Macrotransport of a biologically reacting solute through porous media

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Abstract. A physically based model is developed to study the transport of a solute utilized by microorganisms forming a biofilm coating on soil grains in a porous medium. A wavy-walled channel is used as a geometrical model of a porous medium and a biofilm is attached to the channel wall. Within the biofilm the solute is consumed according to a first-order volumetric rate. A numerical study is performed to obtain the dependence of the macrotransport coefficients on the Peclet number and Damkohler number. It is found that in some cases of practical importance the pore fluid is not well mixed, and mass transport limitations can control macroreaction rates. For diffusion-limited cases (large Damkohler numbers) increased solvent velocity can enhance the macroreaction rate by a factor of almost 3. Mean solute and mean solvent velocities are, in general, not equal, and mean solute velocities can exceed mean solvent velocities by 60% at high Damkohler numbers. These results agree qualitatively with those of a previous numerical study by Edwards et al. [1993]. The results also suggest that due to the spatially variable pore geometry, the biomass nearest the pore throat is more effective at consuming the solute than biomass in the pore chamber. A comparison is made between mass transfer correlations and the results determined for the macroreaction rate coefficient. We find that over a limited range of Peclet numbers a macroscale Sherwood number follows the \( \text{Pe}^{1/3} \) behavior determined from experimental mass transfer correlations and predicted by boundary layer theory.

1. Introduction

In practical applications of groundwater modeling we are interested in describing the solute transport phenomena at a scale much larger than the scale at which the generative underlying processes take place. Typically, the underlying physicochemical processes are best understood and quantified at the small scale. For example, diffusion coefficients or biological reaction rates have succinct descriptions at the pore scale. In practice, however, we make measurements and model transport phenomena at a scale much larger than the pore scale. This research is aimed at furthering our understanding about how, and when, pore-scale processes influence macroscale transport phenomena. One objective of this research is to determine the Darcy-scale macrotransport coefficients for a solute, which at the pore scale is transported by diffusion and advection and is consumed by a first-order volumetric reaction. Solute consumption occurs within a biofilm attached to the porous medium.

The approach presented herein is based on a detailed description of the mechanisms thought to be significant in the biodegradation of a reactive contaminant, including: (1) the pore water velocity field through a channel with spatially variable geometry; (2) spatially variable diffusion in the pore water, biofilm and solid matrix; and (3) first-order volumetric reaction rates confined within a biofilm. A physically based mathematical model representing the above mentioned microscale processes is developed. Then an upscaling procedure, known as the moment method [Shapiro and Brenner, 1988], is employed to obtain the macrotransport parameters which describe the transport of the spatially averaged solute concentration.

Using the moment method to obtain the macrotransport coefficients from the microscale processes requires spatially averaging, over an appropriately large volume, the equations governing the pore-scale solute transport. If \( C \) is the concentration the microorganisms experience in the pore fluid, then the concentration we actually measure and intend to model is

\[
\bar{C} = \frac{1}{V_f} \int_{V_f} C(x, t) \, dx
\]

where \( V_f \) is a representative fluid volume within a bulk volume \( V \) of porous medium. We are interested in how the transport of \( \bar{C} \) depends upon the cumulative and interacting effects of pore-scale structural features (pore geometry), pore-scale transport mechanisms (diffusion, advective mass transfer), and pore-scale reaction rates (reaction rates within a biofilm). After a specified relaxation time it can be shown that the macrotransport equation governing \( \bar{C} \) is [Shapiro and Brenner, 1988]

\[
\frac{\partial \bar{C}}{\partial t} = \nabla \cdot \mathbf{D}^* \nabla \bar{C} - \mathbf{u}^* \cdot \nabla \bar{C} - \gamma^* \bar{C}
\]

where \( \mathbf{D}^* \), \( \mathbf{u}^* \), and \( \gamma^* \) are the constant (or, more precisely, slowly varying) Darcy-scale macrotransport coefficients of dispersion, velocity, and first-order volumetric reaction rate, respectively. Our aim is to study the dependence of these macrotransport coefficients upon the pore-scale mechanisms. A related numerical study was performed by Edwards et al.
308

DYKAAR AND KITANIDIS: MACROTRANSPORT OF BIOLOGICALLY REACTING SOLUTE

Figure 1. Pore-scale conceptual model of a saturated porous medium with biofilm based on the film theory.

[1993] for a two-dimensional model of porous media consisting of circular cylinders. At the cylinder surface the solute undergoes a first-order surface reaction. Edwards et al. [1993] used the same moment method procedure to obtain the governing equations for macrotransport coefficients but different numerical techniques for their evaluation. The effect of packing geometry, microreaction rates, solvent velocities, and molecular diffusion rates on the Darcy-scale macrotransport coefficients was studied. Our determination of macrotransport coefficient dependence upon the microscale processes agrees qualitatively with those reported by Edwards et al. [1993]. Precise, quantitative agreement was not expected because of the differing pore geometries, and that in our model, reactions took place within a biofilm of finite thickness.

The contributions of this paper are the following: (1) our study serves as independent verification of the results found by Edwards et al. [1993] despite the differences in pore geometry and microscale specification of the first-order reaction; (2) we demonstrate the use of a powerful numerical technique for the solution of the nonself-adjoint governing equations; (3) we compare the results of this study to those obtained from experimental mass transfer correlations and boundary layer theory; and (4) our results are put in the context of biologically reactive transport and provide guidelines for when mass transfer limitations might be important and how to adjust the reaction rate to account for such limitations.

2. Background

2.1. Conceptual Models

Mass transport rate limitations at the pore scale arise due to either physical or chemical nonequilibrium [Harmon et al., 1989; Weber et al., 1991]. For example, physical nonequilibrium between aqueous and nonaqueous solute concentrations may play a significant role in aqueous phase mass transport [Miller et al., 1990]. Biological consumption of chemicals can also cause nonequilibrium if the rate of reaction is rapid enough relative to rates of diffusive and convective mass transport resulting in significant concentration gradients [Rifai and Bedient, 1990; Anderson and McCarty, 1994]. Consider the transport of a biologically reactive solute through a porous medium with the microorganisms forming a biofilm on the surfaces of the grains. Figure 1 shows how this system is commonly conceptualized for obtaining the connection between the pore-scale concentrations experienced by the microorganisms and the Darcy-scale concentrations appearing in the macrotransport equations used in models [Jennings et al., 1976; Baveye and Valocchi, 1989]. The porous medium is compartmentalized into a bulk aqueous phase and a boundary layer which separate rates it from a biofilm. The bulk aqueous phase is assumed to be well mixed, so there are no concentration gradients present; all of the transport rate limitations from the bulk aqueous phase to the biofilm are lumped into a diffusional process across the boundary layer.

There is some disagreement in the literature on whether the transport of a biologically reacting solute is significantly influenced by mass transport limitations at the pore scale. Some researchers have included the effects of biologically induced nonequilibrium in Darcy-scale transport models [Widdowson et al., 1988; Chen et al., 1992], while some others have not [Kindred and Celia, 1989; Frind et al., 1990; Malone et al., 1993].

