Analytical solutions of tracer transport in fractured rock associated with precipitation-dissolution reactions

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Abstract

Precipitation-dissolution reactions are important for a number of applications such as isotopic tracer transport in the subsurface. This study develops analytical solutions for tracer transport in both a single-fracture and a multiple-fracture system associated with these reactions under transient and steady state transport conditions. These solutions also take into account advective transport in fractures and molecular diffusion in rock matrix. It is demonstrated that for studying distributions of disturbed tracer concentration (defined as difference between actual concentration and its equilibrium value), effects of precipitation-dissolution reactions are mathematically equivalent to a "decay" process with a decay constant proportional to the corresponding bulk reaction rate. This important feature significantly simplifies our derivation procedure by taking advantage of the existence of analytical solutions to tracer transport associated with radioactive decay in fractured rock. It is also useful for interpreting tracer breakthrough curves, because impact of decay process is relatively easy to analyze. Several illustrative examples (breakthrough curves obtained from analytical solutions) are presented and show that results are considerably sensitive to fracture spacing, matrix diffusion coefficient (fracture surface area), and bulk reaction rate (or "decay" constant), indicating that the relevant flow and transport parameters may be estimated by analyzing tracer signals.

1. Introduction

Tracer transport in fractured rock involves fast and advection-dominated processes in fractures characterized by high permeability and mass transfer between fractures and rock matrix (with negligible permeability) in which chemical reactions may occur as well. Modeling tracer transport in fractured rock is of interest to a number of practical applications, including radionuclide transport in a geological repository (e.g., Sudicky and Frind, 1982), groundwater contamination in fractured aquifers (e.g., Freeze and Cherry, 1979), and interpretation of isotopic tracer transport signals for characterizing flow patterns and fracture-matrix interaction (e.g., DePaolo, 2006).

With the significant advance of computational technology in recent decades, numerical models have been increasingly employed for modeling tracer transport in fractured rock. However, analytical solutions are still playing an important role in evaluating the transport processes for several reasons. First, given significant uncertainties in site characterization and parameter variability for a practical application, analytical solutions have often been used for analyzing field-testing results obtained under controlled conditions (Neretnieks, 2002), because they involve a small number of parameters and are able to capture key transport processes. Second, analytical solutions are generally more useful for providing physical insights into solute transport processes (DePaolo, 2006), because relative importance of key parameters (or parameter combinations) and processes can be explicitly identified from relevant analytical solutions. Third, it is well known that analytical solutions are useful for validating numerical models by comparing numerical and analytical results. The focus of this study is on development of analytical solutions for tracer transport in fractured rock.

A number of analytical solutions for solute transport in fractured rock have been published in the literature. These solutions consider fractured rocks associated with a single and straight fracture or a set of parallel fractures (or other simplified geometry of fractures). Neretnieks (1980) reported a solution for one-dimensional transport in a single fracture without considering longitudinal dispersion. Tang et al. (1981) presented both transient and steady state solutions for a single-fracture system, which were derived using Laplace transforms. Rasmuson and Neretnieks (1981) provided a one-dimensional solution for transport in fractured media consisting of porous blocks separated by fissures (fractures). In their solution, the porous blocks are represented by spheres that have a finite capacity to store a contaminant. Baker (1982) investigated tracer transport in a system of equally spaced fractures separated by slabs of saturated porous rock. However, his work was based on numerical inversion of the Laplace transform. Unlike the study by Baker (1982), Sudicky and Frind (1982) developed general analytical solutions for similar systems using analytical inversion of Laplace transform. Similar analytical solutions for parallel fracture systems were also reported by Maloszewski and Zuber (1985).

In addition to advection and dispersion in fractures and matrix diffusion processes, all the previous studies mentioned above consider chemical reactions such as radioactive decay and adsorption (represented by a retardation factor). To the best of our knowledge, the recent work of DePaolo (2006) probably represents the first effort to develop systematic analytical solutions to tracer transport in fractured rock associated with precipitation-dissolution reactions. That work was particularly focused on describing isotopic tracer transport. Developed relationships between isotopic signals and flow path

properties were demonstrated to be useful for characterizing the corresponding fracture-matrix properties (DePaolo, 2006). However, the analytical solutions of DePaolo (2006) are limited to steady-state transport conditions. Transient solutions are required for describing isotopic tracer transport in more general cases.

