

Fracture-Flow-Enhanced Matrix Diffusion in Solute Transport Through Fractured Porous Media

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Abstract Over the past few decades, significant progress of assessing chemical transport in fractured rocks has been made in laboratory and field investigations as well as in mathematic modeling. In most of these studies, however, matrix diffusion on fracture–matrix surfaces is considered as a process of molecular diffusion only. Mathematical modeling based on this traditional concept often had problems in explaining or predicting tracer transport in fractured rock. In this article, we propose a new conceptual model of fracture-flow-enhanced matrix diffusion, which correlates with fracture-flow velocity. The proposed model incorporates an additional matrix-diffusion process, induced by rapid fluid flow along fractures. According to the boundary-layer theory, fracture-flow-enhanced matrix diffusion may dominate mass-transfer processes at fracture–matrix interfaces, where rapid flow occurs through fractures. The new conceptual model can be easily integrated with analytical solutions, as demonstrated in this article, and numerical models, as we foresee. The new conceptual model is preliminarily validated using laboratory experimental results from a series of tracer breakthrough tests with different velocities in a simple fracture system. Validating of the new model with field experiments in complicated fracture systems and numerical modeling will be explored in future research.

Keywords Matrix diffusion · Solute transport · Contaminant transport · Tracer test · Fractured porous media

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List of Symbols

b	Half aperture of fractures (m)
c	Concentration (kg/m^3)
c, c_i	Simulated concentration (kg/m^3)
c^*	Measured concentration (kg/m^3)
c_f	(Averaged) solute concentration across fractures (kg/m^3)
c_m	Solute concentration of the matrix on the matrix block surface (kg/m^3)
c_o	Constant fracture source solute concentration (kg/m^3)
D	Hydrodynamic dispersion coefficient along fractures (m^2/s)
D_E	Effective enhanced matrix-diffusion coefficient (m^2/s)
D_m	Free-solution molecular diffusion coefficient (m^2/s)
D^*	Effective molecular diffusion coefficient (m^2/s)
h_c	Mass-transfer coefficient at the fracture–matrix interface (m/s)
K_f	Distribution coefficient (m) on fracture surfaces, defined the solute mass adsorbed per unit area of fracture surface divided by solute concentration in solution
n	Exponential
p	Laplace operator
R_f	Fracture-face retardation coefficient
q_c	Mass-transfer flux at the fracture and matrix interface [$\text{kg}/(\text{s}\text{m}^2)$]
v	Mean-flow velocity in fracture (m/s)
\vec{v}	Fracture-flow velocity vector (m/s)
w_i	Weighting factor
α_E	Fracture-flow-enhanced dispersivity ($\text{m}^{2-n}/\text{s}^{1-n}$)
δ_c	Thickness of a concentration boundary (film) layer (m)
δ_h	Velocity boundary-layer thickness (m)
ϕ	Porosity of the matrix
Φ	Objective function of Eq. 10
λ	Decay constant (1/s)
τ	Tortuosity of matrix porous media

1 Introduction

Earlier studies of flow and transport in fractured porous media were motivated primarily by concerns related to petroleum and geothermal energy technologies, as well as interest in groundwater resources from fractured reservoirs (e.g., [Warren and Root 1963](#)). In the 1970s and 1980s, chemical or solute transport through fractured porous media received increasing attention from investigators involved in underground natural-resource recovery, as well as in subsurface contamination and remediation. Since then, fractured rock has been recognized to play an important role in the transport of natural resources or contaminants through subsurface systems. Over the past few decades, significant progress has been made in understanding and modeling transport phenomena in fractured porous media (e.g., [Tang et al. 1981](#); [Sudicky and Frind 1982](#); [Rasmuson et al. 1982](#); [Huyakorn et al. 1983](#); [Pruess and Narasimhan 1985](#); [Berkowitz 2002](#)).

In recent years, interest has grown in investigating solute transport through fractured rock, driven by environmental concerns related to radionuclide transport in fractured formations (e.g., [Liu et al. 2003, 2004a](#); [Hu et al. 2004](#); [Reimus and Callahan 2007](#)). Moreover, suitability evaluations for underground geological storage of high-level radioactive waste in

fractured rock have generated renewed interest in investigations of tracer and radionuclide transport in a fractured geological system. In addition, application of tracer tests, including environmental tracers and man-made gas- and liquid-tracer injection, has become a standard technique in characterizing fractured rock formations. All these investigations and experiments require an in-depth, quantitative understanding of fracture–matrix diffusion and interaction.