The conceptual model depicted in Figure 1 has its roots in the stagnant film theory originally developed by Nernst [Levich, 1962]. The main idea behind the stagnant film theory is that concentration gradients are confined within a thin static liquid layer separating two regions with distinct physical properties, say, at a solid-liquid boundary. All the resistance to mass transfer from the solid surface to the liquid is assumed to occur across the static liquid film and is modeled as a diffusional process. Due to the limitations imposed by a static film in Nernst's theory, it was conceptually generalized to include mass transfer in a moving fluid into a so-called film theory [Levich, 1962]. However, the film theory neglects fluid motion tangential to the solid-liquid boundary, which can be an important mechanism for mass transfer. Both the Nernst theory and the film theory are qualitative descriptions of the mass transfer process; they do not provide a means for the direct computation of the mass flux through the conceptualized thin film. Their usefulness for fluids in motion lies mainly as an empirical descriptor of the true underlying transport mechanisms.

The inadequacies of the film theory for use with moving fluids lead to the application of boundary layer theory [Batchelor, 1979] to establish a more rigorous theoretical framework for describing and understanding convective mass transfer. In the boundary layer model at large Peclet numbers, concentration gradients are assumed large near the particle surface. For cases such as solutes in water, the Schmidt number (see Table 1) is also large, so near the particle surface velocity gradients are assumed to change less quickly than the concentration gradients. Hence a relatively thin concentration boundary layer is assumed to form near the particle surface, across which the velocity gradient is assumed constant.

2.2. Darcy-Scale Transport Modeling With Mass Transfer Limitations

According to both the film theory and boundary layer theory, the rate of mass transfer between two phases is a function of a linear driving force created by a concentration gradient and an interfacial area between the phases. Referring to Figure 1, for a boundary layer of thickness \( \delta \) and a solute with liquid diffusivity \( D \), the mass flux \( J [M/L^2 T] \) through the boundary layer is proportional to the linear driving force supplied by the concentration difference across the boundary layer.

\[
J = \frac{D}{\delta} (C_a - C_b) = k (C_a - C_b)
\]  

(3)

where the constant of proportionality is the mass transfer coefficient \( k[L/T] \). To use this concept in a Darcy-scale transport equation, the interfacial area \( A \) per unit volume of pore fluid \( V_f \) or, specific surface area \( a_s = A/V_f [1/L] \), of the
where \( K \) is the mass transfer rate coefficient.

A recent development in theories for upscaling, there is potential for using a more systematic analysis than that provided by theories yielding mass transfer coefficients, is the extremely complex geometry of the boundary surfaces of individual grains in natural porous media. However, with the recent increases in computational speed, improvements in numerical methods, and refinements in theories for upscaling, there is potential for using a more physically based approach than either the film or boundary layer theories. A physically based model will capture more faithfully the interplay between the macroscopic processes of diffusion, advection, and reaction, which produce the macroscopic phenomena we are interested in.

The upscaling methodology applied in this study to obtain the macrotransport coefficients was developed by Shapiro and Brenner [1986, 1987, 1988] and herein will be called the moment method. The moment method has its roots in the technique originally used by Aris [1956] to analyze dispersion of a conservative solute flowing through a tube. Shapiro and Brenner [1986, 1987, 1988] significantly generalized Aris’s approach for multidimensional flow including first-order chemical reactions in bulk and on boundaries.

### 3. Problem Formulation: Pore-Scale Model

This section contains a description of our pore-scale model. We are restricted, for computational reasons, to use relatively simple geometrical models of a porous medium. However, the selected geometry has at least some of the essential features which might reasonably be thought to affect the macrotransport parameters, such as converging and diverging flows through restrictions and openings.

#### 3.1. Pore Geometry

A wide variety of pore space models have been proposed in an effort to simulate flow and other phenomena in porous media. This work considers an undulating channel, symmetric about its centerline \( x_2 = 0 \). A cell of size \( L_1 \times L_2 \) is shown in Figure 2. The rock matrix is covered by a biofilm of depth \( b \),...
and the height function $h$ specifies the distance between the surface of the biofilm and the centerline $x_2 = 0$. In subsequent numerical experiments the height function is taken to be the sinusoid,

$$h(x_1) = \frac{\bar{w}}{2} + a \cos \left( \frac{2\pi x_1}{L_1} \right)$$

(6)

where $\bar{w}$ is the average channel width and $\bar{w} + 2a$ is the maximum channel width ($a < \bar{w}/2$). Figure 2 shows the base case geometry used in most of the numerical work to follow. The parameter values are provided in the figure caption. The biofilm occupies 29% of the fluid volume $V_f$. The pore size is on the order of a coarse sand [de Marsily, 1986].

### 3.2. Flow Field

Groundwater motion is typically slow, and the fluid is practically incompressible. Low Reynolds number flow through the channel is governed by the Stokes and mass balance equations,

$$\nabla p = \mu \nabla^2 v \quad \nabla \cdot v = 0$$

(7)

where $p$ is the pressure and $\mu$ is the viscosity. The velocity within the biofilm and rock matrix is taken to be zero. There is a no-slip boundary condition at the surface of the biofilm.

A simple and easily evaluated solution to (7) with the no-slip boundary condition is desired for this work. A perturbation solution was found to be suitable for our purposes. Assuming gradual variations in the channel height, a small expansion parameter $\varepsilon$ is identified:

$$\varepsilon = \frac{\bar{w}}{L_1}$$

(8)

Using the fact that the macropressure gradient is the same across any single period of the channel, a series solution to the Stokes equation in powers of $\varepsilon$ for the stream function $\psi[L^2/T]$ is derived:

$$\psi(x) = Q_{\psi}[\psi_0(x) + \varepsilon^2 \psi_2(x) + \varepsilon^4 \psi_4(x) + \cdots]$$

(9)

where $Q_{\psi} = -\bar{p}x\bar{w}^2/12\mu$

The stream function and velocity vector are related by

$$v_1 = \frac{\partial \psi}{\partial x_2} \quad v_2 = -\frac{\partial \psi}{\partial x_1}$$

(10)

The functions $\psi_n$ are the approximate stream functions of order $n$ associated with the corresponding power of the parameter, $\varepsilon^n$. The factor $Q_{\psi}[L^2/T]$ is the flux per unit depth through a straight channel of width $\bar{w}$ and macropressure gradient $\bar{p}$, across one period of the channel. Due to the channel symmetry about the centerline $x_2 = 0$, only the even-ordered terms are nonzero, and terms up to fourth order have been used in this work. The approximate streamfunctions used are provided in the appendix as (A1) through (A3). Due to the assumption of low Reynolds number, or inertialless flow, the approximate stream functions are functions of only the confining geometry $h(x_1)$, while viscosity and macropressure gradient appear only as a scaling factor in (9).

The total flux is given by the difference between the stream function at the upper and lower channel boundary,

$$Q = \psi(x_1, h) - \psi(x_1, -h) = Q_{\psi}[8C_0 + \frac{2}{3} \varepsilon^2 C_2 - \frac{2}{3} \varepsilon^4 C_4 - \cdots]$$

(11)

where the constants $C_0$, $C_2$, and $C_4$ are also given in the appendix as (A4) through (A6). The mean water velocity through the channel is then

$$\bar{v}_1 = \frac{Q}{\bar{w}} = \frac{\bar{w}^2}{12\mu} \left[ 8C_0 - \frac{2}{3} \varepsilon^2 C_2 - \frac{2}{3} \varepsilon^4 C_4 \right]$$

(12)

The terms in braces in (12) are grouped to highlight the fact that at the macroscale, the flow obeys Darcy’s law; that is, the macrovelocity is proportional to the macropressure gradient.