In this paper, we derive analytical solutions to tracer transport in fractured rock associated with precipitation-dissolution reactions under both steady state and transient transport conditions. The derivation is based on the analytical inversions of Laplace transform that are similar to those used by Tang et al. (1981) and Sudicky and Frind (1982). The usefulness of our solutions in describing tracer transport is also demonstrated under a number of conditions.

2. Assumptions and Governing Equations

We will investigate tracer transport in a single fracture or a set of equally spaced identical fractures. Figure 1 shows a multiple-fracture system, with a single-fracture system being considered a special case with infinite fracture spacing. Water flow rate in each fracture is assumed to be constant and downward. Each fracture has a constant aperture that is much smaller than the fracture spacing. Matrix block has homogeneous properties and negligible permeability. Therefore, advection in rock matrix can be ignored. Because of transverse diffusion and dispersion, complete mixing across its width at all times. We also assume that molecular diffusion process within matrix occurs along the direction perpendicular to fractures only. The same assumptions were made in previous studies (e.g., Sudicky and Frind, 1982; DePaolo, 2006). Furthermore, we ignore the longitudinal dispersion and molecular diffusion within a fracture, because these

processes are not important for practical applications (e.g., Neretnieks, 2002) and ignoring these processes can significantly simplify mathematical development of analytical solutions. Following DePaolo (2006), we also consider dissolution rate to be the same as precipitation rate within rock matrix. The justification for this treatment was provided in DePaolo (2006) within the context of isotopic tracer transport.
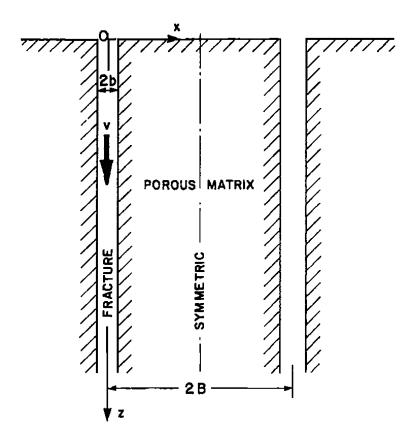

Fig.1. Fracture-matrix system

With above assumptions, tracer transport process in fractured rock can be described by two coupled one-dimensional equations for transport in liquid phase (one for fracture and one for rock matrix) and the third equation for solid phase due to precipitation-dissolution reactions. While the detailed derivation of these equations was given in DePaolo (2006), these equations are briefly discussed herein.

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Based on the mass conservation principle, tracer transport in fractures is described by (Sudicky and Frind, 1982; DePaolo, 2006):

$$\frac{\partial c_f}{\partial t} = -v\frac{\partial c_f}{\partial z} + \frac{D_m \phi_m}{b}\left\langle\frac{\partial c_p}{\partial x}\right\rangle_{x=b} \tag{1}$$

where t is the time (T), z and x are the spatial coordinates (M) (Figure 1), c_f is the tracer concentration in fractures (M/L^3), v is the water velocity in fractures (L/T), D_m is matrix diffusion coefficient defined by molecular diffusion coefficient in free water multiplied by tortuosity (L^2/T), ϕ_m is matrix porosity, c_p is the tracer concentration in matrix pore liquid (M/L^3), and 2b is the fracture aperture (L). The second term on the right hand of the equation describes the flux crossing two fracture walls.

Within the rock matrix, the pore fluid interacts with the solid phase by dissolution-precipitation, and the pore fluid communicates with the fracture fluid by diffusion. The equations describing these processes are given as (DePaolo, 2006):

$$\frac{\partial c_p}{\partial t} = D_m\frac{\partial^2 c_p}{\partial x^2} + R_m M\left(c_s - Kc_p\right) \tag{2}$$

$$\frac{\partial c_s}{\partial t} = -R_m\left(c_s - Kc_p\right) \tag{3}$$

where c_s is the tracer concentration in solid phase (M/L^3), R_m is the bulk reaction rate (1/T) that was also called bulk reaction time constant by DePaolo (2006), K is the distribution coefficient for solid/fluid system, and M is the mass ratio of solid to liquid given by

$$M = \frac{\rho_s\left(1-\phi_m\right)}{\rho_f \phi_m} \tag{4}$$

In Equation (4), ρ_f and ρ_s are fluid and solid density (M/L^3).

