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APPENDIX

CORRELATIONS BETWEEN SHERWOOD, *Sh*, AND PECLET, *Pe*, NUMBERS FOR A SPHERE AND FOR A TUBE SITUATED IN A GRANULAR BED

The Peclet number for a tube and for a sphere are defined respectively as

$$Pe_T = \frac{d_T U_0}{D} = \frac{\bar{d} U_0}{D}; \quad Pe_S = \frac{d_s U_0}{D} \tag{A-1}$$

Hence they may be related by

$$Pe_T = Pe_S \frac{\bar{d}}{d_S} = Pe_S \sqrt{\frac{8 + 4c_1 + 3c_2}{15} \cdot \frac{d_c^2}{d_S^2}} \tag{A-2}$$

Introducing c_2 into Equation (A-2) one obtains

$$Pe_T = Pe_S \left[\frac{8 + 4c_1 + 3c_1^2}{15c_2^2} \right]^{1/2} \tag{A-3}$$

The overall mass transfer rate may be expressed as

$$Q = K_L A \Delta c = \frac{K_L d_e}{D} \frac{D}{d_e} A \Delta c = Sh \frac{D}{d_e} A \Delta c \tag{A-4}$$

Here, d_e is the equivalent diameter and A, the total transfer area. Equation (A-4) for a sphere, becomes

$$Q_S = Sh_S \frac{D}{d_s} A_s \Delta c = Sh_S D(\pi d_S) \Delta c \tag{A-5}$$

while for a tube it reads

$$Q_T = Sh_T \frac{D}{d_T} A_T \Delta c = Sh_T D(\pi L_T) \Delta c \tag{A-6}$$

A mass transfer balance is now performed on a volume of the granular bed of dimensions $(1 \times 1 \times h)$, where $h = c_2 d_c$. The number of pores, n_p, in such a volume is

$$n_p = N_p \cdot c_2 d_c \cdot 1 \cdot 1 \tag{A-7}$$

whereas the number of spheres in the same volume is

$$n_s = \frac{c_2 d_c \cdot 1 \cdot 1 \cdot (1 - \epsilon)}{\frac{\pi d_s^3}{6}} \tag{A-8}$$

Using Equations (A-5 to A-8), the balance yields

$$Q_T \cdot n_p = Q_S \cdot n_s \tag{A-9}$$

and finally, after some algebraic manipulations, one obtains

$$Sh_T = Sh_s \frac{1 - \epsilon}{\epsilon} \cdot \left[\frac{8 + 4c_1 + 3c_1^2}{10c_2^2} \right] \tag{A-10}$$

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Entrance Region (Lévêquelike) Mass Transfer Coefficients in Packed Bed Reactors

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Calculations for the high Peclet number, entrance region (Lévêquelike) packed bed, mass transfer coefficient using a sinusoidal periodically constricted tube model for the void structure of the bed are presented. An inverse cube root dependence of the mass transfer coefficient on the bed depth is predicted. This length dependence is anticipated only at very low Reynolds numbers. Calculations which assume a mixing region between successive periods are also presented. No bed length dependence is anticipated in these coefficients.

The periodically constricted tube model for porous media constitutes a useful model for mass transfer in two-phase, packed-bed reactors. This model was developed by Payatakes and co-workers (1973, 1977) to predict the permeability of a nonconsolidated packed bed. They envisioned the bed as cell structures made of segments of parabolic periodically constricted tubes. A sinusoidal periodically constricted tube (PCT) is used in this work to model the void structure in a bed in order to predict the mass transfer coefficient. The fluid is assumed to be in the viscous flow regime, and the reactant conversion is assumed to be controlled by mass transfer from the

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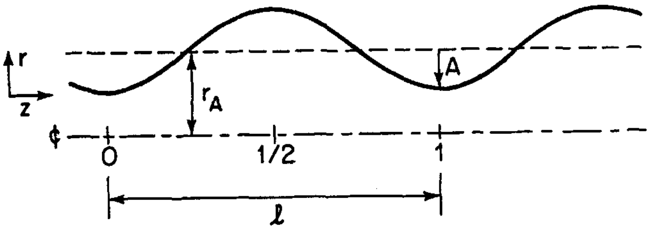

