

Numerical Simulation of In-Situ DNAPL Remediation by Alcohol Flooding

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ABSTRACT

The removal of residual saturations of dense non-aqueous phase liquids (DNAPLs) from below the water table using alcohol solutions is under investigation as a potential remediation tool. Alcohol flooding reduces the interfacial tension (IFT) and density difference between the aqueous and DNAPL phases, and increases the chemical solubility in the aqueous phase. Depending on the partitioning behavior of the alcohol/chemical system, DNAPL can be removed by either mobilization as a separate phase or through enhanced dissolution.

A new three dimensional multiphase numerical simulator has been developed for modeling this process. The code is based on the general TOUGH2 [Pruess, 1991] Integral Finite Difference formulation for multiphase transport with modifications to account for the complex behavior of an alcohol/water/ DNAPL system. The alcohol flood code uses a special equation of state module for computing phase compositions, IFT, saturations, densities, viscosities, relative permeabilities, and capillary pressures during each time step. This equation of state is based on a numerical interpolation of experimentally determined ternary phase data. The code was designed so that it can readily be applied to other three-component, two-phase problems such as surfactant and solvent floods given appropriate ternary data.

Comparisons of simulation results with column experiments performed at Clemson University [Brandes and Farley, 1992] were used to validate the simulator.

INTRODUCTION

Contamination of the saturated zone by dense nonaqueous phase liquids (DNAPLs) such as halogenated organic solvents has become a widespread problem in industrialized countries. These chemicals become trapped as blobs or ganglia in the pore spaces of the soil due to capillary forces. Reducing the residual saturations of the contaminants through conventional waterflooding (pump and treat) has proven to be an inefficient and uneconomical process. Alcohol flooding of these contaminated zones is a promising technology that is currently in the experimental stage. Recent laboratory-scale experiments [Boyd, 1991; Brandes, 1992] have demonstrated the effectiveness of this technology.

Characterizing the process of alcohol flooding is complicated by the unique and varied partitioning behavior of the injected alcohol between the aqueous and DNAPL phases. For this reason and because of the nonlinearity of the governing equations, the application of analytical solutions to multidimensional alcohol flooding problems is limited.

In the past decade, several numerical simulators have been developed and reported for use in environmental remediation which model NAPL transport in multiphase systems [Abriola and Pinder, 1985; Faust, 1985; Baehr and Corapcioglu, 1987; Falta et al., 1992]. None of these simulators contained the capability to handle an added miscible component.

In the petroleum industry, the desire to simulate the processes and mechanisms of tertiary oil recovery led to the development of simulators capable of modeling miscible displacement in the early 1960s. One-dimensional simulators for modeling the recovery of oil with alcohol solutions were reported by Donahue [1963] and by Farouq Ali and Stahl [1965]. The relative high cost of alcohol curtailed further development of solvent flooding simulators. Interest in the mechanisms of surfactant and chemical flooding led to the development of chemical flooding numerical simulators [Pope and Nelson, 1978; Thomas et al., 1984]. The two dimensional simulator for chemical flooding developed by Pope et al. [1981] was improved by Datta Gupta et al. [1986] for three-dimensional flow. This simulator, named UTCHEM, was recently used to simulate the three dimensional remediation of an aquifer contaminated with DNAPLs using surfactants [Pope et al, 1993].

NUMERICAL FORMULATION

Governing Equations

For an isothermal system containing three mass components, three mass balance equations are needed to fully describe the system. There is a mass balance performed on each of the three components: alcohol, water, and chemical. The governing transport equations follow Pruess [1987] with extensions to account for a NAPL phase and for the alcohol and chemical components. The three mass accumulation terms for the three components are based on a sum over the aqueous and NAPL phases. The three mass flux terms, like the mass accumulation terms, are summed over the aqueous and NAPL phases. The mass flux terms are calculated for each component in the aqueous and NAPL phases.

