## THREE-REGION MODEL

We now introduce an intermediate layer, whose permeability exceeds the permeability of the bulk of the porous medium. We now have three regions: (I) a central core, $R < R_c - d_f - d_m$, occupied by a porous medium with permeability $k$; (II) an intermediate region, $R_c - d_f - d_m < R < R_c - d_f$, occupied by a medium with permeability $k_m$, where $k_m > k$; and (III) a wall region, $R_c - d_f < R < R_c$, occupied by pure fluid. As before, we suppose that $d_f$ is of the same order as a particle diameter. The thickness $d_m$ of the intermediate region is assumed to be equal to several particle diameters.

The (superficial) velocity $V_m$ in region II is related to the velocity $V$ in region I by $V_m = (k_m/k)V$. In our new model there will be an increase in volume flux, over that in the old model, of amount $(V_m - V)A_m$, where $A_m$ is the cross-sectional area of region II. Since $Q_0 = \pi R_c^2 V$, and

$$\begin{aligned} A_m &= \pi(R_c - d_f)^2 - \pi(R_c - d_f - d_m)^2 \\ &= \pi d_m(2R_c - 2d_f - d_m) \doteq 2\pi R_c d_m, \end{aligned}$$

we now have, in place of Eq. 3,

$$\frac{Q}{Q_0} = 1 - \frac{d_f}{R_c} F(\alpha, d_f/k_m) + 2(k_m/k - 1)\frac{d_m}{R_c}\,. \tag{14}$$

The last term in this equation is positive and represents a relaxing effect of an increase in permeability due to increase in porosity near the wall. The second to last term represents primarily a restricting effect due to no-slip at the wall.

## CONCLUSIONS

We have developed a model which involves core, intermediate and wall regions, and in this respect it is similar to that of Cohen and Metzner, but is otherwise distinctly different. We have derived an expression for $Q/Q_0$ (Eq. 14) which is essentially linear in the small parameters $d_f/R_c$ and $d_m/R_c$. In this expression the restricting and relaxing contributions to the wall effect are clearly displayed. The parameters $d_f$, $d_m$ and $k_m/k$ may be varied (within limits to fit experimental data. We stop short of doing so here, because our purpose is not to compete directly with the theory of Cohen and Metzner, which already ties in quite well with experiment, but rather to provide an additional vantage point from which to view that theory.

## NOTATION

$A$ = constant of integration, given by Eq. 10
$A_m$ = cross-sectional area of intermediate layer
$d_f, d_m$ = thickness of fluid layer, intermediate layer, respectively
$F$ = function given by Eq. 12
$k$ = permeability of bulk of porous medium
$k_m$ = permeability of intermediate layer
$L$ = length of column
$p$ = pressure
$\Delta p$ = pressure drop across length $L$ of column
$Q, Q_0$ = volume flux through column in presence, absence (respectively) of wall effect
$R$ = radial distance
$R_c$ = radius of cross-section of column
$R_m$ = radius of interface ($R_m = R_c - d_f$)
$r$ = dimensionless radial distance
$U$ = velocity of fluid
$\tilde{U}$ = velocity scale ($\tilde{U} = R_c^2 \Delta p / 4\mu L$)
$u$ = dimensionless velocity of fluid
$V$ = superficial velocity
$V_m$ = superficial velocity in intermediate region
$v$ = dimensionless superficial velocity

### Greek Letters

$\alpha$ = Beavers-Joseph nondimensional constant
$\beta$ = $4\alpha k^{1/2}/R_c$
$\gamma$ = $d_f/k^{1/2}$
$\epsilon$ = $\gamma k^{1/2}/R_c$
$\eta$ = $1 - \epsilon$
$\lambda$ = $\alpha R\ /k^{1/2}$
$\mu$ = dynamic viscosity of fluid

$c$

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# Non-Newtonian Fluid-Particle Mass Transfer in Granular Beds

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There is a wealth of experimental data and empirical correlations for mass transfer in Newtonian fluids flowing through granular beds, but only a few studies on the effect of non-Newtonian flow characteristics have been published so far.

