

One-dimensional column and three-dimensional box flushing of silicone emulsion-enhanced remediation for chlorinated solvent contaminated soils

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Abstract—Aquifer contamination by dense non-aqueous phase liquids such as chlorinated solvents poses a huge threat to human health. Most chlorinated solvents biodegrade slowly under aerobic and anaerobic conditions. Furthermore, chlorinated solvents exist as free phase in aquifers and continuously contaminate groundwater because they have high density and low aqueous solubility. In this study, the feasibility of emulsion-based remediation for field application was investigated using a one-dimensional column and three-dimensional flushing. One-dimensional column experiments were performed to confirm the effects of soil components such as organics, silt, and clay on flushing performance. High organics (12%) and silt/clay (45%) inhibited solubilization of TCE. In three-dimensional flushing of TCE, a diagonal flow of emulsion was observed and downward migration of chlorinated solvents was prevented.

Keywords: Chlorinated Solvents, Flushing, Aquifer, Emulsion, Feasibility, Remediation

INTRODUCTION

Aquifer remediation using surfactant flushing has gained recognition as a promising technology to facilitate the remediation of petroleum contaminants such as gasoline and diesel. The remediation of aquifers polluted by petroleum contaminants requires a huge amount of water and leads to waste water. The application of flushing agents such as surfactants can enhance the effectiveness of aquifer remediation. The success of flushing technologies depends on the ability to deliver flushing fluids to zones of contamination and to capture the resulting dissolved contaminant plume, and in some cases, displaced free product [1]. The delivery of flushing fluids, including mass transfer between contaminants and flushing fluids, has been investigated in laboratory and field-scale experiments [2-6]. In the case of aquifers contaminated by chlorinated solvents, surfactant solutions become denser than water after the solubilization of chlorinated solvents into surfactant solutions, because the density of chlorinated solvents (TCE: 1.463 g/ml, PCE: 1.623 g/ml at 20 °C) is higher than that of water (0.998 g/ml at 20 °C). Taylor et al. [5] reported that the density of Tween 90 solutions increased to 1.002 g/ml (20 °C) after solubilization of perchloroethylene. The increased density of flushing solutions causes the downward flow of these solutions in the subsurface, and secondary contamination of the aquifer can occur by migration of dense solutions containing contaminants. Researchers have attempted to reduce the density of contaminants by adding alcohols or co-solvents [1,7-11]. The mixing of alcohol and chlorinated solvents

results in an increase of the volume (swelling) and a reduction of the density of the organic phase. This increase in volume, by swelling, is also likely to reconnect previously water-entrapped NAPL blobs, which together with the expected reduction in interfacial tension enhances mobilization [12]. However, their effect is usually not significant until the volume-fraction concentration used is above 10% [7-9]. Ladaa et al. [9] studied the partitioning of PCE into an aqueous phase via a co-solvent effect by three alcohols (ethanol, isopropanol, and tertbutyl alcohol) and determined that alcohol acts as a co-solvent only when its concentration in the aqueous phase is above 20 wt%. Damrongsiri et al. [8] reported that dense non-aqueous phase liquids can be modified to be a lighter phase only if an excess amount of alcohol (PCE to butyl alcohol ratio >0.5) exists, consistent with the findings of Kibbey et al. [13].

To overcome the problem of surfactant flushing, we proposed emulsion-enhanced remediation in our previous studies [14,15]. The oil emulsions were prepared by mechanical homogenization, and the solubilizing characteristics of the emulsions were investigated using chlorinated solvents (TCE, PCE, and DCB) in batch experiments [14]. The flow path and solubilizing characteristics of the oil emulsion were observed in a one-dimensional flushing experiment with filtered sand of 20-30 mesh size [15]. These studies revealed that chlorinated solvents can be effectively remediated by use of an oil emulsion. However, the sand used in one-dimensional flushing had low organic content and a uniform particle distribution between 20 and 30 mesh size. Limitations in delivery or mass transfer may be encountered in real field soils containing various fine particles and organic materials or larger scale systems such as two- or three-dimensional systems. Therefore, the effectiveness of emulsion flushing with real field soils or a large-scale system should be investigated to assess the feasibility of emulsion-based

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remediation. In this study, TCE flushing characteristics of a silicone emulsion were investigated in a one-dimensional system with soils having different properties. In addition, the flow path of the silicone emulsion was observed in a three-dimensional system to confirm the effectiveness in transferring the dense contaminants without secondary contamination by downward migration of flushing solutions containing dense contaminants.