Equation of State

In order to describe the miscible behavior of an isothermal, three-component, two-phase system, three primary variables must be chosen. In this simulator, the primary variables used were pressure and the total chemical and alcohol mass fractions. In addition, a complete set of secondary variables must be calculated for the solution of the three coupled mass balance equations. These include mass fractions for the components of each phase, phase saturations, and phase densities. The mass fractions of the components in each phase and the interfacial tensions are numerically interpolated from the representative ternary diagram. For calculating the transport equations, additional parameters such as relative permeabilities, capillary pressures, and viscosities were determined at each time step.

The ternary diagram (shown, for example, in Figure 1) is represented by two data sets, one for the binodal curve and one for the tie lines. The area under the binodal curve represents the two-phase region with the area above the curve representing the single phase region. The slope of the tie lines in the two-phase region determines the alcohol partitioning behavior. An experimentally determined interfacial tension value is assigned to each tie line.

CODE VALIDATION AND APPLICATION

Simulation of Laboratory Column Experiments

Several laboratory-scale alcohol flooding experiments were performed by Brandes and Farley [1992] using columns packed with either glass beads or soil. Ternary diagrams were experimentally determined and constructed for each of the water/alcohol/chemical combinations being investigated [Bergelin et al., 1943; Brandes, 1992]. The experiments were conducted in vertical glass columns with a packing length of 60 cm and an inside diameter of 25 mm.

The columns were contaminated with DNAPL and then waterflooded until residual concentrations were achieved. One pore volume of an alcohol/water solution was then injected into the column in the upflow mode. Waterflooding in the upflow mode commenced immediately after the alcohol flood until the effluent concentrations of the DNAPL and alcohol had stabilized.

For the purpose of validating the ALCFLD simulator, several of the laboratory experiments were modeled numerically. Two simulations are discussed here. These two represented the two different mechanisms of DNAPL removal: enhanced dissolution and separate phase mobilization.

Enhanced dissolution was observed in the isopropyl alcohol (IPA) flood of perchloroethylene (PCE). The ternary diagram for the IPA/PCE/H₂O system, converted to rectilinear coordinates, is shown in Figure 1. Since the tie lines are sloping toward the right, the alcohol will partition preferentially into the aqueous phase. Thus the DNAPL phase will not appreciably swell and will not be mobilized. As the aqueous phase becomes increasingly alcohol rich, any PCE liberated in the column will become dissolved in the aqueous phase.

Separate phase mobilization was observed in the tert-butyl alcohol (TBA) flood of trichloroethylene (TCE). The ternary diagram for the TBA/TCE/H₂O system converted to rectilinear coordinates is also shown in Figure 1. The tie lines higher in the two phase region slope to the left, indicating preferential alcohol partitioning into the DNAPL phase at increasing alcohol concentrations. At lower alcohol levels, there is almost equal partitioning. As the DNAPL phase swells and the interfacial tension is reduced, the globules are mobilized and coalesce into a large bank.

