

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

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Abstract

Hazardous dense nonaqueous phase liquids (DNAPLs) at Department of Energy (DOE) sites pose a significant threat to soil and groundwater. Subsurface chemical heterogeneities may occur at many of these sites as a result of spatial and temporal variations in aqueous phase chemistry, contaminant aging, mineralogy and organic matter. The presence of such heterogeneities may significantly influence DNAPL migration and entrapment in the saturated zone. Despite its importance, the physics of DNAPL flow in chemically heterogeneous systems is poorly understood and, hence, multiphase flow simulators typically assume that subsurface soils are completely water-wet and chemically homogeneous. If this assumption does not hold, then large errors may be introduced into estimates of DNAPL migration and remediation. This poster highlights research funded by the Environmental Management Science Program (EMSP) of DOE aimed at improving our understanding of and ability to simulate the influence of subsurface chemical heterogeneities on DNAPL flow and entrapment. Aqueous phase solution conditions, such as the concentration of surface-active solutes like octanoic acid (OA) and dodecylamine (DDA), were shown to directly affect water-NAPL capillary pressure-saturation relationships as a result of changes in interfacial tension and/or solid phase wettability. Solid phase mineralogy and surface coatings also altered these relations significantly when they impacted solid phase wettability. DNAPL residual saturation was found to systematically vary by 52 to 80% for experimental soils composed of various mass fractions of untreated (water-wet) and organosilane treated (DNAPL-wet) Ottawa sands. Two-dimensional DNAPL infiltration experiments also demonstrated that subsurface chemical heterogeneities significantly influence DNAPL migration as a result of differences in entrapment behavior and capillary barrier effects at interfaces of capillary contrast (chemical or textural). Theoretical models to quantify and describe these experimental data have been developed and incorporated into a two-dimensional multiphase flow simulator. This simulator was used to describe the migration and entrapment of a DNAPL, tetrachloroethylene (PCE), in experimental systems and to conduct numerical experiments in coupled chemically and physically heterogeneous systems at larger scales and over a wider range of heterogeneity characteristics. Experimental and numerical studies indicate that the spatial distribution of subsurface chemical characteristics should be quantified to improve the prediction of DNAPL fate and persistence, and that this knowledge may be of at least equal importance as the intrinsic permeability distribution in some systems. A more complete understanding of the influence of chemical heterogeneities on DNAPL migration and entrapment may lead to improved methods for DNAPL recovery and containment during aquifer remediation operations.

Introduction

Interfacial properties (wettability and interfacial tension) may vary spatially and temporally in a formation due to variations in aqueous phase chemistry, contaminant aging, and/or variations in mineralogy and organic matter distributions. In natural subsurface systems, highly irregular distributions of NAPLs have been observed. These distributions are likely due to the superposition of physical and chemical heterogeneities.



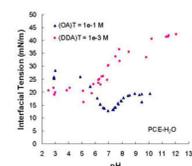
Objective: Explore the influence of chemical heterogeneity on the migration and entrapment of DNAPLs



Interfacial Properties

Aqueous Chemistry - Interfacial Tension

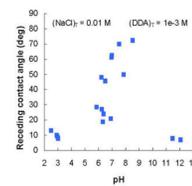
In the presence of dodecylamine (DDA) the interfacial tension increases with increasing pH, whereas the opposite behavior occurs for octanoic acid (OA).



Increasing pH favors the formation of the neutral species of DDA and the anionic (surface active) form of OA.

Aqueous Chemistry - Wettability

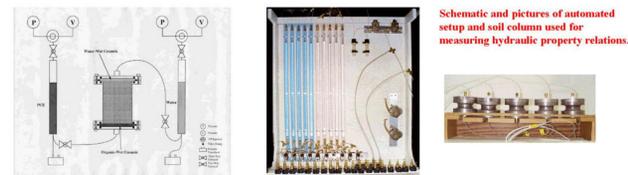
In the presence of DDA the contact angle reaches a maximum near neutral pH. In contrast, for OA the value was much lower (10°) and independent of pH.



As pH increases, the charge density on quartz increases, inducing sorption of DDA and a consequent increase in contact angle. Above pH=10, DDA tends to partition into the organic phase.

Hydraulic Properties

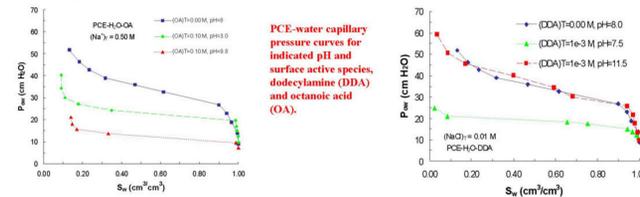
Automated Measurement



Equilibrium liquid pressure and saturations with this apparatus yield the capillary pressure relations, whereas transient outflow measurements are used to determine the relative permeability relations.

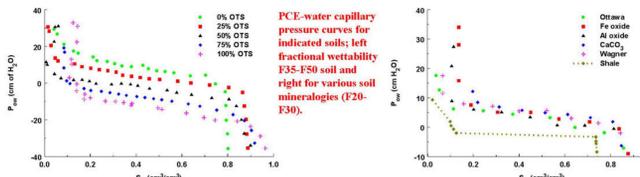
Capillary Pressure Relations - Aqueous Chemistry

Changes in the interfacial properties as a result of the presence of surface active species and changes in system pH influences the hydraulic property relations as shown below.



