Behavior of Dense Immiscible Solvents in Fractured Clay-rich Soils
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Relevance to DOE

This research addresses the goals and missions of several initiatives within DOE, including the plumes and mixed waste focus areas within EM-50. Two of the most important issues facing managers of DNAPL-contaminated sites in fractured, clay-rich deposits are the nature and distribution of DNAPL sources in these materials, and the potential for natural attenuation of plumes derived from these sources. If DNAPL near the site of a spill is found primarily in the larger fractures, there may be some reasonable possibility of recovery of the free-product. However, initial investigations indicate that some DNAPLs may be capable of invading the pores of the fine-grained matrix as an immiscible phase, which would greatly decrease likelihood of recovering much of the free-product. As well, the experiments show that dissolution of the DNAPL and transfer to the fine-grained matrix by diffusion is much more rapid than previously expected. Both of these preliminary findings indicate that DNAPL source removal in fractured clay-rich deposits is likely to be a difficult and slow process. This effects the entire issue of whether DNAPL source zone removal will be considered Technically Impracticable (TI) for methods other than excavation or very aggressive steam/heat/volatilization treatments. The issue of natural attenuation of dissolved phase plumes derived from DNAPLs in fractured clay-rich deposits is still at an early stage of investigation, but there are some promising signs. The first field site to be investigated, at Oak Ridge National Laboratory, shows the presence of TCE degradation products in the shale bedrock just below the saprolite and activity of methanotrophic bacteria, which are often associated with degradation of DNAPLs. Field and laboratory investigations are underway to examine the processes and determine whether the products are indeed due to natural degradation.

Goals and Objectives

The overall goal of the research program is to develop a better understanding of the physical and chemical factors and processes influencing fate and transport of immiscible and dissolved-phase dense solvents in groundwater in fractured, highly weathered clays and shales. These widespread materials are much different, physically and chemically, from granular soils or fractured low porosity rocks, which are the media used for most previous investigations of solvent behavior. The investigations are needed to provide a basic scientific framework for assessment of solvent transport and remediation in fractured clay-rich deposits. Specific experimental objectives include:

1. Determine the nature and distribution of porosity in these materials, and its influence on pressure-saturation behavior for immiscible solvents. This includes determining values for entry pressure, residual saturation, fracture aperture and matrix pore size distribution, as well as assessment of methodologies for measuring/characterizing these parameters.

2. Determine the influence of dissolution, sorption and diffusion into the matrix on long term disappearance of residual solvents in the fractured materials.

3. Assessment of the potential for natural attenuation of common solvents, especially TCE, in these deposits. This includes investigating the natural geochemistry and microbiology of the deposits, and assessing biologically-mediated degradation of solvents in the laboratory and at existing contaminated field sites.

Research Progress

Immiscible Phase Entry and Pressure/Saturation Saprolite Experiments

Air/water entry and pressure-saturation curves have been experimentally measured for an undisturbed column sample of fractured shale saprolite from the Melton Branch experimental site near Oak Ridge National Laboratory (ORNL). These are the most reliable and precise values ever measured in such a material and give a detailed picture of the influence of the pore size distribution in the undisturbed material. Preliminary evaluation of the drainage data indicates that as expected, the largest fractures and/or root holes in the saprolite allow initial entry of air at a pressure significantly lower than that predicted by the calculated hydraulic aperture. Air entry pressures indicate maximum aperture size of 250 to 280 µm, which is much larger than the hydraulic aperture value of 70 µm. This difference is expected because hydraulic aperture values represent an "average" for the entire sample, while air entry values represent the size of the largest fracture. The values clearly show that estimates of DNAPL migration based on hydraulic aperture values are likely to underestimate the actual degree of penetration. Air entry to the fine-grained matrix occurred at approximately 160 cm head of water, which suggests that DNAPLs may also enter the matrix at relatively low pressures. The imbibition curve for the air/water fluid pair has been measured and is currently being evaluated. DNAPL/water entry and pressure-saturation curves are presently being measured for the same soil sample using Fluorinert, a non-hazardous DNAPL. Fluorinert was chosen as a surrogate for TCE partly because of its very low solubility, which allows high resolution pressure-saturation behavior to be experimentally investigated without the having to account for mass losses due to dissolution. Following completion of the air/water and DNAPL/water experiments the data will be compared to determine whether DNAPL/water behavior can be predicted from air/water data. The potential advantage of this approach would be that air/water saturation tests could be carried out safely in the field and possibly be used to predict DNAPL/water behavior.