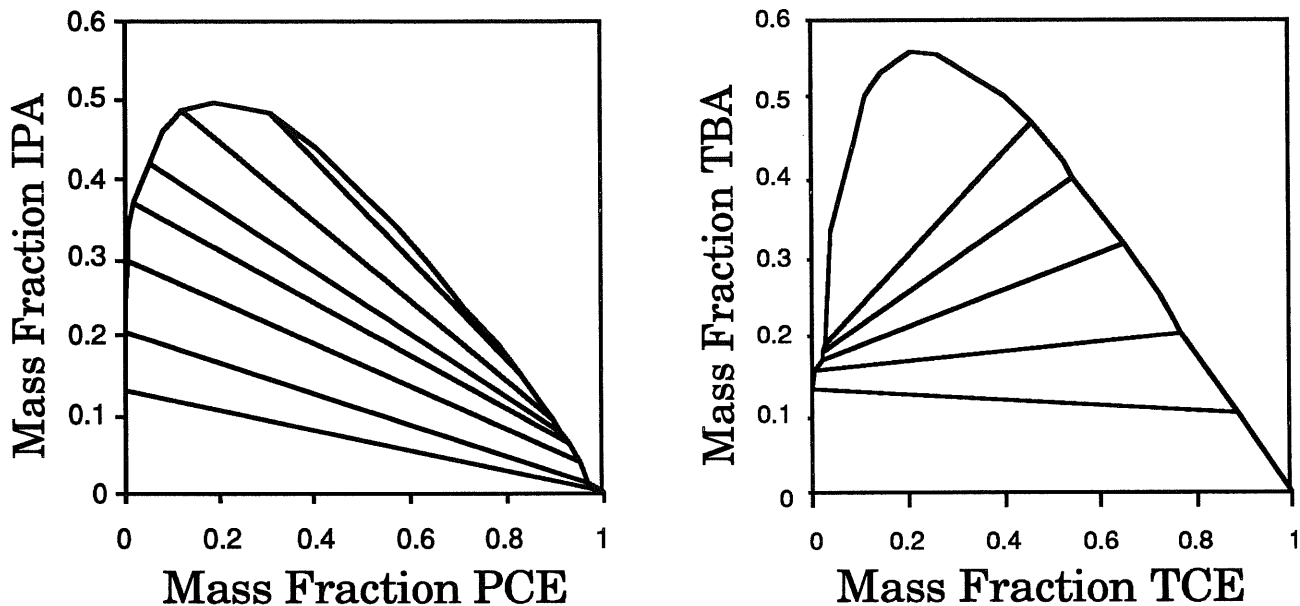


Figure 1. The ternary diagram for the IPA/PCE/H₂O system and the TBA/TCE/H₂O system converted to rectilinear coordinates.

Simulation of Enhanced Dissolution

Experiment one of Brandes [1992] was chosen for the simulation of enhanced dissolution. In this experiment, a 60% (by volume) isopropyl alcohol (IPA) solution was used to flood a column contaminated with residual saturations of PCE. In the experiment, no separate phase DNAPL was observed in the effluent. The saturation of PCE at the beginning of the alcohol flood was experimentally determined to be 16%. This was assumed to be uniformly distributed over the column for the simulation. The results of the simulation at different pore volumes are shown in Figure 2. The levels of NAPL saturation in Figure 2 show the distribution of the total amount of the PCE in *both* phases over the length of the column.

At 0.20 pore volumes (PV), the DNAPL phase was removed from about 3-4 cm of the column, as shown by the NAPL saturation curve in Figure 2. The single phase region continued to grow until reaching a maximum in the simulation at 1.5 PV. Thus, about one-third of the column was cleaned up with the one pore volume of alcohol flood.

At 0.20 PV, there is sharp rise in both the NAPL saturation and the total PCE up to the elevated levels, and then a more gradual return to the residual level. The elevated region delineates the zone of enhanced dissolution. At 0.50 PV, the elevated region has grown significantly and at 1.1 PV, the elevated region extends all the way from the sharp rise to the end of the column. Thus, at 1.1 PV, the maximum concentration of chemical is being produced as effluent. The NAPL saturation is elevated entirely from the slight amount of alcohol partitioning into the DNAPL phase.

At 1.5 PV, the NAPL saturation in the column rises sharply at the phase transition point, levels off at the old residual level and then rises gradually up to the enhanced dissolution region. At this point in the simulation, the follow-up waterflood was stripping the alcohol out of the NAPL and aqueous phases, thus decreasing the NAPL saturation and the corresponding enhanced solubility of chemical in the aqueous phase.

Comparisons of the simulated and observed effluent concentrations are shown in Figure 3. The chemical peaks are matched almost exactly and similar phase behavior is exhibited. In both cases, the alcohol front precedes the chemical front and is elevated over the maximum peak level of the chemical. The chemical front peaks just before one pore volume and maintains this level for almost one pore volume. Since the dissolution process was slow and the column was not fully decontaminated by the one pore volume alcohol flood, as shown by the chemical concentration returning to the residual concentration at 2.0 PV, the enhanced dissolution region was maintained until the waterflood removed

the remaining alcohol from the column. The irregularities in the observed curves after two pore volumes are considered to be artifacts of the experiment.

