An Investigation of the Transport and Fate of Petroleum Hydrocarbons in Homogeneous and Heterogeneous Pore Networks using Flow-Visualization Techniques

by

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Independent Study

Submitted in Partial Fulfillment of the Requirement for the Degree of Master of Science in Hydrology

New Mexico Institute of Mining and Technology

Socorro, New Mexico

May 1, 1989

ACKNOWLEDGMENTS

"He received me in his library, and on my taking leave showed me a shorter way out of the house through a narrow passage which was crossed by a beam overhead. We were still talking as I withdrew, he accompanying me behind, and I turning partly toward him, when he said hastily, 'Stop, stop!' I did not understand him till I felt my head hit against the beam. He was a man that never missed any occasion of giving instruction, and upon this he said to me: 'You are young and have the world before you; *stoop* as you go through it, and you will miss many hard thumps.' This advice thus beat into my head, has frequently been of use to me; and I often think of it when I see pride mortified and misfortunes brought upon people by carrying their heads too high."

- Benjamin Franklin (1784)

The research presented in this report is not due to the sole efforts of any one person, but many. To all those who contributed, many humble thanks are given, all richly deserved: to John Wilson and Steve Conrad, who made this project challenging and fun; to the two other 'Blob Boys', Ed Hagan and Bill Peplinski, for their creative support and input; to Mary Graham, who taught me everything I wanted to know about micromodels and more; and to Teresa, for being there.

This work was supported by grants from the U. S. Environmental Protection Agency, Robert S. Kerr Laboratory and the New Mexico Water Resources Research Institute in Las Cruces, New Mexico.

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ABSTRACT

Organic liquids that are essentially immiscible with water migrate through the subsurface under the influence of capillary, viscous, and buoyancy forces. Although displacement processes are known to be dependent upon a variety of factors, this report focuses on only three: (1) the fluid flow rate, (2) the presence of heterogeneities and, (3) the number of fluid phases present.

The process of organic liquid advance into the subsurface, followed in turn by the displacement and trapping of the organic phase, may be observed using flow visualization techniques. This paper describes and illustrates a flow visualization technique where multiphase displacement experiments were performed within etched glass micromodels. Micromodels are physical models of a pore space network, created by etching a pattern onto two glass plates which are then fused together. The pores have complex three dimensional structure, although the network is only two dimensional. The advantage of performing multiphase flow experiments using micromodels is that they give us the ability to actually see fluids displace one another both in a bulk sense and in individual pores. Displacement photographs of the entire model allow examination of the bulk displacement processes, while photomicrographs taken through an optical microscope permit observation of details on a pore level. Etched glass micromodels provide an excellent method with which to study the mechanisms controlling the transport and capillary trapping of organic liquids because the structure of the pore network and the wettability of the system can be closely controlled. This technique also allows the distribution of the organic phase within the pore space to be observed under two- and three-phase conditions.

Descriptions of the micromodel manufacturing process, as well as the experimental procedures used to run the completed micromodels, are provided in the experimental methods section of the report. Then, in the results section, micromodel experiments are presented which compare 'homogeneous soils' versus 'heterogeneous soils' at several flow rates. Finally, three-phase micromodel experiments are presented and compared to the analogous two-phase case.

INTRODUCTION

Hydrocarbons and other non-aqueous phase organic liquids comprise a significant portion of the subsurface contaminants found at hazardous waste sites and leaking underground storage tank sites (e.g., Burmaster and Harris, 1982; Chaffee and Weimar, 1983; Convery, 1979; EPA, 1980, 1982, 1983; Feenstra and Coburn, 1986; Jercinovic, 1984; Maugh, 1979; McKee et al., 1972; J. R. Roberts et al., 1982; Villaume, 1988; Williams and Wilder, 1971). Usually released at or near the surface, these organic liquid contaminants are largely immiscible with water and therefore travel through the subsurface as a separate liquid phase. As the organic phase moves through the vadose zone, a portion of its volume is immobilized by capillary forces (Schwille, 1967, 1981, 1984, 1988; van Dam, 1967; de Pastrovich et al., 1979). The remainder passes on, and if the volume of the organic phase is large enough, it eventually reaches the water table. At the water table, the organic phase spreads laterally if it is less dense than water, or it continues to move downward though the saturated zone if it is more dense than water. In both cases, the organic phase migrates down gradient with the ambient groundwater flow. At the leading edge of a plume of organic liquid contaminants, organic liquid displaces water as it advances through the aquifer. At the trailing edge of the plume, the organic liquid becomes displaced by water, and its saturation and permeability is reduced until it becomes discontinuous and immobile within the pore space. The amount of organic liquid left behind is called the residual organic saturation, and is measured as the volume of organic liquid trapped in the pores relative to the volume of the pores. Eventually, the entire volume of an organic liquid spill may become immobilized by this process (Wilson and Conrad, 1984).

The organic liquid phase is sometimes referred to as being immiscible with water and air. Although that expression is used here, it is important to realize that small concentrations of the various components of the organic phase volatilize into the air phase and dissolve into the water phase. In the saturated zone, a halo of dissolved organic components precedes the immiscible phase in its migration. Even when the so-called immiscible organic liquid has been immobilized by capillary trapping, the passing groundwater dissolves some of the residual. In effect, the capillary-trapped organic liquid phase acts as a continuing source of dissolved organic pollutants. In the vadose zone, the residual saturation also acts as a source of organic vapors to the air phase (Schwille, 1967, 1981; de Pastrovich et al., 1979).

Development of improved technologies to clean up organic pollutants depends in large part on developing an ability to understand and predict the migration of liquid, vapor, and dissolved organics. In particular, there is a need to understand how the residual organic liquid is trapped and how it can be hydraulically mobilized or otherwise removed. A paucity of experimental results regarding these issues makes site characterization conjectural, predictive modelling unreliable, and remediation design of organic liquid leak or waste sites less effective than might be possible.

The process of organic liquid advance into the subsurface, followed in turn by the displacement and trapping of the organic phase, may be observed using flow visualization techni

experiments using micromodels is that they give us the ability to actually see fluids displace one another both in a bulk sense and in individual pores. Displacement photographs of the entire model allow examination of the bulk displacement processes, while photomicrographs taken through an optical microscope permit observation of details on a pore level. Etched glass micromodels provide an excellent method with which to study the mechanisms controlling the transport and capillary trapping of organic liquids because the structure of the pore network and the wettability of the system can be closely controlled. This technique also allows the distribution of the organic phase within the pore space to be observed under two- and three-phase conditions.

Although displacement processes are known to be dependent upon a variety of factors, this report describes micromodel experiments that focused on only three: (1) the fluid flow rate, (2) the presence of heterogeneities and, (3) the number of fluid phases present. Descriptions of the micromodel manufacturing process, as well as the experimental procedures used to run the completed micromodels, are provided in the experimental methods section of the report. Then, in the results section, micromodel experiments are presented which compare 'homogeneous soils' versus 'heterogeneous soils' at several flow rates. Finally, three-phase micromodel experiments are presented and compared to the analogous two-phase case.

EXPERIMENTAL METHODS

Mattax and Kyte introduced the 'capillary micromodel' in 1961 as a method to make detailed observations of fluid interface movements. Their technique allowed them to precisely control the pore geometry and its variability; factors difficult to control in bead-pack models. They created their models by first mechanically scribing pore-network patterns on a wax-coated plate, and then by contacting the exposed glass surface with hydrofluoric acid. Unfortunately, this method relied on the patience and manual dexterity of the model maker. Davis and Jones (1968), Chatzis (1982), and McKellar and Wardlaw (1982) improved the manufacturing process by adapting a common photo-etching procedure to glass. By generating a pore-network pattern by photo-reproduction instead of by mechanical means, they were able to manufacture large, complex models with pore sizes that approximated those found in oil reservoir rocks. Their technique, similar to one used for making printed circuits in the electronics industry, involved 'photographing' the desired patterns on glass plates coated with an ultraviolet-sensitive resin and etching the plates with hydrofluoric acid. The micromodel construction procedures described below were modifications of Chatzis's methods as well as those developed by Eastman Kodak (1975, 1979).

MICROMODEL CONSTRUCTION

The manufacture of micromodels was a difficult process that initially required an enormous investment of time and effort to learn. However, once the technique was perfected, the whole construction process lasted only three or four days. To make a micromodel, a glass mirror, stripped of its protective enamel backing to reveal a copper layer, was first coated with a photosensitive resin. Then, a transparency of a desired pore-network pattern was placed on the coated mirror surface and was exposed with ultraviolet light. The unexposed resin beneath the opaque portions of the pattern was removed with xylene. The copper beneath the pattern was removed with nitric acid, and the glass beneath the copper was etched with hydrofluoric acid (HF). Lastly, a mirror-image pattern was etched on another piece of mirror, and the two etched halves were fused together in a muffle furnace to form the completed micromodel.

Pattern Preparation

Pore-network patterns were created by modifying commercially available drafting pattern films with drafting pens. A local photographer reduced each pattern to a standard size and transferred it and a mirror image to plastic transparencies. The emulsion side of each transparency contacted the coated glass plates; transparencies laid emulsion-side up on a plate allowed too much light to leak under the pattern during exposure to UV light. The patterns included 'reservoirs' at each end of the network through which fluids were added and removed in the completed micromodel. An example of a pore-network pattern is shown in Figure 1.

