Reduction Kinetics of Swelling Wustite Particles

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Because metallic iron is considerably denser than wustite, wustite particles might be expected to shrink during reduction; however, considerable swelling, perhaps as much as 33% increase in diameter, is observed (*1, 2*). The present single-particle model which accounts for particle shrinkage or swelling during reduction assumes the following:

1. Reactant transport inwards, surface reaction, and product transport outwards all operate in series.
2. Surface reaction mechanism is first order and reversible.
3. Void fraction of the product iron layer is constant.

Oxygen removal is represented by

$$CO + Fe_xO = CO_2 + x\ Fe$$

Therefore, stoichiometry requires

$$\dot{n}_{CO} = \dot{n}_O = -\dot{n}_{CO_2} \tag{1}$$

Spherical symmetry is assumed because there is a sharp interface between iron and wustite at a radius x_i such that there is no oxygen for $x > x_i$ and no metallic iron for $x < x_i$. The fraction of reduction F is related to the interface radius by

$$F = 1 - \left(\frac{x_i}{x_o}\right)^3$$

Equations describing external mass transfer, diffusion in the porous iron layer, and reaction are developed very briefly because further details are available (*13*). Then, the relation between the unreacted core radius x_o and the instantaneous pellet radius x_s is derived and an excellent approximation made, thus permitting analytical solution of the resulting integral. Finally, this model is compared to the constant diameter one.

MODEL DEVELOPMENT

Transport and kinetic fluxes in the external boundary layer, the reduced shell, and at the unreduced core surface are now described individually and then combined.

External Resistance

Transport of carbon monoxide from the bulk gas to the particle outer surface may be written as

$$\dot{n}_{CO} = -\left(\frac{k^m{}_{CO}}{RT}\,4\pi x_s^2\right)(p^b{}_{CO} - p^s{}_{CO}) = \dot{n}_O \tag{2}$$

The opposing carbon dioxide transport may be expressed as

$$\dot{n}_{CO_2} = \left(\frac{k^m{}_{CO_2}}{RT}\,4\pi x_s^2\right)(p^s{}_{CO_2} - p^b{}_{CO_2}) = -\dot{n}_O \tag{3}$$

The external mass transfer coefficient is given by (*4*)

$$\frac{k_j{}^m}{\mathcal{D}}\,2\,x_s = N_{Sh} = 2.0 + 0.60\,(N_{Re})^{1/2}(N_{Sc})^{1/3} \tag{4}$$

In most cases, the Sherwood or mass transfer Nusselt number is between 3 and 5.

Substituting for $k_j{}^m$ in Equations (2) and (3) and dividing Equation (3) by K_e we get

$$-\dot{n}_O\left\{\frac{RT}{2\pi\,\mathcal{D}\,x_s\,[2.0 + 0.6\,(N_{Re})^{1/2}(N_{Sc})^{1/3}]}\right\} = p^b{}_{CO} - p^s{}_{CO} \tag{5}$$

$$-\dot{n}_O\left\{\frac{RT}{2\pi\,\mathcal{D}\,x_s\,K_e\,[2.0 + 0.6\,(N_{Re})^{1/2}(N_{Sc})^{1/3}]}\right\} = \frac{p^b{}_{CO_2} - p^s{}_{CO_2}}{K_e} \tag{6}$$

Shell Layer Diffusion Resistance

The standard quasi steady state approximation is assumed valid for either expanding or contracting pellets. That is, $\dot{n}_i$ is not of function of x for any $x_i \leqq x \leqq x_s$. Therefore

$$\dot{n}_{CO} = -(4\pi x^2)\left(\frac{\mathcal{D}^{eff}_{CO}}{RT}\right)\frac{dp_{CO}}{dx} \tag{7}$$

and

$$\dot{n}_{CO_2} = -\left(\frac{4\pi x^2\,\mathcal{D}^{eff}_{CO_2}}{RT}\right)\frac{dp_{CO_2}}{dx} \tag{8}$$

