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Dissolution of dense non-aqueous phase liquids in vertical fractures: effect of finger residuals and dead-end pools

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Abstract. Understanding the dissolution behavior of dense non-aqueous phase liquids (DNAPLs) in rock fractures under different entrapment conditions is important for remediation activities and any related predictive modeling. This study investigates DNAPL dissolution in variable aperture fractures under two important entrapment configurations, namely, entrapped residual blobs from gravity fingering and pooling in a dead-end fracture. We performed a physical dissolution experiment of residual DNAPL blobs in a vertical analog fracture using light transmission techniques. A high-resolution mechanistic (physically-based) numerical model has been developed which is shown to excellently reproduce the experimentally observed DNAPL dissolution. We subsequently applied the model to simulate dissolution of the residual blobs under different water flushing velocities. The simulated relationship between the Sherwood number Sh and Peclet number Pe could be well fitted with a simple power-law function ($Sh = 1.43Pe^{0.43}$). To investigate mass transfer from dead-end pools, another type of trapping in rock fractures, entrapment and dissolution of DNAPL in a vertical dead-end fracture was simulated. As the entrapped pool dissolves, the depth of the interface between the DNAPL and the flowing water increases linearly with decreasing DNAPL saturation. The interfacial area remains more or less constant as DNAPL saturation decreases, unlike in the case of residual DNAPL blobs. The decreasing depth of the contact interface changes the flow field and causes decreasing water flow velocity above the top of the DNAPL pool, suggesting the dependence of the mass transfer rate on the depth of the interface, or alternatively, the remaining mass percentage in the fracture. Simulation results show that the resultant Sherwood number Sh is significantly smaller than in the case of residual blobs for any given Peclet number, indicating slower mass transfer. The results also show

that the Sh can be well fitted with a power-law function of Pe and remaining mass percentage. The obtained relationships of dimensionless groups concerning the mass transfer characteristics at the level of individual fractures can be further used in predictive modeling of dissolution at a larger (fracture network) scale.

Keywords: fracture; fingering; mass transfer; entrapment configuration; source depletion; contaminant flux; modeling.

1. Introduction

Accidental spills of dense non-aqueous phase liquids (DNAPLs) such as trichloroethylene (TCE) and tetrachloroethylene (PCE) constitute frequently encountered groundwater contamination problems (Mackay and Cherry, 1989; Kueper and McWhorter, 1991; Esposito and Thomson, 1999). Released DNAPLs can penetrate unconsolidated sediments and enter fractured aquifers. Documented field studies and remediation activities for DNAPL contaminated sites (e.g., Dusilek et al., 2001; Werner and Helmke, 2003; U.S. EPA, 2005; McGuire et al., 2006; Cho et al., 2008) have demonstrated significant difficulties and challenges in remediating DNAPL source zones in fractured subsurface environment. This can be attributed to the complexity of the fractured media, as the locations of permeable fractures and DNAPL containing fractures are typically not exactly known, and often connectivity between the injection and extraction wells cannot be assured (U.S. EPA, 2005), as in the unconsolidated media. It is often impractical to remove sufficient DNAPL mass by the aggressive physical and chemical source-zone treatment (e.g., pump and treat, thermal treatment, surfactant flushing, bioaugmented remediation and *in situ* chemical oxidation), for which reason there is an increasing interest in passive treatment or monitored natural attenuation

(Illman and Alvarez, 2009; McLaren et al., 2012; Blum et al., 2011). Risk assessment and performance evaluation for this remediation alternative require a comprehensive understanding of the DNAPL dissolution process in fractured media.

Entrapment and dissolution behavior of DNAPLs in fractured media is complicated due to the heterogeneity at different scales, arising from aperture variability within individual fractures as well as from fracture connectivity in a network. When released into fractured rocks, DNAPLs will migrate under the influence of gravitational, viscous, and capillary forces until they get trapped in dead-end fractures or become immobilized as residual blobs along the migration pathways. Various factors, including release scenarios, fluid properties (i.e. interfacial tension, density and viscosity), aperture variability, and orientation and connectivity of fractures, affect the DNAPL entrapment architecture which has a strong impact on the subsequent dissolution process. Incorporating well-studied column scale mass transfer correlations, field scale simulation studies for DNAPL source depletion in heterogeneous unconsolidated media (e.g., Parker and Park, 2004; Saenton and Illangasekare, 2007) have gained useful insights linking contaminant mass flux to the DNAPL entrapment architecture. But for fractured media, this kind of upscaling analysis for mass transfer is not yet in place, as DNAPL dissolution at the single-fracture scale needs to be thoroughly studied for a number of different trapping conditions. The focus of this paper is the effect of trapping conditions on mass transfer in individual fractures, as a building block for improved understanding of contaminant mass flux from a fracture network.

Natural rock fractures have variable apertures (Brown, 1995; Hakami and Larsson, 1996), which causes fluid trapping for immiscible displacement and phase interference

for two-phase flow. Presence of two fluids within a fracture reduces permeability to each phase (Pruess and Tsang, 1990; Persoff and Pruess, 1995; Detwiler et al., 2005). This permeability reduction is usually represented by the relative permeability, which is the ratio of the permeability in two-phase flow to that in single-phase flow. Predicting the relative permeability (or the average flowing velocity) is important for understanding the dissolution of an entrapped phase into the flowing phase. Experimental studies with horizontal fractures (e.g., Reitsma and Kueper, 1994; Persoff and Pruess, 1995; Chen and Horne, 2006) have been conducted to characterize flow structures and to describe the two-phase relative permeabilities.

