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The influence of surface sorption on dispersion in
parallel plate fractures

Christoph Wels ¹, Leslie Smith ^{*}, Roger Beckie

*Geological Engineering Program, Department of Earth and Ocean Sciences, University of British Columbia,
6339 Stores Road, Vancouver, BC V6T 2B4, Canada*



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The influence of surface sorption on dispersion in parallel plate fractures

Christoph Wels¹, Leslie Smith^{*}, Roger Beckie

*Geological Engineering Program, Department of Earth and Ocean Sciences, University of British Columbia,
6339 Stores Road, Vancouver, BC V6T 2B4, Canada*

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Abstract

Solute transport in a parallel plate fracture is simulated using a random walk model which accounts explicitly for sorption onto the fracture walls. With the hypothesis that solute must move into the vicinity of the fracture wall in order to participate in the sorption process, three implications follow. (1) In comparison to a nonreactive solute, a sorbing solute requires a greater entrance length along the fracture before transverse homogenization is established. The increase in this entrance length is proportional to the surface retardation factor. (2) At short transport distances, surface sorption leads to a high degree of non-uniform retardation. The transport distance required to establish uniform retardation of the entire solute mass varies greatly with geometric conditions and sorption strength. (3) Surface sorption results in enhanced longitudinal spreading of the solute mass in transport regimes which favor advective transport along the fracture relative to transverse diffusion across the fracture aperture. At distances greater than that required for transverse homogenization, an effective longitudinal dispersion coefficient can be defined that describes this enhanced dispersion for a wide range of fluid velocities. The magnitude of enhanced dispersion increases with sorption strength. © 1997 Elsevier Science B.V.

Keywords: Groundwater; Fractures; Adsorption; Dispersion

1. Introduction

Our objective in this paper is to examine the conditions under which a conventional form of the advection dispersion equation is a valid description of the transport of a sorbing contaminant in a parallel-sided fracture. In an open fracture of constant aperture

^{*} Corresponding author.

¹ Present address: Robertson GeoConsultants Inc., Vancouver, B.C.

b , a nonreactive solute disperses under the combined influence of molecular diffusion and the parabolic velocity profile between the fracture walls, a process known as Taylor dispersion (Taylor, 1953, 1954). Beyond an entrance length L_{crit} required to eliminate concentration variations perpendicular to flow, dispersion is Fickian and transport can be approximated by an advection–dispersion equation with a longitudinal dispersion coefficient D_L given as (Aris, 1956):

$$D_L = D_m + \frac{u^2 b^2}{210 D_m} \quad (1)$$

where u is the mean fluid velocity and D_m is the molecular diffusion coefficient. The entrance length L_{crit} for this asymptotic dispersion coefficient to apply is given as (Kessler and Hunt, 1994):

$$L_{\text{crit}} = \frac{6}{\pi^2} \frac{u b^2}{D_m} \quad (2)$$

Hull et al. (1987) used this same relationship with a proportionality constant of 0.125 (instead of $6 \pi^{-2}$) to characterize the applicability of the Fickian dispersion model.

We analyze transport in a vertical section through a horizontal fracture, with uniform conditions assumed in the plane of the fracture (Fig. 1). For simplicity, we assume an impermeable host rock so that diffusion into and sorption within the matrix can be neglected. With fast, linear, and reversible sorption onto the fracture walls, solute transport can be described by the one-dimensional form of the advection–dispersion equation (e.g. Tang et al., 1981):

$$R_a \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \quad (3)$$

where C is the concentration of the solute in solution, the longitudinal dispersion coefficient D_L is given by Eq. (1), and R_a is the surface retardation factor, given as:

$$R_a = 1 + \frac{2 K_a}{b} \quad (4)$$

K_a is the surface distribution coefficient, its value can be estimated from static sorption experiments (e.g. Vandergraaf et al., 1988). The use of a constant retardation factor in Eq. (3) implies that retardation of the entire mass of solute is uniform, that is, each segment of a plume is retarded to the same degree. It is also implicit in Eq. (3) that there is no interaction between surface sorption and dispersion; that is, the magnitude of D_L is independent of the sorption strength K_a of the solute.

Few studies have considered possible interactions between surface sorption and dispersion in parallel-sided fractures. Laboratory migration experiments using machined, constant-aperture fractures suggest that sorbing solutes exhibit significantly more dispersion than nonreactive solutes (e.g. Vandergraaf et al., 1988; Hölttä et al., 1991; Wels et al., 1996). Possible reasons for this enhanced dispersion include (1) spatial variability in sorption sites, (2) non-equilibrium sorption, and/or (3) other non-ideal sorption effects such as non-linear or partially irreversible sorption. Kessler and Hunt (1994) present an

analysis of dispersion in a single fracture that in many regards is similar to the case we examine here. They extended the calculations of Aris (1959) describing longitudinal dispersion of a solute flowing in two annular regions of arbitrary shape to characterize asymptotic longitudinal dispersion of a solute migrating in a planar fracture partially clogged by porous material. Within the porous coating, solutes are subject to advection (at a uniform velocity), dispersion, diffusion, and sorption (assuming a linear isotherm). They presented an analytic expression for the asymptotic longitudinal dispersion coefficient in the form of a mass-weighted sum of the contributions to dispersion from transport both in the open fracture and the porous coating. Their expression includes a term characterizing the enhanced dispersion that arises from a disequilibrium between the mass flux of a sorbing solute in the porous material, and that migrating within the open region of the fracture. Our analysis differs from that of Kessler and Hunt in that we do not explicitly model a two-layer system with mass-weighted contributions to dispersion from each layer; solutes sorbed to the fracture wall are immobile in our formulation. Our evaluation of dispersion describes only the mobile fraction in an open fracture. We focus on the enhanced dispersion that originates from incomplete transverse mixing that can occur in certain velocity regimes if it is assumed that solutes only sorb when they are in close vicinity to the fracture wall.

The hypothesis that sorption occurs only at the fracture wall (or at least in close proximity of it), and that solute must move into the vicinity of the fracture wall in order to participate in the sorption process, imposes constraints on the application of the one-dimensional model, Eq. (3). We present numerical migration experiments which suggest that, in comparison to a nonreactive solute, a sorbing solute requires a greater entrance length along the fracture before transverse homogenization is established. Furthermore, surface sorption results in a significant enhancement of dispersion under transport conditions which favour advective transport along the fracture relative to transverse diffusion across the fracture aperture. An effective dispersion coefficient is derived to account for this enhanced dispersion. This enhanced dispersion also leads to nonuniform retardation, with the extent of the nonuniformity depending upon the relative magnitude of advective and diffusive mass transfer, the surface retardation factor, and the travel distance along the fracture.