Hasegawa and Izuchi [1983] used an identical perturbation technique to obtain the stream function for a channel geometry different than the one used here, and the reader is referred to their work for more details about the derivation. Hasegawa and Izuchi [1983] report good agreement between the perturbation solution and a finite difference discretization and numerical solution of (7). We note that each approximate stream function $\psi_n$ given in (A1) through (A3) individually satisfies the mass balance condition and the boundary conditions.

To evaluate the stream function, one only needs to determine the derivatives of $h(x_1)$ shown in (A1) through (A3) and perform the integrations given by (A4) through (A6) to get the constants $C_0$, $C_2$, and $C_4$. An example flow field used later is shown in Figure 3. To emphasize, since the fluid is assumed inertialless, the streamline contour shapes shown do not change with applied macropressure gradient; only the total flux $Q$ will vary. For this particular pore geometry viscous eddies appear in the pore chamber. Moffatt [1964] was the first to predict the presence of viscous eddies in creeping flow near a sharp corner. Subsequent experimental [Van Dyke, 1982] and numerical [Pozrikidis, 1987] studies on viscous eddies have been performed for a variety of boundary geometries. In this particular case the viscous eddies shown in Figure 3 are quite weak and may be an artifact of the perturbation solution. From the stream function the velocity field is found using (10), while the total flux through the channel is given by (11), and average pore water velocity is found from (12).

### 3.3. Microbial Distribution and Biochemical Kinetics

#### 3.3.1. Biofilm model

The spatial distribution of attached microorganisms in the pore space of a porous medium is cur-
Figure 3. Streamlines for the base case geometry defined in Figure 2. The total flux through the channel is $Q$, and the solid lines are spaced $Q/8$. The dotted lines are spaced $Q/80$, and only four above and below the streamlines $+Q/2$ and $-Q/2$ are shown to visually resolve the flow near the viscous eddies.

Currently the subject of debate [Rittmann, 1993]. Some researchers support the view that bacteria form continuous biofilms on the surface of the porous medium structure at the solid-liquid interface [Williamson and McCarty, 1976; Taylor and Jaffe, 1990; Cunningham et al., 1991]. Other evidence suggests that bacteria colonize the pore space in isolated aggregates [Vandevivere and Baveye, 1992]. Both views of microbial colonization may be valid, and the reconciliation may lie in distinguishing between different environmental conditions [Rittmann, 1993]. In this study the bacteria are assumed to form a continuous biofilm on the surface of the rock matrix.

Biofilms being about 97% water by mass, solute diffusion coefficients in the biofilm are near their aqueous values, typically between 80% and 100% [Williamson and McCarty, 1976]. In this study the solute diffusion coefficient within the biofilm is taken as 80% of its aqueous value. Since the biofilm is permeable, it is possible that bulk water motion through the porous medium may induce flow in the biofilm. In the absence of experimental data, water within the biofilm is assumed to be stagnant in this work. Nonzero water velocities in the biofilm may readily be included in this model if deemed important.

3.3.2. Microbial kinetics. The composition of the biomass within the biofilm is probably quite complex. The biomass may be composed of several fractions with differing biological properties. For example, the biomass may consist of an active fraction which can consume the solute and an inert fraction resulting from cellular decay [Anderson and McCarty, 1994]. The active and inert fractions may also exhibit a particular spatial structure, with the active fraction being nearest the biofilm surface and decreasing with depth to the rock matrix. For simplicity the biofilm is assumed to be uniform and composed of all active cells. This model could be used to explore the effects of biofilm composition on macrotransport parameters, but it is not the focus of this study. Spatially variable biofilm composition can be included in this model as a spatially variable volumetric reaction rate within the biofilm.

The microbial kinetics within the biofilm are described by a Monod relationship [Pavlostathis and Giraldo-Gomez, 1991],

$$\frac{dC}{dt} = -\alpha C \quad C \ll K_s \quad (13)$$

where $k[1/T]$ is the maximum utilization rate for the solute, $X_s[M/L^3]$ is the dry biomass density, and $K_s[M/L^3]$ is the half-saturation constant for the solute. At most groundwater remediation sites the concentration of the contaminant in solution is relatively low compared to its half-saturation coefficient [Semprini and McCarty, 1992]. Then the kinetic equation above becomes approximately first-order,

$$\frac{dC}{dt} = -\alpha C \quad C \ll K_s \quad (14)$$

where the first-order reaction rate within the biofilm is

$$\alpha = \frac{kX_s}{K_s} \quad (15)$$

To obtain the first-order volumetric reaction rate within the biofilm given by (15), we will need estimates for $k$, $X_s$, and $K_s$ which will depend on the particular environment and microorganisms.

As an example, for methanotrophic biofilms we have the following values. The biofilm density has been measured to be about 0.03 g/cm$^3$ [Arvin, 1991]. For trichloroethylene (TCE) $k = 3.1 \times 10^{-5}$ s$^{-1}$ and $K_s = 4.2 \times 10^{-7}$ g/cm$^3$, while for methane $k = 3.6 \times 10^{-5}$ s$^{-1}$ and $K_s = 0.3 \times 10^{-7}$ g/cm$^3$ [Anderson and McCarty, 1994]. Using these values in (15) yields $\alpha = 2.2$ s$^{-1}$ for TCE and $\alpha = 36$ s$^{-1}$ for methane.

3.4. Governing Equations

Application of the moment method to obtain the macrotransport coefficients consists of the following steps [Shapiro and Brenner, 1988].

3.4.1. Microscale definition. The moment method requires that the medium and associated parameters be periodic so a representative unit cell can be identified. Within a unit cell the microtransport equation must be completely specified. The unit cell for $0 \leq x_1 \leq L_1$ and $0 \leq x_2 \leq L_2$ is shown in Figure 2, and the microtransport equation within the cell is

$$\frac{\partial C(x, t)}{\partial t} = \frac{\partial}{\partial x_1} \left( D(x) \frac{\partial C(x, t)}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( D(x) \frac{\partial C(x, t)}{\partial x_2} \right) - v_1(x) \frac{\partial C(x, t)}{\partial x_1} - v_2(x) \frac{\partial C(x, t)}{\partial x_2} - \gamma(x) C(x, t) \quad (16)$$

Referring to Figure 2, the parameter values in (16) are the following:

In the channel water

$$D(x) = D \quad v_1(x) = \frac{\partial \psi}{\partial x_2} \quad v_2(x) = -\frac{\partial \psi}{\partial x_1} \quad \gamma(x) = 0 \quad (17a)$$

In the biofilm

$$D(x) = 0.8D \quad v_1(x) = 0 \quad v_2(x) = 0 \quad \gamma(x) = \alpha \quad (17b)$$

In the rock matrix

$$D(x) = 0 \quad v_1(x) = 0 \quad v_2(x) = 0 \quad \gamma(x) = 0 \quad (17c)$$

3.4.2. Eigenvalue problem. The following eigenvalue problem must be solved within the unit cell
\[ \frac{\partial}{\partial x_1} \left( D(x) \frac{\partial E(x)}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( D(x) \frac{\partial E(x)}{\partial x_2} \right) - v_1(x) \frac{\partial E(x)}{\partial x_1} - v_2(x) \frac{\partial E(x)}{\partial x_2} - \gamma(x) E(x) = -\lambda E(x) \]  

