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PROJECT DESCRIPTION

1.0 SUMMARY OF OBJECTIVES

We propose to continue our collaborative research focused on advanced technologies for subsurface contamination problems. Our approach combines new multi-phase flow theory, novel laboratory experiments, and non-traditional computational simulators to investigate practical approaches to include interfacial areas in descriptions of subsurface contaminant transport and remediation. Because all inter-phase mass transfer occurs at fluid-fluid interfaces, and it is this inter-phase mass transfer that leads to the difficult, long-term ground-water contamination problems, it is critical to include interfacial behavior in the problem description. This is currently lacking in all standard models of complex ground-water contamination problems. In our earlier project, we developed tools appropriate for inclusion of interfacial areas under equilibrium conditions. These include advanced laboratory techniques and targeted computational experiments that validated certain key theoretical conjectures. However, it has become clear that to include interfacial behavior fully into a description of the multi-phase flow and contamination problems, the fully dynamic case must be considered. Therefore, we need to develop both experimental and computational tools that can capture the dynamic nature of interfacial movements. Development and application of such tools will allow the theory to be evaluated, and will lead to significant improvements in our understanding of complex subsurface contamination problems, thereby allowing us to develop and evaluate improved remediation technologies.

We propose to combine theoretical, experimental, and computational research efforts to achieve the following goals:

- Develop new experimental techniques to measure interface dynamics, under realistic conditions of movement in porous media.
- Develop new computational algorithms that properly incorporate interface dynamics, and that include wedges and films of wetting fluid.
- Test existing theory and develop new theory, in conjunction with the experiments and the computations, to provide practical definitions to fundamental terms like dynamic capillary pressure and average interfacial velocity.
- Synthesize the results of the experimental, computational, and theoretical investigations to develop a new model for multi-phase flow and contaminant transport in contaminated soils and ground waters. Compare this new approach to standard methods and evaluate the potential improvements in terms of soil characterization and remediation evaluation.

The results of this research will provide guidance regarding fundamental questions of remediation efficacy. We will examine how interfacial areas need to be characterized, and under what conditions their dynamics need to be included in practical analyses of subsurface contamination problems. Given that these interfaces are the source of contaminants to the aqueous phase, it is important that we continue our ongoing investigations of the role of these

interfaces in contamination problems, the influence of dynamics in their overall description, and the significance of their evolution during important problems like dissolution of non-aqueous phase liquids and their subsequent long-term environmental transport. The proposed research will allow us to extend our earlier work on equilibrium relationships between interfacial area, capillary pressure, and saturation, to include the critical component of interface dynamics.

2. INTRODUCTION

The subsurface environment is critical to many important environmental processes, from water storage and transmission, to nutrient cycling, to global energy balances. Human activities that involve use of earth resources, such as agricultural practices and fossil energy production, are central to modern human existence. However, these activities also introduce contaminants into the subsurface environment, and produce other detrimental environmental effects. In order to realize the beneficial uses of environmental resources, while mitigating the anthropogenic consequences of those activities, certain basic knowledge is needed regarding the mechanisms of fluid and contaminant movement in the subsurface.

The desire to exploit resources, and the concomitant need to mitigate detrimental environmental effects associated with such exploitation, has fueled much of the ongoing research into subsurface flow and transport processes. This has had, and continues to have, significant scientific implications. But it also has enormous economic implications. The legacy of environmental problems resulting from production of nuclear weapons at Department of Energy sites has been well-documented (DOE, 1989; 1995). Contamination of soils, sediments, and ground water with non-aqueous-phase liquid (NAPL) pollutants is one of the most widespread problems for both DOE and the nation at large. The volume of contamination at DOE facilities exceeds 2500 billion liters of contaminated ground water and 200 million cubic meters of contaminated soil (DOE, 1995). Spread over 130 installations, the life-cycle clean-up costs are expected to exceed 300 billion dollars and take up to 100 years to complete. While evolving technologies provide some hope for significant improvements in these estimates, many research questions remain to be answered before these figures can be brought into a manageable range of both cost and time.

We have been addressing the general problem of NAPL migration in subsurface environments using a combination of theoretical developments, novel laboratory experiments, and specific computational modeling. These have highlighted the importance of interfacial area, and provided tools to quantify this variable, to assess its importance, and to incorporate it into models that include fundamental underlying processes such as inter-phase mass transfer and dissolution of NAPL's into flowing ground waters. Research we have pursued collaboratively under previous DOE funding is described in the next section. We then present motivation for the current proposal, including descriptions of the problems we propose to solve. This is followed by a list of specific research tasks to be pursued in the proposed research. We believe that the theoretical results are now well described, that new experimental techniques will allow for rapid measurements of important variables, and that new computational models will allow us to address important issues related to interfacial dynamics and their effects on the overall flow system.

3. PREVIOUS RESEARCH BY PI'S UNDER DOE FUNDING

The simultaneous flow of multiple fluids in the subsurface is central to problems in the unsaturated zone, and to a variety of problems in the deeper subsurface. These problems are characterized by the existence of multiple fluids, each of which exists at a different pressure. At the pore scale, fluid-fluid interfaces separate the fluid phases, and serve to support the pressure differences via interfacial tension. While these interfaces play a central role in multi-fluid porous media systems, they have received remarkably little attention in the historical literature, and terms involving interfacial area are absent from all classical equations of multi-phase flow. In part this can be attributed to the difficulty in measuring interfacial areas, and in part it can be attributed to the complexity of the theory associated with inclusion of interfacial areas.

In our previous DOE project, each of the PI's contributed to a concerted and coordinated effort to expand our understanding of the roles played by fluid-fluid and fluid-solid interfaces. We developed techniques to measure interfacial areas in porous media, to incorporate certain interfacial area terms into the governing equations for multi-phase flow, and to develop novel computational tools to quantify interfacial areas and to explore and test certain theoretical results.

The theoretical results built on the earlier volume averaging approach developed by Gray and coworkers (Hassanisadeh and Gray, 1993). The new results have shown that specific interfacial area, defined as total interfacial area per unit volume of porous medium, must be included in the thermodynamic description of the multi-phase system. If specific interfacial area is not included, then obvious thermodynamic inconsistencies arise (see Gray et al., 1999). Only when interfacial area is included in the description, along with other geometric measures like phase saturation, does the resulting set of governing equations conform to physical observations. The proper incorporation of interfacial areas into the theory is accomplished through the development of conservation equations for those interfaces, followed by postulation of a constitutive theory that closes the equation set. These extensions of current practice that allow for improved description of the system physics carry with them the burden of the need for additional information to quantify parameters in the constitutive equations. Thus the theory has been performed in conjunction with network modeling and experimental investigations designed to provide those parameters and some macroscale thermodynamic relations.

While the theoretical results point to the need for a wide range of experimental measurements, until recently there have been essentially no experimental techniques to determine interfacial areas. Montemagno and coworkers (Montemagno and Gray, 1994, Montemagno and Yu Ma, 1999) developed a novel experimental procedure to measure interfacial areas within a sample of porous medium based on non-destructive imaging. Non-destructive imaging technique has gain extreme interests and development during past 30 years. But most of the matured techniques including X-ray tomography (Wang et al. 1984) and magnetic resonance imaging (Zeev et al. 1993) suffer from limitations in resolution (at the order of mm) regarding to the pore-scale characterization of the multiphase system that may require micron meter resolution. Fluorescence microscopy (FM), including conventional FM and Laser Scanning Confocal Microscopy (LSCM) is only suited for the study of specimens which are thin in the z direction due to their limited working distance (the longest z distance from the focal plane to the objectives)(~ 200μm) (Pawley, 1990). While the study of multiphase flow in porous media requires a larger working distance to insure statistical representative measurement and to

eliminate sample boundary effects. Developed by Montemagno and Gray (1994), Photoluminescent Volumetric Imaging (PVI) system provides a non-destructive and high resolution obtaining of 3D micro-geometry information in the form of 3D digital images over a Representative Elementary Volume (REV) in both x-y and z-x planes.

A typical PVI experiment includes a modeled transparent multiphase porous media system. The porous media system is comprised of optical-quality quartz sand and two or more immiscible fluids matched to the refractive index of quartz sand. The fluids are doped with property-selective fluorophores that are excited by electromagnetic energy in the form of coherent laser light sheets. Excitation patterns within successive sheets of laser light are then captured as computer images. To allow the solid, non-aqueous, and aqueous phases to be distinguished in the data collection process, both of the fluid phases must be doped with fluorophores with different Stoke shifts.

An optical schematic of the PVI measurement system is illustrated in Fig. 1. To acquire an image, first a single-frequency coherent light beam is generated with an Argon-ion laser. The laser beam has a wavelength of 488nm with a total power of approximately 750mW. This 1.5mm light beam is then expanded to a diameter of 25mm with a collimating beam expander. The expanded light beam is then collapsed along the y-axis by a long focal length cylindrical lens to form a light sheet. This light sheet is focused to achieve a y-axis thickness of 20μm over a length of approximately 15mm and a height of 30mm. The light sheet is then directed through the measurement cell orthogonal to the imaging system.

