

**A QUANTITATIVE EXPERIMENTAL INVESTIGATION OF THE  
PHYSICAL PROCESSES RESPONSIBLE FOR DETERMINING  
RESIDUAL ORGANIC LIQUID SATURATIONS IN POROUS MEDIA**

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## ABSTRACT

The ubiquitous use of petroleum hydrocarbons and their organic components has led to widespread groundwater contamination problems. The organic liquids are often essentially immiscible with water and air. When spilled at the surface, they travel downward through the soil as a separate phase. As an organic liquid percolates toward the water table, a sizable percentage of it is trapped by capillary forces in the pore spaces of a soil. This trapped liquid, referred to as residual saturation, can act as a continuous source of contaminant, by slowly dissolving into the water, or diffusing into the air. A better understanding of the physical processes controlling organic liquid trapping must be achieved before effective aquifer remediation schemes can be designed. With this in mind, laboratory soil column experiments were performed to determine the residual organic liquid saturation in various soils. Experiments designed to measure the volume of liquid trapped in the saturated zone were run with six organic liquids to compare residual saturations between liquids. Measurements of residual organic liquid saturations using Soltrol were made in three soils in an attempt to compare residual saturations between soils. Column experiments measuring equilibrium fluid saturations of three-phases (air, water, and organic liquid) in the vadose zone at various elevations above the water table were also conducted. A vertical distribution of fluids in the vadose zone was achieved using the three-phase experimental results.

No correlation was found between residual organic liquid saturation and viscosity, density, or interfacial tension over the range of fluid properties for the organic liquids used in the experiments. This suggests the possibility of using a relatively safe organic liquid to predict the behavior of a more toxic organic liquid. The amount of Soltrol trapped in a particular soil varied from 4% for an organic rich loam to 27% for a dune sand. The three-phase experiments revealed that the vadose zone traps approximately one-third the quantity of organic liquid trapped in the saturated zone. The decrease in residual saturation is due to relative wettability changes associated with the presence of air.

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# CHAPTER 1

## INTRODUCTION

### SCOPE OF PROBLEM

Since the first successful oil well was drilled in Titusville, Pennsylvania on August 28, 1859 by Colonel E.L. Drake, mankind has in all probability been contaminating surface and ground waters of the Earth with petroleum products (Williamson and Baum, 1959). The impact of this discovery on the Earth's environment has only recently been fully realized. Petroleum (oil) supplied the vital source of inexpensive energy used to power the industrial revolution. Associated with the economic and population growth of the country was the rise of the transportation industry. This industry, of which every automobile owner is a part, is responsible for a major portion of the hydrocarbon related groundwater contamination problems facing society today. This study will focus primarily on contaminants commonly found in motor fuels and engine lubricants.

The post World War II boom of the transportation industry, fueled by the expansion of the Interstate highway system, led to a great increase in the number of gas stations dotting the roadside across the country. Many of the gasoline storage tanks at these service stations were constructed of steel with no corrosion protection and over a period of time may have lost their structural integrity and begun to leak fuel into the subsurface. The EPA estimates that of the 3.5 million or more underground storage tanks in the United States, 10-30% may be leaking (Dowd, 1984). Each year millions of gallons of gasoline are lost due to spills and leaks from tanks such as these (Jercinovic, 1984). Underground storage tanks, however, are just one potential source of gasoline pollution. Any activity or facility involved with the distribution and storage of petroleum, including pipelines, tanker

trucks, railroad cars, refineries, disposal pits, and above ground storage tanks are possible avenues for hydrocarbon pollution.

Even the smallest quantities of petroleum products can pose a legitimate threat to groundwater supplies. Almost undetectable, concentrations of some organic compounds contained in petroleum products, are sufficient to cause closure of a water supply well. As an example, the Federal maximum concentration limit allowed in safe drinking water for benzene, a common organic compound found in gasoline suspected of causing cancer, is five parts per billion (ppb) (EPA, 1987).

The importance of maintaining the cleanliness and safety of our groundwater for drinking can not be overemphasized. As the population of the country has risen, the percentage of groundwater used for drinking water has equaled surface water usage. Consumption of ground water has increased 140% between 1950 and 1975 (Burmester and Harris, 1982). Ground water now accounts for approximately 50% of the drinking water used in the United States, with 75% of major U.S. Cities depending on ground water for most of their supply (Pye, 1984).

The ubiquitous usage of petroleum products has contributed to widespread groundwater contamination. Discoveries of polluted groundwater, affecting people across the country from coast to coast, are publicized almost daily. As an example of the vast nature of the problem one only needs to look at the geographic distribution of Superfund sites. The 786 current and proposed Superfund sites on the EPA National Priorities List (NPL)(EPA,1984) encompass 48 of the 50 states, only Nevada and Alaska do not have sites on the NPL. Many of these Superfund sites, are contaminated by fuels and organic solvents derived from petroleum.

The percentage of usable ground water contaminated nationwide has been estimated to be as high as 2% (OTA, 1984). In densely populated, highly industrialized areas an even larger percentage of water may be contaminated to the

level it is unfit for human consumption. Recent Federal studies (Community Water Supply Survey, EPA, 1984) indicate that 45% of public water systems, relying on ground water and serving more than 10,000 people, contained volatile organic chemicals (OTA, 1984).

A populous state such as New York reported 1606 petroleum spill incidents in 1979 alone. From 1973 to 1979, 12,961,000 gallons of motor fuel were estimated to have been spilled in New York State (Jercinovic, 1984). Urbanized regions are not the only areas at risk. New Mexico, a state with a relatively small population documented 261 cases of petroleum contamination incidents between 1972 and 1984. The number of reported incidents is on the low side because they fail to include contamination events we don't yet know about.

The number of people affected by a single catastrophic contamination event can range into the thousands. A few large contamination events involving hydrocarbons are listed below.

- In 1968 the city of Los Angeles was forced to terminate production from a large well field due to a gasoline spill of 250,000 gallons caused by a pipeline leak (Williams, 1972).
- In Pennsylvania over 104 water wells were seriously damaged as a result of 200 hydrocarbon spills over a 2 1/2 year period from 1972 to 1974, effecting 800,000 people (Osgood, 1974).
- An estimated 500,000 gallons of oil near the U.S. Naval Station in Norfolk Virginia was released over decades into the subsurface. An oil skim that appeared in the neighboring harbor was attributed to this accumulation of oil in the subsurface (Sylvester and Landon, 1982).
- Almost 40,000 gallons leaked from an underground storage at a service station in Albuquerque, NM over a three month period in mid-1981. The leak contaminated the subsurface and resulted in explosive levels of gasoline vapors in a nearby residence (Jercinovic, 1984)

Some examples of other major contamination events involving hazardous waste storage and disposal, but not necessarily hydrocarbons, are listed below.

- Seven municipal wells, supplying 40% of Atlantic City's tap water, were closed due to contamination from "Price's Pit", a 26 acre landfill into which more than 9 million gallons of industrial wastes and organic solvents were dumped (Burmester and Harris, 1982).
- Contamination of groundwater, because of improper storage of 10,000 drums and 150,000 gallons of hazardous waste at a Chem-Dyne site, occurred beneath a ten acre site in downtown Hamilton, Ohio (EPA, 1983).
- More than 200 billion gallons of hazardous waste, enough to inundate Manhattan to a depth of 40 feet, have been poured into unlined pits and lagoons at Hanford Weapons plant in Richland, Washington. Toxic seepage has contaminated the underground aquifer over an area of 100 square miles (Satchell, 1989)

Groundwater pollution is probably more widespread and affects more people than believed. Polluted ground water, unlike surface water can not be seen and the old adage "out of site out of mind" appeared, until recently, to be the prevalent attitude. Sizable quantities of pollutants may already be present in ground water but have not yet been detected. The time between emplacement of the contaminant and discovery of the problem often takes months or years due to the relatively low velocity of groundwater. Unfortunately, nearly all contamination events are discovered only after a water supply has been polluted. Once a water supply has been contaminated, complete removal of the hydrocarbon contaminant may be an impossibility (Wilson and Conrad, 1984).

Only recently, maybe as a consequence of numerous widely publicized pollution incidents within the last 20 years, have we begun to fully realize the impact humans have on ground water quality. We are now understanding that



groundwater is not an infinite resource, its availability, similar to fossil fuels, is limited.

## **BACKGROUND**

An organic liquid spilled or leaked at the surface percolates downward into the soil. As the organic liquid travels through a soil containing air and water phases, under the influence of viscous, gravity, and capillary forces, a substantial amount is physically immobilized by capillary forces. The immobilized organic liquid, over time, may partition into the water, air, and soil phases. Once the organics have partitioned into another phase, they migrate with that phase. The movement of organics dissolved into the water phase is governed by the advection–dispersion equation. Organics volatilized into the air phase are subject to similar transport mechanisms. Soils with a high organic carbon content often adsorb significant quantities of organics. These organics may later be released or desorbed into the water phase as the concentration of the organic in the water phase decreases.

The topic of solute transport has been investigated thoroughly by researchers and several of the major transport mechanisms are believed to be fairly well understood. In contrast, multi–phase transport of organic liquids has been virtually ignored by the hydrologic research community in the United States, although it has been the subject of empirical studies in Europe (e.g., Schwille, 1967, 1981, 1984, and 1988; van Dam, 1967). The difficulties associated with quantifying multi–phase fluid behavior in porous media may be part of the reason for the apparent neglect of such an important issue by hydrology oriented researchers.

Through over sixty years of experimentation, petroleum engineering has amassed considerable expertise in multi-phase transport and the mechanics of

residual organic phase trapping and mobilization (Uren et al., 1927). But, until recently, this research was ignored by scientists concerned with near surface organic phase transport, and relatively little of this technology has been applied to recovering organic hazardous wastes and petroleum hydrocarbons released in the near-surface environment. Problems exist with the technology transfer because petroleum researchers investigate oil recovery in subsurface environments vastly different from those occurring at contamination sites at or near the surface. They examine porous media systems having much lower permeabilities than the unconsolidated sediments found at contamination sites. Oil recovery from reservoirs also occurs under much larger pressure gradients than can be produced in soils at the surface. Nevertheless, this research project borrows extensively from recent work conducted at New Mexico Institute Mining and Technology's Petroleum Research Recovery Center investigating enhanced oil recovery methods in petroleum reservoirs.

Within the last ten years, American researchers have conducted experiments addressing organic phase transport in porous media. Convery (1979) ran gravity drainage experiments on a long column to relate organic liquid retention in the vadose zone with grain size and sorting. Eames (1981) used a short soil core centrifuging method to measure residuals in the vadose zone. Eckberg and Sunada (1984) used gamma radiation attenuation and bulk soil electrical resistivity to measure three-phase fluid saturations at various times and at multiple elevations above a water table following a simulated petroleum spill. Ferrand et al. (1986) demonstrated the applicability of a technique using gamma ray attenuation to measure halogenated hydrocarbons under multi-phase conditions. Cary, McBride, and Simmons (1989) met with limited success when they performed experiments to test the ability of multiphase flow theory to predict the infiltration and redistribution of wetting and non-wetting fluids. Lenhard and Parker (1988)

developed an experimental apparatus capable of directly measuring multiple fluid saturations and pressures.

Some simple numerical simulations of multi-phase transport have been developed. These focus on immiscible transport of continuous phases. Residual organic liquids, trapped by capillary forces, are often ignored, although sometimes treated as a source of dissolved contamination (Faust, 1985). This research effort mirrors the state of the art of petroleum engineering's 'black oil' models. A few researchers (notably Baehr and Corapcioglu, 1984 and 1987; Corapcioglu and Baehr, 1987; Abriola and Pinder, 1985a,b; and Pinder and Abriola, 1986) are looking into interphase transfer, including the volatilization and solution of organic components, using computer simulations. This again reflects the state of the art in petroleum engineering, where so-called compositional models are used to examine enhanced recovery techniques.

Based on similar models in petroleum reservoir engineering, Parker et al. (1987) proposed a functional relationship between fluid pressures, saturations, and permeabilities of two- or three-phase porous media systems, and these functional relationships have been implemented in a multi-phase numerical flow model (Kuppusamy et al., 1987). The model has since been extended to include the effects of hysteresis and non-wetting phase trapping (Parker and Lenhard, 1987; and Lenhard and Parker, 1987a). The results of concurrent laboratory work were used to validate the model (Lenhard and Parker, 1987b,c,d; and Lenhard et al., 1987).

## **OBJECTIVE OF RESEARCH**

The purpose of this project is to investigate the physical processes responsible for the entrapment of organic liquids in the subsurface. Laboratory experiments, developed by Conrad (1986), using short soil columns, were designed to simulate

the behavior of an essentially immiscible fluid as it percolates downward through the soil. Residual saturations of organic liquids were measured under saturated and vadose zone conditions. Two-phase and three-phase fluid relationships were examined within the saturated zone and vadose zone, respectively.

This Independent Study investigates the behavior of residual organic liquid, because it often constitutes the most troublesome part of organic pollution (Wilson and Conrad, 1984) by acting as a continual source of dissolved or vapor phase organics. It is important to understand the processes responsible for organic liquid trapping so aquifer remediation schemes can be reasonably (economically and physically) designed. The lack of effective strategies dealing with the clean up of a separate organic phase can be traced to the minimal amount of knowledge the scientific community has collected concerning organic phase movement and distribution in the subsurface. This study, hopefully, will contribute to the understanding of multi-phase flow in a near-surface environment.

The main objectives of this study are:

- 1) Measure the amount of organic liquid trapped as residual saturation in the saturated zone and vadose zone.
- 2) Determine if any relationships exist between fluid properties and quantity of organic liquid trapped in the saturated zone.
- 3) Determine if Soltrol can be used to predict residual saturation of other organic liquids.
- 4) Investigate the vertical distribution of oil, water and air trapped in the vadose zone.

To achieve these objectives the following experiments were conducted. Saturated zone experiments were designed to simulate an organic liquid moving into the saturated zone beneath the water table, then ambient groundwater flow displacing some organic liquid, leaving behind trapped organic liquid at residual saturation. Residual saturations of six organic liquids (Soltrol-130, kerosene,

gasoline, p-xylene, n-decane, and tetrachloroethylene) were determined in the Sevilleta soil. Experiments were also conducted to analyze the multi-phase distribution of air, oil, and water in the vadose zone. A vertical profile of the three phase saturation within the unsaturated zone was reconstructed using experimentally derived results.

## CHAPTER 2

### PRINCIPLES OF FLUID TRAPPING

#### ORGANIC LIQUID MOVEMENT

Many hazardous waste sites, and most leaking underground storage tanks, involve non-aqueous phase organic liquids (e.g., Burmaster and Harris, 1982; Chaffee and Weimar, 1983; Convery, 1979; EPA, 1980,1982,1983; Feenstra and Coburn, 1986; J.R.Roberts et al., 1982; Jercinovic, 1984; Maugh, 1979 ; McKee et al., 1972; Villaume, 1988; Williams and Wilder, 1971). These essentially immiscible liquids, usually released at or near the surface, move downward through the vadose zone toward the water table. Migrating as a separate phase from the air and water already present in the vadose zone, some of the organic liquid is immobilized within the pore space by capillary forces. If the volume of organic liquid is large enough it eventually reaches the water table. There the organic liquid spreads laterally along the water table if it is less dense than water (see right side of Figure 2-1). In instances involving an organic liquid more dense than water, it continues to move downward into the saturated zone (the left side of Figure 2-1). In both cases the organic liquid migrates down-gradient with the ambient groundwater flow. As it moves into the water saturated pores beneath the water table more organic liquid is immobilized by capillary forces (Schwille, 1967, 1981, 1984, 1988; van Dam, 1967; de Pastrovich et al., 1979). In the saturated zone the immobilized organic liquid remains as small, disconnected pockets of liquid, sometimes called 'blobs', no longer connected to the main body of organic liquid. Organic liquid, however, is usually immobilized in the vadose zone in the form of thin films or pendular rings.

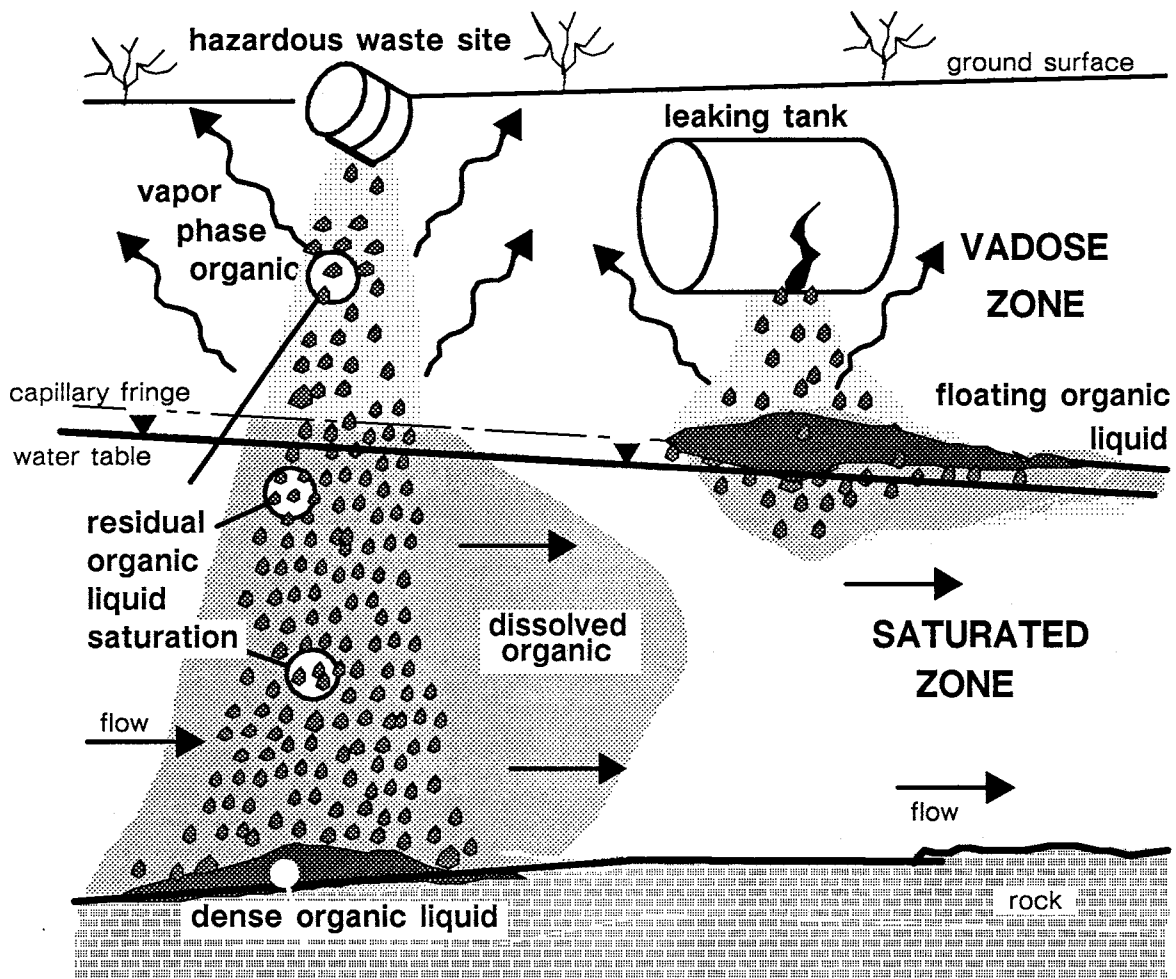


FIGURE 2-1. Migration pattern for an organic liquid more dense than water (left), and less dense water (right) (from Wilson et al., 1989).