(18)

for smallest eigenvalue \( \lambda_0 \) and the associated eigenfunction \( E(x) \). The boundary conditions for \( E(x) \) are periodic:

\[ E(L_{x_1}/2, x_2) - E(-L_{x_1}/2, x_2) = 0 \]  

(19a)

\[ E(x_1, L_{x_2}/2) - E(x_1, -L_{x_2}/2) = 0 \]  

(19b)

In general, another related eigenvalue problem, called the adjoint eigenvalue problem, must also be solved for a spatial weight function \( A(x) \) [Shapiro and Brenner, 1988]. The adjoint eigenvalue problem is given by (18), except that the signs on the velocity terms are positive. Due to the geometrical symmetry of this problem about the \( x_2 = 0 \) centerline, the solution to the adjoint eigenvalue problem is

\[ A(L_1 - x_1, x_2) = E(x_1, x_2) \]  

(20)

3.4.3. Macroelection rate. The macroreaction rate coefficient is the smallest eigenvalue,

\[ \gamma^* = \lambda_0 \]  

(21)

3.4.4. Normalization. Normalize the eigenfunctions \( E \) and \( A \) using the pair of normalization conditions,

\[ \int_{\gamma} E(x) \, dx = 1 \quad \int_{\gamma} A(x) E(x) \, dx = 1 \]  

(22)

3.4.5. Macrovelocity. The macrovelocity in direction \( x_1 \) is found by evaluating the following integral over the unit cell,

\[ u_1^* = \int_{\gamma} \left[ -A(x) D(x) \frac{\partial E(x)}{\partial x_1} + A(x) E(x) v_1(x) \right] \right. \]  

\[ + E(x) D(x) \frac{\partial A(x)}{\partial x_1} \right] \, dx_1 \, dx_2 \]  

(23)

The macrovelocity in direction \( x_2 \) is zero since the rock is impermeable.

3.4.6. Macrodistribution. Computation of the streamwise dispersion coefficient \( D_{1,1}^* \) is a two-step procedure. First, solve the differential equation for the spatial function \( B_1(x) \):

\[ \frac{\partial}{\partial x_1} \left( D(x) \frac{\partial B_1(x)}{\partial x_1} \right) + \frac{\partial}{\partial x_2} \left( D(x) \frac{\partial B_1(x)}{\partial x_2} \right) - v_1(x) \frac{\partial B_1(x)}{\partial x_1} - v_2(x) \frac{\partial B_1(x)}{\partial x_2} - \gamma(x) B_1(x) + \gamma^* B_1 \]  

\[ = E(x) \left[ u_1^* - v_1(x) \right] + 2D(x) \frac{\partial E(x)}{\partial x_1} + E(x) \frac{\partial D(x)}{\partial x_1} \]  

(24)

The boundary conditions for \( B_1(x) \) are periodic, as shown in (19a) and (19b) for \( E(x) \). Second, the desired element of the dispersion matrix is found by performing the integration

\[ D_{1,1}^* = \int_{\gamma} \left[ -A(x) D(x) \frac{\partial B_1(x)}{\partial x_1} + A(x) B_1(x) v_1(x) - u_1^* \right] \right. \]  

\[ + B_1(x) D(x) \frac{\partial A(x)}{\partial x_1} \right] \, dx_1 \, dx_2 \]  

(25)

3.5. Numerical Solution for the Macrotransport Coefficients

A numerical solution scheme capable of computing the desired macrotransport coefficients given an arbitrary set of microscale input parameters and periodic boundary conditions on the unit cell faces is outlined. Developing a robust numerical solution for this problem is a formidable task and some aspects of the numerical solution scheme presented are areas of current research. Aspects of this problem which make numerical solutions particularly challenging are the following: (1) the partial differential equations to solve are not self-adjoint; (2) a large number of discretization points are required to adequately represent the microscale features of the flow domain; and (3) the potentially very large values of the \( Pe \) number.

The eigenvalue problem given by (18) was discretized using second-order accurate, centered finite differences [Ames, 1977]. Iterative methods were used to solve for the smallest eigenvalue and associated eigenfunction [Golub and Van Loan, 1989]. Each iteration of the inverse iteration algorithm requires the solution of a system of linear algebraic equations, written in the usual matrix notation as

\[ Cz = f \]  

(26)

where \( C \) is the coefficient matrix, \( z \) is the vector of unknowns, and \( f \) is the right-hand side forcing function. Due to the presence of the advective term, the partial differential equations are, in general, not self-adjoint, and therefore the matrix \( C \) is not symmetric. Iterative solutions to nonsymmetric large, sparse systems of equations is an area of active research. The method used here to solve (26) is called quasi-minimal residuals (QMR) [Freund and Nachtigal, 1991]. QMR is a conjugate-gradient-type algorithm for nonsymmetric coefficient matrices. Like conjugate gradients, QMR requires a subroutine to perform matrix-vector multiplications, but it also requires matrix transpose-vector multiplications. The convergence rate of QMR is very dependent upon the eigenvalue distribution of the matrix \( C \); the more clustered the eigenvalues are about 1, the faster the convergence. Rates of convergence can be greatly improved with the proper preconditioning of the matrix \( C \) [Freund et al., 1992]. A tridiagonal preconditioner is used in this work and found to be moderately effective. Typically the inverse iteration procedure converged in about four or five iterations.

Equation (24) is solved similarly, discretized using the same finite differences procedure and the resulting matrix equation solved using preconditioned QMR. The integrations of (23) and (25) are performed using the rectangle rule of integration. The results were checked against an analytic solution in the case where the channel walls are flat [Lungu and Moffatt, 1982; Shapiro and Brenner, 1988]. Analytic solutions for flow in complicated geometries are not available in the literature.
4. Results and Discussion

The main results of this section show how the macrotransport coefficients depend upon the relevant dimensionless numbers. Unless otherwise stated, the pore geometry used is that shown in Figure 2 and the velocity field through the pore is shown in Figure 3. Our results agree qualitatively with those of Edwards et al. [1993]; precise quantitative agreement is neither expected nor obtained because of the respective differences in pore geometries and spatial distribution of reaction sites between our problem and that studied by Edwards et al. [1993]. The results are presented in terms of the relevant dimensionless numbers which are defined in Table 1. The reader is reminded that while the $Re$ number does not appear explicitly in the subsequent plots, figures, and discussion, it is assumed to be small. The $Re$ number can be obtained using the relation $Re = Pe/Sc$.

4.1. Normalized Solute Distribution

After sufficient time has elapsed and the solute has had time to sample the microscale variability, the eigenfunction $E(x)$ can be given the following physical interpretation. The spatial function $E$ is a normalized solute distribution, and it represents the solute distribution after averaging over a large number of representative pores or unit cells. The idea is similar to that of a nondimensional, fully developed temperature profile discussed in the heat transfer literature [Kays and Crawford, 1993]. The relaxation time required for the solute to attain this distribution is of the order $L^2/D$, which is a few minutes for coarse sand or fine gravel and much shorter for fine sand. The normalized solute distribution $E$ is the key for gaining insight into how the microscale processes interact to produce the macroscale phenomena we observe. From plots of $E$ one can see how microscale processes affect the long-term distribution of mass within the pores, which in turn is an important factor in determining and understanding the long-time macroscale behavior of concentration.