For isotopic tracer transport processes with typical R_m values, DePaolo (2006) demonstrated that solid phase concentration c_s hardly changes because of low tracer concentration in the liquid phase in natural fracture rocks. Therefore, he assumed c_s to be constant during developing steady-state solutions for tracer transport. In this study, we follow the similar treatment and therefore need to solve Equations (1) and (2) only (as a result of assuming c_s to be a constant) for modeling tracer transport in liquid phase.

For convenience, we introduce the following variables:

$$C_p = c_p - \frac{c_s}{K} \tag{5-1}$$

$$C_f = c_f - \frac{c_s}{K} \tag{5-2}$$

$$\lambda = R_m M K \tag{5-3}$$

Note that under equilibrium conditions, $C_f = C_p = 0$; C_f and C_p can be considered as concentration disturbances to equilibrium concentration fields, because they represent differences between tracer concentrations and their equilibrium values. Combining Equations (1), (2) and (5) yields

$$\frac{\partial C_f}{\partial t} = -v \frac{\partial C_f}{\partial z} + \frac{D_m \phi_m}{b} \left\langle \frac{\partial C_p}{\partial x} \right\rangle_{x=b} \tag{6}$$

$$\frac{\partial C_p}{\partial t} = D_m \frac{\partial^2 C_p}{\partial x^2} - \lambda C_p \tag{7}$$

It is of interest to note that the transformed equations (6) and (7) are mathematically equivalent to equations describing a tracer transport subject to a decay process (with the decay constant λ) occurring in the matrix block only. As will be demonstrated later, this feature is important for obtaining our analytical solutions based on the existing solutions

describing tracer transport subject to radioactive decay in fractured rock, such as those derived by Tang et al. (1981) and Sudicky and Frind (1982).

Assuming the existence of equilibrium at t = 0 and considering a continuous injection case, we can have initial and boundary conditions for (6):

$$C_f(z,0) = 0 \tag{8-1}$$

$$C_f(0,t) = C_0 \tag{8-2}$$

$$C_f(\infty,t) = 0 \tag{8-3}$$

The initial and boundary condition for the matrix equation (7) are

$$C_p(x,z,0) = 0 \tag{9-1}$$

$$C_p(b,z,t) = C_f(z,t) \tag{9-2}$$

$$\frac{\partial C_p}{\partial x}(B,z,t) = 0 \tag{9-3}$$

The coupling of the matrix to the fracture is expressed by (9-2). Note that (9-3) is applied to multiple-fracture systems. For a single-fracture system, it may be replaced by (Tang et al., 1981)

$$C_p(\infty,z,t) = 0 \tag{9-4}$$

3. Analytical Solutions for a Single-Fracture System

We will start with deriving analytical solutions for a single-fracture system. Although a single-fracture system rarely exists in reality, it is a good approximation for many realistic fractured rocks when tracer penetration depth is much smaller than fracture spacing, because in this case, effects of surrounding fractures can be ignored. Analytical solutions are obtained with the strategy used by Tang et al. (1981) and Sudicky and Frind

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(1982) for developing analytical solutions to radioactive tracer transport in fractured rock. Specifically, we apply Laplace transform to (7) and solve the transformed equation in Laplace space first, and then apply Laplace transform to (6). The transformed equations are coupled through the term describing mass transfer between fractures and rock matrix and Equation (9-2). Finally, solutions in the Laplace space are inverted.

Applying Laplace transform to (7) yields

$$pC_p' = D_m \frac{d^2 C_p'}{dx^2} - \lambda C_p' \tag{10}$$

where C_p' is the Laplace transformation of C_p and given by

$$C_p' = \int_0^\infty \exp(-pt) C_p(x, z, t) dt \tag{11}$$

Considering boundary conditions (9-2) and (9-4), the solution to ordinary partial differential equation (10) is obtained as

$$C_p' = C_f' \exp\left\{ -EP^{1/2}(x - b) \right\} \tag{12}$$

where

$$E = D_m^{-1/2} \tag{13}$$

$$P = p + \lambda \tag{14}$$

and C_f' is the Laplace transformation of C_f. Based on (12), we have

$$\left\langle \frac{dC_p'}{dx} \right\rangle_{x=b} = -EP^{1/2} C_f' \tag{15}$$

Applying the Laplace transform to (6) yields

$$pC_f' + v \frac{dC_f'}{dz} = \frac{\phi_m D_m}{b} \left\langle \frac{dC_p'}{dx} \right\rangle_{x=b} \tag{16}$$