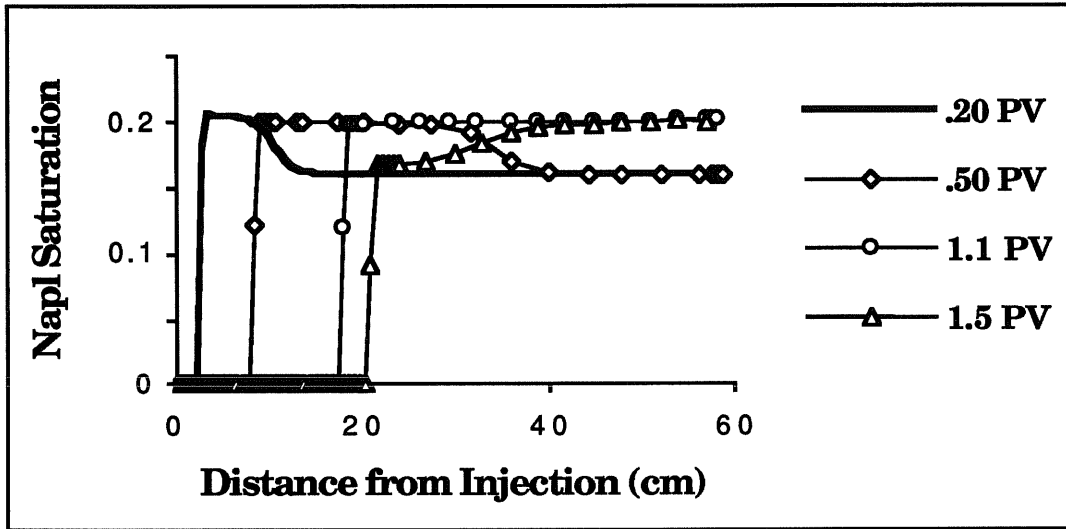


Figure 2. The NAPL saturations at different pore volumes for the simulation of a 60% IPA solution flood of a column contaminated with residual saturations of PCE.

