i is Biot number defined as $B_i = 2r_o h_t/k_e$.

The dimensionless differential equations and their corresponding initial and boundary conditions expressed by Eqs. (2) to (8) completely describe the reaction rate and the temperature change with reaction time and spatial coordinates for a single ilmenite pellet during oxidation.

The fractional conversion of the oxidation of the ilmenite pellet is given by Eq. (9).

$$x = 1 - \eta_i^3 \quad (9)$$

3.2. Determination of Parameters

The mass transfer coefficient k_f and the convective heat transfer coefficient h_c through the stagnant gaseous

film around the pellet were estimated according to Ranz-Marshall's correlations.⁷⁾

$$N_{Sh} = 2.0 + 0.6 N_{Re}^{1/2} N_{Sc}^{1/3} \quad (10-a)$$

$$N_{Nu} = 2.0 + 0.6 N_{Re}^{1/2} N_{Pr}^{1/3} \quad (10-b)$$

where, $N_{Sh} = 2k_f r_o/D$, $N_{Re} = 2Ur_o/\nu$, $N_{Sc} = \nu/D$, $N_{Nu} = 2h_c r_o/k_g$, $N_{Pr} = c_{pg}\mu/k_g$, and $\nu = \mu/\rho_g$.

The molecular diffusivity D and viscosity μ of oxygen were estimated with Chapman-Enskog's equation⁸⁾ and Bird *et al.*'s equation,⁸⁾ respectively.

$$D = 5.9958 \times 10^{-24} \frac{(2T^3/M)^{1/2}}{\rho \sigma^2 \Omega_D} \quad (11)$$

$$\mu = 8.4411 \times 10^{-25} \frac{(MT)^{1/2}}{\sigma^2 \Omega_\mu} \quad (12)$$

The thermal conductivity of oxygen k_g was predicted with Eucken's equation.⁸⁾

$$k_g = (C_{pg} + 5/4 R/M)\mu \quad (13)$$

At high temperature, radiation is also an important process for heat transfer, the radiative heat transfer coefficient h_r was approximately determined by applying Stefan-Boltzmann's equation.⁷⁾

$$h_r = e\sigma_b(T_s^2 + T_b^2)(T_s + T_b) \quad (14)$$

Emissivity e was selected as 0.8 which made the calculated results agree best with that measured experimentally.

In the calculation for the oxidation with diluted oxygen, the parameters such as molecular diffusivity, viscosity, and thermal conductivity of gaseous species were substituted with their corresponding values of the O_2-N_2 system and their estimation methods were similar to what described above. The viscosity and thermal conductivity of the gaseous mixture were then calculated with Wilke's equation,⁹⁾ Eq. (15), and Manson *et al.*'s equation,⁸⁾ Eq. (16), respectively.

Viscosity of the gas mixture:

$$\mu_{mix} = \sum_{i=1}^n \frac{y_i \mu_i}{\sum_{j=1}^n y_j \phi_{ij}} \quad (15)$$

Thermal conductivity of the gas mixture:

$$k_{e,mix} = \sum_{i=1}^n \frac{y_i k_{ei}}{\sum_{j=1}^n y_j \Phi_{ij}} \quad (16)$$

in Eqs. (15) and (16),

$$\Phi_{ij} = \left(\frac{1}{8} \right)^{1/2} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (17)$$

The values of k_f and h_c calculated according to Eqs. (10) to (13) and Eqs. (15) to (17) show that they are almost independent of the composition of the O_2-N_2 mixture.

In the case of the oxidation with pure oxygen, the inward mass transport flux can be expressed as $N_{O_2} = -C/(RT)dp/dr$.¹⁰⁾ The coefficient C was approximated with the effective self diffusivity of oxygen defined

by Eq. (18), because the component of viscous flow is smaller than that of diffusion.

$$D_{e,O_2} = D_{O_2}(\epsilon_p/\tau_p) \quad \dots\dots\dots (18)$$

where D_{O_2} is the self diffusivity of oxygen. The structure parameter (ϵ_p/τ_p) was measured experimentally using 9.8mol% O_2-N_2 so as to avoid the influence of reaction heat.²⁾ In the calculation for the oxidation of the ilmenite pellet with diluted oxygen, the experimental results measured with 9.8mol% O_2-N_2 were directly applied. The effective thermal conductivity and specific heat

capacity as well as thermal diffusivity of both the unreacted core and the product layer were measured at 1173 K which was the mean value of the experimental temperature range.