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Substituting (15) into (16), we obtain the following solution to (16)

$$C_f' = \frac{C_0}{p}\exp(-\frac{pz}{v})\exp\left(-\frac{P^{1/2}z}{vF}\right)$$

(17)

where

$$F = \frac{b}{\phi_m D_m^{1/2}}$$

(18)

The original tracer concentration C_f can be given in terms of the inverse transform L^{-1}

as

$$C_f = L^{-1}(C_f') = \exp\left(\frac{\lambda z}{v}\right)L^{-1}\left[\exp\left(-\frac{\lambda z}{v}\right)C_f'\right]$$

(19)

Taking advantage of the fact that the inverse transform of $\exp\left(-\frac{\lambda z}{v}\right)C_f'$, $C_r(z,t)$, was

already reported by Tang et al. (1981) in their Equations (41) and (42). Thus, C_f can be

directly obtained by multiplying $C_r(z,t)$ by $\exp\left(\frac{\lambda z}{v}\right)$ and the final result is

$$\frac{C_f}{C_0} = 0 \qquad T < 0$$

(20-1)

$$\frac{C_f}{C_0} = \frac{1}{2}[\exp\left(-\frac{\lambda^{1/2}z}{vF}\right)erfc\left(\frac{z}{2vFT} - \lambda^{1/2}T\right)$$
$$+ \exp\left(\frac{\lambda^{1/2}z}{vF}\right)erfc\left(\frac{z}{2vFT} + \lambda^{1/2}T\right)]$$

$$T > 0 \qquad (20\text{-}2)$$

Where

$$T = \left(t - \frac{z}{v}\right)^{1/2}$$

(20-3)

The relation between C_f and C_r can be interpreted in the following way. The latter is the concentration at a location z in the fracture for a tracer with decay constant λ. As previously indicated, C_f may also be mathematically viewed as a tracer concentration (in the fracture) associated with decay constant λ, while the decay occurs in the matrix only. Consider two tracer particles that initially have the same mass m_0 and are released from fracture inlet (z = 0). They have exactly the same transport path. The first one is subject to decay in both fracture and the matrix, and the second one to decay in rock matrix only. When they reach a given location z within a fracture, the mass for the first particle will become $m_0 \exp\left(-\lambda\left[\tau_m + \tau_f\right]\right)$, τ_m and $\tau_f = \dfrac{z}{v}$ are particle residence times (T) in matrix and fracture, respectively, and the mass for the second particle is $m_0 \exp\left(-\lambda\tau_m\right)$. Ratio of the corresponding tracer concentrations is the same as the ratio of particle masses (i.e., $\exp\left(-\dfrac{\lambda z}{v}\right)$). However, it should be emphasized that although C_f can be mathematically viewed to be subject to decay in rock matrix, it is the dissolution-precipitation reaction, rather than real decay, that occurs in rock matrix for the problem under consideration.

To study isotopic tracer transport in fractured rock, DePaolo (2006) introduced a parameter of the diffusive reaction length given by

$$L = \left(\frac{D_m}{\lambda}\right)^{1/2} \tag{21}$$

This reaction length (L) has the property that diffusion through the pore fluid is faster than reaction at length scales smaller than L, and reaction is faster than diffusion at length scales greater than L (DePaolo, 2006). In some practical applications, it is also often useful to relate tracer concentration signals to fracture surface areas, because the surface

areas are important parameters for mass and heat transfer between mobile fluid in fractures and rock matrix. Under steady state flow conditions, we have the following conservation equation for fluid volume in fractures

$$Q\tau_f = Ab \tag{22}$$

where Q is fluid flux in a fracture (L^3/T), and A is the fracture surface area (L^2). In terms of diffusive reaction length and fracture surface area, (20) can be rewritten as

$$\frac{C_f}{C_0} = 0 \qquad T < 0 \tag{23-1}$$

$$\frac{C_f}{C_0} = \frac{1}{2}[\exp\left(-\frac{AD_m\phi_m}{LQ}\right)erfc\left(\frac{AD_m^{1/2}\phi_m}{2QT} - \frac{D_m^{1/2}}{L}T\right)$$

$$T > 0 \tag{23-2}$$

$$+ \exp\left(\frac{AD_m\phi_m}{LQ}\right)erfc\left(\frac{AD_m^{1/2}\phi_m}{2QT} + \frac{D_m^{1/2}}{L}T\right)]$$