EXPERIMENTAL

1. Materials

For the preparation of emulsion, silicone oil (Sigma-Aldrich, USA) of 5 cS was used. Emulsions were prepared by emulsification of an aqueous oil solution using a homogenizer (HMZ-20DN, Global Lab., Korea) at a rate of 8,000 rpm for 15 minutes. As a chlorinated contaminant, trichloroethylene (TCE, Sigma-Aldrich, USA) was used.

2. One-dimensional Column Experiment

Flushing experiments were conducted in a one-dimensional column (30 mm×160 mm, Kontes, USA). Three types of soils were collected from the field. Particles larger than 2 mm were eliminated and then dried at 105 °C for further use. The properties of the soils used in this study are summarized in Table 1. The column was filled with soils under vibration and then installed perpendicularly. Deionized water of more than 20 pore volume was then flowed upwardly at a flow rate of 1 ml/min from the bottom of the column to remove the air from soils. After the column was saturated with water, 1 pore volume of TCE was injected to the column at a flow rate of 1 ml/min, from bottom to top. To confirm the contamination of the column soil by TCE visually, a red dyeing agent (Oil Red-O, Sigma-Aldrich, USA) was used. The contamination of the soils by TCE can be observed visually. After the contamination, excess deionized water of more than 30 pore volume was passed through the column from top to bottom, and free TCE was removed from the soil in the column. Consequently, residual saturation was achieved. For emulsion flushing, an emulsion was prepared with 2% (v/v) silicone oil by homogenization at a rate of 8,000 rpm for 15 minutes. The emulsion was injected to a one-dimensional column upwardly at 1 ml/min. The effluents from the one-dimensional column were continuously collected in 20 ml glass vials.

3. Three-dimensional Flushing Experiment

A photograph of the three-dimensional box is shown in Fig. 1. The dimensions of the three-dimensional box are 20 cm (height)×20 cm (length)×20 cm (width). To observe the flow path of the emulsion with three-dimensional conditions, jumunjin filtered sand, which has low organic content (<0.3%) and a uniform size distribution of 20-30 mesh size, was filled in the box. The total amount

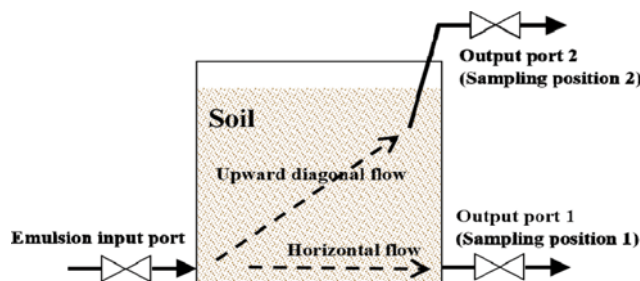


Fig. 1. Schematic diagram of three-dimensional flushing system.

of sand was 8.5 kg and the pore volume (P.V.) was 2.5 L. Initially, an excess amount of deionized water was flowed from left to right to stabilize the flow. Contamination was then carried out by injecting TCE of 15 ml in the middle of box for 1 hour. TCE was allowed to redistribute for at least 24 hrs. For the flushing, a 2% (v/v) silicone emulsion prepared by homogenization at 8,000 rpm for 15 min was injected at 5 ml/min. Every effluent of 250 ml was analyzed. The flow rate was controlled by a peristaltic pump (Masterflex, USA).

4. Analysis

The concentrations of TCE and dyeing agent were measured by a HPLC (Waters, Milford, USA) with a C18 column (4.6×250 mm, Waters, USA) and a UV detector (490E, Waters, USA) at a wavelength of 214 nm. Elution was carried out with 85% (v/v) acetonitrile at a flow rate of 1.0 ml/min. The concentrations of silicone oil adsorbed to the soil were analyzed by using an HPLC/RI (Waters, Milford, USA) with a Petro XL column (250×4.6 mm, Genesis, Hengoed, UK). Elution was performed using 100% hexane at a flow rate of 1.0 ml/min.

RESULTS AND DISCUSSION

1. One-dimensional Flushing with Real Soils

The results of flushing with three real soils are described in Fig. 2. In a previous study on emulsion flushing with jumunjin filtered sand [15], solubilization of TCE slowly progressed during the initial lag phase of flushing (<200 ml or 6 pore volume), even though the effluent concentration was above the aqueous solubility of TCE (1,099 ppm at 25 °C). Slow solubilization of TCE was also observed in emulsion flushing with real soils. Flushing with soil A showed similar results with that of jumunjin filtered sand because the properties of soil A were similar with those of jumunjin filtered sand.