The variable apertures within a single fracture yield different influences of capillary, gravitational, and viscous forces, which control the fluid displacement and entrapment (Glass et al., 2001). DNAPL entrapment structures determine the DNAPL-water interfacial area, a key parameter for predicting interphase mass transfer. Based on DNAPL dissolution experiments in natural fractures, Dickson and Thomson (2003) developed a Sherwood-type empirical mass transfer correlation for the dissolution behavior at the fracture scale. Schaefer et al. (2009) performed DNAPL dissolution experiments for four sandstone fractures and measured the interfacial area by using an interfacial tracer. Detwiler et al. (2001) developed a DNAPL dissolution model that explicitly incorporates the pore scale geometry of the entrapped DNAPL and its evolution during dissolution. The model demonstrated excellent agreement with comparison to high-resolution DNAPL dissolution experiments in an analog variable-aperture fracture. In a recent study, Detwiler et al. (2009) investigated the influence of initial entrapped phase geometry and flowing phase velocity on the dissolution processes, and developed

fracture-scale constitutive relationships describing dependences of interfacial area on entrapped phase saturation, and intrinsic mass transfer rate on Peclet number. The aperture variability within a fracture is often characterized by geostatistical parameters such as variance, correlation length and anisotropy ratio (Keller et al., 1999; Lee et al., 2003). How these parameters affect the DNAPL entrapment and dissolution behavior is of interest for modeling and prediction at a larger scale. A recent study by Yang et al. (2012b) showed that increasing aperture standard deviation and/or decreasing correlation length lead to larger amounts of entrapped DNAPL as well as larger sizes of DNAPL blobs, and subsequently cause longer times for complete dissolution. Interphase mass transfer between the DNAPL and the water is also a fundamental component of the remediation processes which are often applied to enhance the mass transfer rates through chemical or biological reactions (e.g., Tunnicliffe and Thomson, 2004; Schaefer et al., 2010; Chambon et al., 2010; Manoli et al., 2012).

Besides being trapped by capillary forces along the fingered pathways, DNAPLs can also be held stagnant due to fracture termination and/or loss of hydraulic connectivity to other fractures. Occurrences of vertical dead-end fractures can provide regions of a fractured network that accept DNAPLs due to density effects, yet do not contribute to the global flow within the network (Reynolds and Kueper, 2003). Depending on the fracture network characteristics, the volume of DNAPL entrapped in the dead-end fractures can be large. The critical height for DNAPL entry into a partially saturated, dead-end fracture was experimentally studied by Su and Javandel (2004). Experiments and simulations by Ji et al. (2003) showed that ambient groundwater flow can significantly affect DNAPL migration paths in a fracture network. Remediation of entrapped contaminants in dead-

end fractures will be extremely challenging due to the difficulty of successful delivery of a remediating agent to these regions (Yeo et al., 2003). Dissolution of DNAPL in dead-end fractures is expected to be significantly slower than that in well-connected fracture planes, since there is limited contact between the DNAPL and the flowing water due to water bypassing. In a DNAPL-contaminated fractured aquifer, a likely scenario is that the trapped residual blobs have already dissolved but the DNAPL trapped in dead-end fractures keeps generating mass flux at low concentrations. This was shown by VanderKwaak and Sudicky (1996) who performed numerical simulations for a case of TCE dissolution in a fracture network with low porosity granite matrix.

Entrapment as residual blobs along gravity fingers and accumulation as pools in dead-end fractures are two important DNAPL retention mechanisms in a fracture network. Although the aforementioned experimental and numerical studies have provided improved understandings on DNAPL dissolution in fractured media, they have not considered the case of dissolution of residual blobs resulting from gravity fingering. Furthermore, to the best of our knowledge, detailed quantitative analysis of dissolution kinetics of entrapped DNAPLs in dead-end fractures has not been reported in the literature. In this study, we combine a physical experiment and mechanistic numerical modeling analysis to investigate the dissolution of DNAPL under these two entrapment scenarios, namely residual blobs from fingering and dead-end pools. The objective is to quantify the fracture-scale mass transfer characteristics for both scenarios by experimental and numerical studies at a detailed (resolved to $\sim 100\ \mu\text{m}$) scale.

2. Experiment on dissolution of entrapped residual blobs from fingering

We performed a physical TCE-dissolution experiment in a vertical transparent analog fracture. TCE was injected from the top port of the fracture and the injection resulted in fingering and entrapped (residual) TCE blobs along the fingers. Measurement of the aperture field and TCE distribution were conducted by using light transmission techniques (see Detwiler et al., 1999), which enabled us to quantify the dissolution mass transfer from the residual blobs. The experiment was also used to test a computational model which will be described in Section 3.

