Photoluminescent volumetric imaging: A technique for the exploration of multiphase flow and transport in porous media

Carlo D. Montemagno and William G. Gray

Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN

Abstract. A new measurement technique, photoluminescent volumetric imaging (PVI), has been developed for the visualization and quantification of multiphase flows and interface behavior in porous media. For this technique, a transparent, multiphase porous-medium system is constructed of optical-quality quartz sand, and two immiscible fluids matched to the optical refractive index of fused silica. Doping the fluids with property-selective fluorophores allows planar areas of the system to be successively excited with a shaped laser light to reveal the structure of the system. The resulting illumination is recorded by a high-resolution, cooled, slow scan charged-coupled device (CCD) camera. The planar digital images produced are then processed to generate a true three-dimensional data set that allows for quantitative study of the distribution of phases and interfaces within the porous medium. Sample volumes up to 125 mm^3 in size with a resolution of better than 1 μm have been measured. Because of the large sample size and the high resolution of the measured data, geometric, flow, and phase interface information can be visualized and extracted at both subpore and system scales.

Introduction

Investigation of the processes associated with the flow of fluids in porous media has application in biophysics, ceramic and petroleum engineering, agronomy, and hydrology. Researchers rely upon the prevailing fundamental physical laws that are used to describe the fate and transport of fluid in porous media. The physical theories supporting many disciplines are based upon the simple empirical relation proposed by *Darcy* [1856] from crude observations of single phase flow in a porous medium. Because of the difficulties involved in measuring physical processes in a porous medium, the extension of Darcy's law to multiphase flow has been done heuristically without support of fundamental theory. This path of development has resulted in little theoretical advance in the understanding of how processes that can be described at the subpore scale are evident at a spatial scale encompassing tens or hundreds of pore diameters.

Major impediments to the implementation of recent mathematical advances [*Gray and Hassanizadeh*, 1989, 1991; *Hassanizadeh and Gray*, 1990] in the description of multiphase flow through porous media are the extensive data necessary to characterize the performance of these systems. Typically, a porous medium is a solid that exhibits structural variations encompassing length scales which vary over several orders of magnitude. These structural variations control the movement and distribution of phase interfaces which, in turn, control the flow of the fluids through the medium. Thus, pore scale measurements of the interfacial area and pore geometry are required over a representative 3-D volume of porous medium with a characteristic length much greater than the pore scale.

The difficulties in acquiring accurate measurements of the various physical variables that control the behavior of multiphase systems stem from inherent conflicts between the information requirements necessary for understanding the flow process and the for characterizing the physical attributes of the porous medium/fluid system. Additionally, since a multiphase porous medium is a nonlinear complex system, the behavior of this system is dependent on both the characteristics of any forcing placed upon it and also upon the initial energy state of the system. Consequently, full characterization of a porous media system requires that interfacial area and phase saturation measurements be made at different initial and final energy states. Currently available measurement technologies can not satisfy these requirements.

Nondestructive practices for characterizing multiphase porous media typically concentrate on measuring phenomena at either the pore scale or at some larger continuum scale. At the porous medium scale, gross system properties such as bulk phase capillary pressure and fluid flow are measured directly [*Ferrand et al.*, 1990]. However, direct measurement of phase saturations within the porous medium is not possible without disturbing the sample. Indirect determinations of phase saturations have been accomplished by measuring the change in mass of a sample, by measuring the change in attenuation of gamma ray energy [*Ferrand et. al.*, 1989], and through 3-D imaging technology such as x-ray tomography [*Wang et al.*, 1984] or magnetic resonance imaging [*Zeev et al.*, 1993]. However, because of inherent resolution limitations in the physics associated with these techniques, fine distributions (i.e. less than 2 mm^2) of the fluids are not discernible [*Vinegar and Wellington*, 1987]. Consequently, none of the listed techniques is capable of providing an accurate measure of phase interfacial areas or pore structure.