Using the properties of $erfc(\infty) = 0$ and $erfc(-\infty) = 2$, we can easily obtain the steady-state solution by letting $T \to \infty$:

$$\frac{C_f}{C_0} = \exp\left(-\frac{\lambda^{1/2}z}{vF}\right) = \exp\left(-\frac{AD_m\phi_m}{LQ}\right) \tag{24}$$

4. Analytical Solutions for a Multiple-Fracture System

In the previous section, we derived analytical solutions for a single-fracture system which is a good approximation of many realistic fractured rocks when the tracer transport within fracture does not significantly interact with tracer transport in surrounding fractures. However, for relatively small fracture spacing and/or long tracer travel times, interactions between adjacent fractures become important. In this case, solutions for

multiple-fracture systems are needed for modeling tracer transport in fractured rock. Similar procedure for solving tracer transport problem in a single fracture system is followed here for a multiple-fracture system. Also note that governing equations are the same for both fracture systems except for some boundary conditions.

We first solve transformed tracer transport equation for rock matrix. The general solution to the transformed equation (10) is of the form (Sudicky and Frind, 1982)

$$C_p' = C_1 \cosh\left\{-EP^{1/2}(B-x)\right\} + C_2 \sinh\left\{-EP^{1/2}(B-x)\right\} \tag{25}$$

Based on boundary condition (9-3), we have $C_2 = 0$. Using boundary condition (9-2), we obtain C_1 and (25) becomes

$$C_p' = C_f' \frac{\cosh\left\{EP^{1/2}(B-x)\right\}}{\cosh\left\{\sigma P^{1/2}\right\}} \tag{26}$$

where again C_f' is the Laplace transformation of C_f and

$$\sigma = E(B-b) \tag{27}$$

The coupling between transformed tracer transport equations for fractures and matrix is done through the concentration gradient term in (16). In this case, that term is

$$\left\langle \frac{dC_p'}{dx} \right\rangle_{x=b} = -EP^{1/2}C_f'\tanh\left(\sigma P^{1/2}\right) \tag{28}$$

Then the transformed equation for tracer transport in fracture (Equation 16) becomes

$$pC_f' + v\frac{dC_f'}{dz} = -\frac{\phi_m D_m}{b}EP^{1/2}\tanh\left(\sigma P^{1/2}\right)C_f' \tag{29}$$

Solution to the above equation subject to boundary condition defined by (8-2) is

$$C_f' = \frac{C_0}{p}\exp(-\frac{pz}{v})\exp\left(-\omega P^{1/2}\tanh\left(\sigma P^{1/2}\right)\right) \tag{30}$$

where

$$\omega = \frac{\phi_m D_m^{1/2} z}{bv} \tag{31}$$

The original tracer concentration C_f can be determined by the inverse transform of $C_f{}'$.

The inverse transform of $C_f{}'\exp\left(-\dfrac{\lambda z}{v}\right)$ was already derived by Sudicky and Frind

(1982). (See their Equation 35.) Thus, C_f can be easily determined as the inverse

transform of Sudicky and Frind (1982) multiplied by $\exp\left(\dfrac{\lambda z}{v}\right)$:

$$\frac{C_f}{C_0} = 0 \qquad T^0 < 0 \tag{32-1}$$

$$\frac{C_f}{C_0} = \frac{1}{\pi}\exp\left(\frac{2\lambda z}{v}\right)\int_0^\infty I d\varepsilon \qquad T^0 > 0 \tag{32-2}$$

where

$$I = \frac{\varepsilon}{\lambda^2 + \varepsilon^4/4}\exp\left(\varepsilon_R{}^0\right)\left[\exp\left(-\lambda T^0\right)\left\{\frac{\varepsilon^2}{2}\sin\left(\varepsilon_I{}^0\right) - \lambda\cos\left(\varepsilon_I{}^0\right)\right\} + \frac{\varepsilon^2}{2}\sin\left(\Omega^0\right) + \lambda\cos\left(\Omega^0\right)\right]$$

