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**Effects of Dual-Scale Diffusive
Property Heterogeneity on
Effective Matrix Diffusion
Coefficient for Fractured Rock**

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Abstract

Matrix diffusion can significantly retard solute transport in fractured formations. Understanding matrix diffusion is crucial for predicting the arrival time, peak concentration, and tail of a contaminant breakthrough curve. Previous studies show that (1) the effective matrix diffusion coefficient may be scale dependent, and (2) a multi-rate diffusion process may result in a time-dependent effective matrix diffusion coefficient. This study examines how heterogeneities of diffusion properties affect the effective matrix diffusion coefficient. The study focuses on two types of heterogeneity in a channelized flow system: (1) interchannel heterogeneity, and (2) intrachannel heterogeneity. The three objectives of this study are (1) to examine if it is appropriate to use a single, effective matrix diffusion coefficient in a standard solution model to predict breakthrough curves (BTC) in a fractured formation, and how this effective value is related to the degree of variability of the matrix diffusion coefficient; (2) to examine if the observed scale dependence of the effective matrix diffusion coefficient is caused by heterogeneity in diffusion properties; and (3) to examine whether the multi-rate diffusion process results in the observed time dependence of the effective matrix diffusion coefficient. The results show that the use of a single effective matrix diffusion coefficient is appropriate only if the inter- and intrachannel variability of diffusion properties is small. The scale dependence of the effective matrix diffusion coefficient is not caused by either type of the studied heterogeneity. Finally, the multi-rate diffusion process does not result in the time dependence of the effective matrix diffusion coefficient.

1. Introduction

Advection, dispersion, and matrix diffusion are the main physical processes affecting contaminant transport in fractured rock. Because the flow velocity in the rock matrix is much slower than the flow velocity in fractures, advection occurs primarily within the fracture network. However, matrix diffusion can significantly retard solute transport in fractured rock [Bodvarsson *et al.*, 2000; Guimera and Carrera, 2000; Jardine *et al.*, 1999; Liu *et al.*, 2004a; Neretnieks, 2002]. Therefore, understanding the diffusion of contaminants from fractures into the matrix is essential for predicting the arrival time, maximum contaminant concentration, and the tail at a given location.

The effective matrix diffusion coefficient, defined as the molecular diffusion coefficient in free water multiplied by matrix tortuosity, is a key parameter in determining matrix diffusion processes. Recent studies have found that effective matrix diffusion coefficients obtained from field-scale tracer tests are significantly larger than those from laboratory measurements [Andersson *et al.*, 2004; Liu *et al.*, 2004a; Liu *et al.*, 2003; Liu *et al.*, 2004b; Neretnieks, 2002; Shapiro, 2001; Zhou *et al.*, 2005]. By compiling effective matrix diffusion values observed from different test sites, Liu *et al.* [2004a] and Zhou *et al.* [2005] reported that the effective matrix diffusion coefficient may be scale dependent and increase with testing scale. However, the mechanisms behind this potential scale dependence are not clear at present.

Water flow and solute transport processes in fractured rock are complicated by heterogeneities at different scales and the complex geometry of fracture networks. Although different conceptual models for flow and transport in fractured rock exist, many studies indicate that the flow pattern is mainly characterized by discrete flow channels [Neretnieks, 2002; Tsang and Neretnieks, 1998]. Fluids in different channels are not very well mixed (at least in a typical

field test), except at the influent and effluent points, where the mixing of different channels is induced by pumping [Neretnieks, 2002]. Different channels having different flow and transport properties induces heterogeneity that impacts contaminant migration. In this study we refer to this kind of heterogeneity as interchannel heterogeneity.

Matrix diffusion processes in fractured rock are conceptually similar to mass-transfer processes between “mobile” and “immobile” zones in porous media. The conceptual model of mobile/immobile zones was proposed by *Dean* [1963] and later extended by *van Genuchten and Wierenga* [1976]. In this model, the liquid phase in porous media is partitioned into mobile and immobile zones. Advection dominates in the mobile zone, while transfer of solute into and out of the immobile zone is controlled by diffusion. The rate of mass transfer between the two zones is assumed to be proportional to the difference in concentration between the two liquid zones, with the proportionality referred to as a first-order mass-transfer rate coefficient. When the mass transfer is caused purely by molecular diffusion, this mass-transfer rate coefficient is conceptually similar to (and thus can be converted to) the effective matrix diffusion coefficient in fractured rock.

There exists an improved version of the mobile/immobile zone model, called the multi-rate diffusion model [*Haggerty and Gorelick*, 1995; *Haggerty and Gorelick*, 1998; *van Genuchten et al.*, 1984]. As a result of heterogeneity at the pore scale—which we refer to as intrachannel heterogeneity—the mass-transfer coefficient in the multi-rate diffusion model is modeled by a distribution of rate coefficients, rather than by a single value. *Haggerty and Gorelick* [1995] demonstrated that a multi-rate mass-transfer model simultaneously represents various mass-transfer processes in a porous medium, and the rate models of mass transfer are mathematically equivalent to the diffusion models of mass transfer. The two most-often-used

distributions of diffusion-rate coefficients are the gamma distribution and the lognormal distribution. *Haggerty and Gorelick* [1998] investigated different distribution functions and concluded that their experimental data were well represented when using a lognormal distribution of diffusion-rate coefficients.

