**Reactive solute transport in a filled single fracture-matrix system
under unilateral and radial flows**

A manuscript prepared for *Advances in Water Resources*

Renjie Zhou¹, Hongbin Zhan^{1, 2*}, Kewei Chen¹

¹Department of Geology and Geophysics, Texas A&M University, College Station,

TX77843-3115, USA. Email: zhan@geos.tamu.edu (Hongbin Zhan)

²School of Environmental Studies, China University of Geosciences, Wuhan, Hubei, 430074, P.

R. China

(*Corresponding author)

Abstract: The study of transport processes in a single fracture is the basis of understanding transport in complex fractured networks. Many single fractures in the field are filled with sediments, and the transport in such filled single fractures has received much less attention up to present. When the fracture is partially filled with sediments, a mobile-immobile approach is considered necessary. This study deals with a coupled three-domain transport problem using mobile and immobile domains to characterize a filled single fracture and a matrix domain to characterize the rock body. Mathematical models are developed for such a coupled three-domain transport problem with new semi-analytical solutions to analyze the spatial-temporal concentration and mass distributions in the fracture and rock matrix with the help of Laplace transforms. This study addresses transport in a filled fracture-matrix system under two different flow conditions: unilateral flow, and radial flow. The new solutions have been tested extensively against previous solutions under various special settings and are proven to be robust and accurate. This study has the following findings: 1) Longitudinal dispersion in the fracture often plays an important role in such a coupled system in unilateral flow, 2) Mass partitions in three domains follow similar patterns in respect to the influence of fracture apertures, mobile/immobile ratios, and first-order mass transfer rates, 3) The system is most sensitive to the dispersivity and least sensitive to the first-order mass transfer rate and the mobile/immobile ratio in the unilateral flow model over a wide range of time scales (if the longitudinal dispersivity and Darcian flow velocity remain constant), 4) The system is most sensitive to the dispersivity, less sensitive to the mobile/immobile ratio, and least sensitive to the first-order mass transfer rate in the radial flow model (if the radial dispersivity and injection rate remain constant).

Keywords: fracture-matrix system; reactive solute transport; injection well; mobile-immobile model

1. Introduction

Transport in fractured media has been considered as an important research subject by many scholars for more than three decades because of its broad range of applications in different disciplines [1, 2], for instance, for dealing with problems such as the disposal of radioactive materials, CO₂ geological sequestration and storage [3], and groundwater pollution in fractured reservoirs [4]. Since fractures are much more permeable than the surrounding rock matrix [5], fractures have the potential for being the most effective pathways for solute migration. For this reason, transport in the rock matrix is often highly simplified in mathematical models, for instance, limited to a diffusion-dominating process [6]. Specifically, some experiments have been designed and conducted to confirm that advective transport in the rock matrix can often be ignored but diffusive transport in the rock matrix must be considered in most cases [1, 7].

Understanding transport in a single fracture is the foundation of understanding transport in fracture networks [6, 8]. Analytical solutions developed at the scale of fracture-matrix systems can be applied directly to models of solute transport in fracture networks. This is the case for the particle-tracking methods developed by Dershowitz and Miller [9] and Cvetkovic et al. [10] and reviewed by Noetinger et al. [11]. The solutions developed for a single fracture-matrix system can also be extended rather straightforwardly to deal with transport in fractured rocks with multiple parallel fractures which may or may not have the same apertures, as demonstrated in details by Sudicky and Frind [12], Zhu et al. [13], and others.

There are multiple reasons to explain why investigators are interested in single fracture transport. First, this is the simplest possible fracture transport case that may be solved using an analytical approach, which can offer insights on various transport processes. Such analytical or semi-analytical solutions may serve the purpose of benchmarking numerical solutions developed

for transport in a fracture-matrix system, which may suffer from non-negligible (and often hidden) numerical errors, partially because of the sharp differences of fracture and rock matrix parameters [2]. One may consult Seo and Mittal [14] for numerical challenges related to sharp interfaces (such as along a fracture-matrix boundary). Also, a thin fracture, often with an aperture on the order of millimeter or less, requires a very fine grid to discretize the fracture in numerical simulations which may not be practical for dealing with large-scale field transport problems [15]. Secondly, a single fracture offers simple enough setting to test different transport theories related to a fracture-matrix system. Thirdly, isolated single fractures exist in real geological settings [16, 17]. Because of its importance, significant effort has been put into conducting tracer transport experiments in single fractures [18, 19], in addition to the theoretical works that will be briefly reviewed in the following.

A widely-used analytical solution of contaminant transport in a single fracture system was proposed by Tang et al. [6]. Chen [20] also derived an approximate solution for radial transport from an injection well into a single fracture. Theoretical studies of transport in a single open fracture have been reported by numerous investigators, including Moreno et al. [16], and Esposito and Thomson [19]. In the above-mentioned studies, fractures were assumed to be open without infillings.

However, fracture infillings are commonly observed in real applications [21, 22]. Wealthall et al. [21] conducted an investigation of fractures filled with sediments and compared the preferential flow pathways in such filled fractures to those in an equivalent open (unfilled) fractures. Kemp et al. [23] evaluated filled fractures in Permo-Triassic sandstones in southwest Scotland and presented a sampling method for such fractures. Bradner and Murdoch [22] investigated the gas-phase permeability in sand-filled fractures in a soil vapor extraction system.

A filled fracture usually has a different transport behavior from an open one. For instance, Lunati et al. [24] found that a propagation front was smoother in single fractures filled with glass beads at extremely low flow velocity, compared to those in open fractures. The existence of infilling materials often leads to disconnections or dead-end water pockets between pore spaces within a fracture, which can be regarded as immobile domains [25, 26]. Such a problem cannot be dealt with using the advection-dispersion equation (ADE) which is commonly used for dealing with transport in homogeneous porous media or open fractures, as done by Tang et al. [6] for unilateral flow, and by Chen [20] for radial flow. Regarding to transport in an open fracture, there is much evidence showing that ADE performs poorly, and cannot explain the so-called non-Fickian transport phenomena such as the early breakthrough and long tailing of the breakthrough curves (BTCs), that can, however, be satisfactorily explained with mobile-immobile models (MIM) as first proposed by van Genuchten and Wierenga [27].

The objective of this study is to develop new mobile-immobile models for two types of transport problems in a filled single fracture-matrix system, which has not been attempted before. The following transport processes are considered: advection, longitudinal dispersion, first-order reaction, and linear sorption in the fracture; transverse molecular diffusion, first-order reaction, and linear sorption in the rock matrix; first-order mass transfer between the mobile and immobile domains in the filled fracture. The first model concerns a unilateral flow field; while the second model concerns a radial flow field caused by an injection/pumping well.

2. The conceptual model and physical setup

In this study, a filled single fracture is oriented horizontally with a constant aperture $2b$ and extends sufficiently far from the domain of interest. The fracture is bounded by a rock matrix whose permeability is at least several orders of magnitude less than that of the fracture. The rock

matrix is wide enough so that the effect of the limit boundary of the rock matrix can be ignored. This is justified, as the primary transport process in the rock matrix is often limited to regions close to the fracture since it is a much slower process.

Fig. 1. The conceptual model of unilateral flow.

In this model, a constant-rate unilateral flow field from left to right is established (Fig. 1). A Cartesian coordinate system is used with the origin at the intercept of the left boundary and the middle of the fracture. The x -axis is along the same direction with the unilateral flow, and the z -axis is vertically upward. The y -axis is perpendicular to the x -axis and is horizontal as well. A solute source is located at $x=0$ with a constant concentration C_0 and extends to sufficiently far distance from the domain of interest along the y -axis. Thus, the problem can be conceptualized as a two-dimensional (2D) model in the xz plane. Such a simple boundary condition at $x=0$ (constant concentration) can be relaxed later to accommodate more realistic boundary types, such as prescribed time-dependent concentration (first-type), prescribed flux (second-type), or Robin (third-type). Two points are notable. First, the fracture aperture is so small that the vertical mixing throughout the fracture aperture is completed almost instantaneously, thus transverse dispersion in the fracture along the z -axis has no discernible effect on transport processes in the fracture-matrix system and is not considered. Roubinet et al. [1] further reported that longitudinal

diffusion in the rock matrix affected solute transport only when the Peclet number was very low (less than 0.01). Rezaei et al. [28] also investigated the horizontal dispersion in the aquitard (HDA) on reactive solute transport in an aquifer-aquitard system, which is similar to the fracture-matrix system investigated here except that slow water flow (advection) in aquitard was considered by Rezaei et al. [28] and water flow in matrix is excluded in this study. Rezaei et al. [28] concluded that HDA was negligible for most practical cases of transport. Therefore, longitudinal diffusion in the rock matrix is neglected in both models of this study. Secondly, despite the fact that the fracture is filled, it could still be very porous and very permeable.

Fig. 2. The conceptual model of radial flow.