The immobilized volume is referred to as 'residual oil saturation' in petroleum reservoir engineering, and is measured as the volume of organic liquid trapped in the pores relative to the volume of the pores. Organic liquid at residual saturation can occupy from 15% to 50% of the pore space in petroleum reservoir rocks under conditions that are roughly equivalent to those in the groundwater saturated zone (Melrose and Brandner, 1974). At a spill or hazardous waste site the entire volume of organic liquid can be exhausted by this immobilization, although if the volume of organic liquid is large enough, it continues to migrate down-gradient where it

becomes a threat to the safety of drinking water or agricultural water supplies (Schwille, 1967, 1981; de Pastrovich et al., 1979). This paper refers to the immobilized organic liquid as 'residual organic liquid'. As described later in this paper, the actual spatial distribution of the residual saturation within the pore space is completely different in the vadose and saturated zones.

The definitions used to quantify the fluid volume in a porous media, as previously stated, are taken from petroleum engineering research.

Organic liquid saturation is measured as the volume of organic liquid per unit void volume, measured over a representative elementary volume of the porous media:

$$S_o = \frac{V_{\text{organic liquid}}}{V_{\text{voids}}} \quad (2-1)$$

where the "o" indicates the organic liquid. The immobilized organic liquid saturation or residual saturation is defined by:

$$S_{or} = \frac{V_{\text{immobilized organic liquid}}}{V_{\text{voids}}} \quad (2-2)$$

where the "r" indicates residual. In the saturated zone the water saturation is given by:

$$S_w = 1.0 - S_o \quad (2-3)$$

Another measure of residual saturation often used in organic liquid pollution studies is the volumetric retention (e.g., de Pastrovich, 1979; Schwille, 1967):

$$R = \frac{\text{liters of residual organic liquid}}{\text{cubic meters of soil}} = S_{or} \times n \times 10^3 \quad (2-4)$$

where  $n$  is the soil porosity.



The organic liquid phase is often assumed to be immiscible with water and air. But in reality small concentrations of the various components of the organic phase volatilize into the air phase and dissolve into the water phase. For instance, when infiltrating rainwater passes through the zone of residual organic, or through the layer of organic on the water table it picks up soluble components of the oil and transports them into the groundwater system (van Der Waarden et al., 1971). Even when the so-called immiscible organic liquid has been immobilized by capillary trapping, the passing groundwater dissolves some of the residual. A 'halo' of dissolved organic components precedes the immiscible phase as it moves down gradient (Figure 2-1). Similarly, in the vadose zone, volatilized organic liquid migrates by gaseous diffusion and advection, becoming a source of organic components to air or water pollution, and a possible explosion hazard.

In large spills and leaks it is apparent that much of the liquid organic remains as a liquid, some is volatilized and a little is dissolved (Wilson and Conrad, 1984). Though small in volume, the volatilized or dissolved components are usually the ones that cause problems. The organic liquid phase acts as a continuing source of dissolved organic pollutants (Tuck et al., 1988). To restore an aquifer polluted by organics the trapped organic phase must be removed or isolated from the groundwater.

A variety of aquifer restoration techniques exist, yet they are often ineffective in removing trapped organic liquids. Biological and physical methods of reducing the organic phase have been attempted with varying degrees of success. Biological methods, relying upon microorganisms to break down the contaminant into harmless compounds are often used, but the microbes generally consume only the dissolved organic. Moreover, some organic chemicals are extremely resistant to biodegradation. PCBs, for example, biodegrade very slowly, or not at all in the

subsurface (J.R.Roberts et al., 1982). Wilson and Conrad (1984) evaluated the applicability of hydraulically sweeping the organic liquid out with water and concluded this approach often leaves a significant amount of organic liquid in the soil. Because of the failure of restoration methods to fully remove the pollutant, containment is often adopted as part of a restoration strategy. Hydraulic containment (e.g., Wilson, 1984), often in combination with structural barriers such as a slurry wall, is becoming standard practice.

In the vadose zone, induced volatilization may help reduce the residual volume for lighter organics, but is not effective for heavier ones (Burris et al., 1986). As a general rule, the lighter the organic liquid, the more volatile it is. For small pollution events the contaminated soil can be removed, then disposed of, or treated and replaced.

## **TRAPPING MECHANISMS**

The understanding of physical processes responsible for trapping the organic phase needs to be improved before effective restoration techniques can be utilized. In this discussion, research conducted by petroleum engineers examining enhanced oil recovery techniques, specifically looking at pore scale residual oil, is used to explain the mechanisms controlling organic phase trapping. The forces acting in a multi-phase system and the mechanisms by which immiscible fluids are immobilized within a pore network are investigated. Most of the following discussion on trapping mechanisms is taken from Wilson et al., 1989.

Many factors determine the pore scale mechanism of trapping: the geometry of the pore network; fluid-fluid properties such as interfacial tension, and density ratio; fluid-soil interfacial properties which determine wetting behavior (capillary forces); the water phase pressure gradient (viscous forces) and its alignment with

gravity (buoyancy forces) (Morrow and Songkran, 1981). The capillary force is proportional to the interfacial tension at the fluid-fluid interface and the strength of fluid wetting to the solid surface, and inversely proportional to the pore size. Viscous or dynamic forces are proportional to the permeability and to the pressure gradient, while buoyancy is a gravitational force proportional to the density difference between the fluids. According to Demond (1988) it is the capillary force which is responsible for the segregation of two phases into separate pore networks. In a three-phase system, viscous and buoyancy forces exert much greater influence over fluid movement.

Residual organic liquid appears to be trapped within a porous media by either or both of two major mechanisms: snap-off and by-passing (Mohanty et al., 1980; Chatzis et al., 1983; Wilson and Conrad, 1984). The concepts of interfacial tension, wettability, and capillarity are briefly reviewed below, and then used to describe non-wetting fluid trapping mechanisms for two fluid phases in a pore network.

### **Interfacial Tension**

In the interior of a homogeneous fluid, a molecule is surrounded on all sides by identical molecules exerting cohesive forces between one another. At the interface between two immiscible fluids however, there are few if any like molecules across the interface. A molecule at the interface is attracted to molecules of its own phase by a force greater than the force attracting it to molecules of the 'immiscible' phase across the interface. The cohesive forces acting on a molecule inside a fluid phase, and on a molecule at the interface (liquid-gas or liquid-liquid) between fluid phases are illustrated in Figure 2-2. This unbalanced force draws molecules along the interface inward and results in the

tendency for the fluid-fluid interface to contract. If the interface is stretched, it acts like an elastic membrane. The restoring force seeking to minimize the interfacial area between the two immiscible fluids, is called the interfacial tension,  $\sigma$ . The IFT of a liquid with its own vapor is defined as surface tension,  $\gamma$ .

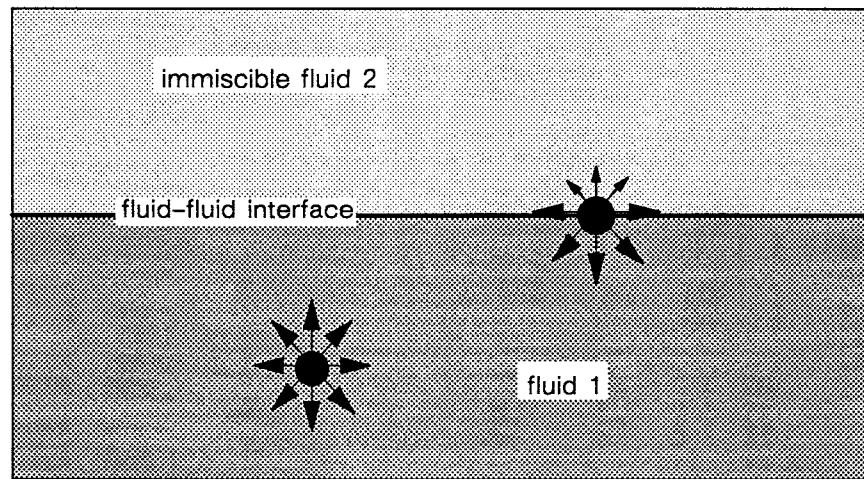
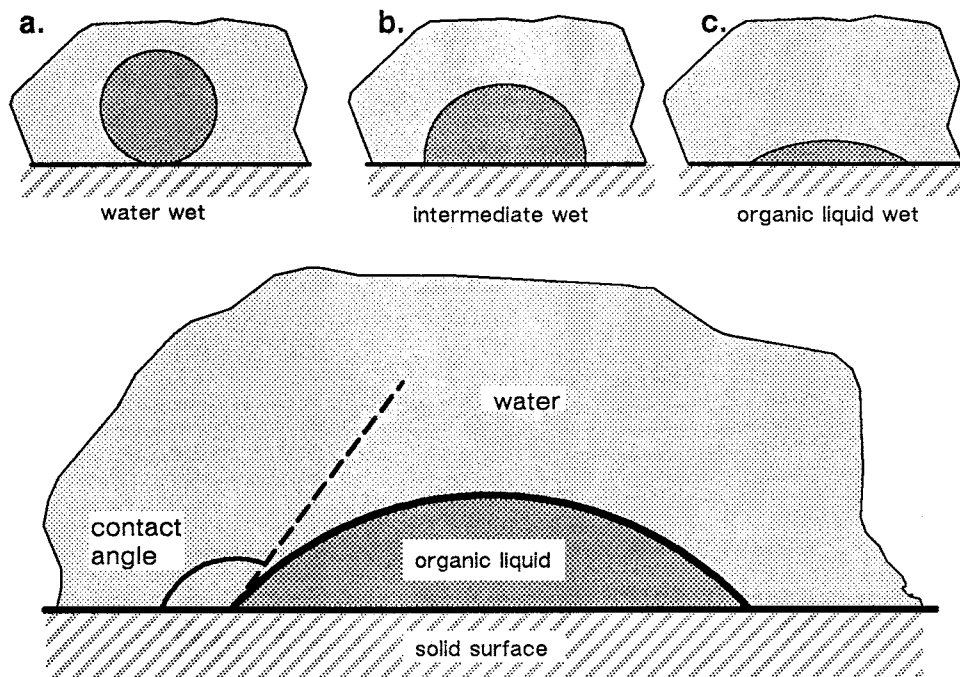


FIGURE 2-2. Cohesive forces acting on a molecule inside a fluid and at its interface with another, immiscible fluid (after Hillel, 1980).

### Wettability

Wettability refers to the relative affinity of the soil for the various fluids — water, air, and the organic phase. On a solid surface, exposed to two different fluids, it can be measured by contact angle (see Figure 2-3). Melrose and Brandner (1974) claim that contact angles are the only unambiguous measure of wettability. As an example of a contact angle, on clean glass, liquid water forms an acute contact angle  $\theta$  of about  $25.5^\circ$  in the presence of air. Water is a strong wetting fluid relative to air for this surface, but not necessarily for other surfaces, such as TFE (tetrafluoroethylene). Morrow (1975) measured the contact angle of water on surfaces with varying degrees of roughness. Contact angles for a number of organic liquids on various surfaces were tabulated by Demond (1988). Several



**FIGURE 2-3. Contact angle measurement on a clean, smooth solid surface.**  
(from Wilson et al., 1989)

common methods for measuring contact angles are summarized by Adamson (1982). Hysteresis in contact angle measurements is common, so both advancing and receding angles are often measured. Despite their widespread use to define wettability, there is some question as to how representative contact angle measurements are since they do not take into account the effect of surface roughness, heterogeneity, and pore geometry (Anderson, 1986b).

Figure 2-4 illustrates a possible configuration of two immiscible fluid phases in contact with the solid phase (walls) of a cylindrical tube. In this example fluid 1 is the more wetting fluid or has more affinity for the solid surface than does fluid 2.

### Capillarity

Related to wettability and interfacial tension is the contact angle. As a result of the contact angle, a meniscus is formed between immiscible fluid phases in

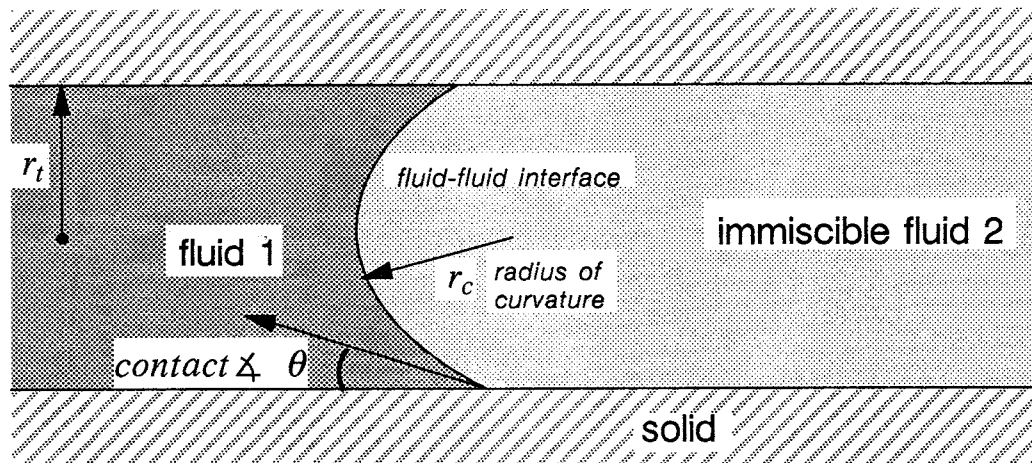


FIGURE 2-4. Hydrostatic equilibrium of two fluid phases in contact with a solid phase (after Melrose and Brandner, 1974).

contact with a solid (Figure 2-4). A pressure difference occurs across the interface separating the fluids due to the occurrence of curvature. The larger the pressure difference, the greater the curvature of the interface. The narrower the tube, the smaller the radius of curvature.

$$P_c = P_{nw} - P_w = \sigma C = \frac{2\sigma}{r_c} = \frac{2\sigma \cos \theta}{r_t} \quad (2-5)$$

where:  $P_c$  = capillary pressure

$P_w$  = pressure in the wetting phase (fluid 1 in the figure)

$P_{nw}$  = pressure in the non-wetting phase (fluid 2 in the figure)

$\sigma$  = fluid-fluid interfacial tension

$C$  = curvature of the fluid-fluid interface

$r_c$  = radius of curvature

$\theta$  = contact angle, measured through the wetting fluid

$r_t$  = radius of capillary tube

The most common example used to illustrate capillarity is that of the capillary rise of water in a straight thin tube (Figure 2-5). A liquid with an acute contact angle (e.g. water on glass) will form a concave meniscus with the air, and therefore the liquid pressure under the meniscus ( $P_w$ ) will be smaller than the

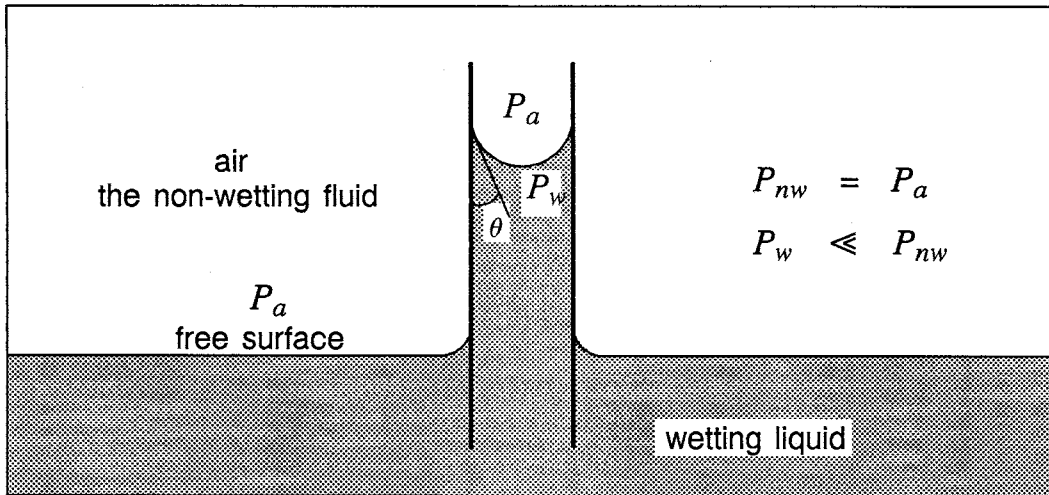


FIGURE 2-5. Capillary rise in a slim tube (from Wilson et al., 1989).

atmospheric pressure ( $P_a$ ). The pressure difference between the wetting fluid (water) and non-wetting fluid (air), at the interface inside the tube, causes the water to rise into the tube, above the level of the free surface until the atmospheric pressure is countered by the hydrostatic pressure of the water column in the tube (Hillel, 1981). The capillary pressure can be thought of as a measure of the tendency of the porous media to suck in the wetting phase and repel the non-wetting phase.

These same processes operate on the pore scale in saturated, and unsaturated, porous media, but the relative influence of the forces is different. The capillary fringe is a notable example. Also, the interplay of the various wettabilities and interfacial tensions of different fluids, and the capillary forces they give rise to, leads to trapping of fluids within pores, as the fluids migrate through, or drain out of, a system. These capillarity induced trapping mechanisms are discussed next.

## Snap-off

Snap-off occurs as non-wetting fluid (organic liquid) in a pore is displaced by wetting fluid (water) from a pore body into a pore throat. The mechanism strongly depends on wettability and aspect ratio — the ratio of pore-body diameter to pore-throat diameter (Wardlaw, 1982).

