

PORE-SCALE SIMULATION OF DISPERSION AND REACTION ALONG A TRANSVERSE MIXING ZONE IN TWO-DIMENSIONAL HETEROGENEOUS POROUS MEDIUM COMPOSED OF RANDOMLY DISTRIBUTED CIRCULAR AND ELLIPTICAL CYLINDERS

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ABSTRACT

Several studies have demonstrated the important role played by transverse dispersion along the lateral fringe of chemical plumes in porous media. For example, the success of natural and engineered in-situ remediation relies on the transverse mixing of reactive chemicals or nutrients. Field, laboratory, and theoretical studies have also demonstrated that the length scale of transverse mixing zones can be very small, often on the order of millimeters or centimeters. In order to study dispersion, mixing and reaction at this scale, we have developed a pore-scale modeling approach that consists of the following: (a) geometric construction of a packed bed of randomly sized, shaped and randomly oriented grains; (b) solution for the steady flow field by the Lattice-Boltzmann method; and (c) solution for the steady-state distribution of reactive chemicals using a finite volume code. Due to the extreme computational burden of pore-scale simulation, we restrict our modeling to two space dimensions. We illustrate our approach through a steady-state system of two reactants injected side-by-side parallel to the mean flow direction; a kinetic bi-molecular reaction rate law is assumed. We first estimate the transverse dispersion coefficient through comparison of a continuum-scale model to the pore-scale simulation of the spread of a nonreactive solute. We then simulate the reactive case for different flow rates and compute the product formed by the reaction. We investigate whether use of the transverse dispersion coefficient gives the proper degree of mixing to accurately simulate the amount of product formed in the system. The results are compared with available experimental evidence and theoretical findings. Our results indicate that transverse dispersion coefficients that describe spreading of nonreactive solutes also may be used to model transverse mixing and reaction.

Keywords: mixing; pore-size heterogeneity; dispersivity; transport; pore-scale transport.

1. INTRODUCTION

Many risk-based strategies for managing groundwater pollution rely upon intrinsic in-situ biodegradation of organic contaminant plumes. Field and laboratory studies have shown that the overall rate of biodegradation is controlled by transverse mixing of electron donors and acceptors (e.g., hydro-carbons and oxygen) that are present at the interfaces between the ambient groundwater and the contaminant plume, thus indicating

a localized development of steep concentration gradients [e.g., Rahman et al., 2005; Jose and Cirpka, 2004]. These steep gradients lead to conditions where the transverse mixing rate is more important than the intrinsic biodegradation kinetics. As a result, it is often reasonable to assume an instantaneous reaction rate between two binary reactants when studying intrinsic biodegradation of contaminant plumes. Liedl et al. (2005) and Ham et al., (2004) have studied plume evolution under these conditions. It is also reasonable to focus on steady state plume conditions due to its importance for risk management. Liedl et al. (2005) and others have shown that longitudinal dispersivity has practically no effect on steady-state plume length, and therefore in this paper we focus only on transversal dispersion. Traditionally, reactive transport is modeled through a continuum-based approach where all solute concentrations are averaged over some representative elementary volume (REV) [Bear 1972; and Dagan 1989]. Recent studies indicate that such a continuum-based approach may not be adequate for understanding reactive transport. For instance, through an image based quantification of instantaneous colorimetric reactions, Gramling et al., (2002) showed that the dispersive term in the advection-dispersion equation can overpredict pore-scale mixing, and thereby overpredict overall chemical reaction. This same conclusion was reached earlier by Raje and Kapoor (2000) who investigated bimolecular reaction at the interface of two moving solutes in a one-dimensional column displacement experiment. They indicated that such an over prediction is due to ignoring the impact of sub-REV concentration gradients on local reaction rates. Scheibe et al., (2001) also reported some field-scale discrepancies. Recently, Acharya et al. (2006a,b) showed that longitudinal dispersion coefficient is a function of the variance of pore size distribution, however, these effects have not yet been fully quantified for transversal mixing.

Several studies [e.g., Rahman, 2005; Jose and Cirpka, 2004; Raje and Kapoor, 2000; Gramling et al., 2002] have discussed the difference between solute spreading and mixing. The former is what is normally quantified by mechanical dispersion of a nonreactive solute. These studies have indicated that longitudinal mechanical dispersion overestimates the amount of mixing. In this paper we investigate whether the same phenomenon occurs in the transversal direction, and hence the apparent transversal dispersion for reactive transport $D_{T,R}$ and conservative nonreactive transport $D_{T,NR}$ may be different.