2.1. Description of the analog fracture

The transparent analog fracture was made by placing two 20×20 cm pieces of textured glass in contact. Each piece of glass is 8 mm thick. A schematic of the fracture cell is shown in Fig. 1a. The four edges were sealed with cement and then covered with a layer of silicone. Prior to sealing, three fluid ports were attached to three of the edges. The port attached to top edge was used for injection of TCE and were capped during the dissolution process. The fracture cell was held vertical and water was allowed to flow from the left hand side to the right hand side. In order to distribute the inflow water evenly along the left-side boundary, a half-cylinder-shaped groove was etched on each fracture surface in the vicinity of the left edge, which created an inner hollow cylinder of 6 mm diameter. This was also done for the outflow (right side) boundary.

Following the methodology presented by Detwiler et al. (1999), a light transmission system was used to measure the aperture and delineate the TCE phase. The system includes a 12-bit charge-coupled device (CCD) camera (AVT Pike F421B) with a spatial resolution of 2048×2048 pixels in front of the fracture and a uniform, planar light source

(Phlox light-emitting diode backlight) producing constant light behind the fracture. The experiment was conducted in a dark box. The fracture was first filled with deionized water and then flooded with at least 100 fracture volumes of 0.0625 g/L FD&C Brilliant Blue #1 dyed water. Light intensities were measured by the sensor of the CCD camera both for the fracture with clean water and with dyed water. To minimize the error due to random noise produced by the sensor, 256 images were taken and averaged each time when the light intensities were measured. The aperture field was then determined by directly applying the Beer-Lambert law (see Detwiler et al., 1999). We obtained aperture measurements for an area of $17.7\text{ cm} \times 17.7\text{ cm}$ with 1800×1800 pixels.

The details of the aperture field measurements are summarized in Table 1 while Fig. 1b shows a gray image of the measured aperture field. The aperture field approximately follows a normal distribution with a standard deviation of 0.12 mm (Fig. 2a). The spatial correlation in the aperture field is characterized by plotting the semivariograms. Fig. 2b shows that the semivariogram in the horizontal direction is well represented by an exponential function with a correlation length of about 4.1 mm. For the vertical direction, the semivariogram increases with the separation distance and does not reach a plateau. This is because a slightly increasing trend exists for the mean aperture in the vertical direction.

2.2. DNAPL dissolution experiment

After the aperture field was measured, 1.0 mL TCE was injected from the port on the top boundary using a glass syringe (Hamilton) with a rate of about 0.5 mL/min. The injection created downward fingered flow of TCE which also resulted in entrapped TCE blob along the finger tracks. The difference in light absorbance for the pure TCE and the

dyed water provided contrast in light intensities that were captured by the CCD camera. This enabled differentiation of the DNAPL and the dyed water by subsequent image processing. About a half (0.525 mL) of the injected TCE reached the bottom and formed a large continuous blob. The rest of the injected TCE was trapped by capillary forces as residual blobs. Fig. 1c shows a binary image of the TCE entrapment configuration. Note that part of the large blob at the bottom was outside of the recorded area by the camera and is not shown in Fig. 1c. The large blob will be excluded from the analyses of DNAPL saturation, interfacial area and mass transfer characteristics. The focus of the experiment was to quantify the dissolution process of the residual DNAPL blobs which showed significant variability in sizes and shapes.

The water (with zero TCE concentration) inflow rate from the left-hand side boundary was kept at 0.1 mL/min during the dissolution experiment. The CCD camera was then programmed to take pictures regularly at an interval of 2 hours. Given the ability of the experimental setup to accurately measure the aperture field and the DNAPL mass in the fracture (see methodology developed in Detwiler et al., 1999; 2001), we were able to quantify the transient mass transfer rate and therefore did not measure the effluent TCE concentration. The dissolution experiment was run for 17 days.

3. Model for dissolution of entrapped DNAPL

The full three-dimensional (3D) equations describing the dissolution of a single-component DNAPL into water in variable-aperture fracture were discussed by Detwiler et al. (2001). Using the approximation of quasi-steady state and depth-averaging for single phase flow and transport, Detwiler et al. (2001) developed a two-dimensional (2D) numerical model which couples water flow, dissolved species transport, interphase mass

transfer and DNAPL-water interface movement. The model was demonstrated to be able to reproduce their experimental results well for DNAPL dissolution within a horizontal fracture. The modeling approach used in this study is similar to that of Detwiler et al. (2001) except that here we consider vertical fractures with gravity effects and apply a new algorithm (Yang et al., 2012a) for tracking the DNAPL-water interface shrinkage. In the following we briefly describe the numerical model for DNAPL dissolution and mass transport.

The water flow in a variable-aperture fracture is approximated by the well-known 2D Reynolds equation:

$$\nabla \cdot (b\mathbf{v}) = 0 \quad (1)$$

where b is the local aperture and the average flow velocity is given by

$$\mathbf{v} = -\frac{k\rho_w g}{\mu} \nabla h \quad (2)$$

where h is the local pressure head, k is the local permeability (calculated as $b^2/12$ according to the cubic law), ρ_w is the density of the water, μ is the viscosity of the water, and g is the gravitational acceleration constant. Due to the presence of the entrapped non-aqueous phase, the fluid-fluid interface renders a zero-gradient (no-flow) boundary for the flowing phase.