Consider the case of water displacing an organic liquid from a tube with a non-uniform pore diameter, as shown in Figures 2-6 and 2-7. The walls of the tube are smooth and strongly water wet. The water contact angle is acute, the water-organic liquid interface is curved, and the water phase 'wicks' along the pore wall. In high aspect ratio pores, the pore throats are much smaller than the pore

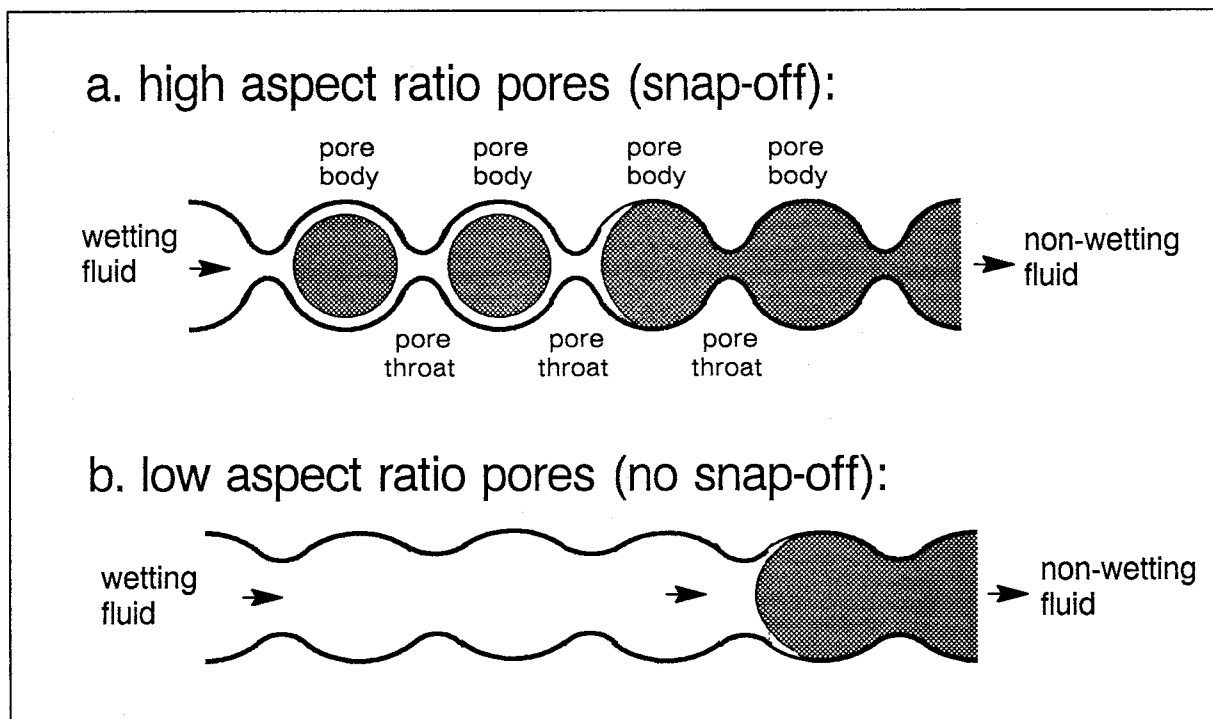


FIGURE 2-6. Effect of pore aspect ratio on organic liquid trapping in a tube of non-uniform diameter (after Chatzis et al., 1983).



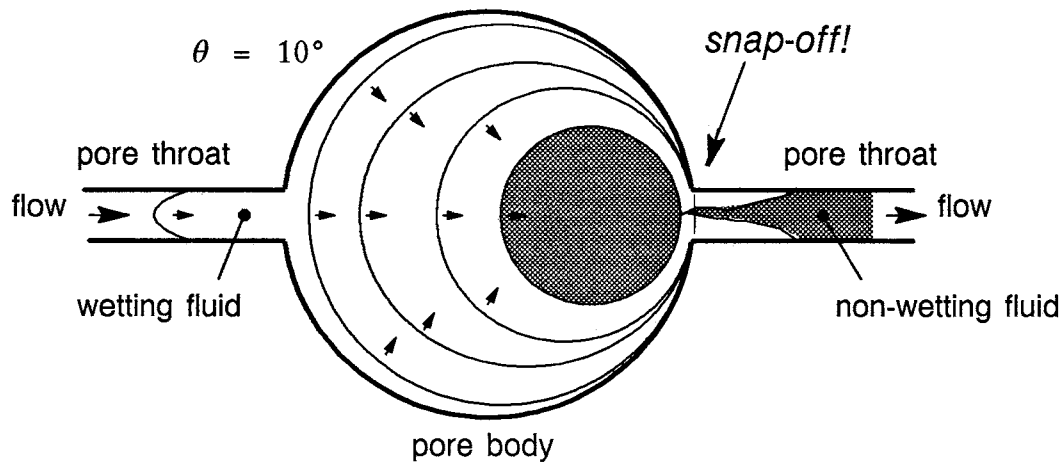


FIGURE 2-7. Wetting fluid displacing a non-wetting fluid from a circular, high aspect ratio pore under strongly wet conditions (after Wardlaw, 1982).

bodies (Figure 2-6a and Figure 2-7). When the thin layer of water phase reaches the exit pore throat, a large blob of organic liquid still remains in the pore (Figure 2-7). Snap-off occurs as the water continues through the exit throat leaving behind the now disconnected singlet blob. In a sequence of high aspect ratio pores, a singlet blob is trapped by snap-off in each pore (Figure 2-6a). Pores in uniform sized glass bead packs have a high aspect ratio, explaining the prevalence for singlet blobs observed by Morrow and Chatzis (1982) and Chatzis et al. (1983). For low aspect ratio pores, in which the pore throats are almost as large as the pore bodies, it is possible to completely displace the organic liquid, as shown in Figure 2-6b.

Trapping, in addition to pore geometry is also a function of wetting and contact angle. The combined effect of contact angle and pore geometry control the curvature of a fluid-fluid interface and determine the potential for snap-off (Wardlaw, 1982). Figure 2-8 depicts an interface with a 90 degree contact angle passing from a pore throat through a high aspect ratio pore body with smooth

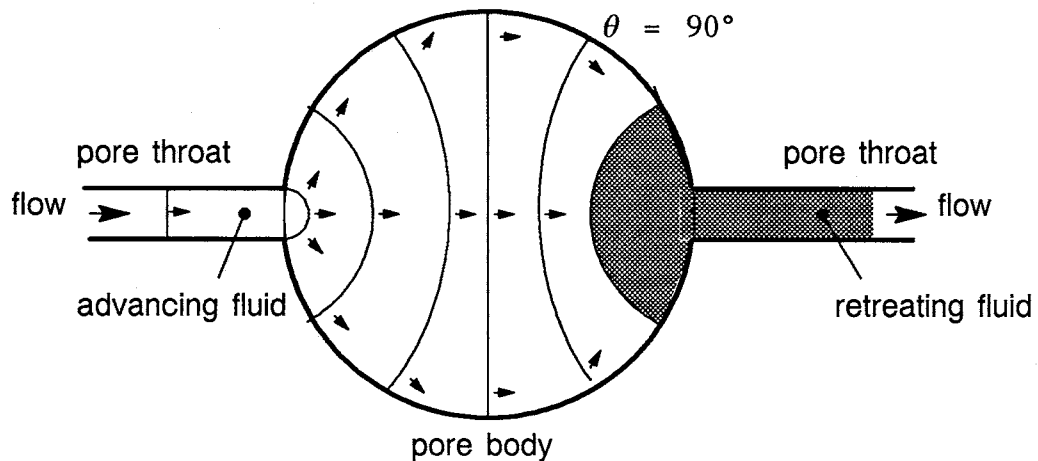


FIGURE 2-8. One fluid displacing another from a circular, high aspect ratio pore, under intermediate wetting conditions (after Wardlaw, 1982).

walls. The intermediate contact angle of  $90^\circ$  causes the curvature of the interface to remain relatively small. As the interface reaches the exit throat, little organic phase remains in the pore and no trapping occurs (Wardlaw, 1982). In rough walled pores, there is probably some trapping of the retreating phase in the asperities along the wall (see Figure 2-9).

### By-passing

A second mechanism used to explain immiscible fluid phase trapping is by-passing. The pore doublet model (Figure 2-10) has been used to describe this trapping mechanism on a microscopic scale (Chatzis and Dullien, 1983; and Chatzis et al., 1983). A pore doublet consists of a tube which splits into two pores, one generally narrower than the other, and then rejoins. The pore doublet concept is used here to describe organic phase trapping by the mechanism referred to as 'by-passing'.

Figure 2-10 depicts a wetting phase (water) displacing a non-wetting organic phase in a pore doublet under several different circumstances. The pore walls are

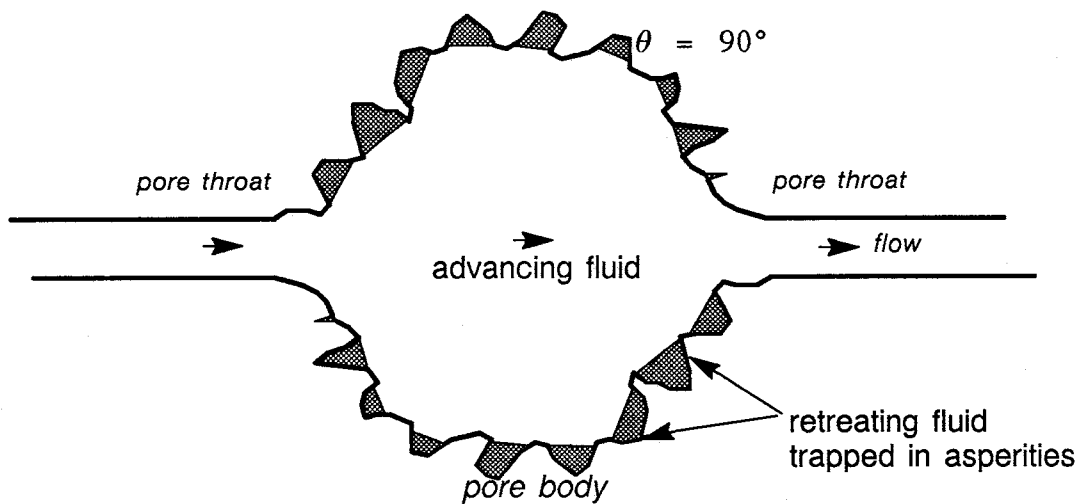


FIGURE 2-9. Final condition after an advancing fluid displaced a retreating fluid from a rough-walled pore under intermediate wetting conditions (after Wardlaw, 1982).

smooth and strongly water wet. Figure 2-10a demonstrates circumstances under which no trapping occurs. The advancing water phase enters the narrower pore opening first (stage 1). In each pore, the total pressure drop driving flow is the sum of the capillary pressure and the dynamic pressure drop caused by flow (Moore and Slobod, 1956). For the pore doublet to have any physical meaning, the flow rates (and dynamic pressure drop) should be low enough to approximate aquifer conditions. On a pore scale, under such conditions, capillary forces are much larger than the dynamic viscous forces. Capillarity then controls advance of the wetting front causing water to initially fill the narrower pore (Chatzis and Dullien, 1983). The water-organic interface remains stable at the entrance to the wider pore (stage 2). When the water reaches the downstream node (where the pores rejoin), it forms a stable meniscus with the organic liquid because the cross-section at the downstream node is greater than at the entrance to the wider pore. In instances where a stable meniscus can be maintained at the downstream node, water can then push organic out of the wider pore (stage 3). The menisci rejoin at the

downstream node (stage 4). In this case, the water has displaced the organic liquid completely from the pore doublet and no trapping has occurred.

The displacement sequence for the pore doublet shown in Figure 2-10b illustrates the by-passing mechanism of trapping. As before, the water enters the narrower pore first. However, as water reaches the downstream node, it does not stop because no stable interface is formed (Figure 2-10b, stage 2). The organic liquid in the wider pore has become disconnected from the main body of organic liquid and is now unable to drain from the pore. This liquid has become 'by-passed' by the advancing water (stage 3).

Figure 2-10c uses a pore doublet model to demonstrate both snap-off and by-passing trapping mechanisms. Once again, water enters the narrower pore first

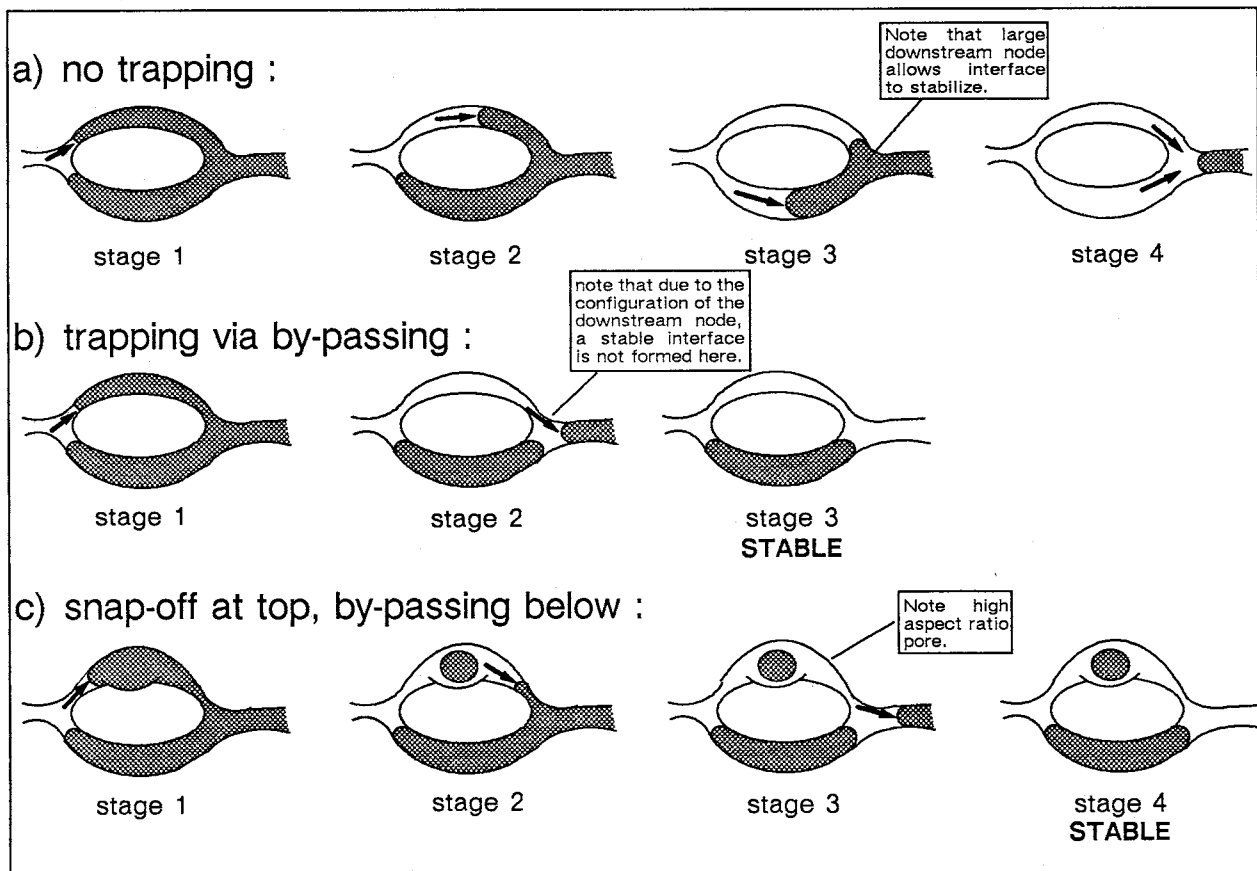


FIGURE 2-10. Sketches illustrating trapping mechanisms using the pore doublet model (after Chatzis et al., 1983)

(stage 1). Due to the high aspect ratio in the narrower pore, snap-off occurs (stage 2). Water continues to move through the narrower pore and through the downstream node. No stable meniscus is formed and organic liquid in the wider pore is by-passed (stages 3 and 4).

While the pore doublet model allows the organic liquid to be by-passed in at most one pore, in a porous medium the organic phase in several pores may be collectively by-passed leaving an organic blob which extends over several pores. In contrast, blobs trapped by snap-off extend over one pore only. Peplinski (1989) using styrene as the organic phase, was able to determine the size and shape of organic liquid at residual saturation in Sevilleta sand. The styrene solidified when heated, enabling it to retain the same shape as when it was trapped as a liquid. The soil was dissolved in hydrofluoric acid, leaving behind the resistant styrene blobs. The simple singlet observed in Figure 2-11, was probably trapped by snap-off. By-passing probably played a dominate role in trapping the complex blobs of Figure 2-12. As pore aspect ratio decreases, the proportion of organic liquid trapped by by-passing, relative to snap-off, increases, and blobs become larger and more complex. Soil or rock heterogeneity also encourages trapping through by-passing (see Chatzis et al., 1983).

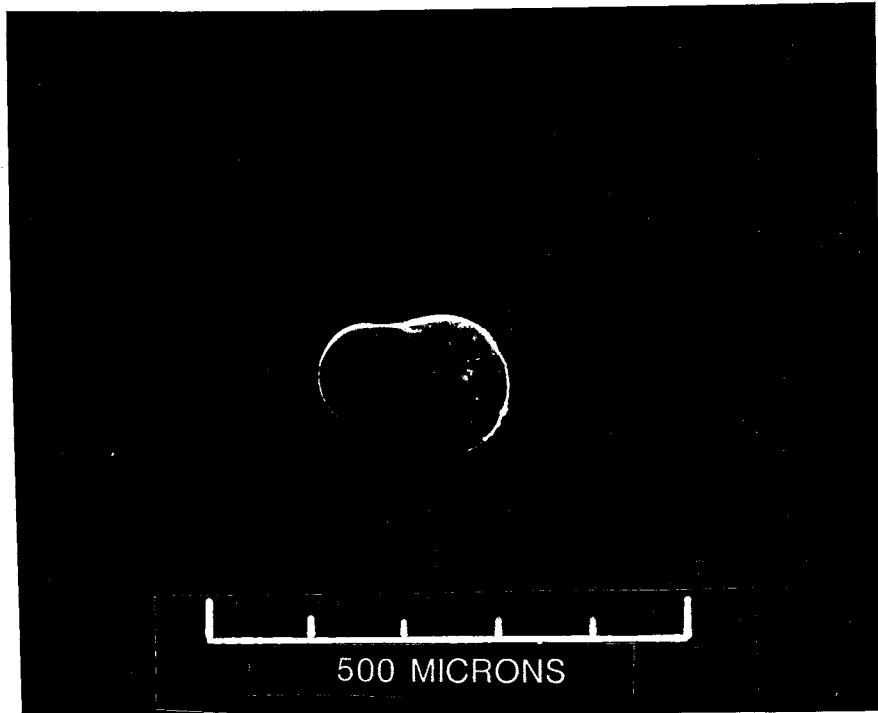


Figure 2-11. Organic liquid blob probably trapped by snap-off (Peplinski, 1989).



