Nonideal behavior during complete dissolution of organic immiscible liquid 1. Natural porous media

A.E. Russo[a], M.K. Mahal[a], M.L. Brusseau[a,b,*]

[a] Department of Soil, Water and Environmental Science, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, USA
[b] Department of Hydrology and Water Resources, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, USA

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ABSTRACT

Experiments were conducted to investigate the complete dissolution of organic immiscible liquid residing within natural porous media. Organic-liquid dissolution was investigated by conducting experiments with homogeneously packed columns containing a residual saturation of organic liquid (trichloroethene). The porous media used comprised different textures (ranges of particle-size distributions) and organic-carbon contents. The dissolution behavior that was observed for the soil and aquifer sediment systems deviated from the behavior typically observed for systems composed of ideal sands. Specifically, multi-step elution curves were observed, with multiple extended periods of relatively constant contaminant flux. This behavior was more pronounced for the two media with larger particle-size distributions. Conversely, this type of dissolution behavior was not observed for the control system, which consisted of a well-sorted sand. It is hypothesized that the pore-scale configuration of the organic liquid and of the flow field is more complex for the poorly sorted media, and that this greater complexity constrains dissolution dynamics, leading to the observed nonideal behavior.

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1. Introduction

Organic liquids are a persistent source of groundwater contamination at many hazardous waste sites. Understanding the mechanisms mediating the dissolution of organic liquids, and attendant source-zone mass flux, is critical for accurate risk assessment and effective remediation of sites contaminated by organic liquids. One issue of particular significance for organic-liquid-contaminated source zones is characterizing mass-removal behavior and associated mass-flux dynamics over long time frames [1]. Addressing and managing mass flux over the long term is central to reducing site risk.

The distribution, mass-transfer dynamics, and mass flux of organic liquids in the subsurface have been examined in numerous studies conducted over the past few decades. Thus, there exists a significant level of information and understanding about the behavior of organic-liquid contaminants in the subsurface. However, the current understanding of mass-transfer and mass-flux processes is far from complete, and many challenges remain [1]. For example, experiments to investigate the dissolution behavior of organic liquids have been conducted at the column, intermediate, and field scale (e.g. [2–20]). However, the laboratory experiments have been conducted using primarily glass beads or well-sorted sands, while relatively few have been conducted using natural soils and aquifer sediments (e.g. [10,11,16]). Additionally, few of these experiments have examined complete mass removal and associated long-term mass flux behavior (e.g. [10,16]). The objective of this study was to examine dissolution behavior for systems composed of natural soils and aquifer sediments, with a specific focus on characterizing long-term mass-flux behavior associated with complete dissolution of the organic liquid.

2. Materials and methods

2.1. Materials

Trichloroethene (TCE) (Aldrich Chemical Co., Inc., Milwaukee, WI) was used as the model organic liquid, given its widespread presence as a groundwater contaminant. Pentafluorobenzoic acid (PFBA) (Aldrich Chemical Co., Inc.) was used as a conservative tracer to determine the hydrodynamic properties of the columns. Calcium chloride (0.01 N) electrolyte solution was used as the aqueous solution for all experiments. Five natural porous media with varying compositions and particle-size distributions were used for the experiments. These included a sandy sub-soil collected from Alachua County, FL (Eustis), a silty soil from Pima County, AZ (Hayhook), a high organic-carbon content soil from Pima County, AZ

* Corresponding author at: Department of Soil, Water and Environmental Science, University of Arizona, 429 Shantz Building, Tucson, AZ 85721, USA.
Tel.: +1 520 621 3244; fax: +1 520 621 1647.
E-mail address: brusseau@ag.arizona.edu (M.L. Brusseau).

Table 1
Properties of porous media.

