NOTATION

$f(x, y)$ = general function of dependent variables x and y
$g(x, y, \epsilon)$ = general function of dependent variables x, y and of parameter ϵ
t = independent variable
t_l = boundary layer length
$w(x, y)$ = general function of dependent variables x and y
x = nonstiff dependent variable
x_0, x_1 = nonstiff outer variables
X_0, X_1 = nonstiff inner variables
y = stiff dependent variable
y_0, y_1 = stiff outer variables
Y_0, Y_1 = stiff inner variables

Greek Letters

ϵ = bookkeeping indication of degree of stiffness
ζ = initial condition on nonstiff variable
η = initial condition on stiff variable
α = dimensionless constant
λ_i = ith eigenvalue
ρ = spectral radius
τ = expanded inner t scale, t/ϵ

Subscripts

x = partial derivative with respect to x
y = partial derivative with respect to y
0 = zeroth-order expansion in ϵ
1 = first-order expansion in ϵ

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Prediction of "Tortuosity Factors" from Pore Structure Data

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In a recent paper the author has proposed a new network permeability model of porous media (Dullien, 1975) consisting of a set of cubic networks of arbitrary orientation with respect to the macroscopic flow direction. This model has resulted in the following formula to predict permeabilities:

$$k_m = \frac{\epsilon}{96\, \Sigma_i \Sigma_j V_{ij}} \sum_i \frac{(\Sigma_j V_{ij}/D_j^2)^2}{\Sigma_j V_{ij}/D_j^6} \tag{1}$$

where ϵ is the porosity corresponding to the pores considered in the calculations and V_{ij} is the volume of the pores of diameter D_j, the entry to which is controlled by pore necks of diameter D_i. The bivariate pore size distribution V_{ij} can be estimated from the mercury intrusion porosimetry and the photomicrographic pore size distribution curves of the sample. In the same paper the author has shown that a cubic network of capillary tubes has isotropic permeability which is independent of the orientation of the network. The calculations have shown that the network behaves in every orientation as if 1/3 of the tubes were conducting, resulting in the factor 3 × 32 in the denominator of Equation (1). In other treatments (Haring and Greenkorn, 1970; Johnson and Stewart, 1965; Wiggs, 1958), it has been shown that for pores of random orientation also a factor of 1/3 results as compared with the factor 1 for the case when all the pores are lined up parallel to the macroscopic flow direction. Often it has been the custom to call the reciprocal of this factor tortuosity T.

Equation (1) has been applied successfully to highly compacted materials of very different permeabilities (Dullien, 1975).

In the case of pore diffusion and of electric conductivity measurements in porous media, a different kind of tortuosity X has been defined by the equation (Wyllie and Rose, 1950; Cornell and Katz, 1953)

$$F = \frac{X}{\epsilon} \tag{2}$$

where

$$F \equiv \frac{D_{12}}{D_{12,\mathrm{eff}}} = \frac{\rho_0}{\rho_w} \tag{3}$$

Here D_{12} is the binary diffusion coefficient in a mixture of substances 1 and 2, and $D_{12,\mathrm{eff}}$ is the corresponding effective diffusion coefficient measured in the porous solid. ρ_0 is the specific resistance of the porous medium to the flow of the electric current through a conducting fluid filling the entire pore space and ρ_w is the resistivity of the conducting fluid in the bulk state. F is often called the *resistivity factor.*

The tortuosity X defined by Equation (2), unlike the tortuosity T, depends on the degree of constrictedness of the capillaries. This can be easily demonstrated on the example of a porous medium consisting of identical parallel capillaries with periodic step changes in their diameter. For this kind of porous medium, the tortuosity T is equal to 1. For X, however, the following expression is readily obtained by using Equations (2) and (3):