The quasi-steady, two-dimensional equation for dissolved mass transport within a variable-aperture fracture is described by (Detwiler et al., 2001):

$$\nabla \cdot (b\mathbf{v}C) = \nabla \cdot (b\mathbf{D}_{\text{eff}} \cdot \nabla C) \quad (3)$$

where C is the depth-averaged concentration and $\mathbf{D}_{\text{eff}}$ is the effective dispersion tensor.

According to the discussions by Detwiler et al. (2001), $\mathbf{D}_{\text{eff}}$ is taken to be equal to the

molecular diffusion coefficient D_m . The DNAPL-water interfaces impose a boundary condition as $C = C_{eq}$ where C_{eq} is the solubility (equilibrium) concentration. Local mass fluxes from the entrapped DNAPL to the flowing water are calculated as

$$j = D_m \nabla C \cdot \mathbf{n} \quad (4)$$

where $\mathbf{n}$ is the vector normal to the fluid-fluid interface. Integrating equation (4) for the local interfaces along the perimeter of each DNAPL blob gives the mass transfer fluxes for the individual blobs. It should be pointed out that by this approach the mass transfer into the wetting films is ignored. This can be justified by the fact that the wetting films are relative stagnant (with transmissivity as least 3 orders of magnitude smaller than regions occupied solely by the flowing phase) and of little wetting phase volume in the fracture (Detwiler et al., 2009), provided that solute diffusion into the rock matrix is negligible.

Dissolution of the entrapped DNAPL into the flowing water alters the flow velocity field. As a result, equations (1) to (4) need to be coupled. That is, each time after transport and mass transfer is solved the water flow solution needs to be updated. We numerically solve the flow and transport equations using a centered finite difference scheme during each time step. The amount of mass that is removed due to dissolution from each DNAPL blob in each time step is equal to the integrated mass transfer rate for each blob multiplied by the time step size Δt . Dissolution of the individual entrapped blobs results in shrinkage of these regions and subsequent small-scale movement of the interfaces which is controlled by interplay of capillary, gravitational and viscous forces (Detwiler et al., 2009). This interface movement process is taken into account by coupling the mass transfer results obtained from the solution of the advective-diffusive

equation to a newly developed invasion percolation (IP) algorithm (Yang et al., 2012a) in which the local capillary pressure is calculated using both the aperture-spanning curvature and the in-plane curvature. The local in-plane curvature is determined by an adaptive circle fitting approach.

Numerical simulations for DNAPL dissolution using the algorithm described above require specifying appropriate boundary conditions. In this study, the relevant boundary conditions for the flow simulations were specified according to the experimental condition, i.e., constant water flux along the inflow boundary, constant head along the outflow boundary and no flow boundaries for the other two sides parallel to the mean water flow direction. The boundary conditions for the transport simulations were zero concentration at the inflow boundary, $\partial C / \partial x = 0$ at the outflow boundary and no flux for the other boundary segments.

4. Modeling DNAPL entrapment in dead-end fractures

While a physical experiment on dissolution of entrapped residuals from DNAPL fingers is described in Section 2, experiments on DNAPL entrapment and dissolution in vertical dead-end fractures were not attempted because of the restriction imposed by the especially long time-frame. Instead, we take advantage of the developed computational model and simulate DNAPL entrapment and dissolution in dead-end fractures.

Although the downward movement of DNAPL in a vertical variable-aperture fracture is in general a complicated process with possible characteristics such as fingering, fragmentation and pulsation, the filling of a vertical dead-end fracture may be modeled as a slow and stable process, since the main displacement direction will be upwards (against gravitational direction) once the DNAPL has reached the bottom.

In this study, we simulate the entrapment of DNAPL in dead-end fractures using a modified IP model as presented in Yang et al. (2012a). We consider a case of single dead-end fracture where the lower halves of the side boundaries are closed and the DNAPL infiltrates from the middle part of the top boundary. The dead-end filling process is stopped once the DNAPL reaches the open part of the side boundaries. Fig. 3a shows an example of the aperture fields used for the simulations of DNAPL entrapment and dissolution in dead-end fractures. To generate the aperture fields, we used a fast inverse Fourier transform algorithm, based on the power spectrum model proposed by Brown (1995). The 512×512 aperture field in Fig. 3a has a mean aperture of 0.3 mm, standard deviation σ_b of 0.075 mm and grid spacing of 0.3 mm. The statistical parameters of the generated aperture field fall within the range reported in the literature on aperture measurements and fracture surface characterization (e.g., Hakami and Larsson, 1996; Brown, 1995). The simulated configuration of DNAPL entrapment for this fracture is presented in Fig. 3b. Note that we have removed the DNAPL finger above the pool in the dead-end because it is expected that the finger will be dissolved within a much shorter time than the dead-end pool. The dead-end DNAPL pool constitutes a volume percentage of 44% of the whole fracture void space (fracture scale DNAPL saturation S_n is equal to 0.44).