Figure 1. The wall of a PCT generated by $r_w(z) = r_A - A\cos(2\pi z)$. All lengths are dimensionless with respect to the period length l.

fluid to the particle surface. In previous communications, we have presented calculations using this model for the mass transfer coefficient in the high (Fedkiw and Newman, 1977) and low (Fedkiw and Newman, 1978*a*) Péclet number, deep-bed asymptotic limit. These limiting values can be used in their appropriately defined ranges (as suggested by Karabelas et al., 1971), or they can be empirically combined to cover the intermediate Péclet number range. This approach is similar to that taken by Sørensen and Stewart (1974) who, in their pioneering work, solved the convective-diffusion equation in a simple cubic packed bed of uniform sized spheres. In this note, the high Péclet number, entrance region (Lévêquelike) mass transfer coefficient calculations are presented. The term entrance region is used here to designate that region where a concentration boundary layer has started to grow along the wall of the packing or particles but has not yet completely filled the flow passage.

A note similar to this was presented by Tardos et al. (1976). They presented calculations for the mass transfer coefficient under the stated restrictions using various sphere-in-a-cell models for the void structure in the bed. As will be seen, in the creeping flow regime these models are inherently different from the conduit model which predicts a length dependent coefficient.

MATHEMATICAL FORMULATION

Figure 1 represents a segment of a sinusoidal PCT. The bed is conceptualized as a matrix of these tubes. The well-known straight conduit model results when the amplitude of the tube wall oscillation equals zero. The tube parameters may be determined by the procedure suggested by Payatakes et al. (1973).

The effective mass transfer coefficient k_m is defined as

$$\frac{c_L}{c_F} = \exp\left(-ak_mL/v\right) \tag{1}$$

where c_F and c_L are the reactant concentration far upstream and downstream of the reactor, respectively. Since the axial dispersive flux becomes negligible compared to the convective flux at high Péclet numbers, Equation (1) can be generated by integrating the one-dimensional model for the bed, wherein k_m is analogous to a first-order rate constant. The distinction between this coefficient and the film coefficient k_f which appears as the first-order rate constant in the one-dimensional model of the bed which includes a dispersive flux should be pointed out. Only in the high Péclet number limit do these two coefficients become indistinguishable. [See Fedkiw and Newman (1978*b*) for a more thorough discussion.]

Consider a single PCT of length L. A mass balance for the reactant across the tube (inlet to outlet) can be written as

$$q_T[c_F - c_L] = \text{rate of moles reacted at tube wall} \tag{2}$$

The bed is assumed to be homogeneous; thus the reactant concentrations of Equation (2) are equal to those of Equation (1). The right side of Equation (2) can be calculated by solving the appropriate form of the convective-diffusion equation. We shall demonstrate shortly how this calculation is carried out, but let us express the result of this step in terms of an average Sherwood number for the tube

$$\langle Sh \rangle = \langle N_w \rangle \frac{2r_{Ad}}{\mathcal{D}_0 c_F} \tag{3}$$

In the high Péclet number limit, combining Equations (1), (2), and (3), we get

$$\frac{k_m aL}{v} \cong \frac{\langle Sh \rangle}{2r_{Ad}\langle v_{Ad}\rangle/\mathcal{D}_0}\,\frac{SA_L}{\pi r^2_{Ad}} \tag{4}$$

The bed Sherwood number (a dimensionless mass transfer coefficient) can be written by relating the superficial velocity v to the average velocity in the tube $\langle v_{Ad}\rangle$:

$$\langle v_{Ad}\rangle = \frac{v}{\epsilon}\left[1 + \frac{1}{2}(A/r_A)^2\right] \tag{5}$$