Bhavaraju et al. (1978) and Kawase and Ulbrecht (1981) treated mass transfer in non-Newtonian flows through multiparticle systems by using a cell model. The applicability of their results is, however, restricted to very low Reynolds numbers. No models for high Reynolds number region have been reported so far.

The objective of this note is to discuss the effects of non-Newtonian flow behavior at high Reynolds numbers on the mass transfer in granular beds using the boundary layer model which was applied successfully to the case of Newtonian fluids by Carberry (1960). The development of the model starts with considering the flow past a flat plate first, and this will be then amended by modifying the average velocity appropriately. The predictions of the theory will be then compared with experimental data on mass transfer to power-law fluids in granular beds obtained by Kumar and Upadhyay (1980, 1981).

## BOUNDARY LAYER MODEL

### Mass Transfer from a Flat Plate

The laminar flow of a non-Newtonian fluid past a flat plate is considered first. The convective diffusion equation is

$$u\frac{\partial c}{\partial x} = \mathcal{D}\frac{\partial^2 c}{\partial y^2} \tag{1}$$

which must be solved subject to the boundary conditions

$$c = c_\infty \quad \text{at} \quad x = 0 \tag{2a}$$

$$c = c_w \quad \text{at} \quad y = 0 \tag{2b}$$

$$c = c_\infty \quad \text{at} \quad y = \infty \tag{2c}$$

To portray the non-Newtonian flow characteristics, we shall choose the well-known power-law model

$$\tau_{xy} = K\left(\frac{\partial u}{\partial y}\right)^n \tag{3}$$

A commonly used velocity profile for the flow past a flat plate is the cubic parabola (Skelland, 1967)

$$\frac{u}{u_\infty} = \frac{3}{2}\left(\frac{y}{\delta}\right) - \frac{1}{2}\left(\frac{y}{\delta}\right)^3 \tag{4}$$

but, in certain cases, it is justifiable to drop the cubic term and use a linear profile instead. If the Schmidt number is large enough (as in the case for liquids), the concentration boundary layer is much thinner over a given surface than the momentum boundary layer. Therefore, it can be assumed that the velocity component in the concentration boundary layer is approximated by the linear term of Eq. 4 (Kramers and Krayger, 1956; Acrivos et al., 1960).

The approximate linear velocity at a given distance $x$ from the leading edge of the plate is given as (Skelland, 1967)

$$\frac{u}{u_\infty} = \frac{3}{2}\frac{y}{\left\{\frac{280}{39}(n+1)\left(\frac{3}{2}\right)^n\right\}^{1/(n+1)}\left(\frac{x^n u_\infty^{2-n}\rho}{K}\right)^{-1/(n+1)}x} \tag{5}$$

Equation 1 can be solved readily by the technique for Newtonian fluids used by Mixon and Carberry (1960).

The average transfer coefficient becomes

$$\bar{k} = \frac{\int_0^x \frac{-\mathcal{D}\partial c/\partial y|_{y=0}}{\Delta c}dx}{x}$$

$$= 2^{-1/(n+1)}A_1(n)u_\infty{}^{1/(n+1)}X^{-(n+2)/3(n+1)}D^{2/3}/(K/\rho)^{1/3(n+1)} \tag{6}$$

where

$$A_1(n) = \frac{9(n+1)}{2n+1}\frac{1}{\Gamma(1/3)} \times \left[\frac{2^{(2-n)(m+1)}(n+2)}{3(n+1)\left\{\frac{280}{39}(n+1)\left(\frac{3}{2}\right)^n\right\}^{1/n+1}}\right]^{1/3}$$