$$\tag{32-3}$$

$$\varepsilon_R{}^0 = -\frac{\omega\varepsilon}{2}\left(\frac{\sinh(\sigma\varepsilon) - \sin(\sigma\varepsilon)}{\cosh(\sigma\varepsilon) + \cos(\sigma\varepsilon)}\right) \tag{32-4}$$

$$\varepsilon_I{}^0 = \frac{\varepsilon^2 T^0}{2} - \frac{\omega\varepsilon}{2}\left(\frac{\sinh(\sigma\varepsilon) + \sin(\sigma\varepsilon)}{\cosh(\sigma\varepsilon) + \cos(\sigma\varepsilon)}\right) \tag{32-5}$$

$$\Omega^0 = -\frac{\omega\varepsilon}{2}\left(\frac{\sinh(\sigma\varepsilon) + \sin(\sigma\varepsilon)}{\cosh(\sigma\varepsilon) + \cos(\sigma\varepsilon)}\right) \tag{32-6}$$

$$T^0 = t - \frac{z}{v} \tag{32-7}$$

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Similar to the analytical solutions to the single-fracture system as discussed in the previous section, Equation (32) can also be written in terms of diffusive reaction length defined in (21), fracture surface area A and liquid flux Q. In this case, we have

$$\frac{C_f}{C_0} = 0 \qquad T^0 < 0 \tag{33-1}$$

$$\frac{C_f}{C_0} = \frac{1}{\pi} \exp\left(\frac{2AD_m^{\,2}b}{L^2 Q}\right) \int_0^\infty I d\varepsilon \qquad T^0 > 0 \tag{33-2}$$

$$\omega = \frac{\phi_m D^{1/2} A}{Q} \tag{33-3}$$

$$T^0 = t - \frac{Ab}{Q} \tag{33-4}$$

It seems to be difficult to derive steady state solutions from (32) or (33), because these transient solutions involves an integration from 0 to ∞. An alternative way to derive steady state solutions is to directly use governing equations (6) and (7) for tracer transport. While DePaolo (2006) obtained steady state solutions for a multiple-fracture system in terms of both Laplace transform and Fourier series representation, this paper offers a more straightforward approach to derive them.

Under steady-state conditions, Equation (7) becomes

$$\frac{d^2 C_p}{dy^2} = \frac{C_p}{L^2} \tag{34}$$

where

$$y = x - b \tag{35}$$

Solution to (34) is of the form

$$C_p = C_1' \exp(\frac{y}{L}) + C_2' \exp(-\frac{y}{L}) \tag{36}$$

The constants, C_1' and C_2', are obtained by substituting boundary conditions defined in Equations (9-2) and (9-3) into the above equation. Then Equation (36) becomes

$$\frac{C_p}{C_f} = \frac{\exp(\frac{y}{L}) + \exp(\frac{B-b-y}{L})}{1 + \exp(\frac{B-b}{L})} \tag{37}$$

The (matrix) tracer concentration gradient at fracture wall can be expressed as

$$\left\langle \frac{\partial C_p}{\partial y} \right\rangle_{y=0} = \left\langle \frac{\partial C_p}{\partial x} \right\rangle_{x=b} = -\frac{C_f}{L} \left[\frac{\exp(\frac{B-b}{L}) - 1}{\exp(\frac{B-b}{L}) + 1} \right] \tag{38}$$

Substituting the above equation into steady-state version of equation (6) for tracer transport in fractures yields

$$v \frac{dC_f}{dz} = -\frac{D_m \phi_m C_f}{bL} \left[\frac{\exp(\frac{B-b}{L}) - 1}{\exp(\frac{B-b}{L}) + 1} \right] \tag{39}$$

Solution to the above equation subject to boundary condition defined by Equation (9-2) is

$$\frac{C_f}{C_0} = \exp\left\{ -\frac{D_m \phi_m z}{bvL} \left[\frac{\exp\left(\frac{B-b}{L}\right) - 1}{\exp\left(\frac{B-b}{L}\right) + 1} \right] \right\} = \exp\left\{ -\frac{\lambda^{1/2} z}{Fv} \left[\frac{\exp\left(\frac{B-b}{L}\right) - 1}{\exp\left(\frac{B-b}{L}\right) + 1} \right] \right\} \tag{40}$$

Equation (40) is essentially the same as the steady state analytical solution derived by DePaolo (2006). As expected, for $B \to \infty$, Equation (40) is reduced to Equation (24) that gives the steady-state solution for a single-fracture system.

