Dissolution of entrapped DNAPLs in variable aperture fractures: experimental data and empirical model

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Dissolution of Entrapped DNAPLs in Variable Aperture Fractures: Experimental Data and Empirical Model

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An appreciation of the dissolution from entrapped nonaqueous phase liquids (NAPLs) in fractures is essential as we attempt to understand and predict the fate of NAPLs present in fractured rock systems. Eight long-term dissolution experiments using 1,1,1-trichloroethane and trichloroethylene were conducted in two laboratory-scale dolomitic limestone variable aperture fractures under various conditions. Between 560 and 2600 fracture volumes of water were passed through the fractures resulting in the removal of 10–60% of the initial mass trapped. The effluent concentration profiles revealed three distinct and characteristic stages of dissolution: an initial pseudosteady stage, a transient stage, and a tailing stage. On average, 8% of the initial volume of NAPL present was removed during the initial pseudosteady stage. Data from the dissolution experiments were used in conjunction with statistical techniques to develop a continuous empirical model describing the initial pseudosteady and transient stages of dissolution. The model was used to successfully replicate effluent concentration data from two separate and independent dissolution experiments. The experimental results provide an indication of the dissolved and entrapped NAPL behavior at the scale of a single fracture.

Introduction

Dense nonaqueous phase liquid (DNAPL) releases to the subsurface often occur over fractured geologic deposits and can migrate through fracture networks under the influence of gravitational, viscous, and capillary forces. Capillary forces act to resist the forward movement of flowing DNAPL and are responsible for separating and immobilizing DNAPL masses from the continuous DNAPL phase. Once released into the subsurface, the DNAPL will continue to migrate until the entire volume is trapped as residual ganglia or until it reaches a capillary barrier that it cannot penetrate. The trapped DNAPL dissolves into the surrounding aqueous phase and eventually forms a plume within the fracture network and the porous matrix and represents a potential long-term source of contamination.

The remediation of fractured rock masses is exceptionally difficult to achieve because the complex fracture network makes it nearly impossible to predict or accurately characterize the spatial location and distribution (residual vs continuous) of the DNAPL. Additionally, there has been no general agreement among researchers regarding mass transfer and contaminant transport model formulations that correctly account for all dominant processes occurring in fractured porous media systems (1). Remediation strategies currently used in fractured rock are similar to those used in porous media (2) and of these technologies are fundamentally based on the mass transfer process (e.g., pump and treat, soil vapor extraction, in-situ air sparging), which presently is poorly understood in fractured rock systems.

In the absence of remedial actions, the mass transfer process influences the length of time that a DNAPL entrapped in fracture planes will persist and the magnitude of the dissolved phase plume. It has been shown that DNAPL disappearance from a fracture is only significantly affected by matrix diffusion in relatively porous environments (3, 4). Esposito and Thomson (5) developed a numerical model to simulate nonequilibrium dissolution and aqueous phase transport in a variable aperture fracture and coupled it with an existing two-phase flow model (6). They showed that the model can be used to predict both the dissolution and dissolution processes that occur within a fracture plane. Glass and Nicholl (7) simulated fracture plane using etched glass to study the dissolution of an entrapped air phase and were not able to explain their results using any existing conceptual dissolution models. Based on both experimental and simulation results, Detwiler et al. (8) used a simple exponential relationship with a constant bulk mass transfer coefficient to model the temporal change in DNAPL saturation in a variable aperture fracture.

Although the various investigations discussed above were motivated by the ultimate need to understand DNAPL behavior in fractures at the field scale (i.e., fracture networks), this cannot be accomplished without first understanding the behavior and developing tools to characterize dissolution at the scale of a single fracture. With this goal in mind, the investigation presented in this paper had two primary objectives: (1) to conduct a series of long-term single variable aperture fracture physical model experiments to yield representative dissolution profiles subject to a range of fluid flow and entrapment conditions and (2) to use these experimental data to develop a continuous empirical model describing the bulk mass transfer rate from entrapped DNAPLs in single variable-aperture fracture planes.

Materials and Methods

Experimental Apparatus. The fracture planes employed in these experiments originated from a dolomitic limestone outcrop located near Kingston, Ontario. This formation was selected due to the presence of prominent stylolites and bedding planes, which provide convenient planes of weakness for inducing fractures. Rock samples were removed from the outcrop using a Quick Cut saw (TS 350, Stihl) equipped with a diamond-tipped blade and returned to the laboratory where tension fractures were induced using the method described by Reitsma and Kueper (9). This method of inducing tension fractures in rock samples is similar to the manner in which natural extension fractures are formed by weathering or stress relief. Two fractures were used in this

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The experimental apparatus, illustrated in Figure 1, consisted of glass end caps fixed to the upstream and downstream ends of a horizontally oriented fracture. Each end cap was equipped with two glass spigots located at the highest and lowest points on the end cap to allow for the separation and drainage of multiple fluid phases. Plastic steel (10210, Devcon) was used to seal the remaining two edges of the fracture plane creating no-flow boundaries. A peristaltic pump (E650MG, Cole Parmer) was employed to inject fluid into the fracture plane, while fluid exited the system through the effluent end cap allowing any DNAPL exiting the fracture plane to flow through this tube and collect at the bottom of the flask. The second stainless steel tube allowed water displaced by the DNAPL to exit the flask and flow through the system toward the constant hydraulic head.

