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The Migration and Entrapment of DNAPLs in Physically and Chemically Heterogeneous Porous Media

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Research Objective

The migration and entrapment of dense nonaqueous phase liquids (DNAPLs) at hazardous waste sites is typically believed to be controlled by physical heterogeneities. This belief is based upon the assumption that permeability and capillary properties are determined by soil texture. These transport properties however, also depend on porous media wettability characteristics, which may vary spatially in a formation due to variations in aqueous phase chemistry, contaminant aging, and/or variations in mineralogy and organic matter distributions. The overall objective of this research is to investigate the influence of such coupled physical and chemical heterogeneities on the migration and entrapment of DNAPLs in the saturated zone. This research includes laboratory and numerical investigations for a matrix of organic contaminants and solid media encompassing a range of wettability characteristics. Specific objectives include: (1) quantification of system wettability and interfacial tensions; (2) determination of transport property relations; (3) two-dimensional infiltration experiments; (4) modification of a continuum based multiphase flow simulator to account for physical heterogeneity, saturation independent and saturation dependent wettability, and concentration dependent wettability and interfacial tension; and (5) utilization of this model to explore the potential influence of coupled physical and chemical heterogeneities on the migration of DNAPLs and the development of innovative remediation schemes. The accomplishment of the above research objectives will facilitate the characterization and remediation of contaminated field sites.

Research Progress and Implications

This section summarizes research conducted towards the accomplishment of goals (1), (2), (4), and (5) during the first 1.5 years of this 3-year project. Goal (3) builds upon results from the other objectives and will be initiated in the coming year.

To address objective (1), a series of experiments have been conducted for xylene-water-quartz systems using the representative surface-active agents, dodecylamine (DDA) and octanoic acid (OA). DDA and OA exhibit pH dependent acid-base speciation in aqueous solution, which results in aqueous chemistry-dependent interfacial tension and/or wettability in these systems. When the neutral species of DDA ($\text{pH} > 10$) and OA ($\text{pH} < 5$) prevailed, minimal changes were observed because of preferential partitioning of DDA and OA into the NAPL. In contrast, the cationic form of DDA ($\text{pH} < 10$) sorbed both to quartz which altered the wettability from water-wet to neutral and to the NAPL-water interface. The anionic form of OA ($\text{pH} > 5$) sorbed only to the NAPL-water interface which lowered the interfacial tension by as much as 50%. Results from these studies will facilitate the quantification of aqueous phase chemistry effects on DNAPL migration and remediation.

To address (2), capillary pressure relations have been measured for a representative DNAPL (tetrachloroethylene), water, and synthetic and natural fractional wettability porous medium systems using a modified pressure cell apparatus. Results indicate that as the organic-wet fraction of a soil increases, for a given saturation and saturation history, the residual water saturation increases and the organic liquid-water capillary pressure decreases, becoming negative during imbibition. Work has also been directed towards the design and construction of an automated apparatus to measure the hydraulic property relations on a number of columns in parallel. Construction is now complete and experimental protocols have been established for its operation. Equilibrium liquid pressure and saturations measured with this apparatus will yield capillary pressure relations, whereas transient

outflow measurements will be used to determine the relative permeability relations, in conjunction with history matching procedures. The multiphase flow simulator discussed below has been successfully coupled with a nonlinear least-squares fitting routine for this purpose. Research to address (2) will lead to the development of improved methods to predict, model, and economically measure hydraulic property relations which are required by multiphase flow and transport simulators.

Considerable progress has been made towards the accomplishment of goals (4) and (5). A two-dimensional multiphase flow simulator has been modified to account for coupled physical and chemical aquifer heterogeneity. Saturation independent and saturation dependent wettability effects on the hysteretic hydraulic property relations are currently included, but the simulator does not yet account for concentration dependent wettability and interfacial tension. The implemented hydraulic property model and available experimental data suggest that, for a given saturation and saturation history, increasing the contact angle or organic-wet fraction of a porous media tends to: (1) decrease the organic-water capillary pressure; (2) decrease the organic relative permeability; (3) decrease the amount of organic entrapped by water; (4) increase the water relative permeability; and (5) increase the amount of organic retained as an immobile film coating solid surfaces. This simulator has been employed to investigate the potential influence of coupled physical and chemical heterogeneity on DNAPL flow and entrapment. For reasonable ranges of wettability characteristics, simulations suggest that spatial variations in wettability can have a dramatic impact on DNAPL distributions. In physically homogeneous systems, increasing the contact angle or organic-wet fraction of a soil produces a prolonged slow migration of the DNAPL creating larger contaminated aquifer regions with lower organic saturations. In coupled physically and chemically heterogeneous systems, interfaces of capillary property contrast (soil texture or soil wettabilities) lead to higher organic saturations, increased lateral spreading, and decreased depths of organic liquid infiltration.

Planned Activities

Future work will investigate whether OA and DDA have a similar effect on interfacial properties when tetrachloroethylene is the NAPL. Experimental research efforts will also focus on the determination, quantification, and prediction of capillary and relative permeability relations for variously wetted synthetic and natural porous media. Results from these studies will be utilized in the development and design stages of the two-dimensional organic liquid infiltration experiments which will be initiated this year. Numerical modeling efforts will initially be directed towards the simulation of transient outflow experiments (to determine the relative permeability relations), and then two-dimensional infiltration experiments. Modifications to the simulator to account for concentration-dependent interfacial tension and wettability will be made as information and insight is gained from the above mentioned experiments.

Other Access To Information

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