5. Results

5.1. Experiment results and comparison with dissolution simulation for residual blobs from fingering

Tracking the DNAPL volume during the dissolution experiment was done by continuous monitoring of the DNAPL distributions by the CCD camera. The residual

DNAPL saturation (S_{nr}) is defined as the DNAPL volume in the form of residual blobs divided by the fracture volume. Fig. 4a presents the evolution of S_{nr} over the dissolution period. During the 17-day long dissolution experiment, S_{nr} dropped from the initial 0.034 to 0.0065. It can be seen in Fig. 4a that the rate of S_{nr} decrease gradually reduces. This reflects the fact that the specific DNAPL-water interfacial area (a_i) decreases with S_{nr} as is evident in Fig. 4b. Note that the specific interfacial area here was not a direct measurement and does not include the interface between the DNAPL and the water films along the fracture walls. Rather, we estimated the interfacial area by integrating the measured apertures along the DNAPL perimeters from the DNAPL-water binary images, following the method by Detwiler et al. (2001). Because of the relative small amount of DNAPL mass trapped as residual form the estimated initial specific interfacial area ($\sim 0.45 \text{ cm}^{-1}$) is also small in comparison to the interfacial area measurement in the literature. For instance, Schaefer et al. (2009) reported specific interfacial area measurements ranging between 19 and 57 cm^{-1} for DNAPL saturations from 0.19 to 0.52 in sandstone fractures, using an interfacial tracer method.

Numerical simulations for entrapped DNAPL blobs under both gravity-neutral and gravity-stabilized conditions (Detwiler et al., 2009) showed that a_i can be approximated as a linear function of DNAPL saturation for a wide range of saturation values. Here, it is shown in Fig. 4b that, for small saturation values corresponding to residual blobs from gravity destabilized fingering, a linear relationship fits the $S_{nr} - a_i$ data with root mean squared error (RMSE) of 0.021, while a power law relationship ($a_i = 6.37 S_{nr}^{0.8}$) seems to substantially improve the fitting with RMSE of 0.007.

We also simulated the DNAPL dissolution in the measured aperture field using the computational algorithm described in Section 3. The experimentally measured DNAPL distribution (Fig. 1c) was used as the initial condition. The simulation parameters are presented in Table 2. Note that we coarsened the originally measured aperture field by a factor of 2 for both directions, yet maintained high resolution for the simulations. This resulted in a grid spacing of 0.197 mm and gave a reasonable number of grid cells (810,000) for equations (1-4) to be efficiently solved on a PC. The water inflow rate was 0.1 mL/min. Applying the boundary conditions described in Section 3, we obtained an initial concentration field as shown in Fig. 5a. Fig. 4a presents the simulated S_{nr} reduction by dissolution over the experiment duration. It can be seen that application of the modeling approach for DNAPL dissolution gives results that closely follow the experimental observations. Comparison of the blob shapes and the interfacial area between the simulated and the experimental results also showed good agreement (not shown here for space considerations). This further supports the contention that the introduced mechanistic model (which links depth-averaged flow and transport with interphase mass transfer and physically based entrapped blob shrinkage) can realistically simulate DNAPL dissolution in vertical variable-aperture fractures.

5.2. Effect of aqueous phase flow rate

The water flow velocities through the fracture influence the dissolved TCE concentration field and thus the local interphase mass transfer which is driven by the concentration gradient at the immediate vicinity of the fluid-fluid interface. It is of interest to quantify the effect of water velocity on the mass transfer at the fracture scale. The good agreement between the simulated and experimental results of the DNAPL

dissolution supports the further use of the modeling approach (Section 3) for investigation of mass transfer under different water flow rates.

DNAPL dissolution was simulated for a series of flow rates ranging from 0.005 to 2.5 mL/min. These flow rates correspond to dimensionless Peclet numbers (Pe , which weighs the relative magnitude of advective to diffusive transport and is defined as $Pe = q\langle b \rangle / D_m$, where q is the average water flow velocity and $\langle b \rangle$ is the mean aperture) ranging from about 0.6 to 295. Fig. 5b shows the simulated TCE concentration field for water flow rate of 1.0 mL/min (10 times of the flow rate in the dissolution experiment). Fig. 6 presents the simulated change of residual DNAPL saturation in the fracture (S_{nr}) with time for different flow rates. It can be seen that the complete mass removal after 16 days is only achieved with the highest flow rate 2.5 mL/min ($Pe = 295$). For the low flow rate of 0.02 mL/min ($Pe = 2.4$) only about half of the DNAPL mass is removed.

In order to quantify the dependence of the mass transfer rate coefficient on the flow rate, we apply the simplified analytical solution to 1-D steady-state advective-reactive transport equation (Parker and Park, 2004) to the initial flow and transport solution. The simplified equation is:

$$\frac{C_{out}}{C_{eq}} = 1 - \exp\left(-\frac{KL_s}{q}\right) \quad (5)$$

where C_{out}/C_{eq} is the flux-weighted outflow concentration normalized to solubility concentration, K is the bulk mass transfer rate coefficient and is often used to represent the product of k_i (the intrinsic mass transfer rate coefficient) and a_i , and L_s is the source zone length in the mean flow direction (L_s is 3.9 cm for experimental entrapment configuration). The intrinsic mass transfer rate coefficient can also be expressed using the

dimensionless Sherwood number (Sh) defined as $Sh = k_i \langle b \rangle / D_m$. Rewriting equation (5) in terms of Sh and Pe yields:

$$Sh = \frac{-Pe}{a_i L_s} \ln\left(1 - \frac{C_{out}}{C_{eq}}\right) . \quad (6)$$