A Marriott bottle DNAPL release system consisting of stainless steel tubing was used to release DNAPL into the fracture under a constant hydraulic head. The stainless steel tube transferred atmospheric pressure to the fluid at the bottom of the separatory funnel, enabling the entire contents of the funnel to be released under a constant hydraulic head independent of the fluid level in the funnel. The separatory funnel was also equipped with a stopcock to control flow from the system. To retain any free phase exiting the downstream end of the fracture a DNAPL collection system consisting of an Erlenmeyer flask equipped with a rubber stopper and two stainless steel tubes was used. One stainless steel tube connected the Erlenmeyer flask to the lower spigot of the effluent end cap allowing any DNAPL exiting the fracture plane to flow through this tube and collect at the bottom of the flask. The second stainless steel tube allowed water displaced by the DNAPL to exit the flask and flow through the system toward the constant hydraulic head flow apparatus.

Materials. To avoid dissolution of the fracture planes, all water injected into the fracture planes was Milli-Q water buffered to a pH of 7.5–8.0 using sodium carbonate (BDH assured Na2CO3, VWR Canlab). This water was then autoclaved to inactivate any microbial contaminants, equilibrated to room temperature, and degassed to prevent gas formation within the fracture plane. Bromide (Br−, BDH assured NaBr, VWR Canlab) served as the conservative tracer, and 1,1,1-trichloroethane (1,1,1-TCA, 99.5% pure Omnisolv grade, VWR Canlab) and trichloroethylene (TCE, 99.5% pure Omnisolv grade, VWR Canlab) were used as the model immiscible liquids. The 1,1,1-TCA and TCE were dyed with Sudan IV (11) for visual observation purposes. The relevant physical properties of both 1,1,1-TCA and TCE are listed in Table 2. The sessile drop method (11) was used to measure the wetting angles with respect to buffered water on a smooth slab of dolomitic limestone. The interfacial tensions were measured with respect to buffered water using axisymmetric drop shape analysis (11). A comparison of these measurements with values reported in the literature revealed that the Sudan IV dye had a negligible effect on the physical properties of these compounds.

Experimental Methods – Fracture Plane Characterization Experiments. Porosity and fraction of organic carbon (foc) measurements were used to characterize the rock matrix. The porosity was measured using the International Society for Rock Mechanics suggested method for determining

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**TABLE 1. Fracture Plane Characteristics**

<table>
<thead>
<tr>
<th>property</th>
<th>fracture 1</th>
<th>fracture 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>length in direction of flow (cm)</td>
<td>30.0</td>
<td>54.6</td>
</tr>
<tr>
<td>width perpendicular to flow (cm)</td>
<td>22.5</td>
<td>28.58</td>
</tr>
<tr>
<td>matrix porosity (%)</td>
<td>0.059</td>
<td>0.031</td>
</tr>
<tr>
<td>hydraulic aperture, e_h (μm)</td>
<td>350 ± 22a</td>
<td>192 ± 8a</td>
</tr>
<tr>
<td>mass balance aperture, e_m (μm)</td>
<td>1274 ± 22b</td>
<td>954 ± 23b</td>
</tr>
<tr>
<td>frictional loss aperture, e_f (μm)</td>
<td>180 ± 2b</td>
<td>93 ± 2b</td>
</tr>
</tbody>
</table>

* Error based on the 95% confidence interval. a Error based on one standard deviation, calculated using the equation for propagation of error given by Blom (27).
porosity (12), while the $f_{oc}$ was determined by a method developed according to Churcher and Dickhout (13). In general, the matrix porosity was determined to be <1% and the $f_{oc} < 0.06\%$ (Table 1).

The aperture fields were characterized by three different equivalent apertures derived from hydraulic and tracer studies. Each hydraulic test was conducted under saturated conditions and involved injecting water through the fracture at a constant specific discharge and measuring the hydraulic head loss across the fracture plane. Hydraulic tests were repeated at various specific discharges for each fracture plane.

Each tracer test was run under saturated conditions with a uniform flow rate and a constant influent concentration of Br$. Samples were withdrawn from the effluent sampling cell every two to three minutes for the duration of the experiment. Each tracer study was continued until complete breakthrough was achieved as determined by the effluent concentration equaling the influent concentration. The effluent concentration profiles were used to determine the equivalent tracer apertures of each experimental fracture plane.

The effluent samples were analyzed for Br$ concentration using an ion chromatograph (AI-450, Dionex) equipped with a conductivity detector. An ion exchange column (AS4A-SC, Supelco) was inserted through the septa of the GC vials to allow the sample to equilibrate with the headspace at room temperature for a minimum of 2 h. A SPME fiber (100 μm polydimethylsiloxane, Supelco) was inserted through the septa and exposed to the headspace for five minutes, allowing the organic phase to partition onto the fiber. The fiber was then inserted into a GC (6890, Hewlett-Packard) equipped with a split/splitless injector used in splitless mode (200 °C), a flame ionization detector (FID), and an electron capture detector (ECD). The column (HP-5, Hewlett-Packard) was 30 m in length with a diameter of 0.25 mm and a phase thickness of 0.32 μm. Helium (He) was used as the carrier gas. The MDL for 1,1,1-TCA was 1.32 mg/L on the FID and 1.18 mg/L on the ECD, while the MDL for TCE was 1.30 mg/L on the FID and 1.2 μg/L on the ECD.

