

## DNAPL Removal Mechanisms and Mass Transfer Characteristics during Cosolvent-Air Flooding

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### ABSTRACT

The concurrent injection of cosolvent and air, a cosolvent-air (CA) flood was recently suggested for a dense nonaqueous phase liquid (DNAPL) remediation technology. The objectives of this study were to elucidate the DNAPL removal mechanisms of the CA flood and to quantify mass transfer rate coefficients during CA flooding. DNAPL removal mechanisms were examined by evaluating the effects of air flow rate and DNAPL solubility and visually documented at a pore-scale. Two serial processes, immiscible displacement and dissolution, were experimentally and visually documented during CA flooding. Mass transfer rate coefficients ( $K$ ) were computed from the data showing PCE saturation versus time. Results showed that CA floods exhibited higher  $K$  values than cosolvent floods without concurrent air injection. (This document has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.)

**Key words:** dense nonaqueous phase liquid, remediation, groundwater, cosolvent, porous media

### 1. Introduction

Groundwater contamination by dense nonaqueous phase liquids (DNAPLs) presents a formidable challenge. Because conventional recovery methods such as water flooding have shown little success at removing DNAPLs, cosolvent flooding may be applied to contaminated sites using a mixture of alcohol and water as the primary flushing agents. The efficacy of cosolvent flooding is a function of the degree of mixing between the injected remedial fluid and the resident DNAPL. Poor mixing may occur because of non-uniform flow of remedial fluids and non-uniform distribution of trapped DNAPL. Non-uniform fluid displacement can be a result of spatial variability of hydrodynamic properties of the porous medium or differences between fluid properties of resident and displacing fluids.

Air having low viscosity and density clearly exhibits preferential flow in porous media. Remediation techniques and systems may potentially be designed to take

advantage of these processes to improve contact between trapped DNAPL and remedial fluids. The goal of this study was to evaluate the influence of co-injected air on the dynamics of cosolvent displacement and subsequent DNAPL mobilization and dissolution. The study investigated DNAPL removal mechanisms by evaluating the effects of air flow rate and DNAPL solubility on DNAPL removal. The mechanisms were visually documented at a pore scale.

Dissolution of DNAPL blobs has been represented with a linear driving force model [1]

$$-\rho_n \phi \frac{\partial S_n}{\partial t} = K(C_s - C) \quad (1)$$

where  $\rho_n$  and  $S_n$  are DNAPL density and saturation, respectively;  $\phi$  is the porosity;  $t$  is time;  $K$  is the mass transfer rate coefficient ( $= k a$ ;  $k$  is the mass transfer coefficient and  $a$  is the specific interfacial area);  $C_s$  is the solubility of DNAPL and  $C$  is the DNAPL concentration in the aqueous phase. This study obtained  $K$  from the DNAPL saturation data as a function of time.

## 2. Material and Methods

The homogeneous micromodel used in this study was made of etched glass and was fabricated at U.S. EPAs Robert S. Kerr Environmental Research Center, Ada, Oklahoma. The pore volume (PV) and porosity of the porous medium excluding the influent and effluent reservoirs were 0.95 ml and 0.64, respectively. The intrinsic permeability of the micromodel was  $2.43 \pm 0.09 \times 10^{-7} \text{ cm}^2$ . The effective permeability of the micromodel at an average PCE saturation of 0.32 was  $3.58 \pm 0.05 \times 10^{-8} \text{ cm}^2$ .

Tetrachloroethylene (PCE) was the DNAPL selected for this study. PCE (99.9%) containing 0.5 g/liter Oil Red O dye was placed in the micromodel as a stable residual PCE saturation. Remedial cosolvent fluids were injected at a rate of 0.02 ml/min ( $q = 0.96 \text{ m/day}$ ) in either cosolvent-air (CA) flooding or cosolvent (CS) flooding. Air for CA flooding was continuously injected with cosolvent. Two air flow rates, 0.04 and 0.1 ml/min, were evaluated. Three cosolvent solutions (50% ethanol/50% water, 70% ethanol/30% water, and 90% ethanol/10% water, by volume) were used for evaluation.

Live images were taken via a video camera mounted on a stereoscope (Zeiss SV11). Images were captured with a frame grabber and analyzed using an image analysis software package (Optimas v.6.5, Media Cybernetics Inc.). Areas and perimeters of PCE blobs were quantified with the aid of the image analysis software.