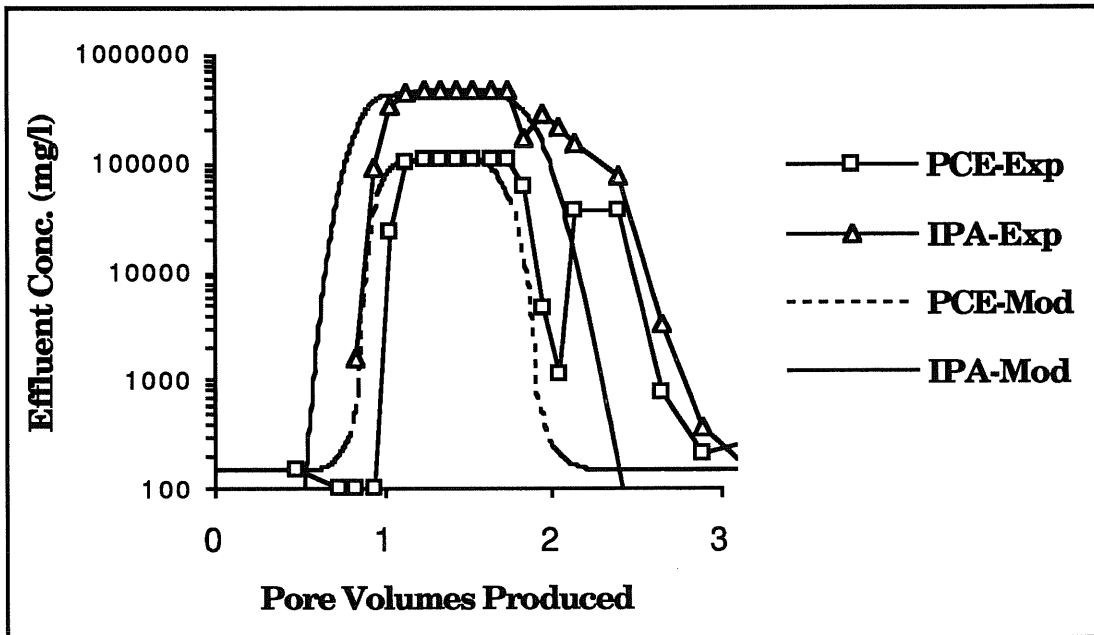


Figure 3. The simulated and observed effluent concentrations for a 60% IPA solution flood of a column contaminated with residual saturations of PCE.

Simulation of Separate Phase Mobilization

Experiment seven of Brandes [1992] was used as a comparison for the simulation of separate phase mobilization. In the experiment, a 70% (by volume) solution of tert-butanol (TBA) was injected upward into a fully saturated column contaminated with residual saturations of trichloroethylene (TCE). The saturation of TCE at the beginning of the alcohol flood was determined to be 15%. The experimental results indicated that large quantities of separate phase DNAPL were produced and that all the detectable chemical in the column was removed.

Figure 4 shows the trend of the NAPL saturations over the column at different pore volumes. This Figure demonstrates how the mobilized bank of DNAPL moves through the column over time and is eventually produced at high concentrations. Note at increasing pore volumes, the lateral width of the bank increases as the region affected by the alcohol flood grows. The saturations rise quite sharply at the point of the phase transition to a relatively high value, and maintain that level before dropping off fairly sharply near the front of the alcohol flood. The high value attained by the saturation in this simulation, compared to the height of the maximum NAPL saturation in Figure 2, shows that there is preferential partitioning of alcohol into the DNAPL phase. The rounding of the fronts at higher pore volumes results from dispersion of the alcohol flood.

At 0.25 PV, about 10 cm of the column had been converted to single phase conditions. Contrast this with the enhanced dissolution case in Figure 2, where only about 4 cm of the column was single phase at this point in the simulation. In the enhanced dissolution case, 0.75 PV of effluent had to be produced before 10 cm of the column was converted to single phase. The separate phase mobilization process is much more efficient at remediating contaminated soils. At one pore volume, high concentrations of chemical were being produced. After 1.5 PV, the simulator predicted total removal of the DNAPL phase from the column. There is still a slight amount of chemical left in the column at 1.5 PV, as shown in Figure 4, but it is dissolved in the aqueous phase and will be removed by the waterflood.

The overall behavior shown in Figure 4 is attributed to liberated chemical coalescing at the front of the DNAPL bank. This is in contrast with the enhanced dissolution case where the chemical was uniformly distributed over the alcohol swollen aqueous phase.

Figure 5 gives direct comparisons of the experimental and simulated effluent results. As shown, there is good correlation between the two figures. The TCE and alcohol are produced as sharp fronts at high concentrations as predicted. The simulated TBA effluent concentrations did not fall off after three pore volumes as was observed in the laboratory, but this can be attributed to the use of a log scale which accentuates the effects of numerical dispersion at higher pore volumes. The overall behavior is being modeled. Both curves show complete removal of TCE within two pore volumes.