The conceptual model of radial flow is the same as that of unilateral flow but with the following exceptions (Fig. 2). A radial flow field rather than a unilateral flow field is established due to an injection/pumping well with a constant rate Q (positive for injection and negative for pumping). Accordingly, a cylindrical coordinate system rather than a Cartesian coordinate system is utilized with the radial r -axis horizontally outward while the z -axis is vertically upward and along the center of the well, with the origin located at the intercept point of the horizontal

symmetry plane of the fracture and the z -axis (see Fig. 2). Groundwater flow is driven only by the injection/pumping well, without any other regional flow presented for the radial flow model.

3. Mathematical solutions

Based on the conceptual models described above, one can establish the mathematical models for both unilateral and radial flows. As two different coordinate systems are employed, the mathematical models are quite different. We will start with the unilateral flow model, followed by the radial flow model. Since the investigated system is symmetric which respect to the plane of $z=0$, we will only discuss the half-plane above $z=0$ hereinafter.

3.1 Mathematical model of unilateral flow

Reactive solute transport in a filled single fracture and rock matrix system can be described as three governing equations:

$$\theta_m R_1 \frac{\partial C_m}{\partial t} + \theta_{im} R_2 \frac{\partial C_{im}}{\partial t} = \theta_m D_m \frac{\partial^2 C_m}{\partial x^2} - \theta_m v_m \frac{\partial C_m}{\partial x} - \theta_m \lambda_1 R_1 C_m - \frac{q_m}{b} , \quad (1)$$

$$\theta_{im} R_2 \frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}) - \theta_{im} \lambda_2 R_2 C_{im} , \quad (2)$$

$$R_3 \frac{\partial C_k}{\partial t} = D_d \frac{\partial^2 C_k}{\partial z^2} - \lambda_3 R_3 C_k . \quad (3)$$

where C_m [M/L³] and C_{im} [M/L³] are the concentrations in the mobile and immobile domains in the fracture, respectively; C_k [M/L³] is the concentration in the rock matrix; b [L] is the fracture half-aperture; v_m [L/T] is the groundwater velocity in the mobile domain, which equals q/θ_m ; q [L/T] is the Darcian velocity; λ [1/T] is the decay constant which is defined as $\ln 2/t_{1/2}$ where $t_{1/2}$ is the half-life of the radionuclide or biodegradable species; θ_m and θ_{im} are the mobile and

immobile water contents, respectively, and the sum of θ_m and θ_{im} is the total porosity of the fracture; ω [1/T] is the first-order mass transfer rate between the mobile and immobile domains; R is the retardation factor (constant); the subscripts 1, 2 and 3 of R and λ refer to the mobile domain of the fracture, the immobile domain of the fracture, and the matrix, respectively; D_m [L^2/T] is the longitudinal dispersion coefficient in the fracture, and it can be further expressed as:

$$D_m = \alpha_L v_m + D^* , \quad (4)$$

where α_L [L] is the longitudinal dispersivity while D^* [L^2/T] is the effective molecular diffusion coefficient in the mobile domain, which is usually much smaller than $\alpha_L v_m$ and can be ignored; D_d [L^2/T] is the effective molecular diffusion coefficient in the rock matrix; q_m [M/ L^2T] is the diffusive mass flux between the fracture and the rock matrix, and is expressed based on Fick's law:

$$q_m = -\theta_k D_d \left(\frac{\partial C_k}{\partial z} \right) \bigg|_{z=b} , \quad (5)$$

where θ_k is the porosity of the rock matrix.

Eqs. (1)-(3) refer to the governing equations in the mobile domain of the fracture, mass transfer between the mobile and immobile domains of the fracture, and the governing equation in the rock matrix, respectively.

There are a few notable points about Eqs. (1)-(3). First, different decay constants are used for the mobile and immobile domains, as well as for the rock matrix, which are likely to have different reaction rate constants [13]. For example, biodegradation would be affected by water temperature, type and content of organic compounds, oxygen concentration and other factors [29,

30]. Some of these factors could be different in the mobile and immobile domains of a fracture and matrix.

Secondly, the retardation factors in the mobile and immobile domains of a fracture could be different [31, 32]. The retardation factors of the mobile and immobile domains are defined as $R_1 = 1 + \rho_m K_m / \theta_m$; $R_2 = 1 + \rho_{im} K_{im} / \theta_{im}$, where ρ_m and ρ_{im} are the partial bulk densities of the mobile and immobile domains, respectively; K_m and K_{im} are the distribution coefficients for each domain and represent the mass of solute absorbed per unit volume of solid divided by the concentration of the solute in the fracture. Since the bulk density, distribution coefficient and porosity in the rock matrix may be different from those in the fracture, the retardation factor of the rock matrix could be very different from that of the fracture.

As multiple parameters are involved in the mathematical models illustrated above, it is necessary to elaborate on the parameter determination process for model application. This will be addressed later in Section 4.4.

Experimental and theoretical efforts have been made by many scholars to understand the possible existence of concentration discontinuity at the sharp interface between the fracture and the rock matrix [33, 34]. Such a phenomenon may occur if there are possible mass accumulations when solutes cross from one medium to another [35]. However, no experimental evidence of mass accumulation at the sharp interface is available to support this conjecture [36]. Thus, the concentration discontinuity at the fracture-matrix interface is not considered in this study. The above equations are supplemented with a continuity equation at the fracture-matrix interface and initial and boundary conditions to close the system. At any point on the interface between the fracture and rock matrix, the concentration is continuous, thus one has:

$$C_m(x, t) = C_k(x, z = b, t) . \quad (6)$$

The fracture-matrix system is assumed to be free from solute at the beginning, thus the initial conditions are:

$$C_m(x, t = 0) = C_{im}(x, t = 0) = C_k(z, t = 0) = 0 . \quad (7)$$

The remaining boundary conditions are as follows:

$$C_m(x \rightarrow \infty, t) = C_{im}(x \rightarrow \infty, t) = 0 , \quad (8)$$

$$C_m(x = 0, t) = C_0 , \quad (9)$$

$$C_k(z \rightarrow \infty, t) = 0 . \quad (10)$$

Eqs. (8) and (10) imply that the fracture is infinitely long and the rock matrix is infinitely thick, which avoid the effect of the finite boundary. Eq. (9) defines a constant concentration source in the mobile domain of the fracture at $x=0$.

3.1.1 Solutions of the unilateral flow model

To solve Eqs. (1)-(10), the Laplace transform will be used to transform the problems in the real-time domain to those in the Laplace domain. The benefit of this approach is to convert partial differential equations (which are usually difficult to deal with) into ordinary differential equations by removing the time-derivative terms from the equations. After solving the boundary value problems (BVP), one can obtain analytical solutions of the problems in the Laplace domain. After this step, one needs to apply an inverse Laplace transform technique, which has to be numerical for the problems addressed here, to finally obtain solutions in the real-time domain.

Before conducting the Laplace transform, it is helpful to convert the equations into their dimensionless forms that have fewer numbers of independent variables and are more reflective of the systems involved, as commonly done in dynamic analysis [37, 38].

The Laplace-domain solutions are obtained as follows while the detailed derivations are provided in Appendix A of the supplementary files:

$$\overline{C_{mD}} = \frac{1}{p} \exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right), \quad (11)$$

$$\overline{C_{imD}} = \frac{1}{p} \frac{\omega}{\frac{\theta_{im} R_2 p}{\alpha} + \omega + \lambda_2 \theta_{im} R_2} \exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D\right), \quad (12)$$

$$\overline{C_{kD}} = \frac{1}{p} \exp\left(\frac{Pe - \sqrt{Pe^2 + 4k_1}}{2} x_D + \sqrt{\lambda_3 \alpha + p} \left(\sqrt{\frac{R_3 D_m}{R_1 D_d}} - z_D\right)\right). \quad (13)$$

Where the subscript D denotes the terms in dimensionless formats hereinafter,

$$k_1 = p + p \times \frac{\theta_1 R_2}{R_1} \times \frac{\omega}{\frac{\theta_{im} R_2 p}{\alpha} + \omega + \lambda_2 \theta_{im} R_2} + \lambda_1 \alpha + \alpha_1 \sqrt{\lambda_3 \alpha + p}, \text{ and the Peclet number } (Pe) \text{ and all}$$

other terms are explained in the supplementary files.

3.1.2 Steady-state solutions

For some transport problems, it is possible to obtain steady-state solutions that are usually much simpler than the transient solutions. The steady-state solutions will be particularly useful for assessing the long-term transport behavior, thus they are sometimes required for screening and/or designing long-term monitoring and remediation plans.