Figure 2-12. Complex shaped organic liquid possibly trapped by by-passing (Peplinski, 1989).

## Capillary and Bond Number

In some instances the capillary forces which cause trapping can be overcome by the viscous pressure gradient or buoyancy forces or a combination of these forces, reducing the residual organic liquid saturation. The ratio of viscous forces to capillary forces is known as the capillary number,  $N_c$ , while the ratio of gravity forces to capillary forces is the Bond number,  $N_B$ :

$$N_c = \frac{k \nabla P_w}{\sigma} \quad (2-6)$$

$$N_B = \frac{\Delta \rho g R^2}{\sigma} \quad (2-7)$$

where:  $k$  = intrinsic (absolute) permeability of soil (cm<sup>2</sup>)  
 $\nabla P_w$  = water phase pressure gradient (g/cm<sup>2</sup>-sec<sup>2</sup>)  
 $\sigma$  = interfacial tension between the fluids (dynes/cm)  
 $\Delta \rho$  = density difference between fluids (g/cm<sup>3</sup>)  
 $g$  = acceleration of gravity (cm/sec<sup>2</sup>)  
 $R$  = representative grain radius (cm)

This representation of the capillary number assumes that the hydrostatic forces are negligible. The ratio of forces represented by the capillary number can also be given in terms of the Darcy velocity in the water phase (see, e.g., Taber, 1981):

$$N_c = \frac{q_w \mu_w}{\sigma} \quad (2-8)$$

where:  $q_w$  = specific discharge (darcy velocity) of the water phase (cm/sec)  
 $\mu_w$  = viscosity of water (g/cm-sec)

Morrow and Songkran (1981) demonstrated that if the viscous or buoyancy forces relative to the capillary forces are increased above a critical value a reduction in residual saturation occurs. Once the capillary number or Bond

Number exceeds a critical value, the residual saturation decreases as the number is increased. Chatzis and Morrow (1981) performed a large number of experiments using sandstone cores to explore this relationship between capillary number and organic liquid saturation. The gradient or flow rate across the core was increased in a stepwise manner, and at each step residual organic liquid production was observed. A typical curve for the sandstone is shown as the left-hand curve in Figure 2-13. Above the critical capillary number,  $N_c^*$ , viscous forces associated with higher flow rates, begin to overcome the capillary forces resulting in a reduction of the residual saturation. The critical capillary number at which the residual saturation began to decrease was typically  $N_c^* \approx 2 \times 10^{-5}$  for sandstones.  $N_c^{**}$  denotes the capillary number necessary to displace all of the blobs;  $N_c^{**} \approx 1.3 \times 10^{-3}$ . The relationship in Figure 2-13 holds for a wide variety of sandstones and organic fluids, provided that the organic liquid is the non-wetting

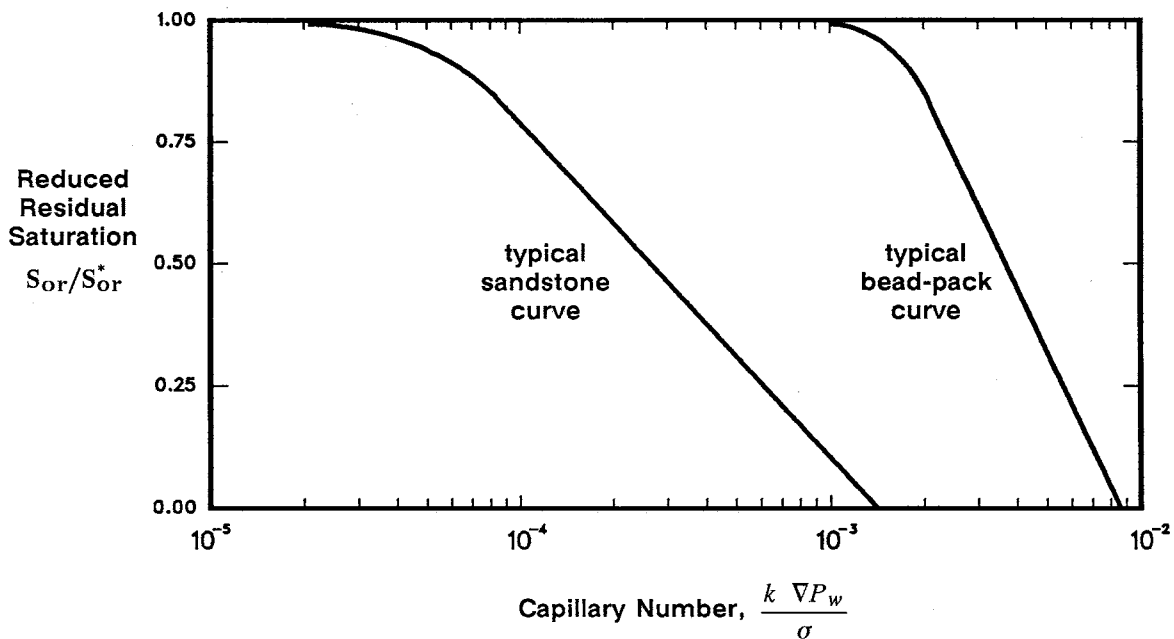


FIGURE 2-13. Relationship between residual saturation and capillary number for sandstones and glass beads. The sandstone curve is from Chatzis and Morrow (1981); the bead-pack curve is based on work reported in Morrow and Chatzis (1982).



fluid. In Figure 2-13, the residual saturation is normalized by its initial value,  $s_{or}^*$ , which is the residual saturation measured in the soil column experiments.

A similar set of experiments were performed with glass beads by Morrow and Chatzis (1982). Using a variety of sizes of uniform beads, and various organic liquids another correlation was obtained (Figure 2-13). For glass beads a significantly larger capillary number (i.e. more gradient) is required to mobilize the residual liquid. The reason for this can be explained by the larger aspect ratio of the bead pack relative to the sandstones. Sintering the beads (melting them together slightly) reduces the aspect ratio and produces a curve much closer to the sandstone curve (Morrow and Chatzis, 1982).

Morrow and Songkran (1981) correlated the combined effect of gravity and viscous forces to residual saturation. They determined residual saturation could be correlated with a simple linear combination of Bond number and Capillary number. These numbers can be combined to yield the relationship shown below.

$$\frac{F_v + F_b}{F_c} = \text{the ratio of viscous plus gravity forces to capillary forces.}$$

A qualitative plot of residual saturation versus this relationship (Figure 2-14) shows that as the viscous and buoyancy forces are increased, while the capillary force is held constant, the residual saturation initially remains the same. But when the critical value is exceeded, the residual saturation begins to decrease.

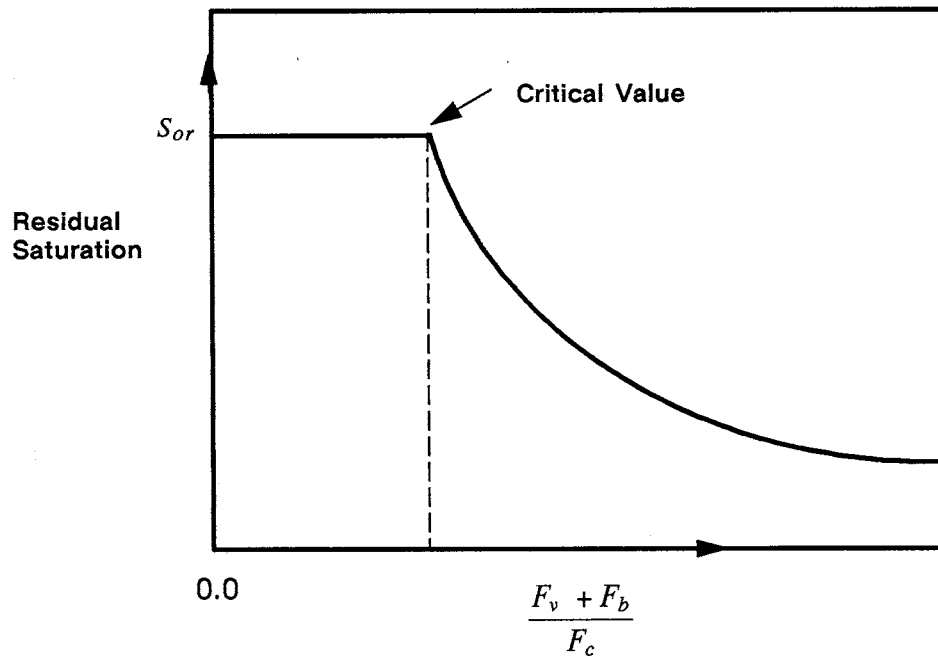


Figure 2-14 Residual saturation versus the ratio of viscous and buoyancy forces to capillary forces (After Morrow and Songkran, 1981).

In the saturated zone experiments trapping takes place beneath the critical value so organic liquid residual saturation is at a maximum. In the vadose zone experiments however, the critical value is often exceeded. The combined effect of viscous and buoyancy forces overcome capillary forces at some locations, reducing the residual organic liquid saturation of the system. The correlation between the capillary force and the buoyancy force and its effect on residual organic liquid saturation is discussed in greater detail in Chapter 6.

## CHAPTER 3

### EXPERIMENTAL METHODS

Column experiments were performed to measure the residual organic liquid saturations of soils under either vadose zone or saturated zone conditions, providing a direct means to compare the amount of organic liquid trapped in the vadose zone to the amount trapped in the saturated zone. The soil used in the experiments was a uniform, medium-sized, quartz sand. Soltrol-130, a mixture of C<sub>10</sub> to C<sub>13</sub> isoparaffins with negligible solubility in water, served as the organic phase. The aqueous fluid used in the experiments was water with 3000 ppm calcium chloride added to prevent dispersion of clays. In other saturated-zone experiments, either kerosene, regular leaded gasoline, p-xylene, or tetrachloroethylene was used as the organic phase to directly compare the differences in residual saturations to different classes of organic pollutants. Residual saturations were also measured for several soils under saturated-zone conditions and these results were compared to the results of other researchers.

A short glass chromatographic column with threaded Teflon™ tetrafluoroethylene endcaps was used to contain the soil sample. The glass column had an inside diameter of 5 cm and an effective internal length of about 5 cm. The column was kept short so that variations in saturation over the length of the column would be minimized. Semi-permeable membranes were used on the lower endcap to prevent capillary end effects. A paper filter placed on the upper endcap prevented clay-sized particles from leaving the column. During an experiment, the change in column mass was used, in conjunction with the known density difference between the fluids, to measure saturations. Soils and liquids were exposed only to glass, Teflon, and chemically resistant tubing during the experiments.

In the saturated zone experiments, organic liquid was introduced into a water-saturated soil sample until the so-called irreducible water saturation was reached. Water was then re-introduced into the soil displacing most of the organic liquid, but leaving behind some discontinuous blobs of organic liquid trapped by capillary forces. The fraction of the pore space occupied by these trapped blobs is the residual saturation. The experiment represents a scenario in which organic liquid percolates into the saturated zone and is, in turn, displaced by ambient groundwater flow, leaving behind a residual organic liquid saturation.

In the vadose zone experiments, an initially water-saturated soil sample was drained with air under an applied suction until an equilibrium was reached. The drained soil represented vadose zone conditions in which the pore space is occupied by both air and water. As organic liquid was introduced (simulating a spill or leak), it displaced air and water as it percolated through the soil. Organic liquid was then drained from the soil under an applied suction, simulating the downward movement of organic liquid as it passes through the vadose zone toward the water table. Again, capillarity caused some organic liquid to become trapped in the pore space.

In this chapter the fluids and soils used in these experiments are described and the rationale behind the choices is given. A description of the experimental apparatus is presented, followed by an explanation of the experimental procedures designed to determine the residual organic liquid saturation under saturated and vadose zone conditions. The chapter is concluded by discussing the limitations of the apparatus and possible errors that may occur when conducting these experiments.

## FLUIDS AND SOILS

The aqueous fluid used in all experiments was distilled, de-ionized, de-aired water with 3000 ppm  $\text{CaCl}_2$  added to prevent dispersion of clays.

Soltrol-130, a mixture of  $\text{C}_{10}$  to  $\text{C}_{13}$  isoparaffins produced by Phillips 66 Company was the organic liquid used to debug the apparatus and develop the experimental procedure. It is a colorless, combustible liquid having a mild odor and negligible solubility in water. Soltrol-130 proved to be the ideal fluid for debugging because of its relatively low solubility, volatility, and toxicity. For these desirable qualities and because of the need to hold all variables but the independent variable of interest constant, Soltrol-130 was used in all experiments comparing residual saturations in the saturated zone to those in the vadose zone, and for all comparisons of residual saturations between soils.

The other organic liquids selected for use in the experiments were chosen to be representative of several classes of organic liquid pollutants often present at landfills, hazardous waste sites, and accidental spills. Saturated zone residual organic liquid saturations were determined for six organic liquids; three of the liquids were mixtures (regular leaded gasoline, kerosene, and Soltrol-130), and three were single-component liquids. Of the single-component liquids, n-decane was chosen to represent straight-chain aliphatics, p-xylene was chosen to represent aromatics, and tetrachloroethylene (PCE) was chosen to represent halogenated hydrocarbons. Selection of a particular chemical to represent a given class of chemicals was based on the volatility and solubility of the organic liquid, as well as the density difference between the organic liquid and water. Low volatility and solubility were desired to avoid competing physical processes. A large density difference between the organic liquid and water was desired because the soil

columns were weighed to measure the fluid saturations. Larger density differences between the fluids led to more accurate measurement of the saturations. Solubility, volatility, and toxicity values for some organic liquids are presented in Appendix E.

Gasoline leakage from thousands of storage tanks and spills, incurred during transportation and distribution of the fuel, is responsible for a large number of the groundwater contamination incidents reported today. Gasoline and its individual components (as represented by xylene for the lighter aromatic fraction and decane for the less volatile fraction) were considered for investigation because of gasoline's abundant use and misuse.

Kerosene is very similar in composition to the aviation fuel used in military aircraft and long-distance passenger-carrying aircraft. Groundwater contamination problems have occurred from spills of aviation fuel at airfields and military bases around the country.

PCE, commonly used as a solvent and degreaser, was one of two chemical carcinogens, TCE was the other, found most often in groundwater according to a report compiled in 1980 by the EPA Office of Drinking Water (Burmester & Harris, 1982). PCE, because of its relatively low solubility and volatility, was chosen to represent the class of organic liquids denser than water.

Sevilleta sand was selected as the soil used to refine the experimental apparatus and procedure. Once again because of the need to hold all variables but the independent variable of interest constant, this soil was used in all experiments comparing residual saturations in the saturated zone to those in the vadose zone, and for all comparisons of residual saturations between organic liquids. The Sevilleta sand is a well sorted, medium aeolian sand, taken from a sand dune in

the Sevilleta Wildlife Refuge, located 15 miles north of Socorro, New Mexico. This sand was chosen for three reasons:

- 1) It is a uniform, homogeneous soil with a fairly high hydraulic conductivity, a low percentage of fine particles, and a very low organic content. These properties made the Sevilleta sand easy to use during the testing and fine tuning of the experimental technique.
- 2) The sand is easy to obtain. The Hydrology program maintains a field site at the location from which the soil is taken.
- 3) The Sevilleta sand has been previously in several hydrologic studies here at Tech. This permitted a comparison of soil characterization results with those of previous studies conducted at New Mexico Tech.

The Traverse City soil, a sandy soil similar to the Sevilleta sand, was also used in saturated zone experiments. The soil was supplied by the EPA's Kerr lab from their biodegradation field demonstration site at a Coast Guard Air Station in Traverse City, Michigan.

Palouse loam, an agricultural soil from eastern Washington, was used as a third soil in the saturated zone experiments. The Palouse soil provided a good contrast to the Sevilleta and Traverse City soils because of its much finer texture (15% sand, 80% silt, 5% clay) and its higher organic carbon content of 1.5%. Unfortunately, the Palouse loam was found to be inappropriate for use in these experiments and pointed out some of the limitations of the apparatus. The fine-grained nature of the soil made it difficult to work with. The column had to be packed dry, because the Palouse loam became a gooey, unmanageable ooze when wet. Dry packing increased the length of time required to de-air the column by two to three weeks. The small pores present in this fine-grained soil made it difficult to

supply sufficient pressure to force organic liquid into the soil. Cracks in the soil, formed when the top endcap was tightened down, were also a common problem. More about the problems encountered in using the Palouse loam can be found later in a discussion of the limitations of the apparatus.

### EXPERIMENTAL APPARATUS

Each apparatus used in the experiments consisted of a short glass chromatographic column with tetrafluoroethylene (TFE) endcaps (Figure 3-1), and associated plumbing. The glass column and TFE endcaps were manufactured by Ace Glass, Inc. The glass column was specially fabricated to our specifications: 5

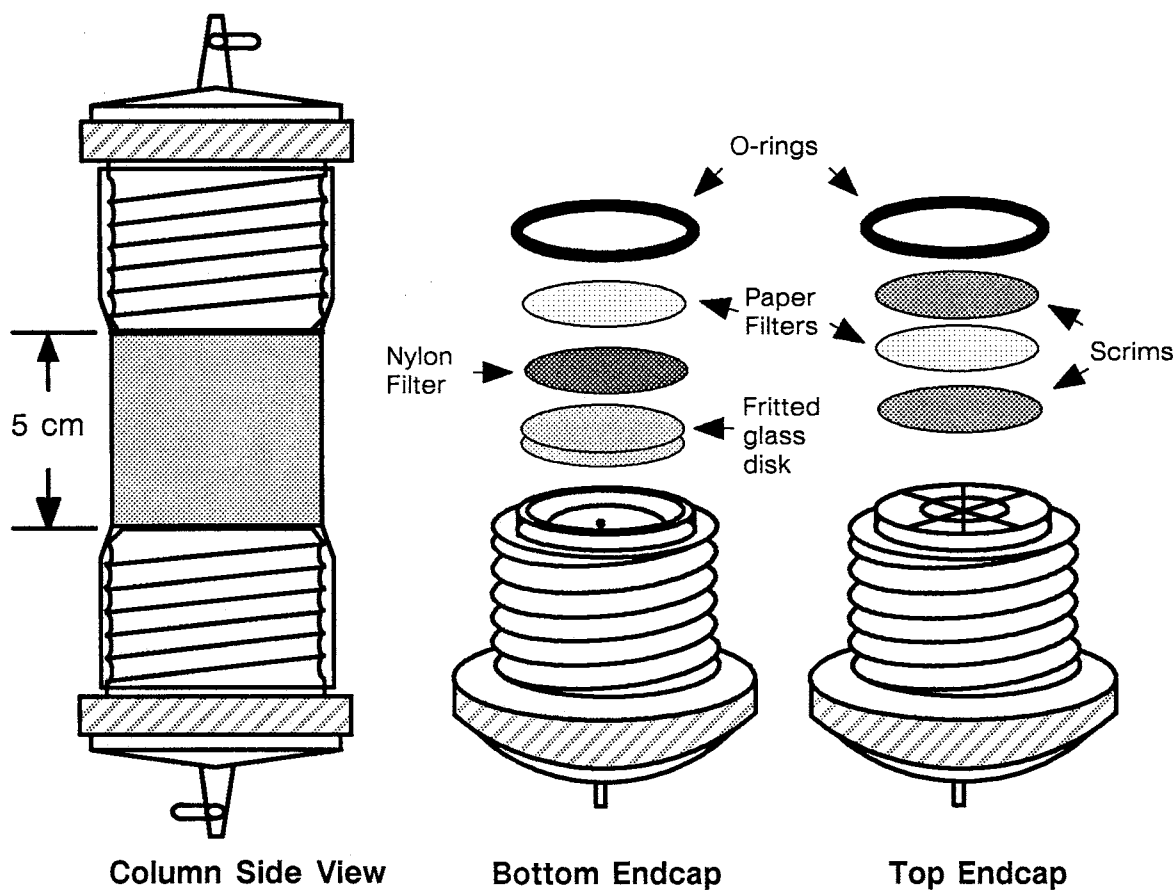


FIGURE 3-1. The short column apparatus, with blow-up views of the endcaps and filters.



cm inside diameter and 5 cm effective internal length between TFE endcaps. The effective column length was kept short to decrease saturation variation within the soil column. The endcaps were screwed into threaded ends on the glass column and sealed against the column with chemically resistant o-rings.