Recently, *Haggerty et al.* [2004] compiled a large number of first-order mass-transfer rate coefficients estimated from test results. They found that the estimated rate coefficient depends on the test duration (t_{exp}) and is correlated to the advection residence time ($t_{\text{ad}} = L/v$, where L is the distance from the injection to the effluent point, and v is the average pore-water velocity). This time dependence of the rate coefficient is possibly a result of the underlying correlation between t_{exp} and t_{ad} . A larger mass-transfer rate coefficient corresponds to a smaller t_{exp} or t_{ad} . One of the possible explanations for the time dependence (given by *Haggerty et al.* [2004]) is that some tests were analyzed using a single-rate diffusion model even though the system exhibited multiple time scales for mass transfer.

Note that multi-rate diffusion processes have recently been used also for the analysis of tracer transport in fractured rock [*Haggerty et al.*, 2004]. In contrast to the observations of *Haggerty et al.* [2004], *Zhou et al.* [2005] did not find a correlation between test duration and the estimated effective matrix diffusion coefficient for a number of fractured rock sites. Therefore, the question arises whether the dependence on test duration observed by *Haggerty et al.* [2004] holds for fractured rocks with multiple time scales of mass transfer.

In this paper, we focus on the effects of two types of heterogeneity in diffusion properties (i.e., the interchannel heterogeneity—heterogeneity between individual flow channels, and the intrachannel heterogeneity—heterogeneity within an individual flow channel) on the effective matrix diffusion coefficient for fractured rock. More specifically, our goals are (1) to examine if

it is appropriate to use a single effective matrix diffusion coefficient in a standard solution model to predict breakthrough curves (BTC) in a fractured formation, and how this effective value is related to the degree of variability of the matrix diffusion coefficient, (2) to examine if the effective matrix diffusion coefficient changes with scale, which would indicate that the observed scale dependence of the effective matrix diffusion coefficient is caused by heterogeneity in diffusion properties, and (3) to examine whether the multi-rate diffusion process results in the observed time dependence of the effective matrix diffusion coefficient.

The effects of hydrodynamic dispersion are excluded from this study, because the interplay between matrix diffusion and dispersion within the fracture network makes the interpretation of numerical and experimental results difficult and ambiguous. Retardation due to sorption is also ignored in order to be able to separate and identify the effects of matrix diffusion heterogeneity on BTCs in fractured rock. However, in a real system, both dispersion and sorption may be important and should be considered.

2. Problem Setup

A simple fracture system, illustrated in Figure 1, is used in this study. The system consists of a fracture oriented in the x direction, embedded in matrix rock. Panel A shows a cross-sectional view of the fracture in the x - z plane, and Panel B shows the y - z plane. Flow is one-dimensional in the x direction. The fracture aperture is denoted as b , and a unit length is taken in the y direction. Water is assumed to flow along the fracture with a constant velocity. Tracer is applied using a Dirac input function, i.e., a contaminant of mass M_0 is instantaneously released at location $x = 0$ and time $t = 0$, so the concentration at $x = 0$ is:

$$c_0 = \frac{M_0}{bv} \delta(0) \quad (1)$$

where v is the flow velocity and $\delta(t)$ is the Dirac delta function. While most of the contaminant is transported by advective flow in the fracture, some contaminant mass is transferred from the fracture into the matrix by molecular diffusion. In our numerical experiments, we assume a negligible hydrodynamic dispersion (local dispersion) in the fracture and use a conservative tracer. We also assume complete mixing across the fracture aperture. Matrix porosity is 0.15, fracture aperture is 4.0×10^{-4} m, and flow velocity is 2.5×10^{-3} m/s.

Figure 1. Schematics of a single fracture system

Based on these assumptions, the solution to the transport equation subject to the above Dirac input injection is given by *Tang et al.* [1981]:

$$c(x, t) = \frac{M_0 k}{bv \sqrt{\pi} (t - t_w)^{3/2}} \exp\left(-\frac{k^2}{t - t_w}\right) \theta(t - t_w) \quad (2)$$

where: $c(x, t)$ is the contaminant concentration at location x and time t ;

$t_w = \frac{L}{v}$ is the residence time, where L is the distance between the contaminant release point and location x ;

$k = \frac{\phi_m \sqrt{D_m t_w}}{b}$, where D_m is the matrix diffusion coefficient and ϕ_m is the matrix porosity; and

$$\theta(t) = \begin{cases} 0 & t < 0 \\ 1 & t \geq 0 \end{cases}.$$

3. Interchannel Heterogeneity

Flow and transport processes in fractured rock occur along individual flow channels within a fracture network [Neretnieks, 2002]. As mentioned above, interchannel heterogeneity

results from different flow channels having different flow and transport properties. In this study, we use a simplified conceptualized flow model to investigate the effects of interchannel heterogeneity on diffusive properties. Specifically, we consider a simplified multichannel system, in which each flow channel has uniform properties and does not mix with any other channels except at influent and effluent points. These channels have the same length, width, fracture aperture, and other properties, but different matrix diffusion coefficients.

