

Application of Steam Flushing for Remediation of Multicomponent DNAPL Subsurface Contamination

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Summary

The effectiveness of steam flushing for removal of dense nonaqueous phase liquids (DNAPL) that are comprised of mixtures of high and low volatility organic compounds was investigated in laboratory experiments and numerical modelling. Removal of a mixture of monochlorobenzene (MCB) and DDT by steam flushing were conducted in a two-dimensional (110.5 cm by 57.5 cm) tank containing coarse silica sand and a fine silica sand capillary barrier. A three-dimensional finite difference model for three-phase (water-gas-nonaqueous phase liquid) flow and transport with energy transport and fully temperature dependent fluid properties and interphase partitioning was applied to elucidate the important mechanisms operative in the laboratory experiments and to investigate the field scale implementation of steam flushing for removal of multicomponent DNAPL contamination from the subsurface.

In the laboratory and modelling studies steam flushing resulted in very little DDT removal. Initial MCB removal rates were high, but removal rates declined exponentially as MCB was removed from the DNAPL and the MCB effective vapour pressure decreased. DNAPL persisting through steam flushing may move downwards through capillary barriers desaturated by water vapourization. Downward movement is limited by the high viscosity of the DNAPL as it cools beyond the steam zone.

Results of this study indicate that several pore volumes (as condensate) of steam may be required to achieve high levels of removal of volatile organics from DNAPL containing substantial amounts of low volatility compounds. The consequences of downward DNAPL movement must be considered in implementation of steam flushing for removal of multicomponent DNAPL from the subsurface.

Introduction

At many sites of soil and groundwater contamination, the contamination consists of dense nonaqueous phase liquids (DNAPL) that are mixtures of organic compounds with a wide range of solubilities and volatilities. Remediation of these DNAPL is very challenging due to the complex dependence of their physicochemical properties on DNAPL composition. In particular, the less soluble and less volatile organic compounds may be the most recalcitrant to both biotic and abiotic remediation methods. Thermal remediation methods, such as steam flushing have shown great promise for the removal of volatile organic compounds from the subsurface. However, as the volatility of the organic compounds decreases the rates of removal will decrease, requiring longer remediation times and higher remediation costs.

Compounds such as DDT and a number of polyaromatic hydrocarbons which are solid at ambient temperature, are often dissolved in dense nonaqueous phase liquids (DNAPL), and comprise a fraction of the DNAPL that has low vapour pressures at temperatures typical of steam flushing. Consequently, these low volatility compounds, can only be removed in any significant amount by hydraulic displacement of the DNAPL. As steam flushing preferentially strips the more volatile compounds from the DNAPL the effective solubility and vapour pressure of these compounds decreases (as predicted by Raoult's Law). This results in decreasing rates of removal of the volatile compounds and a prolonged period of remediation to reach acceptable levels of remediation. As significant saturations of DNAPL may persist throughout steam

flushing, downward movement of the DNAPL into capillary barriers can still be of concern, due to desaturation of the capillary barriers from water vapourization. However, the low volatility organic compounds typically have high viscosities and may even be solid at ambient aquifer temperatures, limiting their movement once they reach the bottom of the steam zone.

In this study the application of steam flushing for remediation of a mixture of monochlorobenzene (MCB) and DDT is investigated through bench scale laboratory studies and numerical modelling. MCB is a volatile organic compound, with a boiling point of 132 C and a solubility of approximately 500 mg/L. In contrast, DDT has a solubility of 0.03 mg/L and pure compound melting and boiling points of 110 C, and 260 C, respectively. The laboratory and modelling studies focus on the impact of the DDT in the DNAPL on MCB removal, and the potential for downward mobilization of the DNAPL through capillary barriers.

Experimental Methods

The steam flushing experiments were conducted in the laboratory cell used by She and Sleep (1998). This cell is 110.5 cm long, 57.5 cm high, and 10 cm thick. One side of the cell was 1.8 cm thick tempered glass, covered by 6 mm Lexan, while the other side was 6 mm thick 304 stainless steel (see Figure 1). The cell was equipped with thermocouples, pressure transducers, and sampling ports, all installed in the stainless steel side of the cell. The cell also contains a steam injection well and an extraction well, both located above the capillary barrier. Effluent from the extraction well was passed through a condenser to a Tedlar bag placed on a weigh scale. For this study, the cell was wet packed with F75 silica sand, with an 8 cm thick F110 silica sand barrier placed approximately in the middle of the cell. 300 mL of a DNAPL mixture of 50 weight percent of MCB and DDT was added to the cell at the location shown in Figure 1. Three days after the addition of the DNAPL, steam flushing was initiated at an average rate of 3.5 kg/hr with an approximate pressure of 65 kPa and temperature of 120C.