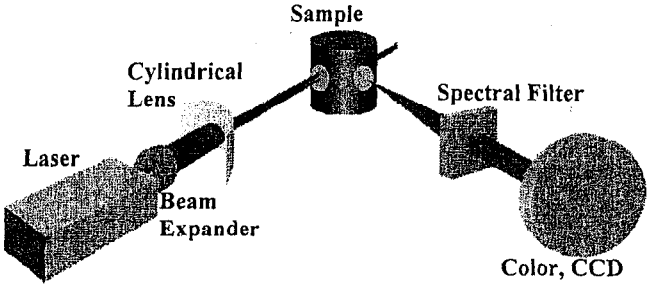
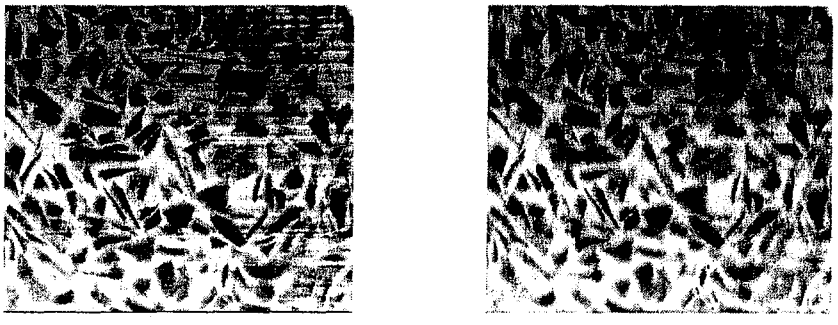


Fig. 1 Schematic of PVI system

The imaging system consists of a long-range (about 12cm working distance) microscope and a spectral filter assembly, which is interfaced to CCD camera that acquires the image. After each image is recorded, precision translators move the measurement cell to reposition the focal plane of the laser light sheet within the sample volume so that another image may be recorded. The translators used in the described apparatus will position the measurement cell to a precision of 100nm with a repeatable accuracy of 1μm over a 25mm translation. Typical resolutions of the whole system of 5μm and over volumes greater than $120mm^3$ have been achieved.
Figure 2 (a) shows an original PVI image in gray level.

With the development of the pore scale imaging technique, quantitative image analysis tools are in great need and are key points in obtaining valid measurements from the raw data. Before saturation, phase interfacial area, pore structure can be measured directly from the image, noises have to be first eliminated and the image need to be segmented into interested components such as solid phase, wetting phase and non-wetting phase. Because no available commercial software

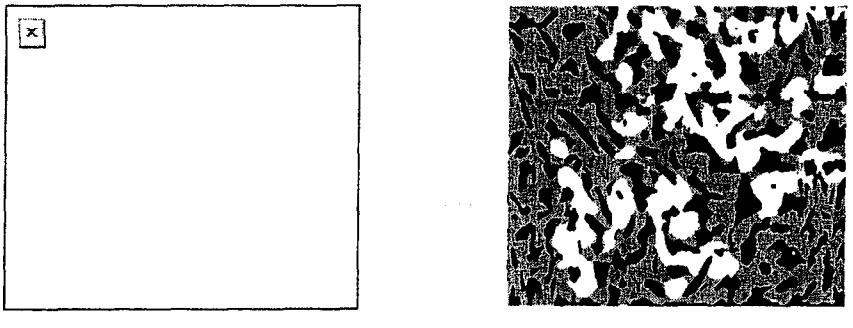
is capable of accurately analyzing the produced images, new noise elimination and automatic image segmentation algorithms were developed and implemented by Montemagno and coworkers (Ma and Montemagno, 1998; Montemagno and Ma, 1999; Montemagno and Ma, 2000). The major noise of PVI images comes from a non-perfect index match of the fluids and solid phase. The noise appears in thin strips in the image. Common techniques such as mean and Fourier Transform filtering do not yield acceptable results because the fine geometries present in the image are severely affected and distorted. A spatial filter sensitive to the thin strip pattern was designed and the noise in the image was filtered without a significant reduction in the geometric information present in the image (Montemagno and Yu Ma,1999). Figure 2(b) shows the resulting noise-reduced image.



(a) Original PVI image in gray level (b) After noise elimination

Figure 2

Segmentation of the PVI Images into the various phase components was difficult due to the fact that the all of the image metrics varied with intensity through out the image. Thus no simple threshold value can be found for automatic segmentation. Montemagno and coworker (1999) developed a dynamic segmentation algorithm both in gray scale and RGB space. The algorithm is based on the local statistics of image intensity and thus overcomes the non-homogeneity problem. Figure 3 (a) shows an original PVI image in RGB, in which green color is for the nonwetting phase, red color is for the wetting phase and the dark color for the solid phase. Figure 3(b) shows the segmented components with white color stands for nonwetting, gray for wetting and black for nonwetting phase.



(a) One slice of PVI (red:wetting; green: nonwetting; dark:soild) (b) Segmented (gray: wetting; white: nonwetting; black: solid)

Figure 3

After segmentation, the interfacial areas between wetting and nonwetting (α_{wn}), wetting and solids (α_{ws}) and nonwetting and solids (α_{ns}) can be computed from the image. Traditional method used in computer graphics is based on a marching cube algorithm which uses tessellated triangles to simulate the surface. The areas of the triangles are added to produce a measure of the surface area. Unfortunately, this method is very sensitive to surface noise which is quite common in digital images because of digitizing error. This noise becomes most significant when the object is small in size such as the interface between two fluids in a pore throat. We used a novel approach to compute the interfacial area by adapting the relationship between specific surface area and the 2-point correlation function proposed by Berryman (1987).

Under the assumption of *statistical homogeneity* of the porous media, assume $f(\bar{x})=0$ *or* 1 is a binary function describing the characteristic of the porous media. When $f(\bar{x})=1$, $\bar{x}$ is in the pore space and when $f(\bar{x})=0$, $\bar{x}$ is in the solid space. Then the 2-point correlation function of the porous media is defined as:

$$C_2 = \int_{-\infty}^{\infty} f(\bar{x}) f(\bar{x}+\bar{r}) d\bar{x} = FFT^{-1}[F(\bar{k})F(\bar{k})]$$

Angular Average of the correlation function:

$$A_2 = \frac{1}{4\pi}\int d\varphi d\theta \sin\theta \; C_2(r\hat{r})$$

Specific surface area:

$$a = -4\lim_{r\to 0}\frac{dA_2(r)}{dr}$$

$C_2(\bar{r})$ and A_2 are computed directly from the digital images using FFTs.

By using this technique the specific areas are computed by using all information associated with the object instead of only using its surface, consequently a more accurate measure of its surface can be expected. This was demonstrated through experimentation (Montemagno & Yu Ma, 1999).

However, direct application of the Berryman relationship can only determine the specific area between 2 components. The Berryman relation between specific surface area and the 2-ponit correlation function is based on the analysis of binary images in which the image can only have two components with pixel values of 0 or 1. To calculate the specific surface areas between more than two components (eg. wetting, nonwetting phases and solid), a new transform was developed.

Assume there are P components in the image F of $M \times N$. Then F can be transformed into P new images which are represented by $Z = \{Z_1, Z_2, Z_3, \ldots Z_P)$ in which Z_k is a binary image consists of two components: component k as 1 and the remaining components as 0. If we calculate the specific surface areas from $Z_1, Z_2, Z_3 \ldots Z_P$, the values we get are the specific areas between the component k and the remaining components. We use a_{kr} to stand for these values, in which r represent the remaining components $k=1,2,,,P$. The following P equations can be derived straightforwardly:

$$a_{kr} = \sum_{i \neq k} a_{ki}$$

where $k=1,2,...P$

With a_{kr} computed from the 2-point correlation function of the transformed image $Z_1, Z_2 \ldots Z_P$, these linear equations can be solved. In the case of three components: wetting fluid, non-wetting fluid and solid, the solution is the following:

$a_{ws}=(a_{wr}-a_{nr}+a_{sr})/2$

$a_{ns}=(a_{sr}-a_{wr}+a_{nr})/2$

$a_{wn}=(a_{wr}-a_{sr}+a_{nr})/2$

where a_{nr}, a_{wr} and a_{sr} represent the specific surface areas between non-wetting and the remaining (solids plus wetting), wetting and the remaining (non-wetting plus solids) and solids and the remaining (wetting plus non-wetting) components respectively.

The development of the discussed image processing algorithms has resulted in the accurate measurement of phase interface areas using the PVI experimental methodology and the enhancement of our ability to extract the geometric information necessary to generate realistic pore network systems. These achievements directly supported the recent advances in pore-scale network modeling resulting from the efforts of Celia and coworkers (Dahle and Celia, 1999; Held and Celia, 2000).

