Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

Project ID: 55395

Stephan H. Conrad, Sandia National Laboratories

Robert J. Glass, Sandia National Laboratories

Executive Summary

Spilled solvents have created pervasive groundwater contamination problems across the DOE complex because of their ubiquitous use, their toxicity and persistence in the environment, combined with the difficulty of recovering them from the subsurface. Because organic solvents are more dense than water and immiscible with water, they are commonly referred to as DNAPLs (dense non-aqueous phase liquids). They migrate below the water table downward and laterally under the influence of gravity, capillary, and viscous forces. Variations in media texture that the DNAPLs encounter as they migrate can have a profound influence on the migration path. This interplay between textural heterogeneities and driving forces complicates the migration of the DNAPLs and therefore it is not straightforward to predict the locations in the aquifer at which the spilled DNAPLs may ultimately reside. Uncertainties in the region of solvent contamination translate into higher remediation costs as the remedial system must be designed in light of these uncertainties. In an effort to clean up spilled DNAPLs, several remediation approaches are currently under development. Chemically enhanced solubilization, alcohol displacement, in situ oxidation, and air sparging are among the most promising. Many of these techniques have already undergone preliminary field demonstrations. However, results from such field demonstrations cannot be extrapolated to predict remedial performance under the wide range of field conditions to be encountered at spill sites across the DOE complex. Indeed, these techniques have not yet had the opportunity to be sufficiently tested and quantitatively compared in well-controlled laboratory experiments under heterogeneous conditions indicative of what can be expected in the field. In addition, the numerical simulation techniques used to predict DNAPL migration and remediation treatments have yet to be adequately verified through comparison against laboratory experiments conducted in heterogeneous media.

Research Objective

Our research effort has been designed as broad and crosscutting. The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. There are two major aspects to the DNAPL problem: finding them (migration) and cleaning them up (remediation). We have been working on both. By designing lab experiments within heterogeneous porous media analogous to field conditions, we have been able to directly observe DNAPL initial migration and subsequent interactions between injected remedial agents and the DNAPL. In these experiments we have identified critical mechanisms having important implications affecting both the initial migration and the successfulness of remedial processes.
Research Progress and Implications

For migration, we have found the influence of heterogeneities to yield high DNAPL saturation “pools” of a wide range of sizes, corresponding to the effects imposed by textural variations between geologic facies. These pools are interconnected by fingers where very little DNAPL resides. When viscous forces are low, we discovered the DNAPL structure to pulsate at both the pore scale within fingers and at the unit scale within large pools due to a capillary-gravity pulsation mechanism. We have shown that this pulsation can lead to multiple DNAPL migration pathways in time. We have built pore scale invasion mechanisms into a new modeling approach, a form of Modified Invasion Percolation or MIP model. Our simulations yield results that closely track the migration behavior seen in our experiments. Remediation experiments have shown both the successes and pitfalls of surfactants and in situ oxidation in the presence of even small pools. In the case of IFT lowering surfactants, a capillary bellows mechanism pushes DNAPL from the pool upstream into the flood where it then falls and can become caught within the lowest permeability units where it is bypassed by solubilization. For in situ oxidizers, DNAPL is not mobilized, however, the reaction product builds a low permeability rind around all the pools, isolating them from future oxidation. We also noted that the use of partitioning interwell tracer tests (PITT) to determine DNAPL saturations also has the potential to cause some mobilization of DNAPL from pools. As pools are expected at these and larger scales within any aquifer, such characterization and remediation methods must be used with caution.

From our research, we believe the following “products” and/or increased understanding to be of immediate and critical use to DOE DNAPL spill sites and cleanup efforts:

1. A fundamentally new and physically correct model (MIP) for DNAPL migration has been formulated, implemented and tested. This model can be extended to include the contact angle aging process found in mixed DNAPLs and combined with miscible transport codes to model DNAPL mobilization on IFT lowering and subsequent solubilization.
2. A series of length scales for DNAPL structure (i.e., pool height, finger diameter, and pulsation location) have been derived as a function of capillary, gravity and viscous forces within a heterogeneous media. These length scales can be combined to form the basis of a large scale structural growth model for DNAPL migration as well as the design of remediation applications.
3. The importance of heterogeneity to cause local saturations much higher than residual to be distributed throughout an aquifer has been clearly demonstrated. This multiple scale pool structure will largely control DNAPL migration extent and critically influence remediation attempts. Both DNAPL delineation before remediation and remediation design must be accomplished with this critical structure in mind.
4. Most importantly, we emphasize caution and advocate a restrained approach to site remediation at this time. Use of surfactants that cause excessive IFT reduction can cause the downward mobilization of the DNAPL and its penetration of low permeability layers. Such a scenario may have already happened at DOE site pilot tests. Since full recovery of surfactant is never achieved, the migration of this fluid down gradient will continue to mobilize DNAPL far outside of the region where it was originally used. Thus, all of these remediation approaches must be carefully considered prior to field implementation so that an existing contamination situation is not made worse.

Planned Activities

We have found that liquid phase DNAPL movement in the context of heterogeneities, initially, during redistribution, and subsequently mobilized in the presence of characterization and remediation fluids is the critical determiner of remediation success or failure. Therefore, we now focus our research primarily on liquid phase movement in the context of heterogeneity and place lower priority on the consideration of DNAPL removal due to subsequent solubilization or oxidation. If during remediation, we can keep the DNAPL from mobilizing to undesirable locations, then we believe remediation schemes can be optimized to remove it. Therefore, we must understand and constrain mobilization within the heterogeneous system so that remediation can, “first do no harm.” Since mobilization is brought on by IFT reduction (through the introduction of surfactants or alcohols) and since these
remain among the most promising remedial techniques, we will focus our primary research effort toward continued study of them. However, we will also begin to consider the issue of dirty or mixed DNAPLs and we will construct a demonstration experiment of air sparging in the context of heterogeneous aquifers.

**Information Access (publications)**

Manuscripts submitted for publication, pre-prints available from the PIs:


