Progress Report

Establishing a Quantitative Functional Relationship Between Capillary Pressure, Saturation and Interfacial Area

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Project Objectives

There is a fundamental knowledge gap associated with the in *situ* remediation of non-aqueous phase pollutants. Currently it is not possible to accurately determine the interfacial surface area of non-aqueous contaminants. As a result it is impossible to 1) accurately establish the health and environmental risk associated with the pollution: 2) precisely quantify and evaluate the potential efficacy of various *in situ* treatment technologies; and 3) conduct reliable performance assessments of the applied remediation technology during and after the clean-up. The global goal of this investigation is to try to remedy these shortcomings through the development of a formalized functional relationship between interfacial area (a), phase saturation (S) and capillary pressure (P,). The development of this relationship will allow the direct determination of the fluid-fluid interfacial area from field measurements.

Quantitative knowledge of the surface area of the non-aqueous phase pollutant facilitates accurate predictions of both the rate of dissolution and the contact area available for treatment. In addition. if saturation and capillary pressure measurements are made during the remediation process. both the spatial and temporal effectiveness of the remediation technology can be quantified. This information can then be used to optimize the restoration program.

The project objective will be achieved through an integrated and focused research program that is comprised of theoretical computational and experimental efforts. These efforts are organized into a framework of four tasks:

1. Improve on newly developed laboratory techniques to quantify and directly measure the functional relationship between phase interfacial area (a). saturation (S) and capillary pressure (P_c).
2. Develop new computational algorithms in conjunction with laboratory measurements to predict P_c, S and *a*.
3. Test existing theory and develop new theory to describe the relationship between P_c, S and *a* at the large scale.
4. Synthesize the results of the experimental. computational and theoretical investigative efforts to develop a generic model based upon an intrinsic soil metric to describe the functional dependence of P_c, S and a.

Project Status

Task 1: Improve on newly developed laboratory techniques to quantify and directly measure the functional relationship between phase interfacial area (a), saturation (S) and capillary pressure (P,)

Accurate. reproducible measurements of fluid-fluid phase area within a porous media over long time periods is technically very challenging. Photoluminescent Volumetric Imaging (PVI), a new optical measurement technique has been applied to this problem. To successfully meet the demands of this research program extensive improvements to the PVI measurement technique had to be made. In particular, significant improvements to the fluorophore-fluid system were needed to ensure the stability of the physical system over the measurement period associated with each experiment (-3 months); the measurement chamber had to be redesigned to both eliminate environmental impacts on the model porous medium and to facilitate independent saturation measurements; the excitation beam optics needed improvement to meet the accuracy requirements for this project; and new image process algorithms had to be development to insure that the generated results could be analyzed and reproduced by investigators not associated with this project.

Approximately twenty fluorophore pairs were evaluated for use in this project. The criteria used for selection of the fluorophores included; 1) an evaluation of the probe's emission and excitation spectrum for potential second order interactions, 2) a comparison of the relative quantum efficiency in solution between fluorophore pairs, 3) the long term chemical stability of the fluorophores, and 4) the diffusion rate of the fluorophores across the fluid-fluid interface. The selected multiphase porous medium uses a 200 nmol concentration of Kiton Red (a laser dye) dissolved first in methanol then in the aqueous fluid OHZB. The non-aqueous fluid in the system is the silicon oil S1056 doped with a 100 nmol concentration of the biological membrane probe DiO dissolved in MEK.

The excitation beam optics were redesigned to reduce the beam waist of the laser light sheet from approximately 33 μm to 17 μm. This afforded improved resolution of the image volume by virtually eliminating the production of measurement degrading out of focus light. To accommodate the changes in the shape of the excitation light beam. the measurement cell needed to be redesigned. In the redesign of the measurement cell we incorporated a system for the independent measurement of the fluid saturations. This provides a quality check on the values of phase saturation calculated from the processing of the image data.

We evaluated two different techniques for extracting the phase interfacial area from the PVI image data, One technique calculated the interfacial area from a summation of an isosurface generated by a 27 point tessellation of the 3-D data set. The other technique extracted the information using a 3-D two point autocorrelation analysis. The results of this evaluation found that for irregular surfaces, such as those found in porous media systems, the autocorrelation analysis had an overall accuracy of approximately 2% in comparison to an accuracy of only 10% for isosurface generated areas. There are also significant savings in manpower and computational costs associated with using the autocorrelation analysis. Consequently, autocorrelation analysis will be the method used to calculated phase inter-facial areas.