Reaction rate constant k was determined with experimental data measured by using 9.8mol% O_2-N_2 according to the mixed-control isothermal kinetic model, details of which were reported previously.²⁾ Because the thermodynamic properties of pseudorutile ($Fe_2Ti_3O_9$) is not available, the reaction heat ΔH° , equilibrium constant K and equilibrium concentration of oxygen c^* of reaction (1) were estimated as first approximation according to the following reaction:

and the corresponding thermodynamic properties were from Ref. 11).

The temperature dependence of all of these parameters were illustrated in Figs. 2 through 4.

3.3. Numerical Analysis

The differential equations were solved numerically by means of finite difference approximation. For simplicity, the variables in the above-mentioned dimensionless differential equations were expressed in their dimensional forms and the corresponding expressions for energy conservation, Eqs. (3) to (8), were listed in Eqs. (20).

The uniformly distributed n grids were generated in such a way that the pellet center was taken as the origin and that at the external surface as number n . Two-point forward difference approximation and three-point central approximation were used for time derivative and for spatial derivative, respectively. Because of its convergence, the fully implicit scheme was adopted in the following calculation.¹²⁾

(a) at pellet center:

$$\begin{aligned} b_c T_o + c_c T_1 &= f_c \\ b_c &= 1 + 6F_{or} \\ c_c &= -6F_{or} \\ f_c &= T_o^{(old)} \end{aligned} \quad \dots\dots\dots (20-a)$$

(b) within the unreacted core:

$$\begin{aligned} a_r T_{j-1} + b_r T_j + c_r T_{j+1} &= f_r \\ a_r &= -r_{j-1/2}^2 F_{or} \\ b_r &= r_j^2 + r_{j-1/2}^2 F_{or} + r_{j+1/2}^2 F_{or} \\ c_r &= -r_{j+1/2}^2 F_{or} \\ f_r &= r_j^2 T_j^{(old)} \\ (j &= 1, 2, 3, \dots, i-1) \end{aligned} \quad \dots\dots\dots (20-b)$$

(c) at the reacting interface:

$$\begin{aligned} a_i T_{i-1} + b_i T_i + c_i T_{i+1} &= f_i \\ a_i &= -r_{i-1/2}^2 k_{er} / \Delta r \\ b_i &= r_i^2 (\rho_{ar} c_{pr} + \rho_{ap} c_{pp}) \Delta r / (2 \Delta t) \\ &\quad + r_{i-1/2}^2 k_{er} / \Delta r + r_{i+1/2}^2 k_{ep} / \Delta r \\ c_i &= -r_{i+1/2}^2 k_{ep} / \Delta r \end{aligned} \quad \dots\dots\dots (20-c)$$

Fig. 2. Temperature dependence of the main kinetic parameters.
 $r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³·s⁻¹.

Fig. 3. Temperature dependence of the thermodynamic properties for the oxidation of ilmenite.

Fig. 4. Temperature dependence of heat transfer coefficients.
 $r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³·s⁻¹, $T_b = 1073$ K

$$f_i = [r_i^2 \rho_{ar} x_s (-\Delta H^0) / M_s] \Delta r / \Delta t \\ + [r_i^2 (\rho_{ar} c_{pr} + \rho_{ap} c_{pp}) \Delta r] / (2 \Delta t) T_i^{(old)}$$

(d) throughout product layer:

$$a_p T_{j-1} + b_p T_j + c_p T_{j+1} = f_p \\ a_p = -r_{j-1/2}^2 F_{op} \\ b_p = r_j^2 + r_{j-1/2}^2 F_{op} + r_{j+1/2}^2 F_{op} \\ c_p = -r_{j+1/2}^2 F_{op} \\ f_p = r_j^2 T_j^{(old)} \\ (j = i+1, i+2, \dots, n-1)$$