Haggerty et al. [2001] suggested that the distribution of diffusion rate coefficients may be defined in any appropriate manner. Most commonly, diffusion rate coefficients are characterized by a statistical distribution. For interchannel heterogeneity, we investigate two kinds of distributions for matrix diffusion coefficient. First, we assume a distribution that allows us to derive an analytical solution at the effluent point, given the solution for a single-channel flow system. Then we compare the form of the analytical solution with the single-channel model to see whether specifying a single effective matrix diffusion coefficient is appropriate to capture transport and matrix diffusion when interchannel heterogeneity exists. Even through the assumption of this distribution may not be physically justified, we nevertheless can obtain some insights from the corresponding analytical solution. Secondly, we use a lognormal distribution, as suggested by *Haggerty et al.* [2001]. A numerical experiment is performed to examine the existence and appropriateness of using a single effective matrix diffusion coefficient.

For the first analysis, we define $a = \frac{k}{t_w} = \frac{\phi_m \sqrt{D_m}}{b}$ (see Equation 2), and assume a follows a normal distribution (which is equivalent to $\sqrt{D_m}$ having a normal distribution, since ϕ_m and b are considered constant). When $t > t_w$ we can rewrite Equation (2) as:

$$c(x, t) = \frac{M_0 t_w a}{bv \sqrt{\pi} (t - t_w)^{3/2}} \exp\left(-\frac{t_w^2 a^2}{t - t_w}\right) \quad (3)$$

The probability density function for a is given by:

$$f(a) = \frac{1}{\sigma \sqrt{2\pi}} \exp\left[-\frac{(a - \bar{a})^2}{2\sigma^2}\right] \quad (4)$$

where σ is the standard deviation of a , and $\bar{a}$ is the arithmetic mean of a . So the average concentration at the effluent point is:

$$\begin{aligned} \bar{c}(x, t) &= \frac{M_0 t_w}{bv \sqrt{\pi} (t - t_w)^{3/2}} \int_{-\infty}^{+\infty} \frac{a}{\sigma \sqrt{2\pi}} \exp\left[-\frac{t_w^2 A^2}{t - t_w} - \frac{(a - \bar{a})^2}{2\sigma^2}\right] da \\ &= \frac{M_0 t_w \bar{a}}{bv \sqrt{\pi} (t - t_w + 2t_w^2 \sigma^2)^{3/2}} \exp\left[-\frac{t_w^2 \bar{a}^2}{t - t_w + 2t_w^2 \sigma^2}\right] \end{aligned} \quad (5)$$

Let $T_w = t_w - 2t_w^2 \sigma^2$. Inserting T_w into Equation (5) yields

$$\bar{c}(x, t) = \frac{M_0 \frac{T_w}{1 - 2t_w \sigma^2} \bar{a}}{bv \sqrt{\pi} (t - T_w)^{3/2}} \exp\left[-\frac{\left(\frac{T_w}{1 - 2t_w \sigma^2}\right)^2 \bar{a}^2}{t - T_w}\right] \quad (6)$$

Comparing Equations. (3) and (6), we can conclude that (unless the standard deviation is very small), a single effective matrix diffusion coefficient is unlikely to exist for the analytical solution given by Equation (3).

This analysis assumed that the square root of the matrix diffusion coefficient is normally distributed. It may be more reasonable to assume a lognormal distribution for the matrix diffusion coefficient (for details, see *Haggerty et al.* [2001]). In the second analysis, we use a Monte Carlo method, in which the matrix diffusion coefficient for each channel is sampled from a lognormal distribution. Then the BTC for each channel is calculated and an average BTC is obtained. An effective matrix diffusion coefficient is determined by fitting the BTC calculated

using Equation (2) to this average BTC, assuming complete mixing at the effluent point. This step is conducted using iTOUGH2-TRAT [Zhou, 2005]. The iTOUGH2-TRAT program was developed to calibrate transport parameters using BTCs observed in field (or laboratory) tracer test(s). It is based on iTOUGH2, a program using inverse modeling for parameter estimation and uncertainty analysis [Finsterle, 1999]. Six analytical models for tracer transport with different flow configurations and boundary conditions are implemented in iTOUGH2-TRAT. For our calibration purpose, we use the solution given by Tang *et al.* [1981] as Equation (2), the analytical solution for a single fracture embedded in a porous rock without dispersion.

In the numerical experiment we use a mean of -12 for $\ln(D_m)$, where D_m has units of m^2/h , corresponding to a geometric mean of D_m of $1.71 \times 10^{-9} \text{ m}^2/\text{s}$. For the base case, we assume a standard deviation for $\ln(D_m)$ of 0.598 , which yields an arithmetic mean for D_m of $2.04 \times 10^{-9} \text{ m}^2/\text{s}$. (These values are taken from Fleming and Haggerty [2001].) Three effluent points at $L = 5 \text{ m}$, 50 m , and 500 m are used in the numerical experiment.

