Environmental Management Science Program

Project ID Number 55083

Behavior of Dense, Immiscible Solvents in Fractured Clay-Rich Soils

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June 1, 1998

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Research Objective

This research project addresses the nature and and distribution of DNAPL sources (typically chlorinated solvents) in fractured clays or shales and the potential for natural attenuation of plumes derived from these sources. Specific goals include: 1) determining whether typical DNAPLs can penetrate fractures and the fine-grained matrix pore structure for head values within the range expected for a typical DNAPL spill; 2) investigate methods of measuring or estimating fracture or matrix entry pressure and pressure-saturation curves for these materials; 3) experimentally determine whether DNAPL residuals in fractures can be significantly depleted by dissolution and diffusion into the fine-grained matrix over the time-frame relevant to many contaminant investigation and remediation programs; and 4) assess potential for natural attenuation of common DNAPLs (TCE and its degradation products) in these deposits. Preliminary investigations indicate that DNAPL source removal will be a much more difficult and slower process for fractured clay-rich deposits than for granular deposits. These basic research investigations are needed to build the scientific framework for assessment of remediation options or for determining whether remediation, at least for the source zone, should be considered Technically Impractible (TI).

Research Progress and Implications

This report summarizes progress made during the first 1.7 years of a 3-year project. The project investigates the behavior of DNAPLs in two fractured clay-rich materials: weathered shales at Oak Ridge National Lab. in east Tennessee; and weathered glacial till in southern Ontario. The materials, although very different in origin, are similar in terms of fracturing, porosity and hydraulic conductivity and DNAPLs are expected to behave in similar fashions in the two materials. This allows the researchers to share their expertise, as well as helping to determine whether the findings of these studies are applicable to a broader spectrum of fractured clay-rich materials. Results to date for the major sub-projects are briefly described below:

Weathered and Fractured Shale Column Experiments

Air/water and DNAPL/water entry and pressure-saturation curves have been experimentally measured for an undisturbed column sample of fractured weathered shale from Oak Ridge National Laboratory (ORNL). The DNAPL used for the experiments was a non-hazardous compound manufactured under the trade name Fluorinert FC-40. Preliminary evaluation of the results indicate that air/water data can be used, along with appropriate scaling factors based on the differences in fluid properties, to estimate DNAPL behavior. This is significant, because it raises the possibility that field scale air/water measurements could be used as a non-hazardous means of predicting DNAPL/water relationships. At capillary pressure head values of 5-8 cm the DNAPL first entered the fractures and at 160-210 cm it began to enter the fine-grained matrix. These are well within the range of head values expected for even a small DNAPL spill, so it indicates that at many sites DNAPL is likely to

enter both the fractures and the matrix. Investigations of pore size distribution using mercury porosimetry indicate that pore-throat sizes range from 3 nm to 8000 nm, which are smaller than the maximum size indicated by the column experiments, but this is likely related to the small size of the samples used for porosimetry.

