1 of 1

PROGRESS REPORT**Experimental Assessment and Modeling of Organic Compound Interphase Mass-Transfer Rates in Multiphase Subsurface Systems****Co-Principle Investigators**

Walter J. Weber, Jr.
Linda M. Abriola

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Department of Energy
Grant Number: DE-FG02-89ER60844

March 15, 1990

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

During the initial eight month period of this grant, work has been conducted on all facets of the project. Significant progress has been made in the design, construction and testing of the experimental apparatus. Investigation of methods for characterizing the physical forms of non-aqueous phase liquid (NAPL) residuals (globules or 'blobs') has led to a narrowing of possible approaches. Development of a numerical simulator that accommodates multiphase transport with mass transfer rate interactions is well underway.

Experimental Apparatus

The experimental apparatus and instrumentation for the NAPL dissolution experiments has been purchased and assembled. To provide dedicated laboratory space for the interfacial area experiments, which will be run in parallel to these column studies (see discussion below), a recycle hood was also purchased with grant funds. The initial experimental design is consistent with details described in the proposal.

A schematic of the experimental setup is shown in Figure 1. Dissolution experiments are conducted in a 15-cm diameter glass column that is designed to accommodate adjustable sand depths between 5 and 100 cm. It is planned to perform experiments with a variety of well-sorted and well-graded sands. The bottom sand support is an innovative composite of porous teflon and glass frits that enables separation of water and NAPL effluents. This separation provides for independent estimates of residual saturation and mass balance checks. Presently the top sand support is a thin layer of large diameter glass beads intended to aid in distributing flow uniformly across the sand column.

Residual saturation of the NAPL is established in the sand by sequentially introducing water and NAPL with a high pressure pump designed to provide accurate flow over a large range of resistances. The distribution of NAPL blobs is measured by gamma ray attenuation. A relatively low cost temporary support stand has been constructed to facilitate the NAPL saturation measurements designed to gain preliminary information upon which more refined tests can be predicated. The column is mounted in the center of a rigid stand, and the gamma source and detector are mounted on a frame that moves both vertically and radially. Gamma ray attenuation measurements are attainable over the entire soil thickness and through all vertical cross sections. It is anticipated that experience with the performance of this apparatus in the initial experimental phase will lead to design and fabrication of a more sophisticated support stand in the second year of this award period. Budget funds have been allocated for this purpose. The improved design will facilitate computer control of the equipment and experiments.

Once residual saturation of NAPL has been attained, a constant water flux is established through the column. High pressure liquid chromatography with a UV spectrometer detector is used to measure organic concentrations in the aqueous phase effluent. These aqueous phase effluent concentrations are then employed to assess the extent of interphase mass transfer. Ultimately these data will be used develop correlations between mass transfer parameters and measurable soil and chemical properties.

Gamma Ray Attenuation

A significant effort has been made in modifying the gamma ray attenuation instrument to reduce measurement drift. Early saturation measurements were found to drift by as much as 15% over time. The problem of drift was found to be related to an excessive photon count rate on the detector. Over time this causes 'detector fatigue', resulting in measurement drift. The detector count rate is adjustable by beam collimation, whereby the window of the gamma entry and exit ports is narrowed.

Modifications to the gamma detector have been completed and include an adjustable collimation. This approach allows minimization of drift for any type of porous medium within the glass column. Initial tests show that measurement drift has been reduced to a level of approximately 1% per day. At this level, saturation measurements can be corrected by calibrating the count rate with a standard brass plate absorber before and after each experiment. Data retrieval software which will facilitate gamma ray attenuation measurements has been developed and tested. The software is designed to electronically collect and store the gamma detector counts, and also performs real time averaging of detector counts over specified time periods.

The gamma ray attenuation device is presently being used to determine the mass attenuation coefficients for water and each of the study sands and NAPLs. These coefficients are required for relating detector counts and NAPL residual saturation in the water/NAPL/sand system.

Initial Column Tests

Performance of the column and associated equipment has been tested in experiments examining the formation of residual saturation of NAPL in Ottawa sand. Separate experiments have been conducted with hexane (SG<1) and trichloroethylene (TCE, SG>1). Both experiments successfully produced residual NAPL blobs within the Ottawa sand. The initial tests generally demonstrated that the column and associated equipment are functioning satisfactorily. Results suggest that the experimental setup provides the necessary capability for collection of mass transfer information on dissolution of residual NAPL blobs. Some minor problems with design and construction of the column were revealed in these experiments, however. These are discussed below, together with planned remedies.

A flaw in the construction of the bottom support was uncovered in the TCE experiment. The hexane experiment was conducted first, and in this run the bottom support functioned well, providing separation of the aqueous phase and NAPL effluents. However with TCE, it was observed that the epoxy resin used to bond the glass frits and porous teflon forming the bottom support was weakened. Consequently, leaks formed between the TCE and water effluent drains and separation of the water/NAPL mixture was incomplete. Because this phenomenon was not observed in the hexane run, it is believed related to the chemical interaction of TCE and the epoxy resin. The problem will be remedied by use of alternative resins having greater chemical resistance to the organic solvents under study.

