MATHEMATICAL ANALYSIS OF KINETICS OF SOLID-CONSUMING REACTION

TADASHI CHIDA AND TEIRIKI TADAKI
Department of Chemical Engineering,
Tohoku University, Sendai 980

Solid-consuming reactions were analyzed theoretically with a modified structural model in which a pellet consists of a large number of spherical, non-porous particles and the radius of the particle and that of the pellet decrease with time. This model was applied to carbon gasification with carbon dioxide and the leaching of hematite with hydrochloric acid in aqueous solution. The theoretical results are consistent with the experimental ones.

Introduction

The mechanisms of solid-consuming reactions, such as gasification of carbon with carbon dioxide and leaching of metal oxide with acid, are so complicated that a mathematical analysis is very difficult, because the effect of change in solid structure during the course of the reaction cannot be ignored. In recent years, Petersen7), Hashimoto and Silveston3), Yoshida and Kunii13), and Ramachandran and Smith9) have proposed pore models accounting for changes in pore geometry with reaction. Also, Ramachandran and Smith9) have proposed a particle pellet model in which a pellet is assumed to be an assembly of spherical non-porous particles (of uniform size at the beginning of a reaction), and the reaction occurs by diffusion of gaseous reactant into the pellet to the reactive surface of a particle. Owing to swelling or shrinking of particles, the particle radii and the void fraction change during the course of the reaction.

Using this model, Ramachandran and Smith9) accounted for the effects of changes of solid structure on the overall reaction rates. However, they assumed that the radius of the pellet does not change. This assumption is inconsistent with the fact that the particle radius changes during the course of the reaction.

The authors have proposed a modified structural model for mathematical analysis of the solid-consuming reaction of a slab-like solid21). In this model, the thickness of a solid changes with reaction. This paper describes the modified structural model for the case of a spherical pellet in which the radius of the pellet is assumed to change during the course of reaction. This model is compared with the experimental results of gasification of carbon with carbon dioxide and the leaching of hematite with hydrochloric acid in aqueous solution.

1. Mathematical Formulation of the Model

Assume that a spherical pellet of radius $R_0$ consists of fine dense particles of radius $r_0$ as shown in Fig. 1. A reaction occurs on the geometrical surface of the particles. Suppose the reaction is of the form

$A(gas\ or\ liquid) + S(solid) \rightarrow 2B(gas\ or\ liquid)$

and the disappearance rate of component A is expressed as

$$(-r_A) = kC_A$$

where $k$ is the reaction rate constant and $C_A$ is the concentration of A.

Also, assume the following restrictions.

(1) The reaction occurs at pseudo-steady state.
(2) The particle radius $r_0$ is sufficiently smaller than the pellet radius $R_0$.
(3) The net flux which results from the change in moles due to reaction is negligible.
(4) The centers of the particles are fixed.
(5) The temperature gradient within the pellet is negligible.
(6) The effective diffusivity $D_{eff}$ is estimated by using the following equation11):

$$D_{eff} = \frac{D_{eff}}{1 + \frac{r_0}{R_0}}$$

Fig. 1 Schematic representation of pellet
\[ D_{\text{m}} = \varepsilon^2 D_{\text{A}} \quad (2) \]

where \( \varepsilon \) is the void fraction and \( D_{\text{A}} \) is the molecular diffusivity in a pore.

The mass conservation expression for \( A \) within the pellet and the boundary conditions are

\[ \frac{d}{dX} \left( D_{\text{A}} \varepsilon^2 \frac{dY}{dX} \right) - P_s X^2 Z^2 Y = 0 \quad (3) \]

\[ \frac{dY}{dX} = 0 \quad \text{at} \quad X = 0 \quad (4) \]

\[ \frac{dY}{dX} = -\frac{N_f K_f}{D_{\text{m}}^*} (Y - 1) \quad \text{at} \quad X = X^* \quad (5) \]

where

\[ X = R/R_0, \quad X^* = R^*/R_0, \quad Y = C_A/C_{A,0}, \quad Z = r/r_0, \]

\[ D_{\text{m}} = D_{\text{A}}/D_{\text{A},0} = (\varepsilon/\varepsilon_0)^2, \quad P_s = N_s P, \quad N_s = k_r D_{\text{A}}/D_{\text{A},0} \]

\[ P = 4\pi R^2 r_0 n_0 \rho_{\text{A}} \]

\[ N_f = k_f^* r_0 D_{\text{A},0} \quad \text{and} \quad K_f = k_f/k_f^* \]

The gas-film mass transfer coefficient \( k_f \) must be changed with pellet radius \( R^* \), but these values can be evaluated using the Ranz and Marshall equation

\[ Sh = 2 + 0.6 (Re)^{1/3} (Sc)^{1/3} \quad (6) \]

where \( Sh = k_f (2R^2)/D_{\text{A},0}, \quad Re = (2R^2)\mu\rho/\mu \quad \text{and} \quad Sc = \rho_D/\rho_{\text{A}}. \]

That is,

\[ K_f = (Sh/(Sh_0))/X^* \quad (7) \]

where \( Sh_0 \) is \( Sh \) at \( R^* = R_0 \).