DNAPL Natural Attenuation Field Site in Shale and Weathered Shale

A field facility at the Oak Ridge National Laboratory is serving as an extraordinary example of how natural attenuation processes can reduce the off-site transport of chlorinated organics in a fractured and slightly weathered shale. The field facility consists of a 35 m long transect of multilevel sampling wells located in a discharge zone adjacent to existing waste trenches that contain organic contaminants. The wells indicate the presence of a fast flowing fracture regime and a fine-grained matrix regime with very slow flow. VOC and dissolved gas concentrations are highest in two large waste trenches located directly upgradient from the monitoring wells. Along the monitoring transect there is a decrease in solvent concentrations with distance from the trench, with TCE disappearing approximately 10 m from the end of the waste trenches and 1,2-DCE disappearing 35 m away, just before the groundwater discharges from a seep. VC and ethylene are still present at the seep, with ethylene showing peak concentrations at this locale. These results are strong indicators that anaerobic reduction of the chlorinated organics is occurring. In addition, the presence of high concentrations of methane throughout the site is also an indication of anaerobic conditions. Since ethylene concentrations are 100 fold larger than the chlorinated organics, the extent of anaerobic reduction is extraordinary. Another interesting finding is that the concentration of chlorinated organics is slightly higher in the matrix relative to the fracture regime, whereas the concentration of ethylene is lower in the matrix relative to the fracture regime. These results suggest that the fracture regime is slightly more effective in the anaerobic reduction of the chlorinated organics. Temporal variability of TCE and its degradation products is slight, with a general increasing concentration trend of chlorinated organics and dissolved gases as the site hydraulic gradient increases (a response to increased storm events during the winter and spring months). This may imply that the intrinsic bioremediation scenario at the site is less effective at higher discharge rates. Bacterial population data collected from the site indicate various populations of methanotrophs, total heterotrophs, and some sulfate reducing bacteria. The methanogenic population was not determined. The presence of methane oxidizers (methanotrophs) suggests possible zones of oxygenated groundwater which is confirmed with on- site DO measurements. Thus it appears there are two mechanisms of biological removal of chlorinated organic compounds occurring at the site. One pathway involves anaerobic dechlorination of TCE to VC and ethylene, and the other pathway involves oxidation of TCE to ethane via methane-oxidizing bacteria. Since both ethane and VC are present as possible degradation products of TCE, it is probable that both mechanisms are operative. At present it is not clear whether these processes are operating mainly in the relatively unweathered bedrock, where most of the wells are located, or whether they are also active in the upper few meters of highly weathered shale.

Fractured Till Column Experiments

An initial laboratory investigation of entry of immiscible TCE into a large (0.5 m x 0.5 m) cylindrical sample of fractured till, and its subsequent dissolution and diffusion into the matrix has been completed and a manuscript based on this research has been submitted to a major journal, Water Resources Research. After hydraulic testing of the sample, which yielded a mean hydraulic fracture aperture of 5 to 6 μm, immiscible-phase trichloroethene (TCE) was introduced to the column by incrementally increasing the head until entry occurred, which was followed shortly afterwards by discharge of TCE out of the bottom of the column. The entry-pressure corresponded to a calculated fracture aperture of 17 μm, which although larger than the hydraulically-determined value is still consistent, because it represents the aperture of the largest fractured, rather than an “averaged” value. The sample was allowed to sit for approximately three weeks and then was dismantled and the distribution of immiscible phase TCE in the fractures was determined by mapping of the dyed-TCE. Distribution of the dissolved phase TCE was determined using a miniature core sampling technique and subsequent extraction of dissolved TCE from the cores. After less than 1 month,

there was very little TCE remaining in the fractures. Concentration measurements from the miniature core samples showed that most of the mass of TCE had dissolved and diffused in the matrix where it formed a “halo” around the fractures. This rapid disappearance has several major implications for detection and clean-up of DNAPLs in fractured clays: first, the absence of immiscible DNAPL in monitoring wells or cores samples does not necessarily imply that the well or borehole has missed the DNAPL source zone; and second, remediation strategies aimed at removing the immiscible phase DNAPL are likely to be ineffective if there has been sufficient time since the initial spill for a significant portion of the DNAPL mass to diffuse into the matrix. Once in the matrix the dissolved DNAPL can still diffuse back into the fractures, but its removal will be largely diffusion-controlled.

Planned Activities

Weathered and Fractured Shale Column Experiments - two series of column experiments are in the preparation stage. The first will be to determine whether TCE residuals in fractures are rapidly depleted by dissolution and diffusion, as was observed in the experiments in fractured till. The second experiment will involve a simulated TCE spill in an undisturbed column of fractured and weathered shale, followed by flushing of the column with clean groundwater for a period of approximately one year to simulate natural flushing or remediation using pump and treat. The effluent will be monitored for TCE and degradation products and a mass balance will be carried out. Related to this, microcosm studies of TCE degradation and sorption will be carried out using the weathered soil to further study factors influencing the fate of the spilled TCE.

Natural Attenuation Field Site - This year we are planning to further characterize the plume and conduct a survey of bacterial populations in the groundwater using 16s rDNA analysis. The objective is to link specific bacterial populations with anaerobic dechlorination of TCE and its daughter products.

Till Columns - A second fractured till column is being set up for carrying out a multi-component DNAPL injection, to examine the influence of mixtures on entry-pressure and dissolution.

Other Access To Information

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