239 To obtain the steady-state solutions for the unilateral flow model, one must fulfill the
 240 following condition:

$$241 \quad \frac{\partial C_{mD}}{\partial t_D} = \frac{\partial C_{imD}}{\partial t_D} = \frac{\partial C_{kD}}{\partial t_D} = 0 . \quad (14)$$

242 Eq. (14) indicates that the concentrations would no longer change with time any more after
 243 reaching steady state, which simplifies Eqs. (1) and (2) to ordinary differential equations. The
 244 steady-state solutions can be reached by substituting Eq. (14) into Eqs. (1)-(3), or taking
 245 advantage of the following identity: $f(t_D \rightarrow \infty) = \lim_{p \rightarrow 0} (pF(p))$, where $F(p)$ is the Laplace
 246 transform of $f(t_D)$ and $f(t_D \rightarrow \infty)$ is the steady-state solution of $f(t_D)$. In this case, $F(p)$
 247 corresponds to the solutions in the Laplace domain (Eqs.(11)-(13)). Thus, the steady-state
 248 solutions of the mobile and immobile domains of the fracture and the matrix are derived by
 249 calculating the limitations of $p\overline{C_{mD}}$, $p\overline{C_{imD}}$ and $p\overline{C_{kD}}$ as p approaches 0.

250 The analytical solutions for C_{mD} , C_{imD} and C_{kD} at steady state can be derived as follows:

$$251 \quad C_{mD} = \exp \left(\frac{Pe - \sqrt{Pe^2 + 4(\lambda_1 \alpha + \alpha_1 \sqrt{\alpha \lambda_3})}}{2} x_D \right) , \quad (15)$$

$$252 \quad C_{imD} = \frac{\omega}{\omega + \theta_{im} \lambda_2 R_2} \exp \left(\frac{Pe - \sqrt{Pe^2 + 4(\lambda_1 \alpha + \alpha_1 \sqrt{\alpha \lambda_3})}}{2} x_D \right) , \quad (16)$$

$$253 \quad C_{kD} = \exp \left(\frac{Pe - \sqrt{Pe^2 + 4(\lambda_1 \alpha + \alpha_1 \sqrt{\alpha \lambda_3})}}{2} x_D - \sqrt{\lambda_3 \alpha} \left(z_D - \sqrt{\frac{R_3 D_m}{R_1 D_d}} \right) \right) . \quad (17)$$

254 It is interesting to point out that the steady-state solutions of Eqs. (15)-(17) are all exponential
 255 decay functions of spatial coordinates, and are closely related to the Peclet number (Pe) in the
 256 fracture, in addition to other factors.

257 **3.2 Mathematical radial flow model**

258 In the radial flow model, the solute is discharged into a filled fracture-matrix system from an
 259 injection well at a constant rate Q [L^3/T]. r_0 [L] is the radius of the well. The velocity of the
 260 background regional groundwater flow is ignored. Thus, the steady-state flow velocity in the
 261 mobile zone of the fracture is only caused by the injection well, which is expressed as:

$$262 \quad v_m = \frac{A}{r}, \quad (18)$$

263 where $A = \frac{Q}{4\pi b\theta_e}$, and θ_e is the effective porosity in the fracture, which equals the mobile water
 264 content θ_m in this study.

265 The flow velocity is steady with time but variable with radial distance from the well. The
 266 radial hydrodynamic dispersion coefficient D_r [L^2/T] is expressed as [38]:

$$267 \quad D_r = dv_m = \frac{dA}{r}, \quad (19)$$

268 where d [L] is the radial dispersivity. The governing equations in the mobile and immobile
 269 domains of the fracture can be written as follows:

$$270 \quad \theta_m R_1 \frac{\partial C_m}{\partial t} + \theta_{im} R_2 \frac{\partial C_{im}}{\partial t} = \theta_m D_r \frac{\partial^2 C_m}{\partial r^2} - \theta_m \frac{A}{r} \frac{\partial C_m}{\partial r} - \theta_m \lambda_1 R_1 C_m - \frac{q_m}{b}, \quad (20)$$

$$271 \quad \theta_{im} R_2 \frac{\partial C_{im}}{\partial t} = \omega(C_m - C_{im}) - \theta_{im} \lambda_2 R_2 C_{im}, \quad (21)$$

where the diffusive flux between the fracture and matrix, q_m , has the same expression as above in Eq. (5) in the unilateral flow model and The governing equation for the reactive solute transport in the rock matrix is the same as above in Eq. (3). The boundary conditions of the filled fracture-matrix system in the radial flow model are expressed as follows:

$$C_m(r \rightarrow \infty, t) = C_{im}(r \rightarrow \infty, t) = 0 , \quad (22)$$

$$C_m(r = r_0, t) = C_0 . \quad (23)$$

The boundary condition for the matrix is the same as Eq. (10). Eq. (22) specifies that the effect of the system boundary is infinite in the r axis. The boundary condition given in Eq. (23) illustrates that the source concentration at the injection well remains constant C_0 . This boundary condition can be replaced with other boundary types such as time-dependent prescribed concentration, flux prescribed (second-type), or Robin (third-type), if needed. The initial conditions for the fracture and rock matrix are the same as Eq. (7). At the interface between the fracture and rock matrix, the continuity relationship holds (see Eq. (6) in the unilateral flow model).

3.2.1 Solutions of the radial flow model

The solutions in the Laplace domain are obtained as follows while the full derivations are provided in Appendix B of the supplementary files:

$$\overline{C_{mD}} = \frac{1}{p} \exp\left(\frac{1}{2}(r_D - r_{0D})\right) \frac{Ai\left[\beta^{1/3}\left(r_D + (4\beta)^{-1}\right)\right]}{Ai\left[\beta^{1/3}\left(r_{0D} + (4\beta)^{-1}\right)\right]} , \quad (24)$$

$$\overline{C_{imD}} = \frac{1}{p} \frac{\omega}{\frac{\theta_{im} p R_2}{\tau} + \omega + \lambda_2 \theta_{im} R_2} \exp\left(\frac{1}{2}(r_D - r_{0D})\right) \frac{Ai\left[\beta^{1/3}\left(r_D + (4\beta)^{-1}\right)\right]}{Ai\left[\beta^{1/3}\left(r_{0D} + (4\beta)^{-1}\right)\right]}, \quad (25)$$

$$\overline{C_{kD}} = \frac{1}{p} \exp\left(\frac{1}{2}(r_D - r_{0D}) - \sqrt{\tau\lambda_3 + p}\left(z_D - \frac{b}{d} \sqrt{\frac{R_3 A}{R_1 D_d}}\right)\right) \frac{Ai\left[\beta^{1/3}\left(r_D + (4\beta)^{-1}\right)\right]}{Ai\left[\beta^{1/3}\left(r_{0D} + (4\beta)^{-1}\right)\right]}, \quad (26)$$

$$\text{where } \beta = \left(\tau\lambda_1 + \tau_1 \sqrt{\tau\lambda_3 + p} + p + \frac{\theta_1 p \omega R_2}{\left(\frac{\theta_{im} p R_2}{\tau} + \omega + \lambda_2 \theta_{im} R_2\right) R_1} \right), A_i \text{ is the so-called Airy function.}$$

3.2.2 Steady-state solutions

Similar to the derivation of the steady-state solutions of the unilateral flow model, to reach the steady state, Eq. (14) must be fulfilled. The analytical solutions of the concentration distribution in the mobile domain (Eq. (27)), immobile domain (Eq. (28)) and rock matrix (Eq. (29)) can be obtained in the real-time domain as follows:

$$C_{msD} = \exp\left(\frac{1}{2}(r_D - r_{0D})\right) \frac{Ai\left[\beta_1^{1/3}\left(r_D + (4\beta_1)^{-1}\right)\right]}{Ai\left[\beta_1^{1/3}\left(r_{0D} + (4\beta_1)^{-1}\right)\right]}, \quad (27)$$

$$C_{imsD} = \frac{\omega}{\omega + \lambda_2 \theta_{im} R_2} \exp\left(\frac{1}{2}(r_D - r_{0D})\right) \frac{Ai\left[\beta_1^{1/3}\left(r_D + (4\beta_1)^{-1}\right)\right]}{Ai\left[\beta_1^{1/3}\left(r_{0D} + (4\beta_1)^{-1}\right)\right]}, \quad (28)$$

$$C_{ksD} = \exp\left(\frac{1}{2}(r_D - r_{0D}) - \sqrt{\tau\lambda_3}\left(z_D - \frac{b}{d} \sqrt{\frac{R_3 A}{R_1 D_d}}\right)\right) \frac{Ai\left[\beta_1^{1/3}\left(r_D + (4\beta_1)^{-1}\right)\right]}{Ai\left[\beta_1^{1/3}\left(r_{0D} + (4\beta_1)^{-1}\right)\right]}, \quad (29)$$

301 where $\beta_1 = (\tau\lambda_1 + \tau_1\sqrt{\tau\lambda_3})$.