Since the 1970s, while understanding fracture–matrix interaction has been the focus of investigation into flow and transport processes in fractured rock, matrix diffusion has been gradually recognized as one of the most important mechanisms that control radionuclide transport processes in fractured rock (e.g., Neretnieks 1980; Neretnieks et al. 1982; Maloszewski and Zuber 1993; Liu et al. 2004a). Even in the laboratory, fracture–matrix diffusion is also found to be dominant (Neretnieks et al. 1982; Sudicky et al. 1985; Wu and Pruess 2000). However, field tracer tests (e.g., Liu et al. 2003, 2004a) have shown that fracture–matrix interaction through matrix diffusion may be too large (or “enhanced”) to be explained by traditional advection–diffusion theory. In order to match tracer experimental results from a large-scale field test, Liu et al. (2003) had to increase fracture–matrix interfacial areas by a factor of 2–4, or to significantly increase effective matrix diffusion. Several studies have been carried out to look into why such enhanced matrix diffusion occurs at fracture–matrix interfaces, with mechanisms ranging from scale dependency of the effective matrix-diffusion coefficient (Liu et al. 2004b) to possible effects of small-scale fractures or large fracture–matrix interaction areas (Wu et al. 2004).

Even with the significant progress made in laboratory and field investigations, as well as in mathematical modeling, matrix diffusion on fracture–matrix surfaces has been exclusively considered as a molecular diffusion process only. As a result, mathematical modeling approaches based on this traditional concept have had difficulty in matching or explaining laboratory and field testing results (e.g., Neretnieks et al. 1982; Starr et al. 1985; Maloszewski and Zuber 1993; Liu et al. 2003, 2004a). Here, we propose an additional matrix-diffusion mechanism: matrix-diffusion enhancement induced by rapid fluid flow within fractures. According to the boundary-layer or film theory (e.g., Bird et al. 1960; Fahien 1983), fracture-flow-enhanced matrix diffusion may dominate mass-transfer processes at fracture–matrix interfaces, because rapid flow along fractures results in high velocity or large concentration gradients at and near fracture–matrix interfaces, enhancing matrix diffusion on matrix surfaces. In this article, we present a new formulation of the conceptual model for such enhanced fracture–matrix diffusion, and its implementation is discussed using existing analytical solutions and numerical models. The new model can be easily integrated with existing analytical solutions, as demonstrated in this article; we foresee that integrating the model with numerical model is not difficult. In addition, we use the enhanced matrix diffusion concept to analyze laboratory experimental results from nonreactive and reactive tracer breakthrough tests, in an effort of preliminary validation of the new conceptual model. The model is considered validated by the experiment results of a simple fracture system, because the experiment results with different velocities are explained reasonably well by the model using a consistent set of parameters. If the fracture-flow-enhanced matrix diffusion is ignored as in Starr et al. (1985), the model parameters must be adjusted for different velocities to obtain the same level of fitting to the experimental results. Further validating the new conceptual model using field experiment in complicated fracture system (e.g., fractured network) and using numerical models will be conducted in the future research.

2 Physical Consideration and Conceptual Model

The schematic of vertical fracture–matrix systems under study is shown in Fig. 1. A fracture is subject to fluid flow with an averaged velocity of v , in which a boundary layer of laminar flow may be created (Fig. 1a) or the flow becomes fully developed within the fracture (Fig. 1b). For simplicity, it is assumed that fluid flow occurs only within fractures, the matrix is impermeable, and mass transfer across fracture–matrix interfaces and within the matrix is by diffusion only. As shown in Fig. 1a, a concentration profile, $c(x)$, with a concentration boundary (film) layer develops along the vertical fracture–matrix interface at depth. According to the boundary-layer or film theory (e.g., [Fahien 1983](#)), the mass transfer (q_c) of solute per unit area at the fracture and matrix interface is given by

$$q_c = h_c(c_f - c_m) \approx \frac{D_m(c_f - c_m)}{\delta_c}, \quad (1)$$

where h_c is the mass-transfer coefficient at the fracture–matrix interface; c_f is the (averaged) solute concentration across fractures; c_m is the solute concentration of the matrix on the matrix block surface; and δ_c is the thickness of a concentrated boundary (film) layer for mass transfer (Fig. 1a). Equation 1 indicates that the mass-transfer coefficient h_c (similar to the heat-transfer coefficient in advective heat transfer) is determined by the free-solution molecular diffusion coefficient, D_m , of the matrix, divided by the effective concentration-layer (film) thickness (Fig. 1a) δ_c

$$h_c \approx \frac{D_m}{\delta_c}. \quad (2)$$

Note that the concentration boundary-layer thickness δ_c is related to the velocity boundary-layer thickness (δ_h , Fig. 1a), in general, while the latter in turn depends on fracture-flow velocity or Reynolds number, among other variables.

