EMSP Progress Report:

Physics of DNAPL Migration and Remediation in the Presence of Heterogeneities

Stephen Conrad and Robert Glass
Sandia National Laboratories

Research Summary

We are in the process of conducting well-controlled laboratory experiments to better understand the physics of DNAPL migration and remediation in the presence of heterogeneities. These experiments are being used to develop and test an upscaled percolation model, a new approach for modeling DNAPL migration. In addition, numerical simulators under current use in evaluating remediation techniques will be compared against our remediation experiments. We are making use of our unique experimental capabilities in the Subsurface Flow and Transport Processes Laboratory at Sandia to conduct controlled, systematic, repeatable experiments that first consider the physics of DNAPL migration in initially water-saturated, heterogeneous porous media and then evaluate the efficacy of a suite of promising remediation techniques for remediating DNAPLs from heterogeneous aquifers. The results of the migration experiments are being used to test and continue development of new modeling approaches based on upscaled percolation theory developed by us. The remediation experiments include visual and quantitative measures of each remediation technique's performance. The results of the remediation experiments will be used to test, for the first time, within heterogeneous media, the quantitative performance of remediation design codes (two-phase flow codes that incorporate compositional models).

Research Objectives and Progress to Date

Under each objective, we begin by restating what we promised that we would accomplish over the course of the three year project, followed by a description of the progress to date.

Objective I: Develop fundamental understanding of the physics of DNAPL migration processes within heterogeneous porous media.

1.1 Conduct a suite of two-dimensional thin slab physical experiments within controlled and systematically varied heterogeneous porous media at scales up to one meter. Vary system parameters to consider a range of capillary and bond numbers within these heterogeneous porous structures.

We have made use of our 2D experimental system where we can fully visualize DNAPL migration within a saturated, heterogeneous sand slab. Such 2-D experiments are required because systematic 3-D experiments are prohibitively expensive to conduct. and impossible to monitor to yield DNAPL migration as a function of time at a resolution that yield increased understanding and allows us to test our numerical simulators.

In our experiments we have used silica sands (Accusand as used in OHER's Subsurface Science Program) as they are representative of many aquifers. have a relatively uniform chemistry, allow application of our transmitted light techniques and can be purchased in narrow distributions that allow us to mix up the distributions that we require for systematic variation of two-phase flow properties. The grain size distribution controls the pore size distribution to yield different DNAPL/water pressure saturation curves. In previous work. we found that air/water pressure saturation curves were sufficient to obtain the pore size distributions needed to implement the percolation code. We have measured the hysteretic air/water pressure saturation curves to calculate the pressure distributions for both DNAPL invasion and drainage for the three experimental sands. These properties have been measured in situ within our sand chambers using methods developed in our lab.

We have begun to explore the effects of macro heterogeneities (such as discrete formation-scale features like facies). For one particular heterogeneous structure that we have created. we have conduct a suite of experiments where fluid/fluid inter-facial tension, fluid/fluid density differences and DNAPL invasion rates have been systematically varied to consider a range of relative importance of capillary, viscous, and gravity forces as embodied in the Bond and capillary numbers. Variation in the capillary number has been achieved by varying the flow rate. Because the variation in Bond number is largely controlled by density differences and interfacial tensions, we have run identical experiments using a variety of fluids spanning a range of densities and interfacial tensions. We have conducted a suite of experiments within this one heterogeneous structure composed of three different sands under conditions of low capillary number for three fluid/fluid systems: air/water, Soltrol/water. TCE/water. Interfacial tensions have been measured for the fluid/fluid pairs used in the experiments. The method for predicting the percolation parameters from pressures saturation curves has been refined and simulations of the experiments are largely complete. We have found excellent agreement between the results of these experiments and the results of our percolation modeling. In March, we completed the final TCE experiment needed to write a paper for submission to a technical journal describing this work. Preparation of this manuscript is currently ongoing. We are also in the process of writing a paper that describes how the use of our upscaled percolation model can be used within a Monte Carlo analysis to help determine DNAPL location by creating a probability map of where the DNAPLs might reside. Such a map could be used in conjunction with any DNAPL detection technology to suggest the most profitable sampling locations.