These can be integrated between x_s and x_i and p^i and p^s to give

$$\dot{n}_O\left(\frac{RT}{\mathcal{D}^{eff}_{CO}\,4\pi}\right)\left(\frac{x_s - x_i}{x_s\,x_i}\right) = p^s{}_{CO} - p^i{}_{CO} \tag{9}$$

and

$$\dot{n}_O\left(\frac{RT}{\mathcal{D}^{eff}_{CO}\,4\pi}\right)\left(\frac{x_s - x_i}{x_i\,x_s}\right)\left(\frac{1}{K_e}\right) = \frac{p^i{}_{CO_2} - p^s{}_{CO_2}}{K_e} \tag{10}$$

Reaction Resistance

The reduction of wustite with carbon monoxide to produce iron and carbon dioxide is assumed to be first order and reversible; therefore

$$-\dot{n}_O\left(\frac{RT}{k_r 4\pi x_i^2}\right) = p^i{}_{CO} - \frac{p^i{}_{CO_2}}{K_e} \tag{11}$$

If Equations (5), (6), (9), (10), and (11) are added, and $\dot{n}_O$ is replaced by $c_O 4\pi x_i^2\,\dfrac{dx_i}{dt}$, then

$$\frac{dx_i}{dt} = \left(\frac{1}{RT\,c_O}\right)\left(p^b{}_{CO} - \frac{p^b{}_{CO_2}}{K_e}\right)\left[\frac{-1}{\dfrac{x_i^2}{x_s\alpha} + \dfrac{x_i\,(x_s - x_i)}{x_s\beta} + \dfrac{1}{k_r}}\right] \tag{12}$$

$$\alpha = \frac{0.5\,\mathcal{D}\,K_e\,[2.0 + 0.6\,N_{Re}{}^{1/2}\,(N_{Sc})^{1/3}]_{CO}\,[2.0 + 0.6\,N_{Re}{}^{1/2}\,N_{Sc}{}^{1/2}]_{CO_2}}{[2.0 + 0.6\,N_{Re}{}^{1/2}\,N_{Sc}{}^{1/3}]_{CO_2}\,K_e + [2.0 + 0.6\,N_{Re}{}^{1/2}\,N_{Sc}{}^{1/3}]_{CO}} \tag{13}$$

$$\beta = \frac{K_e\, \mathcal{D}^{\mathrm{eff}}_{\mathrm{CO}} \quad \mathcal{D}^{\mathrm{eff}}_{\mathrm{CO_2}}}{K_e\, \mathcal{D}^{\mathrm{eff}}_{\mathrm{CO_2}} + \mathcal{D}^{\mathrm{eff}}_{\mathrm{CO}}} \tag{14}$$

After considerable thought, the change in x_s with time was related to the unreacted core radius x_i. The problem of swelling is quite complex, and it is not possible to describe it exactly. As a good approximation, the void fraction of the reduced iron layer is assumed constant for any $x > x_i$ and any time > 0. Thus
mass Fe in shell = initial mass Fe as wustite
— mass Fe in core as wustite

$$\frac{4}{3}\pi(x_s^3 - x_i^3)\,\rho_{\mathrm{Fe}}\,(1 - V_{\mathrm{Fe}})$$

$$= \frac{4}{3}\pi\, x_o^3\, \rho_w f\,(1 - V_w) - \frac{4}{3}\pi\, x_i^3\, \rho_w f\,(1 - V_w) \tag{15}$$

Simplifying and solving for x_s we get

$$x_s = [\gamma\ x_o^3 + (1 - \gamma)\ x_i^3]^{1/3} \tag{16}$$

where

$$\gamma = \frac{\rho_w\,(1 - V_w)\,f}{\rho_{\mathrm{Fe}}\,(1 - V_{\mathrm{Fe}})} \tag{17}$$

Note that $\gamma > 1$ refers to particle expansion, while $\gamma < 1$ indicates contraction.