Figure 1: Laboratory cell used for steam flushing experiments

Modelling Methods

The model developed includes the three-phase (gas, water, organic) flow and transport of energy and an arbitrary number of species with equilibrium interphase mass transfer. Sleep and McClure (1996) gave the species molar balance equation describing the movement of species α in fluid phase β as:

$$\sum_{\beta=1}^3 \left\{ \frac{\partial}{\partial t} [\rho_{\beta} x_{\alpha\beta} (\phi S_{\beta} + K_{\alpha\beta,d} \rho_b)] + \nabla \cdot [\rho_{\beta} x_{\alpha\beta} \mathbf{q}_{\beta}] + \nabla \cdot [\phi S_{\beta} \mathbf{J}_{\alpha\beta}^D] - r_{\alpha\beta} - \Gamma_{\alpha\beta} \right\} = 0 \quad (1)$$

where ρ_{β} is molar phase density (n/L^3), $x_{\alpha\beta}$ is species α mole fraction in phase β , ϕ is porosity, S_{β} is phase saturation, $K_{\alpha\beta,d}$ is the linear sorption coefficient for species α in phase β and ρ_b is the bulk mass density of the soil phase (M/L^3). \mathbf{q}_{β} is the molar-averaged Darcy velocity vector for phase β (L/T), $\mathbf{J}_{\alpha\beta}^D$ is the dispersive molar flux vector for species α relative to the other molar-averaged velocity ($n/L^2 T$), $r_{\alpha\beta}$ represents interphase transfer of species α to or from phase β ($n/L^3 T$), and $\Gamma_{\alpha\beta}$ represents sources and sinks of species α to or from phase β ($n/L^3 T$).

Interphase partitioning of species in the model was based on Henry's law and Dalton's law assuming equilibrium conditions exist between phases. The relationship between mole fractions of a species α in water ($x_{\alpha w}$), gas ($x_{\alpha g}$), and organic ($x_{\alpha o}$) phases was given by

$$x_{\alpha w} H = x_{\alpha g} p_g = x_{\alpha o} P_{\alpha}^v \quad (2)$$

where H is Henry's constant ($M/L T^2$), p_g is the gas phase pressure ($M/L T^2$), and P_{α}^v is the vapor pressure of species α ($M/L T^2$).

Equation 1 in combination with the heat transport equation (Carrigan and Nitao, 2000) were discretized using three-dimensional finite differences, and were implemented for an arbitrary number of organic and inorganic species. Water may be present in the aqueous and gaseous phases, organic compounds may be in any of the organic, aqueous, or gaseous phases. Air may partition between the gas and water phases. Temperature dependent vapour pressures and Henry's Law constants were calculated from the Antoine equation. Viscosities of the DNAPL were temperature and composition dependent. Temperature dependence of capillary pressures was calculated using the correlations of She and Sleep (1998).

Results

With the injection of steam in the laboratory cell, effluent MCB aqueous phase concentrations increased from 25 to the MCB solubility limit. After 100 minutes of steam injection, just prior to steam breakthrough at 110 minutes, DNAPL was present in the effluent exiting the condenser. Approximately 57% of the DNAPL added was recovered, with a composition of 87% MCB. At the end of 4 hours of steam flushing, 17.4 kg of condensate were produced, representing approximately two times the pore volume of the region above the capillary barrier in the cell. At this point, effluent aqueous phase MCB concentrations were approximately 100 mg/L. Concentrations of MCB below the capillary barrier increased from 3 mg/L after 1 hour of steam flushing to 140 mg/L in measurements made after the cessation of steam flushing.