The calibrated effective matrix diffusion coefficient is $1.58 \times 10^{-9} \text{ m}^2/\text{s}$ for all three effluent points. The sampling of the matrix diffusion coefficient for a given distribution is performed using Latin Hypercube sampling (LHS) [Zhang and Pinder, 2003], a method that is more efficient than the traditional Monte Carlo method. In this method, the probability distribution curve for a variable is divided into N_{LHS} intervals of equal probability, where N_{LHS} is equal to the total number of realizations being generated. Then, a realization is sampled from each interval.

A total of 10 channels are used in the analysis. Increasing the number of channels does not change the estimated matrix diffusion coefficient significantly (e.g., for the base case, the

calibrated value changes only slightly to $1.575 \times 10^{-9} \text{ m}^2/\text{s}$ for 50,000 channels); 10 channels are therefore considered reasonable.

In Figure 2, we plot both the average BTC from all channels and the BTC from Equation (2) using the calibrated effective matrix diffusion coefficient for the effluent point at $L = 5$. For a standard deviation of 0.598, the calibrated curve does not fit the peak well, whereas the tail is very well reproduced. The root mean square error (defined as $RMSE = \left[\sum_m r^2 / (m - n) \right]^{1/2}$, where r is the residual at each calibration point, $m = 200$ is the total number of calibration points, and $n = 1$ is the number of estimated parameters) is 1.81, which is approximately 8% of the peak and 20% of the average concentration values. Whether such an average fitting error is acceptable depends on the prediction accuracy required by the specific application.

The analysis was repeated for standard deviations of 0.3 and 0.8. A good fit is achieved and acceptable for a standard deviation of 0.3, but not for 0.8. When the standard deviation is 0.3, the differences between the calibrated effective matrix diffusion coefficients evaluated at the three effluent points are insignificant, i.e., no scale dependence is observed. Therefore, for a standard deviation on the order of 0.3, an effective matrix diffusion coefficient can be found and used to estimate the entire BTC. Moreover, when $\ln(D_m)$ has a standard deviation on the order of 0.6, an effective matrix diffusion coefficient may be found and used to estimate the tail of the BTC. However, if the peak of the BTC is very important, this single effective value cannot be used. When the standard deviation of $\ln(D_m)$ is small and the single effective matrix diffusion coefficient can be estimated, no scale dependence of matrix diffusion coefficients caused by small interchannel heterogeneity can be observed.

4. Intrachannel Heterogeneity

In addition to interchannel heterogeneity, variability in diffusive mass-transfer properties *within* a flow channel also plays an important role for solute transport. In this study, we apply a particle-tracking method to capture the intrachannel heterogeneity of the matrix diffusion coefficient. The particle-tracking method has been used in many studies for different purposes [Tsang and Doughty, 2003; Tsang and Tsang, 2001; Yamashita and Kimura, 1990]. Based on the approach of Yamashita and Kimura [1990], we incorporate the intrachannel heterogeneity of the matrix diffusion coefficient for a solution to tracer transport through a single fracture.

Given the solution in Equation (2), we can integrate the mass flux $F = cbv$ from $t = 0$ to t_v , which yields

$$\int_0^{t_v} F(L, t) dt = M_0 \operatorname{erfc}\left(\frac{k}{\sqrt{t_v - t_w}}\right) \quad (7)$$

As t_v goes to infinity, this integration converges to the total released mass M_0 . The ratio F/M_0 can be treated as the probability density function of the contaminant travel time, and $\operatorname{erfc}\left(\frac{k}{\sqrt{t_v - t_w}}\right)$ is the cumulative distribution function (CDF) for the contaminant travel time.

This is the starting point of the particle-tracking method suggested by Yamashita and Kimura [1990] to solve radionuclide transport in fractured porous media. The basic idea of the method is illustrated in Figure 3, where (3a) represents a BTC at location $x = L$, and (3b) represents the corresponding CDF for the contaminant travel time. In both figures, contaminant travel time is plotted on the x-axis. Assume that we divide the CDF of the travel time into 20 equal intervals as shown in Figure 3b (only part of the CDF is shown in this schematic figure, because the curve

gets very flat as it approaches 1) and find the corresponding travel-time interval Δt_v (time length between two adjacent times of the CDF).

The procedure of the particle-tracking method includes the following steps:

1. Release a total number of N particles at $x = 0$.
2. For each particle, generate a random number R from a uniform distribution in the interval $[0, 1]$, and solve for the particle travel time t_v from (see Figure 3b):

$$R = \operatorname{erfc} \left(\frac{k}{\sqrt{t_v - t_w}} \right) \quad (8)$$

Repeat Step 2 for all N particles.

3. Determine the experiment end time t_{end} (the travel time of the slowest particle) at the effluent point. Plot the histogram of particle arriving times.
4. Given that M particles arrive at $x = L$ between times t_1 and t_2 , the average concentration at $x = L$ at time $t = (t_1 + t_2)/2$ is calculated as:

$$c_0 = \frac{M}{N} \frac{M_0}{bv(t_2 - t_1)} \quad (9)$$

The average concentration is calculated for each time interval, resulting in the BTC at $x = L$.