The void fraction \( \varepsilon \) can be estimated as

\[ \varepsilon = 1 - (1 - \varepsilon_0)Z^2 \quad (8) \]

And the changing rate of the dimensionless radius \( Z \) is of the form

\[ \frac{dZ}{dT} = -N_s Y \quad (9) \]

where \( T \) is the dimensionless time, \( sD_r c_{A,0}/\rho f \varepsilon \). The position of the pellet surface \((X = X^*)\) is given as the position where the particle radius equals zero, that is,

\[ X^* = X|_{\varepsilon = 0} \quad (10) \]

The initial conditions are

\[ Z = 1 \quad \text{and} \quad X^* = 1 \quad \text{at} \quad T = 0 \quad (11) \]

These Eqs. (3)–(11) can be solved by the numerical method as follows. At \( T = 0 \), the solution of Eqs. (3)–(5) is

\[ Y = \frac{N_f}{X} \sinh \left( \sqrt{P_r} X \right) \quad (12) \]

At \( T > 0 \), if \( X^* \) equals unity, the finite difference forms of Eq. (3) are obtained as

\[ C_1 Y_{i-1} + A_1 Y_i + B_1 Y_{i+1} = 0 \quad (i = 2, \ldots, I) \quad (13) \]

where

\[ A_1 = -2 - P_s (D_{\text{A}}^2) \]

\[ B_1 = 1 + (D_{\text{e},i-1} - D_{\text{e},i-1})/4D_{\text{e}}, (DX)/X_i \]

\[ C_1 = 1 - (D_{\text{e},i-1} - D_{\text{e},i-1})/4D_{\text{e}} - (DX)/X_i, (DX)/X_i = 1/I \]

And using the boundary conditions, Eqs. (4) and (5), the following equations are obtained:

\[ A_1 Y_i + B_1 Y_{i+1} = D_{\text{e},i} \quad (14) \]

\[ C_1 Y_{i-1} + A_1 Y_i + B_1 Y_{i+1} = D_{\text{e},i+1} \quad (15) \]

where

\[ A_1 = 1 + P_s (D_{\text{A}}^2)Z^2 |D_{\text{e},i} \]

\[ B_1 = -1, \quad A_1 = 1 + P_s (D_{\text{A}}^2)Z^2 |D_{\text{e},i+1}| \]

\[ \times \left( 1 + (D_{\text{e},i+1} - D_{\text{e},i})/2D_{\text{e},i+1} + (DX)/X_i \right) \]

\[ C_1 = -1 \quad \text{and} \quad D_{\text{e},i+1} = (DX)N_f K_f \]

\[ \times \left( 1 + (D_{\text{e},i+1} - D_{\text{e},i})/2D_{\text{e},i+1} + (DX)/X_i \right) \]

From Eqs. (13)–(15), discrete values of \( Y \) can be calculated by the Thomas method. Then the values of the dimensionless particle radius \( Z \) can be calculated as

\[ Z_i^* = Z_i - N_s Y_i (\Delta T) \quad (16) \]

where \( Z_i^* \) is the new value of \( Z_i \), after the time \( \Delta T \).

\( Z_i \) will be negative sooner or later. The negative value of \( Z_i \) means that the particles disappear at the point \( X = X_i \). The position of the pellet surface \((X = X^*)\) can be calculated as follows. If \( Z_{i+1} < 0 \) and \( Z_i \geq 0 \), \( X^* \) is between \( X_i \) and \( X_{i+1} \). Then, \( X^* \) is obtained as the position where \( Z = 0 \), using the value of \( Z \) at the positions \( X_{i+1} \), \( X_i \), \( X_{i+1} \), and assuming \( Z \) as a quadratic equation of position \( X \).

When \( X^* < 1 \), Eq. (15) cannot be used. Equation (5) must be applied at the position \( X^* \). First, set \( I_t \) as \( X_{t+1}^* \). Then, \( X^* < 1 \) is obtained as the position where \( Z = 0 \), using the values of \( Z \) at the positions \( X_{i+1} \), \( X_i \), \( X_{i+1} \), and assuming \( Z \) as a quadratic equation of position \( X \).