The objective of this study is to quantify $D_{T,NR}$ and $D_{T,R}$ for various pore-scale heterogeneities and transport regimes. In this work we use a homogeneous porous medium composed of staggered cylinders as a reference medium, and compare the results to a heterogeneous medium composed of differently shaped, oriented, and sized cylinders of the same porosity. We quantify $D_{T,NR}$ for these two media by injecting a conservative solute into the domain. Then we allow two side-by-side flowing solutes to react at their interface and quantify the product. By fitting the numerically simulated product with an analytical solution [Nambi et al., 2003], $D_{T,R}$ can be estimated. We present a comparative analysis of $D_{T,NR}$ and $D_{T,R}$ for different transport regimes characterized by Péclet number (Pe).

2. MODELS

We assume the two solutes A and B react and form the product AB, according to the reaction $S_A A + S_B B \rightarrow S_{AB} AB$, where $S_{\{i\}}$ is the stoichiometric coefficient. Symbols

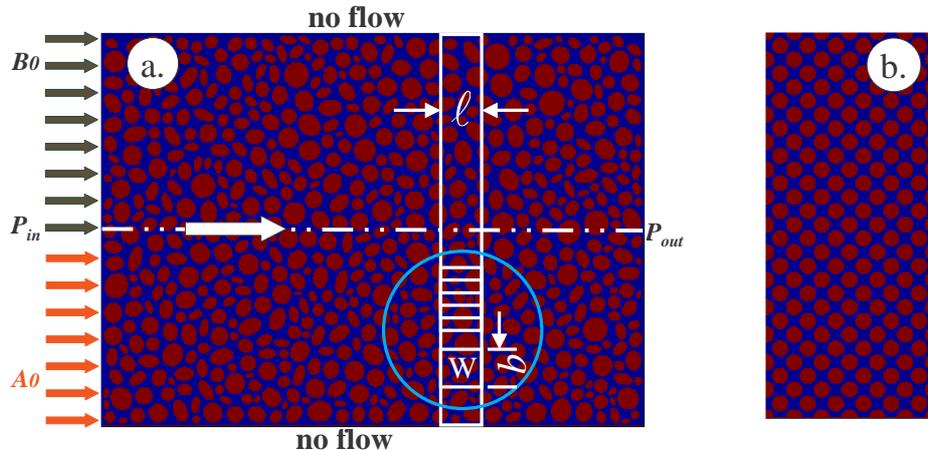


FIGURE 1. A schematic of 2D porous media. (a) Heterogeneous porous medium composed of differently shaped, sized and oriented cylinders. Shown are the no flow boundaries (“no flow”), fixed pressures at the inlet (P_{in}) and outlet (P_{out}), concentrations of the electron “donor” and “acceptor” A_0 and B_0 at the inlet, flow direction (from left to right), averaging window (W) of size $\ell \times b$. (b) A sample of homogeneous medium composed of staggered uniformly sized cylinders. Solid phase is colored light gray (red in color print) and fluid is colored dark gray (blue in color print).

A , B and AB denote respectively concentrations of solutes A, B, and the product AB. The model describing steady state transport of these reactants and the product in porous media can be expressed by the advection-dispersion-reaction equations, i.e.

$$\begin{aligned} \nabla \cdot \vec{v}A - D_A \cdot \nabla^2 A &= -S_A \gamma \\ \nabla \cdot \vec{v}B - D_B \cdot \nabla^2 B &= -S_B \gamma \\ \nabla \cdot \vec{v}AB - D_{AB} \cdot \nabla^2 AB &= S_{AB} \gamma, \end{aligned} \quad (1)$$

where the velocity field \vec{v} is defined by the steady state Stokes equation [Knutson et al., 2001]. The symbol γ denotes the reaction rate. For a bi-molecular reaction $\gamma = k[A][B]$, where k is a rate constant. The symbol $D_{\{.\}}$ denotes molecular diffusion coefficients of the participating species (A, B and AB).