Even though the PVI technique provides a fascinating approach for measurement of interfacial areas and characterization of the pore space, it is extremely time consuming and difficult to implement the displacement experiments. Because many measurements are needed to perform just one complete experiment, alternate approaches are clearly needed. To address this need, specific computational models have been developed by Celia and coworkers (Reeves and Celia, 1996; Rajaram et al., 1997; Celia et al., 1998; Gray et al., 1999; Fischer et al., 1999; Held and Celia, 2000a,b,c). These models are based on explicit representation of the pore space and subsequent tracking of every individual fluid-fluid interface through the pore network. These tracking calculations, based on an assumption of interface equilibrium, move the interfaces from one equilibrium state to another. Once this is accomplished for all interfaces, for an imposed set of fluid pressures, the percent of the pore space occupied by each fluid can be computed. This is the fluid saturation. Given a definition of capillary pressure as the difference between the phase pressures (assume two fluid phases), the data pair of phase saturation and capillary pressure provides one data point in the traditional relationship between saturation and capillary pressure.

The resulting relationship between saturation and capillary pressure exhibits all of the characteristics observed in experiments, including finite entry pressures, nonlinearity, hysteresis, and nonzero residual saturations. These models provide good estimates to measured curves for unconsolidated materials (Rajaram et al., 1997; Fischer and Celia, 1999). They also provide good estimates to other standard nonlinear relationships such as relative permeability as a function of saturation. While these results are intriguing, one of the most powerful uses of these kinds of models involves quantification of variables that cannot be measured. Because each fluid-fluid interface is defined explicitly, interfacial areas may be calculated readily. By including interfacial areas with the saturation and capillary pressure values, relationships between these three variables can be derived. This has allowed us to explore questions regarding the nature of hysteresis, the possibility that hysteresis can be eliminated with an expanded view

of the multi-phase system, and the underlying definition of capillary pressure as it applies to practical multi-phase systems. We have also expanded our calculations to include additional variables, such as measures of contact line lengths, where the contact line is defined as the line defining the intersection of two fluid and one solid phase.

In the work of Fischer and Celia (1999), which expands on the earlier work of Rajaram et al. (1997), we considered how relatively standard measurements involving the main branches of the Pc-S relationship can be used to estimate pore-size distributions for both the pore bodies and pore throats. In Fischer and Celia (1999), as well as Fischer et al. (1999), an automated optimization procedure is presented which derives the appropriate pore-size distributions by including the pore-scale simulator as part of the algorithm. This greatly improves more traditional approaches that are based on simple bundles of tubes. To test the efficacy of the estimation approach, we used the resulting network model to predict both relative and absolute permeabilities for a variety of porous media types. Results demonstrated that for unconsolidated materials, very good results were obtained. We parameterized the resulting relationships using the standard procedures of soil physics, based on the van Genuchten models, and found excellent behavior for van Genuchten exponent, n, greater than about 3. For lower values, the pore-size distributions were less successful. Our overall experience indicates that in this range of materials with lower n values, we need to include strong spatial correlation and, for lower n values, larger-scale structure into the network. We are continuing to pursue solutions to this problem, in the context of physically-based displacement rules and network descriptions that include more complex structures.

One of the intriguing conjectures that has arisen from the theoretical work involving interfacial areas is the idea that hysteresis between drainage and imbibition may be eliminated by proper inclusion of interfacial area in an expanded representation of the traditional relationship between capillary pressure and saturation. That is, the surfaces that define the expanded relation involving Pc, S, and A, when defined for drainage scanning curves and for imbibition scanning curves, should coincide in the case of no hysteresis. Our initial efforts to test this conjecture showed that hysteresis in fact is not eliminated: the drainage and imbibition surfaces defining the relationship between Pc, S, and A did not coincide, despite the fact that they are smooth and well behaved. However, we have recently reexamined this question by making use of the following observations. When the process of imbibition is modeled, the mathematical rules for when a fluid-fluid interface will invade a particular pore element are complicated by several physical mechanisms that are not present in the drainage process.

The two significant mechanisms are snap-off (or choke-off), and local fluid configuration. Snap-off refers to a process whereby pore throats may fill with wetting fluid, ahead of any invading front of wetting phase. While this process is relatively well understood, its mathematical description involves certain parameters that need to be determined. These parameters have been estimated by several different research groups. Each has measured different values, leading to a range of values that are considered to be physically plausible. Similarly, the effects of local fluid configuration have also been quantified, and again a range of parameters appears to be physically plausible.

In our earlier tests for hysteresis, we chose one set of parameters to describe the imbibition process, and used those parameters in all of our simulations (see, for example, Reeves, 1997). We have recently reexamined this issue by asking the following question: Is there a set of physically plausible rules for both snap-off and local fluid configuration, for which hysteresis between drainage and imbibition is eliminated in the expanded relationship between Pc, S, and A. We found that for the pore network under study, which corresponded to a fairly uniform sand, that in fact we can find a plausible set of parameters for which hysteresis is eliminated. This work is described in detail in the publication Held and Celia (2000a). This research, driven directly by the theoretical work of Gray and coworkers, has a number of possible implications. In particular, the expanded set of governing equations may ultimately lead to a simplified description of the system by elimination of hysteresis effects that are prominent in traditional descriptions of the system.

In the paper of Held and Celia (2000a), we also presented relationships between contact line length, capillary pressure, and saturation. This is the first time contact line has been quantified, and the first time its functional dependence has been explored. We found that behavior of contact line length was similar to that of interfacial area, both in terms of its functional dependence and in terms of its hysteretic behavior. When we eliminated hysteresis in interfacial area between drainage and imbibition, we also eliminated hysteresis in contact line length. This implies that inclusion of contact line length in equations for multi-phase flow may add little to the overall system description, because the overall effects are already captured by the interfacial area terms. Again this points to potential simplifications in the new theory.

We have also used the network models to examine the fundamental definition of capillary pressure, and how it should be defined in practical terms. That is, if we have a description of the porous medium such that explicit locations of all interfaces are known, and fluid pressures have been calculated, how should the volume-averaged capillary pressure be computed? Traditional laboratory measurements use imposed boundary pressures as the phase pressures for individual fluids. In Held and Celia (2000b), we have shown the regions of saturation where this definition is acceptable. More importantly, we have shown the conditions under which this definition is not applicable. We have redefined volume averaged capillary pressure, based on extensive discussions with W. Gray and C. Montemagno, as the areal average defined over all fluid-fluid interfaces. Given this definition, we defined (for the first time) the complete Pc-S curve, including saturation ranges between residual and zero saturation. In addition, we calculated interfacial areas and relative permeabilities in this range of saturations. Among other things, we observe that capillary pressure is not unbounded, as is usually shown on Pc-S curves in virtually all textbooks and research papers. There are definite bounds, which can be computed directly by the network model (given our modified definition of Pc). We also observe that the Pc-S curve no longer remains monotonic, in the extended saturation region. This may have implications for traditional simulators, which involve the derivative of saturation with respect to Pc as a coefficient in the equations. These traditional equations cannot apply to the region between residual and zero saturation for any fluid phase. While we have chosen a heuristic definition of average capillary pressure, which seems to be the most plausible, we still have not reconciled this 'practical' definition with the theoretical definition involving derivatives of free energies. If we are to move to calculations of dynamic capillary pressures and include interface dynamics

(see discussion below), this definition needs to be examined more closely, and theoretical guidance needs to be developed for the computational models.

The calculation of Pc-S-A (and relative permeability) relationships that covered the entire range of saturations required a physically-based mechanism to achieve saturations below residual. To this end, we developed a model for dissolution of a residual phase in the presence of a flowing phase. Notice that this allows us to compute the capillary pressures and saturations, as well as interfacial areas, over the saturation ranges of interest. It also provides us with much more information regarding dissolution dynamics for non-aqueous phase liquids (NAPL's). In Held and Celia (2000c), we describe our algorithm for dissolution and subsequent miscible transport in the aqueous phase. Included in this is our first attempt to incorporate interfacial dynamics, in this case driven by mass loss due to inter-phase mass transfer. This interface algorithm is based on a simple volume balance, constrained by local pore geometry. However, the displacement algorithm used to generate the residual saturation was still based on quasi-static displacements.

While we have continued to use traditional, quasi-static network models to investigate fundamental questions about the new theoretical results, we have also recognized the need to expand the kinds of network models that we are using. To this end, we began to develop an entirely new set of computational network model, to allow incorporation of realistic geometric descriptions, and to incorporate interface dynamics into the simulators. The network geometry in these new simulators is very general, allowing for a variety of pore elements and an arbitrary connectivity of those elements. These models have been written to interact directly with the pore imaging that is possible with the advanced techniques developed as part of the experimental efforts of this proposal. We have also recognized the importance of dynamics in regard to interface movement. In part this is driven by fundamental questions regarding time scales and assumptions of equilibrium, and in part it is driven by the need to quantify certain terms in the equations that arise from the new theory. These terms include average interfacial velocities as well as net generation of new interfacial area.