302 **4. Validation and results**

303 Now all transient solutions for both models are derived in the Laplace domain. Analytical
304 inverse Laplace transforms might result in complex multiple integrations which can only be
305 calculated with numerical methods [6, 20, 39]. Therefore, a numerical inverse Laplace transform
306 technique is adopted here to compute the spatial-temporal concentration distributions. The de
307 Hoog et al. [40] algorithm, which has been successfully used in solute transport problems before
308 [41, 42], is selected to conduct the numerical inverse Laplace transform here. It accelerates the
309 convergence of the Fourier series resulting from the inversion integral and ensures the accuracy
310 by reducing errors [40]. The results obtained from the de Hoog algorithm are then tested against
311 other analytical solutions: those from Tang et al. [6] and Zhu et al. [13] for unilateral flow, and
312 the other from Chen [20] for radial flow.

313 **4.1 BTC analysis**

314 To better illustrate the above derived solutions, an example is used to analyze BTCs of the
315 mobile domain in the fracture. The parameters used in the example are taken from previous
316 studies [6, 43], which dealt with similar transport problems without considering fracture
317 infillings. The same parameters are used for example calculations of both models:

318 $2b = 100 \mu\text{m}$; $\theta_k = 0.01$; $t_{1/2} = 12.35 \text{ yrs}$; $R_1 = 1$; $R_2 = 1$; $R_3 = 1$; $D_d = 1.38 \times 10^{-5} \text{ m}^2/\text{d}$;
319 $\alpha_L = 0.5 \text{ m}$; $d = 0.5 \text{ m}$; $\omega = 0.9/\text{d}$; $\theta_m + \theta_{im} = 0.9$.

320 In the unilateral flow model, the Darcian velocity (q) of the groundwater in the mobile
321 domain of the fracture is 0.01 m/d , which can be used to calculate the flow velocity of

groundwater (v_m). In the radial flow model, the constant injection rate (Q) is $0.001 \text{ m}^3/\text{d}$, and the radius of the wellbore (r_0) is 0.11 m . The default mobile/immobile ratio in the following calculation is set to be 10 (or $\theta_m=0.818$ and $\theta_{im}=0.0818$). For computations involving different mobile/immobile ratios, θ_m and θ_{im} will change accordingly with the constraint of $\theta_m+\theta_{im}=0.9$. A sample point of $(0.5 \text{ m}, 0 \text{ m})$ is picked in the fracture for the discussion of BTCs. The selection of such a point is rather arbitrary, thus the results obtained are general in nature.

It is worthwhile to note that some related studies use a fixed dispersion coefficient (D_m) [6, 27] while others use a fixed longitudinal dispersivity (α_L) [44, 45] for analyzing the transport process. As Eq. (4) shows, the relationship between D_m and α_L can be simplified as $D_m = \alpha_L v_m = \alpha_L q / \theta_m$, if neglecting the molecular diffusion coefficient. Figs. 3A and 3B respectively show BTCs for the unilateral flow model with a fixed longitudinal dispersivity of 0.5 m and a fixed dispersion coefficient of $0.00611 \text{ m}^2/\text{d}$ which is computed with $\alpha_L=0.5 \text{ m}$, $q=0.01 \text{ m}/\text{d}$, and $\theta_m=0.818$. Fig. 4A shows BTCs for the radial flow model with a radial dispersivity of 0.5 m and an injection rate of $Q=0.001 \text{ m}^3/\text{d}$. To distinguish curves which are superposed on a linear scale, Fig. 3C and Fig. 4B are plotted on a semi-log scale corresponding to Fig.3B and Fig. 4A, respectively.

It is also useful to know different time scales associated with the problems in order to understand the different transport behavior under unilateral and radial flows. These two models are under different conditions: the unilateral flow model refers to an ambient condition while the radial flow model corresponds to a forced hydraulic condition. The time scale of the radial flow model is about three orders of magnitude smaller than that of the unilateral flow model. For the chosen first-order mass transfer rate of $\omega = 0.9 \text{ day}^{-1}$, the time scale for the mass transfer between

the mobile and immobile domains is around $1/\omega \approx 1.1$ days. Now one looks at the θ_m / θ_{im} ratios of 10, 5, and 1 as used in Figs. 3A-3C for unilateral flow, when the Darcian velocity is kept at 0.01 m/d and $\theta_m + \theta_{im}$ is kept at 0.9, such three θ_m / θ_{im} ratios will lead to advective transport times to the point of interest (0.5 m, 0 m) to be 40.9 days, 37.5 days, and 22.5 days, respectively. For radial transport shown in Figs. 4A-4B, the advective transport time needed to a radial distance r from a well with an injection rate of Q is: $T = 0.5r^2 / A$, where A is defined after Eq. (19). One then looks at the θ_m / θ_{im} ratios of 10, 5, and 1 as used in Figs. 4A-4B and finds that the advective transport times to a point of (0.5 m, 0 m) with Q of 0.001 m³/day and $\theta_m + \theta_{im}$ of 0.9 will be 0.0642 days (or 1.54 hrs), 0.0589 days (or 1.41 hrs), and 0.0353 days (or 0.85 hrs), respectively.

The solutions of Tang et al. [6] (for unilateral flow) and Chen [20] (for radial flow) can be regarded as special cases of this study by assuming $\theta_m = 1$ and $\theta_{im} = 0$. In other words, there is no immobile domain and the fracture is open with a porosity of 1. The solution of Tang et al. [6] is included in Figs. 3A-3C while the solution of Chen [20] is included in Figs. 4A-4B. As can be seen from these figures, excellent agreements are reached for both cases when neglecting the immobile domain of the fracture and assigning identical reaction rates and retardation factors for the fracture and the matrix.

In Fig. 3A, BTCs in the unilateral flow model are nearly unaffected by the mobile/immobile ratios if the longitudinal dispersivity is fixed. This observation can be explained as follows. Under a fixed longitudinal dispersivity, the flux terms on the right side of Eq. (1) become

$$\alpha_L q \frac{\partial^2 C_m}{\partial x^2} - q \frac{\partial C_m}{\partial x}, \text{ which have no relation with the mobile/immobile ratio that is mainly related}$$

to the partition of mass storage change terms on the left side of Eq. (1). The advective transport time scales in Fig. 3A (in the range of 40.9 days to 22.5 days) are much longer than the mass transfer time scale between the mobile and immobile domains (around 1.1 days). Therefore, concentrations in the mobile and immobile domains have nearly reached equilibrium, i.e., the rates of mobile and immobile concentration changes with time become nearly the same, which renders the left side of Eq. (1) $\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} \approx (\theta_m + \theta_{im}) \frac{\partial C_m}{\partial t} = 0.9 \frac{\partial C_m}{\partial t}$. This implies that Eq. (1) is now essentially insensitive to the mobile/immobile ratio under these conditions. However, one has to be aware that the assumption of a fixed longitudinal dispersivity may not always hold if the mobile/immobile ratio is changing. This is because a change in the mobile/immobile ratio will inevitably change the pore structure and velocity variation which control the longitudinal dispersivity. This suggests that the fixed longitudinal dispersivity assumption under various mobile/immobile ratios can only be regarded as a simplification of actual problems.

In Figs. 3B-3C, the BTCs are plotted with a fixed dispersion coefficient but with different mobile/immobile ratios in unilateral flow. In contrast to Fig. 3A, one can see that the BTCs are moderately sensitive to the mobile/immobile ratios. Since D_m equals $\alpha_L q / \theta_m$ when neglecting the molecular diffusion, thus a fixed D_m is equivalent to state that longitudinal dispersivity (α_L) is proportional to the mobile water content (θ_m). This is understandable because a greater mobile water content might mean a greater velocity variation in the mobile domain, which leads to a larger longitudinal dispersivity. However, the proportionality of α_L versus θ_m is rather idealized and is better treated as a simplification of actual problems.

It is also interesting to compare the influence of the mobile/immobile ratio on the BTCs in Figs. 3B-3C and Figs. 4A-4B. Figs. 3B-3C show that the solute moves slower under a smaller mobile/immobile ratio in unilateral flow while Figs. 4A-4B indicate that it travels faster with a smaller mobile/immobile ratio in radial flow. The results of Figs. 3B-3C and 4A-4B shed light on different perspectives of transport in unilateral flow as well as radial flow, and they can be explained as follows. First, from above time scale calculation, one can see that for Figs. 3B-3C, the advective transport times to the point of interest (0.5 m, 0 m) are all much longer than the time scale of mobile/immobile mass transfer, thus the mass partition between the mobile and immobile domains has nearly reached equilibrium. Therefore, a smaller mobile/immobile ratio simply means a greater portion of mass stored in the immobile domain and a larger retardation effect over the transport in the mobile domain, which is clearly manifested in Figs. 3B-3C. Secondly, quite different from Figs. 3B-3C, the advective transport times to the point of interest (0.5 m, 0 m) in Figs. 4A-4B are considerably smaller than the mass transfer time scale. In other words, the mass transfer between the mobile and immobile domains has not yet had enough time to reach equilibrium. Therefore, a smaller mobile/immobile ratio means a smaller percentage of mass being transferred to the immobile domain, which results in a greater concentration in the mobile domain, as demonstrated in Figs. 4A-4B. Furthermore, as the advective transport times for three different mobile/immobile ratios are not much different from each other in radial flow (varying between 1.54 hrs to 0.85 hrs) in respect to the mass transfer time scale (around 1.1 days), the results for the three θ_m / θ_{im} ratios in Figs. 4A-4B are clustered quite closely.