Porous media	Sand %	Silt %	Clay %	Bulk density (g/cm^3)	Porosity	Median grain diameter (d_{50}, mm)	Organic-carbon content (% OC)	Uniformity coefficient (UC)[a]	R[b]
Well-sorted sand	100	–	–	1.67	0.37	0.35	0.03	1	~1
Borden soil	96.2	2	1.8	1.74	0.34	0.21	0.03	1.9	1.5
Eustis soil	95.9	1	4.4	1.69	0.36	0.27	0.38	2.3	2.4
Hayhook soil	85.5	4.3	10.2	1.64	0.38	0.26	0.08	16	1.3
Mt. Lemmon soil	60	24	16	1.17	0.56	0.11	10	22.6	8.2

[a] UC = d_{60}/d_{10}.
[b] R = retardation factor.

(Mt. Lemmon), and an aquifer sediment from Ontario, Canada (Borden). A well-sorted natural quartz sand (45/50 Accusand) was used as a control, representative of the type of porous medium used in most prior column studies of organic-liquid dissolution. The media encompass a range of particle-size distributions (reflected by the uniformity coefficients) and organic-carbon contents (Table 1). The columns, tubing, and fittings were constructed of stainless steel. Most of the experiments were conducted using columns that are 2.5 cm in diameter and 7 cm in length (referred to as the "medium-sized" columns). Additional experiments were conducted using two other sizes, 0.5 cm diameter by 4 cm long (small) and 7.6 cm diameter by 11 cm long (large).

2.2. Methods

The columns were uniformly packed with dry porous media. After packing, the columns were saturated by injecting de-aired aqueous solution into the bottom of the column. The flowrate was slowly increased from the equivalent pore-water velocity of 5–25 cm/h over 48 h. Complete saturation was assumed once a constant mass was attained for the column. A non-reactive tracer test was then conducted to determine hydrodynamic properties of the system. Additionally, experiments were conducted using aqueous solutions of TCE to characterize the contribution of sorption/desorption to transport and elution of TCE. These experiments were conducted by continuously injecting tracer solution until the effluent concentration of the tracer (PFBA or TCE) equaled the input concentration. Tracer-free aqueous solution was then injected until the effluent tracer concentration reached the detection limit.

To establish residual saturation for the dissolution experiments, pure-phase TCE was injected into the bottom of the vertically placed water-saturated column using a gas-tight syringe attached to a syringe pump (Sage Model 355). The volume and flowrate of injection was selected to achieve the targeted saturation. Following the injection, the mobile-phase TCE was removed via injection of two pore volumes of a saturated TCE solution into the top of the column at approximately 5 cm/h, followed by ten pore volumes at a pore-water velocity of approximately 60 cm/h. The capillary number for this displacement process was approximately 10^{-6}, consistent with previously published studies and which has been shown to produce stable, discontinuous (residual) distributions of nonwetting liquids [21,22]. Final values for TCE fluid saturation were determined by moment analysis using the effluent data collected during the dissolution experiments.

The dissolution experiments were conducted in duplicate or triplicate for each porous medium. An additional set of experiments was conducted with the Hayhook medium to evaluate the impacts of organic-liquid saturation level and representative elementary volume (REV) on mass-removal behavior. Dissolution was initiated by flushing the column with de-aired aqueous solution at a flowrate equivalent to a mean pore-water velocity of approximately 20 cm/h. The solution was pumped into the column from the bottom (the same direction in which organic liquid was injected into the column) using an HPLC pump. The original endplates (distribution plate and porous frits) were replaced with clean endplates while dissolution remained in the steady-state stage, approximately 20 pore volumes after dissolution began, to reduce the impact of TCE entrapped in the endplates on mass flux. Effluent samples were collected with 2-ml or 5-ml glass syringes (Popper & Sons, Inc., New Hyde Park, NY) and diluted as needed.