Experimental Methods – Dissolution Experiments. A series of physical model dissolution experiments was conducted under a range of experimental conditions to determine the effects of aqueous specific discharge, entrapped DNAPL saturation, and aperture field characteristics on the mass transfer process.

The dissolution experiments were conducted by first releasing 200 mL of DNAPL at a constant capillary pressure into the saturated fracture plane. Water was then flushed through the fracture plane at high Capillary numbers to mobilize as much of the DNAPL as possible. The resulting mass of entrapped DNAPL was estimated from mass balance calculations. Finally, water was flushed through the fracture plane under a range of specific discharges. Samples were withdrawn from the upstream and downstream sampling cells at regular intervals (every 2–6 h over the first week and then every 24–48 h for the remainder of the experiment). Between experiments, the remaining DNAPL was removed from each fracture plane by first desaturating the system and then sparging it with air. Following resaturation of each fracture, hydraulic tests confirmed that the hydraulic aperture remained unchanged, and aqueous samples were used to ensure that background DNAPL concentrations resulting from the previous experiment were insignificant.

Solid-phase microextraction (SPME) in combination with gas chromatography (GC) was used to determine the concentration of 1,1,1-TCA and TCE. The samples were transferred into 1.2 mL glass screw capped GC vials and then sparging it with air. Following resaturation of each fracture, hydraulic tests confirmed that the hydraulic aperture remained unchanged, and aqueous samples were used to ensure that background DNAPL concentrations resulting from the previous experiment were insignificant.

Fracture Plane Characterization Experiments. The hydraulic test data were used to estimate the hydraulic aperture, $e_h (L)$, which is defined as the equivalent parallel plate aperture required to satisfy the bulk cubic law as given by (14)

$$ e_h = \frac{12Q}{\rho g W \Delta H} $$

where $\mu (M\cdot L^{-1}\cdot T^{-1})$ is the dynamic viscosity, $L (L)$ is the fracture length in the direction of flow, $W (L)$ is the fracture width perpendicular to the direction of flow, $\rho (M\cdot L^{-3})$ is the fluid density, $g (L\cdot T^{-2})$ is the acceleration due to gravity, and $\Delta H (L)$ is the hydraulic head loss across the fracture plane.

The results of the tracer tests were interpreted using both the mass balance method and the fractional loss method. The mass balance aperture, $e_{mb} (L)$, is a measure of the equivalent aperture required to balance a known volume of fluid over the aerial extent of the tracer transport and is based on the mean residence time (15) given by

$$ e_{mb} = \frac{Q t_m}{\rho g W} $$

where $t_m (T)$ is the mean residence time calculated through moment analysis on the tracer breakthrough curve. The fractional loss aperture, $e (L)$, is based on the expression of

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**TABLE 2. Physical and Chemical Properties of Organic Compounds**

<table>
<thead>
<tr>
<th>property</th>
<th>symbol</th>
<th>units</th>
<th>1,1,1 TCA</th>
<th>TCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>density</td>
<td>$\rho$</td>
<td>g·mL$^{-1}$</td>
<td>1.33$^d$</td>
<td>1.46$^d$</td>
</tr>
<tr>
<td>solubility</td>
<td>$C_s$</td>
<td>mg·L$^{-1}$</td>
<td>1300$^f$</td>
<td>1100$^f$</td>
</tr>
<tr>
<td>interfacial tension</td>
<td>$\gamma_{ln-w}$</td>
<td>dynes·cm$^{-1}$</td>
<td>36.7$^c$</td>
<td>29$^c$</td>
</tr>
<tr>
<td>viscosity</td>
<td>$\mu$</td>
<td>g·cm$^{-1}$·s$^{-1}$</td>
<td>0.62$^d$</td>
<td>0.39$^d$</td>
</tr>
<tr>
<td>wetting angle</td>
<td>$\theta$</td>
<td>degrees</td>
<td>21$^c$</td>
<td>20$^c$</td>
</tr>
<tr>
<td>diffusion coefficient</td>
<td>$D_0$</td>
<td>cm$^2$·s$^{-1}$</td>
<td>8 × 10$^{-6}$</td>
<td>8.5 × 10$^{-6}$</td>
</tr>
</tbody>
</table>

$^a$ Measured property with Sudan IV ($T = 20–25 ^\circ C$). $^b$ Measured property (with Sudan IV) with respect to Milli-Q water ($T = 20–25 ^\circ C$). $^c$ Measured property (with Sudan IV) with respect to Milli-Q water and dolomitic limestone ($T = 20–25 ^\circ C$). $^d$ Reference 28.
used in this study are comparatively large. Although the range of extreme apertures within the fracture planes represents the lower end of this spectrum. This indicates that the tracer aperture ratios indicate a smaller range of extreme aperture regions. A parallel plate fracture, which has no pathways and solute transport. Smaller tracer aperture ratios indicate a larger range of extreme aperture regions, and larger tracer aperture ratios indicate a smaller range of extreme aperture regions. A parallel plate fracture, which has no dependence on the hydraulic head difference across the fracture plane, and thus are weighted towards the smaller apertures encountered along the flow path. Conversely, the mass balance aperture is not sensitive to the hydraulic head loss across the fracture plane but to the storage of tracer mass in the void space, which occurs in the larger aperture regions. The mass balance aperture therefore represents an average aperture along the tracer transport flow path and provides the best estimate of the arithmetic mean aperture (15).