2. Transport models

In a parallel-plate fracture (Fig. 1(a)) solutes are transported by two mechanisms: (1) advection by the fluid according to the Poiseuille velocity profile and (2) molecular diffusion. For a fracture aspect ratio greater than approximately 12, the transport problem is essentially two-dimensional (e.g. Hull et al., 1987)

$$\frac{\partial C}{\partial t} = D_m \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right) - \frac{3}{2} u \left(1 - \frac{y^2}{a^2} \right) \frac{\partial C}{\partial x} \quad (5)$$

where a is the half-aperture of the fracture (Fig. 1(b)). The process of fast, linear, and

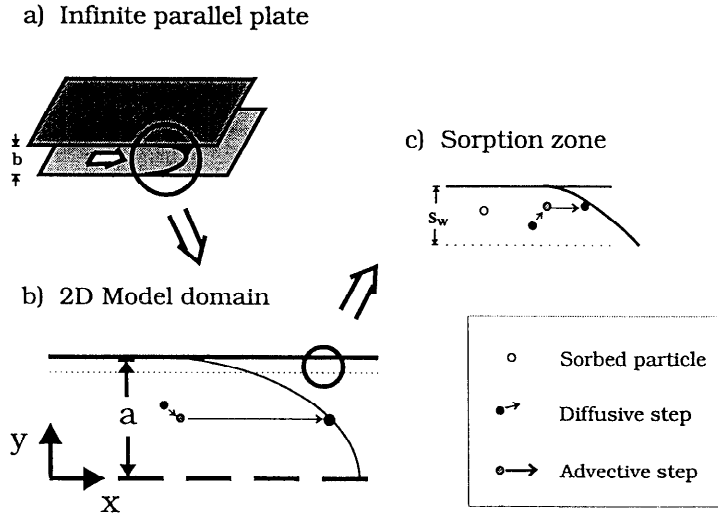


Fig. 1. Conceptualization of reactive solute transport in a parallel plate fracture.

reversible sorption to the fracture walls is described by the following boundary condition

$$C_s = CK_a|_{y=a} \quad (6)$$

where C is the dissolved solute concentration in proximity of the surface and C_s is the surface solute concentration (mass sorbed per unit area) on the fracture wall. Eq. (5) and (6) are a finer-scale description of transport than the one-dimensional formulation in Eq. (3) and (4). By modeling transport at this finer scale, we identify the conditions for a sorbing solute that govern the application of the one-dimensional model.

A random walk method is used to simulate the movement of nonreactive and sorbing solutes in a parallel-plate fracture. This method is well-suited to study dispersion phenomena because the processes of molecular diffusion (probabilistic), advection (deterministic), and sorption (probabilistic) are modeled explicitly. The transport of a solute by advection and diffusion is modeled by moving a large number of particles (N_p) according to a random walk with steps (e.g. Kinzelbach, 1988):

$$x_p(t + \Delta t) = x_p(t) + Z_1\sqrt{2D_m\Delta t} + v(y_p)\Delta t \quad (7a)$$

and

$$y_p(t + \Delta t) = y_p(t) + Z_2\sqrt{2D_m\Delta t} \quad (7b)$$

where x_p , y_p are the longitudinal and transverse position of a particle, respectively, t is the time step, and Z_1 , Z_2 are random normal variates with mean zero and variance one. The local particle velocity $v(y_p)$ is determined from the Poiseuille velocity profile:

$$v(y_p) = \frac{3}{2}u\left(1 - \frac{y_p^2}{a^2}\right) \quad (8)$$

In the limit of large numbers of particles and small time steps, the frequency distribution obtained from the random walk model (Eqs. 7(a) and (b)) satisfies the nonreactive transport Eq. (5).

This methodology has been extended to account for surface sorption onto the fracture wall. A "sorption zone" is defined within a small distance s_w of the fracture wall in which surface sorption is assumed to take place (Fig. 1(c)). The use of a (relatively small) sorption zone near the fracture wall is consistent with the working hypothesis that surface sorption influences only those solute particles in close proximity of the fracture wall. In this conceptualization, sorption occurs (strictly speaking) only at the fracture surface (see boundary condition (Eq. (6))). From a theoretical point-of-view an ionic solute would have to either hit the surface directly for sorption to occur or at least move within the thickness of the electric double layer for surface complexation or ion exchange to occur. In either case, the distance from the fracture wall within which a solute particle may sorb is probably not greater than several tens of nanometers. A discretization at this scale is not feasible in the particle tracking code. As noted below, a larger sorption width on the order of the distance a particle may travel by diffusion in a few time steps can be considered acceptable.

With the random walk method, we need to express the partitioning of solute between the fracture surface and the aqueous phase (Eq. (6)) in terms of the number of particles assigned to each phase. Let N denote the number of particles per unit area of sorption zone, and N_s the number of particles sorbed from within this zone. The partitioning of particles between the surface and the aqueous phase is given by a partitioning coefficient K_p :

$$K_p = \frac{K_a}{s_w} = \frac{N_s}{N} \quad (9)$$

In words, the partitioning of particles is proportional to K_a and the surface area-to-volume ratio of the sorption zone (with the surface-area-to-volume ratio equal to $1/s_w$ in a two-dimensional description). As s_w is reduced, K_p must increase to maintain the specified sorption strength K_a . When evaluating the partitioning of solute onto the fracture wall, K_p is treated as a uniform parameter, independent of particle position within the sorption zone.

This partitioning of particles between surface and solution is modeled probabilistically (e.g. Kinzelbach, 1988). Every particle is assigned an additional state variable $s_p(t)$ indicating whether the particle is in the dissolved state ($s_p(t) = 0$) or in the sorbed state ($s_p(t) = 1$). Every time step, particles residing within the sorption zone (i.e. y_p is within a distance s_w from the fracture wall; see Fig. 1(c)) are evaluated for a transition between the dissolved and the sorbed state according to the following transition probabilities:

$$p_{0,1} = \frac{K_p}{1 + K_p}; p_{1,0} = \frac{1}{1 + K_p} \quad (10)$$

These transition probabilities describe equilibrium sorption and are consistent with the more general transition probabilities for a first-order rate controlled sorption reaction used by Valocchi and Quinodoz (1989). The use of the equilibrium transition probabilities (Eq. (10)) assumes that the time scale of sorption is much smaller than the time scale of advection (local equilibrium).