(e) at the external surface:

$$a_b T_{n-1} + b_b T_n = f_b \\ a_b = -r_{n-1/2}^2 F_{op} \\ b_b = r_n^2 + r_{n-1/2}^2 F_{op} + r_n^2 h_t \Delta r / k_{ep} F_{op} + r_n^2 / 2 \\ f_b = r_n^2 h_t \Delta r / k_{ep} F_{op} T_b + r_n^2 / 2 T_s^{(old)}$$

where, F_{or} and F_{op} are the grid Fourier number for both unreacted core and product shell, respectively.

$$F_{or} = \alpha_r \Delta t / (\Delta r)^2 \quad (21-a)$$

$$F_{op} = \alpha_p \Delta t / (\Delta r)^2 \quad (21-b)$$

The $(n+1)$ simultaneous linear equations expressed by Eqs. (20) were solved by means of TDMA (Tridiagonal matrix algorithm).¹²⁾ The reaction front shrank $\Delta r = r_o/n$ inwardly for each calculation step. When reaction front was at r_i , the corresponding time increment Δt , fractional conversion x , and temperature distribution within the pellet were determined according to Eqs. (2), (9) and (20), respectively. Because some of the coefficients of Eqs. (20) also depended on the unknown temperatures, they were determined by means of optimized SOR (Successive over-relaxation) iteration¹²⁾ within each calculation step. During calculation, the mass transfer coefficient (k_f), the effective diffusivity (D_e) and the reaction rate constant (k) were calculated with the following temperature values, $(T_b + T_s)/2$, $(T_s + T_i)/2$ and T_i , respectively.

$$T_j^{(new)} = T_j^{(old)} + \omega (T_j^{(new)} - T_j^{(old)}) \\ (j = 0, 1, 2, \dots, n) \quad (22)$$

The optimal value of ω was found to be near 1.95.

In the actual calculation, the value n was chosen as 200 and the final difference $|T^{(new)} - T^{(old)}|$ was less than 0.05 K. The above-mentioned calculation was repeated until the reaction finished and the solution completely described the temperature change with reaction time and spatial coordinates as well as the relationship of fractional conversion *versus* reaction time.

4. Discussion

4.1. Validity of the Unsteady Nonisothermal Kinetic Model

It is easy to understand that isothermal kinetic model can not successfully interpret the oxidation kinetics of the ilmenite pellet with pure oxygen because of the appreciable temperature rise.

Fig. 5. Comparison of the measured fractional conversion with the calculated ones.

$r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³·s⁻¹, $c_b = 11.36$ mol·m⁻³

Fig. 6. Comparison of the measured pellet surface temperature with those of calculation for the oxidation with pure oxygen.

$r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³·s⁻¹, $c_b = 11.36$ mol·m⁻³

Figure 5 compares the calculated fractional conversion with that of measurement, which shows satisfactory agreement except in the final stage. The reason for the slight deviation occurring in the later stage was mainly attributed to the estimation of the reaction heat and other parameters.

Figure 6 shows the comparison between calculated and measured surface temperature of the pellet. It was very difficult to get complete agreement between both of them, however, fairly good result was obtained.

The essential improvement of the unsteady non-isothermal kinetic model mentioned above is that it brings the heat accumulation term into the equations of energy conservation. The effect of this term is quantitatively evaluated as follows.

The rate of heat loss to the pellet surroundings and that of heat accumulation inside the pellet can be expressed by Eqs. (23) and (24), respectively.

$$v_l = 4\pi r_o^2 h_t (T_s - T_b) \quad (23)$$

$$v_a = 4\pi \left(\int_0^{r_i} r^2 \rho_{ar} c_{pr} \frac{\partial T}{\partial t} dr + \int_{r_i}^{r_o} r^2 \rho_{ap} c_{pp} \frac{\partial T}{\partial t} dr \right) \quad (24)$$

Fig. 7. Effect of heat accumulation on heat balance.
 $r_o = 6.38 \times 10^{-3} \text{ m}$, $Q = 1.67 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$, $c_b = 11.36 \text{ mol} \cdot \text{m}^{-3}$, $T_b = 1073 \text{ K}$