We then find

$$Sh_B = \frac{\epsilon k_m}{a\mathcal{D}_0} = \frac{\langle Sh \rangle}{4}\left(\frac{2\epsilon}{ar_{Ad}}\right)^2 \left\{\frac{SA_L}{2\pi r_{Ad}L\left[1 + \frac{1}{2}(A/r_A)^2\right]}\right\} \tag{6}$$

In order to calculate the mass transfer coefficient from Equation (6), a value for the average Sherwood number ($\langle Sh \rangle$) in a tube must be determined. This may be found by applying a Lighthill (1950) transformation to the convective-diffusion equation. The axial diffusive flux is assumed to be negligible, and the velocity profile is taken to be linear near the wall. The governing equation may be found in Newman's text (1973) and is

$$\langle Sh \rangle = \frac{\pi}{3\Gamma(4/3)}\,\frac{2r_{Ad}}{SA_L\mathcal{D}_0}\left[9\mathcal{D}_0\int_0^{x_d} r_{wd}\sqrt{r_{wd}\beta_d}\,dx_d\right]^{2/3} \tag{7}$$

The integral is carried out along the boundary-layer coordinate x, measured along the surface of the tube. The radius of the tube is r_{wd}, and β_d is the normal derivative of the velocity at the wall. This may be found by appropriate differentiation of the stream function solutions found in Fedkiw and Newman (1977). In a dimensionless form, this derivative is expressed as

$$r_A\frac{\partial v_t}{\partial n} = 4\left(\frac{r_A}{r_w}\right)^3(1 + r_w'^2)\left[1 - \sum_{k=1}^{NCP} A_k(z)\phi_k(1)\right] \tag{8}$$

Equation (7) may be inserted into Equation (6), and, after some rearranging, this results in an expression for the macroscopic quantity k_m in terms of the measurable parameters aL, ϵ, Pe_B, and the microscopic model parameters r_A and A/r_A

$$\frac{\epsilon k_m}{a\mathcal{D}_0} = \frac{9^{2/3}}{3\Gamma(4/3)4^{1/3}}\,I^{2/3}\left\{\frac{2\epsilon}{ar_{Ad}\sqrt{1 + \frac{1}{2}(A/r_A)^2}}\right\}^{4/3}$$

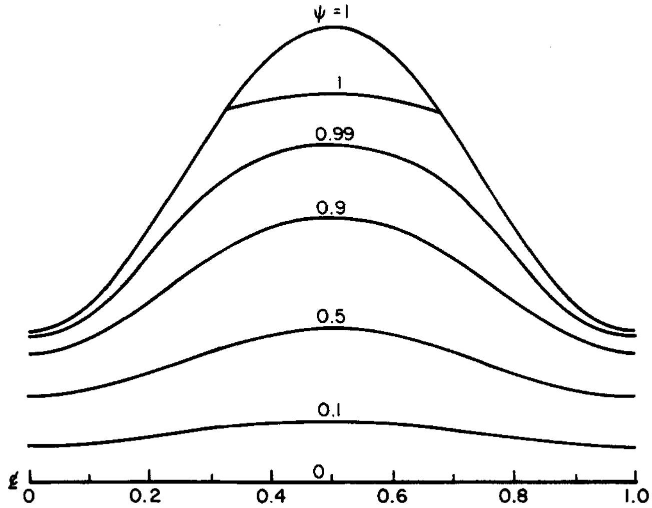

Figure 2. Streamlines in a sinusoidal PCT with $r_A = 0.5$, $A/r_A = 0.5$.

$$\left(\frac{\epsilon v}{aLa\mathcal{D}_0}\right)^{1/3} \quad (9)$$

where

$$I = \int_0^{1/2} \frac{r_w}{r_A} \sqrt{(1 + r_w'^2)\,\frac{r_w}{r_A}\, r_A \frac{\partial v_t}{\partial n}}\, dz \quad (10)$$

It has been assumed in deriving Equation (9) that L/l is an integer.

