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NONIDEAL BEHAVIOR DURING COMPLETE DISSOLUTION OF ORGANIC IMMISCIBLE LIQUID: 1. IDEAL POROUS MEDIA

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Abstract

Column experiments were conducted using ideal natural sands and stainless-steel beads to examine the complete dissolution behavior of an organic immiscible liquid. Trichloroethene (TCE) was used as the representative organic liquid. The elution curves exhibited multi-step behavior, with multiple extended periods of relatively constant contaminant flux. These secondary steady-state stages occurred at concentrations several orders-of-magnitude below aqueous solubility for the well-sorted sands. In contrast, the secondary steady-state stages occurred within one log of aqueous solubility for the poorly-sorted sand. The nonideal behavior is hypothesized to result from constraints to hydraulic accessibility of the organic liquid to flowing water, which may be expected to be mediated by the pore-scale configuration of the flow field and the fluid phases.

Keywords

NAPL; mass transfer; elution curves; transport

1. INTRODUCTION

Organic liquid contaminants such as chlorinated solvents and hydrocarbon fuels occur at many hazardous waste sites. It is well documented that the presence of organic-liquid contamination greatly increases the risk posed by the site, as well as the complexity and cost of site remediation. Understanding the dissolution and mass-flux behavior associated with these contaminants will allow for better site characterization and more effective site remediation [1–4].

A number of experiments have been conducted to elucidate dissolution behavior of organic immiscible liquids at the column scale. The majority of these experiments have been conducted using glass beads and well-sorted sands. Mass-removal behavior typically observed for such systems consists of an initial period (commonly referred to as the steady-state stage) wherein effluent concentrations remain at aqueous-solubility levels, followed by a rapid monotonic decrease in concentration (see Figure 1). However, as discussed recently [5], such ideal behavior is not always observed. For example, multi-step elution curves have been observed for systems comprising poorly-sorted media [5]. An example of this nonideal elution behavior is presented in Figure 1. Inspection of this figure shows that a secondary steady-state stage associated with organic-liquid dissolution occurs at approximately 0.01 relative concentration. This is several orders of magnitude higher than the elution tailing

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associated with rate-limited desorption, which is evident in the data set obtained from a miscible-displacement experiment (see Figure 1).

Estimates of mass-removal times and magnitudes of mass flux are clearly dependent upon the nature of the dissolution process. Thus, it is important to fully understand the conditions under which ideal or nonideal behavior may be observed. As illustrated by the data presented in Figure 1, robust investigations of contaminant mass-removal behavior require experiments to be conducted such that essentially complete mass removal is attained. However, the elution behavior associated with complete mass removal has been examined in only a few prior dissolution studies [e.g., 5–8]. Thus, a question exists as to whether or not the behavior typically observed for experiments conducted using sands or glass beads in prior studies may be a manifestation of the absence of low-concentration data.

The purpose of this research was to examine dissolution behavior of an organic liquid for systems comprised of well-sorted sands. Three well-sorted sands of different grain size were used. A poorly-sorted sand comprised of a mixture of the well-sorted sands was also used to evaluate the impact of grain-size distribution. The experiments were conducted in such a manner to allow characterization of low-concentration elution behavior associated with complete mass removal.

2. MATERIALS AND METHODS

2.1 Materials

The following natural, commercially available silica sands were used: 20/30 mesh Accusand, 40/50 mesh Accusand, 100/140 mesh Granusil (Unimin Corporation). To examine the impact of sorting, a poorly-sorted sand comprised of combinations of the various size fractions was also used. In addition, stainless-steel beads were used as an ideal medium (perfect spheres with no significant surface roughness) for baseline comparison. The uniformity coefficient and median particle size for these media are presented in Table 1.

Trichloroethene (TCE) was used as the representative organic liquid (Aldrich Chemical Co., Inc., Milwaukee, WI). An electrolyte solution comprised of 0.01 N CaCl_2 was used as the aqueous medium (Spectrum Chemical Manufacturing Corporation, Gardena, CA). Pentafluorobenzoic acid (PFBA) (Aldrich Chemical Co., Inc., Milwaukee, WI) was used as a conservative tracer to determine the hydrodynamic properties of the columns. Experiments were conducted with 7-cm long, 2.1-cm I.D. stainless-steel columns.

2.2 Methods

The columns were packed in steps, and then were saturated with de-aired electrolyte solution. Complete saturation was assumed when a constant mass was achieved for the column. Miscible-displacement experiments were conducted with PFBA to characterize hydrodynamic properties of the packed columns. These experiments were conducted before and after the residual saturation of organic liquid was established. For the latter experiments, a TCE-saturated solution was used to prevent dissolution of residual organic liquid.

Miscible-displacement experiments were conducted to characterize the contribution of sorption/desorption to transport and elution of TCE. These experiments were conducted by continuously injecting an aqueous solution of TCE until the effluent concentration equaled the input concentration. Following the injection, a TCE-free electrolyte solution was injected until the effluent concentration reached the detection limit.