We have also begun to explore the effects of micro heterogeneities (such as micro layering and crossbedding found within lithologic units). Over the course of the summer and fall, we have begun conducting a series of experiments to examine the effects of small scale heterogeneities on larger scale DNAPL migration behavior. We have four objectives for this work:

1. to observe the effect of these heterogeneities on DNAPL migration behavior.
2. to begin to speculate about the role of small-scale heterogeneities on larger-scale migration behavior.
3. to further test the ability of our upscaled percolation model to accurately simulate DNAPL migration.
4. to see if we might be able to propose some reasonable effective properties for field-scale block sizes containing smaller-scale heterogeneities within them.

In an initial series of experiments. micro structures have been varied through their "intensity" in terms of property variation across individual laminae. The "intensity" of laminations is controlled by the grain size distribution supplied to the automated sand filler (the wider the distribution, the greater the "intensity"). One experiment that considers the effect of

microstructures on buoyant immiscible displacements is shown in Figure 2. This experiment is discussed in more detail under objective 1.3 below. Results obtained suggest that the degree of small-scale heterogeneities (in the form of lateral laminations) affect effective block saturations and may well affect accessibility rules for the upscaled percolations. Additionally, in these laminated systems we see that effective block saturations that are much more sensitive to flow rate than in either homogeneous systems or in discrete/macro-scale systems that we have studied previously. In coming months we'll be addressing the implications of this work for percolation simulations of field-scale DNAPL migration behavior.

1.2 Enhance the percolation mode1 to include simultaneous invasion and drainage of each phase within the problem domain. Compare the model predictions to experiments conducted in 1.1 at low capillary number.

In low capillary number systems, there are limits to the DNAPL head that can be built up. Once the head becomes great enough such that the entry pressure at the advancing front is exceeded, DNAPL drainage occurs at the trailing edge. It is not yet known the conditions under which failure to model this simultaneous DNAPL drainage can cause significant errors in simulating migration behavior. It is well known, however, that DNAPL drainage can lead to significant redistribution once the DNAPL spill has abated. In previous work, we have found that new applications of invasion percolation models require experimentation to guide their proper formulation.

The enhancement of percolation model to include this simultaneous invasion and drainage may not be necessary if one is only interested in the final disposition of a spill. It is however required if we are to consider the dynamic evolution of the DNAPL liquid migration in time (or as a function of volume added). Obviously, our development of the percolation model for simultaneous DNAPL invasion and drainage requires iteration and close connection with experiment just as it has in some of our previous work.

Progress to date:

- Code has been written to implement the proposed simultaneous invasion and drainage model.
- We are in the progress of checking the code against a number of test cases to make sure that it is functioning correctly.
- Once this is accomplished, we will begin comparing the code against the experiments that have been conducted to meet objectives 1.1 and 1.3

1.3 Determine the limit of percolation mode1 validity with respect to capillary number. Consider the deviation of model results from both experimental results from 1.1 and simulations with continuum models that include viscous forces.

We expect that most situations of importance to DNAPL movement within an aquifer will be "buffered" from viscous forces. Under many circumstances. DNAPL will have to pass through the vadose zone before slowly building up on top of the water table. When it reaches a height allowing entry into the aquifer, we expect the slow movement and low velocities/capillary numbers to continue. Even in instances where leaks originate at or below the water table. the nature of leaks are such that DNAPL often slowly seeps into the subsurface at low rates that may persist for many years. And of course. viscous pressure gradients will dissipate as the distance from the source increases. In the far field, viscous forces wilt commonly be negligible. Indeed,

these common circumstances are fortuitous for percolation modeling since our percolation model as currently formulated requires viscous forces to be negligible with respect to capillary forces. We have conducted a first set of experiments varying the capillary number in a single heterogeneous sand slab using a gas/water system. In these experiments, we are attempting to determine the bound of validity for upscaled percolation within heterogeneous structures through comparison to experiments conducted in 1.1 where the same heterogeneity structure is created many times and the invasion rate is increased (capillary number increased). Deviation of model results from experimental observation suggest the departure of the upscaled percolation approach from reality at the point at which viscous forces begin to become important.