RESULTS AND DISCUSSION

The bed Sherwood number may be calculated by evaluating the integral I of Equation (10) by the use of Equation (8). In the course of the calculations, it was found that $\partial v_t/\partial n$ became less than zero for certain ranges of the tube parameters. This implies a separational flow pattern. Separation in viscous flow has been reported in the literature by Davis and O'Neil (1977), Moffat (1964), and Ganatos et al. (1978), among others. The Lighthill transformation is not valid when the shear rate becomes negative.

In the worst case for which calculations are presented ($r_A = 1/2$, $A/r_A = 1/2$), the surface area of the tube occluded by the separation zone is 44% of the total surface area. Figure 2 presents the streamlines for this case. In the spirit of numerical simplicity, the shear rate was set identically equal to zero from the separation point to $z = 1/2$ in evaluating the integral I, thus neglecting the complications caused by the flow pattern. This will result in an underestimate in k_m. Those values of the tube parameters for which separation was found are indicated by the dashed line of Figures 3 and 4.

Figure 3 is a plot of the integral I. Figure 4 is a plot of the high Péclet number, entrance region Sherwood number. Both figures use r_A and A/r_A as parameters.

As was found by Chow and Soda (1973), who solved a regular perturbation problem for small values of r_A, the Sherwood number increases with amplitude. However, for larger values of r_A, this trend reverses itself. This identical trend was found for the high Péclet number, deep-bed asymptote.

Equation (9) predicts that the bed Sherwood number decreases as $L^{-1/3}$ for a mass transfer controlled reaction. Sørensen and Stewart (1974a) have also reached the same conclusion. One cannot find conclusive evidence in the literature to substantiate this prediction. Kato et al. (1970) have correlated their data with a packing depth

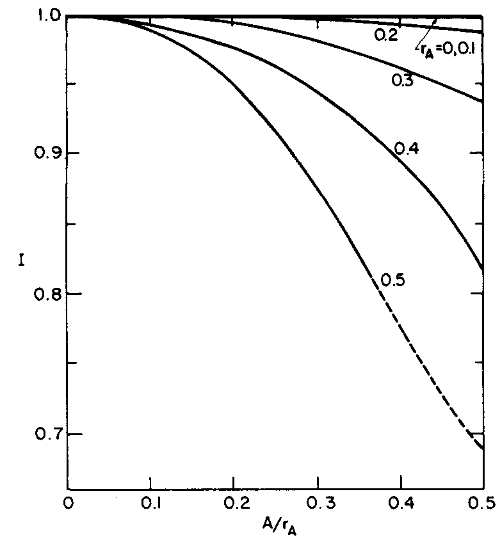

Figure 3. The integral I plotted as a function of the sinusoidal PCT parameters.

factor. There are also indications of a length dependent k_m in the data of Wilson and Geankopolis (1966) and of Alkire and Gracon (1975). For a given flow rate, increasing the packing depth by a factor of 10 will result in a decrease of k_m by 54%. If we consider the nature of experimental measurements of k_m, this difference can easily be obscured by experimental error. Thus, an experiment to ascertain if there is a packing depth effect must be carefully designed.

Tardos et al. (1976) compared their calculations for k_m with the experimental correlation of Wilson and Geankopolis (1966). This latter correlation was developed from data taken from beds with aL values ranging from 3.4 to 27 with ϵ approximately 0.4. If an average aL of 15 is assumed, the PCT model predicts the ratio $Sh_B/Pe_B^{1/3}$ to be in the range 0.214 to 0.304, while Tardos et al. (1976) report a range of this ratio from 0.536 to 0.584 depending upon the cell model used. The Wilson and Geankopolis correlation results in a value of 0.464.