It should be noted that C_{out}/C_{eq} is also dependent on Pe . For sufficiently small Pe so that the diffusion dominates over the advective transport, C_{out}/C_{eq} is expected to be close to 1. For example, the lowest flow rate considered ($Pe=0.6$) gives a value of 0.90 for C_{out}/C_{eq} . Using the information of C_{out}/C_{eq} from the numerical simulations, we plotted Sh against Pe as shown in Fig 7. It can be seen that for $Pe < 20$, Sh increases fast with increasing Pe , meaning that mass transfer in this range of Pe values is limited by the advective transport of the dissolved component. The increasing trend slows down as Pe becomes larger, suggesting that diffusion limited mass transfer is more and more pronounced. The Pe - Sh relationship can be well fitted to the following simple power-law equation:

$$Sh = \alpha_1 Pe^{\alpha_2} \quad (7)$$

With RMSE = 0.49 and the best fitted parameters $\alpha_1 = 1.43$ and $\alpha_2 = 0.43$. For comparison purposes, we have also plotted another relationship ($Sh = 0.7Pe^{0.23}$) inferred from a detailed computational study by Detwiler et al. (2009). The comparison (Fig. 7) indicates that the Sherwood numbers calculated from this study are significantly larger than those presented by Detwiler et al. (2009). This will be further discussed in Chapter 6.

5.3. Dissolution of entrapped DNAPL in a dead-end fracture

As described in Section 4, we simulated DNAPL entrapment in a square dead-end fracture where the lower halves of the side boundaries were closed and the DNAPL gradually filled the dead-end fracture until it reached the open part of the side boundaries.

The DNAPL entrapment configuration is presented in Fig. 3b. The initial entrapped DNAPL saturation S_n in the fracture is 0.44. Subsequently, DNAPL dissolution was simulated by introducing water inflow from the upper half of the left-hand side boundary and allowing water discharge from the upper half of the right-hand side boundary. The other parts of the boundaries were set to be no flow. The parameters used for the dissolution are the same as those listed in Table 2 except that the fracture dimension and the grid spacing are different (described in Section 4).

DNAPL dissolution was simulated for four different water flow rates ranging from 0.01 mL/min to 1.0 mL/min. With the dead-end entrapment configuration, the only contact area between the DNAPL and the flowing water is at the top of the DNAPL pool. This contact interface area normalized by the fracture volume gives a specific interfacial area of 0.16 cm^{-1} . As the DNAPL pool dissolves, the contact interface gradually lowers towards the bottom of the fracture due to gravity effects. Unlike in the case of residual DNAPL blobs, the contact interfacial area remains more or less constant as DNAPL saturation S_n decreases. This is because the interfacial area for mass transfer is largely limited to the top of the pool and the constant mean aperture along the vertical direction can render relative invariant average fluid distribution of a horizontal cross section. We define a depth (d) of the contact surface as the distance in the vertical direction between the mean contact surface and the middle line (at the top of the dead-end part of the fracture). This depth increases linearly with decreasing S_n .

Fig. 8a presents the evolution of DNAPL saturation normalized to initial entrapped saturation S_n/S_{ni} with the total volume of water flow through the fracture (represented by the number of fracture volumes). As expected, with a higher flow rate a larger volume of

water is required for the complete removal of the DNAPL mass in the dead-end fracture, which may suggest the inefficiency of pump-and-treat remediation schemes for this entrapment scenario. The normalized flux-averaged outflow concentration C_{out}/C_{eq} as a function of the contact surface depth is presented in Fig. 8b. It is shown that the C_{out}/C_{eq} values are small (<0.1). This is due to the fact that a significant portion of the water flow bypasses the lower half of the fracture. It can be seen in Fig. 8b that generally C_{out}/C_{eq} decreases with increasing depth of the contact surface. This is because it is less efficient for the water flow to ‘pick up’ the dissolved mass when the contact surface is deeper, not because the contact surface area is getting smaller. Fig. 8b also shows that C_{out}/C_{eq} , an indicator of the effective mass transfer rate, is smaller when the water flow rate is higher.

Based on the C_{out}/C_{eq} data for different flow rates, the Sherwood numbers were calculated according to equation (6). By comparison with the previous case of residual blobs we see that the Sh values are at least an order of magnitude smaller for the dead-end pool case for any given Peclet number. The four different flow rates correspond to Peclet numbers from about 2.3 to 233. Fig. 9 shows the relationship between S_n/S_{ni} and Sh/Pe ($= -\ln(1-C_{out}/C_{eq})/a_i L_s$) for different Pe values. A simple power-law equation was used to fit the data. The equation is:

$$Sh = \beta_1 Pe^{\beta_2} \left(\frac{S_n}{S_{ni}} \right)^{\beta_3} \quad (8)$$

with RMSE = 0.0017 and best-fit parameters $\beta_1 = 0.037$, $\beta_2 = 0.70$ and $\beta_3 = 0.46$. The fitted lines using these parameters show that the equation can reasonably well describe the dissolution process for different flow rates (Fig. 9). Equation (8) indicates that intrinsic mass transfer from a DNAPL pool in a dead-end fracture is dependent both on the flow velocity and the amount of remaining mass. In order to examine how well

Equation (8) generalizes the dead-end pool dissolution scenario, we have simulated DNAPL dissolution in dead-end fractures with different system parameters, including mean aperture, flow velocity, and depth of the entrapped pool. We found that Sh calculated from Equation (8) can well match Sh resulted from the corresponding fine-scale simulations, within a factor of 2.