As shown in Fig. 1a, once boundary layers develop in fractures, the classic boundary-layer theory provides a physical base for fracture-flow-enhanced matrix diffusion (e.g., [Bird et al. 1960](#)); the larger the fracture-flow velocity (or the Reynolds number), the thinner the velocity or concentration boundary layers. Then, the mass-transfer coefficient of (2) becomes larger, leading to larger mass-transfer flux (Eq. 1). In addition, plug or turbulent flow, if it occurs within fractures, could be considered as a special case of the boundary-layer concept, i.e., at plug or turbulent flow, the thickness of the flow boundary “layer” as well as the concentration boundary layer (δ_c) is tiny or infinitesimal. This is because along the matrix solid surface, the velocity is zero, and plug or turbulent flow will create huge velocity and concentration gradients perpendicular to matrix surfaces, which will be compensated by enhanced matrix diffusion into matrix blocks.

In general, fracture apertures in geological formations are very small, normally ranging from micrometers to millimeters, and velocity and/or concentration profiles may become fully developed in fractures (Fig. 1b). In such a case, Eq. 1 may be replaced by the following expression:

$$q_c = h_c[c(x=0) - c_m] \approx \frac{D_m[c(x=0) - c_m]}{b}, \quad (3)$$

where $c(x=0)$ is the concentration at the center of a fracture (x being perpendicular to fractures, Fig. 1b) and b is the half aperture of fractures (See Fig. 1). In this case, the mass-transfer coefficient may be approximated as

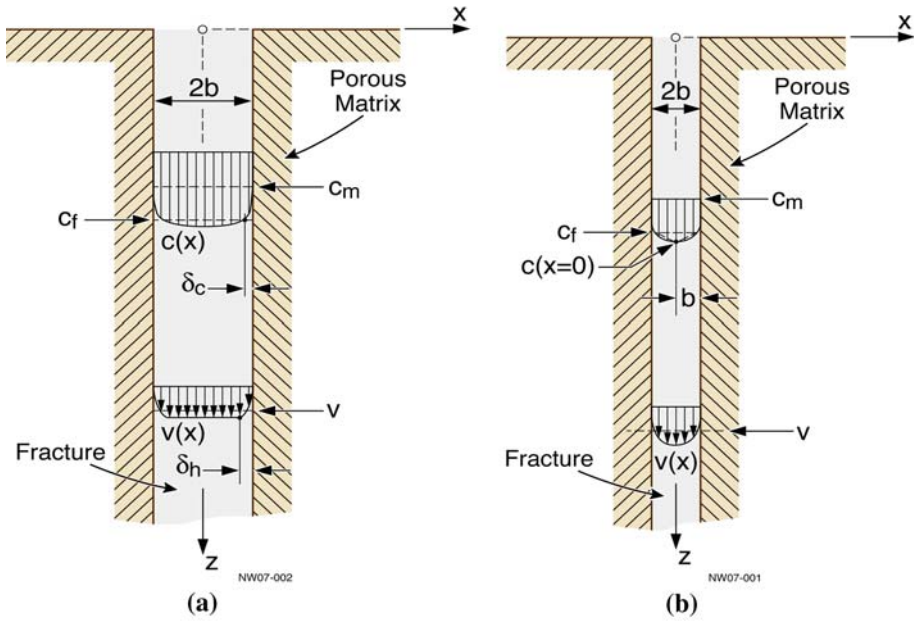


Fig. 1 Fracture–matrix system illustrating concentration and velocity profiles within a fracture, as well as a concentration boundary or film layer at the fracture–matrix interface: **a** velocity boundary layer (thickness = δ_h), and concentration boundary (film) layer (thickness = δ_c) with a large fracture; **b** fully developed flow velocity and concentration profiles ($\delta_c = b$) with a small fracture

$$h_c \approx \frac{D_m}{b}. \tag{4}$$

Note that the mass-transfer coefficient at fracture–matrix interfaces, as defined by Eq. 4, becomes constant. However, the concentration at the center of fractures, $c(x = 0)$, would increase with large fracture-flow velocity under fully developed flow conditions, because advective transport is the strongest along the center stream line of fractures (Fig. 1b), leading to increase in concentration gradients or enhanced diffusion into the matrix, as implicitly described by Eq. 3.

Mass flux continuity at the fracture–matrix interface requires that the mass-transfer rate of (1) or (3) be balanced by actual mass diffused into the matrix. The same amount of mass flux may be described by the following effective enhanced matrix diffusion term:

$$q_c = -D_E \left. \frac{\partial c}{\partial x} \right|_{x=b}. \tag{5}$$

Here, we introduce an effective enhanced matrix-diffusion coefficient D_E to include the enhanced mass-transfer effect, which is induced by fast fracture flow. Specifically, we propose the following expression for calculating the *effective* enhanced matrix-diffusion coefficient as