Special attention should be paid to Fig. 5 for the comparison with Zhu et al.[13], which essentially ignores longitudinal dispersion in the fracture under the unilateral flow scenario, in addition to assigning identical reaction rates and retardation factors for the fracture and the

matrix. Fig. 5 clearly shows that a special case of our model with a zero fracture longitudinal dispersion coefficient yields the same result as the analytical solution of Zhu et al.[13]. Furthermore, our model with non-zero fracture longitudinal dispersion coefficients produces BTCs that are very different from the BTCs produced from Zhu et al.[13]. This suggests that the fracture longitudinal dispersion has a significant influence on solute transport in a single fracture-matrix system, thus should not be neglected. As seen in Fig. 5, a greater fracture longitudinal dispersion allows the contaminant solute to migrate faster in the mobile domain of the fracture.

419 Fig. 3A. The breakthrough curves (BTCs) in the mobile domain of the fracture on a linear scale
 420 at different mobile/immobile ratios at point (0.5 m, 0 m) with a fixed longitudinal dispersivity of
 421 0.5 m and Darcian velocity of 0.01m/d in the unilateral flow model.

422
 423 Fig. 3B. The BTCs in the mobile domain of the fracture on a linear scale at different
 424 mobile/immobile ratios at point (0.5 m, 0 m) with a fixed dispersion coefficient of $0.00611 \text{ m}^2/\text{d}$
 425 and Darcian velocity of 0.01m/d in the unilateral flow model.

426

427 Fig. 3C. The BTCs in the mobile domain of the fracture on a semi-log scale at different
 428 mobile/immobile ratios at point (0.5 m, 0 m) with a fixed dispersion coefficient of $0.00611 \text{ m}^2/\text{d}$
 429 and Darcian velocity of 0.01m/d in the unilateral flow model.

430

431

432 Fig. 4A. The BTCs in the mobile domain of the fracture on a linear scale at different
 433 mobile/immobile ratios at point (0.5 m, 0 m) with a fixed radial dispersivity of 0.5 m and mass
 434 transfer rate of 0.9 /d in the radial flow model.

435

436

Fig. 4B. The BTCs in the mobile domain of the fracture on a semi-log scale at different

437

mobile/immobile ratios at point (0.5 m, 0 m) with a fixed radial dispersivity of 0.5 m and mass

438

transfer rate of 0.9 /d in the radial flow model.

439

440

441 Fig 5. The BTCs in the mobile domain of the fracture on a linear scale with different longitudinal
 442 dispersivities in the fracture at point (0.5 m, 0 m) with a fixed Darcian velocity of 0.01m/d in the
 443 unilateral flow model.

444 4.2 Stored mass calculation

445 As an important indicator of long-term impacts of solute transport in a fracture-matrix
 446 system, solute mass stored in each domain (fracture or matrix) provides very useful information.
 447 To understand the solute mass transported and stored in each domain under the unilateral flow
 448 scenario, the following equations are given:

$$M'_{fm} = \int_0^\infty 2b \times C_m \times \theta_m dx , \quad (30)$$

$$M'_{fim} = \int_0^\infty 2b \times C_{im} \times \theta_{im} dx , \quad (31)$$

$$M'_k = \int_b^\infty \int_0^\infty 2 \times C_k \times \theta_k dx dz , \quad (32)$$

where M'_{fm} , M'_{fim} and M'_k are the mass stored per unit width in the mobile and immobile domains of the fracture and rock matrix, respectively. The actual mass stored in the mobile and immobile domains of the fracture and rock matrix over a width of W can be easily computed as:

$$M_{fm} = M'_{fm} W; M_{fim} = M'_{fim} W; M_k = M'_k W.$$

Similarly, the mass stored in each domain under the radial flow scenario is given as Eqs. (33) -(35):

$$M_{fm} = \int_{r_o}^\infty 2\pi r \times 2b \times C_m \times \theta_m dr , \quad (33)$$

$$M_{fim} = \int_{r_o}^\infty 2\pi r \times 2b \times C_{im} \times \theta_{im} dr , \quad (34)$$

$$M_k = \int_b^\infty \int_{r_0}^\infty 4\pi r \times C_k \times \theta_k dr dz , \quad (35)$$

where M_{fm} , M_{fim} and M_k are the mass stored in the mobile and immobile domains of the fracture and rock matrix, respectively, and $2b$ in Eqs. (30), (31), (33) and (34) is the fracture aperture. Eqs. (32) and (35) consider the mass stored in the upper and lower rock matrix altogether. The calculation details are included in the supplementary files, and all the mass stored ratio figures are plotted under a fixed dispersivity of 0.5 m.

The following Figs. 6-8 exhibit different aspects of the stored mass. In particular, Figs. 6A-6B show the mass stored ratios in the matrix ($M_k / (M_{fm} + M_{fim} + M_k)$) under different fracture apertures for both models. Figs. 7A-7B and 8A-8B are the mass stored ratios in the immobile domain of the fracture ($M_{fim} / (M_{fm} + M_{fim} + M_k)$) under different mobile/immobile ratios and first-order mass transfer rates for both models, respectively.

Basically, all parameters have similar effects under the unilateral flow and radial flow scenarios. Figs. 6A-6B indicate that the influence of the fracture aperture is similar in both models: the ratio of mass stored in the matrix increases sharply at the beginning, and then approaches an asymptotic limit. A smaller fracture aperture corresponds to a higher ratio of mass stored in the matrix. The observations from Figs. 6A-6B can be understood as follows. At the beginning of transport, the rock matrix is free of solute, thus there is a significant (or nearly infinite) concentration gradient across the fracture-matrix interface behind the transport front in the fracture, leading to significant diffusive mass transport from the fracture to the rock matrix and a relatively rapid increase of mass in the rock matrix. When time goes longer, such a concentration gradient across the fracture-matrix interface becomes less, resulting in less diffusive mass transport to the matrix, thus a slower rate of increase of mass stored in the matrix. A smaller fracture aperture means a smaller fracture volume, thus a greater ratio of mass stored in the matrix.

In Figs. 7A-7B, the ratio of mass stored in the immobile domain surges first, after reaching a peak value, it starts to drop slowly and finally approaches an asymptotic limit. The mobile/immobile ratio is a key factor for the mass stored in the immobile domain of the fracture:

a higher mobile/immobile ratio results in a lower ratio of mass stored in the immobile domain of the fracture. Those observations are also understandable.

First of all, one can check the characteristic time scales for mobile-immobile mass transfer in the fracture and diffusive transport to the rock matrix. With the use of a mobile-immobile mass transfer rate of $\omega = 0.9 \text{ d}^{-1}$, the characteristic time for mass transfer between the mobile and immobile domains will be $1/\omega = 1.1 \text{ d}$. Using Eq. (19) in Zhu et al. [13], one can estimate the solute penetration depth into the rock matrix L to be about 2.7 m, based on D_d of $1.38 \times 10^{-5} \text{ m}^2/\text{d}$, a retardation factor of 1, a half-life of 12.34 years, and a four orders of magnitude of concentration reduction in the rock matrix ($\varphi = C_k / C_0 = 0.01\%$). Therefore, the characteristic time for diffusive transport into the rock matrix can be estimated to be $L^2 / (2D_d) = 2.6 \times 10^5 \text{ d}$. One can easily see that the time scale for diffusive transport to the rock matrix is five orders of magnitude longer than the time scale needed for mass transfer between the mobile and immobile domains of the fracture.

At the beginning of transport, the immobile domain of the fracture is free of solute, thus mass transfer from the mobile domain to the immobile domain of the fracture is rapid, resulting in a rapid rise of the ratio of mass stored in the immobile domain, as shown in Figs. 7A-7B. When time is greater than the characteristic time of mobile-immobile mass transfer (about 1.1 d), mass partition between the mobile and immobile domains of the fracture approaches an equilibrium state, and the ratio of mass stored in the immobile domain will reach a peak value at a time similar to the characteristic time of mobile-immobile mass transfer. This is found to be true. For instance, the times corresponding to three peaks in Fig. 7A are 0.41 d, 0.63 d, and 1.24

d, respectively, which are in the same order of magnitude as the characteristic time of mobile-immobile mass transfer of 1.1 d.