Note that the above procedure is applied to cases with constant D_m . The main reason for our choosing this method, instead of using an existing analytical solution, is to be able to incorporate heterogeneity. The procedure is slightly modified to consider the intrachannel heterogeneity, where D_m is different at different locations. We divide the flow path along the fracture into small segments. The flow path encountered by a particle consists of segments with varying matrix diffusion coefficients, and each particle follows a separate flow path. A local D_m (sampled from a distribution curve) is assigned to each segment along the particle's path. Then

the travel time in this segment is calculated for each particle, and the procedure is repeated for each segment. Finally, at the observation point $x = L$, the travel times in all segments are added for each particle, which is the travel time for the particle to travel from $x = 0$ to $x = L$, and the BTC can be calculated for $x = L$.

A lognormal distribution is used to characterize the intrachannel heterogeneity of the matrix diffusion coefficient. The statistics (e.g., the mean and the variance of $\ln(D_m)$) describing the base-case intrachannel heterogeneity are assumed to be the same as those used for describing the base-case interchannel heterogeneity. Note that in general the variance of the intrachannel heterogeneity is expected to be smaller than that of the interchannel heterogeneity, which refers to a somewhat larger scale. The impact of the variance on the estimated effective matrix diffusion coefficients is examined through sensitivity analyses. A total of 50,000 particles is used in our modified particle-tracking method. This number is consider sufficient to yield stable output statistics, as is confirmed by *Yamashita and Kimura* [1990], who did not observe significant differences when using either 20,000 or 200,000 particles.

The size of a segment used in the calculation is 0.05 m. To test the sensitivity of the results to the discretization of the flow path, a high-resolution simulation was performed, in which the flow path of length $L = 5$ m was subdivided into one million segments. The difference between the resulting estimates of the effective matrix diffusion coefficient (2.99×10^{-9} m²/s vs. 3.04×10^{-9} m²/s) is considered insignificant.

Figure 4 shows fitting plots at $L = 5$ m, i.e., the simulated BTC of the heterogeneous system obtained using the particle-tracking method, and the BTC for an equivalent homogeneous system obtained using Equation (2) and the calibrated, effective matrix diffusion coefficient. The two panels of Figure 4 are the results for standard deviations of 0.598 (left) and 1.5 (right),

leading to *RMSEs* of 0.485 and 0.497, respectively. The generally good fit indicates that the heterogeneous system behavior can be reasonably well represented by a homogeneous system with an appropriate effective diffusion parameter. The analysis was repeated by increasing the standard deviations of $\ln(D_m)$ stepwise up to 4.0. Good matches were obtained for standard deviations up to 2.0. For higher standard deviations, Equation (2) is no longer capable of capturing the shape of the entire BTC from the heterogeneous system, leading to a mismatch (underprediction) at early times, which is compensated for in a least-squares sense by an overprediction of the peak concentration value. Again, whether this mismatch is acceptable depends on the application, e.g., whether arrival time or peak values are of interest. The estimated effective matrix diffusion coefficient can be used to estimate the tail of the BTC. When the standard deviation is above 4.0, an obvious mismatch is observed, and the estimated effective parameter should not be used.

The calibrated effective matrix diffusion coefficients for standard deviations of 0.598 and 1.5 are listed in Table 1. Similar to the interchannel heterogeneous cases with small variances, the difference among the calibrated matrix diffusion coefficients at different effluent points is not sufficient enough to indicate scale dependence of the matrix diffusion coefficient. This observation is independent of the variance. Thus, the intrachannel heterogeneity is not the reason for the observed scale dependence of the effective matrix diffusion coefficient.

Based on our numerical experiments, when the standard deviation of $\ln(D_m)$ is less than 4.0, the following formula can be used to estimate the effective matrix diffusion coefficient in the presence of lognormally distributed intrachannel heterogeneity:

$$\hat{D}_m = \exp\left[m + \frac{s^2}{4}\right] \quad (10)$$

where m and s are the mean and the standard deviation of $\ln(D_m)$, respectively. Figure 5 shows that Equation (10) can be used to estimate the effective matrix diffusion coefficient up to a standard deviation of $s = 3$. Recall that for higher standard deviations, the use of an effective matrix diffusion coefficient is questionable, because Equation (2) is an unlikely model of the heterogeneous system.

The coefficient $\hat{D}_m$ calculated using Equation (10) is very close to the effective matrix diffusion coefficient ($\bar{D}_m$) when s is less than 2 (e.g., when $s = 2$, $\hat{D}_m = 4.62 \times 10^{-9} \text{ m}^2/\text{s}$ vs. $\bar{D}_m = 4.64 \times 10^{-9} \text{ m}^2/\text{s}$). Again, as we continue to increase s , the difference between the calculated and the calibrated values starts to increase. Figure 6 is an illustration of three BTCs (at $L = 5 \text{ m}$ and for $s = 3$): the black dots are the simulated data using the modified particle-tracking method, the blue line is the BTC obtained by inserting the calibrated effective matrix diffusion coefficient into Equation (2), and the red line is the BTC obtained using $\hat{D}_m$ estimated by Equation (10). Neither the calibrated diffusion coefficient nor that estimated by Equation (10) give a perfect match to the peak concentration from the heterogeneous system; however, they both match the tail very well.

