h = height of the conical transition from the distributor plate
H = bed height
H_{max} = maximum slugging bed height
U = superficial gas velocity
U_{mf} = superficial minimum fluidization velocity
U_B = bubble velocity

Subscripts

1 = bottom section
2 = expanded section

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Determination of Diffusion Properties of Impervious Layer of a Double Layered Catalyst Pellet

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Deposition of contaminants on the outer surface of a catalyst pellet sometimes results in the formation of impervious or near impervious outer layer. Examples are given in an article by Chou and Hegedus (1978). Characteristics of this impervious layer of the double layered catalyst pellet are such that the thickness of the impervious layer is very small and the porosity very low. As pointed out by Chou and Hegedus, it is very difficult to accurately measure the thickness and porosity of this impervious layer. In order to determine the diffusivities of two layers of a catalyst pellet, Chou and Hegedus (1978) solved on the Laplace domain mass balance equations for each of the two layers of catalyst pellet and a conservation equation for a pellet string reactor. The diffusivities were then determined by minimizing the error between the theoretical frequency response and the experimental frequency response obtained through pulse tests. The thickness and porosity of the near impervious layer independently determined were used for accurate determination of the diffusivities. However, they found that the results are insensitive to the porosity.

In this note, it is shown that the single-pellet chromatography of Smith and co-workers (Suzuki and Smith, 1972; Dogu and Smith, 1975) leads to straightforward determination of the diffusion properties of the impervious layer, such as diffusivity and porosity, and the thickness of the impervious layer. It is also shown that diffusivity of the impervious layer can be determined without the knowledge of thickness and porosity of the impervious layer. We will treat the general case where the retention time for the impervious layer is of the same order of magnitude as that for the unobstructed layer. This general case can be reduced to that of Chou and Hegedus (1978), where the retention time for the near impervious layer is much smaller than that for the unobstructed layer. Diffusion in catalysts with a bipore distribution was studied using transient response by Haynes and Sarma (1973) and Ma and Lee (1976).

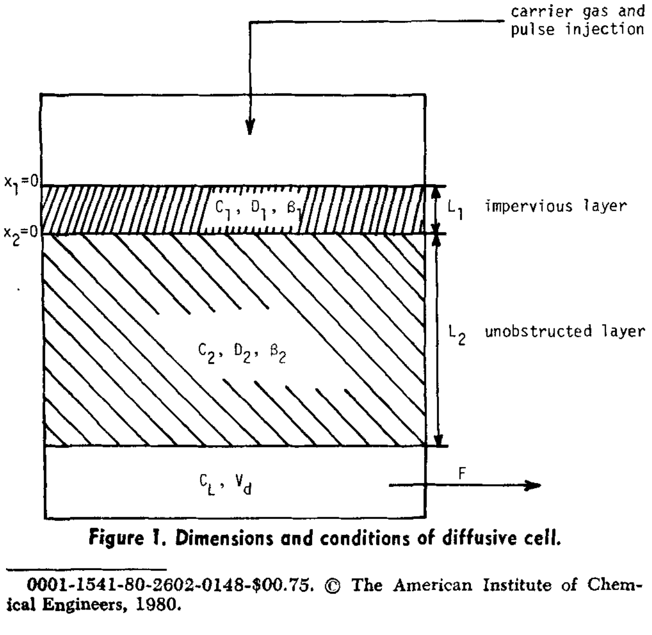

Figure 1. Dimensions and conditions of diffusive cell.

SINGLE-PELLET CHROMATOGRAPHY FOR DOUBLE LAYERED CATALYST PELLETS

Dimension and conditions of a double-layered, single-pellet, diffusion cell are shown in Figure 1. For a nonadsorbed gas, the conservation equation applied to each of the layers can be written in terms of dimensionless variables as follows:

$$\frac{\partial^2 C_1}{\partial z_1^2} = \phi_1^2 \frac{\partial C_1}{\partial t} \tag{1}$$

$$\frac{\partial^2 C_2}{\partial z_2^2} = \phi_2^2 \frac{\partial C_2}{\partial t} \tag{2}$$

where

$$z_i = x_i/L_i \tag{3}$$

$$i = 1, 2$$

$$\phi_i^2 = \beta_i L_i^2/D_i \tag{4}$$

The boundary and initial conditions are (see Figure 1)

$$C_1(0, t) = M\delta(t) \tag{5}$$

$$C_1(1, t) = C_2(0, t) \tag{6}$$

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$$\frac{dC_1(1,t)}{dz_1} = \frac{dC_2(0,t)}{dz_2}\,(d) \tag{7}$$

$$C_1(z,0) = C_2(z,0) = 0 \tag{8}$$

where

$$d = D_2/D_1 \tag{9}$$

The boundary condition at $x_2 = L_2$ is as follows:

$$\frac{dC_2(1,t)}{dz_2} = -\,B_f C_2(1,t) = -\,B_f C_L(t) \tag{10}$$

if the diffusion cell is a continuous cell (Dogu and Smith, 1975)