The major component of soil A was sand and its organic content was as low as 0.6% (Table 1). The organic content of jumunjin filtered sand was less than 0.3% and its size was between 20 and 30 mesh size (600-850 μm). Compared to jumunjin filtered sand

Table 1. Properties of soils used

| Soils | Density (g/cm ³) | Bulk density (g/cm ³) | Porosity | Organic content (%) | Soil composition (%) | | |
|--------|------------------------------|-----------------------------------|----------|---------------------|----------------------|----------------------|------------------|
| | | | | | Sand (2-0.02 mm) | Silt (0.02-0.002 mm) | Clay (<0.002 mm) |
| Soil A | 2.340 | 1.521 | 0.350 | 0.6 | 93.5 | 2.5 | 4.0 |
| Soil B | 2.286 | 1.136 | 0.497 | 3.5 | 75.0 | 15.0 | 10.0 |
| Soil C | 2.254 | 0.789 | 0.650 | 12.1 | 55.0 | 28.0 | 17.0 |

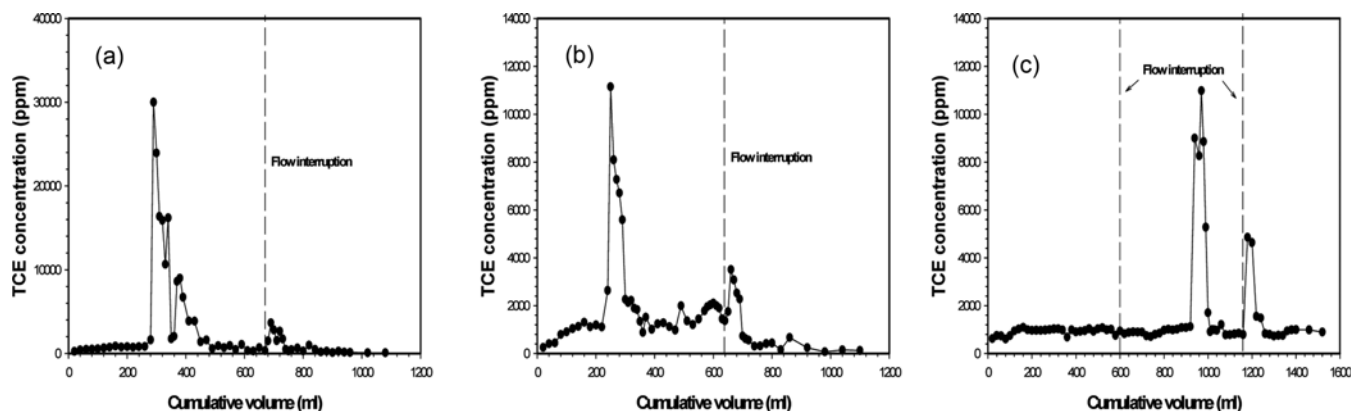


Fig. 2. One-dimensional flushing of TCE with soil A (a), soil B (b) and soil C (c).

and soil A, soil B had relatively high organic content (3.5%) and portion of fine soils (silt and clay); however, the flushing tendency with soil B was not different from the tendencies with jumunjin filtered sand and soil A. In the case of soil C, which had highest organic content (12.1%) and portion of silt and clay, the solubilization of TCE proceeded slowly after flow of 900 ml emulsion. The increase of organics and fine soils led to an increase of pore volume, and thus hydraulic conductivity decreased. The hydraulic conductivities of soil A, B, and C in the column were 0.0115 cm/s, 0.0086 cm/s, and 0.0063 cm/s, respectively. The decrease in hydraulic conductivity causes the slow solubilization of TCE because the saturation of pores within soils slowly progresses. Additionally, the existence of organics leads to strong sorption of TCE on soils. Thus, the solubilization of TCE progressed slowly in soils with high content of organics and fine soils, especially soil C. The organic content and hydraulic conductivity of soil depend on the regional characteristics. The soils of an aquifer generally have low organic content of below 1-2% [16-18], even though some researches showed high organic content over 2% [19,20]. And it was reported that conventional soil flushing was effective in aquifers of hydraulic conductivity ($>10^{-3}$ cm/s) [21]. Therefore, emulsion flushing will be suitable for common aquifers of low organic content ($<1-2\%$) and relatively

high hydraulic conductivity ($>8 \times 10^{-3}$ cm/s).