Beyond the peak value time, both the mobile and immobile domains of the fracture will gradually lose mass due to the diffusive transport to the rock matrix. Such mass loss will result in the decline of the ratio of mass stored in the immobile domain of the fracture. The decline rate of the ratio of mass stored in the immobile domain of the fracture becomes smaller with time because the rate of diffusive transport of mass to the rock matrix drops with time as well. This is evident in Figs. 7A-7B. In respect to different mobile/immobile ratios, the one with a less mobile/immobile ratio means a greater portion of the immobile domain of the fracture, thus a greater ratio of mass stored in the immobile domain of the fracture as well, which is clearly the case in Figs. 7A-7B.

Figs. 8A-8B show the similar patterns of an increasing limb at the beginning, followed by a decreasing limb at the later time for the ratio of mass stored in the immobile domain, as those in Figs. 7A-7B, with the same reasons explained above. A minor point to note is that much larger time scales are used in Fig. 8A (100 d) and Fig. 8B (50 d) than those in Figs. 7A-7B (10 d), thus the plots of Figs. 8A-8B appear differently from Figs. 7A-7B. Furthermore, as Figs. 8A-8B demonstrate, a greater mass transfer rate will lead to significantly greater mass stored in the immobile domain at early time. However, as time increases, mass partition among different domains will reach a nearly equilibrium state, thus the concentration distributions in all domains will remain stable (or at quasi-steady state). Under such a quasi-steady state condition, the mass distributions among different domains are no longer affected by the mass transfer rate, which only plays a role in the transient (or pre-equilibrium) mass transfer processes between the mobile

530 and immobile domains. This is the reason why the curves for different mass transfer rates in Figs.
 531 8A-8B merge after a sufficiently long time of transport.

532

533 Fig. 6A. The mass stored ratio curves of the rock matrix under different half-apertures of the
 534 fracture with a fixed mobile/immobile ratio of 10 and mass transfer rate of 0.9 /d in the unilateral
 535 flow model.

536

537 Fig. 6B. The mass stored ratio curves of the rock matrix under different half-apertures of the
 538 fracture with a fixed mobile/immobile ratio of 10 and mass transfer rate of 0.9 /d in the radial
 539 flow model.

540

541 Fig. 7A. The mass stored ratio curves of the immobile domain of the fracture under different
 542 mobile/immobile ratios with a fixed half-aperture of 5×10^{-5} m and mass transfer rate of 0.9 /d in
 543 the unilateral flow model.

544

545 Fig. 7B. The mass stored ratio curves of the immobile domain of the fracture under different
 546 mobile/immobile ratios with a fixed half-aperture of 5×10^{-5} m and mass transfer rate of 0.9 /d in
 547 the radial flow model.

548

549 Fig. 8A. The mass stored ratio curves of the immobile domain of the fracture under different
 550 mass transfer rates with a fixed half-aperture of 5×10^{-5} m and mass transfer rate of 0.9 /d in the
 551 unilateral flow model.

Fig. 8B. The mass stored ratio curves of the immobile domain of the fracture under different mass transfer rates with a fixed half-aperture of 5×10^{-5} m and mass transfer rate of 0.9 /d in the radial flow model.

4.3 Sensitivity analysis

557

558

559 Fig. 9. The normalized sensitivity in the fracture at (0.5 m, 0 m) in the unilateral flow model.

Fig. 10. The normalized sensitivity in the fracture at (0.5 m, 0 m) in the radial flow model.

The normalized sensitivity analysis proposed by Huang and Yeh [46] and Kabala [47] is a useful tool to analyze the influence of the input parameters on the output results. The main reason to analyze the sensitivity is to understand the relative impact on the output results due to small increments of the input parameters. Normalized sensitivity coefficients of the mobile-domain concentration in response to the relative changes of the given parameters are expressed as:

$$K_{i,j} = X_j \frac{\partial R_i}{\partial X_j}, \quad (36)$$

where K_{ij} is the normalized coefficient for the j -th input parameter X at the i -th time step. The parameter R is a function of the input parameters X_j and t . The partial derivative in the above equation is approximated by a forward differencing equation as follows:

$$\frac{\partial R_i}{\partial X_j} = \frac{R_i(X_j + \Delta X_j) - R_i(X_j)}{\Delta X_j}, \quad (37)$$

where ΔX_j is a small positive increment of the parameter value. In this study, one can assume $\Delta X_j = 10^{-2} \times X_j$.

Several observations can be made from Figs. 9 and 10. First, as shown in Fig. 9 for unilateral flow, the concentration in the mobile domain of the fracture is most sensitive to the longitudinal dispersivity, and nearly insensitive to the first-order mass transfer rate and the mobile/immobile ratio. As shown in Fig. 10 for radial flow, the concentration in the mobile domain of the fracture is most sensitive to the radial dispersivity, less sensitive to the mobile/immobile ratio, and least sensitive to the first-order mass transfer rate. Secondly, the normalized sensitivity curves in both models are time dependent: they sharply increase at the beginning; after reaching peak values, they decline with time and eventually approach their equilibrium state. Based on the sensitivity analysis, it is recommended that great effort should be put on determining the dispersivity value for both unilateral and radial flows as the concentration is most sensitive to this parameter.

4.4 Discussion and further scopes of the study

Several issues are addressed below in respect to the application of the model. The limitations and further scopes of the study are also discussed.

4.4.1 Parameter identification

The parameters involved in the mathematical models of this study may be measured directly or determined via a calibration process. The fracture aperture can be measured using an X-ray CT scanner [48]. It may also be determined indirectly using the so-called “cubic law” if the flow rate and the hydraulic gradient through the fracture can be measured [49]. Darcian velocity in the fracture can be measured directly by the ratio of the total flow rate over the cross-section of flow which is the product of the fracture aperture and the fracture width. Matrix porosity and matrix diffusion coefficient can also be measured directly by diffusion experiments as reported in many previous studies such as Neretnieks [50], Medina and Carrera [51], Boving and Grathwohl [52], and Tachi et al. [53], to name a few. Zhou et al. [54] provided an analysis of forty field-scale effective matrix diffusion experiments and suggested that effective matrix diffusion coefficient was likely to be statistically scale-dependent. Retardation factor in the matrix can also be measured, as reported previously in studies such as Neretnieks [50], Schwartz et al. [55], Dai et al. [56], and Tachi et al. [53]. Retardation factor in the fracture can be measured by comparing a non-sorptive tracer versus a sorptive tracer simultaneously. The decay constant can be calculated if the half-life of the tracer is known. However, complexity rises when the decay constants are different for the matrix and the mobile and immobile domains of the fracture. Such a phenomenon may occur when biodegradation is involved, and this is a subject requires further investigation. The fracture mobile/immobile ratio may be measured using a method proposed by Clothier et al. [57] and others. The mobile/immobile mass transfer rate can be determined following previous studies such as Jaynes et al. [58]. Now the only parameter that is undetermined is the fracture dispersivity, which can be calibrated by fitting the observed BTCs with the theoretical BTCs obtained in this study.

4.4.2 Application to heat transfer problems

Given the similarity of heat transfer and solute transport in the subsurface, the models developed in this study can be applied to heat transfer in fractured rocks. The heat transfer in fractured rocks has seen a wide range of applications such as risk assessment of high-level nuclear waste depository [59], thermal energy development from hot dry hard rocks [60], and temperature-dependent groundwater flow system such as geysers in Yellow Stone National Park [61].

4.4.3 Application to a single fracture with variable apertures

Generally speaking, the models developed in this study cannot be applied directly to a single fracture with variable apertures, because flow and transport in such a fracture could be highly complex. For instance, there is abundant evidence showing that flow and transport in a single fracture with considerable variation of aperture may not be planar. Instead, it follows a few discrete channels (or pipes), as reported by Cacas et al. [62] for investigating the tracer experimental results at the test site of the Fanay-Augères uranium mine, France. Many other studies such as Tsang et al. [63] and Detwiler et al. [64] have provided insightful analysis of flow and transport in variable-aperture fractures, particularly the channel flow and transport phenomena. When the variation of aperture is mild, it is possible to approximate the fracture with a uniform “averaged” aperture, thus the models developed here may be relevant. Nevertheless, further investigation is certainly needed to study transport in a fracture-matrix system with spatially and/or temporally variable aperture in the future.

5. Conclusions

Two different models are proposed to study reactive solute transport in a filled fracture-rock matrix system: one for unilateral flow and one for radial flow. Diffusion to the rock matrix is

taken into consideration for both models, in addition to other processes such as radioactive decay, retardation associated with a linear sorption isotherm, advection and longitudinal dispersion. The investigated system involves coupling of transport in three domains: a mobile domain and an immobile domain for characterizing the filled fracture, and a rock matrix domain serves as the solute sink. Both models are solved using a Laplace transform technique. The developed solutions are proven to be robust and accurate and can be used as benchmarks against numerical simulations of transport in a coupled three-domain system involving a filled single fracture-matrix system.