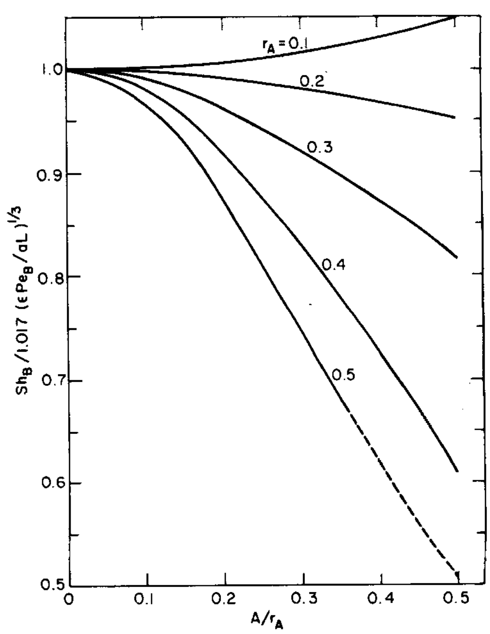

Figure 4. Packed bed, entrance region mass transfer coefficient as a function of the sinusoidal PCT parameters.

It should be emphasized that the packing depth effect is anticipated only at low Reynolds numbers. In creeping flow, the Péclet number is the only physicochemical parameter controlling the mass transfer rate. As the flow rate increases, the Reynolds number also becomes a factor to consider. In the nonviscous flow region, mixing eddies will become a dominant flow structure in the interstices of the packing. Thus, any boundary layer that might form on the surface of the particles is destroyed by the eddies. In this case, the models of a sphere in a cell become physically more appropriate. The conduit model may also be applied here by redefining the length scale over which the average tube Sherwood number is calculated (for example, l instead of L). Kataoka et al. (1972) have carried out such an analysis using the straight tube model. With the aid of Figure 2, it is possible to carry out such an analysis for the sinusoidal PCT.

The fluid is now imagined to be well mixed before it enters a period and remixed after it leaves a period. The Lévêque solution can be applied in each period to calculate the mass transfer coefficient. The length scale over which the Lighthill transformation is applied is l in this case rather than L. Equation (9) still applies after the appropriate substitution. The period length l may be related to the particle diameter by

$$l = \left[\frac{\pi}{6(1-\epsilon)} \right]^{1/3} d_p \qquad (11)$$

as suggested by Payatakes et al. (1973, 1977). Substituting into Equation (10) and introducing the specific interfacial area for d_p, one obtains

$$\frac{\epsilon k_m}{a\mathcal{D}_0} = \frac{9^{2/3}}{3\Gamma(4/3)4^{1/3}} \left[\frac{\epsilon}{[6(1-\epsilon)]^{2/3}} \right]^{1/3} \left(\frac{2\epsilon}{a r_{Ad} \sqrt{1 + \frac{1}{2} (A/r_A)^2}} \right)^{4/3} l^{2/3} \left(\frac{v}{a D_0} \right)^{1/3} \qquad (12)$$

For the reasonable values of $r_A = 0.5$ and $A/r_A = 1/3$, Equation (12) predicts $Sh_B/Pe_B{}^{1/3} = 0.419$.

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NOTATION

A_d = amplitude of PCT wall oscillation, cm
$A_k(z)$ = axial dependent expansion function for stream function
a = specific interfacial surface area, cm^{-1}
c_F = reactant feed concentration, mole/cm^3
c_L = reactant concentration at bed exit, mole/cm^3
$\mathcal{D}_0$ = reactant diffusivity, cm^2/s
k_m = effective mass transfer coefficient, Equation (1), cm/s
l = period length of PCT
L = depth of bed, cm
n = normal to tube wall, dimensionless
$\langle N_w \rangle$ = average reactant flux on tube wall, mole/cm^2 s
q_T = flow rate per tube, cm^3/s
r_{Ad} = average radius of PCT, cm
SA_L = surface area of PCT of length L
$\langle Sh \rangle$ = average Sherwood number in a PCT
Sh_B = packed bed Sherwood number, $\epsilon k_m/a\mathcal{D}_0$
v_t = tangential wall velocity in a PCT
v = superficial velocity in a packed bed, cm/s
ϵ = porosity
ϕ_k = radial dependent expansion function for stream function

Subscript

d = dimensional quantity

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