Pseudosteady State Approximation for Fluid-Solid Reaction and for Extraction in Cylindrical Geometry

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Gas-solid noncatalytic reactions and fluid extraction of a solid from porous or nonporous particles involve moving boundary diffusion. Examples of these types of systems are the reaction of ZnS with O_2 to produce ZnO, regeneration of porous catalyst particles by oxidation with air of deposited carbon, and solvent extraction of kerogen from oil shale particles. In some applications the shape of the element of solid reactant or solute is more nearly cylindrical than spherical or slab-shaped.

Bischoff (1963) has presented results for the reaction case for slab and spherically shaped particles. He obtained an approximate solution of the dynamic equations and compared this with a simple, less exact, pseudosteady state solution. The latter is based on the assumption that the rate of change of the boundary between fluid reactant (or solute) is negligible with respect to the rate of diffusion of the fluid reactant (or solvent). This steady state approximation is accurate when the fluid reactant is a gas at normal concentrations or a liquid at low concentrations. However, the error can be significant if the fluid reactant (or solvent) has a high concentration. This could be the situation in extraction of kerogen from oil shale with a solvent or for fluid-solid reaction. Therefore, it is useful to know the expected error due to the pseudosteady state assumption for cylindrical-shaped solid reactant or solute. In western shales the kerogen is present in layers separated by more or less kerogen-free layers of inert rock. Hence, for granular or even spherical particles, the kerogen layers are approximately in the shape of thin cylindrical disks.

In this note the errors for cylindrical shape are calculated and compared with those of Bischoff for slab and spherical shapes.

A cylindrical disk containing a solid reactant (or solute) S and a surrounding cylindrical fluid region is shown in Figure 1. The concentration c of fluid reactant G (or dissolved solute) in the fluid region is described by the dynamic diffusion equation

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) = \frac{1}{D_e}\frac{\partial c}{\partial t} \tag{1}$$

with boundary conditions

$$c = c_o \quad \text{at } r = r_o \tag{2}$$

$$c = c_s \quad \text{at } r = r_s \tag{3}$$

$$\frac{\partial c}{\partial r} = \left(\frac{\rho_s}{bD_e}\right)\frac{dr_s}{dt} \quad \text{at } r = r_s \tag{4}$$

Equation 4 relates the fluid concentration gradient to the consumption of solid reactant (or solute) expressed in terms of the velocity of the moving interface at r_s. For the extraction application, b is unity, as components G and S are identical; for the reaction case, b is the number of moles of solid reactant S consumed per mole of fluid reactant G, according to the equation

$$G(f) + bS(s) \rightarrow C(s) + D(f) \tag{5}$$

PSEUDOSTEADY STATE SOLUTION

In the steady state approximation the change in concentration with time is taken to be negligible with respect to the change with position in the fluid region. Then the solution of simplified Eq. 1, for constant diffusivity, constant temperature, and constant density ρ_S, is

$$c = A + B \ln r \tag{6}$$

$$c = c_o + (c_s - c_o)\frac{\ln(r/r_o)}{\ln y} \tag{7}$$

where y is the dimensionless position of the interface at r_s; i.e., $y = r_s/r_o$. Equation 7 does not require a rapid reaction rate for which $c_s \rightarrow 0$; the concentration at the interface is c_s, which may be finite.

Differentiating Eq. 7 to obtain dc/dr at $r = r_s$, substituting the result in Eq. 4, and integrating from $t = 0$ to t, one obtains

$$4\left(\frac{bD_e t}{r_o^2}\right)\left(\frac{c_s - c_o}{\rho_s}\right) = 1 - y^2 + 2y^2 \ln y \tag{8}$$

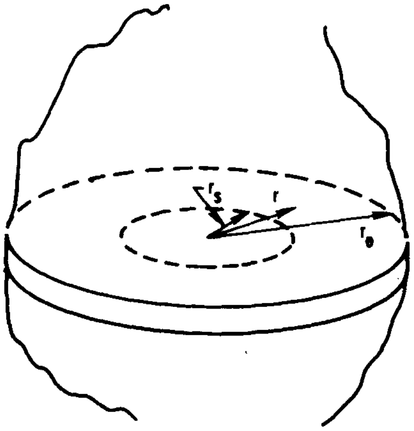

Figure 1. Cylindrical disk of reacting solid (or dissolving solid) of radius r_s in a particle of radius r_o.