Current methods for examination of microscale porous media processes can be divided into two different classes: idealized 2-D approaches geared toward investigating fluid flow and transport processes; and 3-D imaging technologies. The measurement techniques utilizing 2-D physical domains such as sand boxes [*Schwille*, 1988] and etched plates [*Wan and Willison*, 1994] provide valuable qualitative insight into the mechanisms associated with multiphase flow through porous media. However, boundary effects of the confining plates cause the physical system to behave differently from what would be expected in the interior of a 3-D porous medium. Additionally, the relatively small number of pores normally incorporated into these systems significantly reduces both the dynamic range of measurement scales and the system complexity. Therefore, meaningful, quantitative information on the relationship between interfacial area, phase saturations and pore structure cannot be extracted from these techniques. X-ray tomography [*Pyrak-Nolte and Montemagno*, 1994; *Warner et al.*, 1989], magnetic resonance imaging [*Hove et al.*, 1990; *Zeev et al.*, 1993], and synchrotron radiation microtomography [*Spanne et al.*, 1992; *Lindquist et al.*, 1992], are all 3-D imaging techniques that provide quantitative information about multiphase porous media systems. While each of these imaging technologies has merit, they all suffer from inadequacies in either resolution, length scale, or speed of measurement. The general inability of all these measurement methodologies to provide accurate measurements of fluid and solid interfaces at both the pore and continuum scale moti-

vated the development of the new measurement technique, photoluminescent volumetric imaging (PVI).

Materials and Methods

PVI is an optical visualization technique which utilizes a model multiphase porous medium. The transparent porous media system is comprised of optical-quality quartz sand and two immiscible fluids matched to the optical refractive index of fused silica. The fluids are doped with property-selective fluorophores that distribute within the fluids of interest and are excited by electromagnetic energy in the form of coherent laser light sheets. Excitation patterns within successive sheets of laser light are captured as computer images. Because the collected data are two-dimensional projections, the need to generate tomographic reconstructions is eliminated, significantly reducing computational requirements and permitting rapid acquisition of high resolution data over very large areas. Typically, each voxel has a resolution of 5 μm^2 integrated over the light sheet thickness of 100 μm. A resolution scale as fine as 1 μm can be obtained and a sample volume as large as 10 mm^3 can be imaged if appropriate sampling technology is used. However, because of the very large quantity of data that would be generated at such a high resolution, an overall system resolution of 10 μm along each axis is more typical.

To measure dynamically the change in the interface surface areas and phase distributions, the fluid-fluid and fluid-solid interfaces must exhibit a high contrast with the neighboring phases in the visible portion of the electromagnetic spectrum. This condition is achieved by exploiting the molecular charge structure of the fluid-fluid system. Researchers [*Morrison and Weber*, 1987; *Roberts and Tombs*, 1987] have demonstrated that some fluorescent molecular probes will concentrate along the interface between two immiscible liquids. Selection of such a probe and filtering of the energy emitted by the probe allow only the illuminated interface to register on the detector using the PVI technique.

Apparatus

Figure 1 provides an optical schematic of the PVI measurement system. A single-frequency coherent light beam is generated with an argon-ion laser. Typically the laser beam has a wavelength of 514.5 nm with a total power of approximately 750 mW. This 1.5 mm light beam is then expanded to a diameter of 25 mm 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 125 μm over a length of approximately 15 mm and directed through the measurement cell orthogonal to the imaging system.

Within the measurement cell is the model multi-phase porous medium system consisting of optical-quality, fused-silica sand grains and one or more fluids with a refractive index matched to the fused silica. Dissolved in the fluids are property active fluorophores. When excited, these fluorophores emit light at an energy different from the excitation source. Because these fluorophores can be tailored to interact with specific physio-chemical features of the fluids, different structures and properties of the multi-phase system can be measured and visualized.