$$D_E = \phi (D^* + \alpha_E v^n), \tag{6}$$

where the effective molecular diffusion coefficient is $D^* = \tau D_m$ (τ being the tortuosity of the matrix porous medium) and ϕ is porosity of the matrix. In Eq. 6, we introduce the two new parameters, i.e., a constant coefficient α_E and a nonnegative exponential n . In analogy

with hydrodynamic dispersion methodology, α_E is called the fracture-flow-enhanced dispersivity (L^{2-n}/T^{1-n}), while n is a dimensionless variable. Note that in this article, the effective molecular diffusion coefficient of (6) is correlated to fracture-flow velocity, instead of the Reynolds number, despite the fact that thickness of concentration boundary layer is related to the Reynolds number. Using flow velocity instead is for convenience in application, because the Reynolds number is more difficult to define when handling flow through heterogeneous fractures than flow velocity, and the latter is generally known in both analytical and numerical modeling.

The rationale behind Eq. 6 estimating the enhanced fracture–matrix-diffusion process are as follows:

- The effective diffusion coefficient D_E becomes larger with the increase in fracture-flow velocity, to account for the impact of large increases in concentration gradients or enhanced matrix diffusion at fracture–matrix interfaces. No matter what fracture-flow regime is encountered, whether it be boundary layer, fully developed, plug-like, or turbulent, rapid fracture flow will cause large transverse velocity gradients near and at matrix surfaces, leading to large-transverse concentration gradients and then enhanced matrix diffusion locally. This correlation can be explained by the classic boundary-layer theory, if boundary layers develop.
- For the case of very low or zero fracture-flow velocity, the fracture fluid and solute would be well-mixed laterally across the fracture, and the fracture–matrix-diffusion process is dominated by molecular diffusion, i.e., the local equilibrium condition prevails within fractures as well as at fracture–matrix interfaces. In this case, the effective enhanced matrix-diffusion coefficient of (6) is approximately the molecular diffusion coefficient as well.
- In the special case in which the exponential $n = 1$, Eq. 6 becomes symbolically equivalent to the transverse dispersion coefficient from the hydrodynamic dispersion theory in estimating diffusion terms perpendicular to the fracture-flow direction. Note that there is, in general, a fundamental difference between the proposed model of (6) and the traditional transverse dispersion in hydrodynamic dispersion theory, because Eq. 6, applied only for the *fracture–matrix* interface, represents fracture-flow-enhanced matrix diffusion, whereas hydrodynamic dispersion accounts for dispersive processes caused by pore-scale heterogeneity of flow within *porous media*.

The two new parameters, fracture-flow-enhanced dispersivity α_E and exponential n in (6), should be determined empirically from laboratory tests or field studies using site-specific fracture–matrix data. Assuming that matrix diffusion is dominated by rapid fracture flow, as well as several other common used assumptions (fully developed fracture flow, constant concentration, or constant mass flux at fracture–matrix interfaces, etc.), the exponential n could be estimated as $n = 1/2$ for laminar flow in a large aperture fracture or as $n = 4/5$ with turbulent flow. If the mass diffusion process at fracture–matrix interfaces is similar to heat transfer, the range of exponential n could be $0.5 < n < 1.0$, by analog with the heat-transfer coefficients under different flow conditions (Tables 8-2 and 8-3, Ozisik 1985). Note that estimates of exponential n values in heat- and mass-transfer literature are based on many strict assumptions and idealized conditions. In general, fractures in porous media are heterogeneous, with variable apertures, rough surfaces, partial fillings and contacts, and irregular shapes. It may be neither impossible to determine the two parameters theoretically, nor is it considered to be necessary. They should be estimated using curve fitting or other empirical approaches from laboratory and field tests.

3 Model Implementation and Application

In general, diffusive mass-transfer processes across a boundary film, as shown in Fig. 1, lead to a third type of boundary condition, in contrast to the first two types, concentration and flux boundary conditions at fracture–matrix interfaces in the model formulation. The third type boundary condition will introduce some difficulty into the mathematical models. More significantly, one more parameter, mass-transfer coefficient, h_c (in addition to diffusion coefficients), would need to be determined. There would be additional complications when handling heterogeneous fracture networks. Therefore, in the following, we will investigate whether conventional treatment of boundary conditions at fracture–matrix interfaces can be used instead. For example, in analytical solutions, continuity in both concentration and mass flux is imposed (e.g., Tang et al. 1981; Lu et al. 2003), whereas numerical approaches treat fracture–matrix mass exchanges using flux continuity only (e.g., Wu and Pruess 2000). In order to use existing mathematical models and analytical solutions to incorporate fracture-flow-enhanced matrix diffusion, we must rely on the effective enhanced matrix-diffusion coefficient D_E , which is defined to include such fracture-flow diffusion enhancements.