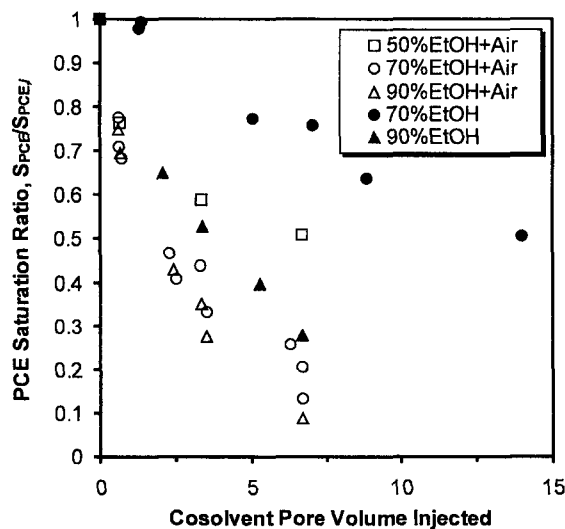
## 3. Results and Discussion

The observed rates of PCE removal as a result of CA or CS flooding are shown in Figure 1. The results are displayed on the basis of volume of injected cosolvent. A mixture of 70% ethanol and air removed 80% of the initial PCE with 6.7 PV of cosolvent. Flushing with an equivalent amount of the cosolvent (6.7 PV) without air removed less than half of the PCE.

Approximately 25% of the PCE was removed by immiscible displacement (PCE mobilization) during the initial phases of the CA floods. The injected air flowed through preferential flow paths, displacing PCE and water before exiting the pore network. PCE residing in the preferential flow paths traversed by air was readily displaced. However, the rate of free-phase PCE eluted from the micromodel decreased with time as a result of depletion of PCE in the preferential flow paths.

Impact of the air flow was evaluated by changing air flow rate. More efficient PCE removal was observed at a higher air flow rate of 0.1 ml/min. However, PCE removal during in the initial period was similar for the two air flow rates (i.e., 0.04 and 0.1 ml/min, data not shown here). PCE mobilization appeared to be independent of air flow rate for these experiments. Because difference in the PCE removal between the two air flow rates became distinct as time elapsed, the higher PCE removal at the higher air flow rate was most likely due to the efficient dissolution resulting from enhanced mixing of cosolvent and DNAPL. Visualization experiments also demonstrated that most of the DNAPL was removed by dissolution.

CA floods with different ethanol contents showed the effects of cosolvent concentration on PCE removal (Fig. 1). The air flow rates were the same, i.e. 0.1 ml/min. PCE removal efficiencies during the initial period of the CA floods were similar, implying similar air-induced PCE displacement. PCE mobilization also appeared to be independent of cosolvent concentration for these experiments. The results show the importance of PCE solubility in the dissolution process. Under the the same air flux, the CA flood with 50% ethanol showed a lower removal rate than floods with higher ethanol contents. It should be noted that PCE solubility in 50% ethanol was one tenth of that of 70% ethanol. Dissolution rates were directly related to PCE solubilities in the remedial fluid.



**FIGURE 1.** Normalized PCE saturations measured during cosolvent-air (CA) flooding and cosolvent (CS) flooding: results are shown on the basis of equivalent volumes of injected cosolvent. Injection ratio of Cosolvent: Air is 1:5.  $S_{PCE,i}$  is the initial PCE saturation.

Figure 2 shows mass transfer coefficients calculated using equation (1) as a function of volumetric content of PCE ( $\theta_n = \text{PCE residual saturation} \times \text{porosity}$ ). CA floods showed higher mass transfer rate coefficients than CS floods. The mass transfer rate coefficients for CA floods were determined from the dissolution phase of the experiments. The results indicate that dissolution of PCE was enhanced by co-injection of air.

The DNAPL removal mechanisms mentioned earlier were evaluated in a random flow pattern micromodel which is a more representative of field conditions. Injected air flowed through the preferential flow paths, displaced PCE residing in these paths, and promoted cosolvent flow in less preferential flow paths. These observations were consistent with results of the impacts of air flow rate and ethanol content on PCE removal.

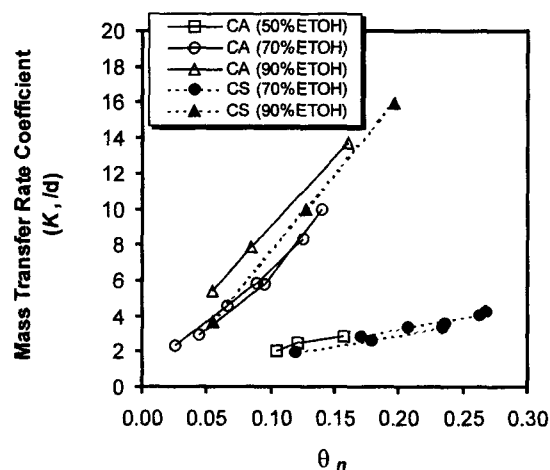


FIGURE 2. Mass transfer rate coefficient as a function of volumetric content of PCE ( $\theta_n$ ).

#### 4. Conclusions

Concurrent injection of cosolvent and air facilitated PCE removal in porous media. Two major removal processes contributed enhanced PCE removal by CA flooding: 1) immiscible displacement of PCE by air, and 2) cosolvent displacement by air from the preferential flow paths. The displacement of gas through the porous medium improves the flow distribution and dynamics of the cosolvent solution in porous media, resulting in improved dissolution.

#### 5. Reference

- [1] Imhoff, P. T., Jaffe, P. R., and Pinder, G. F. "An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media." *Water Resources Research*, 30(2), 307-320, 1993.