As previously mentioned, *Haggerty et al.* [2004] reported that the mass-transfer coefficient in porous media decreases with test duration, but the trend is not obvious for fractured media (see their Figure 1). (Recall that their mass-transfer coefficient is conceptually similar to the effective matrix diffusion coefficient used here.) *Zhou et al.* [2005] indicated that the test-duration dependency is not evident from the analysis of tracer tests conducted in fractured rocks. In these intrachannel heterogeneity experiments with the modified particle-tracking method, we also investigate the relationship between test duration and effective matrix diffusion coefficient

for multi-rate diffusion processes by varying the advection residence time t_{ad} for a flow channel with a lognormal distribution of the matrix diffusion coefficient at each location. The observation point is fixed at $L = 50$ m. In addition to the base case ($s = 0.598$) in which $t_{ad} = 2.0 \times 10^4$ s, we run four cases with an advection residence time t_{ad} of 2.0×10^3 s, 2.0×10^5 s, 2.0×10^6 s, and 2.0×10^7 s, respectively. The resulting effective matrix diffusion coefficients are identical for different advection residence times (or test durations), indicating that the multi-rate diffusion process resulting from pore-scale heterogeneity cannot explain the dependence of the effective matrix diffusion coefficient on test duration, at least not for fractured rock. This result is consistent with the finding of Zhou *et al.* [2005]. A possible reason for the dependence on test duration observed by Haggerty *et al.* [2004] is that the mass-transfer coefficient is overestimated during early periods of the experiment, since at an early stage, the concentration gradient at the interface between the mobile and immobile zone is much sharper than at later stages of the experiment.

5. Discussion and Conclusion

In this paper, we have investigated how two types of heterogeneity in diffusion properties affect solute transport, namely, interchannel heterogeneity and intrachannel heterogeneity. Our first objective was to examine whether it is appropriate to use a single effective matrix diffusion coefficient, in combination with a standard solution model for transport in a homogeneous medium, to predict breakthrough curves (BTC) in a heterogeneous fractured formation. It appears that for both types of heterogeneity we studied, the use of a homogeneous model with an effective matrix diffusion coefficient is appropriate only if the variability is small, e.g., s_{inter} (standard deviation of $\ln(D_m)$ for interchannel heterogeneity) smaller than 0.3–0.6, and s_{intra}

(standard deviation of $\ln(D_m)$ for intrachannel heterogeneity) smaller than 2.0–4.0, assuming a lognormal distribution of the underlying matrix diffusion coefficient. The lower bound should be used for applications where the prediction of both peaks and tails is important, and the upper bound could be used when the tail is of primary interest. The application range of the effective matrix diffusion coefficient for the interchannel heterogeneity seems to be much smaller than that for intrachannel heterogeneity. Fortunately, a property usually has larger variability when it is averaged over a smaller geological area. For intrachannel heterogeneity, when the use of an effective matrix diffusion coefficient is appropriate, it can be estimated from Equation (10), provided that the standard deviation of the underlying matrix diffusion coefficient distribution is known.

The second objective of the study was to examine if the observed scale dependence of the effective matrix diffusion coefficient is caused by heterogeneity in diffusive properties. For both types of heterogeneity, we compared the single effective matrix diffusion coefficients at different effluent points assuming a relatively small variance of $\ln(D_m)$. The difference among the resulting values is small and cannot be considered a consequence of the different study scales. We conclude that the scale dependence is not caused by inter- or intrachannel heterogeneity in the diffusion coefficient. However, it is possible that in some tracer tests or field experiments, particles may not encounter the entire spectrum of diffusion-relevant matrix properties. In other words, the sampling of the local matrix diffusion coefficient may not be complete, which results in a bias in the actual distribution of the matrix diffusion coefficient. The bias may result in an observed scale dependence.

The third objective of the study was to examine whether the multi-rate diffusion process actually results in the observed time dependence of the effective matrix diffusion coefficient. We

compared the effective matrix diffusion coefficients for different advection residence times. Again, no significant difference was observed. The results show that multidiffusion processes cannot cause the test-duration dependence of the effective matrix diffusion coefficient.

The multichannel model was used to incorporate the interchannel heterogeneity, and the particle-tracking method was used to incorporate the intrachannel heterogeneity. The impacts of these two types of heterogeneity have been studied separately, even though they are unlikely to be distinguished in the results of laboratory and field tracer tests. The study still helps us to understand the role of heterogeneity in matrix diffusion processes.

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Figure 1. Schematic of a single fracture system [Yamashita and Kimura, 1990]

Figure 2. The average BTC of the 10 channels vs. the BTC from the calibrated effective matrix diffusion coefficient for the base case

Figure 3. Illustration of the particle-tracking method

Figure 4. The simulated BTC using particle tracking vs. the BTC from the calibrated effective matrix diffusion coefficient: left – $s = 0.598$; right – $s = 1.5$

Figure 5. $\hat{D}_m$ calculated using Equation (10) vs. calibrated $\bar{D}_m$ using Equation (2) for different standard deviation s

Figure 6. Comparison of simulated concentration using particle tracking (PT; black dots), BTC obtained using $\bar{D}_m$ (blue line) and BTC obtained using $\hat{D}_m$ (red line)

Table 1: Effective matrix diffusion coefficient (m^2/s) with intrachannel heterogeneity