If Equation (16) for x_s is substituted into Equation (12), the result is so complex that integration is most unlikely. Alternatively, x_s may be approximated by a Taylor series expansion about $x_i = 0$, and the result including fifth derivatives is

$$\frac{x_s}{x_o} = \gamma^{1/3} + \left(\frac{x_i}{x_o}\right)^3 \left(\frac{\gamma^{-2/3} - \gamma^{1/3}}{3}\right) \tag{18}$$

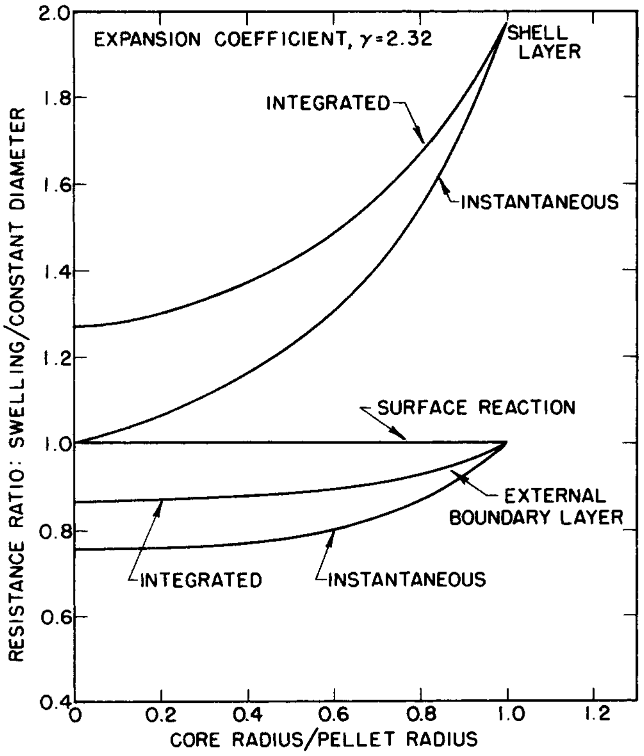

Fig. 1. Comparison of resistances for swelling and for constant sized pellets.

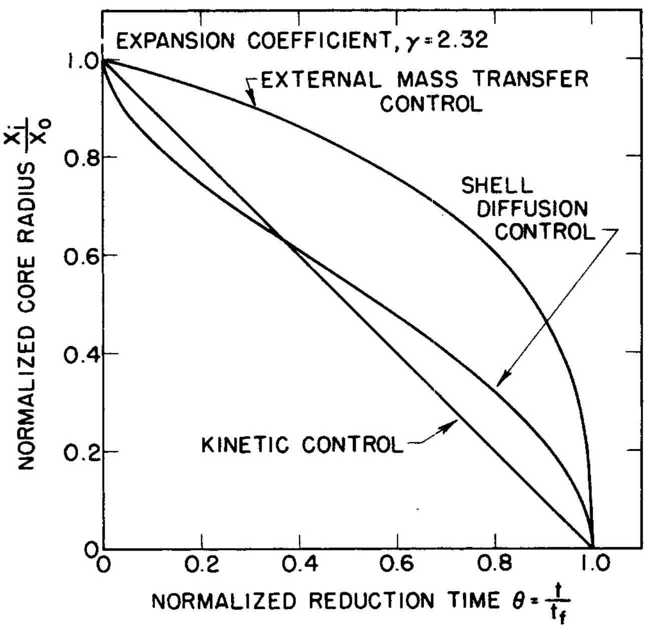

Fig. 2. Reduction rate predictions for single-step models for a sphere that swells during reaction.

This approximation is correct at $x_i = 0$ but about 5% too large at $x_i = x_o$ for a typical γ of 2. But this error occurs at zero time which implies a 5% ash layer at the start of reduction. Clearly this is not satisfactory. However, the expansion would be correct at both end points if the coefficient was changed to $1 - \gamma^{1/3}$. This gives

$$\frac{x_s}{x_o} = \gamma^{1/3} + (1 - \gamma^{1/3}) \left(\frac{x_i}{x_o}\right)^3 \tag{19}$$

The approximation is also improved in the region between the end points. The maximum error is now under 1.5% for $\gamma = 2$, and therefore Equation (19) is used to approximate Equation (16) for $0.5 \leqq \gamma \leqq 2.5$.