Mirror Preparation

Ordinary mirrors are manufactured by coating a piece of glass first with a silver layer, then a copper layer, and finally a protective enamel backing (see Figure 2). Mirrors were used in micromodel construction



FIGURE 1. Pore-network pattern for the homogeneous model.



FIGURE 2. Mirror construction.

FIGURE 3. Mirror with enamel removed to reveal copper surface.

as a matter of convenience: the copper layer provided a binding surface for the photosensitive resin described below, and the enamel backing served to protect the copper during transport and storage. A less convenient alternative to mirror glass would have been to coat plain glass with copper by evaporation in a high-vacuum chamber.

A 5 X 8 inch (12.7 X 20.3 cm) piece of mirror glass was prepared for coating with resin by first placing it, enamel side up, in a hot 50% by weight solution of NaOH to remove the protective backing. The solution was kept as hot as possible without actually boiling (approximately 90° C). During the next 5-10 minutes, the integrity of the enamel was tested by gentle scraping with teflon tongs. When the backing scratched easily, the mirror was taken from solution and the enamel was removed from the plate by gentle rubbing with a Viton-gloved hand under a stream of hot tap water. If the plate was left for greater times in solution, the backing slid off easily with no rubbing necessary; however, for these longer soaking times, the NaOH slightly corroded the copper beneath the enamel layer. If any enamel was left on the plate after the rinse, the

affected portion was reinserted into the solution for a short time and then re-rinsed. Some experimentation was necessary to find a brand of mirror with enamel (Willard mirror glass, for instance) that could be removed completely and easily. After the backing was removed, the plate was rinsed with distilled water and dried in an 80° C oven (see Figure 3).

Pattern Exposure and Development

Kodak Thin Film Resist (KTFR), an ultraviolet-sensitive resin, was used to transfer the pore-network pattern to the mirror surface. In a darkened room, 1 part KTFR by volume to 2 parts xylenes were mixed. A mirror plate stripped of its protective backing was held horizontally, copper side up, and coated with approximately 10 ml of resist mixture. The plate was tipped in various directions to evenly distribute the resin over the copper surface in a layer of uniform thickness (see Figure 4). The plate was tilted vertically and allowed to air dry until the coating was no longer sticky to the touch (generally 20-30 minutes). If long HF etching times were expected, the plate was baked in an 80° C oven for 10 minutes to help the resin adhere to the copper surface. The disadvantage of baking was that the resin was difficult to remove in later steps. Unused coated plates were stored in a dark place.

After the coating was dry, the patterned transparency was placed emulsion-side down on the coated mirror surface, covered with a clear piece of glass to ensure good contact between the pattern and the surface, and placed under a 1600 microwatt per centimeter long-wave ultraviolet light source at a distance of 24.5 cm. The assembly was exposed to the UV source for approximately 12 minutes as illustrated in Figure 5.

Exposure times were found to be a function of the thickness of the resin coating, the intensity of the light source, and the distance of the light source from the plate. A thick coating (an undiluted KTFR mixture) better protected the non-pore areas from HF during the etching step but required greater exposure times than for a thin coating. However, thin coatings made by diluting KTFR with xylene reproduced fine details more faithfully and required smaller exposure times than for thick resist layers. It was also found that exposure time decreased with a shortened distance between the light source and the model, and with increased intensity of the light source. Exposure times were also affected by the age of the resin: the older the bottle of KTFR (on the order of years), the longer the exposure times needed.





FIGURE 5. Pore-network pattern exposed with UV light onto coated copper surface.

When the exposure was complete and while the room lights were still dim, the plate was removed from under the UV light and the surface was sprayed with xylene. The plate was tipped back and forth for about 1 minute to wash away the undeveloped resist representing the pore-network pattern (see Figure 6). The plate was rinsed with warm tap water, then distilled water, after which the normal room lighting was restored. If the pattern was not visible, more xylene was applied, and the plate was rinsed again. The plate was shaken to remove excess water droplets and was placed in an 80° C oven for 10 minutes. The plate was removed and cooled before the next step.



Etching Copper

The cooled model was placed in a 50% by weight solution of HNO_3 for approximately 10 seconds, or until the copper and silver layers unprotected by resist (the pore-network pattern) had dissolved to reveal the underlying glass surface as illustrated in Figure 7. The plate was rinsed quickly with cold tap water and then with distilled water. After the plate had been dried in an 80° C oven, the pattern was examined under a microscope for imperfections. Small undissolved portions of the network were removed carefully with a dental tool or scriber. If necessary, the plate was re-dipped in the HNO₃, then re-rinsed, to remove copper and silver left in the network after the first acid dip.

Etching Pattern in Glass

All areas of glass that were to remain unetched, such as the model edges and back, were coated with excess resist mixture and allowed to dry. The model was placed pattern-side up in a tray of concentrated HF for about 15 minutes. Longer etching times were used for models requiring deeper pores. When the model was removed from solution, it was promptly rinsed in cold water, and the network was scrubbed with a wire brush to remove siliceous deposits formed during etching. The resist was removed with a razor blade, the copper and silver with HNO_3 , and the model was washed with detergent, rinsed with distilled water, and allowed to dry.

Model Assembly

A mirror-image micromodel half was produced by the above methods using a mirror-image transparency. Inlet and outlet ports were drilled with a diamond drill bit in the reservoir areas of one of the

plates. The two halves were aligned under a microscope, and cyanoacrylate glue was wicked in between the plates from the edges to temporarily hold them together. The model was placed in a muffle furnace and fused at 720° C for 15 minutes. Longer fusing times resulted in smoother, smaller pores; however, if a model was left too long in the furnace, some of the pores closed and the network became disconnected. Cross-sectional views of typical micromodel pore bodies and throats by a scanning electron microscope are depicted in Figures 8 through 10.

MICROMODEL EXPERIMENTAL PROCEDURE

In the two-phase micromodel experiments, an initially water-saturated micromodel was flooded with Soltrol at a prescribed rate to simulate the movement of an organic liquid into the saturated zone. After the fluid saturations stabilized, the model was flooded with water at low velocity. The organic liquid still in the model after water injection remained as residual saturation 'blobs': immobile and disconnected pockets of organic liquid which have been trapped by capillary forces. The two-phase experiments represented a scenario in which an organic liquid percolated into the saturated zone, then was displaced by ambient groundwater flow, and finally was left behind as residual organic liquid saturation.

In the three-phase experiments, an initially water-saturated micromodel was drained with air under an applied suction. The magnitude of the applied suction determined the water saturation remaining in the model. Organic liquid was then introduced into the column under low-flow conditions, simulating the infiltration of organic pollutants into the vadose zone. After steady state conditions were reached, the organic liquid was again drained with air. The three-phase experiments represented a scenario where an organic liquid percolated through the vadose zone to the water table, leaving behind trapped organic liquid.

During flooding or drainage, a capillary end effect was sometimes observed at the bottom of the model (see Figure 16, left, for example). A cure to this problem was to alter the pore-network pattern so that it included a series of small pores in one of the end reservoirs (see Figure 11). These small pores, when water-wet, prevented the non-wetting organic phase from passing into the end reservoir, thus building the organic-phase pressure in the model, allowing the wetting phase to drain more completely, and eliminating the end effect.

Model Preparation

Prior to an experiment, the micromodels were cleaned with chromic acid, thoroughly rinsed with distilled and deionized water, and were saturated with the aqueous phase. After the completion of an experiment, the micromodels were evacuated with a vacuum, cleaned once again with chromic acid, and readied for reuse in future experiments.

Fluid Preparation

The fluids used in the micromodel experiments were air, water, and Soltrol-130. Soltrol is a $C_{10} - C_{13}$ hydrocarbon that is less dense (0.753 g/cm³) and slightly more viscous (1.45 cP) than water. The aqueous phase was prepared by combining 10 milliliters of blue food color with one liter of distilled water. The



FIGURE 8. SEM photomicrograph of a pore throat cross-section.



FIGURE 9. SEM photomicrograph of a pore body cross-section.



FIGURE 10. SEM photomicrograph of a cross-section of several pore bodies.



FIGURE 11. Detail of the pore-network pattern for the homogeneous model with the capillary barrier.

organic phase was prepared by combining 0.90 grams Oil Red O with one liter of Soltrol-130, by stirring the mixture for one hour, and then by straining the mixture through a coarse paper filter.

Two-Phase Experimental Procedure

The micromodels were initially saturated with water by connecting each one to a circulating pump and a reservoir of the aqueous phase as shown in Figure 12a. Water was then flushed through the model until all entrapped air was removed. Then, Soltrol was injected at a prescribed rate into each model with a Sage Instruments model 351 syringe pump. After the fluid saturations stabilized, the syringe pump flow direction was reversed and the model was flooded with water. Capillary forces trapped the remaining organic liquid as immobile, disconnected blobs.

Micromodels were oriented either vertically or horizontally during the two-phase experiments. For vertically-positioned micromodel experiments, the syringe pump was connected to the top fitting of the model and was flooded with Soltrol from the top to the bottom (Figure 12b). In the horizontally-oriented experiments, the syringe pump was arbitrarily connected to the left fitting and Soltrol was flooded into the model from left to right (Figure 12c). The pore networks shown in Figures 1 and 14 were run vertically. The network in Figure 15 was run in both the horizontal and vertical positions.