5. Illustrative Examples

Analytical solutions for a single-fracture system and a multiple-fracture system are presented in Sections 3 and 4. Note that focus is on solutions to tracer transport in fractures, rather than in matrix, although impact of rock matrix is exactly considered. This simply because tracer concentration data are often obtained from fractures in practical applications (Neretnieks, 2002; DePaolo, 2006). Analyses of these tracer data are generally used to understand flow and transport processes in fractured rock and to infer values of important parameters characterizing the relevant processes including fracture-matrix interaction.

This section presents several illustrative examples (in terms of breakthrough curves) calculated from the analytical solutions to demonstrate the validity of these solutions and effects of parameter variations on tracer transport. To evaluate analytical solutions for a multiple-fracture system, numerical integration is needed over an interval between 0 and infinity (Equation 32). As indicated by Sudicky and Frind (1982), although the upper limit of the integration extends to infinity, the numerically significant portion of the integrand extends over a much smaller range. They also suggested using a scanning procedure prior to integration to calculate numerically significant range. In this study, the range is determined by $\exp\left(\varepsilon_R{}^0\right) \geq \exp(-20)$. Beyond that range, values for function I (Equation 32) will be extremely small and therefore can be ignored. Within the numerically significant range, the relatively robust Euler integration algorithm is employed. Typically, about several hundred to a couple of thousand subintervals are needed to get satisfactory and oscillation-free results. In this study, we use 5000

subintervals for evaluating analytical solutions to tracer transport in a multiple-fracture system.

The parameter values used in our illustrative examples are typical ones given in DePaolo (2006) for studying isotopic tracer transport in fractured rock. In this study, we use these parameter values for the purpose of demonstrating the usefulness of the analytical solutions, rather than investigating tracer transport in a practical problem. These parameter values are: bulk reactivity R_m = 1.E-5 yr^{-1}, matrix diffusion coefficient D_m = 0.1 m^2 /yr, matrix porosity ϕ_m = 0.01, mass ratio of solid to liquid phase M = 250, distribution coefficient K = 35, advective time in fracture $\frac{z}{v}$ = 0.1 yr., and fracture aperture 2b = 1.E-3 m.

Figure 2 shows tracer breakthrough curves for a multiple-fracture system with half fracture spacing B = 2.0 and 0.5 m, respectively. The relative concentration in this figure and other figures is defined as $\frac{C_f}{C_0}$. For the comparison purpose, a breakthrough curve for a single fracture system is also presented. All these breakthrough curves are obtained using the parameter values given above. For B = 2.0 m, results from the single fracture system (with infinite fracture spacing) and the multiple-fracture system are essentially identical, indicating that for a relatively large fracture spacing, impact of surrounding fractures can be ignored, as expected. This also demonstrates the validity of analytical solutions obtained for the two systems. For relatively short travel time (less than one year), all the breakthrough curves remain essentially the same, because tracer penetration depth during this time period is much smaller than the given fracture spacing values, and therefore tracer transport process is close to that for the single-fracture case. For a travel

time longer than one year, tracer concentration for B = 0.5 m becomes larger than that for B = 2.0, resulting from that interaction between tracer transport from adjacent fractures reduces diffusive transport from fractures into matrix.
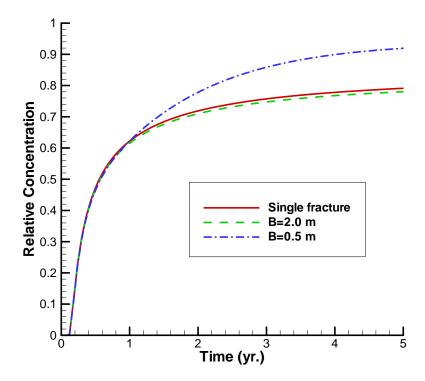

Fig.2. Breakthrough curves for a single fracture system and a multiple fracture system with half fracture spacing B = 2.0 and 0.5 m.