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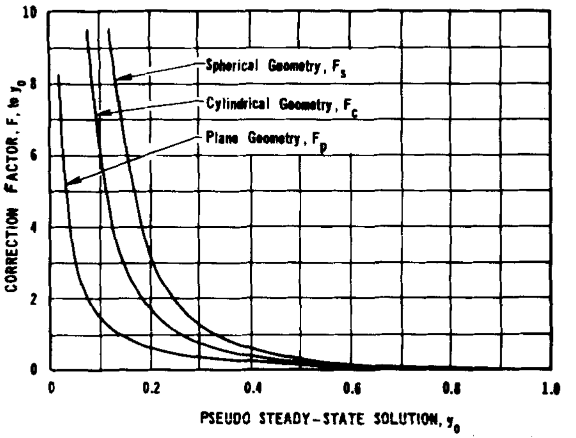

Figure 2. Correction factor *F* to pseudosteady state approximation for various geometries.

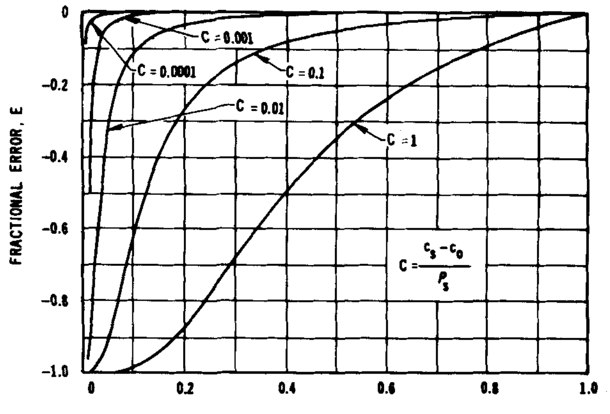

Figure 3. Fraction error of pseudosteady state approximation for cylindrical geometry.

From this pseudosteady state solution y (and r_s) and the conversion of solid S (or fraction extracted) can be calculated for any time.

APPROXIMATE SOLUTION TO DYNAMIC PROBLEM

A solution analogous to Eq. 8, but including the dynamic term in Eq. 1, is required. Apparently an analytical solution is available only for plane geometry. Bischoff (1963) used a perturbation method to obtain an approximate solution, but one more accurate than the steady state result, for a fluid-solid catalytic reaction with planar or spherical particles. We use a similar method for cylindrical geometry for both the reaction and extraction cases. The solution is achieved by letting A and B in the steady state solution, Eq. 6, be functions of time:

$$c = A + B \ln\left(\frac{r}{r_o}\right) + \frac{r^2}{4D_e}\left[\dot{A} - \dot{B}\left(1 - \ln\frac{r}{r_o}\right)\right] + \ldots . \qquad (9)$$

An infinite series is necessary in order that the solution satisfy Eq. 1. $\dot{A}$ and $\dot{B}$ represent derivatives with respect to time. The method, which is described in detail by Bischoff (1963) and Estevez (1983), involves first substituting Eq. 9 in the boundary conditions, Eqs. 2–4, to give three equations in the three unknowns A, B, and y. These unknowns are expanded in series in terms of the perturbation parameter

$$\epsilon = r_o^2/t_c D_e \qquad (10)$$

where t_c is a characteristic time. These series are

$$A = A_o + \epsilon A_1 + \ldots . \qquad (11)$$

$$B = B_o + \epsilon B_1 + \ldots . \qquad (12)$$

$$y = y_o + \epsilon y_1 + \ldots . \qquad (13)$$

Neglecting higher terms in Eqs. 11–13 and retaining the terms shown in Eq. 9, the solution for y is

$$y = y_o\left[1 + \left(\frac{c_s - c_o}{\rho_S}\right)F\right] \qquad (14)$$

where F for our cylindrical geometry is the following function of y_o:

$$F_c = \frac{1}{4y_o^2 \ln(1/y_o)}\left[1 + y_o^2 - \frac{1 - y_o^2}{\ln(1/y_o)}\right] \qquad (15)$$

