

## MODELING ETHANOL-ENHANCED DNAPL REMEDIATION IN A TWO-DIMENSIONAL EXPERIMENTAL SETTING

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### ABSTRACT

The accidental release of organic contaminants in the form of non-aqueous phase liquids (NAPLs) is a widespread and challenging environmental problem. Successful remediation of sites contaminated with NAPLs is essential for the protection of human health. An effective remediation method is the injection of chemical additives (cosolvents) together with water upgradient of the NAPL-contaminated area (flushing). The additives alter the physio-chemical properties of NAPLs, such as interfacial tension, and enhance their solubilities. Solubilized contaminants are carried downgradient and collected through recovery wells. The goal of the work presented here was the development of a numerical model that simulates accurately the experimental results of a DNAPL (TCE) flushing process using ethanol as a cosolvent. The effect of different ethanol contents (0%, 20% and 50%) on the remediation process were tested and evaluated. Experiments were conducted using a two-dimensional sand box, to allow for the impact of density variations on DNAPL mobility. The experimental results were used to calibrate a multiphase flow model based on a modified version of the UTCHEM simulator that includes an interfacial tension calculation. This IFT method enables UTCHEM to accurately simulate the process of ethanol concentration-dependent interfacial tension lowering.

**Keywords:** NAPL remediation, multi-phase modeling, UTCHEM, cosolvent flushing, solubility enhancement, experimental tank

### 1. Introduction

NAPL (Non Aqueous Phase Liquid) migration is a complex process affected by various parameters, the most important of them being gravity forces, which cause vertical migration, and capillary forces, which cause horizontal spreading. NAPLs gradually partition into the groundwater through dissolution causing long-term groundwater contamination (Qin *et al.*, 2009). Since the late 1980's considerable efforts have been directed towards developing new technologies for the remediation of NAPL-contaminated groundwater. Among the more promising technologies that have emerged is in-situ cosolvent flushing which involves the injection of chemical to enhance the solubility of the NAPL and possibly instigate its mobility as a separate phase by reducing the interfacial tension (Imhoff *et al.*, 2003; Agaoglu *et al.*, 2012). The work presented here focuses on the modeling part of a research effort that consists of two components: an experimental component and a modeling component. The overall goal is to demonstrate the effectiveness of enhanced solubilization and potential mobilization of a DNAPL from the subsurface using in-situ flooding techniques. The experimental results were used to calibrate a multiphase flow simulator (UTCHEM). A dense NAPL (TCE) was used in order to account for an extra complication arising from the potential uncontrolled downward migration of DNAPL due to its higher than water density. The flushing solutions consisted of ethanol–water mixtures with ethanol contents of 0%, 20% and 50% by mass.

## **2. Laboratory experiments**

### **2.1. Batch and Tracer Tests**

Batch tests were conducted to characterize the TCE–ethanol-water system. The measured parameters were solubility, miscibility by ternary phase diagram (TPD) and interfacial tension (IFT) as a function of agent concentration. The solubility of TCE in flushing solutions with ethanol contents of 0-60% by volume was determined. The solubility increased from about 1000 ppm at zero ethanol content to almost 50000 ppm at 60% ethanol content (by volume). IFT measurements show that for ethanol contents greater than 60% IFT becomes almost zero. Based on this result, the ethanol contents that were tested for the flushing experiments were 0%, 20% and 50%.

In order to evaluate the transport characteristics of the tank system, tracer tests were performed using 0.01 M NaCl at two different velocities: 3.2 m/day (high) and 1 m/day (low). The breakthrough curve of the non-reactive tracer was used to estimate the dispersion parameters, as well as the porosity of the sand. The longitudinal dispersion coefficients for the high and low velocity tracer experiments were estimated at  $3 \times 10^{-6}$  m<sup>2</sup>/s and  $0.2 \times 10^{-6}$  m<sup>2</sup>/s, respectively, corresponding to an average longitudinal dispersivity of 5 cm. The transverse dispersivity was assumed 10% of the longitudinal dispersivity value. The porosity was estimated at 0.36, which is a typical value for clean sand.

### **2.2. Flushing Tests**

A two-dimensional vertical sand box was used for the flushing experiments, to allow for the impact of density variations on DNAPL mobility. The tank dimensions are 80 cm length by 40 cm height by 5 cm width. Various ports were drilled in the back of the tank, to be used for TCE injection purposes. Three inlet and three outlet ports were drilled at both sides. The purpose of the inlet ports is to make inflow more uniform, while the outlet ports were used for TCE sampling. The main tank (64 cm length by 30 cm height by 5 cm width) that represents the model domain was filled with sand.

Three flushing experiments were conducted with flushing solutions of 0%, 20% and 50% ethanol. A volume of 10 ml dyed TCE was injected into the sand tank through the injection port at the back. After the TCE injection, the flushing solution was injected from the inlet ports at the left side of the tank with velocity close to 3 m/d for all experiments. The total duration of the flushing experiment was 29 h for the 1<sup>st</sup> experiment and 12 h for the 2<sup>nd</sup> and 3<sup>rd</sup> experiments while the sampling frequency was 1 hour for all experiments. The hourly samples were collected from the 3 exit ports and TCE concentrations were calculated. The average values from the three ports were used for model calibration.