Initially, we encountered problems with the gravimetric system for monitoring flow rate in these experiments, but these problems have been solved. We have run these experiments under a variety of flow rates representing a range in capillary number of up to two orders of magnitude and results suggest that while viscous forces are of second order in this range, they do influence experimental results in a number of small ways. Consider Figure 1. The left image in Figure 1 shows the heterogeneous sand pack used for these experiments. We injected CO_2 from the bottom to move upward under buoyant, capillary, and (perhaps) viscous forces. The two images to the right show a difference maps of two experiments run under different flow rates. While the overall gross displacement behavior remains consistent with this capillary dominated system. we do note some second order effects. These images were constructed by continuing to take digital images of the experiments once CO_2 had broken through at the top. Using image analysis techniques, each successive image was subtracted from the one previous. Images were recorded once every 7 seconds. At locations where displacements were still occurring, differences from one image to the next capture these displacements. We then summed all these difference images together to construct the difference maps seen in Figure 1 (lighter colors show where most of the action was still taking place). In an entirely capillary dominated system, once CO, breaks through a steady state should prevail and the difference maps would be almost entirely black (that is, very little difference from one image to the next). Indeed. that is precisely what our difference maps show for experiments run at flow rates below 1 ml/min. However, at 1 ml/min we see a pulsing behavior in which coarse regions at the bottom of the experiment alternately fill and drain as pressure builds until blob of gas escapes through a finer-grained constriction. This pulsing behavior is not seen at still higher flow rates (5 ml/min) but the release of “gas blobs” through the middle portion of the model is seen for both the 1 and 5 ml/min experiments.

We have conducted a similar set of experiments for the micro-heterogeneity (lamination) experiments. One example is shown in Figure 2. The image on the left shows the laminated sand pack. The images to the right of the sand pack show CO, displacements from bottom to top at 1 and 5 ml/min. Note here that the displacements are different from one another signifying that viscous forces are playing some role. Animation of the 5ml/min experiment shows multiple fingers forming concurrently. This behavior would not occur in an entirely capillary dominated system.

While we have gone to some effort to show these second-order viscous effects. our overall conclusion has been that relatively high flow rates are needed before viscous forces become an important factor in DNAPL migration behavior. That is, we are gaining confidence that our upscaled percolation code will prove suitable for modeling the vast majority spill situations.

We continue to show good agreement between the experimental and modeling results as the DNAPL flow velocity is increased from one experimental run to the next. These results suggest

that perhaps fairly high capillary numbers are required before viscous effects become non-negligible. The implication of these encouraging results is that the negligible viscous effect assumption in the percolation model will probably not be violated for the vast majority of DNAPL spill situations.

Objective 2: Develop fundamental understanding of the physics of DNAPL remediation processes within heterogeneous porous media

Through our previous work on DNAPL migration, we have developed a unique experimental system where we can reproduce complicated heterogeneity structures. This system also allows us to conduct experiments for the first time that can compare several competing approaches for DNAPL remediation on equal footing. The combination of DNAPL migration studies and DNAPL remediation studies is also critical in that we can provide realistic initial DNAPL emplacement conditions for the remediation experiments. We emplace the DNAPL through a migration experiment as performed within the context of objective 1, followed by a remediation experiment here in objective 2.

Simulators of remediation processes have not been extensively tested. in part due to the general lack of results from controlled experiments. Verified simulators of remediation processes are sorely needed as remedial selection and design tools. And since sufficient geologic detail is almost always lacking, it is important to understand the errors introduced through paucity of geologic detail.

2.1 Conduct a suite of physical experiments within controlled and systematically varied heterogeneous porous media at scales up to one meter that consider air sparging, alcohol flushing, and surfactant flushing remediation treatments

From our DNAPL migration experiments, we have developed some insight as to how DNAPLs will likely migrate through various assemblages of geologic facies. We have been exploring new chamber packing techniques in order to make reproducible geologic structures for these remediation experiments that are plausible on the scale of the experiment and. in addition. can serve as analogue to a field scale situation. In previous work, we have demonstrated the ability to reproduce heterogeneous sand packs and replicate DNAPL migration experiments. To the best of our knowledge, this capability is unique and not available elsewhere.