3. POROUS MEDIA

Our 2-D porous media are composed of cylinders of either circular or elliptical (with random orientations) or mixture of different shapes. We focus on the phenomenon of product formation in these media both numerically and analytically. Our flow field is given by the Stokes equation and is solved by a Lattice-Boltzmann model (LBM) reported earlier [Knutson et al., 2001]. We use the finite volume code developed by these same authors [Knutson et al., 2005] to solve the transport equation (1). First, we determine transversal dispersion ($D_{T,NR}$) for conservative tracers and compare with the apparent dispersion coefficient of reactive transport ($D_{T,R}$). This is pursued for the homogeneous

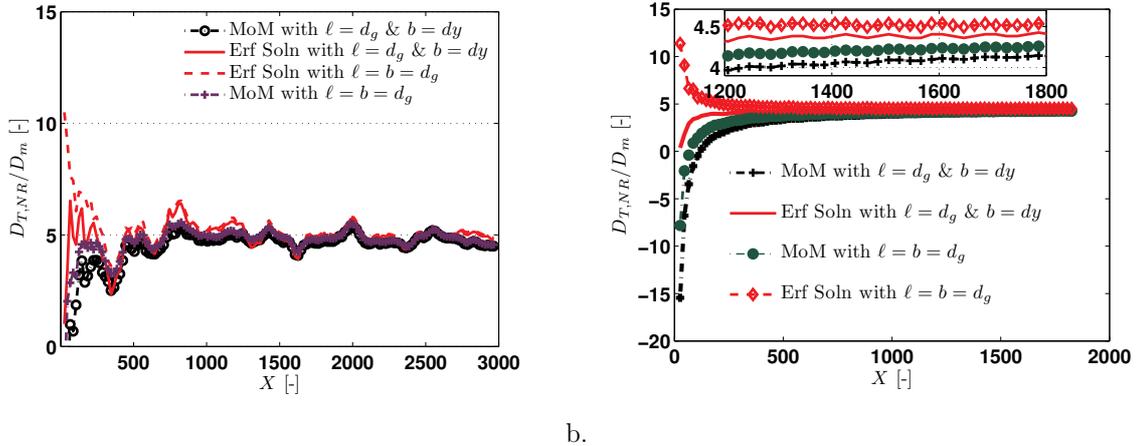


FIGURE 2. Values of $D_{T,NR}/D_m$ at $Pe = 50$ plotted as a function of normalized distance (x/dx) for (a) heterogeneous medium and (b) homogeneous medium. The acronym “MoM” denotes method of moments, whereas the analytical error function solution is denoted with “Erf Soln”.

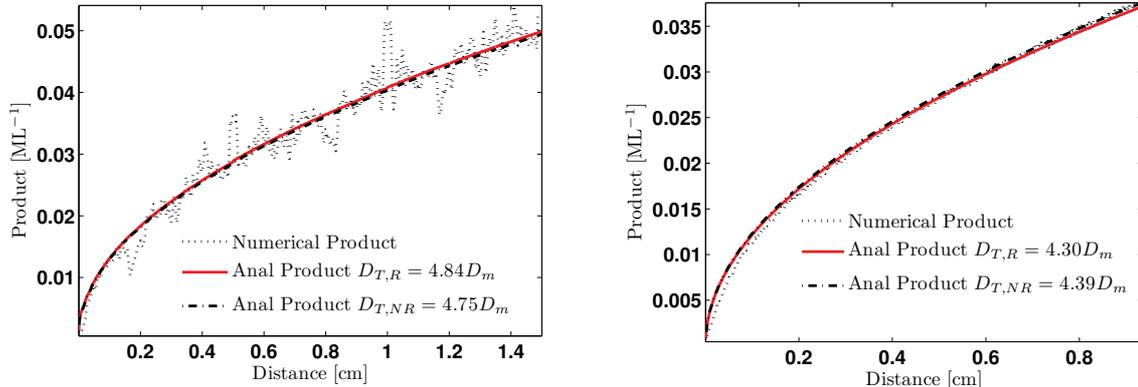
medium composed of staggered circular cylinders as well as for the heterogeneous medium having the same porosity and mean cylinder diameter. A schematic of our heterogeneous porous medium is shown in Figure 1. The porosity of this medium is 49.7%, mean cylinder diameter (d_g) equals $135\mu\text{m}$ and the size of discretization is set at $dx = dy = 5\mu\text{m}$. The standard deviation of grain size distribution of heterogeneous medium is $34\mu\text{m}$. This medium is composed of cylindrical as well as elliptical cylinders with random angles of orientation. We assume such a system represents a packed bed of fine sand. The method creating of such medium deserves a separate discussion, and therefore it is not the focus in this work.