Fig. 8. Temperature distribution within the pellet at different reaction degrees.
 $r_o = 6.38 \times 10^{-3} \text{ m}$, $Q = 1.67 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$, $c_b = 11.36 \text{ mol} \cdot \text{m}^{-3}$, $T_b = 1073 \text{ K}$

R_i and R_a reflecting the relative importance of heat loss and heat accumulation in consuming the reaction heat are defined as follows.

$$R_i = v_i/q \quad \text{and} \quad R_a = v_a/q \quad \dots\dots\dots(25)$$

where q is the heat generation rate, $q = bv_g(-\Delta H^\circ)$. Figure 7 depicts the change of both R_i and R_a in the course of the oxidation of the ilmenite pellet with pure oxygen at 1073 K, and the heat generation rate q is also presented in the figure, which shows that the heat accumulation effect can not be neglected especially in the initial stage. Moreover, as reaction proceeded, the heat generation rate became so small that the whole pellet would be cooled down ($R_a < 0$) rather than heated up.

From what mentioned above, it is easy to understand that the unsteady nonisothermal kinetic model is more suitable for interpreting the kinetic behavior of the oxidation of natural ilmenite pellet with pure oxygen.

4.2. Temperature Distribution

Three representative temperature distributions shown in Fig. 8 correspond to the initial stage, middle stage and near the final stage in the course of oxidation, respectively. This figure shows that the temperature inside the unreacted core is almost uniform except in the initial

Fig. 9. Change of the temperature at external surface, reaction front and the pellet center with reaction time.
 $r_o = 6.38 \times 10^{-3} \text{ m}$, $Q = 1.67 \times 10^{-4} \text{ m}^3 \cdot \text{s}^{-1}$, $c_b = 11.36 \text{ mol} \cdot \text{m}^{-3}$, $T_b = 1073 \text{ K}$

stage, in contrast, relatively greater temperature gradient exists in the product shell. This implies that the heat conduction through the product layer plays an important role in heat transfer. Figure 9 illustrates the temperature change with reaction time at some special positions. Similar to Fig. 8, Fig. 9 also shows that there is a great temperature rise inside the pellet during the oxidation of the ilmenite pellet with pure oxygen, especially in the initial stage. Furthermore, the temperature distribution within the unreacted core is relatively uniform compared to that in the product layer.

4.3. Rate-controlling Step

The expressions for the resistance fraction of each step were derived as follows.¹³⁾

Resistance fraction for mass transfer:

$$R_f = 1/k_f/\Lambda \quad \dots\dots\dots(26)$$

Resistance fraction for intrapellet diffusion:

$$R_d = r_o/D_e(1-\eta_i)/\eta_i/\Lambda \quad \dots\dots\dots(27)$$

Resistance fraction for intrinsic chemical reaction:

$$R_c = 1/(k\eta_i^2)/\Lambda \quad \dots\dots\dots(28)$$

where Λ is the total resistance defined as $\Lambda = 1/k_f + r_o/D_e(1-\eta_i)/\eta_i + 1/(k\eta_i^2)$.

Figure 10 shows the resistance fraction of each step during the oxidation of the ilmenite pellet with pure oxygen. According to this figure, the overall oxidation rate was principally controlled by the intrapellet diffusion of oxygen.

Figure 10 also depicts the change of Biot number during oxidation, which shows that the Biot number is greater than its critical value 0.2⁷⁾ under the experimental condition. This indicates that during the oxidation, heat conduction through the product layer predominated the rate of heat transfer.⁷⁾

4.4. Effect of Oxygen Concentration

It is very difficult for us to completely remove the effect of reaction heat experimentally because energy transfer almost always accompanies with chemical reaction. What is more important is to estimate the deviation of the

Fig. 10.