The light sheet directed into the measurement cell is really a volume of light, 25 mm high, 30 mm long and up to 125 μm thick. Consequently, at any given time all of the fluorophores
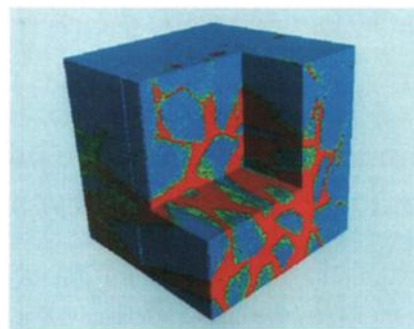

Figure 2. Excavated view of a 125 mm^3 cube of porous medium (blue) saturated with a single fluid.

scan, charge-coupled device (CCD) camera that acquires the image. After an exposure of approximately 100 ms, the CCD system digitizes the image and transfers it to a computer for analysis at a rate of 500 kHz. Resolutions of better than 1 μm and over volumes greater than 125 mm^3 have been achieved.

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. Simultaneously, the imaging system is translated to compensate for the change in optical path length. The translators used in the described apparatus will position the measurement cell to a precision of 100 nm with a repeatable accuracy of 1 μm over a 25 mm translation. Because of the precision with which the measurement cells are moved, each image frame can be referenced to an absolute coordinate system. Consequently, the geometry of the system can be reconstructed and any changes in phase interfaces visualized over time. These images are quantitatively analyzed, and parameters of interest are extracted.

The soil for the translucent porous medium is optical quality fused silica (Corning #7940). The glass is ground and filtered into particle sizes ranging from 710 μm to 63 μm. The glass sand is then cleaned to remove any impurities which might alter its surface properties. A medium with known grain size distribution is constructed by blending the ground glass. This medium is packed in a measurement cell with optically clear sides of a design suitable for the intended experiment.

Four different fluids, produced by R.P. Cargille Laboratories, have been obtained for use in the system. The fluids are all refractive indexed matched (±0.014%) to the fused silica at a wavelength of 514.5 nm and were selected so that the optical dispersion, the change in refractive index with wavelength, of the fluids closely matches that of the fused silica. Two of the fluids are aqueous; one is constructed on a base of silicone oil; and the fourth is a composite of different hydrocarbons. The fluids have a wide range of physical properties so that the physics of a variety of systems can be explored in various pairings of an aqueous and a nonaqueous fluid.

To allow the solid, nonaqueous, and aqueous phases to be distinguished in the data collection process, both of the fluid phases must be doped with fluorophores. Typically the aque-
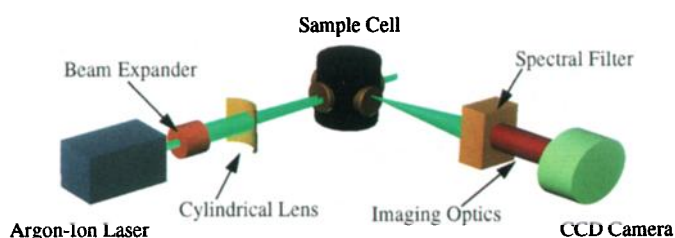

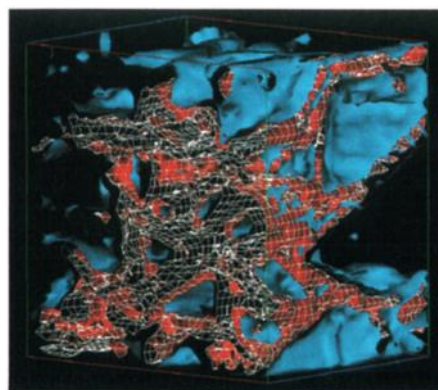**Figure 1.** Schematic of the PVI measurement system.

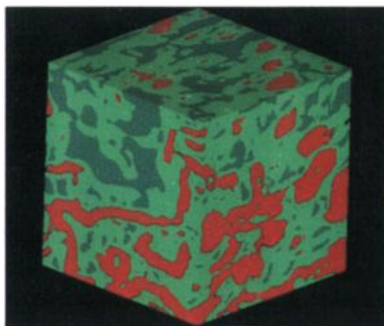**Figure 3.** Mesh imposed on the interface of figure 2.