In the beginning of the flushing experiments, the TCE contaminant plume dimensions were visually determined as 5 cm length and 5 cm height. This information was used in defining the initial NAPL zone in the numerical model.

## **3. Model description**

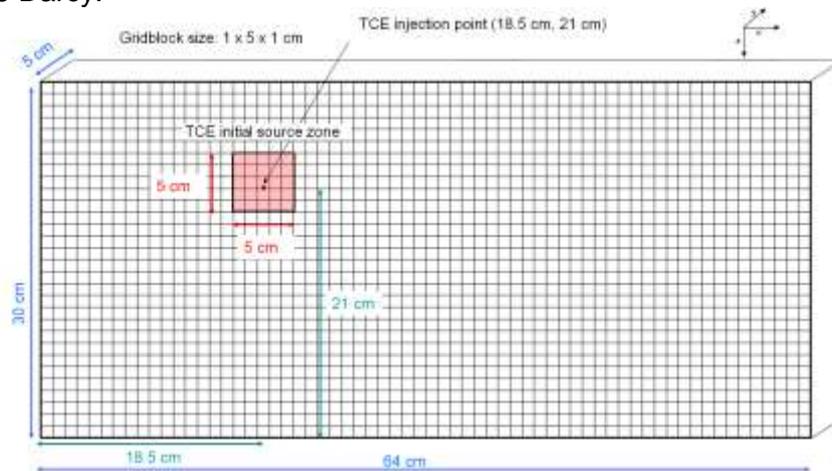
### **3.1. Multiphase flow simulator**

UTCHEM is a three-dimensional, multiphase, multicomponent, compositional, variable temperature, finite-difference numerical model. It was originally developed by Pope and Nelson (1978) to simulate the enhanced recovery of oil using surfactant and polymer processes (Pope and Nelson, 1978) and is one of a very few models that are capable of modeling cosolvent flushing. Roeder and Falta (2001) modified the UTCHEM code, to model unstable conditions which may occur during cosolvent flushing of DNAPLs. A modified version of the multiphase flow simulator UTCHEM-9.0 was used in this modeling study, equipped with the interfacial tension calculation method developed by Li and Fu (1992) that enables UTCHEM to accurately simulate the process of ethanol concentration-dependent interfacial tension lowering. The code modifications were implemented by Liang and Falta (2008).

### 3.2. Numerical model development

In order to simulate the NAPL flushing experiments in the 2D tank, the model domain was discretized by 1920 (30 rows and 64 columns) equally spaced gridblocks. The water saturation was initially assumed 1 everywhere except in the NAPL injection zone that, after visual inspection, was estimated to have dimensions of 5 cm length and 5 cm height. Within the NAPL injection zone the pore volume can be estimated as  $0.36 \times 5 \times 5 \times 5 = 45 \text{ cm}^3$ , leading to a NAPL saturation of 0.22 and water saturation of 0.78 (given that the porosity is 0.36 and the volume of injected NAPL was 10 ml).

Boundary conditions that correspond to water levels of  $h_1 = 30 \text{ cm}$  in the left side of the main tank and  $h_2 = 25 \text{ cm}$  on the right side were used in the form of pseudo-wells controlled by absolute pressure for the flow simulation. The flow calibration was performed by tweaking the experimental value of permeability (18 Darcy) in order to obtain a velocity of 3 m/d, as estimated during the experiment. The new permeability value that was obtained by the calibration process was equal to 16 Darcy.



**Figure 1:** Model discretization and TCE injection point and source zone

**Table 1:** List of key parameters used in the model simulations

Porosity	0.36
Intrinsic Permeability	16 Darcy (calibrated)
Longitudinal dispersivity	5 cm <sup>a</sup>
Transverse dispersivity	0.5 cm <sup>a</sup>
Interfacial Tension for TCE	$K_{li\&fu} = 2^c$ , $X_0 = -3.8$
Capillary pressure parameters	$\lambda = 2^d$ , $P_{bl} = 5.032 \text{ kPa}$
Residual Saturations (low capillary number)	$S_r = 0.2^e$ for all phases
Residual Saturations (high capillary number)	$S_r = 0.05^e$ for all phases