With this conceptualization and treatment, the proposed model of Eqs. 5 and 6 for fracture-flow-enhanced matrix diffusion can be readily implemented into existing analytical solutions and numerical approaches. The following are some examples that show how to incorporate the enhanced matrix-diffusion effects into available or existing mathematical models and solutions.

3.1 Analytical Solutions

Analytical solutions generally assume the same matrix-diffusion coefficients for describing diffusion both at fracture–matrix interfaces and inside the matrix. In order to incorporate the effective enhanced matrix diffusion of (6) using existing analytical solutions, special attention must be paid to distinguish the two types of matrix diffusion processes: (1) enhanced diffusion at fracture–matrix *interfaces* and (2) diffusion *inside* the matrix. With this in mind, for example, the analytical solution, derived by Tang et al. (1981) for solute transport through fractured rock with a single fracture, surrounded by infinitely thick matrix blocks on both sides, can be easily extended to include fracture-flow-enhanced matrix diffusion by revising the constant A to

$$A = \frac{bR}{D_E} \left(\frac{D'}{R'} \right)^{1/2}, \quad (7)$$

where R is the retardation coefficient in fracture and D' and R' are the matrix molecular diffusion and retardation coefficients, respectively, for mass-transfer processes occurring *inside* the matrix.

Using the definition of A in (7), the analytical solution for fracture concentration in the Laplace space \bar{c} with fracture-flow-enhanced matrix diffusion of solute transport through a single-fracture system (Fig. 1) is given in the same form, for example, as Tang et al. (1981):

$$\bar{c} = \frac{c_0}{P - \lambda} \exp(vz) \exp \left[-vz \left\{ 1 + \beta^2 \left| \frac{P^{1/2}}{A} + P \right| \right\}^{1/2} \right], \quad (8)$$

where c_0 is constant fracture solute concentration (M/L^3) at source ($z = 0$, Fig. 1); $P = p + \lambda$; $v = v/2D$ and $\beta^2 = 4R_f D/v^2$, with p being the Laplace operator; v is the mean flow velocity in fracture; λ the decay constant; $D = D_m + \alpha_L v$ the hydrodynamic

dispersion coefficient along fractures; and $R_f = 1 + K_f/b$, called the fracture-face retardation coefficient, with K_f being a distribution coefficient on fracture surfaces.

With the revised definition of A , the analytical solutions in real space can be directly borrowed from [Tang et al. \(1981\)](#) with the same boundary and initial conditions. Using the same definition of A as in (7), the analytical solutions for transport through a parallel-fracture system ([Sudicky and Frind 1982](#)) can be directly extended to include the fracture-flow-enhanced matrix diffusion. These extended analytical solutions within a parallel-fracture system will be used in this study to analyze laboratory data in the following section.

3.2 Numerical Solutions

In comparison to analytical solutions, numerical implementation of the enhanced matrix-diffusion conceptual model is more straightforward. In this case, the effective enhanced matrix-diffusion coefficient, estimated by (6), can be directly used in a numerical model to calculate fracture–matrix-diffusion terms numerically. Considering that fracture flow in a numerical model is often a multidimensional vector, we write the effective enhanced fracture–matrix diffusion coefficient as

$$D_E = \phi(D^* + \alpha_E |\vec{v}|^n). \quad (9)$$

Note that the fracture-flow vector \vec{v} is defined within fractures and is also an unknown in coupled flow and transport processes. Implementation of Eq. 9 may introduce additional nonlinearity resulting from the dependence D_E on fracture-flow velocity when solving a coupled-nonlinear flow and transport problem.

In an ongoing study, the proposed enhanced matrix-diffusion model, Eq. 9, is being tested in the T2R3D code, a member of the TOUGH2 family of codes ([Wu and Pruess 2000](#); [Wu et al. 1996](#)). The numerical code can simulate fracture-flow-enhanced matrix diffusion with different fracture–matrix conceptual models for fracture–matrix interaction, such as double porosity, dual- and multi-continuum, and discrete-fracture modeling approaches. In particular, flow or advective transport within the matrix can also be included in a numerical model by superposing mass fluxes by diffusive and advective processes at fracture–matrix interfaces.

4 Analysis of Laboratory Data

The laboratory results of [Starr et al. \(1985\)](#) and analytical solutions ([Sudicky and Frind 1982](#)) are used in this section to discuss the reasonableness of the proposed physically based model of Eqs. 5 and 6. More specifically, the following analyses of experimental results serve as preliminary validation examples of the concept of fracture-flow-enhanced matrix diffusion.