Change of resistance fraction of each step and Biot number during oxidation of the ilmenite pellet with pure oxygen.
 — $T_b = 1073$ K, --- $T_b = 1123$ K, - - - $T_b = 1173$ K
 $r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³ · s⁻¹, $c_b = 11.36$ mol · m⁻³

Fig. 11. Effect of the bulk concentration of oxygen on the temperature at reaction interface.
 $r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³ · s⁻¹, $T_b = 1073$ K

Fig. 12. Relationship between the maximum temperature inside the pellet and the oxygen concentration in the bulk gaseous phase.
 $r_o = 6.38 \times 10^{-3}$ m, $Q = 1.67 \times 10^{-4}$ m³ · s⁻¹, $c_b = 11.36$ mol · m⁻³

measurements from their real value.

The effect of oxygen concentration on the temperature at the reaction interface is illustrated in Fig. 11 showing that the temperature at reaction front depends strongly on the bulk concentration of oxygen. Moreover, as shown in Fig. 12, when the bulk concentration of oxygen is lower than 10 mol%, $T_{\max}/T_b < 1.03$ as long as the bulk

temperature is between 1073 to 1173 K.

Recalculation of the apparent activation energies with the maximum temperature obtained above showed that the relative error defined by Eqs. (29) for calculating these parameters using the experimental data measured with 9.8mol%O₂-N₂ was less than 1.64% for the apparent activation energy of the intrinsic chemical reaction and smaller than 2.64% for that of intrapellet diffusion.

$$\delta_c = |E_c(T_{\max}) - E_c(T_b)| / E_c(T_b) \dots \dots \dots (29-a)$$

$$\delta_d = |E_d(T_{\max}) - E_d(T_b)| / E_d(T_b) \dots \dots \dots (29-b)$$

It is consequently reasonable to analyze the oxidation of the cement-bonded natural ilmenite pellet with 9.8mol%O₂-N₂ as an isothermal system.

5. Conclusions

(1) The unsteady nonisothermal kinetic model derived in this paper is suitable for interpreting the kinetics of the oxidation of cement-bonded natural ilmenite pellet. The accumulated heat inside the pellet is too great to be neglected in comparison with that lost to its surroundings especially in the initial stage.

(2) The overall oxidation rate was essentially controlled by the intrapellet diffusion of oxygen and the rate of heat transfer was predominated by the heat conduction through the product layer.

(3) When the bulk concentration of oxygen is less than 10 mol%, the oxidation can be reasonably analyzed as an isothermal reaction system. However, during the oxidation with pure oxygen, considerable temperature rise was found in the pellet which affected the oxidation rate.

Nomenclature

b : stoichiometric coefficient of solid reactant in reaction (1) (—)

B_i : Biot number, $B_i = 2r_o h_t / k_e$ (—)

c_b : bulk concentration (mol · m⁻³)

c_i : interface concentration (mol · m⁻³)

c_{pg} : specific heat capacity for gaseous species (J · mol⁻¹ · K⁻¹)

c_{pp}, c_{pr} : specific heat capacity for product layer and unreacted core, respectively (J · kg⁻¹ · K⁻¹)