The series of plots in Figure 4 shows $E$ for a particular $Da$ number and four different $Pe$ numbers. The $Pe$ number is increased in each case by increasing the macropressure gradient across the pore and hence the solvent velocity through the pore. The first quality to notice about all the panels in Figure 4 is that the pore fluid is not well mixed; that is, there are steep gradients in $E$, tending generally from the pore center or centerline down to the biofilm. This means that there are transport limitations from what one would call, in mass transfer terminology, the bulk fluid to the reactive surface. Note that the peak concentration decreases as the velocity increases to $Pe = 100$ and then stays about constant. If we use peak concentration as a gauge of how well the pore fluid is mixed, we see that the increased velocity can help mix the pore fluid.
and thereby reduce solute transport limitations to the biofilm.

At the relatively low velocities of $Pe = 1$, $E$ is distributed almost symmetrically within the pore as shown in Figure 4a. The most likely place to find a solute particle is at the pore center, farthest away from the reactive biofilms. At the pore throat, $E$ is quite low, which means solute in this region is more readily transported to the biofilm. Therefore biomass in the pore throat contributes proportionally more to the observed macroreaction rate than an equivalent amount of biomass in the pore chamber. As the velocity is increased to $Pe = 10$ in Figure 4b, $E$ becomes more asymmetrically distributed. There is a dip in $E$ near the pore entrance, which shows that this region is more effective at getting the solute to the biofilm than the corresponding region at the pore exit. As the velocity is increased still further, we can see evidence of the viscous eddies becoming significant in Figures 4c and 4d. The decrease in $E$ within the eddy, from $Pe = 100$ to $Pe = 1000$, shows how the eddy's rotation increases transport from the chamber fluid to the reactive surface. At very large $Pe$ numbers the differential solute consumption at pore throat and chamber decreases, evidenced by the almost constant value of $E$ along the pore centerline ($x_2 = 0$) in Figure 4d.

The second series of illustrations in Figure 5 shows the effect of changing $Da$ number on $E$. At low values of $Da$, as in Figure 5a, the normalized solute distribution is almost flat. The flatness of $E$ shows that the pore fluid is pretty well mixed, with only minor transport limitations from the pore center to the biofilm, which are most pronounced at the pore throat. As the strength of the reaction or the pore size is increased, which increases the $Da$ number, the gradients in $E$ become much more pronounced. As before, the steep gradients in $E$ show that mass transfer limitations are important in the larger $Da$ number cases. Note also that the peak concentration increases proportionately with the $Da$ number, suggesting how well the pore fluid is mixed.

4.2. Macroreaction Rate Coefficient

It is common practice to present macroreaction rates in terms of effectiveness factors, such as with porous catalyst particles [Sherwood et al., 1975]. For porous particles the effectiveness factor is defined as the actual macroreaction rate divided by the rate of reaction if all reactive sites see the concentration at the particle surface; that is, there are no transport limitations within the particle, and the reaction rate attains its maximum value. A similar concept has been used for biofilms where the permeable biofilm is analogous to the porous particle and the reference concentration is taken as the concentration at the biofilm surface. In our case we desire an effectiveness factor for the entire pore, including the transport limitations within the biofilm. In general, the concentration at the biofilm surface is not constant (since the pore is not flat).
and we will define the effectiveness factor based on the average concentration $\bar{C}$. The macroreaction rate is

$$R_s = \gamma^* \bar{C} \quad (27)$$

while if there are no transport limitations, the maximum rate possible is

$$R_m = \frac{\bar{C}}{V} \int_{V} \gamma(x) \, dx \quad (28)$$

Note that since there are no transport limitations, the solute distribution within the pore is uniform and $\bar{C}$ is also the maximum concentration. The effectiveness factor is the ratio of (27) and (28),

$$\eta = \frac{R_s}{R_m} = \frac{\gamma^*}{(1/V) \int_{V} \gamma(x) \, dx} \quad (29)$$

The effectiveness factor $\eta$ is a dimensionless factor between 0 and 1. For effectiveness factors near 0 the reaction rate is being controlled by transport limitations to the reactive sites, while for effectiveness factors near 1 the reaction is proceeding near its maximum biochemically controlled kinetic rate.

Figure 6 shows the dependence of the effectiveness factor on the $Da$ number at zero velocity. Two pore geometries are shown, a flat pore and cosine pore. Both geometries have the same average width $\bar{w}$. At small $Da$ number, say, less than 10, the reaction rate proceeds near its maximum value, so the effectiveness factor is near unity. Hence for small $Da$ numbers, diffusional limitations are negligible and the reaction rate is controlled by the chemical kinetics within the biofilm as given by (15). As the $Da$ number increases, diffusional limitations become increasingly important, and the actual reaction rate can be reduced by orders of magnitude compared to the maximum chemically controlled kinetic rate. When diffusional transport limitations decide the phenomenological reaction rate, the process is termed diffusion-controlled reaction.

Now, comparing the relative reaction rates between the two pore geometries in Figure 6, we see that the reaction in the cosine pore always proceeds at a higher rate than that in the flat pore. The reason is that at the pore throat, the time it takes for the solute to diffuse from the fluid to the biofilm surface is greatly reduced by the narrow width at the throat. This decrease in the diffusional transport limitations to the reactive site more than compensates for the increase in solute travel time to the biofilm surface inside the wider pore chamber. As noted in the discussion above about the normalized solute distribution, proportionally more of the macroreaction is due to the biomass near the throat. If biomass growth is considered, then the biomass in the vicinity of the throat is consuming more and therefore growing faster than elsewhere. This can potentially have major implications for pore clogging. Since the flow through the channel is controlled by the pore throat, even small amounts of new biomass can drastically reduce the flow through the pore.

Figure 7 shows the effect of solvent velocity on the macroreaction rate coefficient. At small $Pe$ numbers, say less than 1, the effectiveness factor at all $Da$ numbers remains essentially at its respective zero velocity value. Not surprisingly, diffusion is the dominant transport mechanism at small $Pe$ numbers. At larger $Pe$ numbers, say greater than 1, increased solvent velocity will increase the macroreaction rate coefficient. The significance of the velocity in determining the macroreaction rate coefficient depends upon how diffusion-controlled the reaction rate is. When the $Da$ number is small, less than 10, diffusion is relatively rapid, and the increased transport of the solute to the biofilm surface provided by the flowing solvent does not add much to the macroreaction rate. This is also evident from Figure 5a, which shows the pore fluid to be essentially well mixed. For a larger $Da$ number, diffusional transport limitations are more significant, and the moving solvent does enhance the macroreaction rate. Figure 7 shows, as expected, that the velocity has more affect as the $Da$ number increases.

Edwards et al. [1993] found similar qualitative behavior in the macroreaction rate coefficient as that shown in Figure 7. Figure 7 shows that at the maximum $Da$ number studied, 10,000, fluid motion can enhance the macroreaction rate coefficient by a factor of about 3. From Table II of Edwards et al. [1993] one can compute, after removing their nondimensionalization factors, the increase in $\gamma^*$ due to an increase in $Pe$ from 1 to 100 at large $Da$ number. Edwards et al. [1993] find that for the staggered array packing of cylinders $\gamma^*$ is increased by a factor of about 1.75.

Figure 6. Effectiveness factor at zero velocity for two pore geometries. Both geometries have the same average width $\bar{w}$.