[Starr et al. \(1985\)](#) presented an experimental investigation on solute transport in stratified porous media. The experiment was conducted under controlled laboratory conditions by injecting nonreactive and reactive tracers into a thin sand layer bounded by silt layers. In this study, this stratified, heterogeneous laboratory model is conceptualized as a dual-continuum, fracture–matrix medium. The highly permeable sand layer is considered as a “fracture” and the silt portion as “matrix,” because a several-orders-of-magnitude difference exists in permeability between the two media ([Sudicky et al. 1985](#)). More importantly, it is expected that large transverse velocity and concentration gradients develop at and near “matrix” surfaces within fractures, which are an ideal situation for demonstration of the model application.

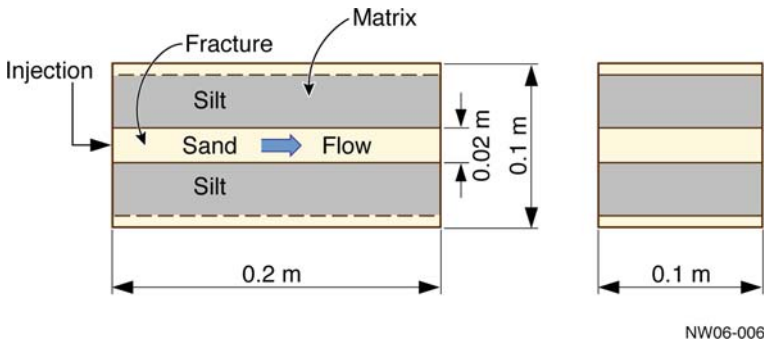


Fig. 2 Laboratory schematic model for bromide (nonreactive) and ^{84}Sr (reactive) tracer injection experiments (Starr et al. 1985)

Table 1 Experimental testing scenarios, pore velocity, and pulse injection periods

Experiment/tracer	Pore velocity (m/day)	Tracer-injection period (day)
Test #1 (Bromide)	0.29	–
Test #2 (^{85}Sr)	1.00	5.18
Test #3 (^{85}Sr)	0.50	8.02
Test #4 (^{85}Sr)	0.25	6.80

We use their experimental results in an effort to test and verify the conceptual model of fracture-flow-enhanced matrix diffusion with solute transport through fractured rock.

The laboratory model of Starr et al. (1985) consists of a plexiglass box containing a sand layer sandwiched between two silt layers, as shown in Fig. 2. The box is 0.2-m long with a 0.1 m \times 0.1 m cross section. The sand layer is 0.02-m thick and situated between the two silt layers, each 0.04 m in thickness. The influent and effluent end caps, through which the displacing liquid, containing a conservative (nonsorbing) tracer, bromide, or a reactive (sorbing) solute, strontium (^{85}Sr), enters or leaves the sand layer, are screened over the sand layer only during a series of continuous-injection or pulse-injection and breakthrough experiments.

Whereas five experiments were conducted (with one conservative and four reactive tracer tests) (Starr et al. 1985), only the first four tracer tests (Table 1) were actually used in their analyses, since the last experiment (with the reactive tracer) was used to repeat the experimental results of Test #2 (or the first ^{85}Sr test) to confirm that the characteristics of the laboratory model did not change with repeated use. Here, we also select the first four tests, i.e., the one conservative and three reactive tracer experimental results that are used in this work, to evaluate our proposed fracture-flow-enhanced matrix-diffusion concept.

In analyzing their laboratory results, involving three reactive tracer experiments at three different velocities, Starr et al. (1985) found that there exist significant discrepancies between model predictions and observed laboratory breakthrough curves for the reactive tracer cases. In particular, they could not use a consistent set of physical parameters with their mathematical model to match the observed data for the same reactive tracers under three different flow velocities. Instead, they had to use velocity-dependent retardation factors for better fitting results, which they concluded to be problematic, since the retardation factor should not vary with velocity for the same system and tracer. They also excluded possible kinetic or nonlocal equilibrium effects from their studies. Since their experiments were well conducted, with highly reproducible results and measurements, the inability to match experimental results

Table 2 Input and fitted parameters used in analyzing laboratory experimental results

<i>Input parameters</i>	
Fracture aperture (sand layer thickness \times sand porosity)	$b = 0.0066$ m
Fracture spacing	$B = 0.0934$ m
Fracture (sand) porosity	$\phi_f = 0.33$
Matrix (silt) porosity	$\phi_m = 0.36$
<i>Fitted parameters</i>	
Effective diffusion coefficient of bromide	$D^* = 6.0 \times 10^{-10}$ m ² /s
Effective diffusion coefficient of strontium (⁸⁵ Sr)	$D^* = 8.9 \times 10^{-10}$ m ² /s
Fracture longitudinal dispersivity	$\alpha_{L,f} = 0.0001$ m
Enhanced dispersivity	$\alpha_E = 2 \times 10^{-5}$ (m ^{1.1} /s ^{0.1})
Enhanced exponential	$n = 0.9$
Fracture retardation coefficient	$R_f = 13$
Matrix retardation coefficient	$R_m = 20$

using their mathematic model with a consistent set of model parameters forced them to speculate that “Some unaccounted for chemical or physical factor has influenced the transport of the reactive solute.”