Multiple approaches were used to ensure that the observed behavior was not an artifact of the system or methods. As noted above, the porous endplates were replaced during the initial steady-state stage for all experiments so that organic liquid trapped in the endplates during column preparation would not influence long-term mass removal. For selected experiments, the endplates were replaced a second time, prior to the start of the secondary steady-state stage. In addition, selected experiments were conducted wherein a stainless steel screen was used in place of the porous endplates. Finally, to confirm whether or not organic liquid was still present in the porous medium at the start of a secondary steady-state stage, an in situ ethanol flush was performed for selected experiments. For these experiments, the columns were flushed continuously with water, in identical fashion to the aqueous flushing experiments, up to the point where the first secondary steady-state region was observed in the corresponding aqueous flushing experiment. At this point, the column was flushed with ethanol, and the effluent was sampled to determine the mass removed. The mass extracted was compared to the mass calculated to be present in the column in the aqueous and sorbed phases. The latter quantity was determined using the K_d value obtained from the miscible-displacement experiments and the measured aqueous concentration (prior to the ethanol flush).

2.3. Chemical analysis

PFBA samples were analyzed using a UV–vis spectrophotometer (SPD-10A Shimadzu) at a wavelength of 262 nm. Aqueous TCE samples, ranging in concentrations from saturation (1300–1400 mg/L) to approximately 10 mg/L were analyzed using a UV–vis spectrophotometer at a wavelength of 232 nm. A GC-ECD (Electron Capture Detector) with headspace autosampler and a Supelco SPB-624 capillary column was used to analyze TCE samples for concentrations below 10 mg/L. GC analysis was also used for samples containing ethanol. The oven temperature was held at 40 °C for 2 min and then increased at a rate of 10 °C/min to a final temperature of 170 °C. The injector temperature was set at 180 °C, and the detector temperature was set at 200 °C. The quantifiable detection limit for this method was approximately 0.5 μg/L.

3. Results

Aqueous miscible-displacement experiments (no organic liquid present) were conducted to determine the impact of sorption/desorption on TCE transport and elution behavior (see Fig. 1a). TCE exhibited different magnitudes of sorption to the porous media (see retardation factors in Table 1). Extended elution tailing was observed starting at concentrations approximately five
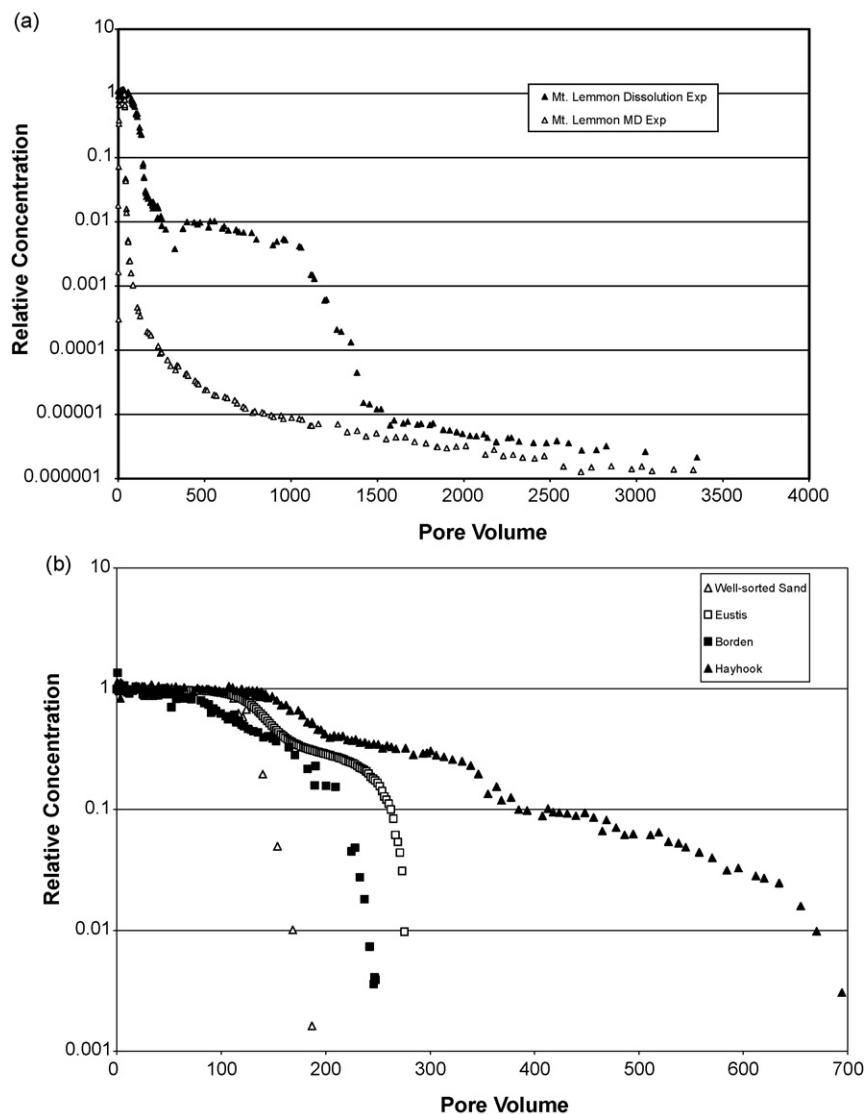
Fig. 1. (a) Elution curves for aqueous miscible-displacement (MD) and organic-liquid dissolution experiments conducted with Mt. Lemmon soil. Pore volumes represents relative time, and relative concentration = C_t/C_o, where C_o is the mean aqueous concentration for the initial steady-state stage of the experiment (equivalent to aqueous solubility). The column for the dissolution experiment contained a residual TCE saturation of 8%. (b) Elution curves for dissolution experiments conducted with the well-sorted sand, Eustis soil, Borden aquifer sediment, and Hayhook soil. The residual TCE saturations were 18.2%, 14.7%, 11.4%, and 20%.