A 5 mm thick fritted-glass disk with a 20 micron average pore diameter was placed into the taper of the bottom endcap as a filter support. A water-wet Magna 66 nylon filter with a 0.22 micron pore diameter, designed to allow water, but prevent organic liquid from leaving the column, was glued along the edges to the fritted-glass disk. A paper filter was placed over the nylon filter to protect the nylon from abrasion by the soil.

A network of small channels approximately 1 mm deep and 1.5 mm wide were machined into the surface of the top endcap in a pattern similar to that shown in Figure 3-1. The grooves allowed for a more uniform flow of fluids between the endcap and the soil. A paper filter which kept fine soil particles from leaving the column, was sandwiched in between two polypropylene scrims and glued to the endcap. The outer scrim kept the paper filter from tearing against the soil when the endcap was screwed down against the soil. The inner scrim decreased clogging by preventing the paper filter from sagging back into the grooves.

In vadose zone experiments, endcaps containing organic-wet filters were used as part of the experimental procedure (as described later in this chapter under 'vadose zone experiments'). Endcaps with organic-wet membranes, which allow organic liquid to pass through but not water or air, were constructed in one of two ways. By the first method, the endcaps were constructed identically to water-wet endcaps but an organic-wet, TFE filter was glued in place instead of a water-wet nylon filter. The TFE filters, purchased from Gelman Sciences, had an average pore diameter of 0.5 microns. By the second method, an organic-wet ceramic disk

was simply glued into place in an endcap, in place of the fritted-glass disk, the membrane, and the paper filter. Because the experimental procedure required these endcaps to be screwed into place against the soil, the TFE membrane could become damaged by abrasion from the soil grains. Use of the much more rugged ceramic disks alleviated this problem.

Devcon 2-ton epoxy was used to glue filters and disks on all endcaps except those used in experiments employing PCE as the organic liquid. Because PCE dissolved the epoxy, silicon sealant was used to attach filters to the endcaps in any experiments involving the use of PCE.

For the saturated and vadose zone experiments to run properly, it was essential that filters maintained their integrity. That is, the nylon filters must allow only water and not organic liquid or air to penetrate under experimental conditions; while the TFE filter or treated ceramic disk must allow organic liquid to pass, but not water or air. Capillary forces held the wetting phase in the pores of the filter, allowing only the wetting phase to pass through. Non-wetting fluids could not pass through the filter, as long as viscous (pressure gradient) or gravity (density differences) forces did not overcome the capillary forces. Under experimental conditions the viscous and gravity forces were small, allowing the integrity of the filters to be maintained. An air-entry test, described in Appendix B, was developed as a simple means to test the integrity of a filter and its glued seal to the endcap.

### **Column Volume Measurement**

Accurate measurement of the column volume was important because it was used in subsequent calculations of bulk density, porosity, pore volume, and fluid saturations. To measure the column volume, the column was weighed empty, filled

with water, and weighed again. The difference between the two weights divided by the density of water yielded the column volume,  $V_c$ . Allowances were made for the volume inside the column occupied by filters, the grooves in the top endcap, and how tightly the endcaps were screwed onto the column to give an 'effective column volume' ( $V_{ce}$ ), the volume occupied by soil and the fluids of interest. What follows is a detailed description of the procedures used to accurately measure the effective column volume.

The mass of the empty column ( $M_e$ ) was determined by weighing the glass column, endcaps with valves, and o-rings using a Mettler PE 1600 balance with 0.01 g accuracy. The bottom endcap was weighed while saturated with water from the filter test, and the top endcap was weighed before the filters were glued into place. The column was then assembled. The bottom endcap was screwed into the glass column and tightened in place using a bench vise. The top endcap was only hand tightened into the glass column at this point. The top endcap and glass column were marked to show this reference alignment. The column was filled with water, and reweighed, making sure no air bubbles were present. The column volume was calculated as:

$$V_c = \frac{M_{w1} - M_e}{\rho_w} \quad (3-1)$$

where:  $M_{w1}$  = mass of the water-filled column (g)

$\rho_w$  = density of water (g/cm<sup>3</sup>)

Packing a column with soil was an imprecise science. The column might have been slightly over-filled with soil one time, slightly under-filled the next. The top endcap could not be screwed down to the reference alignment mark in an over-filled column resulting in a slightly larger volume inside the column.

Conversely, a slightly under-filled column might have been tightened down somewhat further than the reference, resulting in a slightly smaller column volume than the reference volume. To account for this variability in column volume from one packing to the next, a correction factor for endcap tightening was desired. To accomplish this, the valve on the top endcap was opened and the previously hand-tightened endcap was tightened in a bench vise. As the column volume was made smaller by the tightening, water squirted out through the opened valve. A new mark, aligned with the glass column mark, was made on the top endcap. The offset length between marks ( $L_c$ ) was recorded, the column was reweighed, and the new mass ( $M_{w2}$ ) was recorded. The column tightening correction factor ( $C_t$ ) was calculated as:

$$C_t = \frac{M_{w1} - M_{w2}}{L_c \rho_w} \quad (3-2)$$

The volume of the top endcap (including the volume of the grooves, the connecting hole in the endcap, and the valve) was measured in a manner similar to the method used to measure the gross column volume. The endcap was weighed empty, the endcap was filled with a liquid of known density, and the endcap was reweighed. Similar to before, the mass of the full endcap minus the mass of the empty endcap divided by the liquid density provided a measure of volume which could be occupied by fluid in the endcap. Because the endcap was made of Teflon, an organic liquid did a much better job than water of wetting the surface and filling the grooves.

The volume of the filter, scrims, and glue on the top endcap reduced the volume of the column available to sand and fluids and also needed to be accounted for. The volume of the paper filter and the polypropylene scrims was calculated by

simply multiplying the cross-sectional area by the measured thickness. The endcap, filter, and scrims were weighed prior to gluing the filter and scrims onto the endcap. After the glue had hardened, the endcap was reweighed. The difference between the two weights was the weight of the glue, and when divided by the glue density yielded the glue volume. The density of hardened glue was determined using the ASTM D584-83.

The effective column volume was determined by accounting for the volume in the top endcap behind the filters (including grooves, connecting hole, and valve), the volume of the paper filter and scrims on the top endcap, the volume of glue on the top endcap, and the correction for how tightly the top endcap was screwed in place following the soil packing. The effective column volume was calculated as:

$$V_{ce} = V_c - V_{groove} - V_{filter} - V_{glue} - C_t L_s \quad (3-3)$$

where:  $V_{ce}$  = effective column volume (cm<sup>3</sup>)

$V_c$  = original column volume (cm<sup>3</sup>)

$V_{groove}$  = volume of the top endcap grooves (cm<sup>3</sup>)

$V_{filter}$  = volume of the paper filter and polypropylene scrims (cm<sup>3</sup>)

$V_{glue}$  = volume of the glue (cm<sup>3</sup>)

$C_t$  = column tightening correction factor (cm<sup>2</sup>)

$L_s$  = length shy of mark (cm)

### Soil Packing

The glass column was packed by hand in small increments under about 1 cm of water. A previously determined mass of soil was gently poured into a vertically oriented column. The water was controlled by a buret connected to the column through the bottom endcap. The soil was tamped into place using a modified metal spatula (bent flat and turned 90 degrees at one end). The column was packed to a depth of about 5 cm, reaching the top end, just at the base of the upper column

threads. The soil was carefully leveled and the top endcap was screwed into place. If the top endcap alignment mark was offset from the mark on the glass column, the distance was measured as the length shy of mark ( $L_s$ ). The effective column volume was calculated according to equation 3-3.

Occasionally, several attempts at sealing the top endcap needed to be made before the top endcap was successfully screwed into the column and the o-ring was seated properly. After the initial attempt, soil often had to be added or removed from the column before a tight o-ring seal was obtained and the endcap could be tightened in a vise. Any soil removed from the column was oven dried overnight and combined with the leftover soil. The mass of soil in the column,  $M_s$ , was simply the original mass of soil minus any leftover soil.

The mass of soil packed into the column was used in determining the bulk density,  $\rho_b$ , the pore volume,  $V_p$ , and porosity,  $n$ , of the soil pack:

$$\rho_b = \frac{M_s}{V_{ce}} \quad (3-4)$$

$$V_p = V_{ce} - \frac{M_s}{\rho_s} \quad (3-5)$$

$$n = 1 - \frac{M_s}{\rho_s V_{ce}} \quad (3-6)$$

where:  $M_s$  = mass of soil in the column (g)

$\rho_s$  = particle density of the soil (g/cm<sup>3</sup>)

Upon completion of packing, the column was reconnected to the buret tubing to test the top endcap's o-ring seal for water leakage. O-ring leakage was tested by closing the top endcap valve, opening the lower endcap valve and buret valve, and raising the input buret height, thus increasing the pressure on the o-ring seal. It was usually immediately apparent if the seal leaked, requiring the endcap to be refitted. A good o-ring seal was obvious, with the black o-ring appearing flat

against the glass column wall. Only rarely did the seal leak when the top endcap was tightened down using a bench vise. On the other hand, when the top endcap was hand tightened, o-ring seal leakage was more common.

After the column had been tested for leakage, silicon sealant was placed on the outside of the glass column, between it and top endcap. This prevented any change in column mass due to evaporation of any water trapped in the threads between the glass column and top endcap.

### **De-airing**

The column was flooded with 20 to 30 pore volumes of de-aired water in order to remove any gas bubbles trapped in the porous matrix or plumbing. Entrapped gas dissolved into the de-aired water and was carried out of the column. After every 100 ml of water added, the column was disassembled from its plumbing and weighed. The column gained mass as entrapped air was removed from the column and replaced by water. The column mass eventually stabilized as all entrapped air was removed. Three consecutive unchanging measurements of column mass were used to indicate the complete removal of entrapped air. The de-airing of the soil column took anywhere from 5 to 10 days for a sandy soil, and up to 3 weeks for a silty-clay soil. The mass of the column at this point was called the initial column mass ( $M_1$ ). The water-saturated column could now be used for capillary pressure-saturation tests (see Appendix A), the saturated zone experiment, or the vadose zone experiment.

### **SATURATED ZONE EXPERIMENTS**

Saturated zone residual organic liquid saturation was determined by introducing organic liquid into a water saturated soil column (organic liquid flood),

then displacing the organic liquid by water (waterflooding). These experiments simulated conditions beneath the water table.

### Step 1: Organic Liquid Flooding

Once the column had been packed with soil and any entrapped air removed, organic liquid was flooded into the column simulating the movement of organic liquid into the saturated zone. To maintain a stable displacement front, the column was flooded from top to bottom for the case of an organic liquid lighter than water (Figure 3-2). If a denser than water organic liquid such as PCE was used, the

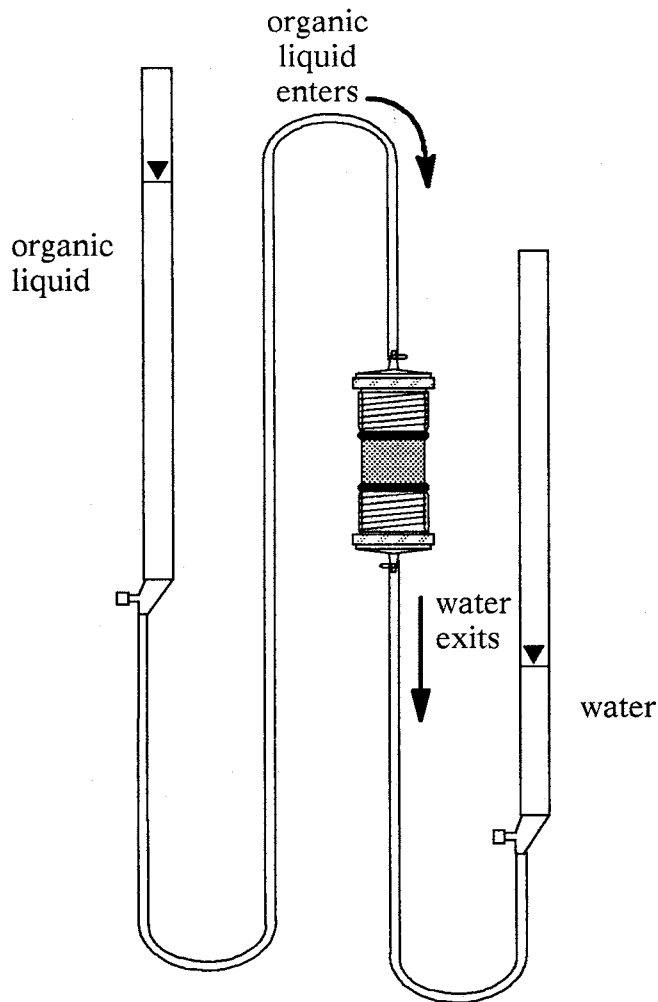


FIGURE 3-2. Step 1: Organic liquid flood into a water saturated column.



column was inverted and flooded from below with organic liquid. The organic liquid was injected under sufficient head to reduce the water saturation to the so-called irreducible water saturation, but the head was kept low enough to prevent organic liquid from breaking through the nylon filter on the bottom endcap.

The burets with organic liquids using a siphoning procedure to reduce aeration of the fluids. To avoid contact with hazardous vapors, p-xylene, tetrachloroethylene, n-decane, and gasoline were siphoned into burets with a vacuum suction under a fume hood. The openings at the top of the burets were sealed to each other by a stopper and tubing arrangement (not shown in Figure 3-2) to close the system and limit emission of fumes.

Organic liquid flooding was continued for at least 24 hours or until the column weight stabilized, indicating that the fluid saturations had reached equilibrium. A stabilization of fluid levels in both the inflow and outflow burets also indicated that the system had reached equilibrium and fluid saturations had stabilized. Fluid production at the bottom endcap was observed to ensure that only water was produced (verifying that the nylon filter had maintained its integrity and no organic liquid had breached the filter). After stabilization, the column was detached from the burets and the column mass,  $M_2$ , was measured (using at least three independent weighings on a Mettler PE 1600 balance with 0.01 g accuracy). The fluid saturations were determined employing the density difference between the organic liquid and water:

$$S_o = \frac{M_1 - M_2}{\Delta \rho V_p} \quad (3-7)$$

$$S_{wr} = 1 - S_o \quad (3-8)$$

where:  $S_o$  = Organic liquid saturation (-)  
 $\Delta\rho$  = Density difference between water,  $\rho_w$ , and organic liquid,  $\rho_o$ , (g/cm<sup>3</sup>)  
 $S_{wr}$  = Residual water saturation (irreducible water saturation,  $S_{wi}$ ) (-)

If an organic liquid heavier than water was used, the formula for organic liquid saturation became:

$$S_o = \frac{M_2 - M_1}{\Delta\rho V_p} \quad (3-9)$$

Modifications to the procedure were made in an attempt to introduce organic liquid (Soltrol) into the Palouse loam soil. Because the soil was fine-grained, compressed air was used to increase the pressure behind the Soltrol and force it into the water-saturated soil column. A tubing line was connected to an air compressor and split with a tee. One split line went to a mercury manometer board to record the pressure and the other line was connected to the buret containing Soltrol, through a stopper inserted on top of the buret. In this manner, a capillary pressure of about 500 cm of water was induced on the Palouse loam.