If the frictional loss aperture is sensitive to the smaller aperture regions, and the mass balance aperture is sensitive to the larger aperture regions, it follows that the tracer aperture ratio, \( \delta \), defined here as

\[
\delta = \frac{e_1}{e_{\text{mb}}}
\]

provides a measure of the range of extreme aperture regions encountered along the flow pathway(s). It is these extreme aperture regions that are responsible for controlling flow pathways and solute transport. Smaller tracer aperture ratios indicate a larger range of extreme aperture regions, and larger tracer aperture ratios indicate a smaller range of extreme aperture regions. A parallel plate fracture, which has no extreme aperture regions, would have a tracer aperture ratio of one. Table 3 presents the tracer aperture ratios for the fracture planes used in this study and ratios calculated from literature data. In general, the calculated tracer aperture ratios varied between 0.1 and 0.7 with the values from this study representing the lower end of this spectrum. This indicates that the range of extreme apertures within the fracture planes used in this study are comparatively large. Although the reason for this is unknown, it may be related to variations in rock type and fracture formation giving rise to different aperture field characteristics or the specific discharge used during tracer studies.

### Dissolution Experiments

Table 4 presents a summary of the experimental conditions and overall mass removal results for each dissolution trial. The first column in Table 4 is the experiment identification number with the first number representing the fracture in which the experiment was conducted and the second number representing the dissolution trial number for that fracture. A conscious effort was undertaken to maintain a consistent mass of trapped DNAPL for each experiment by releasing the DNAPL at the same capillary pressure and flushing at the same Capillary number during the entrapment phase. Despite this effort, some variation in capillary pressures and Capillary numbers did occur between experiments, resulting in a slightly different initial mass of trapped DNAPL in each experiment.

Figure 2(a) presents the normalized concentration profile from exp 2–3 as determined by

\[
C(t) = \frac{C_{\text{eff-trac}}(t) - C_{\text{inf}}(t)}{C_s}
\]

where \( C(t) \) (M·L\(^{-3}\)) is the normalized concentration exiting the fracture plane in excess of the background (or influent) concentration; \( C_s \) (M·L\(^{-3}\)) is the aqueous phase DNAPL saturation concentration (Table 2); and \( C_{\text{inf}}(t) \) (M·L\(^{-3}\)) is the low but nonzero influent DNAPL concentration.

The nonzero influent concentration is an artifact of the DNAPL entrapment methodology, as the DNAPL was released into the fracture plane through the influent end cap. All free phase DNAPL was drained from the influent end cap prior to the commencement of each dissolution experiment; however, the aqueous phase DNAPL could not be removed.

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### Table 3. Summary of Studies Measuring Bulk Aperture Values of Single Fractures

<table>
<thead>
<tr>
<th>Description</th>
<th>Dimensions</th>
<th>( e_{\text{mb}} ) (µm)</th>
<th>( e_1 ) (µm)</th>
<th>( \delta ) [-]</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fracture 1</td>
<td>( W = 22.5 ) cm ( L = 30.0 ) cm</td>
<td>1274</td>
<td>180</td>
<td>0.141</td>
<td>This study</td>
</tr>
<tr>
<td>Fracture 2</td>
<td>( W = 28.6 ) cm ( L = 54.6 ) cm</td>
<td>954</td>
<td>93</td>
<td>0.097</td>
<td>This study</td>
</tr>
<tr>
<td>Natural fracture in shale with dolomite</td>
<td>radius = 15 m</td>
<td>254</td>
<td>140</td>
<td>0.551</td>
<td>16</td>
</tr>
<tr>
<td>Natural fracture in dolomite, borehole test</td>
<td>radius = 20–22 m</td>
<td>1540</td>
<td>360–1030</td>
<td>0.233–0.669</td>
<td>29</td>
</tr>
<tr>
<td>Natural fracture in core sample of Apache Leap Tuff, laboratory test</td>
<td>( W = 20 ) cm ( L = 92.5 ) cm</td>
<td>765</td>
<td>181</td>
<td>0.237</td>
<td>18</td>
</tr>
<tr>
<td>Induced fracture in limestone outcrop sample, laboratory test</td>
<td>( W = 15 ) cm ( L = 25 ) cm</td>
<td>113</td>
<td>41</td>
<td>0.363</td>
<td>25</td>
</tr>
</tbody>
</table>

*Calculated from data provided.

---

### Table 4. Experimental Conditions and Mass Removal Results for the Dissolution Experiments

<table>
<thead>
<tr>
<th>Exp</th>
<th>DNAPL</th>
<th>( \nu ) (m/day)</th>
<th>Initial mass trapped (g)</th>
<th>( FV^a ) filled with DNAPL (%)</th>
<th>( FVs^b ) flushed (–)</th>
<th>Mass removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1–1</td>
<td>TCA</td>
<td>15.47</td>
<td>19.52 ± 0.5²</td>
<td>17.1</td>
<td>870</td>
<td>43.40</td>
</tr>
<tr>
<td>1–2</td>
<td>TCA</td>
<td>22.76</td>
<td>13.09 ± 0.5²</td>
<td>11.4</td>
<td>1265</td>
<td>20.42</td>
</tr>
<tr>
<td>1–3</td>
<td>TCE</td>
<td>97.43</td>
<td>11.49 ± 0.5²</td>
<td>10.0</td>
<td>1575</td>
<td>32.54</td>
</tr>
<tr>
<td>1–4</td>
<td>TCA</td>
<td>58.90</td>
<td>24.09 ± 0.5²</td>
<td>21.1</td>
<td>1805</td>
<td>13.33</td>
</tr>
<tr>
<td>1–5</td>
<td>TCA</td>
<td>17.47</td>
<td>11.66 ± 0.5²</td>
<td>10.2</td>
<td>800</td>
<td>20.21</td>
</tr>
<tr>
<td>2–1</td>
<td>TCA</td>
<td>31.65</td>
<td>32.10 ± 0.5²</td>
<td>16.2</td>
<td>560</td>
<td>39.85</td>
</tr>
<tr>
<td>2–2</td>
<td>TCA</td>
<td>133.91</td>
<td>29.15 ± 0.5²</td>
<td>14.7</td>
<td>1475</td>
<td>62.03</td>
</tr>
<tr>
<td>2–3</td>
<td>TCA</td>
<td>70.40</td>
<td>27.46 ± 0.5²</td>
<td>13.9</td>
<td>2620</td>
<td>48.86</td>
</tr>
</tbody>
</table>