Real Time Radiography - Fracture Visualization in Saprolite

Investigators from ORNL have initiated studies to visualize the fracture network in undisturbed columns of saprolite collected from ORNL. Initial attempts at fracture visualization were conducted using the Real-Time Radiography (RTR) X-ray facility at ORNL. These tests demonstrated that the X-ray equipment could distinguish air-filled fractures from water-filled, but with limited spatial resolution. Further tests will be carried out to determine whether the system will be able to distinguish between water-filled and TCE-filled fractures. We are also in the process of developing a computed tomography (CT) scanning methodology that will be used to visualize the three-dimensional fracture network. CT imaging is expected to provide a finer spatial resolution and, because CT imaging detects density differences, it will likely be better suited to distinguishing between water- and TCE-filled fractures or pores.

Matrix Porosity and Pore Size Investigations in Saprolite

Investigations of porosity and pore size distribution were carried out using saprolite matrix samples from the Melton Branch field site. The investigations used mercury and helium porosimetry methods that have recently been adapted by Drs. J. Dorsch and J. Katsube for investigating the fine pore structure of weakly consolidated mudrock and mudrock saprolite. The study indicates that the effective porosity of the analyzed specimens ranges from 14.0% to 51.4% (based on mercury porosimetry), and from 18.2% to 58.0% (based on helium porosimetry); the grain density ranges from 2.77 g/ml to 2.81 g/ml, whereas the bulk density ranges from 1.27 g/ml to 2.29 g/ml. These values fall between those for saprolite m&rock-fragments and saprolite groundmass from the Nolichucky Shale on the Oak Ridge Reservation, which was analyzed previously. The exception is one specimen with abnormally high effective porosity values and an abnormally low bulk-density value; this specimen most likely indicates more severe weathering which apparently, however, is not tied to the location of the specimen with respect to the present-day surface, but to a difference in lithology instead. Pore-throat sizes of the saprolite specimens range from 3 nm to 8000 nm. Most specimens display a rather broad distribution of pore-throat sizes with one mode (also some weakly developed secondary modes), either skewed to the right or to the left. The shapes of the distribution curves again fall between the shapes encountered for the Nolichucky Shale saprolite (groundmass and mudrock-fragment specimens). The most weathered specimen, however, displays one very pronounced mode commensurate with the vast majority of pore-throat sizes being larger than 1000 nm.

In the studied interval lithologic heterogeneity has proven to be very important. Coherent and rather hard saprolite mudrock-fragments indicate clearly a siliciclastic mudrock as the dominant unweathered precursor. Coherent and blocky, but rather soft and light saprolite fragments probably had a marlstone as an unweathered precursor, whereas plastic-soft clay material is usually linked to a more pure limestone precursor, now completely dissolved away. The petrophysical data summarized above were obtained from the volumetrically most abundant saprolite types: the mudrock fragments and the blocky-light material. The specimen with the abnormal petrophysical values might have been a marlstone with a higher carbonate content, which was lost completely during the chemical weathering.