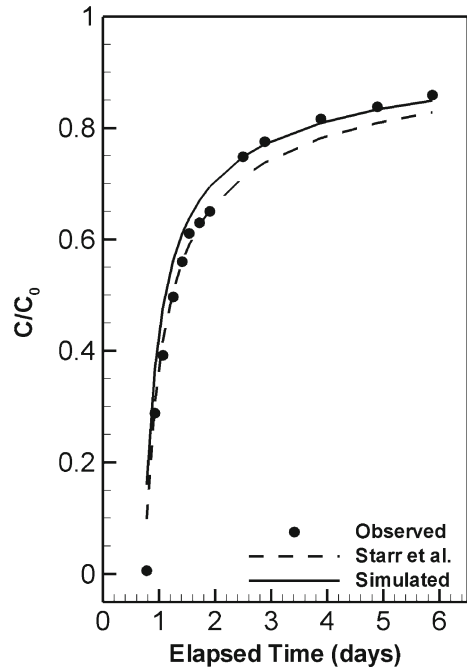
These observations and speculations in part motivate this work. We believe, as we will demonstrate below, that fracture-flow-enhanced fracture–matrix diffusion, which is not included in the original analyses by Starr et al. (1985), may play an important role in solute transport within their experiments. In the following, we will show that we are able to match the reactive-tracer-transport results using a consistent set of parameters with the proposed model, once the fracture-flow-enhanced matrix diffusion is taken into account. In addition, it is found that the same model parameters, fracture-flow-enhanced dispersivity (α_E) and exponential (n), as estimated from reactive tracer transport, are also applicable for nonreactive tracers.

Table 2 lists the model input and fitted parameters used in analyzing laboratory experimental results. We extend the analytical solution of transport through a parallel-fracture system of Sudicky and Frind (1982) to incorporate the fracture-flow-enhanced matrix-diffusion concept, as discussed in Sect. 3. For the three reactive-transport cases of Table 1, the analytical solutions are evaluated using a superposition principle for the time periods following tracer injection pulses (Sudicky et al. 1985). In fitting the experimental results of the four tracer breakthrough tests, we adopt a semi-automatic approach using a least-square-based software PEST (Doherty 2004), combined with trial and error adjustments of parameters. When using the computer-fitting code, PEST adjusts calibrated parameters to minimize an objective function:

$$\Phi = \sum_{i=1}^N (w_i r_i)^2 = \sum_{i=1}^N [w_i (c_i^* - c_i)]^2, \quad (10)$$

which measures the difference between measured and simulated concentration (by the extended analytical solution) denoted by c^* and c , respectively. Weighting factor w_i of measured concentration c_i is related to measurement error of c_i . Assuming that all measured concentrations at each elapsed time are of the same quality, we assign the same weight to all concentration measurements.

Fig. 3 Observed and simulated breakthrough curves for nonreactive tracer. Simulated breakthrough curves include those of Starr et al. (1985) and with fracture-flow-enhanced diffusion



For the case of nonreactive tracer transport, the calibrated or fitted parameters are: effective matrix-diffusion coefficient (D^*), fracture-flow-enhanced dispersivity (α_E), and exponential (n). Figure 3 shows an overall better match to the measurements when the fracture-flow-enhanced matrix-diffusion concept (labeled as “Simulated”) is included and when it is not (labeled as “Starr et al.”). In this case, the total enhancement (defined as the percentage of the 2nd term over the first term, diffusion-only coefficient, in Eq. 6) is 12.7%, indicating matrix diffusion being significantly enlarged by fracture flow.

For the tests of reactive transport, in addition to D^* , α_E , and n , fracture and matrix retardation coefficients are also fitted. The semi-automatic approach combining PEST and trial-and-error parameter calibration is used for Test 3 with velocity 0.5 m/day to obtain the optimum parameters (Table 2) in a least-square sense. These parameters are then used to simulate Tests 2 and 4. The final comparisons for the three tests of reactive transport cases are shown in Fig. 4. Note that a set of consistent physical parameters is estimated and used with the extended analytical solutions in our analyses, e.g., the same two retardation coefficients, R_f and R_m , are used for the three ^{85}Sr transport tests through the fracture–matrix system (Fig. 2). In addition, the same enhanced parameters α_E and n , induced by fracture flow, are found to work for both nonreactive and reactive transport results. Figure 4 shows that accounting for the fracture-flow-enhanced matrix-diffusion concept enables the model to match all three ^{85}Sr breakthrough curves at the three velocities reasonably well, as compared with the fittings by Starr et al. 1985, which unphysically uses different or velocity-dependent retardation factors for the same tracer transport in the same system. Even though comparisons in Fig. 4 indicate that the current work yields a similar good fit when compared with the original Starr et al. work, it is considered significant because the current study is based on the same physically consistent parameters, once incorporating the fracture-flow-enhanced