orders-of-magnitude below the aqueous solubility of TCE. The tails extended for hundreds to thousands of pore volumes, depending upon the particular porous medium. The results of mathematical modeling analyses and batch experiments indicate that this low-concentration elution tailing is caused primarily by rate-limited desorption, with a minor contribution from nonlinear sorption (data not shown).

Extended, low-concentration elution tailing was also observed for the organic-liquid dissolution experiments for all of the media. This is illustrated in Fig. 1a for the Mt. Lemmon medium. The tailing observed for the dissolution experiments is attributed to rate-limited desorption, as has been noted previously [16]. The extended tailing associated with sorption/desorption phenomena occurs at concentrations that are several orders-of-magnitude below the organic-liquid dissolution phenomenon to be addressed below (Fig. 1a). Thus, sorption/desorption will not be considered in the forthcoming analysis, which is focused on behavior associated with organic-liquid dissolution.

The elution curves for the dissolution experiments conducted with the control medium (well-sorted sand) were characterized by

an extended steady-state stage followed by a transient stage comprising a rapid decrease in concentration (Fig. 1b). The steady-state stage extended for approximately 150 pore volumes and comprised concentrations equivalent to aqueous solubility, approximately 1300 mg/L. Such behavior is consistent with that observed in previous dissolution studies using ideal porous media (e.g. [7–10,12]).

Conversely, significantly different elution behavior was observed for the experiments conducted with the soil and aquifer sediments (Figs. 1 and 2). Multi-step elution curves, with multiple periods of relatively constant contaminant flux, were observed for these systems. The secondary steady-state stages extended for several 10–100's of pore volumes, and were characterized by concentrations generally one to two orders-of-magnitude below solubility. The secondary steady-state stages appear to be more pronounced for both the Hayhook and Mt. Lemmon soil experiments, which are the two media with the largest particle-size distributions (largest uniformity coefficients).