Retaining only the subscript zero terms in Eqs. 11–13 gives the steady state solution, that is, Eq. 8. Equation 14 shows that the quantity $(c_s - c_o/P_B)F$ is the factor by which the location of the interface y, as given by the steady state solution, must be corrected to give the second, more exact solution.

RESULTS

For any time t and values of concentrations, density, particle size (r_o), and diffusivity, Eq. 8 can be solved for the location of the interface predicted by the pseudosteady state solution; that is, solved for y_o. Then Eqs. 14 and 15 can be used to calculate the more exact location y of the interface. Figure 2 shows the value of F_c calculated from Eq. 15 and also gives analogous curves for spherical and slab-shaped particles as developed by Bischoff (1963). For these latter cases, F is given by

$$F_s = \frac{1 - y_o}{6y_o^2} \text{ (sphere)} \qquad (16)$$

and

$$F_p = \frac{1 - y_o}{6y_o} \text{ (slab)} \qquad (17)$$

Equation 14 indicates that the error in the steady state approximation is proportional to F. Hence the error is greatest for spherical geometry, while the cylindrical case lies in between the results for plane and spherical geometry.

The fractional error in conversion of solid reactant (or fraction extracted) for the cylindrical particle is given by

$$E = \frac{y_o^2 - y^2}{y^2} \qquad (18)$$

Figure 3 is a plot of this error as a function of the steady state location (y_o) of the interface for different values of the concentration ratio $(c_s - c_o)/\rho_s$. The error becomes large when nearly all of the solid reactant has been consumed ($y \rightarrow 0$). However, this region does not contribute significantly to the total amount reacted. At larger values of y_o the error depends prominently on the concentration ratio. For gas (G)-solid (S) reactions the concentration ratio is small (of the order of 0.001) and the error introduced by assuming pseudosteady state is unimportant. Similar results were obtained by Bischoff (1963) for plane and spherical geometry, with somewhat larger errors for spheres and smaller errors for plane geometry. For liquid extraction of solids, $(c_s - c_o)/\rho_s$ normally will be less than 0.01. Figure 3 indicates that for this case the maximum error would be less than 10% for $y_o > 0.1$. For liquid-solid reactions, where $(c_s - c_o)/\rho_s$ might be of the order of 0.5, the error would be large, so the more exact solution should be used.

ACKNOWLEDGMENT

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NOTATION

A,B = coefficients in Eq. 6, mol/m^3; A_o,B_o and A_1,B_1 are first and second terms in series expansion, Eqs. 11 and 12
$\dot{A},\dot{B}$ = time derivatives of A and B, mol/m^3·s
b = moles of solid reactant per mole of fluid reactant
c = concentrations in the fluid phase, mol/m^3
c_o = concentration at the outer surface r_o of the cylindrical region;
c_s = concentration at the fluid-solid interface, r_s
D_e = effective diffusivity in the fluid, m^2/s
E = fraction error in conversion of solid, defined by Eq. 18
F_c = correction factor to the pseudosteady state solution for cylindrical geometry, defined by Eq. 15; F_s and F_p are for spherical and plane geometry
r = radial distance in fluid region m
r_o = outer radius of the cylindrical region
r_s = radial distance at fluid-solid interface
t = time, s
y = dimensionless radius of the fluid-solid interface, r_s/r_o; y_o = value from pseudosteady state approximation
ϵ = perturbation parameter
ρ_s = density of solid (reactant or component extracted), mol/m^3

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