In all experiments, most of the TCE was flushed out when additional 600 ml of emulsion solution passed through the column after a high concentration of TCE was detected in the effluents. As shown in other studies on flushing [1,5,15,16], low TCE concentrations were detected in the latter phase of flushing due to limited mass transfer between the emulsion and the small amount of residual contaminants after most of the contaminants are flushed out. To enhance the mass transfer in the latter phase of flushing, the flow was interrupted during 12 h after most of the TCE was flushed out. As a result, the effluent concentration increased to about 4,000 ppm due to the enhanced mass transfer by interruption of the flow. Therefore, the stagnation by flow interruption can be one option for enhancing the remediation efficiency of flushing.

2. Three-dimensional Flushing

The emulsion flushing showed high removal efficiencies in one-dimensional flushing with jumunjin filtered sand and field soils, although inhibition of mass transfer in the initial phase of flushing was observed in the experiments with field soils of high organic content. The preferential downward flows of flushing surfactants solution were reported in three-dimensional or field experiments because of the density increase by solubilizing the chlorinated sol-

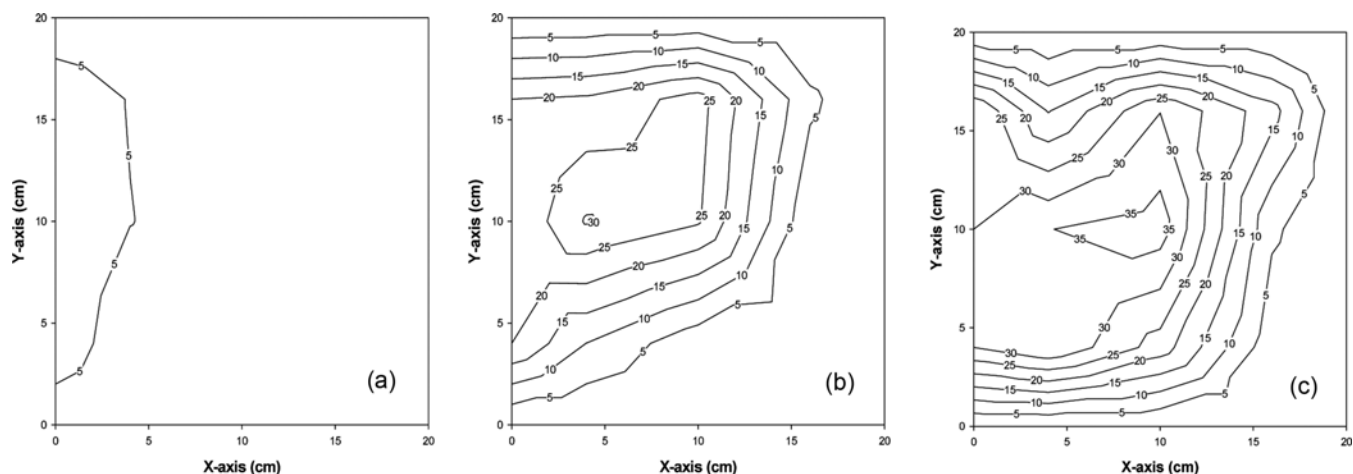


Fig. 3. Brilliant blue G concentration profile at upper area (10 cm height from bottom) after 4 hr (a), after 8 hr (b) and after 12 hr (c).