Microbiological Characterization and Potential for Solvent Degradation in Saprolite

The microbiological characterization and potential degradation of DNAPL in saprolite are being investigated. Biodegradation of organic solvents will depend on whether the solvent exists as a DNAPL or in the dissolved phase and how it is distributed in the deposit (i.e. in fractures, in matrix, sorbed to soil organic, sorbed to soil minerals). Other factors influencing biodegradation of TCE in the soil includes contaminant bioavailablity, the presence of suitable microorganisms, suitable pH and necessary cofactors (nutrients, oxygen inducers, etc.), and the toxicity of the DNAPL and its daughter products. The biodegradation will initially be investigated in a series of batch microcosm experiments and samples of saprolite for initial batch microcosm studies have been collected and characterization begun. The testing will include total aerobic and anaerobic bacterial enumeration, DNA extraction and analysis to determine which degradative genes are present, and mRNA to determine which genes are active. All experiments will be done on bulk material as well as on

fracture surfaces. These will be followed by a DNAPL spill in a large undisturbed column of saprolite, which will then be slowly flushed with clean groundwater for several months to a year. During this period the effluent will be monitored to determine dissolution rates and to look for degradation products. Collection and setup of a preliminary undisturbed saprolite column sample has been carried out and the system is being tested for hydraulic properties and chemical characteristics of the materials to ensure compatibility with the solvents (mainly TCE) used in the experiments. This includes testing and calibration of the necessary sampling and analytical equipment.

Natural Attenuation Field Site in Shale and Saprolite

Investigators at ORNL have preliminary evidence suggesting that natural attenuation processes are controlling the fate and transport of TCE and PCE at a contaminated site in the shale bedrock immediately below the saprolite on the Oak Ridge Reservation. The flow and transport processes at the site have been extremely well characterized in previous studies and recent investigations have begun to characterize the indigenous DNAPL and LNAPL plumes that exist at the site. Significant concentrations of TCE, DCE, VC, and toluene are present within the matrix and fracture regimes of the subsurface media. The concentration of degradation products appears to be 10-50X larger than the concentration of TCE and PCE, which is indicative of degradation. Other indicators of degradation are the presence of methanotrophs and the low levels of methane in the groundwater. Previous evidence presented in the literature indicates that TCE can be degraded by methanotrophs as they consume methane. There is also elevated chloride concentrations at this site relative to neighboring uncontaminated sites, possibly due to TCE degradation. Future research will characterize the spatial and temporal distribution of the DNAPL/LNAPL plumes within the fracture and matrix regimes at the site, and correlate these findings with the microbial ecosystem and groundwater geochemistry present at the site.

TCE Entry and Dissolution Experiments in Till

A cylindrical sample, 0.5 m in diameter and 0.5 m in length. was excavated from a depth of 3.7 to 4.2 m below ground surface in a surficial deposit of desiccation-fractured glaciolacustrine clay. Hydraulic testing provided a saturated hydraulic conductivity of 7×10^{-10} m/s, which is only slightly larger than the matrix hydraulic conductivity. The cubic law applied to this flow test in the conventional manner gave a mean aperture of 4 to 6 µm for the four continuous vertical oxidation-stained fractures in the sample. A column of TCE DNAPL imposed incrementally at the top of the sample provided an entry-pressure-derived aperture equal to 17 µm for an idealized parallel plate fracture. After visible DNAPL breakthrough at the bottom of the sample at 12.5 days, a subsequent 10 day shut-in period was imposed to allow solute diffusion with no advection. The sample was then cut into five horizontal slices for subsampling using a miniature coring device to delineate the diffusion halos of aqueous plus sorbed TCE in the matrix along the fractures where DNAPL had flowed. These halos indicated that DNAPL flowed only through some of the visible, oxidation-stained fractures and that this flow was limited to preferential paths or channels within these fractures. Flow was isolated to only approximately 10% of the total fracture plane. Using the previous hydraulic test results and applying the cubic law only to the aperture segments of apparent

DNAPL flow, an equivalent hydraulic aperture of 7.5 to 12 µm was obtained, which is greater than the conventional mean hydraulic aperture and smaller than the local aperture determined from the DNAPL entry pressure. These differences are large in the context of fluid flux, which is proportional to the aperture cubed. It is unlikely that the presence of such small fractures would be identified in the field using hydraulic test because the bulk hydraulic conductivity of the clay is so close to the matrix conductivity. However, the rapid passage of solvent DNAPL through the fracture network in the column indicates that small-aperture fractures that would probably go undetected at many field sites may allow passage of solvent DNAPL.