BTCs in unilateral flow are nearly unaffected by the mobile/immobile ratio if the longitudinal dispersivity is fixed and the dispersion coefficient is inversely proportional to the mobile water content (see Fig. 3A) while they are moderately affected by the mobile/immobile ratio if the dispersion coefficient is fixed and the longitudinal dispersivity varies proportionally with the mobile water content (see Figs.3B-3C).

The comparison of the unilateral flow model of this study with the previous study of Zhu et al. [13] suggests that the fracture longitudinal dispersion has a significant influence on solute transport in a single fracture-matrix system, thus should not be neglected (see Fig. 5).

For both models, the relative masses stored in the immobile domain of the fracture increase first with time to reach maximum values and then slowly decline with time to approach equilibrium, which depends on the mobile/immobile ratios (see Fig. 7), but appear to be independent of the first-order mass transfer rates (see Fig. 8).

Based on the sensitivity analysis of both models (see Figs. 9-10), it is recommended that great effort should be put on determining the dispersivity value for both unilateral and radial flows as the concentration is most sensitive to this parameter.

Acknowledgements

The comments from four anonymous reviewers are meticulous, constructive, and very useful for us to improve the quality of the manuscript. We sincerely thank them for their unselfish service. This research is partially supported by grants from National Science Foundation of China (Grant Numbers: 41372253, 41521001).

References:

- [1] Roubinet, D., de Dreuzy, J. R., Tartakovsky, D. M. Semi-analytical solutions for solute transport and exchange in fractured porous media. *Water Resources Research*. 48 (2012), doi: 10.1029/2011wr011168.
- [2] Grisak, G. E., Pickens, J. F. An analytical solution for solute transport through fractured media with matrix diffusion. *Journal of Hydrology*. 52 (1981) 47-57, doi: 10.1016/0022-1694(81)90095-0.
- [3] Pouya, A. Three-dimensional flow in fractured porous media: A potential solution based on singular integral equations. *Advances in Water Resources*. 35 (2012) 30-40, doi: 10.1016/j.advwatres.2011.10.009.
- [4] Bodin, J., Delay, F., de Marsily, G. Solute transport in a single fracture with negligible matrix permeability: 1. fundamental mechanisms. *Hydrogeology Journal*. 11 (2003) 418-433, doi: 10.1007/s10040-003-0268-2.
- [5] Wilson, C. R., Witherspoon, P. A. An investigation of laminar flow in fractured porous rocks. Department of Civil Engineering, University of California, 1970.
- [6] Tang, D. H., Frind, E. O., Sudicky, E. A. Contaminant transport in fractured porous-media - analytical solution for a single fracture. *Water Resources Research*. 17 (1981) 555-564, doi: 10.1029/WR017i003p00555.
- [7] Maloszewski, P., Zuber, A. Tracer experiments in fractured rocks - matrix diffusion and the validity of models. *Water Resources Research*. 29 (1993) 2723-2735, doi: 10.1029/93wr00608.

684 [8] Long, J. C. S., Billaux, D. M. From field data to fracture network modeling - an example
685 incorporating spatial structure. *Water Resources Research*. 23 (1987) 1201-1216, doi: DOI
686 10.1029/WR023i007p01201.

687 [9] Dershowitz, W., Miller, I. Dual porosity fracture flow and transport. *Geophysical Research*
688 *Letters*. 22 (1995) 1441-1444.

689 [10] Cvetkovic, V., Painter, S., Outters, N., Selroos, J. Stochastic simulation of radionuclide
690 migration in discretely fractured rock near the Äspö Hard Rock Laboratory. *Water Resources*
691 *Research*. 40 (2004).

692 [11] Noetinger, B., Roubinet, D., Russian, A., Le Borgne, T., Delay, F., Dentz, M., et al.
693 Random walk methods for modeling hydrodynamic transport in porous and fractured media from
694 pore to reservoir scale. *Transport in Porous Media*. (2016) 1-41.

695 [12] Sudicky, E. A., Frind, E. O. Contaminant transport in fractured porous media: Analytical
696 solutions for a system of parallel fractures. *Water Resources Research*. 18 (1982) 1634-1642, doi:
697 10.1029/WR018i006p01634.

698 [13] Zhu, Y. H., Zhan, H. B., Jin, M. G. Analytical solutions of solute transport in a fracture-
699 matrix system with different reaction rates for fracture and matrix. *Journal of Hydrology*. 539
700 (2016) 447-456, doi: 10.1016/j.jhydrol.2016.05.056.

701 [14] Seo, J. H., Mittal, R. A sharp-interface immersed boundary method with improved mass
702 conservation and reduced spurious pressure oscillations. *Journal of Computational Physics*. 230
703 (2011) 7347-7363, doi: 10.1016/j.jcp.2011.06.003.

704 [15] Weatherill, D., Graf, T., Simmons, C. T., Cook, P. G., Therrien, R., Reynolds, D. A.
705 Discretizing the fracture-matrix interface to simulate solute transport. *Ground Water*. 46 (2008)
706 606-615, doi: 10.1111/j.1745-6584.2007.00430.x.

707 [16] Moreno, L., Tsang, Y. W., Tsang, C. F., Hale, F. V., Neretnieks, I. Flow and tracer transport
708 in a single fracture - a stochastic-model and its relation to some field observations. *Water*
709 *Resources Research*. 24 (1988) 2033-2048, doi: 10.1029/WR024i012p02033.

710 [17] Raven, K. G., Novakowski, K. S., Lapcevic, P. A. Interpretation of field tracer tests of a
711 single fracture using a transient solute storage model. *Water Resources Research*. 24 (1988)
712 2019-2032, doi: 10.1029/WR024i012p02019.

713 [18] Brown, S., Caprihan, A., Hardy, R. Experimental observation of fluid flow channels in a
714 single fracture. *Journal of Geophysical Research-Solid Earth*. 103 (1998) 5125-5132, doi:
715 10.1029/97jb03542.

716 [19] Esposito, S. J., Thomson, N. R. Two-phase flow and transport in a single fracture-porous
717 medium system. *Journal of Contaminant Hydrology*. 37 (1999) 319-341, doi: 10.1016/S0169-
718 7722(98)00169-7.

719 [20] Chen, C. S. Solutions for radionuclide transport from an injection well into a single fracture
720 in a porous formation. *Water Resources Research*. 22 (1986) 508-518, doi:
721 10.1029/WR022i004p00508.

722 [21] Wealthall, G. P., Steele, A., Bloomfield, J. P., Moss, R. H., Lerner, D. N. Sediment filled
723 fractures in the Permo-Triassic sandstones of the Cheshire basin: observations and implications
724 for pollutant transport. *Journal of Contaminant Hydrology*. 50 (2001) 41-51.

725 [22] Bradner, G. C., Murdoch, L. C. Effects of skin and hydraulic fractures on SVE wells.
726 *Journal of Contaminant Hydrology*. 77 (2005) 271-297, doi: 10.1016/j.jconhyd.2005.02.001.

727 [23] Kemp, S. J., Pearce, J. M., Oates, D. In-situ sampling of sediment-filled fractures.
728 *Géotechnique*. 53 (2003) 665-668, doi: 10.1680/geot.53.7.665.37388.

729 [24] Lunati, I., Kinzelbach, W., Sørensen, I. Effects of pore volume–transmissivity correlation on
730 transport phenomena. *Journal of Contaminant Hydrology*. 67 (2003) 195-217.

731 [25] Jodar, J., Medina, A., Carrera, J. Gas tracer transport through a heterogeneous fracture zone
732 under two phase flow conditions: Model development and parameter sensitivity. *Advances in*
733 *Water Resources*. 32 (2009) 315-328, doi: 10.1016/j.advwatres.2008.10.008.

734 [26] Qian, J. Z., Chen, Z., Zhan, H. B., Luo, S. H. Solute transport in a filled single fracture
735 under non-Darcian flow. *International Journal of Rock Mechanics and Mining Sciences*. 48
736 (2011) 132-140, doi: 10.1016/j.ijrmms.2010.09.009.

737 [27] Van Genuchten, M. T., Wierenga, P. J. Mass transfer studies in sorbing porous media I.
738 Analytical solutions. *Soil Science Society of America Journal*. 40 (1976) 473-480.

739 [28] Rezaei, A., Zare, M., Zhan, H. Aquitard horizontal dispersion on reactive solute transport in
740 an aquifer–aquitard system. *Transport in Porous Media*. 113 (2016) 695-716.

741 [29] Davis, G. B., Laslett, D., Patterson, B. M., Johnston, C. D. Integrating spatial and temporal
742 oxygen data to improve the quantification of in situ petroleum biodegradation rates. *Journal of*
743 *Environmental Management*. 117 (2013) 42-49, doi: 10.1016/j.jenvman.2012.12.027.

744 [30] Johnson, C. A., Furrer, G. Influence of biodegradation processes on the duration of CaCO_3
745 as a pH buffer in municipal solid waste incinerator bottom ash. *Environmental science &*
746 *technology*. 36 (2002) 215-220.