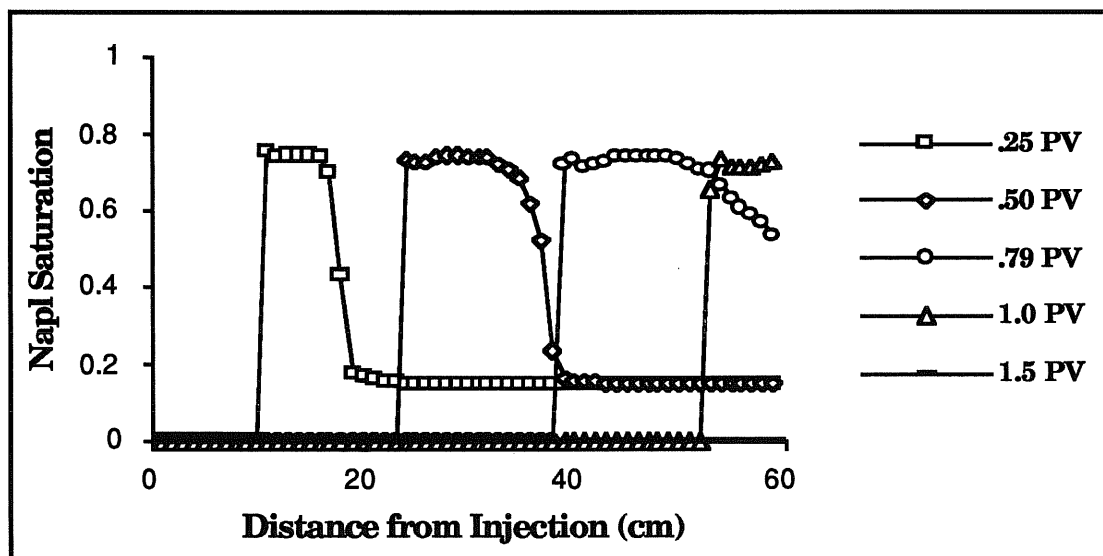


Figure 4. The NAPL saturations at different pore volumes for the simulation of a 70% TBA solution flood of a column contaminated with residual saturations of TCE.

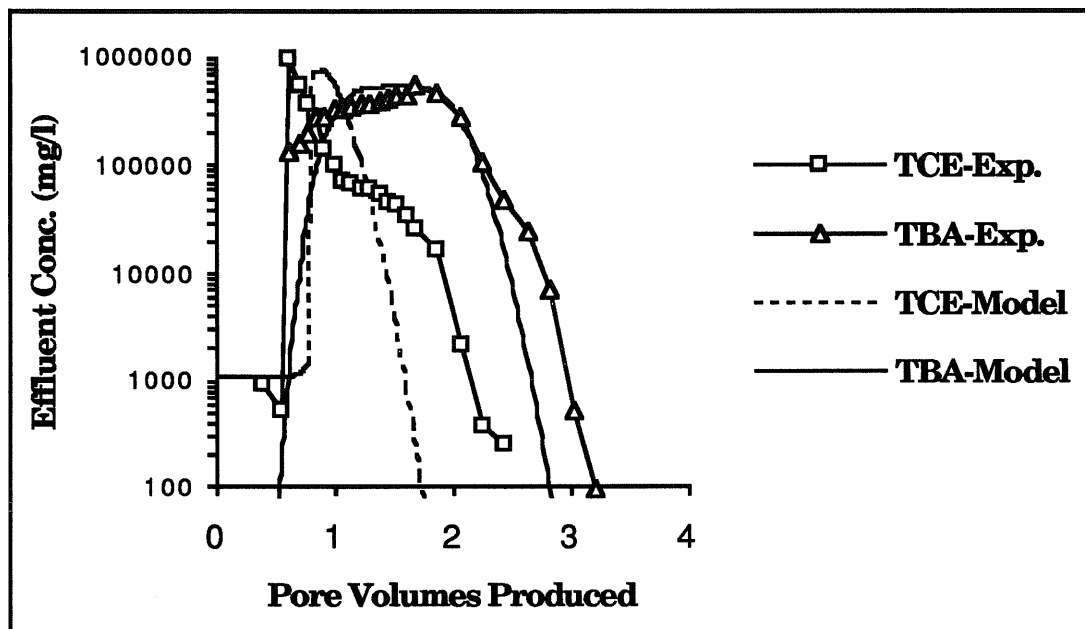


Figure 5. The simulated and observed effluent concentrations for a 70% TBA solution flood of a column contaminated with residual saturations of TCE.

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