$$X = \frac{(1 + x^2 y)(1 + y/x^2)}{(1 + y)^2} \tag{4}$$

where $x = D_l/D_s$ and $y = l_l/l_s$. D_l and D_s is the diameter of the large and small capillary segments, respectively, and l_l and l_s are the corresponding lengths. The same expression was derived a long time ago by Michaels (1959). It is evident from Equation (4) that as x increases without limit, X will also increase indefinitely. This phenomenon can be probably best understood if one imagines that in every continuous capillary path in a porous medium at some point a tiny orifice is installed whose opening is chosen arbitrarily small as compared with the capillary diameter. By this artifice the porosity and the effective path length would be changed only negligibly; nevertheless the value of X could be made arbitrarily great. For this reason the quantity X should not be called *tortuosity* at all because it measures also an effect which is not due to the tortuousness of the paths in the medium. The confusion which has been noted in the literature is exemplified by the following typical statement (Schopper, 1966): "That the rock resistivity exceeds the electrolyte resistivity by the factor F is caused by two effects: first of all, by the reduction of the cross section available for conduction, from bulk cross section A to total pore cross section ϵA; secondly by the fact that the true current path length L_e exceeds the length L of the sample." It is obvious from this statement that the reduction of cross section available for conduction has been equated with the average reduction of cross section due to the presence of the solid matrix. The fact, however, that the effective cross section available for conduction can be much smaller than ϵA because of constrictions in the capillaries has been overlooked.

In the literature on heterogeneous catalysis (Satterfield, 1970), X has been split into the product of two factors

$$X = T \cdot S' \tag{5}$$

where T accounts for increased path length, and S' was called *shape factor.* The misnomer *tortuosity factor* for X, however, is still being used here, too. A better term for S' might be *constriction factor.*

As successful application of the author's network permeability model has shown (Dullien, 1975), the value of the tortuosity T can be expected to be equal to 3 or less. The same network model, however, can be used also to predict the value of X from the bivariate pore size distribution data. The derivation parallels that already published for the permeability calculation; therefore, details will not be given here. For each different controlling segment diameter D_i, a different network i is used. The pore size distribution is also different in each network i. It is assumed that the i networks are independent and, therefore, their conductivities are additive. The orientation of each network with respect to the direction of the macroscopic flux is arbitrary. The total current I_i in an i network is written as the sum of the currents in the capillaries pointing in the x, y, and z coordinate directions

$$I_i = (I_i)_x + (I_i)_y + (I_i)_z \tag{6}$$

After some algebra, one obtains

$$I_i = \frac{3\pi\ \Delta E}{4\rho_w \Sigma_j\, n_{ij}\, l_{ij}/D_j^2}\ (\cot^2\alpha + \cot^2\beta + \cot^2\alpha\,\cot^2\beta) \tag{7}$$

where ΔE is the drop in the potential between the two faces of the sample. l_{ij} is the length and n_{ij} the number, respectively, of capillary segments associated with the volume V_{ij}. α and β are the two angles defining the orientation of the sample with respect to the macroscopic flux. Using Equation (3) and the relations given in Dullien (1975) for the area of the face, the distance between the two faces of the sample in terms of the angles α and β, and the void fraction ϵ_i corresponding to the volume of the tubes in the i network, the final expression for F_i is obtained

$$F_i = \frac{3}{\epsilon}\ \frac{(\Sigma_i \Sigma_j V_{ij})(\Sigma_j V_{ij}/D_j^4)}{(\Sigma_j V_{ij}/D_j^2)^2} \tag{8}$$

From the assumption of additive conductivities of the i networks there follows

$$F = \frac{1}{\Sigma_i\,(1/F_i)} \tag{9}$$

Thus

$$F = \frac{(3/\epsilon)\ \Sigma_i \Sigma_j V_{ij}}{\displaystyle\sum_i \frac{(\Sigma_j V_{ij}/D_j^2)^2}{\Sigma_j V_{ij}/D_j^4}} \tag{10}$$

Comparing this with Equation (2) it is evident that

$$X = \frac{(3)\ \Sigma_i \Sigma_j V_{ij}}{\displaystyle\sum_i \frac{(\Sigma_j V_{ij}/D_j^2)^2}{\Sigma_j V_{ij}/D_j^4}} \tag{11}$$

where 3 is the value of the tortuosity T and the rest of the expression is the constriction factor S'.