As the research pursued under this project proceeded, it became apparent that dynamic models were needed. As such, we began to investigate them, while pursuing the more central computations associated with the traditional quasi-static models. We took this research in several directions, some of which form the basis for the renewal proposal. First, we added some simple dynamics associated with mass transfer across interfaces and subsequent dissolution dynamics, as described earlier (see Held and Celia, 2000c). We have also looked quite closely into different algorithms that allow for inclusion of interfacial dynamics. Our first efforts are described in Dahle and Celia (1999), which reports on a careful, and quite complex, algorithm to track fluid-fluid interfaces dynamically throughout the pore network. Details of the algorithm can be found in the cited publication, and are also summarized in the associated renewal proposal. A subsequent comparison of two different algorithms is reported in the recent paper by Celia et al. (2000). That paper is also discussed in the renewal proposal. At this point, we feel that the options for development of a fully dynamic algorithm are clear. Models used to date are not sufficient to answer the relevant questions associated with interface dynamics, so that we need to develop dynamic models that go beyond what has been done to date. In particular, our dynamic models need to include general geometric structures, to accommodate digitized images provided by PVI, and they need to include wedges and films of wetting fluid, because these are

clearly important to certain dynamic processes. We feel that the experience we have gained under the previous proposal has put us in an excellent position to continue work on dynamic network models. Specific details of the different models, and our proposed approach to construction of an appropriate dynamic model, are presented in the renewal proposal. Given the innovations in measurement technologies that have resulted from the Cornell portion of the research, we are in a unique position to evaluate the dynamic models by comparison to experimental results that can be obtained quickly and relatively easily. We believe that we are positioned to provide fundamentally new insights into the dynamics of fluid-fluid displacements in porous media, and to investigate the importance of these dynamics in the overall mathematical description of multi-phase flow systems.

Realization of the potential present in the new pore-scale models required a means of constructing model pore networks that accurately represent the geometry of real porous media and a method for the rapid experimental verification of the modeling. Our group has accomplished this through the creation of a new generation of 2D micromodels and the development of a new image processing algorithm for mapping the topology and geometry of real pore space into a thin line representation suitable for pore-scale network modeling.

Pore network representation of porous media from images has traditionally been done through a process called 'Skeletonization'. Skeletonization has been an active research area in computer vision motivated by its usefulness in data compression and pattern recognition. Its basic idea is that of eliminating redundant information while retaining only the topological information concerning the shape and structure of the object that can help recognition. Most skeletonization algorithms can be categorized into: (1) iterative thinning (IT), which deletes successive layers of pixels on the contour of the interested object until only a skeleton remains; (2) distance-transform-based thinning (DT), which involves determination of the centers of maximal discs/spheres inscribed in the object. The latter method is also referred to as 'Medial Axis Transform'. The resulting 'skeleton' can be viewed as the central lines or local symmetry axis of the pore space. The term 'medial axis' is also used to denote the local maxima of the distance transform of the image.

Even though this technique has been studied extensively, skeletonization is nontrivial in practice. Selection of the appropriate skeletonization algorithm is application dependent and the appropriateness of the results needs to be carefully examined. Even though IT algorithms are easier to implement, they are non-isotropic. In the situations that the objects have highly convoluted boundaries and are subject to quantization noise, connectivity and geometry may not be preserved. The reason is that only a local 3×3 window is examined in most algorithms, this makes the algorithm incapable of providing global, structural information and results in spurious end points or excessive erosion (broken paths in the skeleton). Although various means have been developed to prevent these problems, most of them involve a tradeoff between spurious branches and excessive erosion.

On the other hand, distance transform based methods are better at preserving connectedness but are more sensitive to contour noise (Lam et al. 1996). In its implementation, when the local maximums of the distance transform is determined inside a 3×3 window, it may not directly form a connected and unit-width thin line. Thus problems arise when trying to obtain a connected and unit-width skeleton. Most distance transform based algorithms require complicated post-

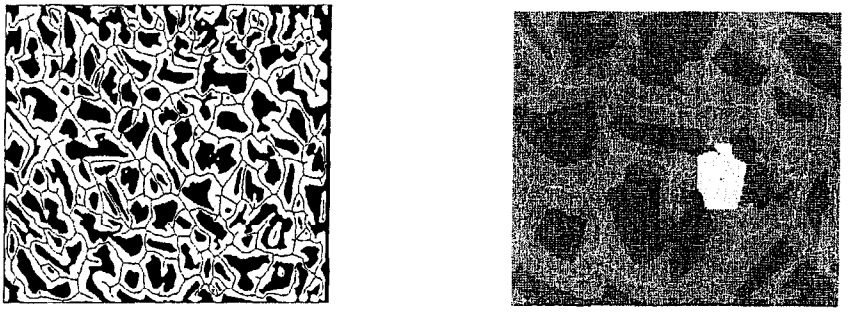
processing including linkage of the broken local maximums, which may incur additional error. The major factors affecting the accuracy are the distance measure used and the method used to find the local maximums of the distance transform (ridge finding).

The requirements for a good skeleton representation pertaining to pore-scale network constructions are that it must:

(1) preserve the connectivity of the pore space.
(2) preserve the geometry of the pore space.
(3) be isotropic or rotationally invariant.
(4) be one pixel /voxel wide (unit-width).

Most available algorithms in literature are motivated by those tasks in computer vision such as character recognition other than pore network construction. The latter has far more complicated object geometry and pays more emphasis on the correctness of overall pore-pore connectivity. Several thinning algorithms including IT based and distance transform based algorithms have been investigated and tried on PVI images, but none of them gave desired performance or they require complicated post-processing.

Montemagno and coworker (Montemagno and Yu Ma, 2000) developed a new distance transform based method for extracting pore space skeleton from digital images. The method employs a fast Euclidean distance transform of the binary image of porous media coupled with a new dynamic algorithm of ridge finding. The new ridge finding algorithm preserves better connectivity of the overall pore space and does not need a subsequent linkage operation. The small features on the contour that result in disjointed small branches from the major skeleton and can be eliminated easily. Same as most distance transform based method, the resulted skeleton is further reduced to one pixel width. The network information is then extracted directly from the skeleton. This method assures good connectivity. Figure 4(a) shows the final skeleton superimposed on the segmented PVI image. The result shows that the new algorithm produced good preservation of connectivity and geometry of the pore space.



(a) Skeleton of pore space superimposed on PVI image (b) Volume partition for individual pore

Figure 4

From the skeleton of the pore space, the connectivity of the pore space, the locations of the pore bodies, the narrowest sites of the pore throat and the pore volume can be extracted. The junctions of the skeleton are regarded as the pore body locations. The pore-pore connectivity is directly

determined by following the skeleton starting from a junction until other junctions are met. Besides junctions, a pore body may reach to an end pixel that may represent the smaller geometry features of the pore space. There is no rule for the extent these features should be included in the network. Further study is needed in this aspect. The end pixel is also recorded in our work. The locations of the narrowest site and the narrowest distance along the connection between two pore bodies are found at the same time.

A relatively difficult parameter to identify is the area (2D)/volume (3D) of each pore and the radii of pore bodies. In commonly used network models, the pore bodies are idealized as circular or spherical shapes and the pore throats are idealized as biconical or cylindrical shapes. While the pore space in real porous media has far more complicated geometry. There is no clearly defined mapping between these two representations. Bakke & Oren (1996) used an average radius for the pore bodies. The contour is searched from the center point of geometry with a rotating radius vector and the searching radii are averaged. This method gives a very coarse approximation and may not be accurate even though 'abnormally' long radii are eliminated because there is no clear and global rule for determining the 'abnormally' long radii and only a limited number of sites along the contours are searched.

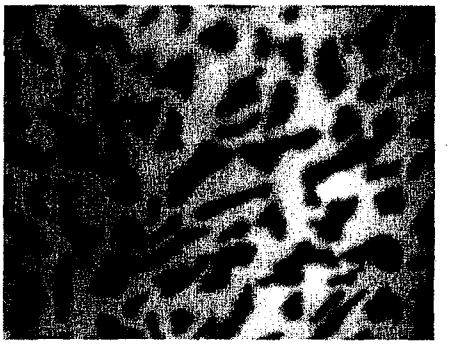
Montemagno and coworker (Montemagno & Yu Ma, 2000) developed a method of calculating the pore area/volume based on the partitioning of the pore space. It is reasonable to regard that the area/volume of the pore space is partitioned and assigned to each pore. By taking advantage of the skeleton and the original binary image, the partitioning is done automatically in the following steps:

(1) The mid-location along each connection between two pore bodies is identified as a partition site and the tangent of the connection line at this mid-location is computed.
(2) For each pore body, perpendicular lines/planes (partition lines/plane) are drawn from its partition sites. The line/plane stops when it hits the contour of the pore space or it meets with another partition line/plane.
(3) A filling algorithm calculates the area/volume enclosed by the partition lines/planes together with the contours of the pore space.

Figure 4(b) shows the area partitioned and assigned to one pore. The calculated area/volume above is the area/volume of an individual pore. It can be further assigned to its representing pore body and pore throats by additional rules related to the specific architecture of the network model. Based on the parameters extracted above, a well-defined and complete network model is constructed. It will be studied and compared with other network models in further proposed study.