FIGURE 12. Two-phase micromodel experimental set-up.

Three-Phase Experimental Procedure

As in the two-phase experiments, the micromodels in the three-phase experiments were de-aired with a circulating pump. With the model positioned vertically, the micromodel was drained with air under a suction applied by a buret, which had been connected to the bottom fitting (Figure 13a). When the syringe pump had been attached to the model's top fitting, organic liquid was introduced into the top of the model to simulate the infiltration of an organic liquid into the unsaturated zone (Figure 13b). After steady state conditions were reached, that is, after the fluid saturations stabilized, the syringe pump was detached from the top fitting and the micromodel was once again drained with air via the buret attached to the model's bottom fitting.



FIGURE 13. Three-phase micromodel experimental set-up.



FIGURE 14. Pore-network pattern for the 'aggregated' model.



FIGURE 15. Pore-network pattern for the heterogeneous 'stringer' model.

RESULTS

Flow visualization techniques were used to illustrate the advance of organic liquid and its subsequent displacement by flowing groundwater in both the saturated and unsaturated zones. The focus of this research was to study how fluid flow rates, the presence of heterogeneities, and the number of fluid phases present affected residual organic phase saturations in a soil. To accomplish this goal, a number of experiments were designed and performed. First, a homogeneous-patterned micromodel was manufactured and run at two flow rates. Then, the homogeneous pattern was altered to create several heterogeneous patterns from which models were made and which were also run at various rates and in various orientations. Ultimately, these heterogeneous experiments were compared to the standard homogeneous case. The homogeneous model was also used in the three-phase experiments described below. All displacement experiments were recorded on videotape and with still film on both the bulk- and pore-level scales.

ORGANIC LIQUID MOVEMENT AND CAPILLARY TRAPPING IN A HOMOGENEOUS POROUS MEDIUM

The pore-network pattern shown in Figure 1 and used in the experiments below is termed 'homogeneous' because it has a similar pore structure throughout. That is, all the pore bodies are of approximately the same diameter, as all the pore throats are of similar width.

Organic Liquid Advance in a Homogeneous Micromodel

A water-wet etched glass micromodel experiment (Figures 1 and 16) serves as good example of the displacement process of organic liquid movement into a water-saturated homogeneous soil. The water-saturated micromodel was oriented vertically, and flooded from the top with red-dyed Soltrol at a relatively slow rate of 0.096 ml/min. The steady state condition, at the end of the organic liquid advancement, is shown in the left-hand photographs of Figures 16 through 18. In these photos, the Soltrol appears red; the water was not dyed. Figure 16 (left) depicts the entire model at steady state, while Figures 17 (left) and 18 (left) are close-ups of the model, also at a steady state condition. Overall the displacement of water was fairly efficient, except at the bottom of the model where a capillary end effect came into play (see Figure 16, left). The residual water saturation occupies several by-passed pockets of the pore network, and also is found in films, rings and wedges in individual pores (see, e.g., Amaefule and Handy, 1982; Dullien et al., 1986; Chatzis et al., 1988). The term 'film' refers to the film of wetting fluid covering all water-wet glass surfaces; 'ring' refers to the pendular rings of wetting fluid found in many of the pore throats; and 'wedge' refers to the wetting fluid in the narrow crevices of the the pores, where the glass plates meet (these films, rings, and wedges are similar to those that are observed in natural porous media - natural pores are not circular, nor are micromodel pores; see also Figure 8). Incidentally, the term 'film' is also used in this report to describe the thin films of non-wetting fluid that spread between air and water phases in three-phase experiments described later.

The capillary end effect is similar to what one would find where a fine sand layer overlies a coarse sand or gravel layer. In this situation, the micromodel pore network represents the upper fine sand layer, and the



FIGURE 16. Organic/water displacement experiment run in the homogeneous micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). Organic liquid is the red fluid. Both photographs depict steady state conditions.



FIGURE 17. Detail from the homogeneous micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). This area is located just below the very center of the model.



FIGURE 18. Yet another detail from the homogeneous micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). This area is located near the top of the model, just to the right of the centerline.

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bottom model reservoir mimics the lower gravel layer. Once the organic liquid breaks through to the lower layer along one or perhaps two flow paths, the remaining organic liquid front retreats slightly. This leaves a few capillary-trapped blobs in the zone at the bottom of the model. The continuing flow of organic liquid takes place through the one or two connected flow paths, which offer less resistance than the many remaining water-saturated pores.

Had a capillary barrier been used at the bottom boundary to reduce the capillary end effect by preventing the organic phase from passing out, the residual water saturation in this model would have been much smaller. A homogeneous model with such a barrier was constructed and indeed, the end effect was completely reduced. Also, less water was trapped in the by-passed water pockets and wedges. Not long ago, Dullien et al. (1986) built a heterogeneous model with a checkered pattern of coarse and fine pore zones. They embedded the inlet and outlet in two of the fine zones, in effect simulating a capillary barrier at the outlet of the model. Their micromodel experiments, and related sandstone core experiments, appear to confirm the hypothesis that residual wetting-phase saturation depends on the outlet boundary condition.

The micromodel experiments illustrated in this paper depict conditions that we were able to reproduce by repeating the experiment. An example of this reproducibility is shown in Figure 19. The photograph in this figure can be compared to Figure 16 (left), and depicts the results of an identical experiment, where Soltrol advanced into the micromodel, displacing water. The character of the saturation pattern is similar for



FIGURE 19. A second experiment in the homogeneous micromodel, depicting conditions at the end of the organic liquid advance — compare to Figure 16 (left). The top of the model is to the left of the photo.

both experiments, only the details vary. The two-phase flow field appears to be a stochastic process, with the same mean behavior, but a different detailed realization for each experimental replication.

Implications for organic liquid migration & its modeling -

The capillary end effect in this model illustrates the significant impact that media heterogeneities can have on the migration of an organic liquid phase. This end effect is not desirable in some laboratory experiments which seek uniform steady state conditions. However, in nature, conditions are not uniform, and the choice of a micromodel (or numerical model) boundary condition at the lower end depends on what the operator wishes to simulate. The use of a capillary barrier boundary is just as arbitrary. It simulates a fine layer, with the soil or network above representing a coarser material. In effect, the freely draining condition of the micromodel experiment illustrated here may be more representative of conditions in aquifers. If there is no barrier to organic-phase migration, as is common with most wells, and the organic phase pressures cannot build up, then the by-passed pockets of water constituting a major portion of the residual water saturation will not drain. In effect, this hypothesis claims that the residual water saturation is not a single 'irreducible' value, but depends on conditions. The use of a single value in a numerical model or simulator could be misleading.

Displacement of Organic Liquid by Water in a Homogeneous Micromodel

After the steady state condition was reached, water was displaced upward through the micromodel at the same rate of 0.096 ml/min, pushing much of the Soltrol out, but leaving behind a capillary-trapped, residual Soltrol saturation. When the model reached a new steady state, additional photos were taken. The right-hand photos of Figures 16 through 18 depict the residual organic liquid left behind after displacement by water. As seen in these photos, the residual organic liquid saturation in these strongly water-wet models is composed of disconnected blobs and ganglia which are fairly evenly distributed throughout the model, and appear to occupy up to 30% of the pore space.

Microscopic Inspection of Blob Size and Shape in Micromodels. Pore Casts. and Blob Casts

Figures 20 and 21 present 'pore scale' close-ups of typical blobs taken from similar experiments conducted in the same micromodel. Figure 20a is a photomicrograph of a blob trapped in a 'pore body'. This blob is referred to as a 'singlet'. The surrounding 'pore throats' are filled with water, the wetting fluid. The trapped singlet is roughly the size of the pore body. Figure 20b depicts a 'doublet', a blob occupying two pore bodies and the pore throat between. Although many blobs have shapes like this singlet and doublet, some are more complex and extend over a number of pore bodies and the connecting pore throats, such as the micromodel blob shown in Figure 21. Other examples of both simple and complex blob shapes can be seen in the right-hand photos of Figures 16 through 18. These more complex shapes include branched blobs with more than two 'ends'.

Peplinski et al. (1989) and Wilson et al. (1989) describe a flow-visualization technique where an organic phase (styrene) is solidified in place within a short TFE column of Sevilleta soil at the conclusion of a displacement experiment (using a displacement procedure similar to that performed in the micromodels), allowing the distribution of organic liquid within the soil to be observed. Photomicrographs of these



FIGURE 20a. Photomicrograph of a singlet blob as observed in the micromodel.



FIGURE 20b. Photomicrograph of a doublet blob as observed in the micromodel.



FIGURE 21. Photomicrograph of a complex blob observed in the micromodel.

polymerized blobs embedded in epoxied pore casts are shown in Figures 22 and 23. Compare the singlet and doublets shown in Figure 22, from the soil column, to those in Figure 20, from the micromodel. The similarity between blob shapes in the two different media gives confidence that micromodels can reasonably be used to simulate the immiscible displacements taking place in the subsurface (Conrad et al., 1989). Figure 23a shows a variety of more complex blobs found in the same pore cast. The pore casts also reveal the position of the blobs within the pore space, and their position relative to the sand grains. In the pore throats, there appears to be only a thin film of water between the blob and the sand grain 'pore wall'. The micromodel mimics this behavior (Figures 20 and 21). However, for pore bodies occupied by organic liquid, there is a difference in the observed behavior between the two visualization methods. Micromodel blobs appear to occupy most of each pore body they are found in, again leaving only a film of water between the blob and the 'pore wall'. Blobs in the Sevilleta pore casts indicate a greater pore body saturation with water, perhaps due to greater surface roughness and irregularities in the pore walls of the Sevilleta sand. This is not surprising since no attempt had been made to achieve similitude between the micromodel network and Sevilleta sand. The greater pore body saturation of water in the Sevilleta sand is also caused partially by the shrinkage of styrene as it polymerizes.