Figure 3 presents tracer breakthrough curves for a single-fracture system with two different L values (Equation 21). The base case corresponds to parameter values given at the beginning of this section and the other curve to the case with a reduced L value (or increased λ value that is 4 times as large as the base-case value). The two curves are very similar at an early time, but become considerably different later. The base case has a smaller λ value, and therefore a higher concentration at a late travel time. This example

demonstrates the usefulness to view effects of precipitation-dissolution reactions as a "decay" process with decay constant λ that is proportional to the bulk reactivity in the matrix (Equation 5-3). The differences between the two curves in Figure 3 result from that tracer mass loss owing to "decay" is time dependent and becomes significant only for a relatively long travel time.
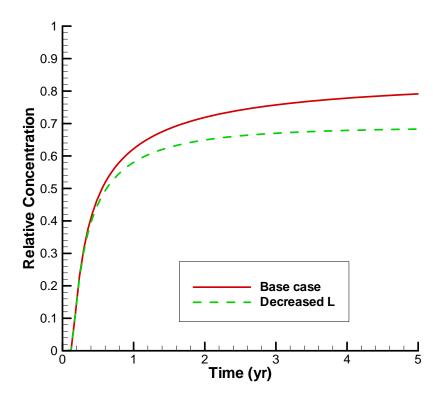
Fig.3. Breakthrough curves for a single fracture system with different L values.

Shown in Figure 4 are breakthrough curves for a single fracture system with different values for matrix diffusion coefficient D_m. The base case and the "increased D_m" case (dashed line) have the same parameter values (given at the beginning of this section) except that the latter has a D_m value that is four times as large as the base case. As expected, a large diffusion coefficient gives relatively low concentration at a given time.

This is because a larger matrix diffusion coefficient increases diffusive tracer transfer between a fracture and its surrounding matrix. An increased fracture-matrix surface area would play the similar role. Figure 4 also includes the third breakthrough curve that has the same (increased) D_m value as the dashed curve, but an increased λ value such that its L value is the same as the base case. Difference between the two "increased D_m" cases is similar to the difference between the two curves shown in Figure 3 as a result of effects of "decay" processes with different λ values.
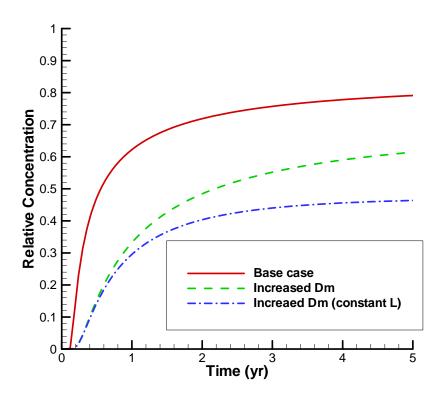
Fig.4. Breakthrough curves for a single fracture system with different D_m values.

5. Conclusions

While significant progress has been made in developing analytical solutions for tracer transport in fractured rock under a variety of conditions, analytical solution for tracer transport associated with precipitation-dissolution reactions are limited in the literature. These reactions are important for a number of applications such as isotopic tracer transport in the subsurface.

This study develops analytical solutions for tracer transport in both a single-fracture and a multiple-fracture system associated with precipitation-dissolution reactions under transient and steady state transport conditions. These solutions also take into account advective transport in fractures and molecular diffusion in rock matrix. It is demonstrated that for studying distributions of disturbed tracer concentration (defined as difference between actual concentration and its equilibrium value), effects of precipitation-dissolution reactions are mathematically equivalent to a "decay" process with a decay constant proportional to the corresponding bulk reaction rate. This important feature significantly simplifies our derivation procedure by taking advantage of the existence of analytical solutions to tracer transport associated with radioactive decay in fractured rock. It is also useful for interpreting tracer breakthrough curves, because impact of decay process is relatively easy to analyze. Several illustrative examples (breakthrough curves obtained from analytical solutions) are presented and show that results are considerably sensitive to fracture spacing, matrix diffusion coefficient (fracture surface area), and bulk reaction rate (or "decay" constant), indicating that the relevant flow and transport parameters may be estimated by analyzing tracer signals.

Finally, our analytical solutions are developed based on several assumptions and approximations. One of them is that change in tracer concentration of the solid phase is not significant. The adequacy of this approximation for isotopic tracer transport was demonstrated in DePaolo (2006). However, for a more general case where this assumption is not valid any more, solutions considering concentration change in the solid phase need to be developed in the future.

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