Rapid verification of the modeling results will be accomplished with the newly developed 2D micromodel system. The micromodels are fabricated out of silicone elastomer from a mold microfabricated from a PVI or other digital image of a porous medium. A mask is first created from the digital image of a porous medium. The mask is then used to selectively expose photoresist on a silicon wafer. The wafer is then plasma etched to finish the creation of the mold. Micromodels are then fabricated by first curing a silicone elastomer on the surface of the mold then removing the elastomer from the mold.

Using this process we are able to fabricate micromodels in large quantities rapidly (<2 hrs), cheaply (< $10.00 ea.) with a very high fidelity to the original porous media structure (feature size <1 μm). In addition we can functionalize the surface of the porous media to make it either water or oil wet, or to make it biologically or chemically active. This new technology provides the opportunity to not only explore the dynamics of multiphase flow but also for the first time to discriminate between biological/chemical and physical processes on the flow of multiphase fluids and the transport of colloid sized particles. Below (Figure 5) is an image of the pores in a 2D microflow cell constructed from a PVI image and an actual flow cell.



(a) Image of pore space in a 2D microflow cell.

(b) Actual elastomer 2D microflow cell

Figure 5

4. MOTIVATION FOR CURRENT PROPOSAL

Standard theory of multi-phase flow in porous media has as important dependent variables the pressures of individual phases, and the relative saturation of each phase. The phase pressures are implicitly defined as volume-averaged pressures, while the saturation is defined as the percentage of pore space occupied by a fluid phase. To close the set of mass and momentum balance equations, the traditional approach assumes that capillary pressure, Pc, is equal to the difference between the nonwetting and wetting phase pressures. Capillary pressure is then assumed to be related algebraically to the phase saturations. This assumption of an algebraic relationship implies that changes in one of the variables (S or Pc) results in instantaneous changes in the other.

The new theory developed by Gray and coworkers (Hassanizadeh and Gray, 1993) points out inconsistencies in the traditional formulations, and adds several new elements that are absent from traditional mathematical descriptions. First, Gray and coworkers observed that specific interfacial area, defined as amount of interfacial area within a representative elementary volume per total volume of porous medium, must be included as a dependent variable in the mathematical formulation. Furthermore, at equilibrium, a relationship must exist between capillary pressure, saturation, and interfacial area. We have explored this relationship recently using theoretical, experimental, and computational tools that were developed specifically for that purpose; see the previous section for additional information. At this point, the general relationships involving interfacial areas, saturation, and capillary pressure have been given a firm

foundation based on theoretical analysis, experimental observations, and computational results. But the focus has been restricted to equilibrium considerations. For example, in the PVI measurements, interfaces were observed and their areas measured only after they reached equilibrium positions. Similarly, in the computational models, only equilibrium states have been considered. Changes from one equilibrium state to another were modeled without consideration of times associated with this change, and no time dimension was included in the calculations.

One of the intriguing aspects of the theory is that it indicates clear time dependence when changing from one state of interface equilibrium to another, and introduces a thermodynamic definition of capillary pressure that is a dynamic variable. Simple thought experiments show this must be true, as interface movements require finite time to occur. From the theoretical point of view, Gray and coworkers have performed analysis that includes dynamics of interface movements. For example, imposition of the second law of thermodynamics to the multi-phase system, and subsequent linearization, leads to an equation that relates capillary pressure to volume-averaged phase pressures and rates of change of phase saturation, viz.

$$\frac{\partial S}{\partial t} = L\left(P_{nw} - P_w - Pc\right)$$

where subscripts *w* and *nw* refer to *w*etting and *n*on*w*etting fluids, respectively. This equation indicates that only at equilibrium, when $\partial S/\partial t = 0$, does capillary pressure equal the difference between volume-averaged phase pressures. In general, Pc does not equal the difference in phase pressures, and this inequality drives changes in saturation. This is a fundamentally different way to look at saturations changes in multi-phase systems, and may have a variety of practical implications for subsurface environmental problems. In order to assess the importance of this dynamic expression, practical methods to define, measure, and compute dynamic capillary pressure must be developed. In addition, both experimental and computational tools need to be developed to quantify phase pressures and interfacial dynamics. Identification of conditions under which the transient effects can be important, and development of tools to test and verify the theory both experimentally and computationally, is a focus of this proposal. Dynamic capillary pressure will be given a practical definition, in terms of measurable variables, and both computational and experimental approaches will be developed to quantify the effects of dynamic capillary pressure.

Because of the importance of interfaces and interfacial areas, conservation equations must be written for the interfaces. Volume averaging techniques are applied to these equations, in the standard way (Haasanizaeh and Gray, 1993), to produce macroscopic governing equations. For example, conservation of mass of the interface leads to an equation of the form

$$\frac{\partial\left(\rho^{\alpha\beta} a^{\alpha\beta}\right)}{\partial t} + \nabla \bullet \left(\rho^{\alpha\beta} a^{\alpha\beta} v^{\alpha\beta}\right) = G^{\alpha\beta}$$

where $\rho^{\alpha\beta}$ is the mass of interfacial area per unit area, $v^{\alpha\beta}$ is the velocity of material in the interface, $a^{\alpha\beta}$ is the interfacial area per unit volume of porous medium, and $G^{\alpha\beta}$ is the rate of change of interfacial area mass per volume as a result of the exchange of mass with the adjacent bulk phases. This equation has important utility, for example, in modeling the amount of surfactant at an interface. It is important to realize that this equation expresses mass conservation. If one considers the mass per area to be constant, then the right side of the equation must still be parameterized to account for the rate of mass transfer to the interface that

will retain this condition as the interface deforms. Thus, even though mass, momentum, and energy equations may be formulated for the interface, additional information is needed to describe the mechanical deformation of the interface itself. Such equations may be developed using constitutive approximations, but these equations must be evaluated, tested, and, most likely, improved. A need exists to develop techniques that measure and quantify the appropriate variables. Only dynamic analyses can provide the needed information. We propose to develop appropriate tools for this purpose using specially designed experiments involving micromodels, and specific computational models involving pore-scale dynamics.

Finally, it has become clear that special attention must be paid to the role of wedges of wetting fluid that form in corners and crevices, and to thin films of wetting fluid that can coat solid surfaces. Wetting fluid in this form will have large area-to-volume ratios, and therefore could play an important role in interfacial analyses. However, these kinds of interfaces are quite distinct from the interfaces associated with dynamic filling or draining of bulk pore spaces. The dynamic interfaces are associated with Haines' jumps, and lead to rapid changes in overall phase saturation. The wedges and films tend to fill or drain relatively slowly, while providing hydraulic connections between otherwise isolated regions of wetting fluid. Thus wedges and films support longer-term dynamics. Proper inclusion of wedges and films in both the theory and the computations, and techniques to measure this type of wetting fluid, remain to be developed and will be explored as part of the proposed work.

5. PROPOSED RESEARCH

We propose to develop a coordinated research effort that combines theoretical, experimental, and computational approaches, with a focus on interfacial dynamics in multi-phase porous media and their practical implication for environmental contamination problems. This work is a natural extension of our ongoing collaborations, and will complement our earlier work on thermodynamic relationships between capillary pressure, saturation, and interfacial areas. We will continue our close research collaboration while pursuing three distinct but closely related areas of research. Details of each are presented below, followed by a description of our planned collaborations and interactions.

5.1 Theoretical Developments in Interfacial Dynamics

The theoretical work that has been performed and the attempts to incorporate that theory into a network model of multiphase flow in porous media has brought to light several issues that require further attention and iteration among the approaches to the problem envisioned here. These issues will be mentioned here as they form the basis for the continuation of the theoretical research.

Dynamic capillary pressures In fact, the description of the capillary pressure is one of the more challenging issues that we have encountered. First, current experimental practice defines measured values of capillary pressure as the pressure difference between fluid reservoirs in contact with a porous medium at equilibrium. The theoretical work has obtained a definition of capillary pressure that is more consistent with a traditional thermodynamic description. The capillary pressure is the interfacial tension multiplied by an average or representative curvature

between the interfaces. In actually writing a constitutive form for the capillary pressure, dependence is on the interfacial tension, saturation, and interfacial area density. Network models are ideally suited to provide information about the two alternative measures of capillary pressure and on the appropriate functional form of the constitutive relation. It is essential that this modeling work proceed as it will offer insight into what is actually being measured in field situations. Effort to correctly define the capillary pressure theoretically and experimentally has been a significant portion of the first phase of this research. An additional issue pertaining to the problem of capillary pressure is the fact that the measured data of capillary pressure vs. saturation in the hydrology literature is for the equilibrium state. In fact, capillary pressure at equilibrium is equal to the pressure difference in the phases adjacent to an interface. However, the shape of this interface adjusts at a finite rate to pressure changes in the phases. Thus information is needed on the dynamic rate of change of the capillary pressure. Indeed, experimental measurements typically allow large adjustment times for reaching equilibrium when measurements of thermodynamic capillary pressure are made. Thus, it seems reasonable that a condition of dynamic capillary pressure – a capillary pressure different from its equilibrium value based on the pressures in the adjacent phases – would exist in cases of drainage or imbibition where the saturation and interfacial areas are changing "rapidly." A constitutive equation that governs the relaxation of the capillary pressure toward equilibrium has been proposed. The dynamic network models will provide insights into the magnitude and functional dependences of the parameters that appear in the theory.