Equation (11) permits the prediction of S' from pore structure data. It is important to point out that whereas Equation (1) for the permeability has the property that the terms corresponding to decreasing controlling pore entry diameters D_i rapidly become insignificant and thus negligible, this is not the case for Equation (11) obtained for X. When calculating permeabilities one can safely neglect the smallest pores, but in the calculation of X the entire range of pore sizes should be covered.

At the present there are no experimental data on F in the case of materials for which the bivariate pore size distribution has been evaluated. Instead, the predictions of Equation (11) have been used to obtain values for the exponent m in the time-honored relationship due to Archie (1942)

$$F = \epsilon^{-m} \tag{12}$$

for the 14 sandstone samples for which the bivariate distribution has been calculated. The values obtained for X range from 7 to 60 and the values of m range from 2.2 to 3.0. In the majority of the cases X is around 10 and m is around 2.5. These values are within the range reported for tightly compacted materials.

NOTATION

A = bulk cross section of sample
D_i = controlling pore entry diameter
D_j = pore diameter
D_l = diameter of large pore segment
D_s = diameter of small pore segment
D_{12} = binary diffusion coefficient
$D_{12,\mathrm{eff}}$ = effective diffusion coefficient
E = electric potential
F = quantity defined by Equation (3)
I = current
k_m = permeability predicted by Dullien's model
l_{ij} = length of a pore segment associated with the volume V_{ij}
l_l = length of a large pore segment
l_s = length of a small pore segment
L = length of sample
L_e = effective path length in sample
m = quantity defined in Equation (12)
n_{ij} = number of pore segments associated with the volume V_{ij}
S' = quantity defined by Equation (5)
T = tortuosity
V_{ij} = bivariate pore volume distribution
x = D_l/D_s
X = quantity defined by Equations (2) and (3)
y = l_l/l_s

Greek Letters

α = angle defining orientation of sample with respect to direction of macroscopic current
β = angle defining orientation of sample with respect to direction of macroscopic current
ϵ = porosity
ρ_0 = specific resistivity of porous medium saturated with electrolyte
ρ_w = specific resistivity of electrolyte

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A Solution for the Oxygen Mass Transfer Problem in Immobilized Enzyme Systems

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The kinetic limitations due to oxygen transfer problems were widely described in chemical and biochemical engineering (Ryu et al., 1973, Topiwala and Hamer, 1973). This subject was especially studied in the field of industrial fermentors. In the growing field of immobilized enzymes, not only has the problem not been solved, but also it has never been clearly studied. Numerous papers (Weetall, 1974) have been devoted to immobilized enzymes and recently reviewed (Gryszkiewicz, 1971; Goldman, 1971).

The aim of this note is to show that in immobilized enzyme systems the oxygen can be generated inside the support itself through another enzyme reaction. The basic principle of the described solution is the existence of substrate and product concentration profiles inside the support (Thomas et al., 1974; Barbotin and Thomas, 1974). In the experimental system glucose-oxidase (E.C. 1.1.3.4.—Sigma) and catalase (E.C. 1.1.1.1.6.—Sigma) are immobilized inside proteic membranes with a co-cross-linking method previously described (Broun et al., 1973). The glucose-oxidase catalyses the transformation of glucose into gluconic acid and H_2O_2 in presence of oxygen. Its kinetics were monitored at *p*H 8, the optimum *p*H for the immobilized enzyme, in a phosphate solution 5.10^{-3}M by injection of NaOH in with a *p*H-stat (Metrohm). Due to the *p*H value and the presence of lactonase, the lactone decomposition is not the limiting stop of the overall reaction. Under steady state conditions, the enzyme activity is given by the measurement of the H^+ production.

The catalase transforms H_2O_2 into water and oxygen. The reaction rate was followed spectrophotometrically at 240 nm. In both experiments performed with free and immobilized catalase and glucose oxidase, activities were respectively 7500 I.U. (with H_2O_2 10^{-2}M) and 250 I.U. (with a glucose solution of 20 g/l) 100-ml bath solution. The Thiele modulus values for the catalase are 186 and 5.8 for the glucose-oxidase. The diffusion coefficients were

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