Of late, we have dedicated serious effort to building the 2’x2’ chamber required to run the remediation experiments. Our initial design was constructed. As is commonly the case with an initial design, we identified some problems. We have since come up with some design solutions, and now we are in the process of constructing the chamber according to the new specifications. In conjunction with this design effort. we have established a protocol – explicit, detailed procedures – for conducting these remediation experiments. Of course. this protocol will likely evolve as we gain experience in running these experiments.

We intend to work closely with the developers of each remediation approach to attempt to optimize the remedial process and show each technique in its best possible light. These experiments will be extremely useful to the remediation developers in helping them understand the physics and chemistry of their remediation processes as they perform under more realistic. less idealized. conditions. Toward that end. in September. Alex Meyer. a professor at Michigan Tech. visited our lab for a week and collaborated with us on a series of experiments looking at

surfactant mobilization and solubilization of DNAPLs. The results of these experiments were very encouraging and the insights gained undoubtedly has helped us design our sand chamber experiments. One example of these experiments is depicted in Figure 3. The image on the left shows a glass micromodel (dimensions 6 inches by 12 inches) with a residual TCE saturation (blue). In the series of three images to the right, the aqueous phase (orange) carries surfactant resulting in the displacement of the TCE. This initially unstable displacement process becomes somewhat more stable over time as the surfactant dissolves TCE it encounters on the lateral sides of the aqueous phase finger. Over time the finger broadens by this process, improving the efficiency of the displacement.

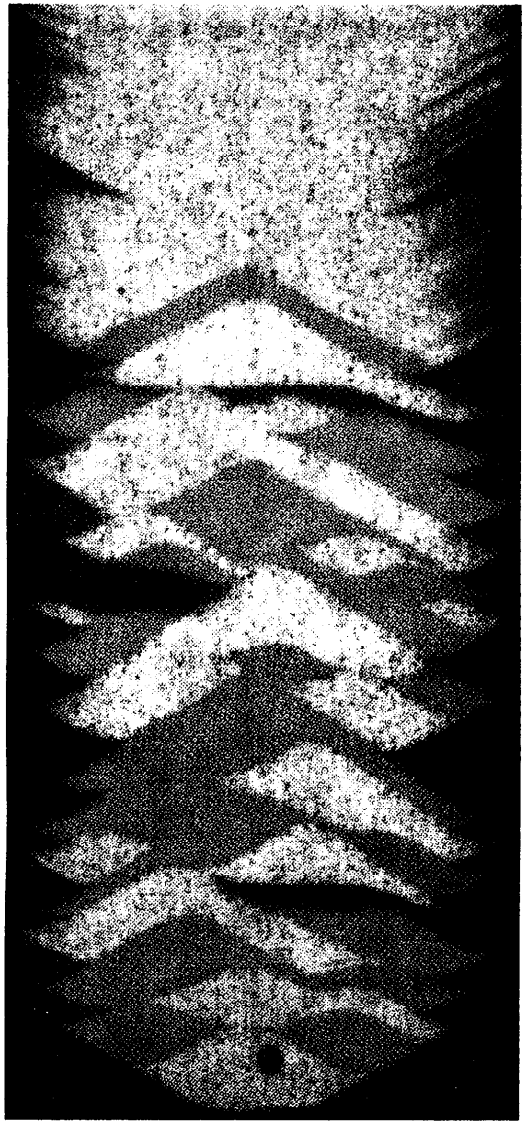
2.2 Apply existing and state-of-the-art compositional models to simulate the results of our remediation experiments

We intend to rely on using currently available models to simulate the remediation processes we observe in the lab. We have identified the model – UTCHEM, a compositional simulator developed by Gary Pope at the University of Texas – we intend to use in attempting to simulate our remedaition processes. We will compare modeling results to the cleanup processes observed in the experiments. Where we identify deficiencies in a model. we will attempt to either suggest or incorporate improvements for the model. Models that are shown to perform well will prove to be extremely useful in designing site-specific remediations, or perhaps as a means for direct comparison between remedial approaches.