Figure 4. Three-phase 550 μm^3 cube constructed from 64^3 data set. 180 μm < grain size < 250 μm. Fused silica is green; aqueous phase is red; non-aqueous phase is blue.

Figure 6. System of figure 4 with only silica phase visible.

ous phase is doped with an active dye that congregates along the fluid-fluid interface. A representative dye used in these studies is the cationic membrane probe octadecylindolcar-bocyanine, $DiIC_{18}$, characterized by a long (18 carbon) alkyl tail. This tail gives the molecule a slight lipophilic character, so that it preferentially distributes itself along the aqueous-nonaqueous interface. This probe has an emission peak at approximately 550 nm. Interestingly, the spectroscopic properties of $DiIC_{18}$ are largely independent of the length of the alkyl tail and more a function of the heteroatoms in the terminal bridge and the fluid in which the molecule is immersed. Consequently, a slightly different Stokes shift, the difference in wavelength between the excitation and emission energies, will occur between the fluorophores aligned along the interface and those within the bulk fluid phase. This property can aid in the identification of the actual location of the interface.

The nonaqueous phase is doped with a proprietary hydrophobic Exciton laser dye, LDS-721, that has an emission Stokes shift outside the emission envelope of $DiIC_{18}$. This dye is characterized by high quantum yields, typically 0.8 - 0.9, and an exceptionally long Stokes shift. LDS-721 has a fluorescence emission maximum at 660 nm. The large difference in Stokes shift between the aqueous and nonaqueous fluid fluorophores aids in the identification and analysis of the various interfaces (fluid-fluid, nonaqueous fluid-solid, and aqueous fluid-solid). Furthermore, because the emission maximum of LDS-721 is significantly above the adsorption maximum of $DiIC_{18}$, secondary emissions are minimized.

Results and Discussion

The equilibrium experiments reported here are intended to demonstrate the PVI technique and establish elementary system operating envelopes. The first experiment was performed with a system consisting of a solid phase and a single aqueous fluid phase doped with $DiIC_{18}$. Initially, the sample cell was partially filled with fluid. A medium composed of glass particles, 500 - 200 μm, was then added. A series of 40 images (512x512 pixels) was taken with the image plane spaced at 125 μm. The field of view for this experiment was 5 mm, for an overall system resolution of 10 μm in each image plane and 125 μm orthogonal to the planes. The total volume measured was 125 mm³.
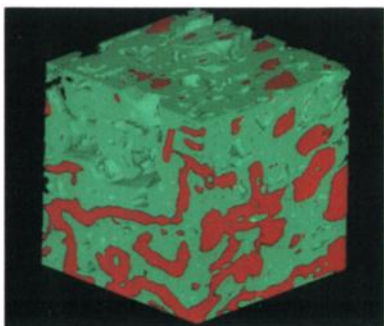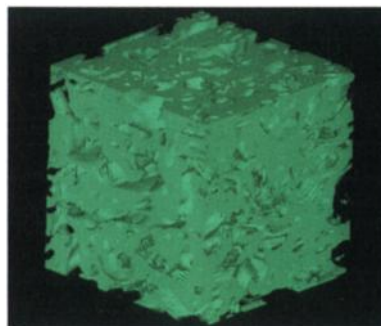
Figure 2 is a direct reconstruction of the raw data with a quarter section removed so that some of the internal details of the data set can be observed. Three regions within the porous medium are readily evident: the solid phase (blue), the fluid phase (red), and the interface between the phases (green). Because the images are registered with high precision, the full structure of the solid-fluid system can be related directly to a set of 3-D coordinates. Consequently, data obtained at the pore scale can be averaged and related directly to information obtained at a larger scale from the same sample.

Figure 3 demonstrates that phase boundaries can be extracted quantitatively from the measured data. It displays an isosurface of the solid-fluid interface with a triangular grid overlay. In this visualization, only a coarse grid is presented in the interest of clarity, and an "internal" surface of the soil grains is shown for reference. The actual full triangular mesh contains over one million nodes. Each node is defined by its coordinates and connectivity information with neighboring nodes. From these data, surface areas and void volumes per volume of medium can be calculated at pore and larger scales. Such information is useful in a variety of applications, including verification of microcontinuum-scale models and pore size distribution correlation analysis.