Equation (17) and the finite difference form at the point \( i = I_t \) give the following equation.

\[ C_{i+1} Y_{i+1} + A_1 Y_i = D_{i+1} \quad (18) \]

where

\[ A_i = -2 - P_s (D_{\text{A}}^2)Z^2 |D_{\text{e},i} \]

\[ B_i = 1 + (D_{\text{e},i-1} - D_{\text{e},i-1})/2D_{\text{e},i+1} + (DX)/X_i \]

\[ C_i = 1 - (D_{\text{e},i-1} - D_{\text{e},i-1})/2D_{\text{e},i+1} + (DX)/X_i \]

Equations (13), (14), and (18) give the values of \( Y_i \) when \( X^* < 1 \).
Fig. 2 Comparison of theoretical results with experimental ones for carbon gasification with carbon dioxide; \( \varepsilon_0 = 0.29, \ P = 1.29 \times 10^7, \ N_f \rightarrow \infty \) and \( K_f = 1 \)

The particle radius \( r_0 \) in the model was evaluated based on the fact that the sum of the initial geometrical surface area of a particle equals the initial internal surface area of the sample, that is, \( r_0 = 1.1 \times 10^{-3} \) cm (which nearly equals \( (L/2) \), where \( L \) is the length of each side of the volume element at the external surface reported by Yoshida and Kunii). The other physical constants except the reaction rate constant \( k \) were determined from the experimental conditions. So, \( \varepsilon_0 = 0.29, \ P = 1.29 \times 10^7, \ N_f \rightarrow \infty, \ K_f = 1 \) and only \( N_k \) was unknown.

In Fig. 2, the solid lines are the theoretical results, which are approximately consistent with the experimental ones shown by the dotted lines. Both the solid and dotted lines are of sigmoid type, though this tendency in the theoretical results (i.e., the solid lines) is smaller than in the experimental ones.

From Fig. 2, the most fittable values of \( N_k \) were obtained at each experimental temperature. Then the reaction rate constants calculated from the values of \( N_k \) are shown in Fig. 3. The values of \( k \) are almost one order smaller than those reported by Yoshida and Kunii, and approach the data for high-purity graphite. This difference may be due to the difference of reaction surface. That is, in the present model the particle surface is the reaction one and so the surface area per unit volume (the specific reaction area) is uniform in the pellet, but in the rectangular pore model used by Yoshida and Kunii the specific reaction area near the pellet surface is smaller than that near the center of the pellet. Therefore, at the pellet surface the reaction area of the pore model is smaller than that of the present model.

3. Application to Leaching of Hematite with Hydrochloric Acid

Another typical example of a solid-consuming reaction is leaching of hematite with hydrochloric acid in aqueous solution as shown the following overall reaction

\[
\text{HCl} + \frac{1}{2} \text{Fe}_2\text{O}_3 \rightarrow \frac{3}{2} \text{FeCl}_3 + \frac{1}{2} \text{H}_2\text{O}
\]

Many investigators have observed "accelerated" and "non-accelerated" types of leaching curve. This difference of types has been explained on the basis of "autocatalysis" or "mechanical decay of solid". Also, Warren and Roach suggested that the grain-to-solid sample size ratio of the oxide being leached is concluded to determine which type of leaching is obtained.

The dotted and dot-dash lines in Fig. 4 are experi...
mental data for the leaching of synthetic hematite with hydrochloric acid. It can be seen from this figure that the curve is a sigmoid type or an accelerated type in the case where the grain-to-solid sample size ratio ($r_0/R_0$) is about 0.023, but not in the case where $r_0/R_0=0.32$.

This difference of leaching curve type can be explained theoretically by the present model. Suppose the reaction of leaching occurs under the assumptions of the model mentioned above*. The values of the physical constants necessary for calculation were estimated from the experimental conditions as follows. $\rho_a=5.1 \text{ g/cm}^3$, $D_a=1.42 \times 10^{-4} \text{ cm}^2/\text{sec}$, $C_{AS}=2.4 \text{ M}$, $r_0=0.0025 \text{ cm}$, $R_0=0.0078$ and $0.11 \text{ cm}$. Only the void fraction $\varepsilon_0$ was unknown (it was not given in the literature). The solid samples were polycrystallines which consist of grains. The grain corresponds to the particle in the present model. Therefore, the interparticle void fraction must be small. Let us set $\varepsilon_0$ equal to 0.005. Then the theoretical curves shown in Fig. 4 were obtained.

It can be seen from Fig. 4 that if the value of $N_k$ equals $6.5 \times 10^{-6}$ the theoretical results are consistent with the experimental ones. Figures 5 and 6 show the changes of void fraction with time. From these figures, it can be seen that the difference in leaching curves is due to the difference in void fraction distributions. That is, in the case where $r_0/R_0=0.023$ (Fig. 5), the void fraction at the sample surface increases with time, and the reaction rate inside the solid sample becomes faster with time. On the other hand, in the case where $r_0/R_0=0.32$ (Fig. 6) the distribution of $\varepsilon$ is so flat that the reaction rate is little accelerated.