Multiple approaches were used to ensure that the observed non-ideal elution behavior was not an artifact of the system or methods, as noted above. The porous endplates were replaced during the
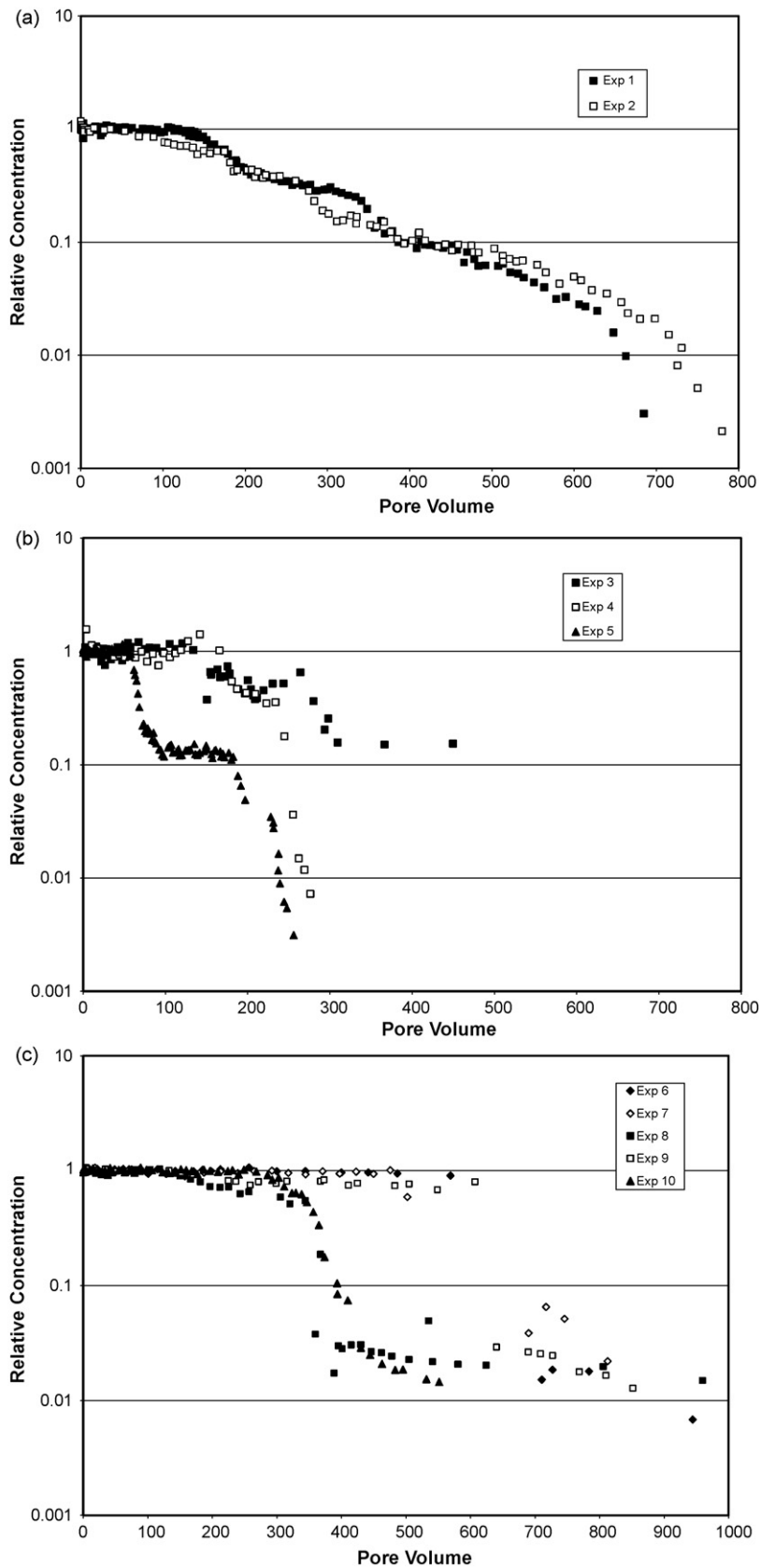
Fig. 2. (a) Elution curves for dissolution experiments conducted with Hayhook soil for columns with medium (~20%) residual TCE saturations. Experiments 1 and 2 were conducted using the medium-sized columns. (b) Elution curves for dissolution experiments conducted with Hayhook soil for columns with low residual TCE saturations. Experiments were conducted using the small columns (experiments 3–4, $S_n \sim 12\%$) as well as the large column (experiment 5, $S_n \sim 8\%$). (c) Elution curves for multiple dissolution experiments conducted with Hayhook soil for experiments with higher (~40%) residual TCE saturations. Experiments 6–10 were conducted using the small columns.