The introduction of water and NAPL into the soil column is a sequential process. The soil is first saturated with water prior to NAPL introduction. Subsequent water flooding establishes the residual NAPL blobs. In the first two column tests the introduction of the denser fluid (water in the hexane experiment and TCE in the TCE experiment) was performed with a pressure head that was insufficient to overcome the soil entry pressure across the entire top soil surface. Consequently, preferential flow paths developed. TCE residuals were not uniform and some NAPL remained along the top soil boundary. These problems will be reduced in future experiments by increasing fluid injection rates.

Pore Characterization and Surface Area Determination

The interfacial mass transfer coefficient depends, in general, only on the physical properties of the system and fluids. Ideally, these physical properties are specified explicitly and not lumped in the mass transfer coefficient itself. Properties that require

separate quantification in this case include the interfacial contact area separating the fluids. In porous media the fluid-fluid interfacial contact area depends not only on the soil properties, but also on the mixing process (i.e. how the fluids are introduced into the soil). Clearly the measurement of a dynamic interfacial contact area within a porous media is a difficult task. Traditional studies of mass transfer in porous media have either focused on quantifying mass transfer coefficients in highly idealized systems or have measured only overall mass transfer factors that combine the information of the mass transfer coefficient and the interfacial surface area into a single parameter. The results of the former are not directly applicable to natural soil systems, and overall transfer factors are both highly system dependent and transient in nature.

A unique feature of this study is the proposed objective of formulating system-independent correlations for mass transfer coefficients. This objective requires development of procedures for measuring interfacial contact area directly or for providing some alternative consistent measurable characterization. A number of approaches have been examined; some have been ruled out and several others will be pursued.

A literature review was conducted into potential methods for direct measurement of interfacial contact area. One possibility is the use of tomography and imaging procedures for surface area measurement. Such methods are commonly used in the medical fields, but have been applied also for measurement of oil saturation in the petroleum industry. The resolution of these techniques, however, is larger than the pore scale. Consequently the techniques are not applicable for examination of surface geometry of small residual blobs. These procedures are no longer under consideration.

Indirect estimates of surface area using network models have also been investigated. This approach uses such models to relate capillary pressure function and interfacial tension measurements with characteristics of pore and throat structures, and then ultimately to simulate residual trapping and surface area formation. One advantage of this approach is that residual saturation and contact area can be related to the properties of the medium and the mixing process. Though these techniques hold promise, there are several potential problems associated with their application. First, a network model that captures all relevant physics controlling residual entrapment and surface area formation has not been developed. Second, laboratory data is required to validate the network model. Consideration of a network model is delayed until a suitable experimental technique has been developed.

An experimental approach which could eliminate the problem of measuring interfacial contact areas would be to use uniform solid spheres of naphthalene and/or benzoic acid as the residual organic. Both of these compounds are solids at room temperature. The known surface area of the solid spheres provides a good approximation of the aqueous phase/organic phase interfacial contact area within the soil column. A series of experiments employing such solid spheres is planned. Although this system is recognized to be highly idealized, it will provide a simple system with which to initiate and develop experimental protocols. The data that are generated will contain minimal uncertainties in surface area determination, and therefore will strongly aid in the formulation of mass transfer coefficient correlation expressions. Uniform spheres of naphthalene or benzoic acid of small diameter are not commercially available. Presently, methods for producing small diameter naphthalene spheres are under development. This work will be conducted in the dedicated space made available by the purchase of a recycle hood.

Polymerization methods developed by the petroleum industry will also be used in this study as an aid in the characterization of interfacial contact area of residual NAPL

blobs. This approach involves the use of a liquid organic polymer (i.e. styrene) as the NAPL phase. After residual NAPL saturation has been established, polymerization with heat and pressure is used to solidify the residual NAPL blobs. The porous matrix is then dissolved using hydrofluoric acid, allowing the geometry of the residuals to be studied. Visual inspection and sieve analysis of the solidified NAPL blobs will be used to quantify the characteristic surface area.

Use of capillary pressure measurements for indirect characterization of interfacial contact area is also under investigation. Capillary pressure measurements inherently reflect characteristics of the pore body and throat structure, which strongly influence the formation of fluid-fluid contact areas. A number of models have been developed that relate capillary pressure measurements with parameters of the porous media. Potentially these parameters, either directly or when combined in some manner, can be used as consistent surrogate representations of interfacial contact area for the mass transfer correlations. Procedures for capillary pressures measurements are well established, and our laboratories are equipped for such measurements.

Development of the Numerical Simulator

Considerable progress has been made on development of a multiphase flow, compositional simulator. A one-dimensional code has been written, and is now being tested and refined. The code solves the coupled flow and transport equations with the finite element method and sequential solution algorithm. With this formulation the transport equations can accommodate rate-limited interphase mass transport processes.

Validation and testing of the simulator has included mass balance error checks, comparisons with analytical solutions for highly simplified problems, and comparisons against a validated commercial package (SUTRA) for slightly more complicated problems. To date, the simulator has performed well in each of these tests. Work is continuing on the examination of solution sensitivity to the extent of interphase mass transfer and on comparisons with a simultaneous solution compositional simulator.

DATE

FILMED

2/10/94

END