Standard deviation of $\ln(D_m)$	$L = 5 \text{ m}$	$L = 50 \text{ m}$	$L = 500 \text{ m}$
0.598	1.86×10^{-9}	1.83×10^{-9}	1.87×10^{-9}
1.5	2.99×10^{-9}	2.96×10^{-9}	2.99×10^{-9}

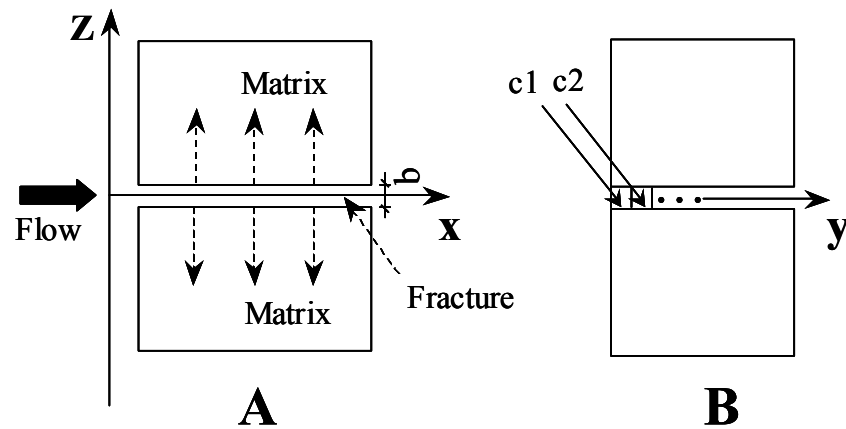


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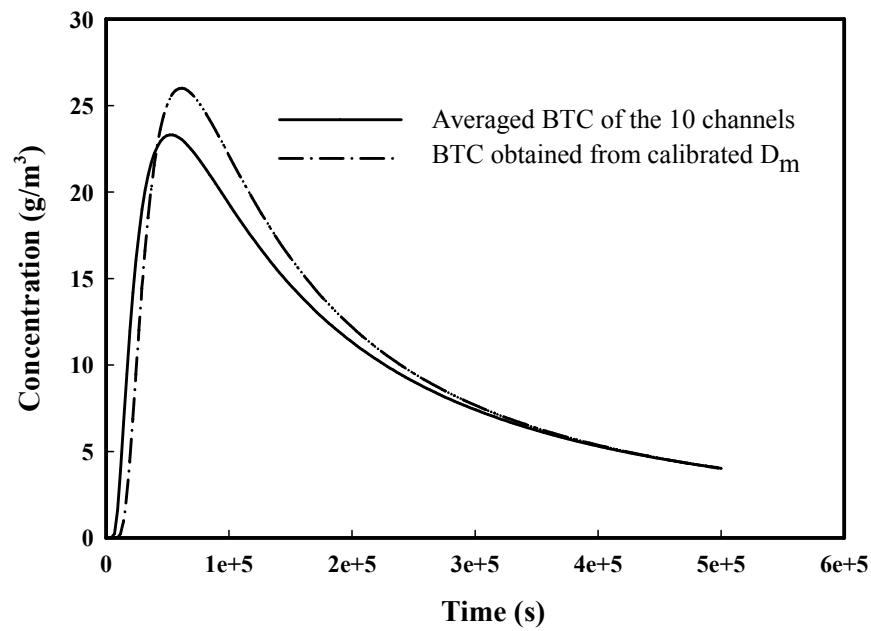