initial steady-state stage for all experiments so that organic liquid trapped in the plates during column preparation would not influence long-term mass-removal behavior. For selected experiments, the endplates were replaced a second time, prior to the start of the secondary steady-state stage, which were still observed. In addition, selected experiments were conducted wherein a stainless steel screen was used in place of the porous endplates. Secondary steady-state stages were observed for these experiments as well. For selected experiments, an in situ ethanol flush was performed to confirm whether or not organic liquid still remained in the porous medium at the start of a secondary steady-state stage. For all cases, the mass extracted during the ethanol flush was one to two orders-of-magnitude greater than the mass calculated to be present in the aqueous and sorbed phases. This indicates that organic liquid was present in the porous medium at the start of a secondary steady-state stage.

Experiments were conducted with the Hayhook soil using columns of three different sizes to evaluate potential impacts of REV limitations on observed behavior. The total system volumes for the small, medium, and large columns were, 1.5, 24, and 500 cm^3, respectively. Multi-step elution curves are observed for all experiments conducted with each of the three columns, as illustrated in Fig. 2a (medium columns) and b (small and large columns). This suggests that the observed nonideal behavior is not an artifact of REV limitations.

Multiple experiments were conducted with the Hayhook soil to examine the impact of organic-liquid saturation on dissolution behavior (Fig. 2). Secondary steady-state stages are observed within approximately one order-of-magnitude of solubility for low (~8–12%) and medium (~20%) saturations (Fig. 2a and b). In contrast, secondary steady-state stages are observed at approximately two orders-of-magnitude below solubility for experiments with high (~40%) saturations (Fig. 2c). The initial steady-state stages associated with the experiments with high saturations are observed to persist for a longer time than those observed for experiments with lower saturations, as would be expected. Examination of the data presented in Fig. 2 shows that multi-step elution curves are observed for all experiments, indicating reproducibility of the nonideal behavior.

The nonideal elution behavior described above, while not discussed in detail, appears to be evident in the results of prior dissolution studies. For example, Powers et al. [8] conducted organic-liquid dissolution experiments using columns packed with Ottawa sand (uniform silica sand) and Wagner soil (uniformity coefficient = 2.42). Multi-step elution curves appear to be exhibited for the experiments conducted with the Wagner soil. Conversely, such behavior is not apparent for the experiments conducted with the uniform sand. Imhoff et al. [10] conducted an organic-liquid dissolution study using columns packed with one of three porous media, glass beads, a mixed sand, and Wagner soil. Multi-step elution curves appear to be exhibited for the experiments conducted with Wagner soil, but not for the experiments conducted with the other two porous media. Bradford et al. [12] conducted dissolution experiments with fractional wettability media established by mixing untreated and octadecyltrichlorosilane-treated Ottawa sands. Multi-step elution curves were observed for experiments employing the medium with the largest particle-size distribution and a fractional wettability of 0.10. Such behavior was not observed for experiments conducted with other fractional wettability media with narrower particles size distributions or with water-wet media. Such behavior was also observed in a study employing a pore-network mathematical model to examine the impact of organic film stability on organic-liquid dissolution in organic-liquid-wetting systems [23]. Ideal elution curves (a single steady-state period followed by a transient stage) were observed for systems with greater film stability, whereas multi-step elution curves were observed for conditions with lesser film stability.