Substitution of x_s from Equation (19) into Equation (12) yields:

$$\int_{x_o}^{x_i} \left[\frac{x_i^2}{\alpha\left(x_o\,\gamma^{1/3} + \left(\frac{1-\gamma^{1/3}}{x_o^2}\right) x_i^3 \right)} + \frac{x_i\left\{ x_o\,\gamma^{1/3} + \left(\frac{1-\gamma^{1/3}}{x_o^2}\right) x_i^3 - x_i \right\}}{\beta\left\{ x_o\,\gamma^{1/3} + \left(\frac{1-\gamma^{1/3}}{x_o^2}\right) x_i^3 \right\}} + \frac{1}{k_r} \right] dx_i \tag{20}$$

$$= \int \left(\frac{-1}{RT\,c_{\mathrm{O}}}\right)\left(p^b{}_{\mathrm{CO}} - \frac{p^b{}_{\mathrm{CO_2}}}{K_e}\right) dt$$

But α changes only 5% over the range of x_i; therefore, it is considered a constant and its average value used.

The function can be integrated by rearranging the first two terms on the left-hand side and by substituting the following standard forms:

$$\int \frac{x^2dx}{a + bx^3} = \frac{1}{3b} \ln (a + bx^3)$$

$$\int \frac{xdx}{a + bx^3} = \frac{-1}{3b\epsilon} \left\{ \frac{1}{2} \ln \frac{(x + \epsilon)^2}{x^2 - \epsilon x + \epsilon^2} - \sqrt{3}\ \tan^{-1} \frac{2x - \epsilon}{\epsilon\sqrt{3}} \right\}$$

TABLE 1. INSTANTANEOUS RESISTANCES, CONTROLLING RESISTANCE RATIO R, CHANGING DIAMETER CASE/CONSTANT DIAMETER CASE

	Reduction regions		
Controlling resistance	Limit $\frac{x_i}{x_o} \to 0$	$0 < \frac{x_i}{x_o} < 1$	Limit $\frac{x_i}{x_o} \to 1$
1) External mass transfer	$R = \gamma^{-1/3}$	$R = \dfrac{1}{\gamma^{1/3} + (1-\gamma^{1/3})\left(\dfrac{x_i}{x_o}\right)^3}$	$R = 1$
2) Shell diff. resistance	$R = 1$	$R = \dfrac{\left\{\gamma^{1/3} + (1-\gamma^{1/3})\left(\dfrac{x_i}{x_o}\right)^3\right\} - \dfrac{x_i}{x_o}}{\left[1 - \dfrac{x_i}{x_o}\right]\left[\gamma^{1/3} + (1-\gamma^{1/3})\left(\dfrac{x_i}{x_o}\right)^3\right]}$	$R = 3\gamma^{1/3} - 2$
3) Kinetic	$R = 1$	$R = 1$	$R = 1$

where $\epsilon = (a/b)^{1/3}$

$$\int \frac{x^4dx}{a+bx^3} = \frac{x^2}{2b} - \frac{a}{b}\int \frac{xdx}{a+bx^3}$$

The final result is

$$\frac{x_o}{3\,\overline{\alpha}\,(1-\gamma^{1/3})} \ln\left\{\gamma^{1/3} + (1-\gamma^{1/3})\left(\frac{x_i}{x_o}\right)^3\right\}$$

$$+ \frac{x_o}{3\,\overline{\beta}\,(1-\gamma^{1/3})}\left[\frac{3\,(1-\gamma^{1/3})}{2}\left(\frac{x_i}{x_o}\right)^2 - 1\right.$$

$$\left. - \ln\left\{\gamma^{1/3} + (1-\gamma^{1/3})\left(\frac{x_i}{x_o}\right)^3\right\}\right]$$

$$+ \frac{x_i - x_o}{x_o\,k_r} = \left(\frac{-1}{x_o\,RTc_O}\right)\left(p^b{}_{CO} - \frac{p^b{}_{CO_2}}{K_e}\right)t \quad (21)$$