\(^a\)Error calculations based on estimated losses. \(^b\)Calculated based on the fracture length, width, and mass balance aperture.

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Three distinct stages of dissolution emerge upon the examination of the effluent concentration profiles: an initial pseudosteady stage, a transient stage, and a tailing stage. The initial pseudosteady stage is characterized by initially high effluent concentrations (10–50% of saturation), which remain relatively constant for several fracture volumes (FVs). The effluent concentrations then gradually decrease as greater volumes of water are passed through the system, indicative of the transient stage of the profile. Eventually the effluent concentrations establish another relatively constant concentration plateau, this time at a much lower concentration, representative of the tailing stage.

The majority of the mass removal occurred during the initial pseudosteady and early transient stages of dissolution. The initial pseudosteady stage typically lasted until an average of 8% of the initial mass trapped was removed, or until the initial volumetric DNAPL saturation Sn(t=0) was reduced by 8% as denoted by Sn8%. This observation is surprisingly consistent with Miller et al. (19) who noted that in unconsolidated porous medium systems the initial pseudosteady stage persists as long as no more than 10% of the initial mass trapped is dissolved. The mass removal rate began to decrease at the onset of the transient stage and had decreased significantly in all experiments after 400–500 FVs of water were flushed through the system. During the transient stage the concentration continued to decrease by 3–6 orders of magnitude until the start of the tailing stage when the effluent concentration remained relatively constant until each experiment was terminated.

Theoretical predictions of the effluent concentration based on the local equilibrium assumption (LEA) are also shown in Figure 2(a). These predictions assume that the effluent concentration remains at the maximum concentration attained in that experiment until all of the trapped mass is removed thereby accounting for flow bypassing and dilution within the system. It is apparent that the local equilibrium assumption is only representative of the initial pseudosteady stage of the dissolution. Clearly, the LEA significantly underpredicts the number of FVs required to remove the mass in each experiment and thus is a poor tool for predicting dissolution in variable aperture fractures.

The lumped mass transfer rate reflects the bulk rate that mass is transferred from the trapped DNAPL within the fracture to the aqueous phase and, in general, can be described by a simple linear mass transfer model written in integrated form as

$$\frac{\Delta M}{\Delta t} = -\lambda(C_{\text{eff}} - C)V_f$$

where $M$ [M] is the mass of DNAPL, $\lambda$ [T$^{-1}$] is the lumped mass transfer coefficient, $C$ [M·L$^{-3}$] is a representative aqueous phase concentration within the fracture plane, and $V_f$ [L$^3$] is the volume of the fracture. The temporal profile of the lumped mass transfer coefficient can be determined from the experimental data by

$$\lambda^{t \rightarrow t+\Delta t} = \frac{Q(C_{\text{eff-frac}} - \overline{C}_{\text{eff}})}{V_f(C_s - C)}$$

with

$$\overline{C} = (C_{\text{inf}} + \overline{C}_{\text{eff-frac}})/2$$

where $C$ [M·L$^{-3}$] represents the mean concentration in the fracture, and the overbar indicates the average value between sampling time level $t$ and $t + \Delta t$. A one-dimensional mass transport analysis indicated that for the Peclet numbers appropriate for these experiments, the most representative aqueous phase concentration within the fracture plane is the mean between the influent and effluent concentration. Figure 2(b) presents the temporal profile of the lumped mass transfer coefficient for exp 2–3. This profile mimics the concentration profile in Figure 2(a), indicating that the bulk mass transfer rate is decreasing as dissolution progresses. At first glance, this observation seems to contradict the work of Detwiler et al. (8), who used an exponential relationship with a constant bulk mass transfer coefficient to describe dissolution in analogue fracture planes. However, Detwiler
TABLE 5. Dimensionless Parameters Employed To Characterize the Mass Transfer Process

<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>formula</th>
<th>physical representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sherwood number (model 1)</td>
<td>$Sh_1$</td>
<td>$\frac{j(r/2)^2}{D_b}$</td>
<td>lumped mass transfer coefficient</td>
</tr>
<tr>
<td>Sherwood number (model 2)</td>
<td>$Sh_2$</td>
<td>$\frac{\lambda\theta_r^2}{D_b}$</td>
<td>lumped mass transfer coefficient</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>$Re$</td>
<td>$\frac{2\nu e_r \rho}{\mu}$</td>
<td>aqueous phase flow rate</td>
</tr>
<tr>
<td>tracer aperture ratio</td>
<td>$\delta$</td>
<td>$\frac{e_i}{e_{tot}}$</td>
<td>initial interfacial area</td>
</tr>
<tr>
<td>normalized aperture saturation</td>
<td>$Sn^+(t)$</td>
<td>$\frac{Sn(t)}{Sn_{8%}}$</td>
<td>dynamic interfacial area</td>
</tr>
</tbody>
</table>