**Conclusion**

A modified structural model for solid-consuming reaction for the case of a spherical solid was proposed. This model was applied to carbon gasification with carbon dioxide and the leaching of hematite with hydrochloric acid.

The theoretical results were almost consistent with the experimental ones. Also, the difference in accelerated and non-accelerated leaching curves was explained by the present model.

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b$</td>
<td>stoichiometric factor</td>
<td>[-]</td>
</tr>
<tr>
<td>$C_A$</td>
<td>concentration of gas A</td>
<td>[mol/cm$^3$]</td>
</tr>
<tr>
<td>$C_{AS}$</td>
<td>bulk concentration</td>
<td>[mol/cm$^3$]</td>
</tr>
<tr>
<td>$D_a$</td>
<td>molecular diffusivity in a pore</td>
<td>[cm$^2$/sec]</td>
</tr>
<tr>
<td>$D_{AS}$</td>
<td>molecular diffusivity</td>
<td>[cm$^2$/sec]</td>
</tr>
<tr>
<td>$D_{eAS}$</td>
<td>effective diffusivity</td>
<td>[cm$^2$/sec]</td>
</tr>
<tr>
<td>$D_{einf}$</td>
<td>initial effective diffusivity</td>
<td>[cm$^2$/sec]</td>
</tr>
<tr>
<td>$D_e$</td>
<td>dimensionless effective diffusivity</td>
<td>[-]</td>
</tr>
<tr>
<td>$r_0$</td>
<td>initial pellet radius</td>
<td>[cm]</td>
</tr>
<tr>
<td>$R_0$</td>
<td>initial pellet radius</td>
<td>[cm]</td>
</tr>
<tr>
<td>$N_k$</td>
<td>dimensionless parameter</td>
<td>[-]</td>
</tr>
<tr>
<td>$k_f$</td>
<td>reaction rate constant</td>
<td>[cm/sec]</td>
</tr>
<tr>
<td>$k_f^o$</td>
<td>gas-film mass transfer coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>$k_f^a$</td>
<td>at $R^*=R_0$</td>
<td>[cm/sec]</td>
</tr>
<tr>
<td>$N_{AS}$</td>
<td>dimensionless parameter</td>
<td>[-]</td>
</tr>
<tr>
<td>$N_{AS}$</td>
<td>dimensionless parameter</td>
<td>[-]</td>
</tr>
<tr>
<td>$n_0$</td>
<td>number density of particle</td>
<td>[1/cm$^3$]</td>
</tr>
<tr>
<td>$P$</td>
<td>dimensionless parameter</td>
<td>[-]</td>
</tr>
<tr>
<td>$P_e$</td>
<td>dimensionless parameter</td>
<td>[cm]</td>
</tr>
<tr>
<td>$R$</td>
<td>radial coordinate</td>
<td>[cm]</td>
</tr>
<tr>
<td>$F$</td>
<td>overall fractional conversion</td>
<td>[-]</td>
</tr>
<tr>
<td>$f$</td>
<td>fractional conversion</td>
<td>[-]</td>
</tr>
</tbody>
</table>

* Pseudo-steady state approximation may be valid in dilute solution cases.
OPTIMUM DESIGN FOR SOLIDS CIRCULATION SYSTEM WITH SHRINKING CORE KINETICS IN BOTH REACTOR AND REGENERATOR

SHOICHI KIMURA, TSUTAO OTAKE
AND OCTAVE LEVENSEPIEL
Department of Chemical Engineering,
Osaka University, Toyonaka 560

The optimum volume ratio of reactor and regenerator which minimizes the total volume of the two is obtained for solids circulation systems where shrinking core kinetics hold for both gas-solid reaction and regeneration. For the general case the optimum volume ratio for a fixed flow rate of solids is represented graphically in terms of reaction and regeneration conditions. For a special case an approximate analytical solution for the minimization is obtained. The procedure to determine the optimum required volume for the reactor and that for the regenerator is also dealt with.

The effect of reaction and regeneration conditions and of solids flow rate on the optimum volumes is discussed.

Introduction

An earlier paper1) developed the performance equations for a system where solids are circulated between reactor and regenerator. In the reactor the solid combined with and removed a component from the gas stream; in the regenerator the captured component was released and the solid was restored to its initial state. The reactor and the regenerator were taken as fluidized beds (mixed flow of solids) and gas-solid reaction and regeneration were both assumed to proceed inward from the surface of the particle (shrinking core model).

The removal of H2S from a coal gasification stream by circulating iron oxide-iron sulfide particles is an example of such a system.

This paper finds the optimum volume ratio of reactor

---

Received October 5, 1978. Correspondence concerning this article should be addressed to S. Kimura. O. Levenspiel is at Dept. of Chem. Eng., Oregon State Univ., Corvallis, Oregon 97331 U.S.A.

---

5) "Kagaku-Benran (Kiso-Hen)", Maruzen, Tokyo (1975).