$$\frac{dC_2(1,t)}{dz_2} = -\,B_c\frac{dC_L}{dt} \tag{11}$$

if the cell is a closed chamber (Suzuki and Smith, 1972), where

$$B_f = \frac{FL_2}{AD_2} \tag{12}$$

$$B_c = \frac{V_d L_2}{AD_2} \tag{13}$$

In writing the boundary condition of Equation (10), we used the argument of Dogu and Smith (1975) that the accumulation term can be made small to be neglected compared to the convective term. Solving the equations on the Laplace domain, we obtain

$$\overline{C}_L = C_2(1,s) = \frac{M}{\cosh(\phi_1\sqrt{s})\left\{\cosh(\phi_2\sqrt{s}) + \dfrac{B_j}{\phi_2\sqrt{s}}\sinh(\phi_2\sqrt{s})\right\} + \dfrac{d\phi_2}{\phi_1}\sinh(\phi_1\sqrt{s})\left\{\sinh(\phi_2\sqrt{s}) + \dfrac{B_j}{\phi_2\sqrt{s}}\cosh(\phi_2\sqrt{s})\right\}} \tag{14}$$

where $B_j = \begin{cases} sB_c & \text{for closed cell} \\ B_f & \text{for continuous cell} \end{cases}$

If the pellet is placed in the diffusion cell with the impervious layer at the bottom of the cell, conservation equations remain the same, the only changes being in the boundary conditions. For this case, we obtain the following expression by merely interchanging the subscripts 1 and 2 in Equation (14):

$$\overline{C}_L' = C_1(1,s) = \frac{M}{\cosh(\phi_2\sqrt{s})\left\{\cosh(\phi_1\sqrt{s}) + \dfrac{B_j'}{\phi_1\sqrt{s}}\sinh(\phi_1\sqrt{s})\right\} + \dfrac{\phi_1}{d\phi_2}\sinh(\phi_2\sqrt{s})\left\{\sinh(\phi_1\sqrt{s}) + \dfrac{B_j'}{\phi_1\sqrt{s}}\cosh(\phi_1\sqrt{s})\right\}} \tag{15}$$

where

$$B_j' = \begin{cases} B_c' = \dfrac{V_d L_1}{AD_1}\,s & \text{for closed cell} \quad (16) \\[2ex] B_f' = \dfrac{FL_1}{AD_1} & \text{for continuous cell} \quad (17) \end{cases}$$

The n^{th} moment function is related to $\overline{C_L}$ (or $\overline{C_L'}$) by

$$m_n = (-1)^n \lim_{s\to 0}\frac{d^n}{ds^n}(\overline{C_L}) = \int_0^\infty t^n\, C_L(t)\,dt \tag{18}$$

where the last term in the equation can be evaluated from the chromatographic peak obtained by introducing pulses to the top of the diffusion cell. If we use Equations (14), (15), and the first equality in Equation (18), the first absolute moment μ $(= m_1/m_0)$ can be obtained, and the results are given in Table 1.

DISCUSSION OF RESULTS

If the experimental procedures of Smith and co-workers are followed, the value of B is much greater than unity. Diffusivity of gas in the unobstructed layer of catalyst pellet (D_2) is several orders of magnitude higher than that in the impervious layer (D_1). Hence, the value of d is much greater than unity. For the near impervious layer that Chou and Hegedus (1978) studied, D_2 was found to be approximately twenty-five times higher than D_1; that is, $d = 25$. Therefore, the first absolute moment given in the second row of Table 1 can be used in actual analysis of pulse response data. For the kind of problem studied by Chou and Hegedus (1978), where the retention time for the near impervious layer is much smaller than that for the unobstructed layer, the first absolute moment can be further reduced to the results given in the last row of Table 1.

It is rather obvious from Table 1 that the closed diffusive cell (Suzuki and Smith, 1972) is much more useful than the continuous (flow) diffusive cell (Dogu and Smith, 1975) in determining the diffusive properties of the impervious layer. In particular, the arrangement of placing the catalyst pellet in a closed cell with the impervious layer at the top of the cell is most useful. Only the knowledge of thickness and porosity of the unobstructed layer, which are easy to measure, is required to determine the effective diffusivity in the impervious layer. Once D_1 is determined, the thickness of the impervious layer L_1 can be obtained from pulse tests, this time with the impervious layer at the bottom of the closed cell, by varying the ratio of dead volume to area (V_d/A) (refer to the expression for μ_c^B in Table 1). Once D_1 and L_1 are known, the porosity of the impervious layer β_1 can be determined from the pulse tests and the expression for μ_c^B. When the retention time for the impervious layer is much less than unity, that is, $\phi_2 >> \phi_1$, effective diffusivity and thickness of the impervious layer can be determined according to the procedures discussed above. However, the porosity of the impervious layer cannot be determined from the pulse tests.