FIGURE 3. Maximum lumped mass transfer coefficient as a function of specific discharge for fracture 1 and fracture 2.

et al. (8) flushed between 290 and 670 FVs of water through their experimental fracture plane, whereas 590–2600 FVs were flushed through the fracture planes in experiments reported here. The first several hundred fracture volumes of each experiment in this study corresponded to the initial pseudosteady and very early transient stages of dissolution, when the bulk mass transfer coefficient is in fact relatively constant. Detwiler et al. (8) noted that the results of some of their numerical simulations suggest that as dissolution pathways become hydraulically connected to the effluent end of the fracture, flow bypassing may cause the bulk mass transfer rate to decrease and their exponential relationship to break down. This statement is consistent with our experimental observations.

Figure 3 presents the maximum lumped mass transfer coefficient estimated in each experimental trial as a function of the specific discharge and reveals two significant phenomena: (1) the maximum lumped mass transfer coefficient increases with increasing specific discharge and appears to be linear over the observed range of data and (2) the maximum lumped mass transfer coefficient varies between fracture planes. The relationship between the mass transfer coefficient and specific discharge indicates that as the specific discharge increases the local concentration gradients within the fracture plane increase causing the maximum lumped mass transfer rate to increase. Since the individual characteristics of the aperture fields control the configuration of the trapped DNAPL and the proximity of the trapped DNAPL to the advective transport pathway(s), it is not surprising to observe that the maximum lumped mass transfer coefficient is fracture dependent.

Model Development. The objective of the empirical modeling component of this investigation was to develop a model capable of describing the lumped mass transfer coefficient over both the initial pseudosteady and transient stages of dissolution under varying conditions.

The model developed, referred to as the Single Fracture Stage Dissolution (SFSD) model, was conceptually based on observations from the dissolution experiments reported here, and the results of various dissolution investigations conducted in unconsolidated porous media (e.g., refs 19 and 20). The SFSD model relates the Sherwood number, Sh (a dimensionless form of the lumped mass transfer coefficient), to various dimensionless numbers (i.e., the Reynolds number, the tracer aperture number, and the normalized aperture saturation) reflective of the various dissolution experiments performed (see Table 5).

The Sherwood number is a ratio that represents the mass transfer rate to the diffusion rate and is the product of the lumped mass transfer coefficient and a characteristic length squared divided by the free water diffusion coefficient. The characteristic length captures the distance across which the mass transport flux must take place (21). Two formulations for the Sherwood number were investigated in this work. The first formulation used one-half the radius of the aerial extent of the fracture plane ($Sh_1$), and the second formulation used the hydraulic aperture as the characteristic length ($Sh_2$). In this study the radius of the aerial extent of the fracture plane is on the order of tens of centimeters, while the hydraulic aperture is on the order of hundreds of micrometers, and thus there is a four-order of magnitude difference between these two lengths. It is postulated that the hydraulic aperture is a more suitable characteristic length for the early stages of dissolution when some of the trapped DNAPL mass is in close proximity to aqueous phase flow pathways and that the radius of the aerial extent of the fracture plane is a more suitable characteristic length for the later stages of dissolution when some DNAPL blobs are completely removed and the remaining DNAPL mass is further away from the aqueous phase flow pathways. For DNAPL blobs in direct contact with flow pathways, the diffusion must take place over the fluid–fluid boundary layer to be removed by the flowing aqueous phase. For DNAPL blobs not in direct contact with an aqueous phase flow pathway, the dissolved phase must diffuse over the distance between the blob and the nearest flow pathway to be removed. Thus, as the distance between a blob and flow pathway increases, the distance over which the mass flux must take place also increases, thereby increasing the length of time that mass will persist.

The mass transfer process is sensitive to the morphology index, which represents the ratio of interfacial area to volume of trapped DNAPL and controls the interfacial area available for dissolution. Since the morphology index is not easily
estimated in most realistic situations and there have been no surrogate measures reported in the literature, a need to develop a suitable surrogate morphology index measure for variable aperture fractures exists. The morphology index is controlled by the trapped DNAPL configuration, which is in turn controlled by regions of extreme aperture variation, thus the tracer aperture ratio (δ) as defined by eq 6 was chosen as a suitable surrogate measure in this work. Although the extreme aperture regions control the initial entrainment geometry, they do not capture the change in the morphology index as dissolution progresses. Therefore, a dynamic parameter, the normalized volumetric aperture saturation (Sn*), was required to fully characterize the interfacial area-to-volume ratio. This parameter represents the volumetric fraction of the aperture field filled with DNAPL normalized to the DNAPL saturation at the transition from the initial pseudosteady stage to the transient stage of the dissolution process. As dissolution progresses, the volume fraction of DNAPL in the fracture will decrease, resulting in a decreased interfacial area-to-volume ratio. Similar formulations have been used in interface studies in unconsolidated porous medium systems (e.g., refs 20 and 22).