If the velocity at the boundary-layer edge, $u_\infty$, is expressed in terms of the average as $u_\infty = 2u_a$, the average Sherwood number is

$$\overline{Sh} = A_1(n)Re_a^*{}^{(n+2)/3(n+1)}Sc_a^*{}^{1/3} \tag{7}$$

For $n = 1$, this equation reduces to

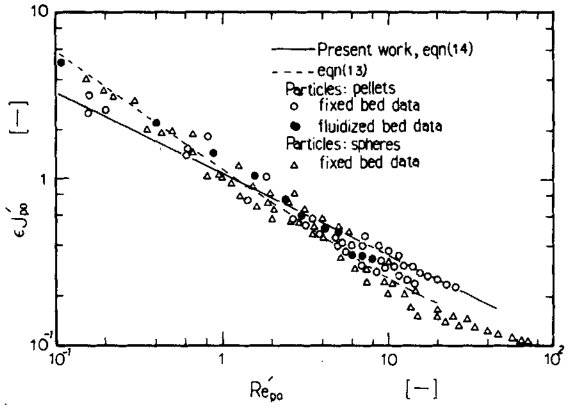

**Figure 1.** $\epsilon J'_{po}$ **vs.** $Re'_{po}$ **(data by Kumar and Upadhyay, 1980, 1981).**

$$\overline{Sh} = 1.20\, Re_a{}^{1/2}Sc^{1/3} \tag{8}$$

which is an equation identical to that derived by Carberry (1960) except for the slightly different coefficient. Carberry's equation

$$\overline{Sh} = 1.15\, Re_a{}^{1/2}Sc^{1/3} \tag{9}$$

was derived using the velocity profile expressed as

$$\frac{u}{u_\infty} = \frac{y}{\sqrt{12\nu x/u_\infty}} \tag{10}$$

in the boundary layer instead of Eq. 5.

### Mass Transfer in a Granular Bed

Equation 9 has been successfully applied in the prediction of Newtonian fluid-particle mass transfer in granular beds (Carberry, 1960). Therefore, it is expected that Eq. 7 can be applied to estimate mass transfer between particles and a non-Newtonian fluid in granular beds with reasonable accuracy.

An approximate average velocity in a granular bed, $u_a$, is given by

$$u_a = \frac{u_o}{\epsilon} \tag{11}$$

where $u_o$ is the superficial velocity and $\epsilon$ the void fraction in a granular bed.

Substituting Eq. 11 into Eq. 7 and using the nomenclature of Carberry (1960), i.e., replacing $x$ by $D_p$, the following relationship may readily be obtained

$$\overline{Sh_p} = A_1(n)\epsilon^{-1/n+1}Re_{po}^*{}^{n+2/3(n+1)}Sc_{po}^*{}^{1/3} \tag{12}$$

Kumar and Upadhyay (1980, 1981) measured the rate of dissolution of benzoic acid particles in granular beds. Fluid used in their experiments is 1% aq. CMC solution and test particles used are pellets and spheres of benzoic acid. They correlated their experimental data with an empirical correlation

$$\epsilon J'_{po} = \frac{0.765}{Re'_{po}{}^{0.82}} + \frac{0.365}{Re'_{po}{}^{0.386}} \tag{13}$$

Equation 12 can be rewritten in the form of the mass transfer factor as

$$\epsilon J'_{po} = A_2(n,\epsilon)Re'_{po}{}^{-2n+1/3(n+1)} \tag{14}$$

where

$$A_2(n,\epsilon) = A_1(n)\epsilon^{n/n+1}\left\{12\frac{(1-\epsilon)}{\epsilon^2}\right\}^{n-1/3(n-1)}\left(\frac{3n+1}{4n}\right)^{n/n+1}$$

Figure 1 compares experimental data of Kumar and Upadhyay (1980, 1981) with our model and with the empirical Eq. 13. A value of $\epsilon = 0.6$ is assumed since Kumar and Upadhyay (1980, 1981) did not report values for the void fraction. The agreement between our model and experimental data, as expected, is very good for 0.01 $<Re'_{po} < 40$. Unfortunately, no other experimental data set is available to assess the range of validity of the proposed model. The Carberry model for Newtonian fluids is valid to about $Re = 1{,}000$. It is particularly important to realize that our Eq. 12 does not contain any adjustable parameters. It may, therefore, be concluded that the present model yields a satisfactory representation of non-Newtonian fluid-particle mass transfer in granular beds.