### **Step 2: Waterflooding**

Following the organic liquid flood, the column was slowly flooded with water at a rate of about 0.3 ml/min to displace the organic liquid. This displacement was intended to simulate the action of ambient groundwater displacing the organic liquid and leaving behind trapped organic liquid at residual saturation. As shown in Figure 3-3, the column was flooded from bottom to top to promote a stable displacement of the less dense organic liquid. When an organic liquid denser than water was used, the column was flooded from above, displacing the denser fluid out the bottom. A syringe pump, or a carefully controlled and monitored buret flow was used to push the water through the column at a low velocity to make sure the displacement proceeded under low Bond number and low capillary number

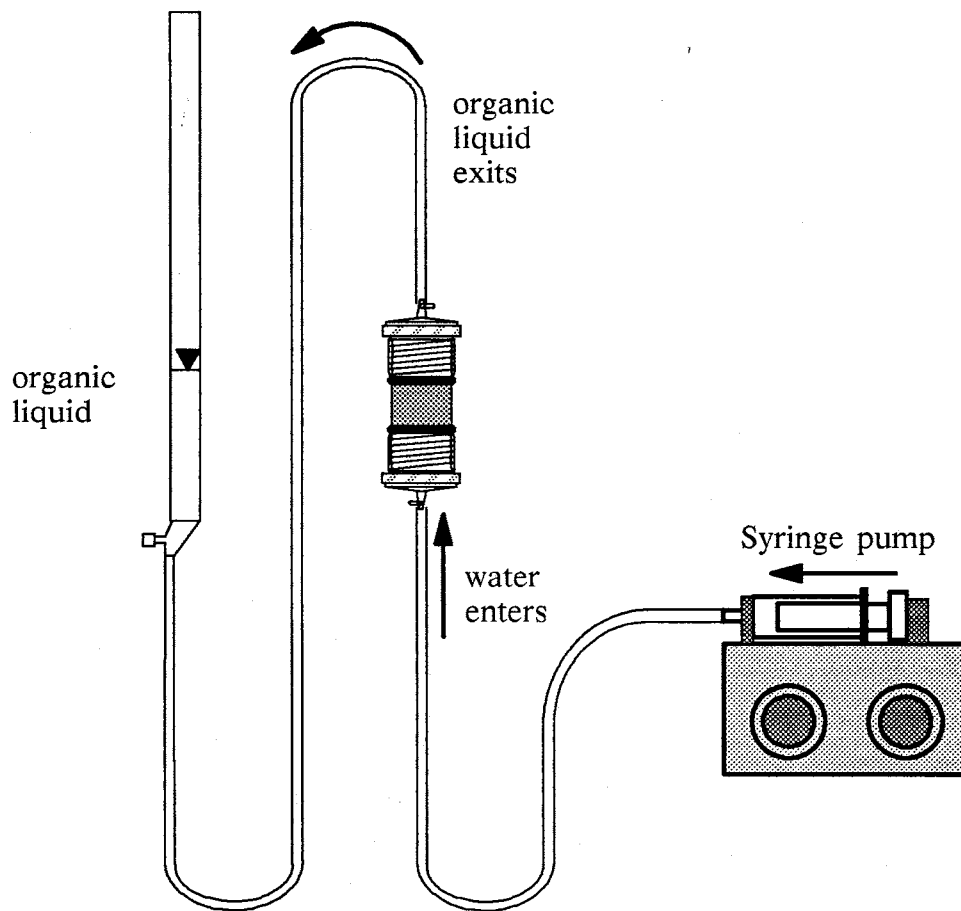


FIGURE 3-3. Step 2: Waterflooding at low velocity to reduce the organic liquid to its residual saturation.

condition. The waterflood continued until no additional organic liquid was produced (as indicated visually through the transparent tubing and by an unchanging column mass). Introduction of about six pore volumes of water through the column was found to be sufficient to reach residual organic liquid saturation. At the conclusion of the waterflood, the column was weighed, the mass ( $M_3$ ) was recorded, and the residual organic liquid saturation was determined:

$$S_{or} = \frac{M_1 - M_3}{\Delta Q V_p} \quad (3-10)$$

$$S_w = 1 - S_{or} \quad (3-11)$$

where:  $S_{or}$  = Residual oil saturation (-)  
 $S_w$  = Final water saturation (-)

When an organic liquid more dense than water was used the formula became:

$$S_{or} = \frac{M_3 - M_1}{\Delta \rho V_p} \quad (3-12)$$

## VADOSE ZONE EXPERIMENTS

The vadose zone experiments were designed to represent organic liquid trapping above the water table where air, water, and organic liquid are simultaneously present. The simulated residual water and organic liquid saturations were obtained under equilibrium conditions, at an equivalent height above the water table. To achieve the aforementioned saturations, water was drained from an initially water saturated, de-aired soil column under an applied suction. Then organic liquid was introduced into the top of the column. Finally, the organic liquid was drained from the column under the same applied suction.

### Step 1: Water Drainage

Beginning with a de-aired, entirely water saturated column of known mass ( $M_1$ ), a suction was placed on the column, draining water through the nylon filter and out the bottom endcap (see Figure 3-4). Air entered through the top endcap, replacing the drained water in the soil's pore space. The water-wet nylon filter allowed water, but not air to pass through the bottom of the column. The suction was applied by lowering the water level in the buret beneath the column in the same fashion as when determining water/air capillary pressure-saturation functions. Figure 3-4 shows the configuration used for applying a suction  $\Delta h$  to the column. The elevation difference  $\Delta h$  was measured from the middle of the soil

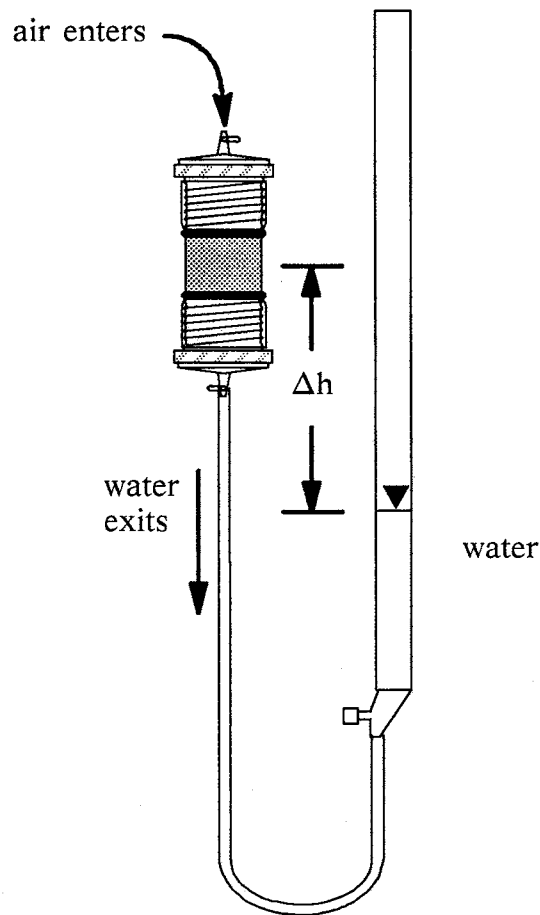


FIGURE 3-4. Step 1: Water being drained with air under an applied suction.

column to the water level in the buret in centimeters of water. Equilibrium was reached when the water level in the buret stabilized and the column weight no longer changed.

Upon reaching equilibrium, the column was weighed and the mass ( $M_4$ ) was recorded. Air saturation was a function of the suction applied and was measured at a particular equilibrium suction as :

$$S_{a,initial} = \frac{M_1 - M_4}{\rho_w V_p} \quad (3-13)$$

$$S_{w,initial} = 1 - S_{a,initial} \quad (3-14)$$

where:

$S_{a,initial}$  = air saturation following water drainage (-)

$S_{w,initial}$  = water saturation following water drainage (-)

The density of water,  $\rho_w$ , was used in the denominator of equation (3-13) instead of the density difference between fluids as in previous equations, because the density of the air was considered to be negligible.

The saturations found by this method were the fluid saturations for the soil under equilibrium conditions  $\Delta h$  centimeters above the water table. The effective column length was kept short (5 cm) to keep fluid saturations relatively constant within the column.

## **Step 2: Organic Liquid Flooding**

Once the water had been drained from the column, organic liquid was introduced to simulate the effect of organic liquid percolating through the vadose zone. Before proceeding with the organic liquid flood, the bottom endcap with the water-wet filter was removed from the column, and replaced with an identical endcap with an organic-wet TFE filter or organic-wet ceramic disk in place of the nylon filter. The TFE filter or ceramic disk was used as a vehicle through which to introduce the organic liquid into the column. In a later step it was used to pull organic liquid from the column under suction. To change endcaps, the column was inverted and the bottom endcap was unscrewed from the soil column. Any soil grains clinging to the paper filter on the bottom endcap were gently brushed back into the column. The replacement endcap with a TFE or ceramic filter was screwed down tightly in place to ensure good contact with the soil. Prior to installation, the TFE or ceramic filter was tested for integrity (Appendix B) and the end reservoir behind the filter was saturated with organic liquid. The column was then reweighed

( $M_5$ ) to account for any difference in the mass of the endcaps. Switching endcaps appeared to cause little disruption of the soil packing.

The column was once again attached to the burets (see Figure 3-5). Organic liquid was introduced through the organic-wet bottom endcap. Because water is more dense and air is less dense than the organic liquid used in the experiments, the column was turned horizontally to inhibit density instabilities that may occur in a vertical displacement. Organic liquid was pushed through the column under low capillary number conditions until no more water or air was produced (verified by a stable column mass,  $M_6$ ). This step usually required about 300 ml of organic

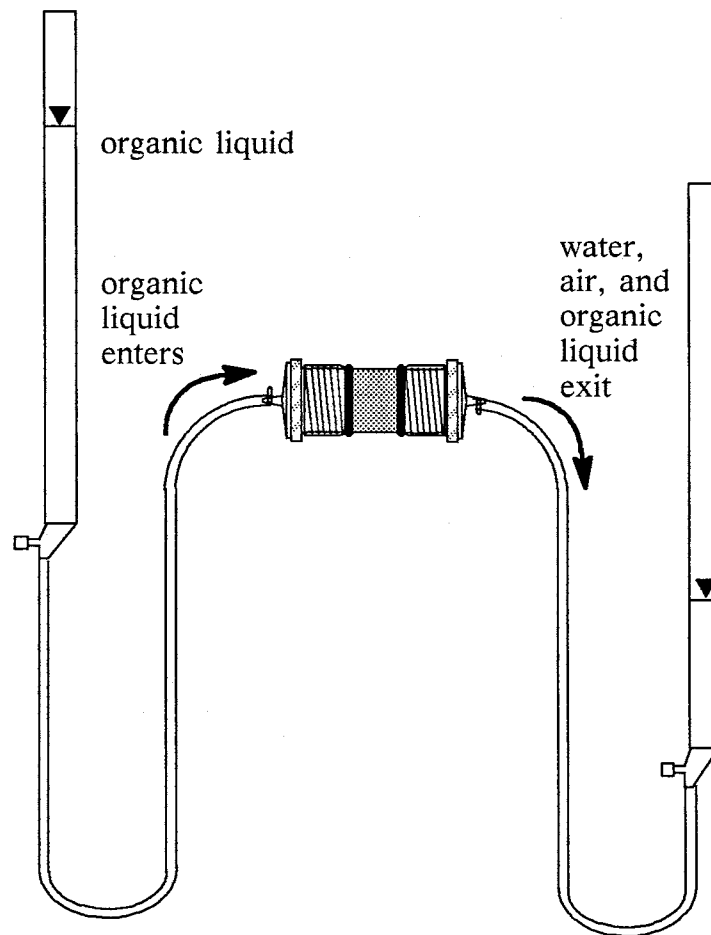


FIGURE 3-5. Step 2: Organic liquid flood in a column already drained by air.

liquid to be pushed through the soil column before the mass stabilized, and took 2 to 3 days to complete.

Once the fluid saturations had equilibrated, the volume of water produced from the soil pack was measured. The volume of water produced was measured by collecting the outflow (water and organic liquid) in a TFE flask and withdrawing the water from the bottom of the flask with a syringe. The water, as well as a small amount of organic liquid pulled into the syringe, was then injected into a graduated cylinder to determine the volume of the water produced ( $V_{wp}$ ). The new water saturation was calculated as:

$$S_w = S_{w,initial} - \frac{V_{wp}}{V_p} \quad (3-15)$$

With the water saturation known, the organic liquid saturation ( $S_o$ ) and the air saturation ( $S_a$ ) could be found using mass measurements of the column before ( $M_5$ ) and after ( $M_6$ ) the organic liquid flood:

$$S_o = \frac{M_6 - M_5 - \rho_w V_{wp}}{\rho_o V_p} \quad (3-16)$$

$$S_a = 1 - S_w - S_o \quad (3-17)$$

### Step 3: Organic Liquid Drainage

In the final step of this process, organic liquid was drained from the column under an applied suction. The organic liquid saturation was reduced to an equilibrium saturation for a given height above the water table. For sufficiently large suctions, this represents the residual organic liquid saturation in the vadose zone. Figure 3-6 shows the set-up for organic liquid drainage. It was very similar to the set-up used earlier in step 1, for draining water from the soil column (Figure 3-4). The drainage was a stable displacement, in which air entered from the top



displacing organic liquid downward through the lower organic-wet filter. The organic-wet filter allowed only organic liquid to drain through the lower endcap. The water saturation remained the same as at the end of the organic liquid flood. The elevation difference,  $\Delta h$ , for this step was equal to the  $\Delta h$  used in the previous water drainage step. For instance, if the suction used in the water drainage step was 70 cm of water, in the organic liquid drainage step the applied suction was 70 cm of organic liquid. Although in each case the fluid column in the buret was dropped the same distance beneath the soil column to induce suction, the capillary pressures induced in each of these steps was not the same. The

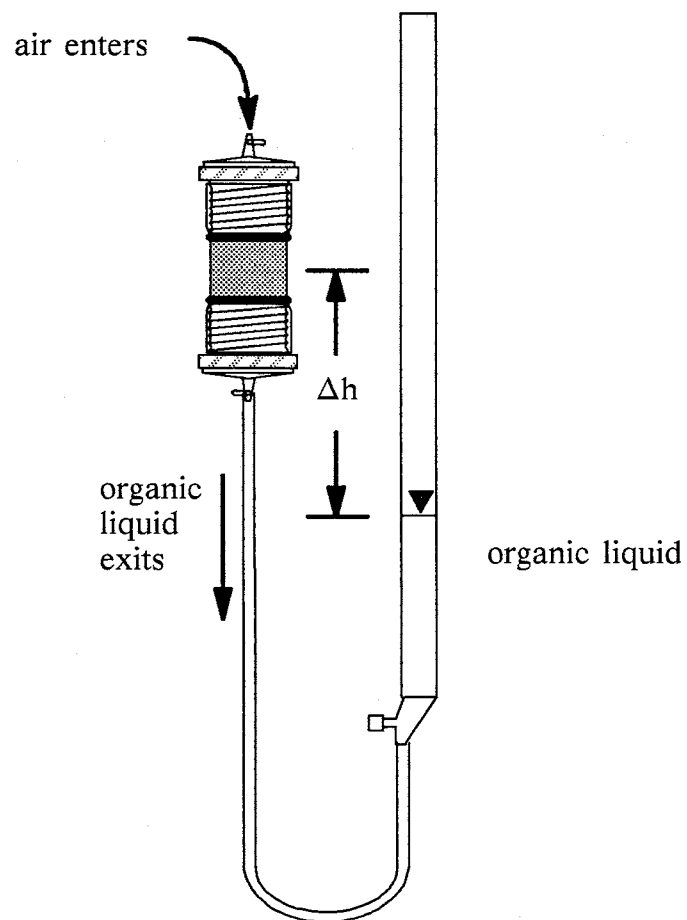


FIGURE 3-6. Step 3: Organic liquid drained by air.

difference in capillary pressures was scaled by the relative densities of the water and organic liquid phases.

The displacement proceeded until the organic liquid and air saturations equilibrated (the water saturation remained unchanged during this step). The equilibrated column was weighed ( $M_7$ ) and the final organic liquid, water and air saturations were determined:

$$S_{or} = \frac{M_7 - M_5 - \rho_w V_{wp}}{\rho_o V_p} \quad (3-18)$$

$$S_a = 1 - S_w - S_{or} \quad (3-19)$$

### POSSIBLE SOURCES OF ERROR

Several sources of experimental error were associated with performing multi-phase flow experiments to determine residual organic liquid saturations. Possible sources of error included:

- incomplete removal of entrapped gas,
- changes in fluid densities due to changes in laboratory temperature,
- lack or loss of filter integrity,
- faulty seals in the system leading to leakage or evaporative losses,
- trapping of fluids in the outflow end reservoir,
- packing variability (from one soil packing to the next), and
- error associated with the precision limits of the measuring devices.

What follows is a brief discussion of each of these sources of error.

#### Entrapped Gas

As soil was packed into a soil column, some gas was trapped in the pore space. For a water-wet system, trapped gas tends to reside in pores which would probably otherwise trap organic liquid (see for instance, Kyte et al., 1956).

Residual saturations measured in the presence of trapped gas would be expected to be lower than residuals measured under strictly two-phase conditions.

Entrapped gas presents other problems because its saturation may not remain constant over the duration of the experiment; some of it may dissolve into the liquid phases. When gravimetric measurements are used to determine fluid saturations, the loss of entrapped gas over the course of the experiment would indicate a lower residual saturation than is actually present (for an organic liquid less dense than water).

Entrapped gas was eliminated by flushing the column with several pore volumes of de-gassed water. As de-gassed water moved through the column, trapped gas dissolved into the water phase and was carried from the column prior to beginning the experiment. The column gained weight as the pore space previously occupied by gas was then occupied by water. All entrapped gas was assumed to be removed once the column weight stabilized.

#### Variable Laboratory Temperature

The worst and most persistent problem encountered during this project was the inability to control temperature variations in the laboratory. As the temperature in the laboratory fluctuated, so too did the densities of the fluids used in experiments, introducing error into gravimetric determinations of fluid saturations. In addition, the observed fluctuations in column weight were larger than could be accounted for by density effects alone. It is believed that as the temperature rose, dissolved gasses came out of solution and were trapped in the soil — this gas may have subsequently redissolved as the temperature fell. The appearance (and redissolution of) trapped gas introduced additional temperature-induced error to

that caused by changes in density alone. This problem was especially acute when liquids containing volatile components, such as gasoline, were used.

Large temperature fluctuations in the laboratory over the course of an experiment led to poor reliability of the results. Residual saturations of Soltrol plotted against temperature variation (Figure 3-7) illustrate the large range in residual saturations that were measured when temperatures were not held constant over the course of an experiment. Results of experiments conducted with small temperature variations ( $< 2^{\circ}\text{C}$ ) show much less scatter than experiments conducted under less controlled temperature conditions.

To remedy the problem of fluctuating temperatures during the experiments, a constant temperature cabinet was designed and constructed by Bill Peplinski and Steve Conrad. Experiments performed within the constant temperature box

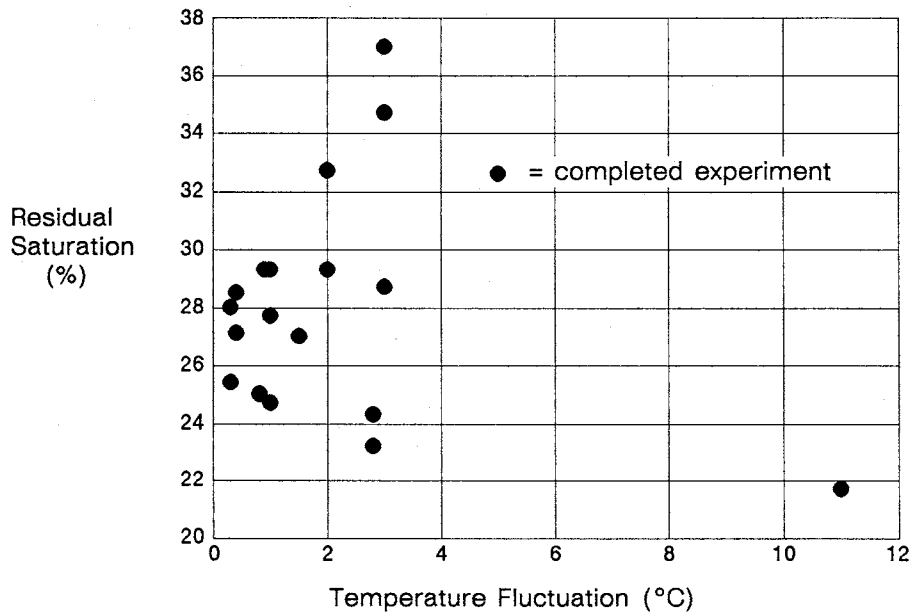


FIGURE 3-7. Temperature range and its effect on the accuracy of results.

displayed a noticeably smaller variation of residual saturations than experiments performed prior to completion of the box.