A piecewise linear regression analysis (23) was performed using the MINITAB statistical software package (release 13.3, MINITAB Inc.) and pertinent dimensionless data from all experiments (except data from exp 1–5 which was retained for model verification), to obtain estimates of the coefficients for the linearized form of a power law relationship given by

\[
Sh = \begin{cases} 
\alpha Re^{\beta_1} \delta^{\beta_2} Sn^*(t)^{\beta_3} & \text{for } Sn^*(t) \geq 1 \\
\alpha Re^{\beta_1} \delta^{\beta_2} Sn^*(t)^{\beta_3} & \text{for } Sn^*(t) \leq 1 
\end{cases}
\]  

where α, β_1, β_2, β_3, and β_4 are the regression coefficients.

This piecewise technique ensured that the SFSD model would adequately represent both the initial pseudosteady (Sn*(t) ≥ 1) and transient (Sn*(t) ≤ 1) stages of dissolution. Additionally, because the relationships presented in eq 12 are equal when Sn*(t) = 1, the model remains continuous over the transition between the initial pseudosteady and transient stages of dissolution. This continuous feature of the developed model is significant in terms of potential future applications, for example its incorporation into a numerical model simulating two-phase flow and contaminant transport in variable aperture fractures. A stepwise regression procedure was performed twice, once for each formulation of the Sherwood number (Table 5), and a significance level of 10% was used to determine the significance of each variable. Table 6(a) presents the optimal models developed by the stepwise regression scheme for each set of coefficients. The quality of fit between the predicted and observed Sherwood numbers is shown in Figure 4 with error bars representing the 90% confidence interval for the model prediction. A residual analysis verified that the errors are normally distributed with constant variance. Plots of the standardized residuals versus the natural logarithm of the predicted Sherwood number, Reynolds number, tracer aperture ratio, and normalized aperture saturation did not reveal any trends thus confirming the assumption of constant variance and indicating that both models are adequate (24). Table 6(b) lists the 90% confidence intervals for the regression parameter estimates for models 1 and 2. All of the parameters are significant at the 90% confidence level, and with the exception of β_3, the confidence intervals are relatively narrow. The confidence interval for β_3 is relatively wide for both models because it was estimated using only 22 initial pseudosteady data points, compared to 79 transient stage data points. Additionally, there was more scatter associated with the initial pseudosteady data than there was with the transient data. The additional scatter in the initial pseudosteady data is caused by a smaller time interval between these data, which magnifies the error associated with the estimation of the temporal derivative in eq 1. Table 6(b) also includes the variance inflation factor (VIF) for each regression parameter in models 1 and 2 and indicates that there is no problem with multicollinearity (24) since the values lie between 1 and 2.

The coefficient of multiple determination is 7% higher for model 2 than for model 1 and indicates that a greater reduction in the variability of the predicted Sherwood number is obtained when the hydraulic aperture is used as the
characteristic length in the calculation of the Sherwood number as opposed to the radius of the aerial extent. This result supports the earlier postulation that the hydraulic aperture is a more suitable characteristic length for the early stages of dissolution when the mass transfer rate is still relatively high due to the proximity of the trapped blobs to the flow pathway(s). There is insufficient tailing data available to confirm if the radius of the aerial extent of the fracture plane is a more suitable characteristic length for the later stages of dissolution when the mass transfer rate decreases due to the distance over which the mass flux must occur. An analysis of the regression parameters and the residuals did not reveal any significant deficiencies in either model, and thus both models are deemed adequate; however, model 2 was chosen as the optimal model based solely on the fact that it has a higher coefficient of multiple determination than model 1.

The developed SFSD model was partially verified by using it to predict effluent concentrations for exp 1–5 (data not used during model development) and for a TCE dissolution fracture experiment performed by Tunnicliffe and Thomson (25). The experimental conditions used by Tunnicliffe and Thomson (25) differed significantly from those used to create the data employed in the development of the SFSD model. Specifically, Tunnicliffe and Thomson (25) used a vertical fracture plane as opposed to a horizontal fracture plane, they released the DNAPL as a point source at the top of the fracture and subsequently conducted a water flush horizontally across the fracture plane, and both the tracer aperture ratio and the Reynolds number used were outside the range of those used in the development of the SFSD model. Additionally, the saturation at the transition from the initial pseudosteady stage to the transient stage of the dissolution profile, for both exp 1–5 and the experiment performed by Tunnicliffe and Thomson (25), was calculated based on 8% of the initial volume of NAPL present, not the actual transition point from the experimental data. Figure 5 illustrates the predicted and observed effluent concentrations for exp 1–5 and the Tunnicliffe and Thomson (25) data. The relative error between the measured and predicted effluent concentration profiles was quantified with the sum of the squared residuals given by

$$\epsilon = \frac{1}{n} \sum_{i=1}^{n} \left( \ln \left( \frac{C_{\text{sat}}}{C_{\text{obs}}} \right)_{\text{obs}} - \ln \left( \frac{C_{\text{sat}}}{C_{\text{pred}}} \right)_{\text{pred}} \right)^2$$

where $[\cdot]$ is the relative error, and $n$ is the number of data points. The relative error for exp 1–5 and for the Tunnicliffe and Thomson (25) data was 0.057 and 0.356, respectively. These relative errors are within the range of those reported for dissolution models in unconsolidated porous media (20, 26). In general, the SFSD model replicated the trends in the observed effluent concentration data and was considered to be a good predictor of the effluent DNAPL concentration profiles. It was encouraging that the SFSD model provided a reasonable prediction of the effluent concentration profile for the Tunnicliffe and Thomson (25) data given that the experimental conditions were considerably different from those under which the SFSD model was developed.