Replicate dissolution experiments were conducted for each porous medium, with the exception of the 45/50 sand, for which five experiments were conducted. Two additional

experiments were conducted for the mixed sand, employing a lower residual saturation of TCE. A residual saturation of TCE was established in each column by first injecting approximately one pore volume of pure-phase TCE into the bottom of a vertically-positioned, water-saturated column using a gas-tight syringe attached to a syringe pump (Sage Model 355). Following the injection, the mobile-phase TCE was displaced by injecting TCE-saturated solution into the top of the column. Two pore volumes of solution were injected at a slow flowrate, followed by ten pore volumes at a fast flowrate (slightly faster than that used during the dissolution experiment). The capillary number ($C_N = q\mu/\sigma$, where q is the specific discharge, μ is the viscosity of water and σ is the interfacial tension) for this displacement process was 10^{-6} , which is consistent with values used in previously published studies to establish a stable, discontinuous distribution of non-wetting fluid. During the injection and displacement steps, pure-phase TCE and TCE-saturated solution were collected and used to determine the initial TCE saturation in the column. The bulk densities, porosities, and initial TCE saturations are reported in Table 1.

After the displacement process, column endplates (frits and distribution plates) were replaced to prevent artifacts due to trapping of organic liquid. A minimum of three pore volumes of TCE-saturated solution was then flushed through the column to ensure that the column remained saturated. Russo et al. [5] present a more in depth discussion of tests performed to ensure that the observed dissolution behavior was not an artifact of the system or experimental conditions. Dissolution was initiated by flushing with an electrolyte solution from the bottom of the column. The flowrate for the experiments was equivalent to a mean pore-water velocity of 27 cm/hr, which is in the range of values associated with regions near extraction wells used for pump and treat applications at contaminated sites. Samples were continuously collected using either a 2-ml or 5-ml glass syringe (Popper and Sons, Inc., New Hyde Park, NY).

At the end of each experiment, the porous media was unpacked from the column and subjected to solvent-extraction analysis to determine the mass of TCE remaining. Dichloromethane (Burdick & Jackson, Co.) was used for all extractions. The extraction samples were placed on a shaker (Orbit Lab-line) at ~100 rpm for 24 hours. The samples were analyzed using GC-FID (gas chromatograph-flame ionization detector) with a quantifiable detection limit of 2.6 mg/L. This translates to an effective detection limit equivalent to approximately 0.05% of the initial TCE mass.

PFBA samples were analyzed using a UV-Vis spectrophotometer (SPD-10A Shimadzu) at a wavelength of 243 nm. Aqueous TCE samples, ranging in concentration from saturation (1200–1400 mg/L) to approximately 1 mg/L were analyzed using UV-Vis at a wavelength of 210 nm. Gas chromatography employing an electron capture detector was used to analyze samples with concentrations below 1 mg/L. The detection limit for this method was 0.1 µg/L.

3. RESULTS

The breakthrough curves for the nonreactive tracer were sharp and symmetrical, indicating relatively ideal hydrodynamic behavior for the packed columns. There was minimal difference in the results for experiments conducted before and after emplacement of the organic liquid, indicating minimal observable impact of the residual saturation on macroscale flow and transport. The results of aqueous miscible-displacement experiments (no organic liquid present) conducted to determine the impact of sorption/desorption on TCE transport and elution behavior indicated very small magnitudes of sorption, as would be expected for these media.

Representative elution curves for dissolution experiments conducted with the well-sorted sands and the stainless-steel beads are presented in Figure 2. The elution curves are characterized by an initial steady-state stage wherein the TCE concentrations are equal to aqueous solubility. This is followed by a transient stage comprising a rapid decrease in concentration. Secondary periods of relatively constant concentration are then observed at concentrations approximately four orders-of-magnitude below solubility. The extents of these secondary steady-state stages vary for the porous media, ranging from several hundred pore volumes for the 45/50 sand to a few ten's of pore volumes for the experiments conducted with 20/30 sand. This nonideal behavior was observed for each of the replicate experiments conducted for each of the sands as well as the stainless-steel beads.

Following the secondary steady-state stages, a rapid decrease in concentration is observed until concentrations reach approximately seven orders-of-magnitude below solubility. At this point, the elution curves exhibit an asymptotic approach towards zero (data not shown). This latter tailing behavior is identical to tailing behavior observed for miscible-displacement experiments (data not shown), wherein no organic liquid is present, and is controlled by sorption/desorption processes as has been noted previously [5,8]. The secondary steady-state stages, which are associated with organic-liquid dissolution, occur at concentrations that are orders of magnitude higher than that at which the desorption-related tailing occurs. The results of the solvent extractions conducted after each experiment showed no measurable TCE remained.