Figure 7. Normalized effectiveness as a function of the $Pe$ number. The effectiveness factor for each $Da$ number is normalized to its respective zero velocity value given in Figure 6.
From Figure 7 it is also evident that the enhancing effect of the velocity on the macroreaction rate coefficient reaches a point of diminishing returns at very large Pe number. There is a relatively large change in the macroreaction rate coefficient from \( Pe = 10 \) to \( Pe = 100 \), but less so from \( Pe = 100 \) to \( Pe = 1000 \). The reason is clear from plots of \( E \); there is a greater redistribution of \( E \) from \( Pe = 10 \) to \( Pe = 100 \) than there is from \( Pe = 100 \) to \( Pe = 1000 \). This phenomenon is explored further in a following section on mass transfer.

4.3. Macrovelocity

The mean velocity of a reactive solute can behave quite differently than that of the more familiar conservative tracer. To begin, consider the transport of an ideal conservative tracer governed by the advection-diffusion equation. Starting from any initial condition and for times greater than the relaxation time (greater than a few minutes), the mean solute velocity is equal to the mean water velocity, as demonstrated by Aris [1956], for flow through tubes. The reason that the solute and solvent travel at the same mean speed is that over the long term, a solute particle is equally likely to be in any solvent due to the random motion caused by molecular diffusion. There is no biasing force, or mechanism, to cause the solute to preferentially sample any one solvent speed over another. Therefore the solute samples all solvent speeds equally and, on average, moves at the average solvent speed. Mathematically, in the language of the moment method, this is expressed as \( E = \text{constant} \).

However, in the reactive case the situation can be quite different. In this case a bias can exist which makes, on average, the solute spend more time in certain streamlines than others. This unequal weighting of solvent velocities causes the solute to travel at a different mean speed than the solvent. Imagine making a slug injection of solute mass in the flowing solvent within a flat pore. As the solute moves downstream it spreads out due to molecular diffusion, and it disappears within the biofilm. A concentration gradient is formed from the centerline of the pore to the biofilm with the highest concentration at the pore centerline, the point most distant from the biomass. Due to the microscale bias created by the reactive biofilm, more solute mass is in the faster moving streamlines at the pore center, and less mass is in the slower moving streamlines near the channel walls. Then, for this particular flat wall geometry, the mean solute speed is greater than that of the solvent [Shapiro and Brenner, 1988].

The strength of the microscale bias can be seen in the function \( E \); the more \( E \) deviates from a constant value, the more unequally the solute will be distributed, and the more possibility there is for differences between mean velocities of solute and solvent.

The situation becomes more interesting for the cosine-shaped pore in this work. Figure 8 shows the normalized mean solute velocity as a function of the (solvent) Pe number for several Da numbers. It is evident that the average solute velocity depends both on the Pe number and the Da number. We first examine the effect of Da number on mean solute velocity. We see that the larger the Da number, the greater the variation in solute velocities over the range of solvent Pe numbers. This phenomenon can be explained by referring to Figure 5 and noting that the microscale biasing effect increases with increasing Da number. Next we examine the effect of solvent Pe number on mean solute velocity. Except for \( Da = 10 \), the other curves in Figure 8 exhibit a crossover point at about \( Pe = 8 \), where the mean solute and solvent velocities are equal. Above \( Pe = 8 \) the macrovelocity exceeds the mean solvent speed \( \bar{v}_1 \). This analysis suggests \( u^*_1 \) can be up to 60% larger than \( \bar{v}_1 \). Below \( Pe = 8 \), excepting \( Da = 10 \), the reverse is true: the macrovelocity is less than the mean solvent speed. In fact, \( u^*_1 \) decreases rapidly to a small fraction of \( \bar{v}_1 \) as the Pe number falls below 1. Edwards et al. [1993] obtain similar results for the mean solute velocity being greater or less than the mean solvent velocity depending on the Pe number at larger Da numbers. For the curve \( Da = 10 \), \( u^*_1 \) remains almost constant at about 75% of \( \bar{v}_1 \) over the range of Pe numbers. This behavior can be explained by recalling that the immobile water within the biofilm occupies about 29% of the pore fluid by volume. For a Da number of 10 the pore fluid is relatively well mixed, so about 29% of the solute mass is also immobilized in the stagnant water in the biofilm.

The reasons for the behavior of \( u^*_1 \) can partially be explained by examining the effect of microscale biasing on the solute distribution \( E \) within the pore. In Figures 4b through 4d for \( Pe = 10, 100, \) and 1000 we see that \( E \) is concentrated along the pore centerline and particularly in the pore throat, where from Figure 3 we know that the solvent speed is greatest. Hence for \( 10 < Da \) and \( 10 < Pe \), the solute preferentially samples the faster moving streamlines, and this explains why \( u^*_1 \) can exceed \( \bar{v}_1 \). However, for \( Pe = 1 \) we see from Figure 4a that \( E \) is greatest at the pore center where the solvent speed is the smallest, and \( E \) is very small in the pore throat where the solvent speed is by far the highest. Then, for small enough Pe numbers (less than about 8) and sufficiently large Da numbers (greater than about 100) \( u^*_1 \) is less than \( \bar{v}_1 \). For example, at \( Da = 1000 \) Figure 8 shows that below \( Pe = 1 \), \( u^*_1 \) is less than 5% of \( \bar{v}_1 \). In the case of small Da, around 10, the microscale bias is slight, as shown in Figure 5a, and \( u^*_1 \) is a very weak function of the solvent Pe number.

4.4. Macrodispersion

For an inert solute, dispersion in the channel is caused by the mechanisms of velocity shear and molecular diffusion. In a channel with flat walls the flow is unidirectional, so the method of moments of Aris [1956] can be readily adapted to this particular geometry. The dispersion coefficient can be found in closed form to be [Wooding, 1960]
Figure 9. Dispersion normalized to the aqueous diffusion coefficient, \( D^*_t / D \), as a function of the Pe number. Two reactive cases of \( Da = 10 \) and 10,000 are compared to the case of parallel plates with no reaction.

\[
D^*_t = \frac{\omega^2 \gamma_c^2}{210D} + D \tag{30}
\]

The first term of (30) is called the Taylor portion of dispersion and is due to the velocity shear. The Taylor contribution to dispersion is proportional to the mean velocity squared and inversely proportional to the molecular diffusion. Shapiro and Brenner [1988] obtain a semianalytic solution for a reactive solute flowing between flat plates and give a thorough comparison with (30).

For a reactive solute flowing through a channel with wavy walls, no closed form solution is available for the dispersion coefficient. Figure 9 shows how the dispersion given by (30) compares with the values computed for the cosine-shaped pore and two different \( Da \) numbers. We see that the effect of the wavy walls with relatively slow reaction (\( Da = 10 \)) increases the dispersion over \( Da = 10,000 \) is to decrease the dispersion. Neither the wavy walls nor the reaction have a major impact on the dispersion coefficient. In the region between \( Pe = 1 \) and 10 all the displayed curves change slope from a constant value to approximately a \( Pe^2 \) dependence. The slope change shows where the dominant contribution to dispersion changes from molecular diffusion to Taylor dispersion.