Figure 23b shows a variety of complex blobs that were produced by first solidifying the residual styrene in place, and then by dissolving the sand matrix away with HF. Although blobs in the blob casts do not show their relationships to sand grains as they do in the pore casts, they demonstrate the complex three-dimensional structure of residual organic liquid saturations.



FIGURE 22a. Photomicrograph of a singlet blob as observed in a pore cast.



FIGURE 22b. Photomicrograph of a doublet blob as observed in a pore cast.



FIGURE 23a. Photomicrographs of complex blobs as observed in a pore cast.



FIGURE 23b. SEM's of several complex blobs as observed as blob casts.

Fast Organic Liquid Advance in a Homogeneous Micromodel

The homogeneous micromodel was rerun at a 'fast' flow rate of 1.5 ml/min, approximately 15 times higher than for the 'slow' experiment. The steady state condition, at the end of the organic liquid advancement, is shown in the left-hand photograph of Figure 24. The organic liquid displacement of water was found to be slightly more efficient than before (compare to Figure 16, left), with a decreased residual water saturation. The faster displacement's larger viscous forces partially overcame capillary forces which resulted in fewer by-passed pockets of water, and possibly less water held in wedges. The capillary end effects were also largely overcome.

This experiment again illustrates the misleading nature of the term 'irreducible water saturation' often used to represent the wetting-phase residual saturation. Whereas the non-wetting phase at its residual saturation is immobile and discontinuous, the wetting phase at residual saturation is still continuous, and is composed of an interconnected network of films, rings, and wedges (see, e.g., Amaefule and Handy, 1982; Dullien et al., 1986; Chatzis et al., 1988). The wetting-phase liquid can move through its interconnected network, draining the films and rings, and further reduce the residual wetting-phase saturation. In petroleum geology and reservoir engineering, the reduced wetting-phase residual saturation can be an important consideration, although it is usually ignored. Several recent experiments in the petroleum field provide some idea of the correlation between non-wetting phase flow and wetting-phase residual for reservoir rocks. The wetting-phase residual appears to be a continuous function of non-wetting phase flow rate, although the flow rate must vary over orders of magnitude before the change in residual is significant (Handy, personal communication, 1988; also see earlier work of Amaefule and Handy, 1982, and Dullien et al., 1986). The micromodel experiments described in this report were not designed to investigate this quantitative correlation. The micromodel experiments shown in this report and in Dullien et al. (1986) provide ample evidence that an increase of the non-wetting phase flow rate leads to a decrease of the wetting phase residual. It may be important to account for flow rate when measuring and modeling the mislabeled 'irreducible water saturation.'

Fast Displacement of Organic Liquid by Water in a Homogeneous Micromodel

The right-hand photo of Figure 24 depicts the residual organic liquid saturation at the completion of a upward displacement by water at the same 'fast' rate of 1.5 ml/min. The residual organic saturation looks similar to that observed after the slow experiment (Figure 16, right), despite the larger amount of organic liquid in storage before the water displacement (compare the left-hand photo in Figure 24 to that in Figure 16). One possible explanation for this increase in efficiency is that in the slow rate experiment the relatively large by-passed water zones remaining after the oil advance (see Figure 16, left) provided pathways for the upwardly-advancing water to by-pass large zones of organic liquid.

ORGANIC LIQUID MOVEMENT AND CAPILLARY TRAPPING IN A HETEROGENEOUS POROUS MEDIA

No soil is truly homogeneous. Soils exhibit spatially-variable properties that are a result of their original deposition and subsequent diagenesis. The importance of this variability on the flow of fluids and the



FIGURE 24. Organic/water displacement experiment run in the homogeneous micromodel at the fast rate: following injection of organic liquid (left), and at residual saturation (right). Once again, both photographs depict steady state conditions. Compare the fluid distributions of this figure to those found in Figure 16.

transport of contaminants has only recently been accepted by most groundwater hydrologists. Gelhar (1986) and Dagan (1986) have reviewed the literature on this topic; conspicuously absent is any discussion of multiphase flow, other than water percolation in a soil with air at a uniform pressure (the Richards' equation approach to two-phase flow). Following this approach, Yeh et al. (1985), Mantoglou and Gelhar (1987), and Abobou et al. (1988) have developed geostatistical-theoretical and computer simulation models that demonstrate the importance of soil stratification on moisture movement in the vadose zone. At high capillary pressures the finer-textured layers and lenses of soil absorb water through capillary forces, while the coarse layers remain relatively dry and impervious. The net result is a hypothesis that the anisotropy of water permeability is a function of saturation. At low water saturations, the fine material is more permeable to water than the coarse material, and water has a preference for horizontal flow along the beds due to capillary forces. At high saturations, the coarse material has the greater water permeability, and gravity forces tend to cause vertical flow. This hypothesis has been verified in the field and in the laboratory by Stephens and Heermann, 1988; Mattson et al., 1988; McCord et al., 1988a,b; and others. A similar observation was made by Schwille (1988) using a hydrocarbon as the wetting phase. Petroleum reservoir engineers have largely ignored spatial variability, although recently they have begun to address the issue. The 1989 SPE Reservoir Simulation Conference has several sessions devoted to the topic, which reservoir engineers refer to as 'reservoir heterogeneity' (Lake and Carroll, 1989; also Moissis et al., 1989; Ewing et al., 1989). Most of this work is focused on miscible displacement, involving the advection and dispersion of chemical components in a single non-homogeneous fluid phase. Earlier, Chatzis et al. (1983) briefly examined the effect of reservoir heterogeneity on immiscible displacement at the pore-network level using heterogeneous glass bead packs. They observed that during water floods, the spatial variation of capillary properties can lead to large scale by-passing of oil-filled, coarse-bead zones. This observation is consistent with the field and laboratory vadose-zone water infiltration studies mentioned above, which showed that air as the non-wetting phase was by-passed in the coarse lenses and layers.

There are several different types of spatial variability that may occur in a soil or rock. This research focused on two types. The first was classified as an 'aggregated soil' (Figure 14), which featured the same pattern as the homogeneous model but where strings of interconnected pores and channels were enlarged. These 'macropores' separated 'clumps' of the smaller pores ('micropores') from one another. The pore network had the character of an aggregated soil in which the clumps of micropores formed the aggregate and the chains of macropores represented the large interstitial channels in between the aggregates. The macropores can also be viewed conceptually as fractures through a consolidated porous rock, where the micropores represent the porous matrix of that rock. The second type of variability investigated concerned stringers or lenses of coarse porous material embedded in a matrix of fine porous material. An example of this heterogeneity is where gravel lenses are buried in a sand matrix. Figure 15 is an illustration of the micromodel pattern used to represent this type of variability. Once again, the pore network was identical to the homogeneous model, but the pores in the coarse zones were enlarged. Both types of heterogeneous micromodels could be said to have bi-modal pore size distributions, with one peak associated with the coarse lenses or macropores, and the second peak associated with the fine matrix or micropores. The coarse lenses were simulated in this report in micromodels, and in short glass and TFE columns filled with Sevilleta soil by Wilson et al., 1989. The 'aggregated' soil heterogeneity was simulated by the micromodel only; there were no analogous short column experiments.

In each laboratory experiment, the heterogeneous sample (micromodel or column) was first saturated with the aqueous phase and then subjected to flooding with the organic liquid (Soltrol or styrene). After the experiment equilibrated the organic liquid was displaced by water, resulting in a residual organic liquid saturation that depended on heterogeneity and fluid flow rates.

Organic Liquid Advance into an Aggregated Pore Micromodel

The organic liquid Soltrol was advanced vertically downward into the water-wet aggregated-pore micromodel at a 'slow' rate of 0.096 ml/min. The experiment was then repeated with a 'fast' rate of 1.5 ml/min. The left side of Figures 25, 26, and 27 depict the steady state conditions in the model at the end of the organic liquid advancement at the slow rate. The close-ups are focused on the same areas depicted earlier for the homogeneous model. The steady state condition for the fast displacement is shown in Figure 28.

The steady state saturations are similar in character for both rates. Capillary forces caused the organic liquid to preferentially travel through the strings of macropores, almost completely by-passing the water-filled micropores. Because very little organic liquid entered the micropore matrix, the organic liquid traveled across the model much more quickly than it did for the same injection rate in the homogeneous model. The by-passing also led to a much higher residual (so-called irreducible) water saturation, and lower 'maximum' organic liquid saturation. It is important to note that the residual water saturations are not truly irreducible saturations for the aggregated case. Had a capillary barrier been employed at the bottom of the model, then drainage would have occurred within the aggregates, and a much lower residual water saturation would have been achieved. However, without the capillary barrier and under 'slow' conditions, essentially all of the micropores were by-passed, while 'fast' flow conditions permitted some organic liquid penetration of the micropores due to the presence of significantly larger viscous forces. The 'fast' flow rate's larger viscous forces also accounted for reduction in capillary end effects at the lower end of the model.