DISCUSSION OF MODEL

The present model as described by Equation (21) may now be compared with Spitzer's results (3) which are now given in similar form:

$$\frac{1}{3\alpha^*}\left\{1 - \left(\frac{x_i}{x_o}\right)^3\right\} + \frac{x_o}{6\beta}\left[1 - 3\left(\frac{x_i}{x_o}\right)^2 + 2\left(\frac{x_i}{x_o}\right)^3\right]$$

$$+ \frac{1}{k_r}\left(1 - \frac{x_i}{x_o}\right) = \frac{t}{RTx_oc_O}\left(p^b{}_{CO} - \frac{p^b{}_{CO_2}}{K_e}\right) \quad (22)$$

The $\overline{\alpha}$ and α^* parameters are related by $\overline{\alpha} = x_o\alpha^*$. All other symbols have the same meaning in both equations. If this substitution is made, and the limit $\gamma \to 1$ is taken, Equation (21) reduces to Equation (22). In both equations, the first left-hand side term is the integrated external mass transfer resistance, the second is ash diffusion resistance, and the last is the kinetic resistance. Note that x_i is an implicit function of t in Equation (21), and there does not appear to be any way to get an explicit function of t.

If a single resistance is controlling, the two models may be compared by the ratio of the resistances. Tables 1 and 2 and Figure 1 give the results for the regions $x_i/x_o = 0$, $0 < x_i/x_o < 1$, $x_i/x_o = 1$ for the three resistances.

Note that both instantaneous and integrated ratios are given for each of the three cases.

For the same operating conditions, same α, β, k_r values and $\gamma = 2$, this model predicts times for complete reduction about 15% greater than those predicted by constant-diameter models. The shape of the $1 - (1 - F)^{1/3}$ vs. θ plot is also changed, with the shell layer resistance becoming important earlier, as is shown in Figure 2.

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NOTATION

c_O = concentration of reducible oxygen in oxide, g.-atoms O/cc.

TABLE 2. INTEGRATED RESISTANCES, CONTROLLING RESISTANCE RATIO R, CHANGING DIAMETER CASE/CONSTANT DIAMETER CASE

	Reduction regions		
Controlling resistance	Limit $\frac{x_i}{x_o} \to 0$	$0 < \frac{x_i}{x_o} \leq 1$	Limit $\frac{x_i}{x_o} \to 1$
1) Ext. mass transfer	$R = \dfrac{-\ln\gamma^{1/3}}{1-\gamma^{1/3}}$	$R = \dfrac{-\ln\left\{\gamma^{1/3} + (1-\gamma^{1/3})\left(\dfrac{x_i}{x_o}\right)^3\right\}}{(1-\gamma^{/13})\left\{1 - \left(\dfrac{x_i}{x_o}\right)^3\right\}}$	$R = 1$
2) Shell diff. resistance	$R = 3 + \dfrac{2\ln\gamma^{1/3}}{(1-\gamma^{1/3})}$	$R = \dfrac{3\left\{1 - \left(\dfrac{x_i}{x_o}\right)^2\right\} + \dfrac{2}{(1-\gamma^{1/3})}\ln\left\{\gamma^{1/3} + (1-\gamma^{1/3})\left(\dfrac{x_i}{x_o}\right)^3\right\}}{1 - 3\left(\dfrac{x_i}{x_o}\right)^2 + 2\left(\dfrac{x_i}{x_o}\right)^3}$	$R = 3\gamma^{1/3} - 2$
3) Kinetic	$R = 1$	$R = 1$	$R = 1$