For a particle in the dissolved state at time t , the particle is moved according to the transport step (Eqs. 7(a) and (b)) before determining the new state variable according to:

$$s_p(t + \Delta t) = \begin{cases} 0 & \text{for } X > p_{0,1} \\ 1 & \text{for } X \leq p_{0,1} \end{cases} \quad (11)$$

where X is a uniformly distributed random variable in the interval $[0,1]$. In contrast, for a particle in the sorbed state at time t there is no movement, i.e. the transport step is replaced by a sorption step:

$$x_p(t + \Delta t) = x_p(t); y_p(t + \Delta t) = y_p(t) \quad (12)$$

and the new state variable is determined according to:

$$s_p(t + \Delta t) = \begin{cases} 0 & \text{for } X \leq p_{1,0} \\ 1 & \text{for } X > p_{1,0} \end{cases} \quad (13)$$

In the limit of a large number of particles (N_p), a small time step (Δt), and a small sorption width (s_w), the frequency distribution obtained from the transport step (Eqs. 7(a) and (b)) combined with the sorption step (Eq. (10)–(13)) simulates two-dimensional transport with surface sorption onto the fracture wall (Eq. (5) and (6)).

At each time step the particle is first moved by diffusion to its new coordinates. Based on the old and new y -coordinate, an average particle velocity in the x -direction is calculated and the particle is moved according to this average fluid velocity. Particles may intersect the fracture wall and center-line only in the diffusive step. Both boundaries represent no-flow boundaries which reflect particles back into the model domain. For particles that reflect off the fracture wall or the centerline, the average particle velocity is given as the average velocity for the path from the old position to the boundary and the path from the boundary to the new position. Note that the time step t is chosen small enough so that a particle cannot leave the sorption zone when reflected off the fracture wall. In this way all particles which “hit” the fracture wall are automatically evaluated for sorption using Eq. (10).

Particles are released into the fracture as a Dirac pulse. A flow-weighted injection is used by releasing particles in proportion to the flow rate at any given transverse position. The transport parameters supplied to the model are four physical parameters (u , D_m , b , L) and one chemical parameter (K_a). Three model parameters (N_p , Δt , s_w) are also required. In general, the larger N_p is and the smaller the values of Δt and s_w , the smoother the breakthrough curve (BTC) and the more accurate the solution. Sensitivity analyses indicated that 2000 particles and a time step small enough to obtain a ratio of sorption width to diffusion distance ($s_w/(2D_m\Delta t)^{1/2}$) greater than four is sufficient to simulate the transport problems discussed here. It was also found that the solution is fairly insensitive to the relative width (a/s_w) of the sorption zone. As a consequence of the parabolic velocity profile (high fluid velocities concentrated close to the center of the fracture) the value of s_w may be as large as 15% of the half aperture without significantly influencing the reactive transport solution. We note that with the use of a larger sorption width, the tendency is to underestimate the degree of enhanced dispersion owing to surface sorption.

Returning to the one-dimensional transport model, Eq. (3) can be written in the non-dimensionalized form:

$$\frac{\partial C}{\partial T^R} = \frac{1}{Pe} \frac{\partial^2 C}{\partial X^2} - \frac{\partial C}{\partial X} \quad (14)$$

where the dimensionless variables are defined as:

$$\begin{aligned} X &= \frac{x}{L} \\ Pe &= \frac{uL}{D_L} \\ T^R &= \frac{ut}{LR_a} \end{aligned} \quad (15)$$

In our application, L is the transport distance of interest, D_L is the longitudinal dispersion coefficient defined in Eq. (1), and Pe is the Peclet number. For nonreactive transport the dimensionless time T^R simplifies to $T = ut/L$ and all other non-dimensional variables remain unchanged.

The solution to Eq. (14) assuming a specified concentration C_0 at the source is (Ogata and Banks, 1961):

$$\frac{C}{C_0} = \frac{1}{2} \operatorname{erfc} \left(\frac{1 - T^R}{2\sqrt{T^R/Pe}} \right) + \frac{1}{2} e^{Pe} \operatorname{erfc} \left(\frac{1 + T^R}{2\sqrt{T^R/Pe}} \right) \quad (16)$$

where we have modified the Ogata–Banks solution to accommodate retardation. In Eq. (16), the solution is linear in C , therefore, this solution is equivalent to the solution for a pulse injection integrated over time (Kreft and Zuber, 1978). Hence, Eq. (16) can be fit to the non-dimensionalized cumulative recovery curves obtained with the random walk model. The cumulative recovery curves eliminate much of the statistical variations present in the instantaneous BTCs, thus simplifying a least squares fitting procedure. Note that only one fitting parameter (Pe) is needed owing to the non-dimensional formulation of the problem.

3. Dispersion of a non-sorbing solute

In this section we will briefly review the transport of a non-sorbing solute to provide a reference for the discussion of the reactive case. Assuming the solute has traveled farther than the entrance length L_{crit} required to establish transverse homogenization, transport of a nonreactive solute is described by the advection–dispersion (Eq. (14)) with the following fracture Peclet number

$$Pe_f = \frac{uL}{D_m + \frac{u^2 b^2}{210 D_m}} \quad (17)$$

Three transport regimes may be distinguished on the basis of the relative magnitude of the two mechanisms of dispersion accounted for in the denominator of Eq. (17). In order to delineate these transport regimes we define a transverse Peclet number as:

$$Pe_t = \frac{ub}{D_m} \quad (18)$$

When the transverse Peclet number is less than approximately 2 the transport regime exhibits ‘‘diffusion-controlled dispersion’’. Under these conditions Taylor dispersion accounts for less than 2% of the longitudinal spreading. In contrast, when the transverse Peclet number is greater than 100, longitudinal diffusion accounts for less than 2% of all longitudinal spreading. The latter transport regime is dominated by Taylor dispersion and the effects of longitudinal diffusion may be ignored. For intermediate values of Pe_t , both mechanisms of dispersion are of similar magnitude and each process needs to be considered explicitly. This transport regime is said to exhibit ‘‘mixed dispersion’’.