In the field, the aggregated pore scenario without the capillary barrier is far more common than the situation with a barrier. For instance, in an aquifer with heterogeneities similar to those described in the experiments above, rarely would wells be packed with material smaller than the average size distribution of the grains in the aquifer, but rather slightly larger so that a larger well screen slot size could be used. In effect, the aggregated micromodel simulates this boundary condition with its large end reservoir.

Implications for spill migration rates and travel distances -

In New England, groundwater consultants commonly distinguish between gasoline leaking from underground tanks in unconsolidated, glacial deposits, and leaks in bedrock. In the unconsolidated deposits, anectdotal evidence suggests that much of the gasoline is trapped by capillary forces, with very limited and slow migration of the liquid gasoline. In bedrock, the gasoline moves quickly and far, with observable liquid gasoline discharges to nearly streams (J. L. Wilson, personal communication, 1988). The aggregated micromodel provides a good analogue to the bedrock situation.

Displacement of Organic Liquid by Water in an Aggregated Pore Micromodel

The right-hand photos in Figures 25 to 28 depict the residual organic liquid left behind after 'slow' and 'fast' upward water floods, respectively. In each case, the residual non-wetting saturation largely consists of



FIGURE 25. Organic/water displacement experiment run in the 'aggregated' micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). Compare to Figure 16.



FIGURE 26. Detail from the 'aggregated' micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). Compare to Figure 17.



FIGURE 27. Another detail from the 'aggregated' micromodel at the slow rate: following injection of organic liquid (left), and at residual saturation (right). Compare to Figure 18.



FIGURE 28. Organic/water displacement experiment run in the 'aggregated' micromodel at the fast rate: following injection of organic liquid (left), and at residual saturation (right). Compare to Figures 24 and 25.

by-passed strings of organic liquid left behind in the macropores. Because advancing organic liquid never initially penetrated the aggregates in the model, very little was subsequently trapped in them, and much smaller residual organic liquid saturations were found in the 'aggregated' model than in the homogeneous model. Perhaps coincidentally, the sweep efficiency (the amount of organic liquid recovered divided by the amount of organic liquid originally in place) was similar for the two models. Displacement of organic liquid from the aggregated micromodel was no more efficient than displacement of organic liquid from the homogeneous model, but the observed residual saturations in the aggregated model were much lower because the amount of organic liquid originally emplaced in this model was so much less than for the homogeneous model.

Increasing the flow rate had a relatively minor effect on the residual saturations, yet there was some difference observed between the two experiments run in the aggregated micromodel. The 'fast' experiment led to a slightly higher residual, with more trapping within the aggregates. When the organic liquid advanced into the model at a 'fast' rate it was able to penetrate into a portion of the some of the aggregates. Later, during the water flood, some of this organic was left behind, even though the water flood occurred under high flow rate conditions with significant viscous forces. The low flow rate water flood led to slightly lower residual organic saturations, not necessarily because it was more efficient, but because there was less organic to be removed. In the field, the 'slow' rate of organic liquid advance might correspond, for example, to a slow leak from an underground storage tank, while the 'fast' rate might be associated with a spill from a tanker accident.

Implications for aquifer remediation -

Two-phase flow experiments conducted in an aggregated micromodel demonstrate that the saturation and spatial distribution of organic liquid found behind an advancing front of free product depends on the combined effects of soil heterogeneity and capillarity. The amount of organic liquid that is ultimately trapped within a unit volume of aquifer is strongly dependent on how much organic liquid was originally emplaced within that volume.

Spilled organics can be expected to move quickly through aquifers which have interconnected macropores or fractures. The organic phase travels preferentially through large pores and fractures by-passing smaller pores in the matrix of these dual porosity systems. The residual saturations left behind following the recovery of free product tend to be comparatively low, but can be expected to extend over a much larger portion of the aquifer.

In this aggregated micromodel, most of the residual organic liquid was trapped as by-passed strings in the macropores. For field sites involving aggregated or cracked soils, or fractured rock, the implications are that it will be difficult to hydraulically remove all of the organic liquid from the cracks and fractures, at least under conditions where the organic liquid is the non-wetting phase of a two fluid phase system. Since real fractures tend to be planar features, rather than the simple linear cracks shown in this micromodel, multiphase flow in the field is considerably more complex than in laboratory micromodel experiments (see, e.g., the videotape by Wilson et al., 1988).

Organic Liquid Advance into a Horizontal Micromodel Containing Lenses of Coarse Pores

Soltrol was also advanced into a horizontally-held 'stringer' micromodel (Figure 15) containing a number of coarse lenses that were oriented parallel to the flow direction. The Soltrol injection was relatively

slow, at 0.096 ml/min. Figure 29 illustrates the process. During the experiment, the front of organic liquid advanced in the finer pore matrix until it encountered a lens, then slowed while most of the incoming organic liquid preferentially traveled through the lenses because capillary forces were lowest in the larger pores. When the lens was full, the front in the fine pores picked up speed again until another lens was encountered. If the front encountered more than one lens at a time, it fed both of them until the one was full, and then supplied only the second. The front in the fine-pore matrix always advanced from the rear; a full lens was never the source for a new front in the fine pores. Because of the role that the lenses played, progress of the advancement was very unsteady, with the fine-matrix front decelerating and accelerating as lenses were encountered. This unsteady flow could be considered as a macroscopic analogy to the Haines' jumps seen on a pore level during the advancement (Haines' jumps on a pore scale were graphically recorded on the videotape by Mason et al., 1988). The final or steady state fluid distribution is shown in Figure 30. Significantly large wetting-phase residual saturation was found in both the coarse- and fine-pore regions. Because of the role of the lenses in the advancement, there were zones of fine material, located between closely spaced coarse lenses, where the water was largely by-passed. Had the coarse lenses extended all the way across the model, the oil advance would have mostly occurred in those coarse areas and not in the fine pores. An analogous field situation occurs where gasoline migrates through the backfill used in utility line trenches.

The horizontal experiment was repeated in the same heterogeneous model but at a faster flow rate of 1 ml/min. As above, the front of organic liquid advanced in the finer-pore matrix until it encountered a lens, then slowed. Even though there was a slight difference in the way the model filled with oil, it did not make much difference in the residual water saturations behind the front in each model. The only difference was that at the faster rate, there was less of an end effect. Since an initial condition containing no end effect was desirable, a flow rate of 1 ml/min became the standard with which to compare the effects of rate on residual organic liquid saturations.

Implications for spill migration rates and travel distances -

Lenses of coarse material embedded in a matrix of fine material (e.g., gravel in sand; sand in silt) will influence the rate and direction of movement of an organic liquid, and create a 'fingering' or 'dispersion' of the location of the immiscible displacement front. The front will 'finger' because of the heterogeneity, and the competition between viscous and capillary forces. This fingering is a function of the length and width of the lenses, and their pore size contrast with the matrix. For continuously varying media represented geostatistically, the equivalent parameters are represented by the covariance or variogram of, say, permeability and other properties. It is currently a controversial issue to determine when the 'fingering' due to heterogeneity, sometimes called 'macrodispersion', dominates over fingering due to viscous or density instabilities caused by a contrast in viscosity or density across the immiscible interface. Most of the work on this topic has been focused on miscible displacement, but is so recent that journal articles have not yet been published. In miscible displacement, local hydrodynamic dispersion is similar in effect to capillarity in immiscible displacement. Transverse mixing caused by either process tends to influence and limit viscous or gravity instabilities, and the 'macrodispersion' caused by heterogeneities.

Displacement of Organic Liquid by Water in a Horizontal Micromodel Containing Coarse Lenses

Figure 31 shows the horizontally-held, heterogeneous 'stringer' model after organic liquid had been displaced by water at a fast rate of 1 ml/min. Since the viscosity of water is lower than that of Soltrol, the



FIGURE 29. Organic/water displacement experiment run in the horizontal 'stringer' micromodel following injection of organic liquid at early time (top), and at later time (bottom).



FIGURE 30. Final residual organic-phase saturation in the horizontal 'stringer' micromodel following injection of organic liquid at a slow rate.

displacement was unstable, and water fingered through the model. The fingering resulted in many oil-filled regions being by-passed in both the fine and coarse zones.

If the flow rate were reduced in the above displacement experiment, capillary forces would begin to dominate over viscous forces. This implies that flow through the micromodel would be confined to the finer pores and that the organic phase in the coarse regions would be by-passed. Such an experiment was run at a flow rate of 0.096 ml/min in the 'stringer' model, and the steady state end result after the water advance is illustrated in Figure 32. During the experiment, the water front moved in the fine pore matrix, splitting as it migrated around each of the organic liquid filled coarse lenses. Very little, if any, non-wetting organic liquid was displaced from the coarse lenses. When the front reached the downstream end of a lens, it closed back together and trapped the non-wetting fluid in the lens via by-passing. There was also typical pore level capillary trapping of blobs in the fine matrix, but it was of much smaller scale, typical of the results seen in the homogeneous model. The residual organic liquid saturation was significantly higher for this heterogeneous model than it was for the homogeneous model because of the large, lens-scale by-passing.