The results displayed in Figure 9 can be explained as follows. The effect of the wavy channel walls is to increase the solute dispersion by increasing the velocity shear, particularly at the narrow throat. Reactions at the channel walls, however, have the opposite effect and tend to reduce dispersion. The gradients in velocity are greatest near the channel walls, since at the channel walls the fluid is held motionless by the no-slip boundary condition. But we see from Figure 5d that the solute spends very little of its time near the walls, since that is precisely where it is being consumed by the biofilm. Hence the reaction keeps the solute out of the flow regions of highest shear and thereby reduces the dispersion. Edwards et al. [1993] find similar qualitative behavior of the macrodispersion coefficient in their two-dimensional model.

5. Comparison With Experimental Mass Transfer Correlations and Boundary Layer Theory

In comparing the results predicted by our model, we focus our attention on the solute mass transfer from the flowing pore water to the biofilm. In the case of a nonreacting solute, data are available from experimental mass transfer correlations on mass transfer from particles to bulk fluid in packed columns. Most experimentally derived mass transfer correlations performed at low \( Re \) numbers and high \( Sc \) numbers involve fitting the data to a correlation of the form

\[
Sh = c + \beta (Pe)^{1/3} \tag{31}
\]

where \( c \) and \( \beta \) are the experimentally determined constants. Wilson and Geankoplis [1966] performed experiments over a range of \( Re \) numbers, 0.0016 \( \leq Re \leq 55 \), and porosities 0.35 \( \leq \theta \leq 0.75 \), and found that \( \beta = 1.09/\theta \). Karabelas et al. [1971] obtained \( \beta = 4.58 \) using a single porosity value of 0.26. As reported here the length scale used in \( Sh \), \( Re \), and \( Pe \) is based on the sphere diameter of the particles used in the packed column, and the velocity appearing in \( Re \) and \( Pe \) is the superficial velocity. Neither Wilson and Geankoplis [1966] nor Karabelas et al. [1971] determined the constant \( c \) in (31) which becomes significant at low \( Pe \) numbers. As the \( Pe \) number tends to zero, the \( Sh \) number must attain a constant nonzero value as molecular diffusion becomes the dominant transport mechanism.

Theoretical mass transfer correlations of the form shown in (31) have been derived using boundary layer theory [Levich, 1962]. In boundary layer theory, gradients of both concentration and momentum are assumed to be confined near the solid-liquid interface and tending toward a constant zero value far enough away from the solid surface. Boundary layer thicknesses of \( \delta_c \) and \( \delta_v \) are associated with the concentration and velocity, respectively. The boundary layer equations for concentration and velocity are of the same form but have a differing diffusivity coefficient, \( D \) and \( v \), respectively. The ratio of the two quantities is the Schmidt number \( Sc = v/D \) and provides information about the relative thickness of the boundary layers. For liquids the \( Sc \) number is large, and we have that \( \delta_v/\delta_c \propto (Sc)^{1/3} \) [Levich, 1962], so for \( Sc = 1000 \), \( \delta_v/\delta_c = 10 \). The theory suggests that the concentration boundary layer is relatively thin, and one of the approximations made in computing mass transfer coefficients is that the velocity gradient normal to the solid surface is constant across the concentration boundary layer. For isolated spheres, Friedlander [1957] found \( \beta = 0.89 \), while Batchelor [1979] obtained \( \beta = 0.99 \). The length scale in the dimensionless numbers is the sphere diameter and the velocity is the mainstream velocity outside the boundary layer. For \( Pe = 0 \), analysis of just the diffusional transport mechanism yields \( Sh = 2 \).

Casting our results for the macroreaction coefficient in terms of a \( Sh \) number can be done as follows. Comparing (2) and (5) and making use of (4) shows that at the macroscale we have the equivalence

\[
a_b k_b (C_a - C) = \gamma * \dot{C} \tag{32}
\]

As mentioned earlier, the concentrations \( C_a \) and \( C_b \) are macroscopic quantities, and we define \( C_a = \bar{C} \) the spatial average concentration in the bulk fluid, and \( C_b \) is the average concentration at the biofilm surface. Solving for the mass transfer coefficient in (32) yields
Define the macroscale Damkohler and Sherwood numbers as

\[ Da^* = \frac{\gamma^* C}{a_s (C - C_b)} \]

Now put (33) into the definition for \( Sh^* \) to get

\[ Sh^* = \frac{\gamma^* C}{a_s^2 D (\bar{C} - C_b)} = Da^* \frac{\bar{C}}{(\bar{C} - C_b)} \]

where use was made of definition for \( Da^* \). At very large microscale \( Da \) numbers, the concentration at the biofilm surface tends to zero and therefore so will the average \( C_b \), as illustrated in Figure 4 for \( Da = 1000 \). With \( C_b = 0 \), (35) becomes

\[ Sh^* = Da^* = \frac{1}{a_s^2 D \gamma^*} \quad Da \to \infty \]

Equation (36) provides the basis for comparison between the macroreaction rate coefficient determined in this work and mass transfer correlations predicting the generic behavior that \( Sh = \beta Pe^{1/3} \). We will use the large-\( Da \) data shown in Figure 7 (\( Da = 10,000 \)) for \( \gamma^* \) in (36). Referring to Figure 2, the specific surface \( a_s \) is twice the arc length of the height function \( \delta \) divided by the fluid volume \( V_f \), which is about \( a_s = 37 \text{ cm}^{-1} \) (within the range of a coarse sand [de Marsily, 1986]). Using the value for the diffusion coefficient of TCE in water of \( D = 9 \times 10^{-6} \text{ cm}^2/\text{s} \), a plot of the macroscale Sherwood number given by (36) is shown in Figure 10. Along with our calculated values is plotted a curve with slope of \( Pe^{1/3} \) made to pass through our calculated values at the point \( Pe = 1 \). It is evident that over the range of \( Pe \) numbers from about 1 to 10 the macroscale Sherwood number (and macroreaction rate coefficient) follows a \( Pe^{1/3} \) curve, as predicted by mass transfer correlations. From Figure 10 we can determine the constant \( \beta = Sh^*/Pe^{1/3} \) by taking the average of the three values within the relevant range, \( Pe = 1, 3, \) and 10, which are \( \beta = 0.46, 0.39, \) and 0.40, respectively. Within a narrow range of \( Pe \) numbers we have the correlation

\[ Sh^* = 0.42 Pe^{1/3} \quad 1 \leq Pe \leq 10 \]

Below \( Pe = 1 \) the macroscopic Sherwood number attains a velocity-independent constant value of about \( Sh^* = 0.44 \).

To isolate the effect of the viscous eddy on mass transfer, it was removed from the flow. This is readily accomplished with the series solution for the stream function (9) by retaining only the zero-order approximate stream function \( \psi_0 \). The approximate stream function \( \psi_0 \) is simply the stream function based on the local width of the channel. Using this flow field, the macroreaction rate was determined for \( Da = 10,600 \) and plotted as a macroscale Sherwood number in Figure 10. We see that without the viscous eddy mass transfer becomes velocity independent above about \( Pe = 100 \).