c_s :	concentration of oxygen at pellet surface ($\text{mol} \cdot \text{m}^{-3}$)	y_i, y_j :	molar fraction of gaseous species (—)
c^* :	equilibrium concentration ($\text{mol} \cdot \text{m}^{-3}$)	α_i :	$\alpha_i = (\alpha_r + \alpha_p)/2$ ($\text{m}^2 \cdot \text{s}^{-1}$)
d_p :	particle diameter, (m)	α_p, α_r :	thermal diffusivity of product layer and unreacted core respectively ($\text{m}^2 \cdot \text{s}^{-1}$)
D :	molecular diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)	γ :	dimensionless heat generation rate (—)
D_e :	effective diffusivity ($\text{m}^2 \cdot \text{s}^{-1}$)	δ :	thickness of the stagnant gaseous film around pellet (m)
$(D_{\text{O}})_{\text{eff}}$:	effective diffusivity of oxygen through the product layer ($\text{m}^2 \cdot \text{s}^{-1}$)	ε :	porosity of pellet (—)
$(D_{\text{O-N}})_{\text{eff}}$:	effective diffusivity of $\text{O}_2\text{-N}_2$ through the product layer ($\text{m}^2 \cdot \text{s}^{-1}$)	ε_p :	porosity of the oxidized layer (—)
e :	emissivity for the oxidized ilmenite pellet (—)	η_i :	dimensionless position of reaction front (—)
E_c, E_d :	apparent activation energies for intrinsic chemical reaction and intrapellet diffusion ($\text{J} \cdot \text{mol}^{-1}$)	η_p, η_r :	dimensionless radial position within product layer and unreacted core (—)
h_c :	convective heat transfer coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$)	$\theta_i, \theta_p, \theta_r$:	dimensionless time (—)
h_r :	radiative heat transfer coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$)	κ :	$(r_o/(r_o + \delta))^2$ (—)
h_t :	total heat transfer coefficient ($\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$)	μ :	gas viscosity ($\text{Pa} \cdot \text{s}$)
ΔH^o :	reaction heat ($\text{J} \cdot \text{mol}^{-1}$)	ν :	kinematic viscosity ($\text{m}^2 \cdot \text{s}^{-1}$)
k :	rate constant ($\text{m} \cdot \text{s}^{-1}$)	ρ_a :	apparent density of pellet ($\text{kg} \cdot \text{m}^{-3}$)
k_e :	$k_e = (k_{ep} + k_{er})/2$ ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	ρ_g :	gas density ($\text{kg} \cdot \text{m}^{-3}$)
k_{ep}, k_{er} :	effective heat conductivity for product layer and unreacted core, respectively ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	ρ_s :	true density of pellet ($\text{kg} \cdot \text{m}^{-3}$)
k_f :	mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)	σ :	collision diameter (m)
k_g :	heat conductivity for gaseous species ($\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$)	σ_b :	Stefan-Boltzmann's constant ($\text{J} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{K}^{-4}$)
M :	molecular weight of gaseous species ($\text{kg} \cdot \text{mol}^{-1}$)	τ_p :	tortuosity factor of the oxidized layer (—)
M_s :	molecular weight of solid reactant ($\text{kg} \cdot \text{mol}^{-1}$)	Ψ_c, Ψ_s :	dimensionless temperature at pellet center and external surface (—)
p :	pressure (Pa)	Ψ_i, Ψ_p, Ψ_r :	dimensionless temperature at reaction front, within product layer and unreacted core (—)
q :	heat generation rate (W)	Ω_D, Ω_μ :	collision integral (—)
Q :	gas flow rate ($\text{m}^3 \cdot \text{s}^{-1}$)		
r_o :	pellet radius (m)		
r_i :	reaction front position (m)		
r_p, r_r :	radial position within product layer and unreacted core (m)		
R :	gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)		
R_f, R_d, R_c :	resistance fraction for mass transfer, intrapellet diffusion and intrinsic chemical reaction (—)		
R_a, R_t :	parameters defined in Eqs. (25)		
S_o :	pellet surface area (m^2)		
t :	time (s)		
t^* :	dimensionless reaction time (—)		
T_b :	bulk temperature (K)		
T_c :	temperature at pellet center (K)		
T_i :	reaction interface temperature (K)		
T_p, T_r :	temperature within product layer and unreacted core (K)		
T_s :	pellet surface temperature (K)		
T_{max} :	maximum temperature inside the pellet (K)		
U :	gas flow velocity ($\text{m} \cdot \text{s}^{-1}$)		
v_g :	reaction rate of gaseous species ($\text{mol} \cdot \text{s}^{-1}$)		
x :	fractional conversion (—)		
x_s :	mass ratio of the solid reactant in the pellet (—)		