A second experiment incorporates multiple fluorophores in a three-phase system. Here the LDS-721 fluorophore is used in a nonaqueous hydrocarbon based fluid. The aqueous fluid fluorophore for this experiment was the highly polar zwitterionic fluorophore N-(3-sulfopropyl)-4-(p-didecylaminostyryl) pyridinium. This fluorophore was selected because of its very low solubility in oil and its low fluorescence in the bulk aqueous phase [Loew and Simpson, 1981]. The molar concentrations for the fluorophores are 1.1 μmole and 0.5 μmole, respectively, for the nonaqueous and aqueous phases. The sample cell cube was partially filled with the aqueous fluid. A mixture with particle sizes ranging from 250 - 180 μm was slowly added until the aqueous fluid surface barely covered the solid. The doped nonaqueous fluid was next overlain on this system. Finally, additional quartz sand was added to the cell until the sand reached the level of the surface of the fluid. The sample cell was then rocked gently to generate some displacement between the two fluid phases.

A total of 89 image planes with a field of view of 4.6 mm were measured at a resolution of 512x512 pixels. These
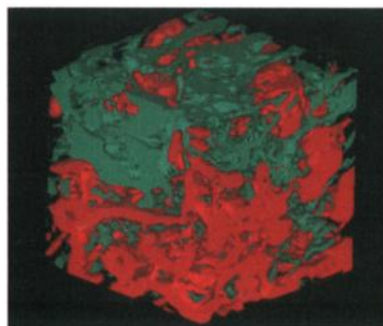

Figure 5. System of figure 4 with nonaqueous phase invisible.

Figure 7. System of figure 4 with solid phase invisible.

image planes were expanded using cubic convolution interpolation to form a virtual 512^3 volumetric data set. This interpolation technique approximates the theoretically optimum sinc interpolation function using cubic polynomials. The interpolated values are calculated by convolving neighboring points with the sinc function. Because of the high computational costs and the small interpixel distances in the image plane compared to the distance between measurement planes, the interpolation was performed on 2-D data slices extracted perpendicular to the image planes. Using the nearest 16 neighboring points, the 512x89 2-D arrays were expanded to 512x512 2-D arrays. These arrays were combined to form the 512^3 volumetric data set. A smaller volume of interest, 64^3 voxels, was extracted in order to illustrate the high level of detail intrinsic to this data set.

Figures 4-7 all have a field of view of approximately 0.55 mm with a resolution of approximately 8.7 μm. Figure 4 shows all three phases. Figures 5 and 6, respectively, display the sample volume with first the nonaqueous phase, then both liquid phases removed. The pore structure of the solid is clearly visible in these renderings. Finally, in Figure 7 the solid is removed from the image so that only the two fluid phases are visible. The three dimensionality and complexity of this multiphase porous medium is clearly evident in these realizations.

One facet of current work is focused on comparing measurements made with PVI to measurements made using more traditional methods. Gravimetric measurements of pore and solid volumes are being compared to the volumes calculated using PVI. Additionally, specific surface area and porosity determined from autocorrelation analysis [Berryman, 1985; Berryman and Blair, 1987] are being compared to surface areas calculated from generated isosurfaces.

As the results of these preliminary experiments demonstrate, the PVI technique can provide great insight into the behavior of fluids in a porous medium. Tailoring the selection of a fluorophore to the physical processes of interest allows a wide range of phenomena to be explored. Interface mass transfer, nonaqueous phase dissolution, and in situ bacterial processes are just a few of the physical systems that could become better understood based on PVI measurements.

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Carlo D. Montemagno, Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556-0767. (e-mail: cmontema@hawk.ce.nd.edu)

William G. Gray, Department of Civil Engineering and Geological Sciences, University of Notre Dame, Notre Dame, IN 46556-0767. (e-mail: William.G.Gray.3@nd.edu)