The developed SFSD model is subject to several limitations including the scale of application, experimental conditions, and fluid properties. The size of the fracture planes used in the development of the SFSD model was on the order of centimeters, whereas a field-scale fracture would likely be on the order of meters to tens of meters in size. This difference in scale has implications on the inherent processes captured in the SFSD model, specifically the aqueous phase flow pathways. In the laboratory experiments, the aqueous phase flow was forced to pass through the fracture planes within centimeters of the trapped DNAPL. At a larger scale, however, it may be possible for the aqueous phase to bypass the area.
containing trapped DNAPL in favor of a hydraulically less resistant route. This flow bypassing would greatly increase the scale over which the diffusive mass flux must occur, seriously altering the dissolution process. The SFSD model was developed at the laboratory scale under a limited range of diffusive flux distances and therefore should only be considered valid at this scale. Although model 2 was more representative of the data collected in these experiments than model 1, it is postulated that model 1 may be more flexible in larger-scale applications. Considering that larger-scale systems may be subject to considerable flow bypassing, it is postulated that the \( r^2 \) term in model 1 (Table 5) may act as a suitable scaling factor for this version of the SFSD model. As the scale of the system increases, the degree of flow bypassing may increase, thereby increasing the distance over which the mass flux must take place. This postulation, however, must be verified using dissolution data collected from various fractures of different scales before it can be applied with any confidence.

The SFSD model was developed using experimental data collected under limited conditions and should only be considered valid under these rather restrictive conditions (0.125 \( \leq \text{Re} \leq 0.874; \delta \sim 0.1; 0.402 \leq \text{Sn}^\ast \leq 1.061)\). The danger of applying the SFSD model outside these ranges without first verifying its applicability is clearly illustrated by considering its dependence on Reynolds number. For a zero Reynolds number (no flow conditions) the SFSD model predicts that no dissolution will occur; however, some dissolution will occur due to diffusive mass transport. Additionally, the SFSD model predicts that the mass transfer rate will increase indefinitely as the Reynolds number increases which is clearly questionable given that it is well-known that mass transfer rate coefficients are insensitive to velocity changes above a certain threshold in unconsolidated porous media (e.g., refs 19 and 22).

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**Nomenclature**

- \( C_{\text{inf}} \): concentration in the influent end cap, M·L\(^{-3}\)
- \( C_{\text{eff}} \): concentration in the effluent end cap, M·L\(^{-3}\)
- \( C_{\text{eff}-\text{frac}} \): concentration exiting the fracture plane, M·L\(^{-3}\)
- \( C_s \): solubility concentration, M·L\(^{-3}\)
- \( C \): mean concentration in the fracture plane, M·L\(^{-3}\)
- \( V \): combined volume of the effluent end cap, recirculation system and sampling cell, L\(^3\)
- \( V_f \): volume of the fracture plane, L\(^3\)
- \( \nu \): specific discharge, L·T\(^{-1}\)
- \( Q \): volumetric flow rate, L\(^3\)·T\(^{-1}\)
- \( \varepsilon_h \): equivalent hydraulic aperture, L
- \( \varepsilon_{mb} \): equivalent mass balance aperture, L
- \( \varepsilon \): equivalent frictional loss aperture, L
- \( \mu \): dynamic viscosity, M·L\(^{-1}\)·T\(^{-1}\)
- \( L \): fracture length in the direction of flow, L
- \( W \): fracture width perpendicular to the direction of flow, L
- \( \rho \): fluid density, M·L\(^{-3}\)
- \( g \): acceleration due to gravity, L·T\(^{-2}\)
- \( \Delta H \): head difference across the fracture plane, L
- \( t_m \): mean residence time, T
- \( \lambda \): lumped mass transfer coefficient, T\(^{-1}\)
- \( M_{\text{trap}} \): initial mass of DNAPL trapped in the fracture plane, M
- \( M_{\text{dis}} \): percent of initial mass trapped removed through dissolution, %
- \( \sigma_{\text{nw}} \): NAPL–water interfacial tension, M·T\(^{-2}\)
- \( \theta \): NAPL–water wetting angle with respect to dolomitic limestone, deg
- \( D_0 \): free water diffusion coefficient, L\(^2\)·T\(^{-1}\)

**Dimensionless Numbers**

- \( \delta \): tracer aperture ratio (\( \varepsilon / \varepsilon_{mb} \))
- \( Sh_1 \): Sherwood number (\( \lambda / (T_g \cdot D_o) \))
- \( Sh_2 \): Sherwood number (\( \lambda \cdot \sigma_{\text{nw}} / D_o \))
- \( Re \): Reynolds number (\( 2 \cdot \varepsilon_{mb} / \mu \))
- \( Sn \): volumetric DNAPL saturation in fracture plane (\( V_{\text{inf}} / (\varepsilon_{mb} \cdot L \cdot W) \))
- \( Sn_{\text{8%}} \): volumetric DNAPL saturation in fracture plane when 8% of initial mass emplaced is dissolved (\( V_{\text{inf}} / (\varepsilon_{mb} \cdot L \cdot W) \))
- \( Sn^* \): normalized volumetric DNAPL saturation in fracture plane (\( Sn / Sn_{\text{8%}} \))
- \( f_{oc} \): (−) fraction of organic carbon

**Literature Cited**

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