6. Discussions and Conclusions

DNAPL dissolution behavior in single fractures under different entrapment scenarios is important for modeling mass flux generation from contaminated fractured rock sites. In the present study we have investigated DNAPL dissolution in a variable aperture fracture under two entrapment configurations, namely, entrapped residuals from gravity fingering and trapped pools in a dead-end fracture closing. These two scenarios are relevant and important for the retention (entrapment) of DNAPL in a fracture network. We first performed a physical experiment of dissolution of residual DNAPL blobs resulting from gravity fingering in a vertical analog fracture whose aperture field was measured in high resolution by light transmission method. Then, a mechanistic process-based numerical model was developed and shown to excellently reproduce the DNAPL dissolution process as observed in the experiment. We subsequently applied the numerical model to simulate dissolution of the residual blobs under different water flushing velocities. The entrapment and dissolution of DNAPL for the case of dead-end fracture was studied by the validated model only, due to time constraint of the physical experiment.

In the experiment, the residual blobs from DNAPL fingering amounted to a saturation S_{nr} of 0.034 in the fracture. Because of the relative small amount of DNAPL mass trapped as residual form the specific interfacial area ($\sim 0.45 \text{ cm}^{-1}$) is also small in comparison to

the interfacial area measurement in the literature. The DNAPL-water interfacial area gradually reduces when the mass dissolves into water. The experimental results show that the specific DNAPL-water interfacial area (a_i) can be well described by a power law function of S_{nr} ($a_i = 6.37 S_{nr}^{0.8}$). It should be noted that the S_{nr} - a_i relationship may not be directly applicable for other fractures with distinctively different aperture statistical properties. However, it adds to the few saturation-interfacial area datasets available in the literature for comparison.

Representation of the fracture-scale interphase mass transfer by a set of simple constitutive relationships of specific interfacial area, relative permeability and Sherwood number has been shown by Detwiler et al. (2009) to adequately describe the dissolution of DNAPL at a larger (e.g. fracture network) scale where each of the entrapped region and the fracture aperture variation are not resolved but represented by averaged estimates. For the residual entrapment conditions studied in Detwiler et al. (2009), the dimensionless Sherwood number Sh (representing intrinsic mass transfer for a given fracture) was shown to be related to Peclet number Pe (representing flow velocity) as $Sh = 0.7Pe^{0.23}$. For the residual blobs from fingering studied here, to investigate the dependence of Sh on Pe , DNAPL dissolution was simulated under different water flow regimes using the measured aperture field and the initial residual blob distribution. The Sherwood number Sh can be well fitted to Pe as $Sh = 1.43Pe^{0.43}$. The results (Fig. 7) suggest that the Sherwood numbers calculated from this study are significantly larger than those presented by Detwiler et al. (2009). However, it needs to be pointed out that the dissolution conditions/scenarios differ in the following respects: (i) in contrast to the residual blobs resulting from gravity fingering in this study ($S_{nr} < 0.04$), the DNAPL

entrapment in Detwiler et al. (2009) is obtained from imbibition process under gravity neutral or stabilized condition ($S_{nr} > 0.15$); (ii) the mean aperture of the fracture ($\langle b \rangle = 0.47$ mm) is larger than that ($\langle b \rangle = 0.2$ mm) considered in Detwiler et al. (2009). However, it should be noted that the difference in mean aperture is only a factor of about 2 and the difference in Sh is almost an order of magnitude for larger Pe values. The difference in the dependence of Sh on Pe may reflect the importance of entrapment condition on mass transfer characteristics.

Boundary conditions of an individual fracture, representing how the fracture is connected to other fractures in a network, have a large impact on DNAPL entrapment and dissolution. To investigate mass transfer characteristics of dead-end pools and the resulting dissolved mass fluxes, we have carried out mechanistic numerical modeling of entrapment and dissolution of DNAPL in a vertical dead-end fracture. A scenario of dead-end fracture with a closed bottom boundary and half-closed side boundary was considered. In this scenario the dead-end fracture has the ability to trap DNAPL to a saturation $S_n = 0.44$ for the whole fracture. As the entrapped DNAPL pool dissolves the depth of the contact interface between DNAPL pool and open water increases linearly with decreasing S_n . The interfacial area remains more or less constant as DNAPL saturation S_n decreases, unlike in the case of residual DNAPL blobs. The increasing depth of the contact interface causes the flowing water to become less and less efficient in picking up the dissolved chemical, suggesting the dependence of the mass transfer rate on the interface depth, or alternatively the remaining mass percentage (S_n/S_{ni}) in the fracture. Simulation results with different water flow velocities show that the resultant Sherwood number Sh is significantly smaller than in the case with residual blobs for any given

Peclet number, indicating slower mass transfer for the case of dead-end pool. The Sherwood numbers can be well fitted with a power-law relationship as a function of Pe and S_n/S_{ni} (Equation 8). In the present scenario, there is significant water flow above the top contact interface of the DNAPL pool within the fracture plane. This is reflected in the power-law relationship (Equation 8) which has an exponent of 0.7 for Pe , indicating a strong dependence of mass transfer on water flow. It should be pointed out that there are other possible water flow scenarios that will lead to different mass transfer characteristics. One example is the case where water only flows in an intersecting fracture above the dead-end fracture. In this case we expect that the mass transfer is diffusion-controlled and not sensitive to the water flow rate.

