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Density-surfactant-motivated removal of DNAPL trapped in dead-end fractures

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Abstract

Three kinds of experiments were conducted to test existing methods and develop an effective methodology for the remediation of DNAPL trapped in vertical dead-end fractures. A water-flushing method failed to remove TCE from vertical dead-end fractures where no fluid flow occurs. A water-flushing experiment implies that existing remediation methods, utilizing water-based remedial fluid such as surfactant-enhanced method, have difficulty in removing DNAPL trapped from the vertical downward dead-end fractures, because of no water flow through dead-end fractures, capillary, and gravity forces. Fluid denser than TCE was injected into the fracture network, but did not displace TCE from the vertical dead-end fractures. Based on the analysis of the experiments, the increase in the density of the dense fluid and the addition of surfactant to the dense fluid were suggested, and this composite dense fluid with surfactant effectively removed TCE from the vertical dead-end fractures.

key word : DNAPL, remediation, dead-end fracture, water flushing, density-enhanced mobilization method, density-surfactant-motivated method

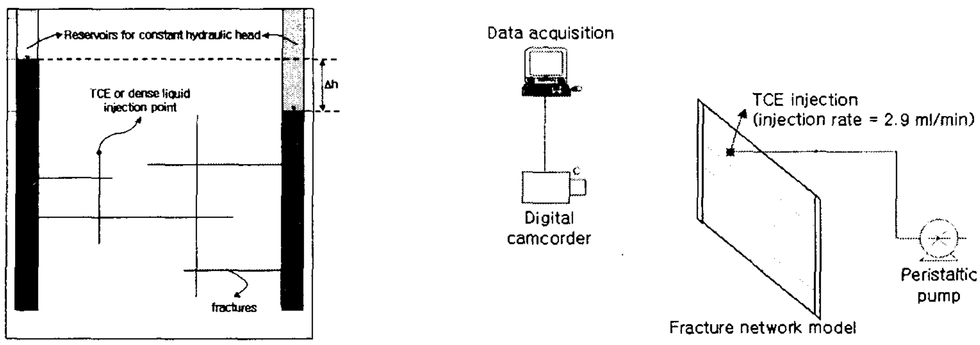
1. Introduction

Dense non-aqueous phase liquid (DNAPL) is a common groundwater contamination source, because of its extensive use in industrial processes. Spilled DNAPL enters ever-present fractures that dissect the bedrock, and is held in rock fractures and downward dead-end fractures for its higher density than water. Trapped DNAPL forms a long-term source of contamination due to its low solubility in water.

Remediation techniques to remove DNAPL contamination usually involve the delivery of remedial fluids to the contamination source; for example, water for pump-and-treat [*Mackay and Cherry*, 1989] and a water-surfactant mixture for the surfactant-enhanced method [*Walker et al.*, 1998]. However, the fractured rock environment makes effective delivery of remedial fluids very difficult to achieve. In particular, remedial fluid is rarely delivered to dead-end fractures because there is no fluid flow. A density-modified displacement method has been suggested on the basis that partitioning of *n*-butanol aqueous solutions into DNAPL reduces DNAPL density and results in a DNAPL phase lighter than the aqueous phase [*Lunn and Kueper*, 1999; *Ramsburg and Pennell*, 2002]. *Miller et al.* [2000] conducted laboratory investigations to test density-enhanced mobilization, where the density-increased flushing solution, by dissolving an additive in the aqueous phase flushing solution, turned DNAPL into LNAPL relative to the surrounding aqueous solution. The former method may not work for removing DNAPL trapped in downward dead-end fractures, because a water-butanol aqueous mixture is not effectively delivered to downward dead-end fractures. The latter has not been tested for rock fractures.

In this work, the focus is given to the development of an effective methodology for removing DNAPL trapped in vertical downward dead-end fractures, which is the most intractable problem. We applied water flushing and density-enhanced mobilization methods to a two-dimensional fracture system with vertical dead-end fractures. A density-enhanced mobilization method was also tested. After evaluating the applicability of the existing remediation methods, an effective remediation methodology is suggested to remove DANPL from vertical downward dead-end fractures.

2. Method



(a) (b)

Figure 1. (a) A fracture network model used for experiments. (b) Schematic diagram of laboratory experiment setup.

Table 1. Fluid properties

Fluid (by weight)	Density	Interfacial Tension (with TCE)
Water[a]	1.00 g/cc	0.0238 N/m
TCE	1.46 g/cc	·
50% water + 50% $CaBr_2$ [b]	1.52 g/cc	0.016056 N/m
39.7% water + 59.5 $CaBr_2$ + 0.8% SDS* [b]	1.67 g/cc	0.007320 N/m

[a] water is dyed with sulforhodamine B.