#### Filter Integrity

Filters that allowed only the wetting phase to pass through were often used to reduce capillary end effects. If filter integrity was not maintained, end effects were not eliminated and the non-wetting fluid could have become trapped in the reservoir behind the filter. In the column-flooding experiments, each filter was tested for integrity prior to use, and paper filters were glued above them to reduce abrasions from the soil which could have caused leakage. For experiments run at low flow rates, ceramic disks were sometimes used instead of filters because of their greater durability.

#### Leaking Seals and Tubing

The endcaps were sealed to the column using o-rings. Each apparatus was pressure tested for leakage prior to use. Volatilization of organic liquid through the tubing occurred when gasoline was used. To prevent introduction of air into the soil column the tubing was inspected regularly for air bubbles. Any air bubbles discovered were subsequently flooded from the tubing.

#### Outlet End Reservoir

In these experiments it was assumed that no organic liquid was trapped in the outlet end reservoir (top endcap), although this assumption was probably not entirely true. By keeping the outlet end reservoir small — less than 1% of the column pore volume — the effects of trapping within the reservoir were negligible.

#### Packing Variability

Variable soil packing from one experimental trial to the next could have lead to some variability in measured residual saturations. Determination of soil bulk

density provided a good measure of the 'tightness' of each packing, but says little about the uniformity of a hand tamped column. Perhaps a mechanical vibrational device could have been used to give more uniform packings.

### Measurement Error

Measurement error, due to the precision limits of measuring devices such as balances, were estimated and propagated through the sequence of calculations. For example, calculations of fluid saturations were dependent upon measures of fluid densities, soil particle density, total soil weight, total column volume, and measures of the column mass at several points in the progress of an experiment. All these measures have some error (or uncertainty) associated with them and these errors are routinely propagated through the calculations used to determine fluid saturations. A worst case error approach which assumed all errors were additive was used for error propagation calculations. Since some measurement errors would be expected to cancel each other out, this worst case approach was a conservative estimate of the total measurement error.

### **LIMITATIONS OF THE TECHNIQUE**

One limitation of the experimental technique was the inability to apply it to fine-grained soils, such as the Palouse loam. The non-wetting phase entry pressure of the Palouse loam was too great to overcome with this technique. A pressure equivalent to more than seven meters of free product was used in an unsuccessful attempt to inject organic liquid into the Palouse loam. Even if it had been possible to inject the organic liquid with sufficient pressure, the entry pressure of the nylon filter on the bottom endcap might have been exceeded, resulting in failure of the filter. In order to accommodate fine-grained soils, the apparatus would have to be re-designed as a high-pressure system, including a

high-pressure fluid delivery pump, a column built to withstand high pressures, and a bottom membrane with a very high non-wetting phase entry pressure.

The inability to inject an organic phase into the Palouse loam did however demonstrate that fine-grained, water-wet soils (which do not shrink in the presence of organics) can serve as an effective barrier to organic liquid movement in the subsurface.

Another limitation of the experimental technique occurred in the vadose zone experiments. Several trials of the vadose zone experiment were run using high applied suctions to measure the saturation of organics left behind a front of organics percolating through the vadose zone high above the water table. Additional vadose zone experiments were performed over a range of applied suctions to determine the saturation distribution in the transition zone between the saturated zone and the vadose zone.

Results from some of these transition zone experiments gave what appear to be unreasonably high equilibrium organic liquid saturations. The limitation of the experimental procedure was that, during the organic liquid drainage step, water was unable to re-imbibe into the soil. Under low applied suctions representing the capillary fringe and just above, re-imbibing water would have displaced organic liquid resulting in lower equilibrium organic saturations than the values measured.

The largest change in forces acting on the organic liquid occurs in the capillary fringe. Unfortunately, the experimental procedure used to measure three-phase saturations over this range was found to be inappropriate. This low suction range is important particularly for organic liquids lighter than water because it is the zone in which organic liquids spread, forming a lens on the water table.

## CHAPTER 4

### CHARACTERIZING EXPERIMENTAL FLUIDS AND SOILS

In this chapter, results of characterization experiments performed to determine properties of the fluids and soils used in the experiments are presented. The chapter, therefore is divided into two main parts — fluids, and soils. Within each part, the methods used for characterization will be described, followed by the characterization results themselves.

#### FLUID CHARACTERIZATION

Measurements of fluid properties such as viscosity, specific gravity, surface tension, and interfacial tension were performed following procedures outlined by the American Society for Testing and Materials (ASTM, 1986). Viscosity was measured with Cannon-Fenske routine viscometers according to ASTM methods D445-83 and D446-85a. Specific gravity measurements were made as described by ASTM method D1429-76 (pycnometer procedure). Adaptations of ASTM procedures D 1590-60 and D 971-82 were used to determine surface tension and aqueous-organic interfacial tensions, respectively, with a Fisher Manual Model 20 tensiometer.

#### Measured fluid properties

A 3000 ppm  $\text{CaCl}_2$  solution was used as the aqueous phase in all column experiments. Distilled, de-ionized water was de-gassed by boiling. Calcium chloride dihydrate was added to the cooled water to bring the concentration to 3000 ppm as described in Appendix C. The solution was stored under a vacuum to keep it de-gassed. The properties of this aqueous phase are given in Table 4-1. The interfacial tensions of all the organic liquids were measured against this fluid.



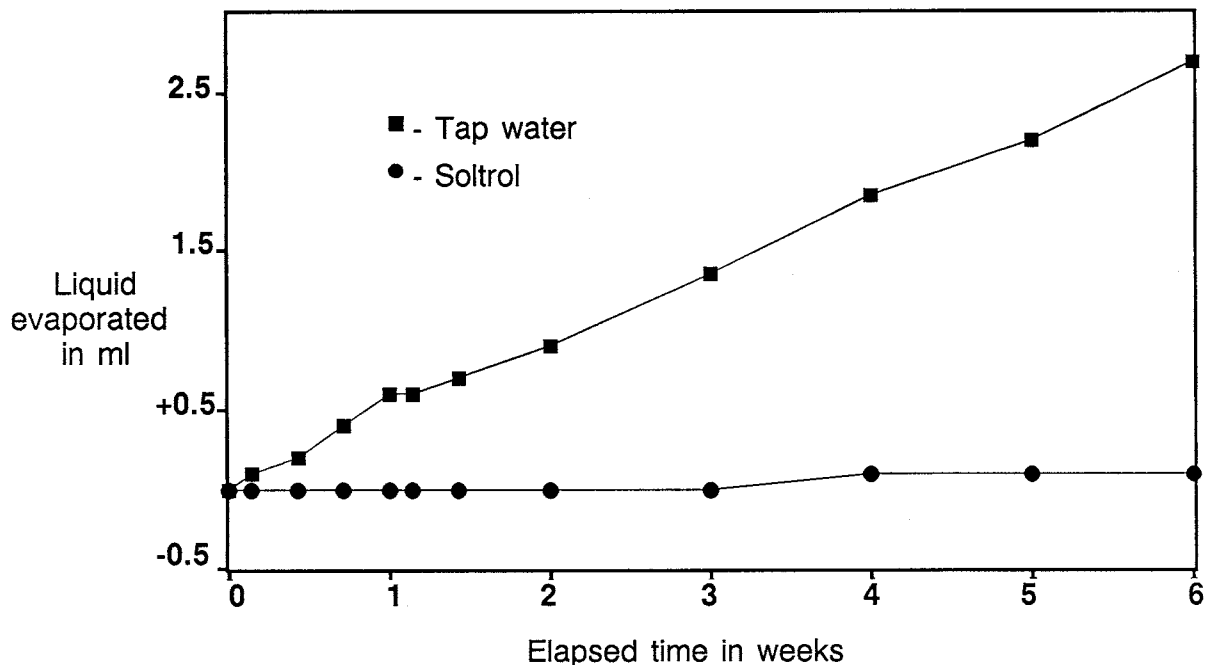


FIGURE 4-1. Qualitative comparison of Soltrol and water volatility.

Soltrol-130, a mixture of  $C_{10}$  to  $C_{13}$  isoparaffins, was the fluid most commonly used as the organic phase in the experiments. It is a colorless, combustible liquid having a mild odor and negligible solubility in water. A simple experiment was conducted to determine the relative volatility of Soltrol to water. Equal amounts of Soltrol and water were placed side by side in identical graduated cylinders and periodically checked visually for liquid loss caused by evaporation. A plot of the results (Figure 4-1) demonstrates the much lower volatility of Soltrol. Other properties of Soltrol as measured in the laboratory are given Table 4-1.

The measured properties of all other liquids used in the laboratory experiments are also shown in Table 4-1.

## SOIL CHARACTERIZATION

Quantitative descriptions of the soils were made, including particle density, particle size analysis, capillary pressure-saturation curves, and wettability. Soil

liquid	specific gravity	density (g/cm <sup>3</sup> )	kinematic viscosity (cst)	dynamic viscosity (cp)	interfacial tension with 0.3% CaCl <sub>2</sub> solution (dynes/cm)	surface tension (dynes/cm)
aqueous phase	1.003±0.002	1.000±0.002	0.98±0.01	0.98 ± 0.01	not applicable	72.0 ± 0.4
Soltrol-130	0.755 ± 0.002	0.753 ± 0.002	1.93 + 0.01	1.45 ± 0.01	47.8 ± 1.2	19.1 ± 0.3
kerosene	0.809 ± 0.002	0.807 ± 0.002	2.15 ± 0.01	1.73 ± 0.01	38.6 ± 1.2	26.8 ± 0.4
gasoline	0.733 ± 0.005	0.731 ± 0.005	0.66 ± 0.01	0.48 ± 0.01	22.9 ± 0.3	20.5 ± 0.3
n-decane	0.729 ± 0.002 <sup>21</sup>	0.727 ± 0.002 <sup>21</sup>	1.25±0.01	0.91 ± 0.01	44.5 ± 1.0	24.9 ± 0.3
benzene	0.877 <sup>20</sup> †	0.877 <sup>20</sup> †	0.745 <sup>20</sup> †	0.652 <sup>20</sup> †	not determined	28.9 <sup>20</sup> †
toluene	0.864±0.002	0.861±0.002	0.685 <sup>20</sup> †	0.590 <sup>20</sup> †	not determined	28.5 ± 0.5
p-xylene	0.858 ± 0.005	0.855 ± 0.005	0.70 ± 0.01	0.60 ± 0.01	35.8 ± 0.8	28.4 <sup>20</sup> †
PCE	1.609 ± 0.005	1.614 ± 0.005	0.54 ± 0.01	0.87 ± 0.01	41.8 ± 0.7	31.7 <sup>20</sup> †
carbon tetrachloride	1.602±0.002	1.599 ± 0.002	0.66 ± 0.01 <sup>21</sup>	1.05 ± 0.01 <sup>21</sup>	32.9 ± 0.8 <sup>21</sup>	28.2 ± 0.3 <sup>21</sup>

† Weast, 1986

TABLE 4-1. Measured properties of fluids used in experiments. All measurements were taken at temperatures between 22°C and 24°C except where noted.

particle densities were determined using ASTM D584-83. Soil particle size distributions were measured using ASTM D422, and the saturated hydraulic conductivities were measured by ASTM D2434. Porosities and bulk densities of the soils were measured at the time of column packing and the methods used are described within the methods section for each experiment. Soil capillary pressure-saturation relationships were determined using the equilibrium method (Vomocil, 1965) described in Appendix A. Wettabilities of the soils to water and

the organic liquid were by the Amott method (Amott, 1959) and the USBM method (Donaldson, 1969).

### Wettability Measurements

Wettability, as mentioned earlier, refers to the relative affinity of the soil for the various fluids — water, air, and the organic phase. Contact angle measurements, because of their relative ease, are often used to determine the wettability of a liquid to a soil. Several common methods for measuring contact angles are summarized by Adamson (1982); often a contact angle cell is used in petroleum engineering studies where the contact angle test is performed under brine (Craig, 1971). A drop of reservoir oil is placed between two polished crystals that are representative of the reservoir rock (usually quartz or calcite) and contact angles are measured. Because of uncertainties associated with contact angle measurements due to their inability to account for surface roughness, heterogeneity, and pore geometry, they were not used in this study. Instead, to measure the bulk wettability of the soils, adaptations of two methods commonly practiced on rock cores in petroleum engineering were employed: the Amott test and the USBM method. Both methods rely upon characteristics of organic-water capillary pressure-saturation curves to determine the wettability of the porous media.

The Amott (1959) test measures the wettability of soil as a function of the displacement properties of the soil-water-oil system. The technique is similar to that required to determine capillary pressure-saturation relationships for two fluid phases. Four displacement operations are performed on the soil, and the ratio of spontaneous imbibition to forced displacement is determined for both the water and organic phases. The four displacements are:

- 1) spontaneous displacement of organic liquid saturated soil column by water.
- 2) forced displacement of organic liquid saturated soil column by water.
- 3) spontaneous displacement of water saturated soil column by organic liquid.
- 4) forced displacement of water saturated soil column by organic liquid.

This test is based on the assumption the wetting fluid will spontaneously imbibe into the core, displacing the non-wetting phase. When the displacement-by-water ratio ( $\delta_w$ ) approaches one and the displacement-by-oil ratio ( $\delta_o$ ) is zero, the core is water-wet. If the opposite is true, the core would be oil-wet. The main problem with the Amott test is its insensitivity at near neutral wettability (Anderson, 1986b).

The USBM test compares the areas under two fluid phase capillary pressure-saturation curves as a measure of average wettability (Donaldson et al., 1969). When a soil is water-wet, the area under the organic-displacing-water capillary pressure curve ( $A_1$ ) is larger than the water-displacing-organic curve ( $A_2$ ). In fact, for a strongly water-wet system, most of the water will spontaneously imbibe into the soil, and the area under the water-displacing-organic curve will be very small. Since the work of fluid displacement is proportional to the areas under the capillary pressure curve (Morrow, 1970), the USBM wettability index in essence measures the ratio of work needed for organic phase to displace water, to the work needed for the opposite displacement. The USBM wettability index,  $W$ , is given as:

$$W = \log \frac{A_1}{A_2} \quad (4-1)$$

Table 4-2 shows the wettability criteria for each of the three quantitative methods.

	WETTABILITY		
	<u>water-wet</u>	<u>intermediate-wet</u>	<u>organic-wet</u>
<b>contact angle</b>			
minimum	0°	60° to 75°	105° to 120°
maximum	60° to 75°	105° to 120°	180°
<b>Amott test</b>			
displacement-by-water ratio ( $\delta_w$ )	positive	zero	zero
displacement-by-oil ratio ( $\delta_o$ )	zero	zero	positive
<b>USBM wettability index, <math>W</math></b>	near 1	near 0	near -1

TABLE 4-2. Relationship between wettability measurement methods (after Anderson, 1986b).

#### Sevilleta Soil

The Sevilleta sand was used in the majority of the experiments and hence, was the most extensively characterized soil. It is obtained locally and has been well studied by researchers at New Mexico Tech. An SEM photomicrograph of a sample of the sand is shown in Figure 4-2. The grains are sub-angular to sub-rounded. The SEM picture shows a particularly angular grain. A mineral characterization of the sand by William Peplinski indicates that it is composed mostly of quartz grains ( $72 \pm 5$  % by number), with lesser amounts of feldspar ( $11 \pm 2\%$ ) and lithic fragments ( $16 \pm 3\%$ ) (see also Wilson et al., 1989). The lithics, generally much smaller in size than the other mineral grains, composed about 5% of the sand by volume. An organic carbon analysis conducted at North Carolina State University (courtesy of Dr. Cass Miller) yielded an organic carbon content of 0.02%, a negligible amount. Karickhoff et al. (1979) state that an organic carbon content of at least 0.1% is needed before nonpolar hydrocarbon adsorption becomes important. Therefore, chemical adsorption, often an important mechanism for immobilizing organics, is not considered significant in this study.



FIGURE 4-2. SEM photomicrograph of Sevilleta sand  
(From Wilson et al., 1989)

The particle density of this sand was determined to be  $2.65 \pm 0.02$  g/cm from five replicate measurements. Six sieve tests were conducted to measure the particle size distribution of the Sevilleta soil. There was excellent agreement between tests with all curves falling essentially on top of one another. The results of one test are presented in Figure 4-3. The particle size distribution classifies the soil as a uniform medium grained sand, with a median particle diameter of about 0.3 mm (300 microns) and a uniformity coefficient ( $d_{60}/d_{10}$ ) of less than 2.