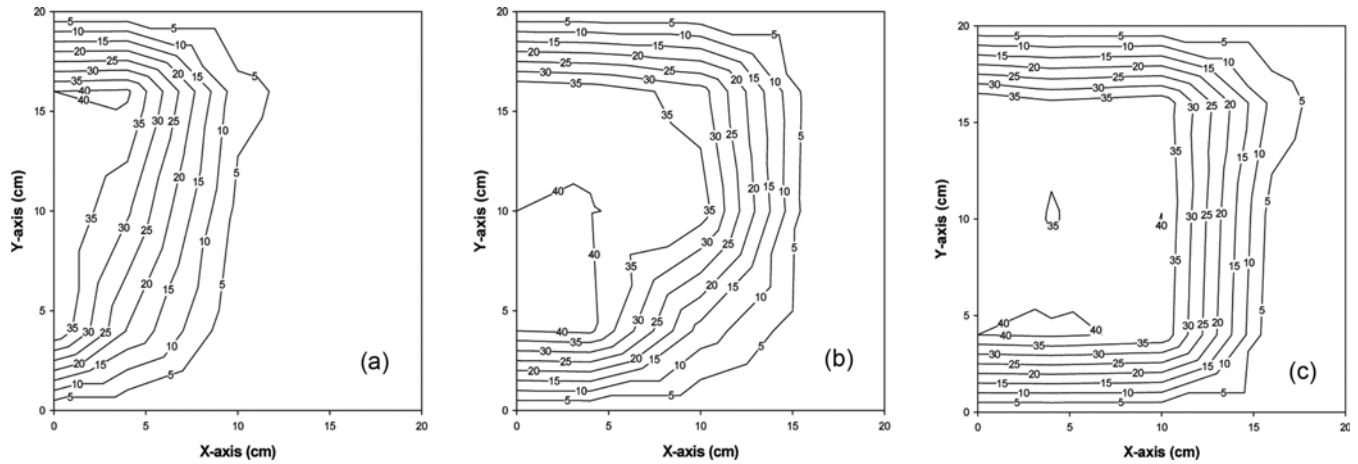


Fig. 4. Brilliant blue G concentration profile at upper area (4 cm height from bottom) after 4 hr (a), after 8 hr (b) and after 12 hr (c).

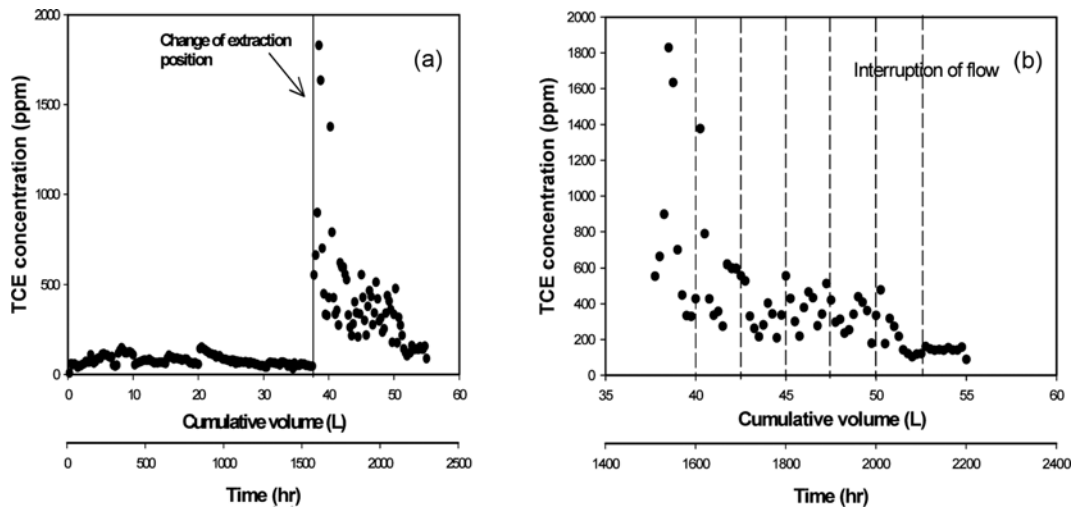


Fig. 5. Flushing of TCE in three-dimensional box (a) and effluent TCE concentration after the change of extraction position (b). Flow was interrupted during 14 hours.

vents [5,17]. Therefore, three-dimensional flushing was performed to observe the emulsion flow containing chlorinated solvents. To view the flow characteristics clearly, jumunjin filtered sand of low organic content and uniform size distribution was used. To visualize the flow, the emulsion was dyed with Brilliant Blue G (Sigma-Aldrich, St. Louis, USA). For the horizontal flow of emulsion within soils, the emulsion was injected from the bottom of the left side of the three-dimensional box and extracted from the bottom of the right side of the box. The samples were taken at two depths: 4 cm and 10 cm height from the bottom. At each depth, 12 samples were taken: every 5 cm in length and every 4 cm in width. Figs. 3 and 4 show the dye concentration within the three-dimensional box after injection of the emulsion. After four hours from the start of emulsion injection, the dye concentration at the bottom (4 cm height) was higher than that at the upper area (10 cm height). However, the dye concentrations at the upper part (10 cm height) became similar to that at the bottom of the box (4 cm height) after 8 and 12 hours from the start of emulsion injection. This means that the emulsion moved upward due to buoyancy force while it passed through soils.