The fracture Peclet number (Eq. (17)) indicates a complex dependence of nonreactive solute transport on the fluid velocity u across the three transport regimes. Fig. 2 shows Pe_f values as a function of u for $b = 400 \mu\text{m}$, $D_m = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and several values of transport distance ($L = 0.02, 0.2$ and 2.0 m). The vertical dashed lines delineate the three transport regimes. In the transport regime of diffusion-controlled dispersion ($u < 1 \times 10^{-5} \text{ ms}^{-1}$) the fracture Peclet number is proportional to fluid velocity indicating a steepening of the BTC with increasing fluid velocities. In the transport regime of Taylor dispersion ($u > 5 \times 10^{-4} \text{ ms}^{-1}$) the Peclet number is

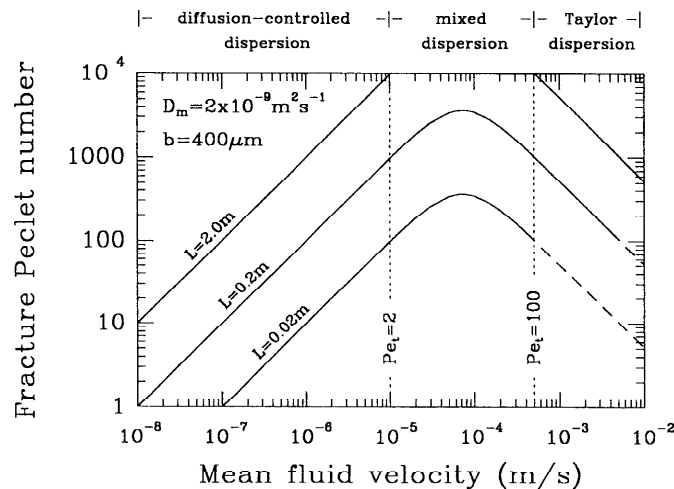


Fig. 2. The fracture Peclet number as a function of mean fluid velocity for $b = 400 \text{ mm}$, $D_m = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and for different transport distances L .

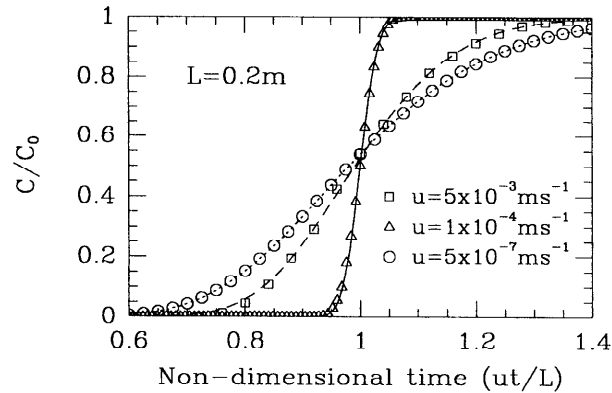


Fig. 3. Simulated breakthrough curves of a conservative solute for mean fluid velocities representing (i) diffusion-controlled dispersion (circles), (ii) mixed dispersion (triangles), and (iii) Taylor dispersion (squares). The lines represent the AD equation using the respective fracture Peclet numbers $Pe_f = 20$ (dotted line), 3450 (solid line), and 105 (dashed line), respectively.

inversely proportional to fluid velocity indicating a broadening of the BTC with increasing fluid velocities. The region of mixed dispersion is a transition zone where the fracture Peclet number is comparatively insensitive to changes in u . Note that the highest fracture Peclet numbers (steepest breakthrough curves) occur in the regime of mixed dispersion. These general observations hold for any transport distance L of interest, provided L is greater than the entrance length L_{crit} .

Fig. 3 shows simulated breakthrough curves of a nonreactive solute for transport conditions representing diffusion-controlled dispersion (circles), mixed dispersion (triangles), and Taylor dispersion (squares). The three transport simulations differ only with respect to fluid velocity. All other physical parameters are constant ($L = 0.2$ m, $b = 400$ μm , $D_m = 2 \times 10^{-9}$ $\text{m}^2 \text{s}^{-1}$). The lines in Fig. 3 are the analytical solution (Eq. (16)) using the respective Peclet number calculated from Eq. (17). Fig. 3 shows that the transport simulations agree well with the analytical solutions based on transverse homogenization, for the cases of diffusion-controlled dispersion and mixed dispersion. In the Taylor regime, with $u = 5 \times 10^{-3}$ ms^{-1} , the analytic approximation of Kessler and Hunt (1994) gives an entrance length, L_{crit} , equal to 0.24 m. The match in the Taylor regime is also good (for $L = 0.2$ m). Thus, our numerical results are consistent with analytic predictions across all three dispersive regimes. Furthermore, they suggest that the entrance length proposed by Kessler and Hunt (1994) provides a conservative approximation of the distance required for transverse homogenization.

Note that the matches to the Ogata–Banks solution (Eq. (16)) were obtained with a flux-weighted injection of particles on the inflow boundary. As shown by Krefl and Zuber (1978), the Ogata–Banks solution applies to a flux-weighted injection with a constant concentration maintained at the source. The Ogata–Banks solution was not matched (for distances beyond L_{crit}) if particles were released uniformly across the inflow boundary. The good match of the numerical and analytical solutions in all three regimes suggests that the asymptotic expression for D_L (Eq. (1)) is not sensitive to the

difference between a flux-weighted particle injection, and the uniform concentration assumed in a derivation by Taylor (1953). We have not investigated the extent to which L_{crit} may be modified by the difference in the upstream boundary condition.

Fig. 3 also demonstrates the relative importance of dispersion compared with advection for the three transport regimes. The transport simulation representing mixed dispersion exhibits a steeper breakthrough curve (larger Pe_f) than the transport simulations representing either Taylor dispersion or ‘‘diffusion-controlled dispersion’’. In other words, the ratio of dispersive transport to advective transport is the lowest in the regime of mixed dispersion. This simulated transport behaviour is accurately predicted by the fracture Peclet number (Eq. (17)) provided the transport distance allows for transverse homogenization (Eq. (2)).

4. Dispersion of a sorbing solute

For discrete fracture models at the network scale, Eq. (3), which does not explicitly model the sorption process, is preferred over Eq. (5) and (6), which describe transport at the sub-fracture scale. In this section we evaluate the conditions under which the reactive transport model (Eq. (3)) is valid in describing transport of a solute that sorbs to the fracture walls. Two questions deserve special attention. First, under which conditions is transverse homogenization of a sorbing solute established? Second, what is the effect of surface sorption on dispersion?