Interfacial velocities The procedure for development of macroscale equations leads to conservation equations for mass, momentum, and energy. These equations have been widely studied for the phases, but the forms that describe these transport processes within an interface are new. The momentum equation describes the momentum of mass in the interface. The external forces are the pressures of the phases and the surface tension effects. However, the momentum equation does not provide direct information on the movement of the interface, only of the mass in the interface. The interfacial movement is an additional problem, one for which constitutive equations must be developed. These equations must account for the normal velocity of the interface (i.e., the motion in the direction perpendicular to the interface) as well as the expansion, contraction, and formation of the interfaces. Distinguishing between the velocity of an interface and the velocity of material associated with the interface is important. The constitutive equations obtained for this mechanical problem are tentative for now, but will be improved through interaction with the dynamic network modeling studies. Certainly, knowledge of these velocities is important for determination of the change of the properties of the system. A clear understanding of interfacial velocity needs to be developed, under the conditions that it is measurable and quantifiable in micromodel experiments and in computational pore-scale models.

Generation term for interfacial area If one works with an interface that has mass and density, then the growth of interfacial area will be related to the transfer of material to the interface and the change in the density (mass per area) of the interface. This situation can be captured using a mass transport equation. The interfacial growth will be related to deformation and movement of the phases adjacent to the interfaces. Note that the volume of the phases are constrained because they must fill a space at all times. However, the amount of area that can be present in a volume is not bounded above. Thus simulation of the generation of area is a complex problem. Some constitutive relations have been proposed in the first stage of this work based on entropy

considerations. However, the theoretical definition of interfacial area generation needs to be clarified and its relationship to interfacial velocities needs to be made explicit. Proposed relations for rates of change of interfacial area need to be studied and parameterized with the aid of well-conceived network models and micromodels.

Film and wedge flow Wedges of wetting fluid may accumulate in corners of pore spaces. These wedges typically have sufficient volume to allow the interfacial curvature to be dominated by capillary forces. Therefore the interfacial curvature is governed by the Young-Laplace equation. Very thin films of wetting fluid are different in that their shape is dominated by local surface forces, and the interface shape no longer follows the Young-Laplace equation. Both of these kinds of wetting phase geometries may be important to both short-term and long-term dynamics in multi-phase systems. Furthermore, the definition of capillary pressure that is based on interfacial curvature does not account for constraints on the fluid-fluid interface that prevent it from taking the expected shape. Additional theoretical development is necessary to distinguish these kinds of volumes and interfacial areas, and to incorporate them into the overall volume-averaged equation set for the multi-phase system. Initial speculation at accounting for this problem at the macroscale indicates that including a dependence of interfacial energy on the properties of the adjacent phases is important. This dependence implicitly adds a measure of the geometry of a phase to the analysis so that formulation includes not only saturation but an indication of whether the phases are present as "blobs" whose boundaries are free to adjust to pressure differences between fluid phases or as "films" whose curvature is impacted by the shape of the solid phase. The extension of the network models to include corners and and films will both motivate additional theoretical development and serve to filter hypotheses for description of the film effects.

5.2 Development and Implementation of Experimental Tools for Interfacial Dynamics

As described in previous sections, PVI provides a non-destructive and high resolution 3D measurement of interfacial area and phase saturations. Previously it has only been used in quasi-static situations. The image acquisition speed is one of the major factor affecting PVI's capability for the measurement of the interfacial dynamics. For quasi-static experiment, the reposition of the translator and the camera are controlled manually. While for dynamic experiments, these need to be done automatically with appropriate speed. In order to measure the new variables associated with interface dynamics such as interface velocity and interface generation term, new fluorophores have to be adopted which are capable of tracking the interface movement in addition to improvements to the experimental equipment. Even with this increased complexity, PVI is still the only tool that offers the promise of directly measuring 3D interface dynamics in real time.

Although interfacial dynamics have not yet been measured, the images of porous media from quasi-static experiments have provided much insight into the pore-scale geometry and its impact on multiphase flow and transport. Quantitative description of the 2D pore structure has been achieved by network extraction from the images through 'skeletonization' algorithms as previously described. These networks will be applied to support future theoretical and experimental network modeling. However, there are still several important aspects associated

with the extraction of pore networks that need further study. The first is that a typical skeleton contains more detailed information such as small branches than necessary to construct the network model. Those branches correspond to the finer geometry or sometime noise on the pore space boundary, which may or may not affect the pore spaces flow and transport properties. Up to now, there has been no measure defining the extent that these features need to be included in the network to preserve the behavioral correspondence between the network and the real system. Consequently, the degree to which a skeleton is pruned remains an open question and must be tested with a series of experiments, in which the interface dynamics of the network models can be compared to that of a physical porous media. A series of 2D micromodels will be fabricated initially from a real porous media image then from "reconstituted" networks with sequentially larger minimum feature sizes. The dynamic multiphase flow properties of each of the micromodels will be compared with computational experiments to identify a metric for reducing the system complexity and still preserve the behaviors of interest.

Another second issue associated with the mapping of porous media to a network model space is the volume partitioning for individual pores. In commonly used network models, the pore bodies are idealized as regular shapes with pore bodies and pore throats while the pore space in real porous media has a far more complicated geometry. There is no clearly defined mapping between these two representations. The validity of the volume partitioning method has also to be tested by experiments. Again a series of specially engineered micromodels with a range of feature sizes and geometries in conjunction with numeric simulations will be used to evaluate the affect that microscale pore geometry has on the accuracy of representing pore bodies in network models as regular geometric structures.

The currently developed skeletonization algorithms need to be extended to 3D to enable the construction of realistic 3D network models. 3D skeletonization has been a challenge due to its different and more complicated geometric properties as compared to 2D systems. Most 2D iterative thinning algorithms cannot be extended straightforwardly to 3D because most 3D thinning conditions are based on the notion that the removal of a contour pixel will not change the local connectivity or genus in its $3\times3\times3$ neighborhood. The requirement for reasonably fast computation means that typically most 3D algorithms execute in parallel on 2D image slices. Consequently, the currently used 3D algorithms are unable to accurately preserve the overall connectivity when applied to complicated geometries such as those associated with porous media. We will expand on our success in the development of new 2D skeletonization algorithms to develop 3D algorithms for extraction pore networks from 3D images of porous media.

Because of the complexity and time-consuming nature of the 3D information acquisition process and the large number of experiments necessary to study interfacial dynamics we expect that most of the experiments will be conducted using our new 2D micromodels. As discussed earlier the new generation 2D micromodels are produced using nano-fabrication techniques. A 2D slice from PVI images of the pore space will be used to make a mask for the 2D micromodels so that results generated from both 2D and 3D systems will be directly comparable. Using this model system in conjunction with dynamic network models we will be able to directly explore and quantitatively describe the fundamental dynamics of multiphase flow. Consequently we expect this micromodel/network model system to ultimately become the "Gold Standard" for the investigation of multiphase fluid dynamics in porous media.

To make the micro-fabricated 2-D flow cell, the usual photolithography process is applied to silicon wafers. First, PVI images or any other pattern of pore space including network patterns are used as masks. The image or pattern from the mask is then transferred to the silicone wafers via exposure of an intermediate photo-resist layer. Next, the wafer is developed and the pattern is etched into the silicon wafer using Reactive Ion Etching (RIE). RIE or plasma etching is used because it etches in a highly anisotropic manner. Consequently the geometry of the pore space is preserved. If a liquid etching process were used the small feature sizes would be lost, the pore sidewalls would not be perpendicular to the surface, and the pore bodies and pore throats would

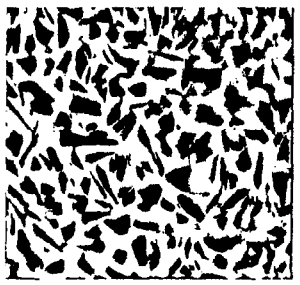


Figure 6: Image of a typical mask made from a PVI image

be made larger than desired. Using this technology feature sizes significantly less than 1 μm can be preserved. The etched wafer becomes the mold from which all of the micromodels are produced.

Once the silicon mold is fabricated the 2D micromodels are produced by pouring a liquid elastomer (General Electric RTV 615) mixture onto the wafer and cured in oven. Once cured (~1 hour) the patterned silicone elastomer sheets are bonded to a smooth elastomer sheet to create the flow cell. The cell is then fixed on a glass base, on which fluid reservoirs are built. The cell is connected to the pressure controlled reservoirs and placed under a fluorescent microscope equipped with a kinetic CCD camera capable of taking images every 5 μsecs. The fluids are doped with fluorescent dyes and images are taken and transferred to a computer to be processing.