747 [31] Parker, J. C., Valocchi, A. J. Constraints on the validity of equilibrium and first - order
748 kinetic transport models in structured soils. *Water Resources Research*. 22 (1986) 399-407.

749 [32] Wierenga, P. J., Vangenuchten, M. T. Solute transport through small and large unsaturated
750 soil columns. *Ground Water*. 27 (1989) 35-42, doi: 10.1111/j.1745-6584.1989.tb00005.x.

751 [33] Leij, F. J., Dane, J. H., Vangenuchten, M. T. Mathematical-analysis of one-dimensional
752 solute transport in a layered soil-profile. Soil Science Society of America Journal. 55 (1991) 944-
753 953.

754 [34] Berkowitz, B., Cortis, A., Dror, I., Scher, H. Laboratory experiments on dispersive transport
755 across interfaces: The role of flow direction. Water Resources Research. 45 (2009), doi:
756 10.1029/2008wr007342.

757 [35] Marseguerra, M., Zoia, A. Normal and anomalous transport across an interface: Monte
758 Carlo and analytical approach. Annals of Nuclear Energy. 33 (2006) 1396-1407, doi:
759 10.1016/j.anucene.2006.09.012.

760 [36] Zhang, X. X., Qi, X. B., Qiao, D. M. Change in macroscopic concentration at the interface
761 between different materials: Continuous or discontinuous. Water Resources Research. 46 (2010),
762 doi: 10.1029/2009wr008853.

763 [37] Simmons, C. T., Fenstemaker, T. R., Sharp, J. M., Jr. Variable-density groundwater flow
764 and solute transport in heterogeneous porous media: approaches, resolutions and future
765 challenges. Journal of Contaminant Hydrology. 52 (2001) 245-275.

766 [38] Bear, J. Dynamics of Fluids in Porous Media. American Else-vier, New York. (1972).

767 [39] Zhan, H., Wen, Z., Huang, G., Sun, D. Analytical solution of two-dimensional solute
768 transport in an aquifer-aquitard system. Journal of Contaminant Hydrology. 107 (2009) 162-174,
769 doi: 10.1016/j.jconhyd.2009.04.010.

770 [40] De Hoog, F. R., Knight, J., Stokes, A. An improved method for numerical inversion of
771 Laplace transforms. SIAM Journal on Scientific and Statistical Computing. 3 (1982) 357-366.

772 [41] Furman, A., Neuman, S. P. Laplace-transform analytic element solution of transient flow in
773 porous media. *Advances in Water Resources*. 26 (2003) 1229-1237, doi:
774 10.1016/j.advwatres.2003.09.003.

775 [42] Wang, Q. R., Zhan, H. B. On different numerical inverse Laplace methods for solute
776 transport problems. *Advances in Water Resources*. 75 (2015) 80-92, doi:
777 10.1016/j.advwatres.2014.11.001.

778 [43] Schumer, R., Benson, D. A., Meerschaert, M. M., Baeumer, B. Fractal mobile/immobile
779 solute transport. *Water Resources Research*. 39 (2003), doi: 10.1029/2003wr002141.

780 [44] Chen, C. S. Analytical solutions for radial dispersion with cauchy boundary at injection well.
781 *Water Resources Research*. 23 (1987) 1217-1224, doi: 10.1029/WR023i007p01217.

782 [45] Dronfield, D. G., Silliman, S. E. Velocity dependence of dispersion for transport through a
783 single fracture of variable roughness. *Water Resources Research*. 29 (1993) 3477-3483, doi:
784 10.1029/93wr01407.

785 [46] Huang, Y. C., Yeh, H. D. The use of sensitivity analysis in on-line aquifer parameter
786 estimation. *Journal of Hydrology*. 335 (2007) 406-418, doi: 10.1016/j.jhydrol.12.007.

787 [47] Kabala, Z. J. Sensitivity analysis of a pumping test on a well with wellbore storage and skin.
788 *Advances in Water Resources*. 24 (2001) 483-504.

789 [48] Johns, R. A., Steude, J. S., Castanier, L. M., Roberts, P. V. Nondestructive measurements of
790 fracture aperture in crystalline rock cores using X-ray computed-tomography. *Journal of*
791 *Geophysical Research-Solid Earth*. 98 (1993) 1889-1900, doi: 10.1029/92jb02298.

792 [49] Witherspoon, P. A., Wang, J. S. Y., Iwai, K., Gale, J. E. Validity of cubic law for fluid-flow
793 in a deformable rock fracture. *Water Resources Research*. 16 (1980) 1016-1024, doi:
794 10.1029/WR016i006p01016.

795 [50] Neretnieks, I. Diffusion in the rock matrix - an important factor in radionuclide retardation.
796 Journal of Geophysical Research. 85 (1980) 4379-4397, doi: 10.1029/JB085iB08p04379.

797 [51] Medina, A., Carrera, J. Coupled estimation of flow and solute transport parameters. Water
798 Resources Research. 32 (1996) 3063-3076, doi: 10.1029/96wr00754.

799 [52] Boving, T. B., Grathwohl, P. Tracer diffusion coefficients in sedimentary rocks: correlation
800 to porosity and hydraulic conductivity. Journal of Contaminant Hydrology. 53 (2001) 85-100,
801 doi: 10.1016/S0169-7722(01)00138-3.

802 [53] Tachi, Y., Ebina, T., Takeda, C., Saito, T., Takahashi, H., Ohuchi, Y., et al. Matrix diffusion
803 and sorption of Cs⁺, Na⁺, I⁻ and HTO in granodiorite: Laboratory-scale results and their
804 extrapolation to the in situ condition. Journal of Contaminant Hydrology. 179 (2015) 10-24, doi:
805 10.1016/j.jconhyd.2015.05.003.

806 [54] Zhou, Q. L., Liu, H. H., Molz, F. J., Zhang, Y. Q., Bodvarsson, G. S. Field-scale effective
807 matrix diffusion coefficient for fractured rock: Results from literature survey. Journal of
808 Contaminant Hydrology. 93 (2007) 161-187, doi: 10.1016/j.jconhyd.2007.02.002.

809 [55] Schwartz, R. C., Juo, A. S. R., McInnes, K. J. Estimating parameters for a dual-porosity
810 model to describe non-equilibrium, reactive transport in a fine-textured soil. Journal of
811 Hydrology. 229 (2000) 149-167, doi: 10.1016/S0022-1694(00)00164-5.

812 [56] Dai, Z. X., Wolfsberg, A., Reimus, P., Deng, H. L., Kwicklis, E., Ding, M., et al.
813 Identification of sorption processes and parameters for radionuclide transport in fractured rock.
814 Journal of Hydrology. 414 (2012) 220-230, doi: 10.1016/j.jhydrol.2011.10.035.

815 [57] Clothier, B., Kirkham, M., McLean, J. In situ measurement of the effective transport volume
816 for solute moving through soil. Soil Science Society of America Journal. 56 (1992) 733-736.

817 [58] Jaynes, D. B., Logsdon, S. D., Horton, R. Field method for measuring mobile immobile
818 water-content and solute transfer rate coefficient. Soil Science Society of America Journal. 59
819 (1995) 352-356.

820 [59] Pruess, K., Wang, J. S. Y., Tsang, Y. W. On thermohydrologic conditions near high-level
821 nuclear wastes emplaced in partially saturated fractured tuff .1. simulation studies with explicit
822 consideration of fracture effects. Water Resources Research. 26 (1990) 1235-1248, doi:
823 10.1029/WR026i006p01235.

824 [60] Tsang, C. F. Coupled hydromechanical-thermochemical processes in rock fractures.
825 Reviews of Geophysics. 29 (1991) 537-551, doi: 10.1029/91rg01832.

826 [61] Fournier, R. O. Geochemistry and dynamics of the Yellowstone National Park hydrothermal
827 system. Annual Review of Earth and Planetary Sciences. 17 (1989) 13-53, doi:
828 10.1146/annurev.earth.17.1.13.

829 [62] Cacas, M. C., Ledoux, E., Demarsily, G., Barbreau, A., Calmels, P., Gaillard, B., et al.
830 Modeling fracture flow with a stochastic discrete fracture network - calibration and validation .2.
831 The transport model. Water Resources Research. 26 (1990) 491-500, doi:
832 10.1029/WR026i003p00491.

833 [63] Tsang, Y. W., Tsang, C. F., Neretnieks, I., Moreno, L. Flow and tracer transport in fractured
834 media - a variable aperture channel model and Its properties. Water Resources Research. 24
835 (1988) 2049-2060, doi: 10.1029/WR024i012p02049.

836 [64] Detwiler, R. L., Rajaram, H., Glass, R. J. Solute transport in variable-aperture fractures: An
837 investigation of the relative importance of Taylor dispersion and macrodispersion. Water
838 Resources Research. 36 (2000) 1611-1625, doi: 10.1029/2000wr900036.

839