Fig. 4 shows simulated breakthrough curves of two solutes with differing sorption strengths ($K_a = 2 \times 10^{-4}$ and 1×10^{-2} m), representing weak retardation ($R_a = 2$) and strong retardation ($R_a = 51$), for otherwise identical transport conditions ($u = 5 \times 10^{-3}$ ms^{-1} , $L = 0.2$ m, $b = 400$ m, $D_m = 2 \times 10^{-9}$ $m^2 s^{-1}$). The BTC for a nonreactive

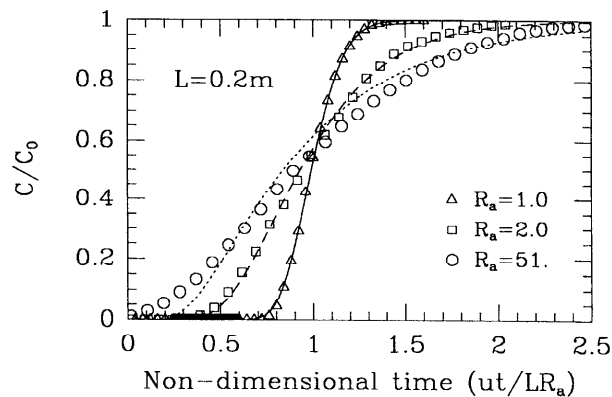


Fig. 4. Simulated breakthrough curves of (i) a conservative solute ($R_a = 1$), (ii) a weakly sorbing solute ($R_a = 2$), and (iii) a strongly sorbing solute ($R_a = 51$). The conservative transport parameters are the same as those used for Taylor dispersion in Fig. 3. The best-fit Peclet number for the weakly and strongly sorbing solute are $Pe = 14.0$ (dashed line) and $Pe = 3.7$ (dotted line), respectively. For the conservative BTC, $Pe_f = 105$ (solid line).

solute is shown for comparison ($R_a = 1$). Note that the breakthrough curves are plotted relative to a dimensionless time for the reactive solute T^R , that is, the dimensionless time $T = ut/L$ is normalized to the surface retardation factor ($T^R = T/R_a$).

Fig. 4 illustrates three key effects of surface sorption on solute transport in a planar fracture. First, the greater retardation owing to a higher sorption strength is described accurately by the surface retardation factor (Eq. (4)). All three BTCs shown in Fig. 4 have the same mean arrival time equal to 1 in dimensionless time T^R . Second, the sorption strength of a solute influences the entrance length required to establish transverse homogenization. Third, Fig. 4 demonstrates that surface sorption leads to enhanced dispersion, that is, there is a greater spread in the reactive BTC relative to the nonreactive BTC.

In our example simulations, a transport distance of 0.2 m is sufficient to establish transverse homogenization for both the nonreactive solute (as indicated by the good fit of the advection–dispersion equation) and the weakly sorbing solute. In contrast, the same fracture length is not sufficient to establish transverse homogenization of the strongly sorbing solute, as indicated by the poorer fit of the retardation model (dotted line, Fig. 4). The transport distance has to be increased by more than an order of magnitude ($L > 10\text{m}$) to obtain a good fit with the advection–dispersion model. These results and additional sensitivity analyses suggest that the increase in the entrance length L_{crit} is of the same magnitude as the surface retardation factor for a given solute. Hence we propose to extend the definition of the entrance length derived by Kessler and Hunt (1994) for the nonreactive case (Eq. (2)) to:

$$L_{\text{crit}}^* = R_a \frac{6}{\pi^2} \frac{ub^2}{D_m} \quad (19)$$

Recall that the entrance length indicates the transport distance necessary to eliminate concentration variations across the fracture aperture. The process of surface sorption limits transverse homogenization because a fraction of the solute mass is sorbed to the surface and cannot participate in advective–diffusive transport. With an increase in sorption strength, more mass is sorbed to the surface at any point in time and the rate of transverse mixing by diffusion is reduced. As a result, a highly sorbing solute requires a greater transport distance to establish transverse homogenization.

The enhanced dispersion is owing to the surface nature of the sorption reaction. In our random walk model particles can only participate in the sorption process when they are in the proximity of the fracture wall, that is, when they are present in the sorption zone s_w . Those particles outside the sorption zone cannot sorb. The localized nature of the sorption reaction increases the range of residence times for solute particles travelling in the fracture, and hence, enhances dispersion. Furthermore, the parabolic velocity profile introduces a negative cross-correlation between local fluid velocity and the potential for sorption. There is a higher probability for a slow-moving solute to sorb than for a fast-moving solute because it is closer to the fracture wall, or more likely to be within the sorption zone s_w . This bias in sorption further increases the spreading of the solute front.

The extent to which dispersion is enhanced by surface sorption can be quantified by determining an effective dispersion coefficient that is based on the Peclet number

obtained from the fit of the advection–dispersion equation to the simulated BTC. Note that this effective dispersion coefficient D_{eff} is always greater than the longitudinal dispersion coefficient D_L which describes hydrodynamic dispersion of a nonreactive solute. In the above example, the effective dispersion coefficient calculated for the weakly sorbing solute is $D_{\text{eff}} = 7.14 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ($Pe = 14.0$) compared with $D_L = 9.5 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ ($Pe = 105$) for a nonreactive solute. In other words, the effective dispersion coefficient for the weakly sorbing solute is approximately 7.5 times greater than the longitudinal dispersion coefficient (i.e. $D_{\text{eff}}/D_L = 7.5$). The effective dispersion coefficient for the strongly sorbing solute should be even greater. However, for the strongly sorbing solute, a value of D_{eff} could not be estimated in this example because the advection–dispersion model does not provide a good fit to the simulated BTC. The estimation and subsequent application of D_{eff} is only meaningful if the transport distance is sufficiently long to ensure homogenization of the sorbing solute in question (see Eq. (19)).

The ratio of D_{eff} to D_L is a surrogate for the increase in dispersion owing to surface sorption beyond the (known) hydrodynamic dispersion in a parallel plate fracture. Fig. 5 shows the ratio of D_{eff} to D_L for the case of a weakly sorbing solute ($R_a = 2$) over a wide range of fluid velocities. First, consider the solid dots which represent values of D_{eff}/D_L determined numerically using the random walk model. The simulations suggest that enhanced dispersion owing to surface sorption is insignificant ($D_{\text{eff}}/D_L = 1.0$) in the transport regime of diffusion-controlled dispersion. In contrast, in a transport regime dominated by Taylor dispersion, longitudinal spreading owing to the surface sorption process is much greater than that owing to hydrodynamic dispersion alone ($D_{\text{eff}}/D_L \gg 1.0$). In this regime the ratio D_{eff}/D_L reaches a plateau value which is nearly independent of fluid velocity (Fig. 5). We will show below that this value depends on the retardation factor; however, it is independent of the transport parameters (u , b , D_m).