4. DETERMINATION OF TRANSVERSAL DISPERSION FOR CONSERVATIVE TRACER

From Eq (1) it is directly seen that local (grid cell scale) concentrations are a function of molecular diffusion ($D_{\{i\}}$) of each participating solutes and the velocity. Diffusion of solute among the tortuous flow paths results in spreading in both the longitudinal and transverse directions; this is the process known as mechanical dispersion [Bear, 1972]. Here, as stressed above, we focus only on the transverse dispersion $D_{T,NR}$. Hence, our aim is to understand how $D_{T,NR}$ is related to the magnitudes of average advection velocities as well as the molecular diffusion properties of the solutes. To include both these properties we define a dimensionless number, commonly known as Péclet number, by

$$Pe = \frac{ud_g}{D_m}, \quad (2)$$

where D_m is the molecular diffusion of the conservative solute, d_g denotes the cylinder diameter, and u is the absolute intrinsic mean velocity (\bar{v}_x) in the primary flow direction. There are several possible methods that can be used for determining $D_{T,NR}$ from the pore-scale concentration data. We present a method based upon fitting an analytical continuum-scale solution to the spatially-averaged concentration field.



a.

b.

FIGURE 3. Per unit length amount of product (m) as a function of distance at $Pe = 50$ for (a) heterogeneous medium and (b) homogeneous medium

For a window W shown in Fig 1, we define the dimensionless concentration \tilde{C} by

$$\tilde{C}(x, y) = \frac{1}{\ell b C_0} \int_{x-\ell/2}^{x+\ell/2} \int_{y-b/2}^{y+b/2} C(x, y) dy dx, \quad (3)$$

where C is the concentration of the conservative solute in the domain, C_0 is the inlet concentration, and ℓ and b are the averaging intervals in the x and y directions, respectively. We test different combinations of ℓ and b . For instance, we could choose $\ell = b = d_g$, $\ell = dx$ and $b = dy$, or $\ell = d_g$ and $b = dy$. Although there is no significant difference which option is used, the third option (strip-wise row-averaging) is more convenient and consistent.

An analytical solution at the continuum scale for \tilde{C} under the assumption of uniform one-dimensional advection and transverse dispersion is computed by using the well-known error function solution

$$\tilde{C} = \frac{1}{2} \operatorname{erfc} \left[\frac{y}{\sqrt{4D_{T,NR}(x/u)}} \right] \text{ for } -\infty < y < \infty, \quad (4)$$

where y is transverse axis (note $y = 0$ denotes the center line) and u mean velocity in the primary flow direction. Note that we assume that the inlet concentration is nonzero and equal to C_0 for $y < 0$.

By using least squares fitting of equation (4) to the “data” computed by equation (3), $D_{T,NR}$ is deduced. Other methods for computing $D_{T,NR}$ include the method of moments (Valocchi, 1989) and the so-called B-field calculation [Brenner, 1980; Edwards et al., 1993]. The B-field calculation is an amicable way of solving the closure problem posed by Whitaker (1966), however, these methods are best suited for periodic porous media. We have developed a method similar to the B-field based on spatio-temporal simulations of concentrations in a porous medium with periodic boundaries. When applied to a periodic medium comprised of equal sized cylinders, the results produced by different methods are not significantly different and agree with the results reported earlier [e.g., Edwards et al., 1993; Hackert et al., 1996].

5. DETERMINATION OF APPARENT TRANSVERSAL DISPERSION FOR REACTIVE TRANSPORT

We take a simple case $D_A = D_B = D_{AB}$ because we can make use of the analytical solution to reactive transport developed by Gramling et al., (2002) and Nambi et al. (2003). This analytical solution also requires an instantaneous reaction rate, so we use very large rate constants. Although the analytical solution requires instantaneous reaction, it can easily be extended to the case of different diffusion coefficients. We use the analytical solution to compute the total transverse integrated product along the flow direction. This is defined as

$$m(x) = \int_{-\infty}^{+\infty} AB(y, x) \cdot 1 \cdot dy, \quad (5)$$

According to the analytical solution for the case, where $D_A = D_B = D_{AB}$, the total product integrated over the cross section is given by

$$m(x) = 2A_0 \sqrt{\frac{x D_{T,NR}}{\pi u}} \quad \text{for } 0 < x < \infty, \quad (6)$$

where A_0 is the input concentration of solute A . This solution is valid at the continuum scale and in this work we argue whether this is also applicable to the spatially averaged product from the pore-scale simulations.