One of the major difficulties of extracting quantitative information from image data is image segmentation. Small changes in thresholding the data can result in dramatic differences in the values calculated for phase saturation and interfacial area. For this reason it is often the case that analytical results can not be reproduced when the same data is analyzed by a different scientist. To avoid this pitfall we have spent a considerable amount of energy to develop an automated thresholding mechanism that takes into account variations in image quality between image slices. The result of this effort is an algorithm that permits the results of this program to be reproduced by any investigator.

The first experiment measuring interfacial area as a function of saturation and capillary pressure was completed in August 1997. Results displaying the first ever experimentally determined interfacial area, saturation, capillary pressure surface were presented at the recent *International Workshop on the Characterization and Measurement of Soil and Hydraulic Properties in Unsaturated Porous Media* held in Riverside Ca this past October. A second experiment is currently underway. In addition, efforts are also being made to digitize the PVI measured pore space so that the results of this and following experiments can be replicated in pore network models under development in this program. Detailed descriptions of the improvements to the PVI system can be found in the M.S. Thesis prepared by Weijun Zang. A complete copy of the dissertation is available upon request.

Task 2: Develop new computational algorithms in conjunction with laboratory measurements to predict P,, S and ***a***

The computational effort of this project is focused on the development and application of pore-scale network models to simulate capillary-dominated displacements in two-fluid porous media. These network models explicitly represent all fluid-fluid interfaces within a model porous medium, and track their motion through the network as a function of imposed capillary pressures. Based on the network geometry and on the interface locations, volume-averaged properties such as volumetric saturations, and interfacial areas per unit volume, may be calculated for given capillary pressures. Relative permeabilities may also be calculated using an assumption of laminar flow within each continuous fluid phase. Therefore, these detailed pore-scale network models provide functional relationships between the volume-averaged variables capillary pressure. saturation, interfacial area, and relative permeability (k,). These models can be used to test various theoretical conjectures regarding two-phase flow in porous media; in turn, these models can be tested by comparison to laboratory experiments.

We have developed computational network models that use two different geometric representations for the pore space. The first is based on spherical pore bodies connected to neighbor pore bodies by bi-conical pore throats, with the pore bodies arranged in a regular lattice pattern (we have used a cubic lattice). The second geometry is based on extraction of the complete pore structure from a packing of solid spheres. To this point, we have restricted the spheres to be mono-sized.

During the first year of this project, we focused on the following areas: (1) Completion of testing and application of the bi-conical pore-scale model for two-fluid displacement, including comprehensive sensitivity analysis and predictions of interfacial areas; (2) Specific applications of the bi-conical model to test certain theoretical conjectures related to interfacial areas, as proposed by co-investigator W.G. Gray; (3) Completion of a sphere-pack-based network model; (4) Testing of the sphere-pack model by comparison to experiments; (5) Application of the sphere-pack model to calculate interfacial areas; and (6) Development of plans to extend the network model to digital geometries. Many of the details of these accomplishments are described in the PhD dissertation of Paul Reeves. A complete copy of the dissertation is available upon request.

Task 3: Test existing theory and develop new theory to describe the relationship between P_c, S and a at the large scale

Although the research involves all three aspects of the problem, the time frame for the experimental work is longer than for the network and continuum modeling. Therefore, in this first year of work, the effort of the continuum approach has been focused primarily on making connections with the network model. During the first year of the research, the following tasks have been addressed:

- Development of an explicit description of the steps that must be undertaken to obtain a model with minimum arbitrariness.

- Derivation of the common line equations of mass, momentum, and energy conservation and of the entropy inequality of the system that includes the common lines.

- Formulation and implementation of a thermodynamic approach that eliminates ambiguity in the description and arbitrariness of selected functional dependence of energy at the macroscale.

- Development of a procedure for relating geometrical quantities such that functional dependence of equation coefficients (such as capillary pressure) are determined and can be extracted from the network models for examination.

- Initial linearization of the flow equations for simple systems that serve as an introduction to the procedure to be implemented for more complex systems.

The developments made in the theoretical framework are allowing for productive interaction with the network modeling effort and will assist in ensuring that parameters measured in the experimental work are appropriate and helpful.

Task 4: Synthesize the results of the experimental, computational and theoretical investigative efforts to develop a generic model based upon an intrinsic soil metric to describe the functional dependence of P,, S and *a*

Currently we have insufficient experimental and computational data to begin work on Task 4. It is anticipated that by the middle of the second project year we will have the information necessary to begin work on this task