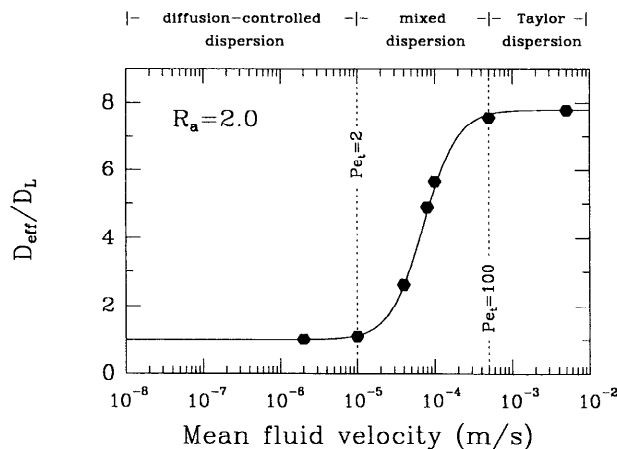


Fig. 5. The ratio D_{eff}/D_L as a function of the mean fluid velocity for a weakly sorbing solute ($R_a = 2$). The solid dots represent results from individual numerical migration experiments. The solid line shows the

For a retardation factor of 2, D_{eff}/D_L is approximately equal to 7.8 in the Taylor regime, which is close to the value ($D_{\text{eff}}/D_L = 7.5$) obtained from the simulation shown in Fig. 4 (for $R_a = 2$). At intermediate fluid velocities the ratio D_{eff}/D_L gradually increases from 1.0 to the plateau value, indicating a strong dependence of the magnitude of enhanced dispersion on fluid velocity in the transport regime of mixed dispersion.

These numerical results are best understood by re-examining the origin of the enhanced dispersion. Longitudinal spreading of the solute plume increases in the presence of surface sorption because the particles in the vicinity of the fracture wall are sorbed preferentially. The negative cross-correlation between local fluid velocity and the probability for sorption further enhances solute dispersion. This additional dispersion is absent only if sorption does not depend on the transverse position of the solute. In theory, this is accomplished when the solute particles mix instantaneously across the fracture. In practice, it is sufficient to require that transverse diffusion is much faster than advection. This condition is met in the transport regime of diffusion-controlled dispersion ($Pe_t < 2$). Here, the fluid velocities are so small that diffusion dominates over advection and instantaneous transverse mixing is approximated.

It is important to distinguish the condition of “instantaneous transverse mixing” of a solute from that of “transverse homogenization”. Transverse homogenization is gradually achieved as the solute front moves along the fracture. In contrast, the applicability of instantaneous transverse mixing is controlled by the transport regime ($Pe_t < 2$) and it is independent of the transport distance. For transport conditions that do not approximate instantaneous transverse mixing ($Pe_t > 2$), enhanced dispersion occurs beyond transport distances sufficient to produce transverse homogenization.

Sensitivity analyses suggest that the magnitude of enhanced dispersion is only influenced by the magnitude of Taylor dispersion. This observation is expressed in the following relationship:

$$D_{\text{eff}} = D_m + c_f \frac{u^2 b^2}{210 D_m} \quad (20)$$

where the proportionality factor c_f is defined as a “dispersion factor”. The above formulation applies only for transport distances sufficiently large to allow for transverse homogenization of the sorbing solute. Eq. (20) is similar in concept to Eq. (18) of Kessler and Hunt (1994), except that we have combined the effects of Taylor dispersion and the enhanced dispersion owing to sorption on the fracture walls into a single parameter.

The solid line in Fig. 5 shows the behaviour of D_{eff}/D_L as a function of the mean fluid velocity, using this definition of the effective dispersion coefficient (Eq. (20)) with $c_f = 7.8$. This line fits the simulated data well in all three transport regimes (Fig. 5). The formulation of an effective dispersion coefficient appears general and applies to a wide range of transport conditions. Note that c_f is best determined in the Taylor regime. In this region longitudinal dispersion owing to molecular diffusion is negligible, and as a result, the ratio D_{eff}/D_L approximates the dispersion factor. The same value for the dispersion factor ($c_f = 7.8$) was obtained in simulations with other combinations of b , u and D_m , suggesting that the magnitude of the dispersion factor depends on the

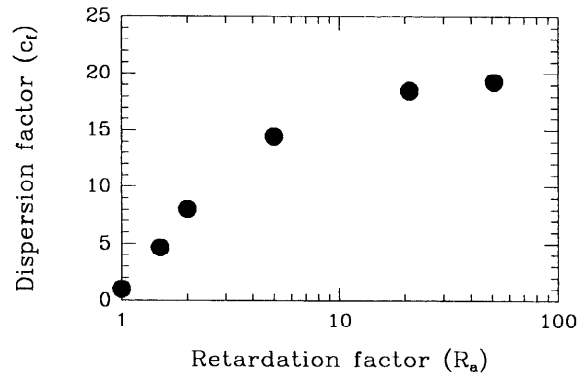


Fig. 6. The dispersion factor c_f determined numerically for a range of retardation factors.

magnitude of Taylor dispersion ($= u^2 b^2 / 210 D_m$) and not on the individual magnitude of the physical parameters b , u and D_m .

Fig. 6 shows the dispersion factor c_f as a function of the surface retardation factor, determined from transport simulations using the random walk model. The results shown in Fig. 6 apply in all transport regimes, provided the transport distance L is greater than the entrance length required to achieve transverse homogenization of the sorbing solute (Eq. (19)). For nonreactive transport the dispersion factor is by definition equal to one. Fig. 6 shows that a higher retardation factor results in a larger dispersion factor, indicating a greater enhanced dispersion owing to surface sorption. For high surface retardation factors, however, the dispersion factor approaches an asymptotic value ($c_f \sim 20$). As noted earlier, the model parameters (N_p , D_t , s_w) influence the accuracy of the reactive transport simulations; a larger value of s_w will tend to underestimate the degree of enhanced dispersion. Limited simulations with a much finer discretization (D_t , s_w) and a greater number of particles (N_p) yield values of the dispersion factor that are 10%–15% higher than the values shown in Fig. 6, but the same pattern of behavior is maintained.