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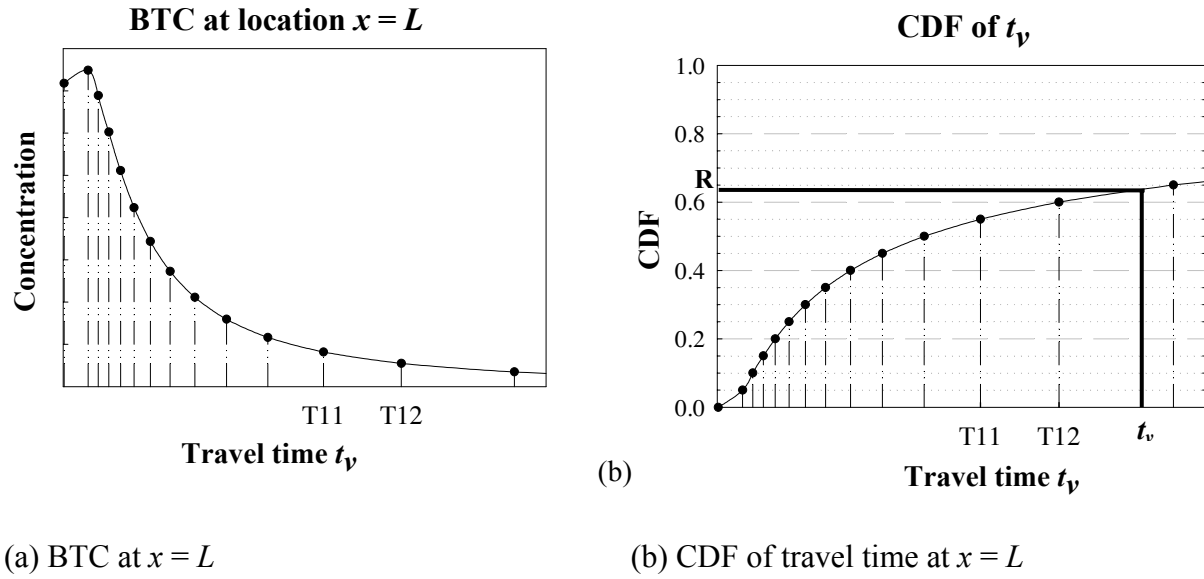
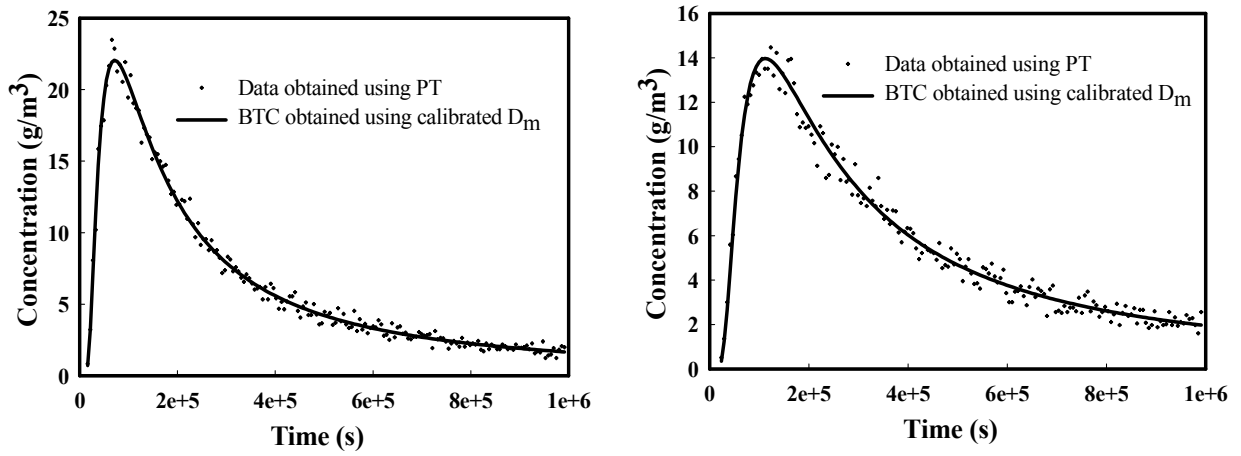


Figure 3. Illustration of the particle-tracking method


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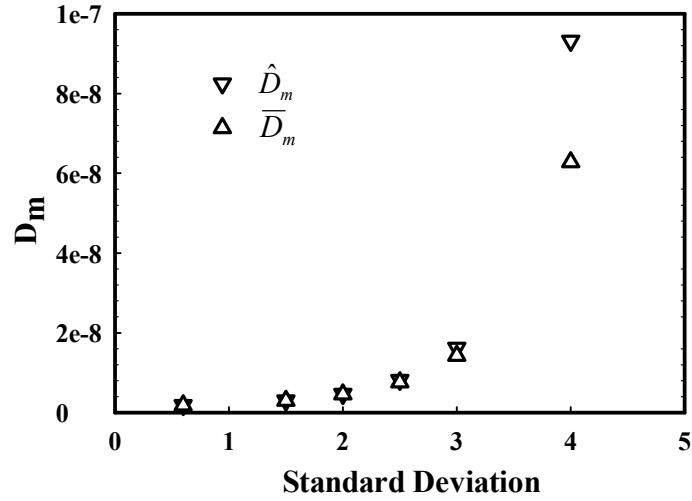


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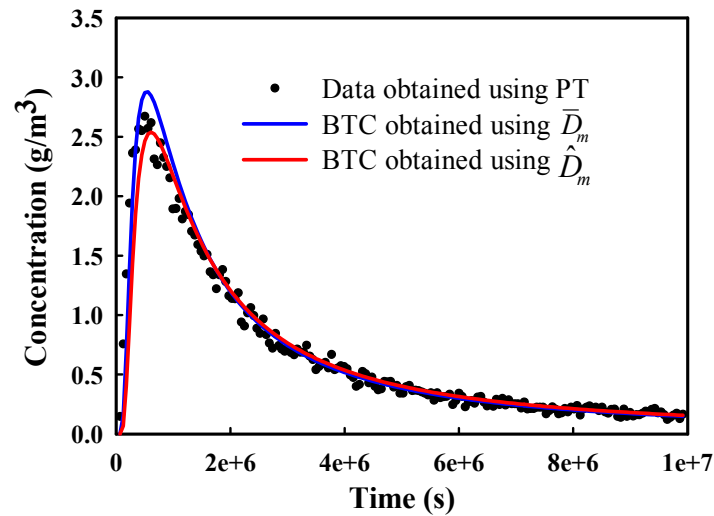


Figure 6. Comparison of simulated concentration using particle tracking (PT; black dots), BTC obtained using $\bar{D}_m$ (blue line) and BTC obtained using $\hat{D}_m$ (red line)