It is also interesting to compare the mass flux – source depletion response for the two entrapment scenarios. For the case of residual blobs, the bulk mass transfer rate coefficient (product of intrinsic mass transfer and specific interfacial area) will be related to the amount of remaining mass with an exponent close to 1 as the interfacial area can be approximated by a linear function of saturation. For the case of dead-end pool, the exponent to the term of remaining mass will be much smaller (0.46 as shown in equation 8 for intrinsic mass transfer), since the interfacial area will be largely insensitive to mass depletion.

It should be pointed out that diffusion of dissolved DNAPL from the fracture to the adjacent rock matrix can play an important role for the liquid contaminant disappearance in fractured media with significant matrix porosity, such as clays and porous rocks (Falta, 2005; Lipson et al., 2005; Parker et al., 1997). In this study, we have focused on DNAPL dissolution in fractures of crystalline rock, a widely exposed geological setting in many

parts of the world. Due to the negligible matrix porosity/permeability the matrix-fracture interaction is not considered here. Additionally, we note that gravity destabilized fingering can be a complex behavior with associated phenomena such as snap-off, fragmentation and pulsation (see e.g., Meakin et al., 1992; Glass and Yarrington, 2003; Su et al., 2004, Loggia et al., 2009). In this respect, more experimental and modeling studies are needed to understand the fluid displacement and entrapment behavior of a dense organic liquid.

In field scale problems individual fractures form a complex network where the fractures may have different orientation and dipping angles as well as different connectivity properties. Thus, a number of very different entrapment scenarios and water flow conditions should be expected. Predictive modeling of DNAPL dissolution and contaminant mass flux generation at the field scale is important in practice. Careful upscaling studies, in which the small (fracture) scale understanding from the previous studies and the present study concerning DNAPL migration and mass transfer characteristics for different entrapment conditions is assimilated, are needed to improve prediction accuracy and reduce uncertainty. This motivates future investigation.

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Table 1. Properties of the measured aperture field

Parameter	Value and unit
Dimensions	177×177 mm
Dimensions, pixels	1800×1800
Pixel size	0.0983 mm
Mean aperture	0.475 mm
Standard deviation	0.120 mm
Correlation length, horizontal direction	4.15 mm
Correlation length, vertical direction	Not defined

Table 2. Parameters for dissolution simulation of the experiment

Parameter	Value and unit
Grid dimension	900×900
Grid spacing	0.197 mm
Time step size	1 hour
Molecular diffusion coefficient (D_m) ^a	9.3×10^{-10} m ² /s
TCE density ^b	1.465 g/cm ³
Solubility (C_{eq}) ^a	1.28 g/L
TCE-water interfacial tension ^b	0.0345 N/m
Contact angle ^{c, d}	48 °

References: a, Detwiler et al. (2001); b, Mercer and Cohen (1990); c, Glass et al. (1998); d, Liechti et al. (1997).

Fig. 1. (a) Schematic of the fracture cell (two-dimensional view) used for the dissolution experiment. (b) Measured aperture field; apertures in unit of mm for the gray scale image. (c) Initial DNAPL entrapment configuration (shown in black) in the vertical fracture.

Fig. 2. (a) Measured fracture apertures follow a normal distribution with a mean of 0.475 mm and standard deviation of 0.12 mm. (b) Semivariogram of the measured fracture aperture field.

Fig. 3. (a) Synthetic aperture field in unit of mm for the dead-end fracture. (b) simulated DNAPL Entrapment in the dead-end fracture.

Fig. 4. (a) Change of residual DNAPL saturation (S_{nr}) over the duration of the dissolution experiment. (b) Specific interfacial area as a function of the residual DNAPL saturation.

Fig. 5. Simulated initial concentration field (g/L) for the experimental DNAPL entrapment configuration. Water flow rate: (a) 0.1 mL/min; (b) 1.0 mL/min.

Fig. 6. Change of residual DNAPL saturation (S_{nr}) with time for different water flow rates.

Fig. 7. Simulated relationship between Pe and Sh (circles) and a fitted curve (dashed line) by equation (6) in comparison to the relationship (solid line) obtained by Detwiler et al. (2009).

Fig. 8. (a) Progression of DNAPL mass normalized to the initial value (represented by S_n/S_{ni}) with numbers of fracture volumes of through-flowing water in the fracture. (b) flux-averaged outflow concentration as a function of the depth of the top contact surface of the DNAPL pool.

Fig. 9. Simulated relationship between S_n/S_{ni} and Sh/Pe for the dead-end pool case. The lines are fitted using equation (8).