Inspection of Figure 10 shows three distinct ranges of \( Pe \) numbers in which different mechanisms for mass transfer become significant. For \( Pe \) less than 1, mass transfer to the biofilm is velocity independent and dominated by molecular diffusion. Within the range \( 1 \leq Pe \leq 10 \) convective mass transfer dominates and follows the \( Pe^{1/3} \) behavior. Above \( Pe = 10 \), convective mass transfer still dominates, but the effect of the viscous eddy begins to become important. Inspection of Figures 4c and 4d shows that at large \( Pe \) numbers the normalized solute distribution \( E \) changes most in the region of the viscous eddy, illustrating that further increases to mass transfer are due to the solute transport ability of the viscous eddy. In the case without the viscous eddy, we see that above about \( Pe = 10 \), mass transfer tapers off rapidly, approaching another velocity-independent region above about \( Pe = 100 \). In both cases, with and without the viscous eddy, this model predicts that above \( Pe = 10 \), convective mass transfer may be less than that suggested by mass transfer correlations.

6. Summary and Conclusion

A model is developed which can determine the macrotransport coefficients of macrodispersion, macrovelocity, and macroscale first-order reaction rate, given the microtransport coefficients and microscale geometry as input. Despite its simplicity, the undulating channel does retain some of the flow characteristics found in real media, such as converging and diverging flow through pore throats and pore chambers. The focus of this work is on the effect pore-scale physical and chemical parameters, expressed as the nondimensional Peclet and Damkohler numbers, have on the macrotransport coefficients.

The upscaling model is based on the moment method of Shapiro and Brenner [1988]. The moment method has a rigorous mathematical foundation and yields equations for the macrotransport coefficients which, in themselves, give insight into the macroscopic implications of the microscale mechanisms. Also, the assumptions made in the derivation are explicit, and most importantly, quantifiable, such as when asymptotically long times are reached. In the application studied here, long time is of the order of a minute, which is relatively rapid compared to other relevant timescales such as biomass growth rates. A disadvantage of the moment method is that the equations to solve can be difficult to evaluate, and in general, nu-
numerical methods are required. The implementation of the numerical solution procedures is not trivial, as the resultant discretized system of equations to solve is typically large and ill-conditioned. The model developed is used to explore the microscale implications on macroscale transport phenomena.

For large Da numbers this model shows that the pore fluid is not well mixed. Steep concentration gradients at the microscale can be produced by transport limitations to the reaction sites. Anderson and McCarty [1994] have investigated the possible reasons for the lower rates of biodegradation of TCE observed in biofilms compared to dispersed growth studies. One possibility for the discrepancy in degradation rates are mass transfer limitations from the bulk water to the biofilm [Anderson and McCarty, 1994]. The significance of mass transfer limitations on observed reaction rates depends on the Da number, as shown in Figure 6. We can estimate the Da number using the pore dimensions shown in Figure 2, where \( \bar{w} = 0.05 \) cm. Using the method of Wilke and Chang [1955] to determine the aqueous diffusion coefficients, we find \( D = 9.0 \times 10^{-6} \text{ cm}^2/\text{s} \) for TCE and \( D = 1.9 \times 10^{-5} \text{ cm}^2/\text{s} \) for methane. Using the definition of the Da number in Table 1 we have \( Da = 600 \) for TCE and \( Da = 4700 \) for methane. In many cases of practical interest, such as when the material is coarse and the reactions relatively fast, as in this case, mass transfer limitations can significantly reduce observed reaction rates. However, the Da number is proportional to the square of the pore dimension and so changes rapidly with grain size. For fine sands the pore dimensions are reduced by about an order of magnitude [de Marsily, 1986], and the Da number is therefore reduced by a factor of 100. Now mass transfer limitations are negligible for TCE and relatively minor for methane, so the pore fluid is essentially well mixed for both compounds. For fine material, pore-scale mass transfer limitations cannot explain the difference between in situ and dispersed growth studies.

Again, when large Da numbers produce concentration gradients within the pore, interesting macrotransport phenomena can result. In particular, the mean solute velocity can be different than the mean solvent velocity, either more or less, depending on the thickness of the microscale reaction [Edwards et al., 1993]. For example, for a diffusion limited reaction \( (Da = 1000) \), the velocity may go from 1.6 times the water velocity near an injection well to 0.05 times away from the injection well, as Figure 8 demonstrates.

Relative rates of solute consumption differ within the pore. The disparity in microscale reaction rates is created by the nonuniformity of the pore geometry. At the one extreme a straight tube or flat channel model of a porous medium does not exhibit spatially dependent reaction rates at the microscale. While in this study it is shown that for a moderately wavy-walled channel, reaction rates are greatest at the pore neck. If the microorganisms reproduce fastest where consumption is greatest, even relatively small amounts of biofilm growth at the pore neck can have significant macroscale consequences. Pore necks can become constricted or clogged, and hydraulic conductivity can be drastically reduced by small changes in biomass. Spatially nonuniform solute consumption can have significant macroscale consequences.

A comparison is made between experimental and theoretical mass transfer correlations for nonreacting solutes, and the results determined for the macroreaction rate coefficient. We find that over a limited range of Pe numbers, a macroscale Sh number follows the \( Pe^{1/3} \) dependency expected by theoretical and experimental mass transfer correlations, while above a limiting Pe number, this model predicts less convective mass transfer.

**Appendix**

The approximate stream functions used in (9) to determine the stream function are given here. The approximate stream functions are dimensionless. All odd-numbered approximate stream functions are zero, and the first three even-numbered ones are

\[
\psi_0(x_1,x_2) = C_0 (6 \xi - 2 \xi^3) \tag{A1}
\]
\[
\psi_1(x_1,x_2) = C_0 \frac{1}{2} (4H_x^2 - HH_{xx})(6 \xi - 2 \xi^3 + \xi) + C_1 \frac{1}{2} \xi^3 (3 - \xi) \tag{A2}
\]
\[
\psi_2(x_1,x_2) = C_0 \frac{1}{2} \left[ (4H_x^2 - HH_{xx})(-450 \xi^7 + 798 \xi^5 - 246 \xi^3 - 102 \xi) + 4HH_{xx}(450 \xi^7 - 1071 \xi^5 + 792 \xi^3 - 171 \xi) + 10H^2HH_{xx}(-18 \xi^7 + 63 \xi^5 - 72 \xi^3 + 27 \xi) + 4H^2H_xHH_{xx}(-60 \xi^7 + 182 \xi^5 - 184 \xi^3 + 62 \xi) + H^3HH_{xxx}(15 \xi^7 - 49 \xi^5 + 53 \xi^3 - 19 \xi) \right] + C_1 \frac{1}{2} \xi^3 (6 \xi^2 - 2 \xi^3 + \xi) + C_1 \frac{1}{2} \xi^3 (3 - \xi) \tag{A3}
\]

where \( X = x_1/l_1 \), \( H = h(X)/\bar{w} \), and \( \xi = x_2/h(X) \), and the constants used above and in (11) are

\[
C_0 = \left[ \int_0^1 \frac{dX}{H^3} \right]^{-1} \tag{A4}
\]
\[
C_2 = C_0 \frac{1}{5} \int_0^1 \frac{H_x^2}{H^3} dX \tag{A5}
\]
\[
C_4 = C_0 \int_0^1 \left[ \frac{352}{525} H_x^2 - \frac{164}{175} H_{xx} - \frac{1}{5} H_x^3 \right] dX \tag{A6}
\]

Differentiation of the height function \( H \) with respect to \( X \) is denoted by the subscript \( X \); for example, \( H_{xxx} \) means \( d^3H/dX^3 \).

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**References**


Anderson, J. E., and P. L. McCarty, Model for treatment of trichlo-