[b] dense fluid is dyed with acid blue.

* SDS: Sodium Doceyl Sulfate

The experiments were conducted using an artificial two-dimensional fracture network model that was made from a 20 cm 15 cm acrylic plate with a thickness of 2 cm (Figure 1a). Fractures in the fracture network have a constant aperture of 0.2 mm. Figure 1b shows the experimental setup. The intended hydraulic head can be achieved using the reservoirs on both sides of the fracture network. Table 1 summarizes all the physical properties of the fluids used in experiments.

3. Results and discussion

Figure 2a and 2b show the TCE locations before and during water flushing. TCE was initially located in horizontal fractures and vertical downward dead-end fractures (Figure 2a). Water was flushed through the fracture network under a hydraulic gradient of 0.4. Water removed TCE located in the horizontal and vertical fractures where water flowed, but

TCE trapped in the vertical dead-end fractures was not removed (Figure 2b). This test showed that water flushing was not effective for DNAPL removal from the vertical downward dead-end fractures through which water does not flow and the remedial fluid should have higher density than that of targeted DNAPL, so as to invade the vertical dead-end fractures. Therefore, density-enhanced mobilization was applied to a fracture network. Dense fluid (a mixture of 50% water and 50% calcium bromide) was introduced into the fracture network, but failed to displace DNAPL from the vertical downward dead-end fractures (Figure 2c). Even though the density of the dense fluid was higher than that of TCE, the injected dense fluid flowed only through the horizontal fractures as observed in a water-flushing experiment, and did not flow into vertical downward dead-end fractures at a fracture junction A (Figure 2c). The MIP model [*Glass et al.*, 2001] showed that the reasons why dense fluid did not flow into vertical downward dead-end fractures were high capillary force between dense fluid and TCE and low gravity force due to small density difference.

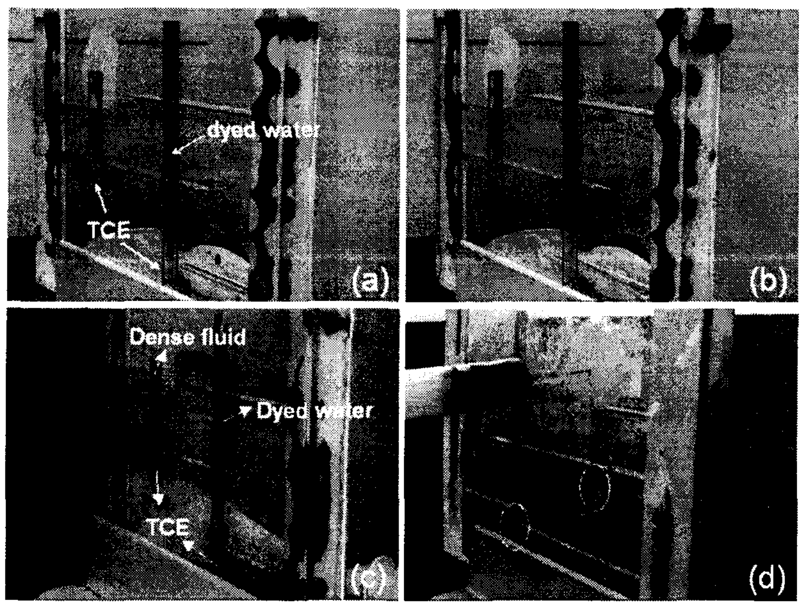


Figure 2. (a) TCE locations before water flushing. (b) TCE residuals after water flushing. (c) Result of density-enhanced mobilization test. (d) Result of density-surfactant motivated test.

SDS surfactant and more calcium bromide were added to give the dense fluid a higher density and a reduced interfacial tension. The density-surfactant-motivated test showed that TCE was successfully being removed from the vertical dead-end fractures by the dense fluid with surfactant (Figure 2d). This methodology was found very effective to remove DNAPL from the downward dead-end fractures.

4. Conclusions

Even though downward dead-end fractures where no fluid flow occurs often exist in rock fracture networks, little research has been done on remediating DNAPL trapped in downward dead-end fractures. Three types of experiments were conducted to test existing remediation methods and develop a methodology effective for DNAPL trapped in vertical downward dead-end fractures. A water-flushing and a density-enhanced mobilization methods were found to have difficulty in removing TCE from vertical dead-end fractures. The analysis of the experiments suggested that the dense fluid with surfactant displaced TCE from vertical downward dead-end fractures more effectively. The density-surfactant-motivated removal technique can therefore be recommended as an effective remediation method for removing DNAPL from the vertical downward dead-end fractures.

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