The procedure of the dynamic measurements in micromodel is designed that the flow cell is first saturated with wetting phase, non-wetting phase is then injected in. Dynamic drainage and imbibition experiment will be performed. The CCD camera takes serial images. The images need to be segmented and the imaging processing algorithms developed in PVI experiment need to be modified to compute the interfacial area and fluid saturations. The difference image between continuous frames can be used to detect the motion of the interfaces and the averaged generation rate of interfacial areas. Edge detection, region growing or other image processing algorithms may be used.

The averaged change rate of interfacial area, can be computed from the change of interfacial area between two continuous frames and the time interval of image acquisition. The averaged velocity can be approximated from the difference of the centroids of the interface positions in two continuous frames and at a known time interval. All these measured variables are averaged terms in a REA. Because of the high degree of integration among the theory, modeling and experimental efforts, the exact form of the measurements will iteratively evolve as the definitions of these variables become more precise.

As we mentioned earlier, it is also possible to functionalize the surface of the "grains" in the micromodel. Consequently we expect to expand the use of this experimental system to investigate the role of surface chemistry in the transport of colloids and to establish the impact of surface wetability on the formation and movement of phase interfaces.

Given the innovations in measurement technologies that have resulted from the Cornell portion of the research, we are in a unique position to evaluate the dynamic models by comparison to experimental results that can be obtained quickly and relatively easily. We believe that we are positioned to provide fundamentally new insights into the dynamics of fluid-fluid displacements in porous media, and to investigate the importance of these dynamics in the overall mathematical description of multi-phase flow systems.

A sequence of 2D micro-models with increasing complexity is going to be constructed. From the simple cylindrical pore throats network used by Dahle and Celia (1999), to circular pore body network model proposed by Blunt and King (1991), to network models extracted from real porous media with randomly located pore bodies and pore throats, and finally to a model made from PVI image of real porous media (fig 2). Several interfacial dynamic properties will be studied including dynamic change in saturation, interfacial area and generation term. The experimental results are going to be compared with the theoretical model. In this way, a justification and comparison of network model can be fulfilled.

5.3 Development and Application of Computational Models for Interfacial Dynamics

Pore-scale network models have provided effective tools to analyze multi-phase porous media systems. These models represent the pore space as a collection of pore bodies and connecting pore throats, and assign sizes of each based on representative pore size distributions, which may include various types of spatial correlation (see, for example, the review article of Celia et al., 1995). The vast majority of these models have used 'quasi-static' descriptions of the fluids, wherein interfaces are moved from one equilibrium position to another in response to changes in phase pressures, but the dynamics of interface motion are ignored. The interfaces are moved based on the equilibrium relationship given by the Young-Laplace equation (Dullien, 1992), which relates capillary pressure to interfacial tension, wettability, and interface curvature. Often these models are used to simulate laboratory measurements such as those associated with traditional pressure cells. The pore-scale models can reproduce traditional measured relationships between capillary pressure (Pc) and saturation (S), as well as relationships between relative permeability and saturation (Dullien, 1992; Rajaram et al., 1997). In addition, they have been used to study various aspects of interfacial area and its relationship to Pc and S, as discussed in earlier sections of this proposal (see for example Reeves and Celia, 1996; Reeves, 1997; Celia et al., 1998; Gray et al., 1999; Held and Celia, 2000a,b,c).

Because of the potential importance of interface dynamics, quasi-static pore-scale network models need to be expanded to include dynamics of interfacial movements. While the vast majority of pore-scale network models have been based on the quasi-static assumption, there are several dynamic models that have been reported in the literature. In these dynamic models, interfaces deemed unstable based on the Young-Laplace criterion are tracked through the

network until a stable position is reached, and the transient movement from one location to another is explicitly described and modeled. While these transient models are more complex computationally, they allow the underlying dynamics associated with interface movements to be incorporated and analyzed explicitly. Examples of these models include the model of Blunt and King (1991), who used a simplified description of the process by assuming volumeless pore throats and zero capillary pressure in the pore bodies; a series of models by Payatakes and coworkers (for example, Constantinides and Payatakes and references therein), which often focused on mobilization of trapped fluids including mechanisms like drop-traffic flows; and more recent models by Aker et al. (1998), Mogensen et al. (1998), Dijkstra et al. (1999), and Dahle and Celia (1999). A comparison of different types of models reported in the literature is given in Celia et al. (2000). We propose to use the most promising features of each of these models, and to add features that will allow for inclusion of processes such as wedge and film flow. The result will be a computational tool that allows for meaningful simulations to provide support for, and testing of, both the theoretical and the experimental parts of the research.

In Celia et al. (2000), we described initial comparisons between two types of models: the first model based on Dahle and Celia (1999), and the second based on the model originally proposed by Blunt and King (1991). In the model of Dahle and Celia (1999), the pore space is represented as a network of cylindrical pore throats, arranged in a cubic lattice. Fluid flows and interface velocities through each pore throat are resolved explicitly. To make the algorithm more tractable, the pore bodies (junctions of pore throats) are assumed to be volumeless, which means that all of the pore volume is distributed within the pore throats. Despite being volumeless, pore bodies are assigned a radius, which is used in certain capillary pressure calculations associated with this algorithm. Figure 7 shows a schematic of this kind of network in two dimensions.

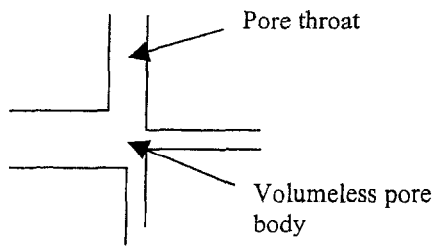


Figure 7 - Network structure for the model based on volumeless pore bodies.

Within any pore throat that contains an interface, the velocity of the interface is computed based on the assumption of laminar flow, coupled with a fixed pressure drop across the interface. The pressure drop is assigned as the limiting capillary pressure from the Young-Laplace equation for the given pore-throat radius. In throats that do not contain an interface, simple Poiseuille flow is assumed. To solve for the interface velocities, and the associated exit times, the pressures in the pore bodies need to be known. These pressures are a function of the interface locations, and must be determined as part of the overall solution strategy. Equations for the pressures are based on mass balances for each of the pore bodies. The assumption of volumeless pore bodies means that the mass balance simply requires the sum of fluxes entering and leaving each pore body to be zero.

Within this algorithm, fluids can become trapped when a second interface begins to invade a pore throat that already contains an interface. This trapped fluid leads to residual saturations for each of the phases. Other aspects of the model are described in detail in Dahle and Celia (1999). In particular, certain displacement rules are employed at the pore bodies to test whether an interface will invade the pore body and continue into connecting throats or become trapped. This is based on assignment of appropriate radii for the pore bodies, although the volume associated with these pore bodies is neglected in the calculations. As such, the algorithm focuses on the pore throats for all of the essential dynamic features of the interface movement.

The second algorithm that we have implemented is based on the original work of Blunt and King (1991). In that model, all of the pore volume is assigned to the pore bodies. Pore throats are assigned characteristic radii, for the purpose of calculating flow resistances, but no volume is assigned to them. This kind of arrangement is shown schematically in Figure 8.

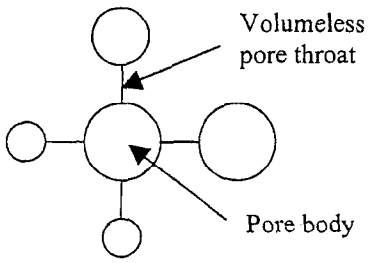


Figure 8 - Network structure for the model based on volumeless pore throats..

Because the throats are volumeless, interfaces are assumed to move through throats instantaneously. Therefore, if the radius of the throat is such that an interface can invade, based on the Young-Laplace criterion, then the interface will displace completely through the throat, and become available for movement into the exit pore body. In the original algorithm of Blunt and King, the pore throats were assumed to be sufficiently large that capillary pressures within the pore bodies were all negligibly small. These considerations lead to a model in which saturations change within each pore body as a result of single-phase flow occurring in all pore throats. In addition, while a given pore body may have any degree of fluid saturation, the assumption of negligible capillary pressure means that only a single pressure is assigned to the pore body. These restrictions lead to a relatively simple computational algorithm. For a given pore body, the change of saturation of, say, the wetting phase, is given by the net flux of wetting fluid into the pore body, such that

$$V_i \frac{\Delta(S_w)_i}{\Delta t} + \sum_{j \in N_i} (Q_w)_{ij} = 0$$

where subscript w denotes the wetting phase, and V_i is the volume of pore body i. Because the pore throats do not have any interfaces within them, the volumetric flow rates Q_{ij} correspond to single-phase, Poiseuille flow, which is still driven by the pressure difference p_j-p_i. As such, the pore-body pressures again need to be determined. To solve for the pressures, the mass-balance equation for the nonwetting phase is written for each pore body, and then the two phase

equations are summed. Given the assumption of incompressible fluids and solid, the sum of the phase saturations is always equal to one, which means that the saturation changes sum to zero. Therefore the resulting equation is of the form

$$\sum_{j \in N_i} \left[(Q_w)_{ij}^{n+1} + (Q_{nw})_{ij}^{n+1} \right] = 0$$

Both the wetting-phase volumetric flow, Q_w, and the nonwetting-phase volumetric flow, Q_{nw}, are related to the pressure differences at the appropriate nodes. In any given pore throat, only one fluid phase is present. That phase is the only one that can have a nonzero flow through that throat. The flow is proportional to the pressure difference across the throat, unless an interface exists at one end of the throat, and that interface cannot enter due to capillary considerations. In that event, the hydraulic conductance of the throat is set to zero for both fluid phases. For the cases when the fluid is not trapped, the conductance for the occupying phase is set to the coefficient appropriate for Poiseuille flow.