## NOTATION

$A_1(n)$ = function of flow index defined by Eq. 6
$A_2(n,\epsilon)$ = function of flow index and void fraction defined by Eq. 14
$c$ = *concentration at any point in the fluid*
$c_w$ = concentration at surface
$c_\infty$ = bulk concentration
$D_p$ = particle diameter
$\mathcal{D}$ = diffusivity coefficient
$J'_{po}$ = $\frac{\bar{k}}{u_o} Sc'_{po}{}^{2/3}$, mass transfer factor
$K$ = consistency index in power-law model
$K'$ = $K\left(\frac{3n+1}{4n}\right)^n$, modified consistency index
$\bar{k}$ = average mass transfer coefficient
$n$ = flow index in power-law model
$Re$ = $xu/\nu$, Reynolds number
$Re^*$ = $x^n u^{2-n} \rho/K$, Reynolds number
$Re'_{po}$ = $D_p^n u_o^{2-n} \rho/K' \left\{12 \frac{(1-\epsilon)}{\epsilon^2}\right\}^{n-1}$, Reynolds number
$Sc$ = $\nu/\mathcal{D}$, Schmidt number
$Sc^*$ = $Kx^{1-n}/u^{1-n}\rho\mathcal{D}$, Schmidt number
$Sc'_{po}$ = $K' \left\{12 \frac{(1-\epsilon)}{\epsilon^2}\right\}^{n-1} D_p^{1-n}/u_o^{1-n}\rho\mathcal{D}$, Schmidt number
$\overline{Sh}$ = $\bar{k}x/\mathcal{D}$, average Sherwood number
$u$ = velocity component along $x$
$u_a$ = average velocity
$u_o$ = superficial velocity
$u_\infty$ = velocity at boundary layer edge
$x$ = distance along the surface
$y$ = distance normal to the surface

### Greek Letters

$\delta$ = hydrodynamic boundary layer thickness
$\epsilon$ = void fraction
$\nu$ = kinematic viscosity
$\rho$ = density
$\tau_{xy}$ = shear stress

### Subscripts

$a$ = based on $u_a$
$p$ = based on $D_p$

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# Activity Coefficients of Mixtures Adsorbed on Heterogeneous Surfaces

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Negative deviations from Raoult's law have been reported for the adsorption of mixtures on heterogeneous surfaces like activated carbon and silica gel (Minka and Myers, 1973; Peisen and Tiren, 1979; Costa, Sotelo, Calleja and Marrón, 1981). In such cases it is impossible to make accurate predictions of mixed gas adsorption equilibria using the method of ideal adsorbed solutions (IAS) (Myers and Prausnitz, 1965; Sircar and Myers, 1973).

The nature of these adsorbed-phase nonidealities is very interesting. For mixtures of aliphatic and aromatic hydrocarbons, the adsorbed solutions exhibit strong negative deviations from Raoult's law. Activity coefficients at infinite dilution are about 0.5 to 0.7, and the curves for activity coefficients are asymmetric about the equimolar composition as shown on Figure 1. This solution behavior is surprising because liquid mixtures of these hydrocarbons have moderate positive deviations from Raoult's law, and the activity coefficients are nearly symmetric about $x_1 = \frac{1}{2}$.

One explanation of this anomalous behavior is that the surface perturbs the interactions of the adsorbed molecules to such an extent that there is no correlation between the excess free energies of adsorbed solutions and bulk liquid solutions. If this were the case, one would expect some mixtures to show positive deviations from Raoult's law and others to show negative deviations. Since all of the excess free energies are negative and uncorrelated with bulk liquid properties, it is possible that the phenomenon is not explained by