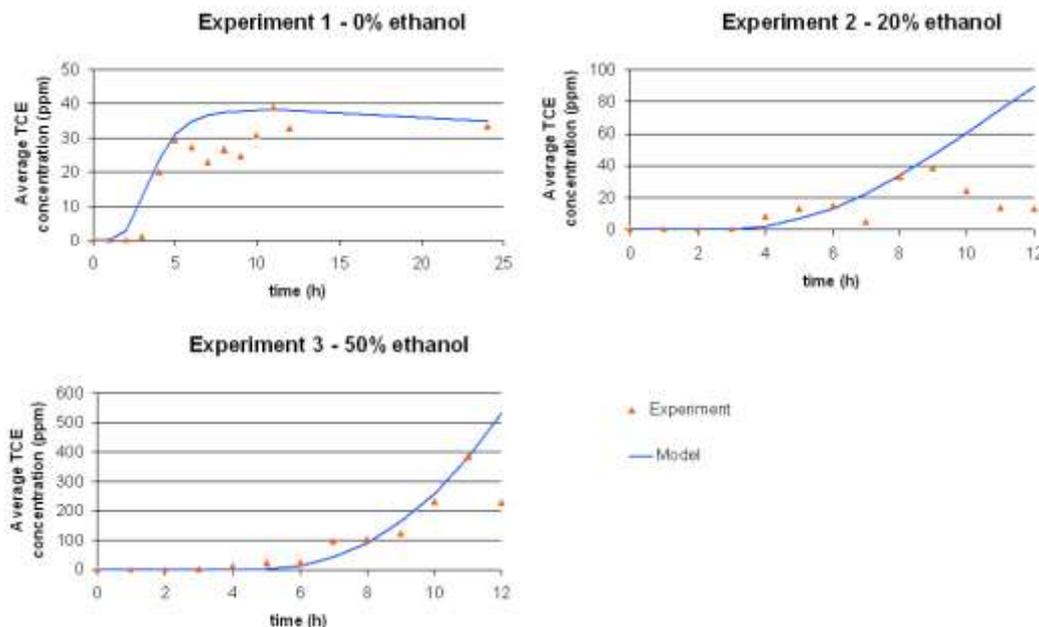
<sup>a</sup>: Longitudinal dispersivity found from tracer test, transverse assumed to be one-tenth of the longitudinal dispersivity, <sup>b</sup>: Value found from TPD experiments, <sup>c</sup>: Based on Li and Fu (1992), <sup>d</sup>: Based on Corey (1994), <sup>e</sup>: Based on Shah *et al.* (1995)

The Brooks–Corey formulation was used to compute the relative permeability of each phase and also the capillary pressure. The pore size distribution index was taken as 2, which is typical for porous media similar to the fine sand used in the experiments (Agaoglu *et al.*, 2012). The enhancement of NAPL solubility using ethanol–water mixtures was calculated from the compositions acquired from an experimental Ternary phase diagram. The models were first tested under equilibrium dissolution conditions but the TCE concentration results were overestimated in all cases. For this reason, non-equilibrium conditions were adopted and the

mass transport model calibration was performed by adjusting the mass transfer coefficient in order to reproduce the experimental results as closely as possible. The key components that were used for the model development are presented in Figure 1 and Table 1.

#### 4. Results

A comparison between the experimental and calibrated model results, in terms of average of the TCE concentration at the three sampling ports, for all experiments (Experiment 1: 0% ethanol, Experiment 2: 20% ethanol and Experiment 3: 50% ethanol) is presented in Figure 2. The enhanced solubilization of TCE with the introduction of ethanol in the flushing solution is evident, leading to higher peak concentrations especially for the 3rd experiment (high ethanol content) as opposed to the water-only flushing experiment. For the 1<sup>st</sup> experiment, the model captures the general behaviour of the TCE effluent concentrations very well, with an RMSE of 7.39 ppm. During the time period of 6-10 hours, the experimental results are lower than the concentrations observed at time  $t=5$  h, which cannot be reproduced by the model, as only increasing concentrations are simulated at that time. For the 2<sup>nd</sup> and 3<sup>rd</sup> experiments, when ethanol is introduced, the early behaviour of the TCE effluent concentration is captured by the model, while it doesn't reproduce well the concentrations observed at later times. The RMSE values for the 2<sup>nd</sup> and 3<sup>rd</sup> experiments are 29.48 ppm and 86.82 ppm, respectively.



**Figure 2:** Experimental and model results for average TCE effluent concentration

#### 5. Conclusions

Three cosolvent flushing experiments of varying ethanol contents (0%, 20% and 50% by mass) were conducted in order to evaluate their effect to TCE dissolution and recovery. The mass transfer coefficient has proved a key parameter for the modeling process. Under the equilibrium assumption, the model results are overestimated in all cases. The importance of this parameter is greatly enhanced considering that the non-equilibrium assumption is even more appropriate under field conditions. A constant mass transfer coefficient was used for the duration of the experiment. The model is able to capture the NAPL behaviour adequately, especially for early times. Given that the model concentrations at later times become much higher than the measured, a decreasing mass transfer coefficient due to a decrease in contact between the flushing solution and the NAPL may be more appropriate for a more accurate model simulation, as suggested by Agaoglu *et al.* (2012). Experiments with lower velocities and intermittent flow

will be also considered in the future in order to assess their impact in NAPL solubility enhancement and recovery.

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