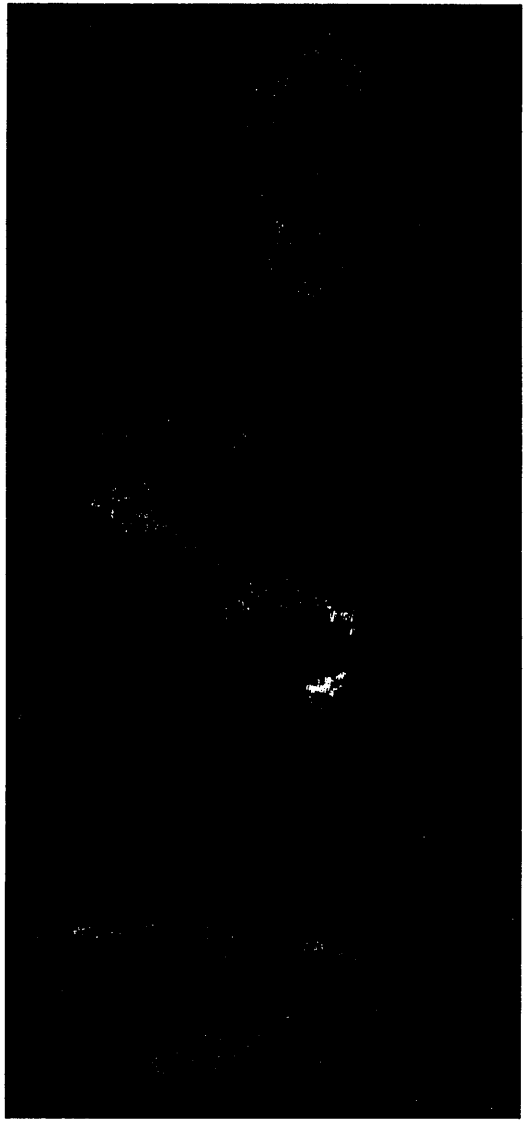
2.3 Develop and test several treatment trains that we hypothesize to yield improved remediation results

In the third year, once we have run the three remedial techniques individually over a wide variety of spill and geologic conditions, we will consider proposing treatment trains for improved cleanup. It is hoped that the strengths of one technique may offset the weaknesses in another. Assuming we observe that this may be the case, we will develop, test. and evaluate promising treatment trains.