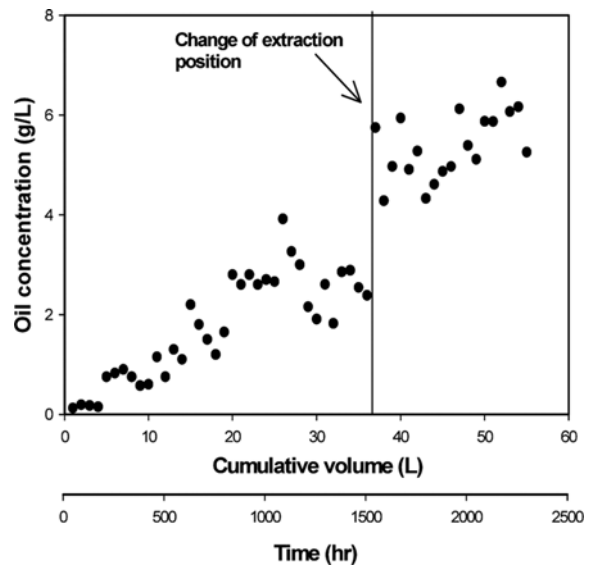


Fig. 6. Silicone oil concentration in flushing effluents.

Thus, the emulsion flowed diagonally upward within the soils and downward flow of the emulsion could be avoided.

Effluent TCE concentration is plotted in Fig. 5. Considering that TCE was distributed in the bottom of the soil, silicone emulsions were initially injected into the bottom of the left side of the box, and the effluents were drawn from the bottom of the right side of the box. As shown in Fig. 6, a low concentration of TCE was detected even though 37.5 L of emulsion (15 P.V.) was flushed out. A low amount of silicone oil was also detected in the effluent (Fig. 6). After flow of 37.5 L (15 P.V.) of emulsion, the position of the extraction well was changed from the bottom of the right side of the box to the upper soil surface in the right side of the box. A high concentration of TCE was then detected in the effluent, and the amount of oils in the effluents increased two-fold by the change of the extraction position. These phenomena were consistent with the flow path observed using a dyeing agent (Brilliant Blue G). This means that the emulsion containing dense contaminants flowed diagonally within soils due to its buoyancy force. Ostrom et al. [24] reported that about 60% of TCE was removed by surfactant flushing from an intermediate-scale flow cell and the missing 40% of TCE might have moved downwards into the fine-grained sand because of pure phase mobilization. The secondary contamination by downward migration of dense contaminants can be minimized by application of emulsion flushing. To enhance the solubilization of TCE in the latter phase of flushing, the flow was interrupted for 14 hours after flow of 2.5 L (1 P.V.) emulsion. The effluent TCE concentration increased about two-fold by interruption of the flow. This effectively enhanced the mass transfer between TCE and the emulsion, but the solubilization of TCE was not enhanced after flow of 50 L (20 P.V.). It has been reported that flushing solutions of 4-30 pore volume were generally used in laboratory and field-scale flushing experiments [4,25-29]. The amount of flushing solution used in the remediation depends on various factors such as physico-chemical properties of soils, degree of contamination, type of contaminant and flushing agent etc. Thus, TCE removal efficiency of 95% was observed by flow of 55 L emulsion (22 P.V.) and 3.9 L emulsion (about 1.6 P.V.) was consumed to remove 1 mL of TCE. Results indicated that 28% of TCE was flushed out by flow of initial 37.5 L emulsion (15 P.V.) and 67% of TCE was flushed out by flow of next 17.5 L emulsion (7 P.V.).

CONCLUSIONS

To evaluate the feasibility of emulsion flushing as an aquifer remediation process, one-dimensional flushing with three real soils of different properties and three-dimensional flushing were investigated. In flushing with soils of high organic, silt, and clay content, the mass transfer between TCE and the emulsion was inhibited by low hydraulic conductivity and strong sorption of TCE by high organic content, and so the solubilization of TCE progressed slowly. Therefore, a large amount of emulsion was required for flushing of TCE in soil with high organic content. However, inhibition of TCE solubilization was not observed with soils below 3.5% organic content and 25% silt and clay. In three-dimensional flushing, diagonal flow of the emulsion caused by its buoyancy force was detected and the flow path of the emulsion did not change after solubiliza-

tion of TCE. Thus, the downward migration of TCE can be prevented. Emulsion flushing can be effectively applied to the remediation of aquifers contaminated by dense contaminants such as chlorinated solvents.

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