Implications for aquifer remediation -

The 'stringer' experiments suggest that the amount and spatial distribution of organic liquid that is ultimately trapped in an aquifer is strongly dependent on the nature of original emplacement and soil heterogeneity. Furthermore, the pumping rate in a remediation well can have a profound effect on the amount of product produced, depending on the rates and heterogeneities involved.



FIGURE 31. Final residual organic-phase saturation in the horizontal 'stringer' micromodel following displacement by water at a fast rate.



FIGURE 32. Final residual organic-phase saturation in the horizontal 'stringer' micromodel following displacement by water at a slow rate.

Organic Liquid Advance into a Vertical Micromodel Containing Lenses of Coarse Pores

In a variation of the 'stringer' experiment, Soltrol was advanced downward into a vertically-held micromodel. The Soltrol injection rate, as before, was relatively slow at 0.096 ml/min. The organic liquid advance was virtually identical to that in the horizontally-held case, except that buoyancy forces played a stabilizing role in this vertical displacement by acting in the opposite direction to the viscous force. The final steady state fluid distribution is shown in Figure 33.

Displacement of Organic Liquid by Water in a Vertical Micromodel Containing Coarse Lenses

Organic liquid was displaced by water from the vertically-oriented model at two rates in two separate experiments. The organic phase from the first micromodel was displaced at a rate of 0.096 ml/min, and the end result is depicted in Figure 34. Oil in the second model (Figure 35) was displaced at a slower rate of 0.002 ml/min. Notice that in each model a significant amount of organic liquid was displaced from the coarse lenses even though the flow rate was low. In the absence of sufficient viscous forces, buoyancy forces



FIGURE 33. Final residual organic-phase saturation in the vertical 'stringer' micromodel following injection of organic liquid.





- FIGURE 34. Final residual organic-phase saturation in the vertical 'stringer' micromodel following displacement by water at a rate of 0.096 ml/min.
- FIGURE 35. Final residual organic-phase saturation in the vertical 'stringer' micromodel following displacement by water at a rate of 0.002 ml/min.

generated by injecting the more dense water phase from below partially overcame the capillary forces which had previously held the organic liquid in the lenses.

Implications for aquifer remediation -

The results vertical 'stringer' micromodel experiments suggest that buoyancy forces, whenever possible, should be incorporated in aquifer remediation schemes so that they aid in the removal of the pollutant.

Displacement of Organic Liquid by Water in Short Columns Containing Lenses of Coarse Sand

This experiment was repeated by W. Peplinski in several short TFE columns using styrene as the organic liquid phase (Peplinski et al., 1989; Wilson et al., 1989). Three cylindrical lenses were simulated by splitting the Sevilleta sand into two fractions with a size 50 sieve. The fine fraction was used to pack the major portion of the column, with the coarse fraction used to construct the three lenses, roughly 3.5 to 4 cm long and 0.9 cm in diameter. The column was held vertically, and styrene was advanced downward slowly. Later, water was injected at the bottom and displaced styrene upward at a relatively slow rate. The residual saturation of styrene was hardened at the end of the water displacement, and pore casts were constructed by replacing the water phase with epoxy. A longitudinal section of the column is shown is Figure 36, as illuminated by an ultraviolet lamp. The coarse lenses contain much greater saturations of styrene than the surrounding fine matrix, and thus verify the micromodel results. The styrene in the coarse sand lenses was by-passed, as was the Soltrol in the micromodel lenses. Even though this column was oriented vertically, buoyancy forces were small and had little effect on the results. The greater density of styrene along with much smaller pore sizes in



FIGURE 36. Longitudinal cross-section of the short TFE column containing coarse lenses. The residual organic phase is light colored.

the sand pack resulted in a much smaller buoyancy force than was encountered in the vertically-oriented micromodel.

ORGANIC LIQUID MOVEMENT AND CAPILLARY TRAPPING IN AN 'UNSATURATED' HOMOGENEOUS POROUS MEDIUM

Figure 37 depicts the portion of the aquifer that includes residual saturation in the vadose zone. Whether an organic liquid is more (left) or less (right) dense than water, it leaves behind a trail of capillary trapped residual in the vadose zone as it makes its way downward toward the capillary fringe. Above the capillary fringe the trapped organic shares the pore space with air and water. The movement of organic liquid through the vadose zone is more complicated (especially on a pore scale) than in the saturated zone. In the vadose zone, a downward percolating organic phase encounters a partly air-filled, partly water-filled pore network. The organic liquid is generally of intermediate wettability — that is, non-wetting relative to water, but wetting relative to air. The organic phase, depending on whether it encounters air or water, can



FIGURE 37. Schematic of residual organic liquid trapped in the vadose zone (after Wilson et al. 1989).

display either wetting or non-wetting behavior. And because of its intermediate wettability, the organic phase tends to be found in between the water phase, which preferentially occupies the smallest pores, and the air phase, which preferentially fills the largest pores. In fact, many organics have low internal cohesion and will spread, forming thin films between the water and air phases. For these reasons, the distribution of residual organic in the vadose zone is much more diverse and complex than in the saturated zone below. A dropping or fluctuating water table can further complicate the behavior of organic liquids in the vadose zone.

Micromodel flow visualization techniques in homogeneous media are used to illustrate the scenario where a large slug of organic liquid percolates vertically downward into the vadose zone. Later, it is drained by air as it continues downward in its migration toward the water table. This scenario was simulated by first saturating a micromodel with water. Then, a vadose zone condition was created by draining the water with air to residual (so-called irreducible) water saturation. An organic liquid was advanced downward into the experimental apparatus, and finally the organic itself was drained by air (or another gas). The trapped organic phase left behind in the vadose zone was observed visually.

Creating the Initial Vadose Zone Condition in a Homogeneous Micromodel

The homogeneous micromodel with the capillary barrier (see Figure 11) was used in this three-phase experiment. The model, oriented vertically with the barrier at the bottom, was imbibed with water from the bottom and then drained with air from the top to achieve the initial vadose zone condition. The water was introduced and drained via a buret. The water was drained under a suction of about 15 cm H₂O, just under the air entry pressure of the capillary barrier. The steady-state condition for the entire model, at the end of drainage, is shown in Figure 38a and a detailed view is shown in Figure 38b. In these photos, the water is blue and the Soltrol is dyed red; the air was colorless. This steady-state condition represents the vadose zone above the transition zone, where water saturation is near its so-called irreducible value. Because the model had fairly large pores and a relatively uniform pore size distribution, not much suction was needed to achieve a fairly complete drainage. Unlike the results obtained from other micromodels, the presence of the capillary barrier at the bottom of the model prevented a capillary end effect. (Capillary end effect was discussed earlier for the case of Soltrol advancing into the same model without a capillary barrier under water-saturated conditions).

Organic Liquid Advance in a Unsaturated, Homogeneous Micromodel

Red-dyed Soltrol was advanced downward into the drained micromodel at a relatively slow rate of 0.096 ml/min. Air and perhaps some water was pushed ahead of the advancing front of organic liquid. Sufficient pressure was achieved to exceed the air-entry pressure of the capillary barrier at the bottom of the model, thus allowing air to escape. Often during this displacement, some organic liquid was observed ahead of the main front of advancing organic liquid; close examination revealed that it had traveled through thin films of organic phase formed between the air and water phases. The steady state condition for the entire model, at the end of the organic liquid advancement, is shown in Figure 39a. A detailed view is offered in Figure 39b. Notice in the detailed photo that the Soltrol has formed thin films between the air and the water. Many organics have relatively little internal cohesion and therefore tend to spread in this fashion, resulting in a reduction of the surface energy of the system. These films are quite often continuous, and keep all the little



FIGURE 38a. Steady state condition in the homogeneous micromodel following drainage by air.

Air and water, detail view.

FIGURE 38b. Detail of the steady state condition in the homogeneous micromodel following drainage by air.

pockets of organic liquid in hydraulic connection. Notice also that the water saturation and distribution remained almost entirely unchanged when compared to the initial vadose zone condition, and that the air phase has been reduced to an entrapped residual non-wetting phase saturation similar to that seen for the organic phase in Figure 16 (right). Because of the presence of air in the vadose zone (in addition to organic liquid and water), the maximum organic liquid saturation achieved in the vadose-zone experiment was not as great as in the saturated-zone case. Compare the organic liquid saturation in Figure 39a to that of Figure 16 (left).

Drainage of Organic Liquid by Air in a Homogeneous Micromodel

In the final step of the experiment, Soltrol was drained from the model by air, representing the continued percolation of the organic phase downward toward the water table. The Soltrol was drained from the model under a small applied suction. This suction is believed to have been insufficient to completely drain the organic phase to its lowest possible saturation, but because Soltrol has a much lower surface tension than water, higher applied suctions would have resulted in air breaking through the capillary barrier.

The final distribution of fluids within the model is shown in Figure 40a, while Figure 40b illustrates the more complex nature of trapping in the vadose zone. Compare Figure 40a to Figure 16 (left) and note that the amount of organic phase retained in the vadose zone is much less than the residual saturation left behind in the saturated zone. Some of the reasons for why this is so will be discussed later in this section.

Organic liquid can be trapped in several different ways in the vadose zone. In particularly dry areas, it can be trapped in pore throats, in small pores, and as films entirely within the air phase. Occasionally,



FIGURE 39a. Steady state condition in the homogeneous micromodel following advance of oil into air and water.