Capillary Pressure Relations - Solid Phase Chemistry

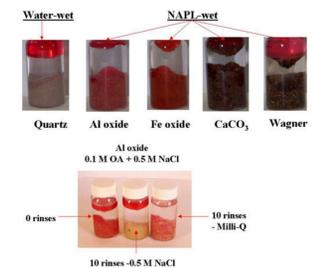
Capillary pressure relations have also been measured for a representative DNAPL (tetrachloroethylene - PCE), water, and synthetic and natural fractional wettability porous medium systems.



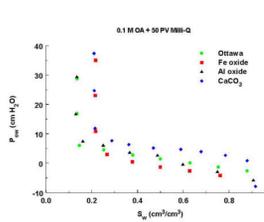
Fractional wettability has a marked influence on the P_{ce}-S_w relations

Capillary Pressure Relations - Aqueous and Solid Phase Chemistry

In the presence of 0.1 M OA wettability alteration occurred for many of the soils. This alteration depended on both the aqueous and solid phase chemistry.



Exposure of the soils to 0.1 M OA followed by extensive flushing with Milli-Q water (50 PV) resulted in wettability alteration for some of the soils (compare above and below figures).

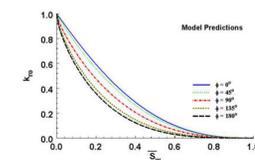


Relative Permeability Relations

Modified Burdine Relative Permeability Model

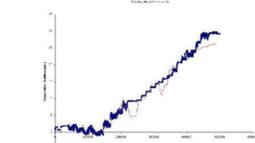
$$k_{r,w} = \left(\frac{S_w - S_{w,c}}{1 - S_{w,c}} \right)^2 \left(\frac{S_w}{1 - S_{w,c}} \right)^2$$

$$k_{r,n} = \left(\frac{S_n - S_{n,c}}{1 - S_{n,c}} \right)^2 \left(\frac{S_n}{1 - S_{n,c}} \right)^2$$



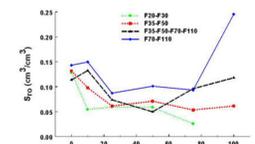
History Matching of Transient Outflow

- Transient Outflow Experiment
- Direct Problem - Numerical Simulator
- Indirect Problem - Nonlinear Least Squares Optimization Routine



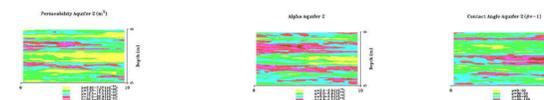
Entrapment

Residual PCE saturations for indicated fractional wettabilities and porous media sieve sizes.

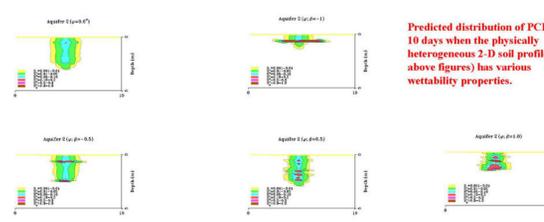


Numerical Simulations

A two-dimensional multiphase flow simulator has been adapted to explore the influence of coupled physical and chemical heterogeneity on DNAPL migration and entrapment in the saturated zone.



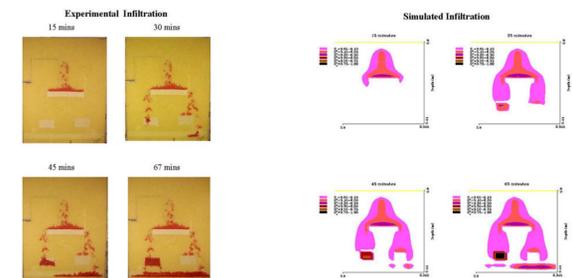
The turning bands method is used to generate an intrinsic permeability distribution with a specified mean and covariance structure (left). Leverett scaling is used to relate capillary properties to the permeability distribution (center). Spatial distributions of chemical heterogeneity are obtained through correlation to the permeability distribution or by specified input (right).



Predicted distribution of PCE after 10 days when the physically heterogeneous 2-D soil profile (see above figures) has various wettability properties.

In coupled physical and chemical heterogeneous systems, simulations suggest that spatial variations in wettability can have a dramatic impact on DNAPL distributions. 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.

PCE Infiltration Experiments



DNAPL-wet layers behave as a very effective capillary barrier, retaining DNAPL and inhibiting its downward migration.

Conclusions

- pH driven changes in speciation, partitioning, and sorption of surface active compounds can significantly influence NAPL interfacial tension and wettability characteristics
- NAPL hydraulic properties depend strongly on subsurface chemical heterogeneity (aqueous chemistry and solid phase mineralogy)
- Residual NAPL saturation tends to decrease with increasing mean grain size and for intermediate wetting conditions
- Interfaces of capillary property contrast lead to higher NAPL saturations, increased lateral spreading, and decreasing depths of NAPL infiltration

Benefits

- Improve our understanding of DNAPL fate
- Enhance the accuracy and flexibility of numerical simulators
- Aid in the characterization of DNAPL waste sources and fate
- Improve the estimation of remediation costs.
- Facilitate the selection of efficient remediation strategies
- Development of innovative technologies for DNAPL remediation and containment

Information Access

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