The evolution of temperatures in the cell predicted by numerical modelling agreed closely with measured values. As with the experiment, the model predicted very little removal of DDT, and a declining rate of MCB removal with time (Figure 2). The model predicted that 0.9 g of MCB

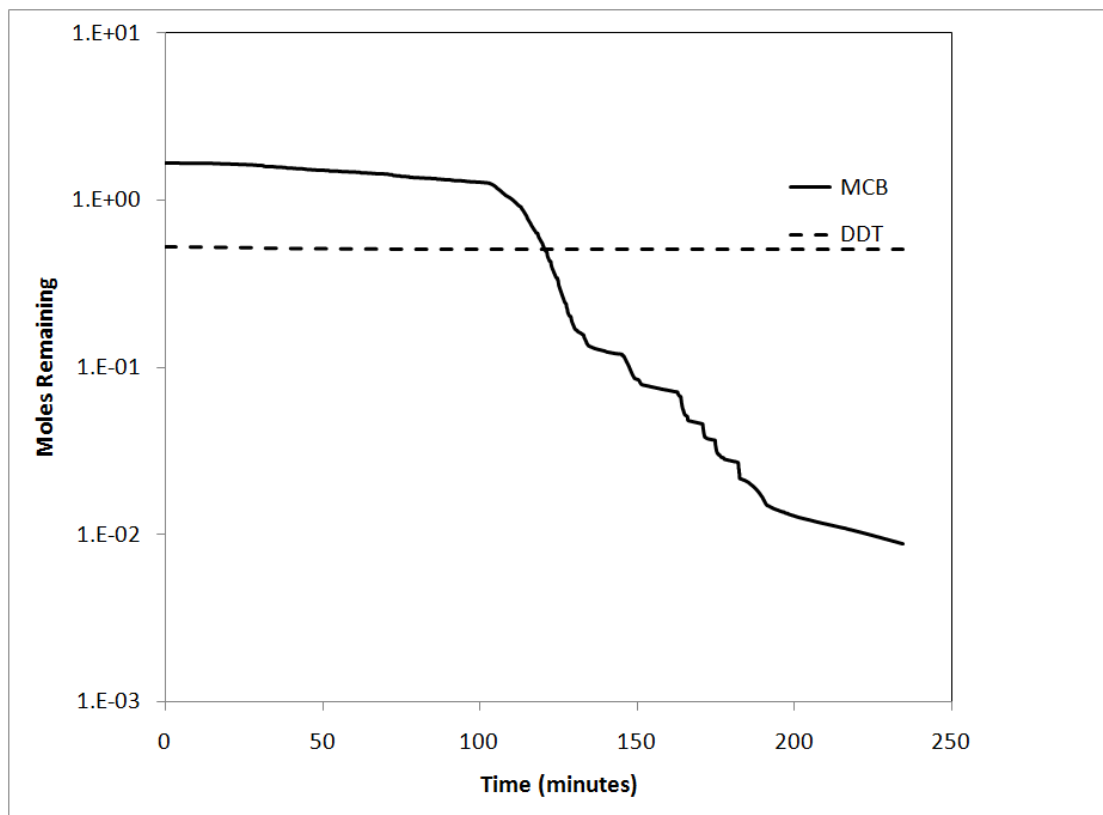


Figure 2: Model predictions of MCB and DDT removal

remained in the cell at the end of 4 hours of steam flushing, producing an effluent MCB concentration of 50 mg/L. The model predictions of higher removal of MCB and lower effluent MCB concentrations are attributed to the model assumptions of interphase equilibrium. The model also predicted the downward movement of the DNAPL (primarily DDT) not removed by steam flushing. Extrapolation of laboratory and modelling results indicates that for the conditions investigated more than 4 pore volumes of steam (as condensate) would be required to remove the remaining MCB. Field scale modelling indicates the importance of well spacing and injection rates to counter the gravity override that occurs with steam flushing due to the density contrast between steam and liquid water.

Conclusions

Steam flushing may remove substantial fractions of volatile organic compounds from multicomponent DNAPL containing low volatility components. However, reductions in effective vapour pressures of the volatile organic compounds as they are preferentially removed from the DNAPL will result in tailing in mass removal and the necessity of several pore volumes of steam flushing. Downward mobilization of low volatility DNAPL not removed by steam flushing and gravity override must both be considered in the design of field scale steam flushing schemes.

References

- Carrigan, C.R. and J.J. Nitao, 2000, Predictive and diagnostic simulation of in situ electrical heating in contaminated, low-permeability soils: *Env. Sci. Technol.*, 34(22), 4835-4841.
- H. Y. She and B. E. Sleep, 1998. The effect of temperature on capillary pressure-saturation relationships for air-water and perchloroethylene-water systems: *Water Resour. Res.* 34(10),2587-2597.
- McClure, P., and B. E. Sleep, 1996, Simulation of bioventing for remediation of organics in groundwater: *ASCE. J. Env. Eng.*, 122(11), 1003-1012.