FIGURE 39b. Detail of the steady state condition in the homogeneous micromodel following advance of oil into air and water.

organic liquid can be trapped — as in a two-phase case — as blobs within the water phase, although this kind of trapping is more likely to occur when the initial water content is relatively high or when infiltrating water follows the organic liquid (for example, when it rains after a spill event). However, due to its intermediate wetting properties and its tendency to spread, organic liquid in the vadose zone is most commonly retained in between the water and air phases. Notice in the detailed photo that although the saturation of the organic phase had been reduced by drainage, the thin films of organic liquid between the air and the water were still present. In contrast to blobs trapped in the saturated zone, the organic phase trapped in the vadose zone remains more or less continuous, with the exception of any organic liquid trapped entirely within the water phase. In this experiment, due to having a relatively low initial water saturation, and because the organic phase readily spread on the water/air interface, the organic phase acted like a wetting phase both in its character of migration and its final distribution within the pore space.

Why Residual Saturations Are Smaller in the Vadose Zone

Hagan et al. (1989) and Wilson et al. (1989), in their short column experiments, found that residual organic liquid saturations are much lower in the vadose zone (at 9.1%) than in the saturated zone (at 27.1%). It is believed that the presence of a third and non-wetting phase, air, along with increased buoyancy forces and decreased capillary forces in the vadose zone, account for this lower residual saturation.

In the subsurface, capillary forces often dominate over the viscous and buoyancy forces that oppose trapping. However, in instances where either viscous, or buoyancy, or a combination of these forces are large enough to overcome capillary forces, the residual organic liquid saturation may be reduced (Morrow



FIGURE 40a. Steady state condition in the homogeneous micromodel following drainage of oil and water by air.



FIGURE 40b. Detail of the steady state condition in the homogeneous micromodel following drainage of oil and water by air.

and Songkran, 1981). Figure 41 illustrates this process. In two curves - one in which a wetting fluid displaces a nonwetting fluid, and the other in which a nonwetting fluid displaces a wetting fluid – the residual saturation is plotted as a function of the ratio of viscous plus buoyancy forces to capillary forces, $(F_v + F_b / F_c)$. For the case when the organic phase is non-wetting (such as when water displaces organic liquid in the saturated zone), beneath a critical value of $(F_v + F_b/F_c)$, viscous and buoyancy forces are small compared to capillary forces and residual saturations are maximum, at a value of Sor. Once the critical value is exceeded, the combination of viscous and buoyancy forces overcome capillary forces at some locations and the residual organic liquid saturation is reduced. Amaefule and Handy (1982) suggest that when displacing a wetting fluid (such as organic liquid being drained by air in the vadose zone), any increase in the capillary number (analogous to our ratio, $(F_v + F_b/F_c)$ will bring about a reduction in trapping. No critical value need be exceeded for a reduction in residual saturation to occur. The difference in displacement behavior for wetting and nonwetting fluids may be attributable to the fact that a wetting fluid is able to remain connected as it is being displaced while a non-wetting fluid breaks into discontinuous blobs. Although it is the intermediate-wetting fluid in the vadose zone, organic liquid will usually remain as a continuous phase, at least through films on the water phase. In this sense it acts as a wetting phase as it is drained by air in the vadose zone.

Residual saturation decreases as the ratio of viscous plus buoyancy forces to capillary forces, $(F_v + F_b/F_c)$, is increased above a critical value. Significantly, most organic pollutants immiscible with water have a much greater buoyancy force in the vadose zone (larger F_b), due to the large fluid density difference with air. The interfacial tension between air and organic in the vadose zone is usually smaller



FIGURE 41. A theoretical plot of trapped organic liquid as dependent upon the ratio of viscous and buoyancy forces over capillary forces when the organic phase is nonwetting (solid line), and when it is the wetting fluid (dashed line). (from Wilson et al., 1989)

than the tension between the organic liquid and water in the saturated zone (smaller F_c). For example, Soltrol-130, the organic liquid used in the micromodel experiments and column studies, has three times the buoyancy forces and 2.5 times less capillary forces in the vadose zone than in the saturated zone (Wilson et al., 1988). Under equivalent conditions, $(F_v + F_b/F_c)$ will be a much larger in the vadose zone compared to the saturated zone. It is speculated that in most cases, $(F_v + F_b/F_c)$ will be greater than critical in the vadose zone, and will be less than critical in the saturated zone. In other words, in the vadose zone buoyancy forces are sufficient to at least partially overcome capillary forces and thereby reduce the residual saturation. Conversely, in the saturated zone, the combined buoyancy and viscous forces are not great enough to overcome the capillary forces and the residual saturation is maximum.

Implications for aquifer remediation -

As discussed earlier in the saturated zone section, the pore-scale distribution of the organic phase influences the partitioning of organic liquid components. Because the organic phase is almost always less wetting than water but more wetting than air, it remains in direct contact with both the air and water allowing for both solubilization into the water phase and especially volatilization into the air phase. And importantly, the formation of thin organic liquid films between the water and air increases the surface area of the organic phase, enhancing the propensity for inter-phase partitioning of organic components. Soil venting of organics in the vadose zone has become an attractive remediation strategy because volatile organics partition easily to the air phase. Figure 42 provides a good example of the large organic/air and organic/water interfaces generated by the organic phase's tendency to spread.



FIGURE 42. Close-up of an organic film in between the water and air phases.

CONCLUSIONS

From the examples of bulk multi-phase flow behavior shown in this report, we can also conclude the following:

- flow visualization techniques employing micromodels provide useful tools with which to examine multi-phase displacement processes on both pore and bulk scales.
- There is a similarity between capillary-trapped blobs and by-passed zones observed in two-phase pore casts and micromodel experiments. This similarity provides some confidence that the micromodels provide a reasonable analogy to multiphase flow in porous media.
- The saturation and spatial distribution of organic liquid found behind an advancing front of organic liquid depends upon the combined effects of soil heterogeneity and capillarity.
- The amount of organic liquid that is ultimately trapped is strongly dependent on the nature of original emplacement.
- Organic liquid selectively travels through the coarser (and more permeable) portions of heterogeneous aquifers.
- At typical aquifer flow velocities, capillary forces can relegate the flow of water to finer-grained regions, by-passing the coarser organic-filled regions.
- Increased recovery of organic liquids from heterogeneous aquifers may be attained by increasing the pumping rate.
- In two-phase organic liquid/water experiments, the capillary-trapped organic liquid is trapped (1) in singlets, by snap-off, and (2) in doublets and more complex shapes, by by-passing. By-passing is also the major mechanism when soil heterogeneities are involved.
- The distribution of the organic phase in the vadose zone is complex, but the propensity for the organic phase to spread as a thin layer between the water and the air makes soil venting of organics in the vadose zone an attractive remediation strategy.

REFERENCES

- Abobou, R., L. W. Gelhar, and D. McLaughlin. 1988. Three-dimensional flow in random porous media. Ralph M. Parsons Laboratory Report 318, Massachusetts Institute of Technology Department of Civil Engineering. 833 pp.
- Amaefule J. O., and L. L. Handy. 1982. The effect of interfacial tensions on relative oil/water permeabilities of consolidated porous media. SPE Journal, vol. 22, no. 3, pp. 371-381.
- Burmaster, D. E., and R. H. Harris. 1982. Groundwater contamination: an emerging threat. Technology Revue, vol.84, no.7, pp. 50-62.
- Chaffee, W. T., and R. A. Weimar. 1983. Remedial programs for ground-water supplies contaminated by gasoline. Third National Symposium on Aquifer Restoration and Ground-Water Monitoring, National Water Well Association, pp. 39-46.
- Chatzis, I. 1982. Photofabrication technique of two1-dimensional glass micromodels. PRRC report #82-12, New Mexico Institute of Mining and Technology, Socorro, NM.
- Chatzis, I., N. R. Morrow, and H. T. Lim. 1983. Magnitude and detailed structure of residual oil saturation. SPE Journal, vol.23, no.2, pp. 311-25.
- Chatzis, I., M. S. Kuntamukkula, and N. R. Morrow. 1988. Effect of capillary number on the microstructure of residual oil in strongly water-wet sandstones. Soc. Pet. Eng. Reservoir Engineering, vol.3, no.3, pp.902-912.
- Conrad, S. H., J. L. Wilson, W. R. Mason, and W. Peplinski. 1989. Observing the transport and fate of petroleum hydrocarbons in soils and in ground water using flow visualization techniques, in Proceedings, Symposium on Environmental Concerns in the Petroleum Industry, American Association of Petroleum Engineers, Palm Springs, CA, May 10, 1989.
- Convery, M. P. 1979. The Behavior and Movement of Petroleum Products in Unconsolidated Surficial Deposits. M.S. Thesis, University of Minnesota.
- Dagan, G. 1986. Statistical theory of groundwater flow and transport: pore to laboratory, laboratory to formation, and formation to regional scale. Water Resources Research, vol.22, no.9, pp.120S-134S.
- Davis, J. A., and S. C. Jones. 1968. Displacement mechanisms of miscellar solutions. Jour. Pet. Tech., Dec. 1968, p. 1415-1428.
- de Pastrovich, T.L., Y.Baradat, R.Barthel, A. Chiarelli, and D.R. Fussell. 1979. Protection of Groundwater from Oil Pollution. Report 3/79, CONCAWE, Den Haag, the Netherlands.
- Dullien, F. A. L., F. S. Y. Lai, and I. F. MacDonald. 1986. Hydraulic continuity of residual wetting phase in porous media. J. Coll. Sci., vol. 109, no. 1, p. 201-218.
- Eastman Kodak Company. 1975. Decorating Glass Using Kodak Photosensitive Resists. Kodak Publication No. P-245, 4 pp.