The increase in the magnitude of enhanced dispersion with increasing sorption strength is consistent with the proposed causes of the enhanced longitudinal spreading. It has been suggested that only a limited fraction of the solute particles (those in immediate vicinity of the fracture wall) participate in surface sorption. With an increase in the sorption strength a greater proportion of the solute mass that is within s_w participates in this limited and biased sorption process and the magnitude of enhanced dispersion increases. The dispersion factor approaches a maximum for highly sorbing solutes (high R_a) where the great majority of the solute particles present in the sorption zone s_w are sorbed to the surface. Here an incremental change in sorption strength has little effect on the partitioning of the solute mass and the resulting enhanced dispersion. Kessler and Hunt (1994) observed a similar asymptotic behavior at higher values of the distribution coefficient for the system they analyzed.

In summary, transport of a sorbing solute in a parallel plate fracture may be modeled using the advection–dispersion equation (Eq. (3)) with the surface retardation factor (Eq.

(4)), given conditions that allow for transverse homogenization of the sorbing solute. The dispersion coefficient describing hydrodynamic dispersion needs to be modified, however, to account for additional dispersion owing to surface sorption. The definition of the effective dispersion coefficient (Eq. (20)) is applicable for a wide range of transport conditions since the dispersion factor is only a function of the sorption strength of the solute (Fig. 6). The magnitude of enhanced dispersion owing to surface sorption increases with sorption strength. The effective dispersion coefficient for a strongly sorbing solute may be up to 20 times greater than the longitudinal dispersion coefficient for a nonreactive solute.

5. Implications for non-uniform retardation

It has been shown that surface sorption results in enhanced longitudinal spreading along a parallel-plate fracture. When viewed at the scale of the entire mass of solute, this enhanced dispersion owing to surface sorption leads to non-uniform retardation, that is, the leading segment of the plume experiences less retardation than the center of the plume and the tail of the plume experiences more retardation. In the following we will demonstrate that the degree of non-uniform retardation depends on the distance that solute travels in a fracture.

The influence of transport distance on non-uniform retardation was studied by comparing the breakthrough curves of a nonreactive solute and a sorbing solute ($R_a = 5.0$), simulated using the random walk model for a range of transport distances ($L = 0.01–1$ m). For any given transport distance we computed three retardation factors; R_5 , R_m , and R_{95} , by comparing the mass arrival times of the 5%, mean, and 95% mass breakthrough fractions in the nonreactive and reactive transport run. The deviation of these retardation factors from the surface retardation factor (Eq. (4)) is a measure for the degree of non-uniform retardation of the solute plume. In addition, the ratio D_{eff}/D_L was computed for any given transport distance to estimate the relative magnitude of enhanced dispersion owing to surface sorption.

Fig. 7 shows the ratio D_{eff}/D_L (upper panel) and the three retardation factors (lower panel) as a function of transport distance. The ratio D_{eff}/D_L is nearly constant indicating that the extent of enhanced dispersion is independent of transport distance. The observed values of D_{eff}/D_L agree well with the independent estimate ($D_{eff}/D_L = 9.8$, dashed line in Fig. 7) obtained using the appropriate dispersion factor from Fig. 6 ($c_f = 14.5$). Note that for transport distances on the order of the entrance length ($L_{crit}^* = 0.25$ m), the observed ratios of D_{eff}/D_L have more uncertainty owing to the poorer fit of the advection–dispersion equation to the simulated breakthrough curves, explaining the fluctuations in the data points.

Although the magnitude of enhanced dispersion is nearly constant, the degree of non-uniform retardation decreases significantly with increasing transport distance (lower panel, Fig. 7). For example, for $L = 0.01$ m the 5% breakthrough fraction experiences only $\sim 60\%$ of the mean retardation ($R_a = 5$) whereas the 95% breakthrough fraction is retarded by a factor of ~ 1.32 more than predicted by the retardation factor. At $L = 0.1$ m, the 5% breakthrough fraction experiences 90% of the mean retardation ($\sim 110\%$ for

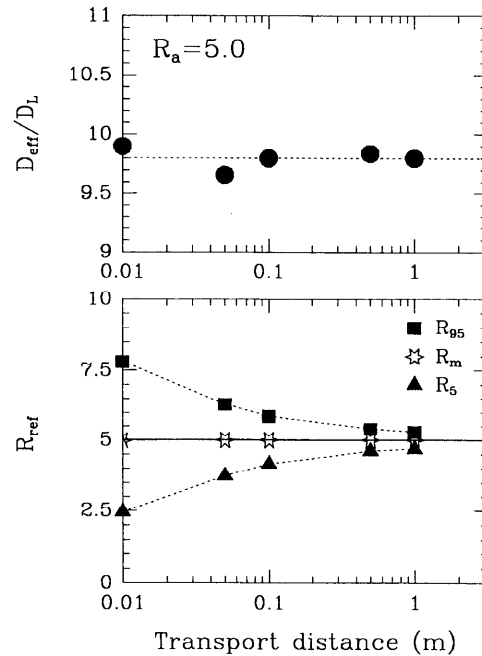


Fig. 7. The ratio D_{eff}/D_L (upper panel) and retardation factors R^{ref} for the 5%, mean, and 95% breakthrough fractions (lower panel) as a function of transport distance for a sorbing solute ($R_a = 5$).

the 95% breakthrough fraction). An additional tenfold increase in L yields essentially uniform retardation, and the three retardation factors are within 5% of the expected retardation predicted by the surface retardation factor (Eq. (4)). Note that the retardation of the mean arrival time is always predicted accurately by (Eq. (4)), independent of transport distance.

The decrease in the degree of non-uniform retardation reflects a reduction in the relative importance of dispersion compared with advective transport at greater transport distances (this reduced importance is expressed as a steepening of the solute breakthrough curve when plotted in non-dimensional time). At small transport distances dispersive transport is a significant component of transport and enhanced dispersion has a strong influence on the retardation of the individual reference breakthrough fractions. In contrast, at long transport distances, the non-dimensional BTCs are very steep, that is, the advective component dominates over the dispersive component. Although the magnitude of enhanced dispersion owing to sorption (expressed by D_{eff}) remains constant it becomes an insignificant component relative to advective transport. Hence, for long transport distances the sorbing solute is essentially transported as an “advective front”. The reduction in the travel velocity of this advective front relative to the mean fluid velocity is then described by the surface retardation factor (Eq. (4)).

The minimum transport distance required to develop a steep solute front of uniform retardation is a function of the degree of enhanced dispersion owing to surface sorption

expressed by the ratio D_{eff}/D_L . In general, the required transport distances are greatest in the transport regime of Taylor dispersion which exhibit a maximum in D_{eff}/D_L (Fig. 5). Similarly, a greater sorption strength (i.e. more retardation) requires a longer transport distance to approximate uniform retardation as a result of more enhanced dispersion (Fig. 6). The required transport distances vary greatly depending on which transport problem is considered. For example, for the transport problem shown in Fig. 7, a transport distance on the order of one meter is required to approximate uniform retardation. In contrast, a highly sorbing solute in a transport regime of Taylor dispersion approximates uniform retardation at a transport distance on the order of several tens of meters.