D = gas diffusivity, sq.cm./sec.
$\mathfrak{D}_j^{eff}$ = effective diffusivity of species j in porous iron layer, sq.cm./sec.
F = fractional reduction
f = weight fraction of iron in wustite
G = mass velocity of approaching gas, g./(sq.cm.)(sec.)
K_e = equilibrium constant for iron-wustite equilibrium, $H_2O/H_{2\,eq}$
k_j^m = mass transfer coefficient for gas j, cm./sec.
k_r = specific rate constant for surface reaction
$\dot{n}_O$ = molar consumption of atomic oxygen, g.-atoms/sec.
$\dot{n}_j$ = molar flow of species j, moles/sec.
N_{Re} = Reynolds number = $2x_oG/\mu$
N_{Sc} = Schmidt number = $\mu/\rho\mathfrak{D}$
N_{Sh} = Sherwood number = $2x_ok_j^m/D$
p_j = partial pressure of species j, atm.
R = gas constant, 82.06, (cc.)(atm.)/(mole)(°K.)
T = temperature, °K. unless otherwise noted
t = reduction time, sec.
V = void fraction in phase
x = distance from the origin in spherical coordinates, cm.
x_i = core radius; distance from origin to reaction interface, cm.
x_o = external radius of oxide sphere, cm.
x_s = radius of pellet initially, cm.

Greek Letters

α = coefficient defined by Equation (13)
$\bar{\alpha}$ = integrated average value of α from $\theta = 0$ to $\theta = \theta$
α^* = $\bar{\alpha}/x_o$
β = coefficient defined by Equation (14)
γ = expansion factor defined by Equation (17)
μ = gas-phase viscosity, poise
ρ = gas-phase density, g./cc.

Superscripts

b = bulk phase value
i = value at reactions interface
m = reduced shell value
s = value at outer surface of pellet
Fe = refers to value for reduced iron shell
F = refers to value for unreduced wustite core

Subscripts

CO = value for carbon monoxide
CO_2 = value for carbon dioxide

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On the Cyclic Operation of Tubular Reactors

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In some cases it may be advantageous to operate a chemical reactor in the unsteady state. Douglas and Rippin (*1*) studied the cyclic operation of a back mix reactor with second-order kinetics and showed that for some values of system parameters the time average conversion of reactant was higher if the reactant concentration in the feed stream varied sinusoidally than if the concentration were held constant at the mean value of the fluctuations. We wish to consider the general problem of cyclic operation of isothermal tubular reactors with back mixing in contrast to their operation in the steady state.

THE UNSTEADY STATE AXIAL DISPERSION MODEL

In this study we are concerned with the isothermal axial dispersion model. This model seems to have been proposed first by Hulburt (*2*) and Danckwerts (*3*), but their analyses were limited to the steady state, although Danckwerts gave a solution to the unsteady state diffusion equation for the case of equimolar counterdiffusion and no reaction. Wehner and Wilhelm (*4*), in their extension of Danckwerts's analysis of the steady state dispersed flow reactor, discussed the applicability of the boundary conditions to the unsteady state as well, but did not give sample solutions. Kramers and Alberda (*5*) reported on the frequency response of the axial diffusion model for plug and laminar flow cases giving input-output amplitude ratio and phase lag diagrams. An alternate formulation of the entrance boundary condition leading to the same approximate solution was published by McHenry and Wilhelm (*6*).

Our formulation follows that of Danckwerts. By assuming constant overall fluid density and constant velocity, the equation of continuity in dimensionless form for a reactant species with second-order kinetics may be written as

$$N_{Pe}^{-1}\frac{\partial^2 x}{\partial \eta^2} - \frac{\partial x}{\partial \eta} - R_{(2)}\,x^2 = N_{Pe}^{-1}\frac{\partial x}{\partial \theta} \qquad (1)$$

For a constant flow rate feed with a sinusoidally varying reactant concentration, a material balance on an infinitesimally thin section around the reactor entrance gives

$$1 + a\sin\omega\,\theta = x(0,\theta) - N_{Pe}^{-1}\frac{\partial}{\partial \eta}x(0,\theta) \qquad (2)$$

Similarly, at the exit

$$\frac{\partial}{\partial \eta}x(1,\theta) = 0 \qquad (3)$$