- Eastman Kodak Company. 1979. Photofabrication Methods with Kodak Photoresists. Kodak Publication No. G-184, 32 pp.
- EPA. 1979. Waste alert. EPA Journal, vol.5, no.2, p.12.
- EPA. 1980. Proposed Groundwater Protection Strategy. Office of Drinking Water, Washington, D.C.
- EPA. 1982. Massive voluntary cleanup to help with hazardous waste removal. EPA Journal, vol.9, no.5, pp.24-5.
- EPA. 1983. Hazardous Waste Site Descriptions: National Priority List Final Rule. Office of Solid Waste and Emergency Response (WH-5624), Washington, D.C., HW-8.1.
- Ewing, R. E., T. F. Russel, and L. C. Young. 1989. An anisotropic coarse-grid dispersion model of heterogeneity and viscous fingering in five-spot miscible displacement that matches experiments and fine-grid models, in Proc. Tenth Annual SPE Symposium on Reservoir Simulation, February 6-8, Houston, TX, pp.447-465.
- Feenstra, S., and J. Coburn. 1986. Subsurface contamination from spills of denser than water chlorinated solvents. Bull. Calif. Water Poll. Control Assoc. vol.23(4), pp.26-34.
- Franklin, Benjamin. 1784. Letter to Samuel Mather (May 12, 1784) in The Autobiography of Benjamin Franklin.
- Gelhar, L. W. 1986. Stochastic subsurface hydrology from theory to applications. Water Resources Research, vol.22, no.9, pp.135S-145S.
- Hagan, E. F. 1989. A quantitative experimental investigation of the physical processes responsible for determining residual organic liquid saturations in porous media. New Mexico Institute of Mining and Technology, Geoscience/Hydrology Section, Open File Report 89-4, 170pp.
- Jercinovic, D. E. 1984. Petroleum-Product Contamination of Soil and Water in New Mexico. Ground Water/Hazardous Waste Bureau, New Mexico Environmental Improvement Division, EID/GWH-84/4.
- Lake, L. W., and H. B. Carroll, Jr. eds. 1986. Reservoir Characterization. Harcourt Brace Jovanovich, Publishers, Orlando, FL., 659pp.
- Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt (eds.). 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.
- Mantoglou, A., and L. W. Gelhar. 1987. Stochastic modeling of large-scale transient unsaturated flow in stratified soils. Water Resources Research, vol.23, no.1, pp.57-68.
- Mason, W. R., S. H. Conrad, and J. L. Wilson. 1988. Micromodel study of organic liquid advance into a soil. presented at Spring 1988 Amer. Geophys. Union. Meeting. Abstract in EOS, vol.69, no.16, pp.370. Order as New Mexico Institute of Mining and Technology, Geoscience/Hydrology Section, Open File Report.
- Mattax, C. C., and J. R. Kyte. 1961. Ever see a water flood? Oil and Gas Jour., Oct. 16, 1961, p. 115-128.

- Mattson, E. D., A. M. Parsons, D. B. Stephens, K. Black, and K. Flanigan. 1988. Field simulation of waste impoundment seepage in the vadose zone, in Proc. FOCUS on Southwestern Ground Water Issues Conference, March 23-25, National Water Well Association, Dublin, OH.
- Maugh II, T. H. 1979. Toxic waste disposal a growing problem. Science, vol.204, pp.819-23.
- McCord, J. T., D. B. Stephens, J. L. Wilson. 1988a. Field-scale variably saturated flow and transport in a sloping uniform porous media: field experiments and numerical simulations, in Proc. International Workshop on Validation of Flow and Transport Models for the Unsaturated Zone. May 23-26, Ruidoso, NM, New Mexico State University.
- McCord, J. T., D. B. Stephens, and J. L. Wilson. 1988b. Field-scale variably saturated flow and transport: the roles of hysteresis and state-dependent anisotropy, in Proc. NATO Advanced Study Institute of Recent Advances in Modeling Hydrologic Systems, July 9-22, Sintra, Portugal.
- McKee, J. E., F. B. Laverty, and R. H. Hertel. 1972. Gasoline in groundwater. Journal of the Water Pollution Control Federation, vol.44, no.2, pp.293-302.
- McKellar, M. and N. C. Wardlaw. 1982. A method of making two-dimensional glass micromodels of pore systems. J. Can. Pet. Tech., July-Aug., 1982, p. 39-41.
- Moissis, D. E., C. A. Miller, and M. F. Wheeler. 1989. Simulation of miscible viscous fingering using a modified method of characteristics: effects of gravity and heterogeneity, in Proc. Tenth Annual SPE Symposium on Reservoir Simulation, February 6-8, Houston, TX, pp.431-446.
- Morrow, N. R., and B. Songkran. 1981. Effect of trapping and buoyancy forces on non-wetting phase trapping in porous media. in *Surface Phenomena in Enhanced Oil Recovery*, D.O.Shah (ed.), Plenum Publishing Corporation.
- Peplinski, W. J. 1989. Simulation of organic liquid saturation using styrene monomer and epoxy resin. New Mexico Institute of Mining and Technology, Geoscience/Hydrology Section, Open File Report 89–1, 35 pp.
- Roberts, J. R., J. A. Cherry, and F. W. Schwartz. 1982. A case study of a chemical spill: polychlorinated biphenyls (PCBs) 1. history, distribution, and surface translocation. Water Resources Research, vol.18, no.3, pp.523-34.
- Schwille, F. 1967. Petroleum contamination of the subsoil a hydrological problem. in *The Joint Problems* of the Oil and Water Industries (P.Hepple ed.), Elsevier, Amsterdam, pp.23-53.
- Schwille, F. 1981. Groundwater pollution in porous media by fluids immiscible with water. in *Quality of Groundwater* (W. van Duijvenbooden et al. eds.), Elsevier, Amsterdam, pp.451-63.
- Schwille, F. 1984. Migration of organic fluids immiscible with water in the unsaturated zone. in *Pollutants in Porous Media: The Unsaturated Zone Between Soil Surface and Groundwater* (B. Yaron, G. Dagan, and T. Goldschmid eds.), Springer-Verlag, New York, pp.27-48.
- Schwille, F. 1988. Dense Chlorinated Solvents in Porous and Fractured Media. Lewis Publishers, Chelsea, MI. 146pp.

- Stephens, D. B., and S. Heermann. 1988. Dependence of anisotropy on saturation in a stratified sand. Water Resources Research, vol.24, no.5, pp.770-778.
- van Dam, J. 1967. The migration of hydrocarbons in water-bearing stratum. in: The Joint Problems of the Oil and Water Industries (P.Hepple ed.), Elsevier, Amsterdam, pp.55-88.
- Villaume, J. F. 1985. Investigations at sites contaminated with dense non-aqueous phase liquids. Groundwater Monitoring Review, vol.5(2),pp.60-74.
- Williams, D. E., and D. G. Wilder. 1971. Gasoline pollution of a ground-water reservoir a case history. Ground Water, vol.9, no.6, pp.50-4.
- Wilson, J. L., and S. H. Conrad. 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? in proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water, NWWA, Houston, TX, pp.274-98.
- Wilson, J. L., S. H. Conrad, E. Hagan, W.R. Mason, and W. Peplinski. 1988. The pore level spatial distribution and saturation of organic liquids in porous media. in proceedings of Petroleum Hydrocarbons and Organic Chemicals in Ground Water, NWWA, Houston, TX, pp.107-133.
- Wilson, J. L., S. H. Conrad, W. R. Mason, W. Peplinski, and E. Hagan. 1989. Laboratory investigation of residual liquid organics from spills, leaks, and the disposal of hazardous wastes in ground water, Technical completion report to the U.S. EPA for work performed under Grant Number EPA CR-813571-01-0, R. S. Kerr Laboratory, Ada, Oklahoma, (in review).
- Wilson, J. L., W. R. Mason, and W. B. Cox. 1988. Flow visualization of two-phase flow in fractures, EOS Trans. AGU 69(16), pp. 355-356. Order as New Mexico Institute of Mining and Technology, Geoscience/Hydrology Section, Open File Report.
- Yeh, T.-C. Jim, L. W. Gelhar, A. L. Gutjahr. 1985a. Stochastic analysis of unsaturated flow in heterogeneous soils, 1, statistically isotropic medium. Water Resources Research, vol.21, no.4, pp.447-456.
- Yeh, T.-C. Jim, L. W. Gelhar, A. L. Gutjahr. 1985b. Stochastic analysis of unsaturated flow in heterogeneous soils, 2, statistically anisotropic media with variable α. Water Resources Research, vol.21, no.4, pp.457-464.
- Yeh, T.-C. Jim, L. W. Gelhar, A. L. Gutjahr. 1985c. Stochastic analysis of unsaturated flow in heterogeneous soils, 3, observations and applications. Water Resources Research, vol.21, no.4, pp.465-472.