REFERENCES

- 1) I. E. Gerey, D. G. Jones and A. F. Reid: *Trans. Inst. Min. Metall.*, **82** (1973), C151.
- 2) K. Sun, M. Ishii, R. Takahashi and J. Yagi: *ISIJ Int.*, **32** (1992), 489.
- 3) K. B. Bischoff: *Chem. Eng. Sci.*, **18** (1963), 711.
- 4) G. S. G. Beveridge and P. J. Goldie: *Chem. Eng. Sci.*, **23** (1968), 913.
- 5) D. Luss and N. R. Amundson: *AIChE J.*, **15** (1969), 194.
- 6) R. H. Spitzer, F. S. Manning and W. O. Philbrook: *Trans. Met. Soc. AIME*, **236** (1966), 726.
- 7) J. Szekeley, J. W. Evans and H. Y. Sohn: *Gas-Solid Reactions*, Academic Press, New York, (1976), 13, 47, 51.
- 8) R. B. Bird, W. E. Stewart and E. N. Lightfoot: *Transport Phenomena*, John Wiley & Sons, Inc., New York, (1960), 259, 24, 258.
- 9) C. R. Wilke: *J. Chem. Phys.*, **18** (1950), 517.
- 10) N. Wakao, S. Otani and J. M. Smith: *AIChE J.*, **11** (1965), 435.
- 11) O. Kubaschewski and C. B. Alcock: *Metallurgical Thermochemistry*, Pergamon Press Ltd., New York, (1979).
- 12) Y. Jaluria and K. E. Torrance: *Computational Heat Transfer*, Hemisphere Publishing Corporation, Washington, (1986), 41, 101.
- 13) A. Moriyama, J. Yagi and I. Muchi: *Trans. Iron Steel Inst. Jpn.*, **7** (1967), 271.

Appendix

At the reaction front, the following local energy conservation must be satisfied.

$$[\text{rate of heat accumulation}] = [\text{net heat entrance rate}] + [\text{heat generation rate}]$$

or written in mathematical expressions as Eq. (A-1).

$$4\pi r_i^2 \Delta r \rho_s c_p \frac{\partial T_i}{\partial t} = 4\pi k_e (r_i + \Delta r)^2 \frac{\partial T}{\partial r} \Big|_{r_i + \Delta r} - 4\pi k_e r_i^2 \frac{\partial T}{\partial r} \Big|_{r_i} + 4\pi (r_i + \theta \Delta r)^2 \Delta r \frac{\rho_s x_s}{M_s} (-\Delta H^o) \frac{dx}{dt},$$

$$(0 < \theta < 1) \dots\dots\dots (A-1)$$

where Δr is the position change of the reaction front, consequently, $4\pi(r_i + \theta \Delta r)^2 \Delta r (\rho_s x_s / M_s) (dx/dt)$ is the instantaneous reaction rate expressed in terms of the consumption of the solid reactant (v_s). According to the stoichiometry of the oxidation,

$$v_s/b = v_g^* \equiv 4\pi v_g \dots\dots\dots (A-2)$$

where v_g^* is the reaction rate expressed in terms of the consumption of gaseous reactant, O_2 . Substituting Eq.

(A-2) into Eq. (A-1) and dividing both sides of Eq. (A-1) with $4\pi \Delta r$ result in Eq. (A-3) when $\Delta r \rightarrow 0$.

$$r_i^2 \rho_s c_p \frac{\partial T_i}{\partial t} = \frac{\partial}{\partial r} \left(k_e r^2 \frac{\partial T}{\partial r} \right) \Big|_{r_i} + r_i^2 \frac{\rho_s x_s}{M_s} (-\Delta H^o) \frac{dx}{dt} \dots\dots\dots (A-3)$$

Equation (A-3) is the dimensional form of Eq. (3). Dividing both sides of Eq. (A-3) with $(k_e T_b)$ and rearranging it according to the dimensionless parameters given in Eq. (A-5) yield Eq. (A-4).

$$\eta_i^2 \frac{\partial \Psi_i}{\partial \theta_i} = \frac{\partial}{\partial \eta} \left(\eta^2 \frac{\partial \Psi}{\partial \eta} \right) \Big|_{\eta_i} + \frac{\partial \gamma}{\partial \eta} \Big|_{\eta_i} \dots\dots\dots (A-4)$$

$$\Psi_i = \frac{T_i}{T_b}, \quad \theta_i = \frac{\alpha t}{r_o^2}, \quad \gamma = \frac{b v_g (-\Delta H^o)}{T_b k_e r_o} \dots\dots\dots (A-5)$$