Use of the continuous diffusive cell would allow us to determine only the diffusive moduli ϕ_1 and ϕ_2. In the special case of ϕ_2 being much greater than ϕ_1, no information on the impervious layer can be obtained. Only the effective diffusivity of the unobstructed catalyst layer can be determined. However, pulse test results of the continuous cell can be used to determine the relative magnitude of the diffusive moduli or the retention time. It follows from Table 1 (second row) that

TABLE 1. FIRST ABSOLUTE MOMENT OF SINGLE-PELLET PULSE RESPONSE

	Closed cell		Continuous cell	
	Impervious layer on top, μ_c^T	Impervious layer on bottom, μ_c^B	Impervious layer on top, μ_f^T	Impervious layer on bottom, μ_f^B
	$\frac{\phi_1^2+\phi_2^2}{2}+B_c+d(\phi_2^2+B_c)$	$\frac{\phi_1^2+\phi_2^2}{2}+B_c'+\frac{1}{d}(\phi_1^2+B_c')$	$\frac{\phi_1^2(1+B_f)/2+\phi_2^2(1+B_f/3)/2+G_1}{1+B_f(1+d)}$ $G_1=\frac{d\phi_2^2}{2}\left[2+B_f+\frac{B_f}{2}\left(\frac{\phi_1}{\phi_2}\right)^2\right]$	$\frac{\phi_2^2(1+B_f')/2+\phi_1^2(1+B_f'/3)/2+G_2}{1+B_f'(1+1/d)}$ $G_2=\frac{\phi_1^2}{2d}\left[2+B_f'+\frac{B_f'}{2}\left(\frac{\phi_2}{\phi_1}\right)^2\right]$
$B_c, B_f, B_c', B_f' >> 1$ and $d >> 1$	$d(\phi_2^2+B_c)=\frac{L_2^2}{D_1}\left[\beta_2+\frac{1}{L_2}\left(\frac{V_d}{A}\right)\right]$	$\frac{\phi_1^2+\phi_2^2}{2}+B_c'=\frac{1}{2}\times\left[\frac{\beta_1L_1^2}{D_1}+\frac{\beta_2L_2^2}{D_2}+\frac{2L_1}{D_1}\left(\frac{V_d}{A}\right)\right]$	$\frac{\phi_1^2}{4}+\frac{\phi_2^2}{2}=\frac{\beta_1L_1^2}{D_1}+\frac{1}{2}\frac{\beta_2L_2^2}{D_2}$	$\frac{\phi_1^2}{6}+\frac{\phi_2^2}{4}=\frac{1}{6}\frac{\beta_1L_1^2}{D_1}+\frac{1}{4}\frac{\beta_2L_2^2}{D_2}$
$B_c, B_f, B_c', B_f' >> 1$ $d >> 1$ and $\phi_2 >> \phi_1$	$\frac{L_2^2}{D_1}\beta_2+\frac{1}{L_2}\left(\frac{V_d}{A}\right)$	$\frac{1}{2}\frac{\beta_2L_2^2}{D_2}+\frac{2L_1}{D_1}\left(\frac{V_d}{A}\right)$	$\frac{1}{2}\frac{\beta_2^2L_2^2}{D_2}$	$\frac{1}{4}\frac{\beta_2L_2^2}{D_2}$
	$B_c'=\frac{V_dL_1}{AD_1},\quad B_c=\frac{V_dL_2}{AD_2}$		$B_f'=\frac{FL_1}{AD_1},\quad B_f=\frac{FL_2}{AD_2}$	

$$\frac{2\mu_f^T-3\mu_f^B}{\mu_f^T}=\frac{1}{2+\left(\frac{\phi_1}{\phi_2}\right)^2} \tag{19}$$

According to Equation (19), experimentally determined first absolute moments would reveal the relative importance of the diffusive moduli. It is understood that the first absolute moments are corrected for other time delays as specified by Suzuki and Smith (1972).

NOTATION

A = cross-sectional area of catalyst pellet
B_f, B_c, B_c', B_f' = quantities defined by Equations (12), (13), (16), and (17), respectively
C = concentration of diffusing gas
C_L = concentration at the end of the diffusive cell, $C_1(1, t)$ or $C_2(1, t)$
$\overline{C_L}$ = Laplace transformed C_L when impervious layer is at the top of diffusive cell
$\overline{C_L}'$ = Laplace transformed C_L when impervious layer is at the bottom of diffusive cell
d = D_2/D_1
D = effective diffusivity
F = volumetric flow rate out of continuous diffusive cell
L_1 = thickness of impervious layer of catalyst pellet
L_2 = thickness of unobstructed layer
m_n = n^{th} moment defined by Equation (18)
M = magnitude of concentration pulse
t = time
V_d = dead volume at the end of diffusive cell
x = axial distance of single pellet as measured from the top
z = normalized axial distance

Greek Letters

β = porosity
δ = Dirac delta function
μ = first absolute moment, m_1/m_0
μ_c^B = μ obtained with impervious layer at the bottom of closed diffusive cell
μ_c^T = μ obtained with impervious layer at the top of closed cell
μ_f^B = μ obtained with impervious layer at the bottom of continuous diffusive cell
μ_f^T = μ obtained with impervious layer at the top of continuous cell
ϕ = diffusive modulus defined by Equation (4)

Subscripts

1 = impervious layer of catalyst pellet
2 = unobstructed layer of catalyst pellet

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