6. Implications for solute transport in rough-walled fractures

In our analysis of the influence of surface sorption on solute dispersion we assumed that the fracture can be approximated by two parallel plates. Natural fracture planes, however, have rough and irregular surfaces. It is uncertain to what extent our results, namely the enhanced dispersion owing to surface sorption, apply to rough and/or partially closed fractures. In principle, surface roughness or partial closure would tend to disturb the uniform flow field that exists in a smooth-walled fracture of constant aperture. These perturbations of the flow field can be expected to result in additional transverse mixing of the solute by advection, and thus, they may reduce the amount of enhanced dispersion owing to surface sorption. In addition, significant variations in fracture aperture may not allow the development of a parabolic velocity profile in the transverse direction. The absence of this velocity profile would further reduce the amount of enhanced dispersion owing to surface sorption.

There is some indication that dispersion in rough-walled fractures is dominated by mechanisms other than Taylor dispersion. Using migration experiments in constant-aperture fractures machined from plexiglass, Dronfield and Silliman (1993) estimated dispersion coefficients for different degrees of fracture roughness. For each fracture roughness, dispersion was proportional to fluid velocity raised to an exponent. The value of the exponent, however, depended strongly on the fracture roughness, ranging from 2.0 for smooth parallel plates to approximately 1.3 for rough plates (Dronfield and Silliman, 1993). Similarly, laboratory migration experiments using rough-walled fractures in granite have indicated that the longitudinal dispersion coefficient is approximately proportional to the mean fluid velocity (Moreno et al., 1985).

The reduced dependence of D_L on fluid velocity observed in rough fracture planes suggests that mixing at junctions connecting different channels within the fracture plane is the dominant dispersion mechanism rather than transverse diffusion across the velocity profile. In this situation, enhanced dispersion owing to limited and biased sorption at the fracture walls may be insignificant. The enhanced dispersion owing to surface sorption may be significant, however, in fractures where flow and transport is dominated by a few open channels. The channeling of flow and transport can be pronounced in rough fractures (e.g. Abelin et al., 1985; Vandergraaf et al., 1994). Enhanced longitudinal spreading owing to surface sorption is more likely to occur in

flow channels, in particular if flow channeling occurs in physical channels of large aperture and/or high flow rates. It has been shown that both of these conditions tend to result in incomplete transverse mixing of the solute, and hence, tend to enhance dispersion.

7. Implications for modeling solute transport at the network scale

Discrete network models typically account for sorption onto the fracture walls by introducing the surface retardation factor (Eq. (4)) for all fracture segments making up the network. Our results indicate that the surface retardation factor provides an accurate description of the reduction in the mean tracer velocity relative to the mean fluid velocity. At the same time, our calculations suggest that surface sorption may result in enhanced dispersion. When using an advection–dispersion equation to describe transport in individual fractures (e.g. Sudicky and McLaren, 1992) the additional dispersion can be accounted for by using an effective dispersion coefficient for a sorbing solute. Our definition of the effective dispersion coefficient (Eq. (20)) could be used under the assumption that the fractures making up the network can be approximated by parallel plates.

When the surface retardation factor (Eq. (4)) is used in network models which consider only advective transport (e.g. Dverstorp et al., 1992; Wels and Smith, 1994), it is implicitly assumed that: (1) dispersion is negligible relative to advection and (2) retardation is uniform in all fracture segments. The presence of enhanced longitudinal spreading of a solute plume at the scale of a single fracture may limit the application of an advection-based transport model. On the one hand, the magnitude of dispersion in each fracture segment would be greater than for the nonreactive case, in particular for a highly sorbing solute, thus potentially compromising assumption (1) for a greater number of fractures. On the other hand, the assumption of uniform retardation could be compromised, in particular in a dense fracture network where the distances between fracture intersections can be very short.

We are not aware of any studies which have focused on the influence of dispersion at the single fracture scale on dispersion at the network scale for the case of a sorbing solute. Based on our results we anticipate that the influence of dispersion at the single fracture scale on dispersion at the network scale may be considerably greater in the presence of surface sorption. This analysis would be further complicated if the network geometry introduces additional non-uniform and/or anisotropic retardation at the network scale (Wels and Smith, 1994). A consideration of non-uniform retardation at the scale of a single fracture may have an influence on non-uniform retardation at the network scale as well.

8. Conclusions

Solute transport in a parallel plate fracture has been simulated using a random walk model which accounts explicitly for sorption onto the fracture walls. Numerical simula-

tions show that the one-dimensional advection–dispersion equation accurately describes solute transport assuming that the condition of transverse homogenization is met. A sorbing solute requires a greater transport distance for transverse homogenization to be achieved than a non-sorbing solute. This increase in the required entrance length is proportional to the surface retardation factor (Eq. (4)). A modified entrance length has been proposed to account for this increase in the entrance length (see Eq. (19)).

Numerical simulations have shown that the surface retardation factor (Eq. (4)) gives an accurate description of the retardation of the mean tracer velocity. However, surface sorption results in enhanced longitudinal spreading of the solute plume. This additional dispersion is caused by (1) limited sorption of the solute plume to the fracture wall owing to slow and incomplete transverse mixing, and (2) biased sorption of slow-moving solute owing to the parabolic velocity profile. Based on numerical simulations an effective dispersion coefficient (Eq. (20)) has been developed which describes this enhanced dispersion for a wide range of fluid velocities. These results suggest that dispersion owing to surface sorption is directly proportional to the magnitude of Taylor dispersion. The increase in dispersion is negligible at very low fluid velocities and reaches a maximum in the range of fluid velocities characteristic of Taylor dispersion. It is further shown that the importance of enhanced dispersion is a function of the sorption strength of the solute, that is, an increase in retardation also results in more enhanced dispersion of the sorbing solute.

At short transport distances, surface sorption results in a high degree of non-uniform retardation. For longer transport distances retardation is essentially uniform since the advective component of transport dominates over the dispersive component. Non-uniform retardation may be an important consideration in the planning and interpretation of migration experiments at the laboratory scale. This effect may also be significant in the retardation of a sorbing contaminant at the network scale in a medium that is densely fractured.

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