Summary of Research Accomplishments

- completed measurements of matrix porosity and pore size distribution in shale saprolite using mercury and helium porosimetry

- measured hydraulic aperture values and air/water entry aperture values and pressure-saturation behavior in a column sample of fractured shale saprolite. DNAPL/water measurements are in progress

- found preliminary evidence that natural intrinsic bioremediation is controlling the fate and transport of DNAPL in a contaminated fractured shale bedrock at ORNL

- measured TCE DNAPL entry pressure and resultant DNAPL entry aperture for column of fractured till and investigated DNAPL channeling within the conductive fractures

- experimentally determined that a typical DNAPL, in this case TCE, can enter and rapidly travel through very small fractures (< 17 µm) in an undisturbed clay till, under applied heads that are typical of field conditions

- found conclusive experimental evidence that dissolution of DNAPL residuals in fractures in clay till and significant diffusion into the clay-rich matrix can occur over relatively short periods (in this case 22.5 days)

Publications, Theses and Abstracts

Related Peer-reviewed Publications (includes those based on closely-related work that began before the present contract)

Hinsby, K., L.D. McKay, P. Jorgensen, M. Lenczewski, and C.P. Gerba, Fracture aperture measurements and migration of solutes, viruses, and immiscible creosote in a column of clay-rich till, Ground Water, 34(6), 1065-1075, 1996.

Allen-King, R.M., L.D. McKay, and M.R. Trudell, Organic carbon dominated TCE sorption in a clay-rich glacial deposit, Ground Water, 35(l), 124-130, 1997.

O'Hara, S.K., B.L. Parker, P.R. Jorgensen and J.A. Cherry. (In Preparation) Trichloroethene DNAPL flow and mass distribution in naturally fractured clay 1: Evidence of aperture variability. For submittal to Water Resources Research.

Theses

O'Hara, SK., Solvent DNAPL flow and matrix diffusion in natural fractured clay: A large column experiment, MS thesis, Univ. of Waterloo, Ontario, Canada, 1997.

Conference Abstracts and Papers

Cropper, S., L.D. McKay, Investigations of air and DNAPL entry in saturated columns of fractured shale saprolite, 41st Annual Midwest Groundwater Confer., Lexington, KY, Sept 29-Oct 1, 1996.

McKay, L.D., An overview of contaminant transport in fractured clay-rich deposits, GSA Annual Meeting, Denver, CO, Oct 28-31, 1996.

O'Hara, S.K. and B.L. Parker. Laboratory study of the effects of molecular diffusion on solvent DNAPL flow in naturally fractured clay using large columns. Presented at the Canadian Association on Water Quality (CAWQ) 32nd Central Canadian Symposium on Water Pollution Research, Burlington, Ontario, Feb 10-11, 1997.

Cropper, S., L.D. McKay, Investigations of air and DNAPL entry and migration in large columns of fractured shale saprolite, 7th TN Water Resour. Symposium, Nashville, TN, Feb 24-26. 1997.

McKay, L.D., Investigations of DNAPL behavior in fractured clay-rich deposits. Annual Meeting of the Solvents in Groundwater Consortium, Toronto, Ontario, October 6-8, 1997.

O'Hara, S.K. and B.L. Parker. Laboratory evidence for fluid channeling in natural fractures using chlorinated solvent DNAPL. GSA Abstracts with Programs, Vol. 29, No. 6, October, 1997.

Cropper, C.S., and L.D. McKay, Investigations of air and DNAPL entry and migration in large saturated columns of fractured shale saprolite, Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Confer. sponsored by API and NGWA, Houston, TX, Nov 12-14, 1997.