The actual solution algorithm involves solution of the resulting set of pressure equations for pore-body pressures, given the fluid distribution at the most recent time step. Once the pressures are determined, flow rates are determined for all of the pore throats. Given these flow rates, the saturation equation is solved for each pore body. Any pore body that becomes completely filled with one phase is allowed to introduce interfaces to all connected throats filled with the other fluid. Each of these throats is subjected to a capillary invasion test, based on the Young-Laplace equation. Throats for which invasion is allowed are filled with the invading fluid; those for which the pressure is not sufficient to allow invasion are marked as trapped for the next time step, and their conductances are set to zero. Once all of the pore-body saturations are updated, the next time step is solved beginning with computation of the pressures at the new time level. Within the structure of this algorithm, the time step size is restricted such that only one pore body is allowed complete its filling during the time step. Therefore, new interfaces are introduced only at one pore body, although updated pressures at other pore bodies may result in previously trapped throats being invaded and thereby freed for flow.

Comparison of Algorithms

These two models represent two relatively opposite approaches to dynamic tracking of interface motions in two-phase flows. The first focuses almost completely on the pore throats, while the second focuses all volume in the pore bodies and neglects virtually all local effects related to two-phase flow. These two different kinds of simplifications to the problem provide a quite different view of the interface motion problem. For a given volume of pore space, this leads to a qualitatively different picture of the pore space. In the first model, explicit interface velocities are resolved, so that meaningful measures of variables like volume-averaged interfacial velocity can be computed. The second model does not really provide an explicit measure of interfacial velocity, so computation of an average measure is difficult. However, it does provide a good picture of fluid distribution within the network, and some estimates of interfacial velocities are possible.

In addition to the conceptual differences between the models, they also differ in computational complexity. The first model, focused on pore throats, involves a fairly complicated computational algorithm that involves several levels of nonlinear iterations (see the algorithm described in Dahle and Celia, 1999). The second algorithm is much less complicated, in part

because the pore-throat volume is neglected, which means the throats are filled with one fluid only, and in part because the capillary pressure in the pore bodies is neglected. A simple implicit-pressure, explicit-saturation (IMPES) type of algorithm linearizes the equations and avoids nonlinear iterations. As such, the algorithm is quite simple to interpret and to code.

Proposed New Algorithm

We propose to continue to develop our dynamic network simulator by including the best features of each of the previous two models, and adding new features to account for wedges of wetting fluid. The presence of wedges of wetting fluid will allow for flow of wetting fluid in pores whose core is occupied by nonwetting fluid. This provides mechanisms for slow drainage, and also allows interfacial areas associated with wedges and films to be modeled explicitly. We will accomplish this by using pore shapes that have edges and corners. For pore bodies, instead of spheres, we will use cubic shapes. For pore throats, we will allow for either rectangular or triangular cross-sectional shapes. We will also allow for arbitrary connection patterns in space, so that we can incorporate images of the pore space into our network description. Overall, the representation of the pore space is a 'general network', where pore bodies and connecting pore throats may be taken from processed images of actual pore geometries, and wherein each pore element can have wedges of wetting fluid that provide hydraulic contact for the wetting phase throughout the network.

Given a network definition, including pore body locations, sizes, and shapes, and associated information for connecting pore throats, the computational algorithm will be based on mass balances written for each of the pore bodies. This is similar to the approach of Blunt and King (1991), except that Blunt and King ignored local capillary pressures within pore bodies. This is consistent with the picture of spherical pore bodies filling with a flat interface. If the pore bodies have a cubic shape, and wedges of wetting fluid are to be taken into account, then this assumption is no longer appropriate. Rather, we need to include local capillary pressures in each pore body. This local pressure will control the interface curvatures within that pore body, and for a given shape of the body, will lead to a specific value of saturation. Morrow and Xie (1999) discuss this for the case of triangular pore throats; similar geometric relationships can be worked out for various shapes of pore bodies and pore throats. The end result is a <u>local</u> relationship between capillary pressure and saturation within a single pore element. This implies an assumption of capillary equilibrium at the scale of an individual interface. This assumption is consistent with the theoretical approach taken by Gray and coworkers, meaning that our computational model will have *scale consistency* with the theory. Numerically, this gives a system of two mass-balance equations at each pore body, with an additional relationship between the pressure difference at the given pore body and the local saturation, where saturation is defined with respect to the volume of an individual pore body.

Next we need to consider how the fluxes that appear in the mass balance equations will be described in terms of phase pressures at the pore bodies. If we assume Poiseulle flow in the pore throats, then we simply need to define resistances to flow in each of the pore throats. But now we are allowing for wetting fluid wedges in the corners of the throats. Therefore in the pore throats that are occupied by a core of nonwetting fluid and wedges of wetting fluid, we need to determine the local saturation in each pore throat, calculate the associated cross-sectional areas occupied by each phase, and then assign resistances to flow in each phase. To do this, we will

rely on simulations of concurrent two-phase flow that are currently being carried out by our colleagues at the Technical University of Delft, The Netherlands (H. Bruining, personal communication, 2000). These detailed computations are providing relative hydraulic conductances for both phases as a function of local interface location within a given pore throat. For throats occupied by only one fluid, then a simple conductance can be computed, which corresponds to simple laminar flow.

If we assume that most of the volume is associated with pore bodies, and that piston displacement within the pore throats occurs instantaneously, then the resulting set of equations looks very much like a standard description of two-phase flow: mass balance equations at each pore body are augmented by a nonlinear relationship between local Pc and S, and a Darcy-type relationship that includes a conductivity term that is a function of local saturation. This is appealing, in that standard solution methods may be employed to solve the system. However, because the equations are written at a scale where the local constitutive relationships are unambiguous (that is, they are consistent with the underlying theory, and the scales over which equilibrium conditions are assumed are explicit), these equations are scale consistent and all terms are based on well-defined physical principles. In addition, because of the explicit geometric representations, the equations can provide detailed information on amounts of interfacial areas, types of interfacial areas (wedge areas versus areas associated with core displacements), and time rates of change of these interfacial areas. All of these terms are important in the new theory. The equations can also provide information about contact line lengths and similar dynamic measures of contact lines.

To implement this type of model, all of the local constitutive relationships need to be worked out, and the model needs to be implemented to compute the appropriate interfacial properties. However, there remains the question of the assumption regarding interface dynamic in the pore throats. If we are building a dynamic network model, can we justify a model that ignores interface dynamics in the pore throats (by assuming it to be instantaneous, such that filling of pore bodies, rather than pore throats, dominates the dynamics)? In addition, if one of our interests is to quantify the volume-averaged interfacial velocity, one of the important components should be interface displacements through the pore throats. Therefore part of our research will involve comprehensive comparisons of models that include interface dynamics in the pore throats (Dahle and Celia, 1999), and those that do not. Initially we will focus on three questions: (1) for simple geometries (spherical pore bodies, cylindrical pore throats, so there are no wetting fluid wedges), what kinds of differences do we see between pore-body-based models and pore-throat-based models? (2) how does each of these models compare to micromodel studies of dynamic two-phase displacements? and (3) If necessary, are there relatively simple ways to include pore-throat displacement dynamics into the general network model that includes more complicated geometries and wedge flows? These questions will be answered by careful comparison of the different types of models, and by careful construction of micromodel test systems and associated comparison between experiments and simulations.

Once we have a dynamic computational model that accounts for all of the important physical processes, we will use the model to evaluate the dynamic nature of the relationship between capillary pressure, saturation, and interfacial area. This includes calculation of the volume-averaged terms appearing in dynamic capillary pressure equation, and evaluation of the

magnitude of the coefficient L in the dynamic equation. It also includes the interfacial velocity terms ($v^{\alpha\beta}$) as well as the interfacial area generation term ($G^{\alpha\beta}$). We will do this for simplified 'test geometries', based on regular lattice structures. We will also do this for networks extracted from pore-space images (Yu Ma REF Here), where the network structure is more random and the shapes more angular. For these kinds of structures, we will have direct comparisons to dynamic experiments performed on two-dimensional networks that are etched into micromodels. The resulting models will therefore be subjected to experimental verification, and be used in more complex, three-dimensional network simulations to test the theoretical developments involving dynamic capillary pressure, interfacial area dynamics, and fundamental definitions of volume-averaged variables like phase pressures and average capillary pressure.

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