The results of an experiment conducted with the mixed sand for the higher TCE saturation are also shown in Figure 2. A secondary steady-state stage is observed at less than one log below solubility, and extends for approximately 400 pore volumes. Russo et al. [5] also observed secondary steady-state stages occurring at less than one log below solubility for dissolution experiments conducted with poorly-sorted soils and aquifer sediments. The mixed-sand medium consists of a mixture of the well-sorted sands used in the experiments discussed above. Thus, geochemical properties (e.g., wettability) of the two sets of media are identical. This suggests that the difference in the magnitude of nonideal behavior observed between the well-sorted and poorly-sorted media is a result of grain-size-distribution effects.

The degree of nonideal behavior observed for a given system can vary significantly among the individual experiments. This is illustrated in Figure 3, wherein are presented the results of the five dissolution experiments conducted for the 45/50 sand. It is observed that both the concentrations at which the secondary steady-state stages occur, and their extent, vary among the five experiments. This diversity likely reflects variability in the specific pore-scale configuration of the pore network and of the organic liquid, which is expected to vary from one column to another.

The observed nonideal behavior is hypothesized to be associated with constraints to hydraulic accessibility of the organic liquid [5,9]. Hydraulic accessibility of the organic liquid is mediated by the configuration of both the organic liquid and the aqueous-phase flow field. Hydraulic accessibility would generally be maximal for a system wherein all organic-liquid/water interfaces are in contact with flowing water, and for which the organic-liquid surface-area-volume ratio is large. To illustrate dissolution behavior for such a system, an experiment was conducted wherein a small volume of TCE (equivalent to a saturation of 1.4%) was mixed with 45/50 sand prior to column packing. For this system, the organic liquid would be expected to occur primarily as thin films surrounding the sand grains. The results of the experiment conducted with this system are shown in Figure 3. No secondary steady-state stages are evident, indicating essentially ideal dissolution behavior.

This observation supports the contention that the nonideal behavior observed for the experiments discussed above is associated with organic-liquid accessibility effects.

4. DISCUSSION AND CONCLUSIONS

Dissolution of an organic liquid was examined for three well-sorted natural sands. Nonideal behavior was observed wherein elution curves comprised multiple periods of relatively constant contaminant flux. The nonideal behavior was observed at effluent concentrations approximately four orders-of-magnitude below aqueous solubility. These concentrations are lower than typically examined in column studies of organic-liquid dissolution. This highlights the value of monitoring complete mass removal when characterizing dissolution dynamics. Secondary steady-state stages were observed at less than one log below solubility for experiments conducted with a poorly-sorted sand, suggesting that the observed nonideal behavior is of greater significance for porous media with larger grain-size distributions.

As discussed above, the observed behavior is hypothesized to be a manifestation of nonideal dissolution phenomena associated with constraints to hydraulic accessibility of the organic liquid. Hydraulic accessibility of the organic liquid is expected to be mediated by the pore-scale configuration of the flow field and the fluid phases. The results of studies using magnetic resonance imaging methods to examine the pore-scale flow field for two-phase systems have shown that pore-water velocity fields are heterogeneous for even the most ideal porous media (i.e., spherical beads comprising a single diameter) [10,11]. Thus, hydraulic-accessibility constraints for organic-liquid dissolution may be expected for even the most ideal media. This is illustrated by the results reported herein for the experiment conducted with stainless-steel beads. It also may be expected 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 therefore exhibit a wider range in degree of hydraulic accessibility, thus explaining the more significant nonideal behavior observed for the poorly-sorted media. Configuration of the fluids at the pore scale is expected to be influenced by such factors as pore-network configuration, wettability, and magnitudes of fluid saturation.

It is now recognized that management of contaminant flux from source zones is critical to long-term stewardship of sites contaminated by organic liquids [1–4]. Estimates of mass-removal times and of magnitudes of mass flux are clearly dependent upon the nature of the dissolution process. Thus, it is important to fully understand the mechanisms responsible for and the impacts of the nonideal dissolution behavior illustrated herein. This nonideal dissolution behavior is one of several processes that may affect long-term mass removal and mass flux. Additional research is required to evaluate the relative significance of this and other relevant processes.

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Figure 1.

Elution curves for organic-liquid dissolution experiments conducted for two porous media (well-sorted sand and Mt. Lemmon soil; the latter is poorly sorted). Also included are the results of a miscible-displacement (MD) experiment (no organic liquid present) conducted for trichloroethene. Data from [5].

Figure 2. Elution curves for organic-liquid dissolution: Experiments conducted with several porous media.

Figure 3. Elution curves for organic-liquid dissolution: Experiments conducted with 45/50 sand. For experiment b, the organic liquid was mixed with the sand prior to packing.

TABLE 1

Physical Properties of Porous Media

Porous Media	Uniformity Coefficient ($U_c=d_{60}/d_{10}$)	Median Grain Diameter d_{50} (mm)	Porosity	Bulk Density (g/cm^3)	Residual Saturation (% S_n)
45/50 Accusand	1.0	0.35	0.37	1.7	11
20/30 Accusand	1.2	0.73	0.35	1.7	10
100/140 Granusil	1.6	0.19	0.38	1.7	22
Mixed Sand	3.5	0.34	0.29	1.9	8, 24
Stainless-Steel Beads	1.0	1.0	0.38	4.9	11