4. Discussion and conclusions

Organic-liquid dissolution experiments were conducted for systems composed of natural soils and aquifer sediments. Elution curves exhibited multi-step behavior, with multiple extended periods of relatively constant contaminant flux. The behavior was observed throughout a range of saturations and was reproducible. A significant amount of organic liquid was still present in the columns when the start of a secondary steady-state stage occurred, ranging from approximately 5% to 18% of the initial mass. These quantities, while relatively small fractions of the initial mass, are evidently sufficient to sustain the relatively extensive secondary steady-state stages observed. The multi-step elution behavior appeared to be greater for the media with larger particle-size distributions, while such behavior was not observed for the well-sorted sand over the effluent concentration range examined. We hypothesize that the observed behavior is a manifestation of nonideal dissolution phenomena, wherein hydraulic accessibility of the organic liquid changes during the dissolution process, and that the change is more significant for the soil and sediment systems due to greater complexity of fluid configuration and distribution at the pore scale.

For discussion purposes, an ideal system with respect to dissolution can be defined wherein the organic liquid occurs solely as single spherical blobs located in the center of pore bodies. Water flows through each pore sequence containing the organic-liquid blobs, thus effecting dissolution uniformly within the system. The hydraulic accessibility of the organic liquid is maximized for such a system, as all surface area of the organic liquid is in contact with flowing water. For such a system, the dissolution front is in theory expected to propagate uniformly down-gradient, with organic-liquid blobs nearest to the influent end of the system being removed prior to the dissolution of down-gradient blobs. There is no change in overall hydraulic accessibility during this ideal dissolution process, and effluent concentrations are thus maintained at maximum (aqueous solubility) values until there is insufficient total mass remaining, at which point they rapidly decrease to zero.

The results of studies using magnetic resonance imaging methods to examine the pore-scale flow field for two-phase systems [24,25] have shown that pore-water velocity fields are heterogeneous for even the most ideal porous media (i.e., spherical glass beads comprising a single diameter). This would seem to be contradictory to the results obtained from prior column-scale dissolution experiments conducted using well-sorted glass beads and sands, which have shown relatively ideal elution curves, indicating that essentially ideal dissolution behavior is observed for such media (at least over the concentration ranges typically examined). In fact, multi-step elution curves have been observed for more ideal (well-sorted) porous media. However, the secondary steady-state stages occurred at much lower concentrations and were less pronounced than for the poorly sorted media [26]. These results suggest that the degree of pore-scale complexity associated with well-sorted glass-bead and sand systems is generally not sufficient to greatly impact overall dissolution behavior.

The results presented herein suggest that the observed nonideal dissolution behavior appears to be more pronounced for media with larger particle-size distributions. It is possible that the pore network and the associated flow field would be more complex for media that have larger particle-size distributions, and that this greater complexity would lead to a more complex pore-scale distribution of the organic liquid. The organic liquid in such systems may exhibit a wider range in degree of hydraulic accessibility. The most accessible mass would likely be removed first during a dissolution event, leaving the lesser accessible mass. Depending upon the spe-

cific pore-scale configuration, the reduction in overall accessibility could be sufficient to cause a significant reduction in the composite effluent concentration, followed by an extended secondary period of relatively constant mass flux.

Additional research is needed to examine the pore-scale processes relevant to the observed phenomenon. For example, the results of a study employing synchrotron X-ray microtomography to characterize dissolution behavior at the pore scale indicated that the dissolution front propagated less uniformly for the Hayhook medium than for the well-sorted sand [27]. The multi-step elution behavior complicates the simulation and prediction of mass removal and mass flux for systems wherein organic-liquid dissolution is significant. Further research is needed to evaluate the ability of typical continuum-based mathematical models to simulate such behavior.

Acknowledgements

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