From the pore-scale simulations we compute amount of product along the transverse zone and to this, by using least squares, we fit the analytical solution given by Eq (6). This fitting will provide us with the apparent transversal dispersion coefficient ($D_{T,R}$). In our work we compare the values of $D_{T,R}$ and $D_{T,NR}$ for different medium and different regimes designated by dimensionless Péclet number Pe .

6. RESULTS

We compute $D_{T,NR}$ and $D_{T,R}$ using the methods described above. For the homogeneous periodic medium comprised by equal sized cylinders, we use a simple method that is essentially the same as computing $D_{T,NR}$ by solving the B-field equation. For the theory of B-field, we refer to Edwards et al. (1993), Souto et al. (1997), Kitanidis (1992), and Wood et al. (2003) and references therein. In this case, our results agree with the results reported in the literature by these and other investigators.

In Table 1, we list the results of a few simulations for two types of porous media: heterogeneous (standard deviation of the grains $34\mu\text{m}$) and homogeneous medium composed of staggered cylinders, i.e., a periodic medium. First the conservative solute is injected into the lower half of the porous domain. Through strip-wise row-averaging (or any other spatial averaging method), we produce a transverse profile of the concentration function. Then we determine the coefficient of (transversal) dispersion for this profile. As already mentioned this can be done either by fitting the error function (4) or method of moments [Valocchi, 1989]. The results do not differ much (see Fig 2), especially at larger distances where the concentration profiles are smooth. Then, letting two solutes A and B react at their interface we accumulate the product AB along the transverse mixing zone. For purpose of comparison with the analytical solution the product is summed up per unit

TABLE 1. Transversal dispersion coefficients for homogeneous and heterogeneous media at different Pe .

Media Pe	Homogeneous			Heterogeneous		
	$D_{T,NR}/D_m$	$D_{T,R}/D_m$	δ	$D_{T,NR}/D_m$	$D_{T,R}/D_m$	δ
10	2.18	2.18	0.00%	1.49*	1.45*	2.68%
50	4.39	4.30	2.05%	4.75	4.84	(1.89%)
100	6.09	5.84	4.11%	8.63	8.57	0.70%
150	7.22	7.06	2.22%	12.32	12.21	0.89%

Note: * This data needs rectification through a wider domain of heterogeneous porous medium. Data in parentheses (..) are negative. $\delta = (D_{T,NR} - D_{T,R}) \times 100/D_{T,NR}$

length per unit fluid volume according to equation (5) and plotted in Fig 3. To this product profile along the x -axis we fit the analytical solution to get $D_{T,R}$. The results shown in the Table indicate that the deviations of $D_{T,NR}$ and $D_{T,R}$ for both cases and for all Péclet numbers are around or less than 4%. However, the deviations of $D_{T,NR}$ or $D_{T,R}$ of heterogeneous medium from the ones of the homogeneous medium are up to 42%.

7. CONCLUSIONS

We can draw some preliminary conclusions based upon the limited results presented in the table. Unlike what others have reported for mixing controlled reactions in longitudinal dispersion systems, we find that $D_{T,NR}$ and $D_{T,R}$ are very close to one another; thus our early conclusion is that the continuum-based approach does not overpredict the product. For better insight we need to simulate transport for a wider variety of grain sizes and other conditions. More interestingly, deviations of the $D_{T,NR}$ (or $D_{T,R}$) values for heterogeneous medium from the one for the homogeneous medium are large (up to 42% for the cases simulated here). Moreover, these deviations increase as a function of Péclet number. These deviations profoundly challenge the common practices of picking a value of $D_{T,NR}$ on the basis of mean grain diameter [e.g., Saffman 1959] or based on Archie's law, which assumes tortuosity as a function of porosity. Note that both the homogeneous and heterogeneous media have the same mean grain diameter and porosity. The results stress that the variance of grain size distribution determines the effective transverse dispersion parameter, whether it is conservative or reactive. Hence, more systematic simulations as well as micro-model experiments are needed to ascertain the relation of $D_{T,NR}$ to Pe , porosity, mean grain size (pore size), the variance of grain sizes, and the orientation of grains.

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