Effects of Capillary Number in Heterogeneous Systems



Heterogeneous Sand Pack

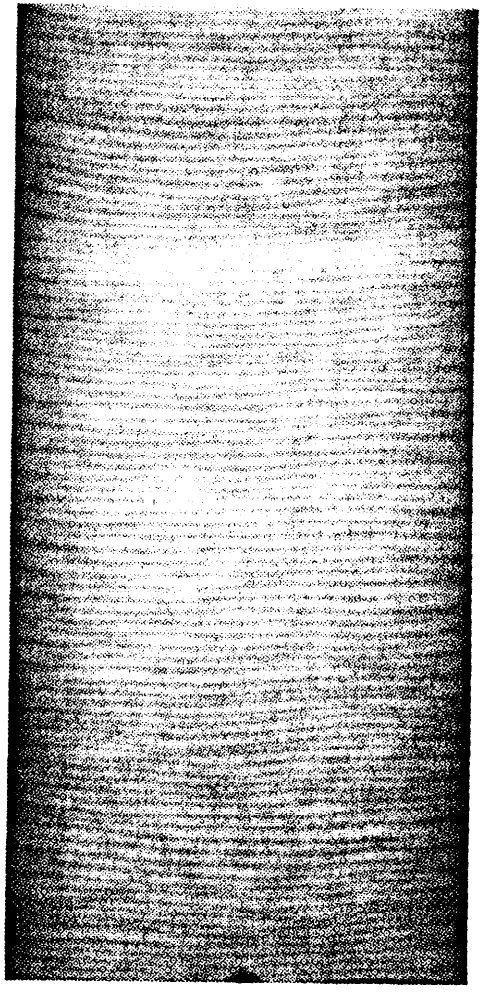


Q = 1 ml/min

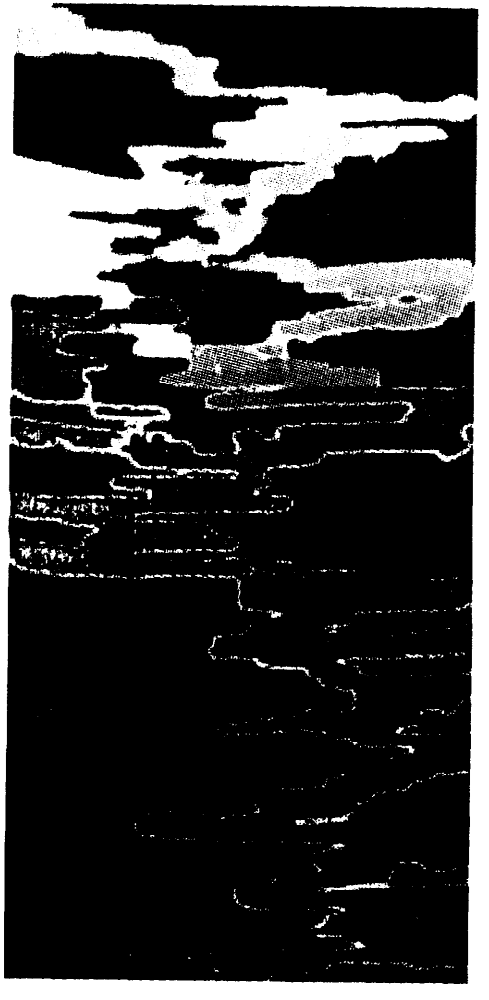
Q = 5 ml/min

Figure 1

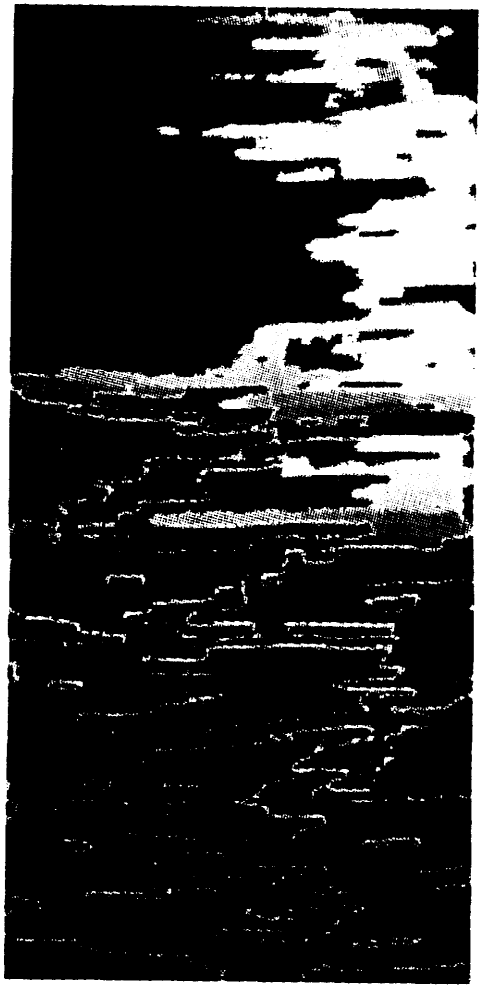
Micro-Heterogeneity Experiment



20-50 Micro-Hetero Sandpack



Q = 1 ml/min



Q = 5 ml/min

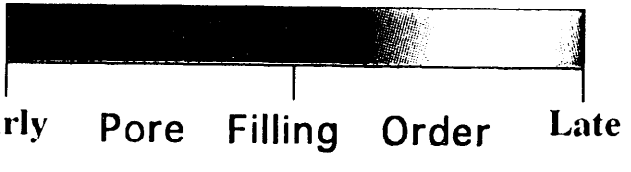


Figure 2

Surfactant Mobilization of Trichloroethylene

Residual TCE **0.25 Pore Volume** **0.75 Pore Volume** **1.5 Pore Volume**

Figure 3