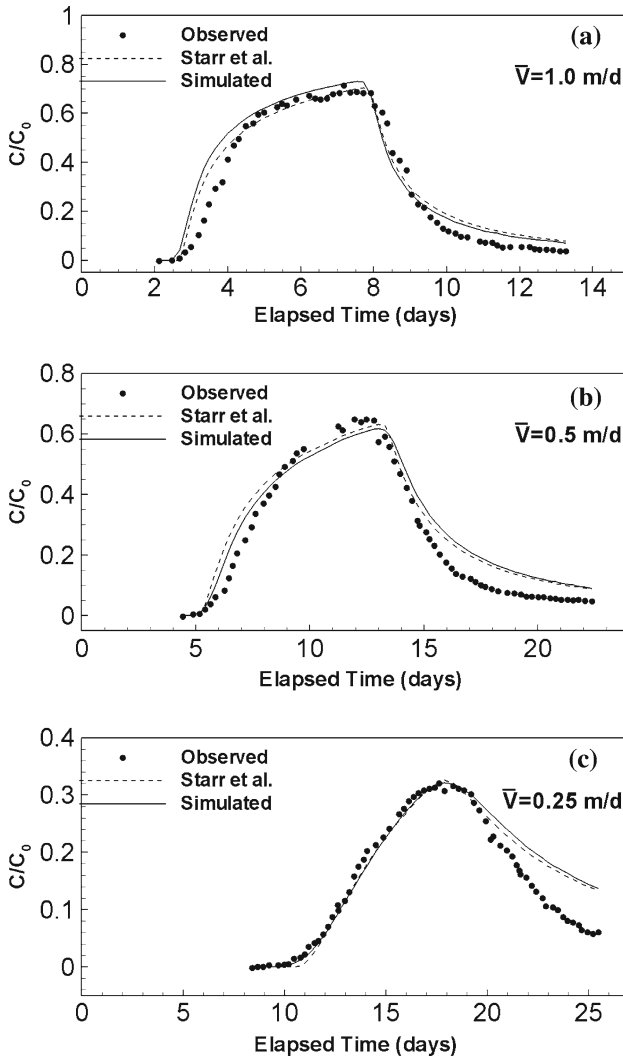


Fig. 4 Observed and simulated breakthrough curves for reactive tracer under three injection flow rates. Simulated breakthrough curves include those of Starr et al. (1985) and with fracture-flow-enhanced diffusion

matrix-diffusion concept. In this case, the enhancements in matrix diffusion by fracture flow are 26.7%, 13.9%, and 7.47%, respectively, for the three velocities of Fig. 4.

As shown in Figs. 3 and 4, the ability to match the laboratory measurements for both nonreactive and reactive tracer transport, using the same flow and transport properties for the same tracer tests, suggests that our proposed fracture-flow-enhanced matrix-diffusion concept is consistent with the behavior of the experimental physical system. However, there are still some inconsistencies when comparing the laboratory and model results, as shown in Fig. 4. In particular, long, smearing tails appear in the model predictions at a later time, when compared against the observations in Fig. 4 for the reactive transport scenario. These phenomena imply that there are still some unaccounted processes in our model, such as the

possible effect of immobile regions around sand grains (e.g., van Genuchten and Dalton 1986). Further discussion of the possible effects of different processes is considered beyond the scope of this study.

5 Concluding Remarks

We present a new matrix diffusion enhancement conceptual model that correlates effective fracture–matrix-diffusion coefficients to fracture-flow velocity. The new conceptual model is physically based on the boundary-layer theory, and it indicates that solute transport by diffusion between fractures and low-permeability matrix can be significantly enhanced and become a dominant factor if rapid flow occurs along the fracture–matrix interface, and if large transverse velocity and concentration gradients are created at fracture–matrix interfaces. We demonstrate that the new proposed mathematical model for describing fracture-flow-enhanced matrix diffusion can be easily incorporated into existing analytical solutions and numerical models to handle solute transport through fractured rock.

In an effort to provide some evidence of preliminary validation of the proposed enhanced matrix diffusion concept, we apply the conceptual model to analyzing laboratory experimental data for nonreactive and reactive tracer breakthrough tests. The experimental analyses indicate that the proposed matrix diffusion enhancement concept can provide not only a better agreement with experimental results for both nonreactive and reactive tracer transport, but also a physically consistent set of flow and transport properties, which cannot otherwise be obtained without incorporating the fracture-flow-enhanced matrix diffusion process. The new conceptual model will be further validated using field experiments in complicated fracture system and using numerical modeling.

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