Eleven replicate measurements of water-saturated hydraulic conductivity ( $K_w$ ) and intrinsic permeability ( $k$ ) were conducted in a constant head permeameter with the following results:

$$K_w = (1.03 \pm 0.20) \times 10^{-2} \text{ cm/sec}$$
$$k = 1.03 \times 10^{-7} \text{ cm}^2 = 104 \text{ darcys}$$

The intrinsic permeability was calculated from saturated hydraulic conductivity by:

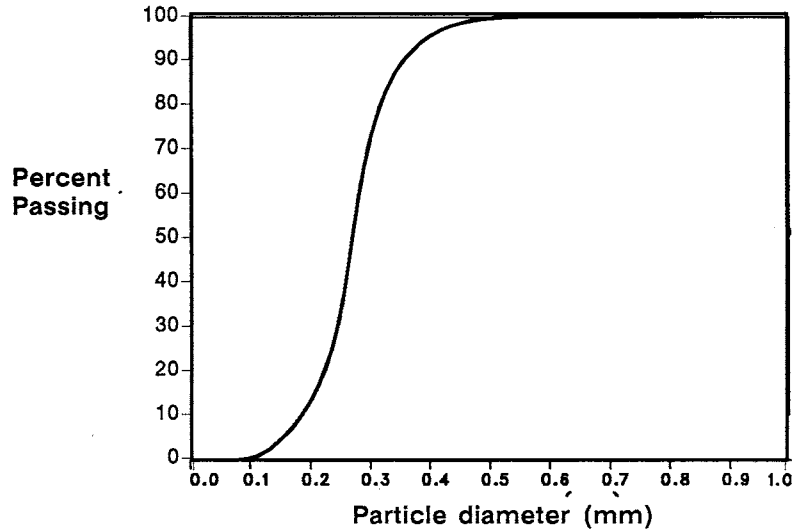


FIGURE 4-3. Particle size analysis of Sevilleta sand.

$$k = \frac{K_w \mu_w}{Q_w g} \quad (4-2)$$

where:  $\mu_w$  = dynamic viscosity of water (0.98 cp)

$Q_w$  = density of water (0.997 g/cm<sup>3</sup>)

$g$  = gravitational constant (981 cm/sec<sup>2</sup>)

Capillary pressure-saturation curves for all fluid pair combinations (air-water, air-organic, and organic-water) were constructed with the Sevilleta soil. Soltrol-130 was used as the organic liquid phase in all trials. The soil capillary pressure-saturation plots from data acquired during 12 experimental trials include:

- **seven organic-water capillary pressure curves**, of which two curves have drainage, imbibition, and secondary drainage cycles, three curves have drainage and imbibition cycles, and two curves have the main drainage branch only;
- **two air-organic capillary pressure curves**, one curve with drainage, imbibition, and secondary drainage cycles, and one curve of the main drainage branch only; and,
- **three air-water capillary pressure curves**, of which two curves have the main drainage and imbibition cycles, and the third curve has the main drainage branch only.

For the air-organic trials, the soil column was packed under organic liquid. Examples of two of these 12 capillary pressure-saturation curves are shown in Figure 4-4. The remaining curves are presented in Appendix G. Data from the saturation-capillary pressure curves are used later in Chapter 6 to evaluate a two-phase scaling technique proposed by Lenhard and Parker (1987c).

Organic liquid-water capillary pressure-saturation curves were also used to determine the wettability of the Sevilleta soil. A typical Soltrol-water capillary pressure-saturation plot (shown in Figure 4-5) was used in conjunction with the Amott and USBM methods to determine the wettability of the Sevilleta soil. The four displacement operations performed in the Amott test were:

- 1) spontaneous displacement of organic liquid by water (corresponding to a capillary pressure of zero on curve 2); point A;
- 2) forced displacement of organic liquid by water (corresponding to the residual organic liquid saturation); point B;
- 3) spontaneous displacement of water by organic liquid (corresponding to a capillary pressure of zero on curve 3); point C; and,
- 4) forced displacement of water by organic liquid (corresponding to irreducible water saturation or residual wetting phase saturation); point D.

Preferentially water-wet soils have displacement ratios,  $\delta_w = (S_{wA} - S_{wD}) / (S_{wB} - S_{wD})$ , approaching 1.0 and displacement-by-organic ratios,  $\delta_o = (S_{wB} - S_{wC}) / (S_{wB} - S_{wD})$ , of zero. Organic liquid-wet soils give reverse results. The Sevilleta soil is strongly water-wet, not only to Soltrol, for which  $\delta_w = 0.98$  and  $\delta_o = 0.0$ , but also presumably for the other organic liquids as well.

The USBM test compares the areas under capillary pressure curves as a measure of wettability. When a soil is water-wet, the area under the organic-displacing-water capillary pressure curve (shaded) is larger than the area under the water-displacing-organic curve (black). In a strongly water-wet system,



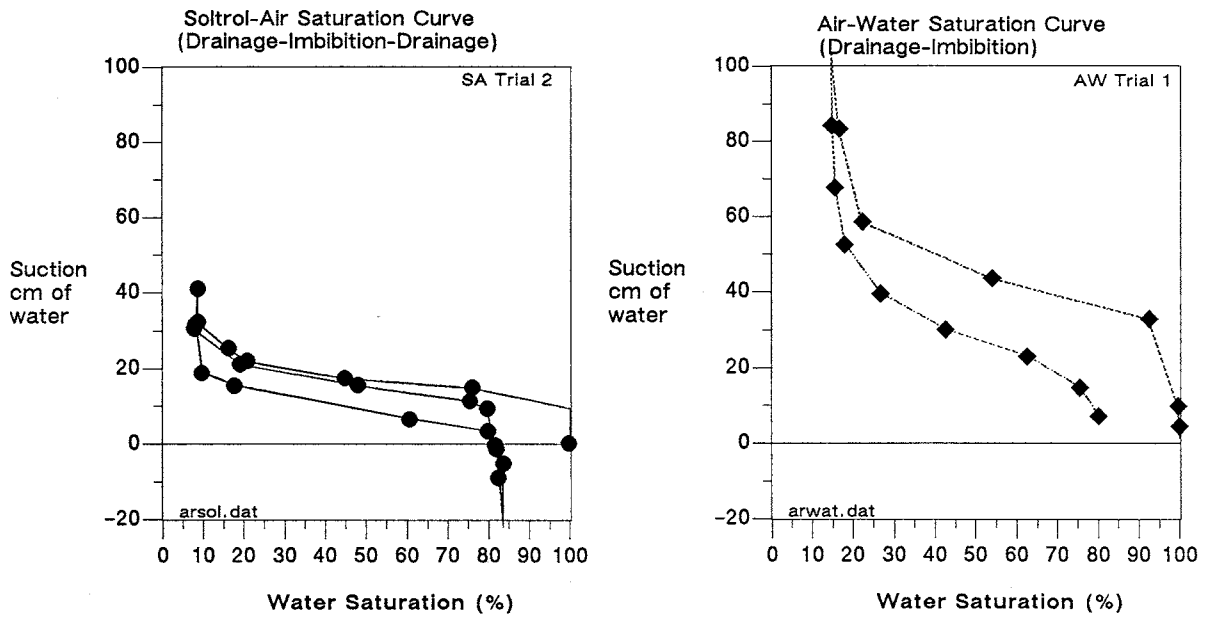


FIGURE 4-4. Typical Sevilleta sand capillary pressure-saturation curves.

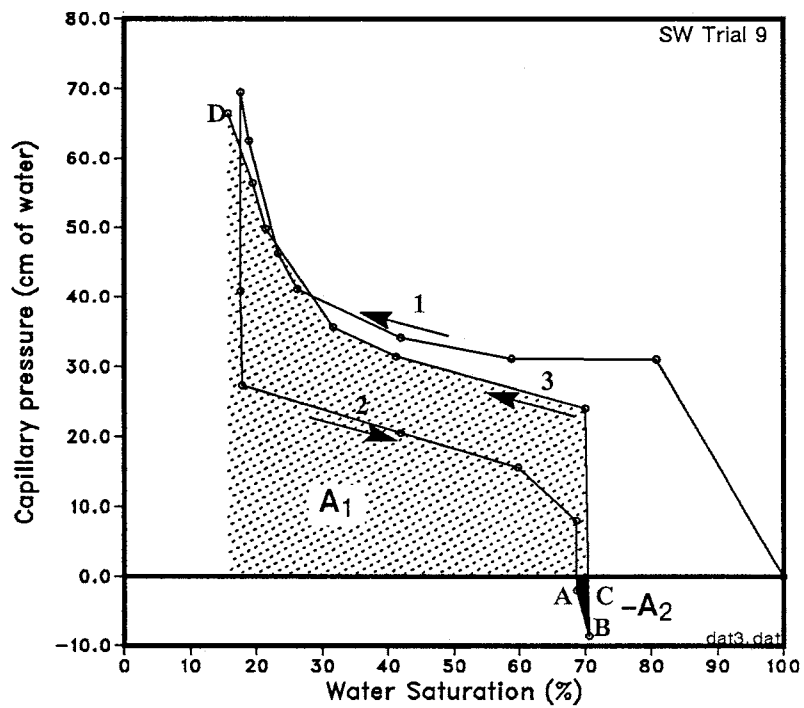


FIGURE 4-5. A typical organic liquid-water capillary pressure-saturation curve used to determine wettability, in this case for Soltrol-130 in Sevilleta sand.

most of the water spontaneously imbibes into the soil, and the area under the water-displacing-organic curve is very small - as is the case for Soltrol in the Sevilleta soil as shown in Figure 4-4.

#### Palouse Loam

The Palouse loam soil, an agricultural soil from eastern Washington, was selected as an alternate soil for use in the saturated zone experiments. The Palouse soil provided a good contrast to the Sevilleta soil because of its much finer texture (15% sand, 80% silt, 5% clay) and its higher organic carbon content, 1.5% (Bowman, 1981). The water-saturated hydraulic conductivity of the soil was measured to be  $5 \times 10^{-6}$  cm/s using a falling head test (Olson and Daniel, 1981), and the particle density was measured to be  $2.67 \pm 0.02$  g/cm<sup>3</sup>.

The fine-grained nature of the soil made it extremely difficult to supply enough pressure to inject a non-wetting phase. Despite the inability to run capillary pressure curves for the Palouse loam, it can be surmised from the high non-wetting phase entry pressures that the soil is strongly water wet, and could serve as an effective barrier to movement of an organic phase.

#### Traverse City Soil

The Traverse City soil sample is from a Superfund fuel spill site at a U. S. Coast Guard Air Station in Traverse City, Michigan. It was collected at a depth of about 120 inches below the surface, in the unsaturated zone, about 4 inches above the water table. The soil is a clean, beach sand, composed primarily of sub-rounded to rounded quartz grains, with some dolomite and igneous and metamorphic particles (Twenter, 1985). It has a particle density of  $2.65 \pm 0.01$  g/cm<sup>3</sup> and a saturated hydraulic conductivity of  $1.0 \times 10^{-2}$  cm/s. An organic

carbon analysis conducted on soil samples from a nearby well indicated the soil had an organic carbon content of about 0.01% (Twenter, 1985).

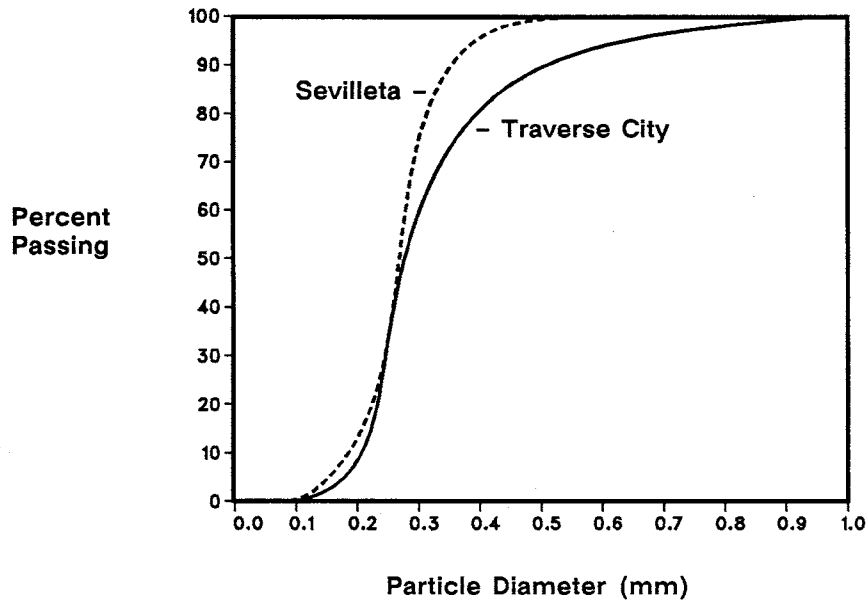


Figure 4-6. Particle size analysis of Traverse City Soil compared to Sevilleta Soil.

The results of Traverse City and Sevilleta soil sieve analyses are plotted in Figure 4-6. From the plot it is apparent the Traverse City Soil is slightly coarser grained and more graded than the Sevilleta Sand. The Traverse City soil can be classified as a medium grained soil with a uniformity coefficient ( $d_{60}/d_{10}$ ) less than 2. The short tail on both curves indicates that the soils contain a very small percentage of fine sized particles.

## CHAPTER 5

### SATURATED ZONE RESULTS AND DISCUSSION

Figure 5-1 depicts the portion of the aquifer that includes residual saturation in the saturated zone. For an organic liquid more dense than water (left below), the slug of organic leaves behind a zone of capillary trapped residual as it makes its way downward toward the bottom barrier, and then laterally along that barrier. Within and below the capillary fringe the trapped organic shares the pore space only with water. In this saturated zone there is no air phase. This so-called

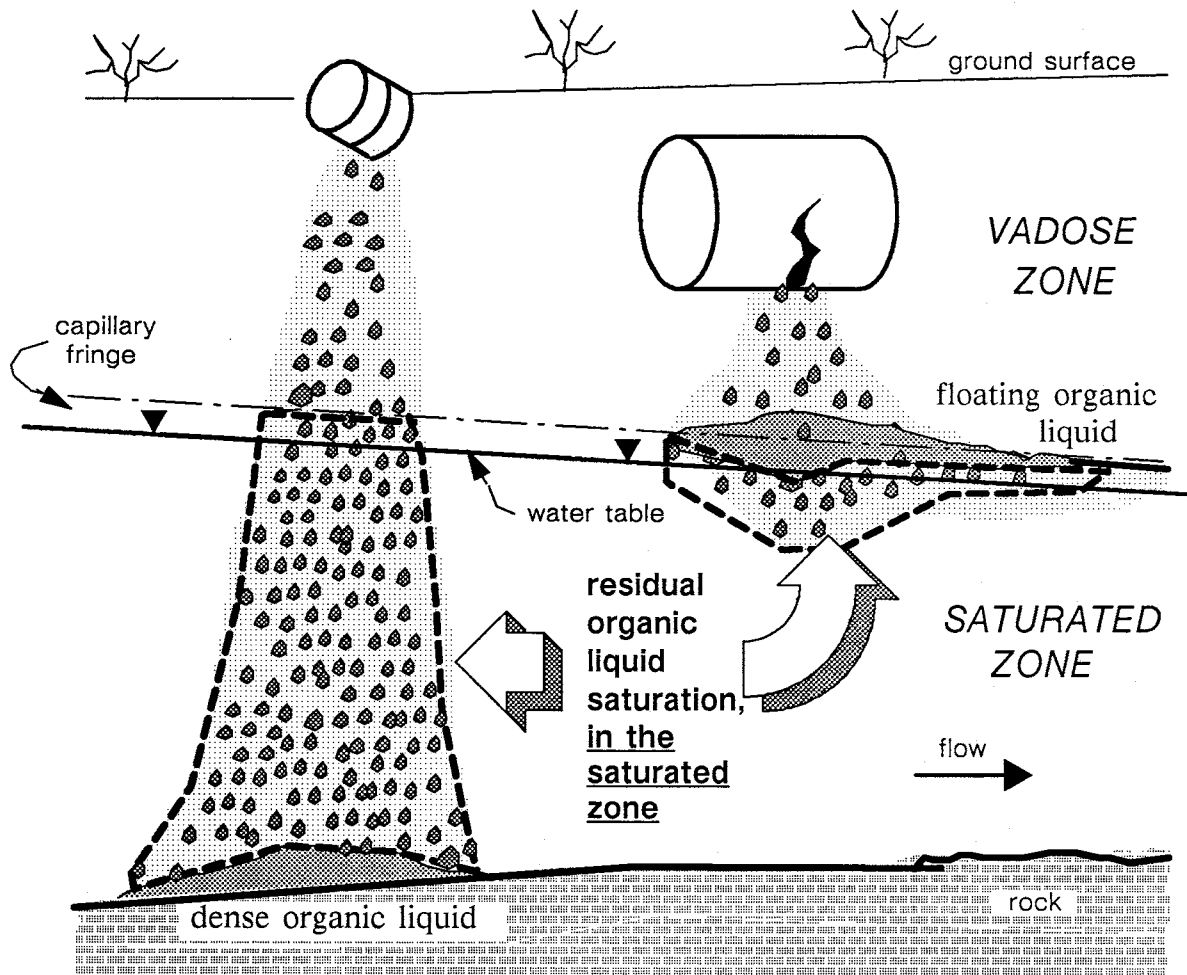


FIGURE 5-1. Schematic of residual organic liquid trapped in the saturated zone. Not clearly shown is the residual organic liquid trapped in the capillary fringe portion of the saturated zone (from Wilson et al., 1989).

saturated zone residual is the subject of this section. When an organic liquid less dense than water reaches the capillary fringe and water table, its weight can depress them (right side of Figure 5-1). Later, as the organic phase redistributes laterally and the water table rebounds trapped organics are left behind, within the saturated zone defined by the capillary fringe and water table. A rising water table can also lead to the same type of saturated zone organic liquid trapping.

Experiments to determine organic liquid residual saturations were conducted following the procedure documented earlier in the Chapter 3. In each experiment a water saturated soil column was flooded with organic liquid to simulate the movement of an organic liquid into the saturated zone. After the fluid saturations stabilized, the column was flooded with water at a low velocity to displace organic liquid. Six pore volumes of water were found to be sufficient to reach a stable organic liquid residual saturation.

The chapter is divided into three sections based on soil type. Within each section, results are presented in table form for every organic liquid tested. The tables include measured values for maximum organic liquid saturation,  $S_o$ , residual organic liquid saturation,  $S_{or}$ , sample porosity,  $n$ , and bulk density,  $\rho_b$ . The porosity and bulk density measurements provide information useful for indicating the variability in soil packing from column to column.

## SEVILLETA SAND RESULTS

Residual saturations for six organic liquids were experimentally determined using Sevilleta sand. A large amount of data concerning Soltrol exists because it was the fluid chosen to debug the experimental apparatus. Four to six trials were conducted for the other organic liquids to determine an average residual saturation.

Tables 5-1 and 5-2 summarize the experimental results for Soltrol as the non-wetting fluid. Many of the earlier Soltrol experiments were run without the benefit of a constant temperature cabinet. This is noted in the second column of Table 5-2, and the difference between maximum and minimum temperatures during the course of the experiment is given in the last column. As discussed in Chapter 3, those experiments with large temperature fluctuations provided less reliable results. In particular, it can be seen from Table 5-2 that the two experiments with the largest temperature fluctuations also had the largest estimated porosity and extreme estimates of residual saturation. Sample statistics for the twenty-two experiments are presented in Table 5-1, with data divided into three categories: a) all experiments; b) thirteen experiments conducted with good temperature control ( $\Delta t < 2^\circ\text{C}$ ); and c) nine experiments conducted with poor temperature control ( $\Delta t > 2^\circ\text{C}$ ). Error measurements, using a worst case error approach in which all errors were assumed additive and propagated through the calculations, are given in Table 5-2. Comparing these estimates to the sample standard deviations suggests that the thirteen temperature controlled experiments account for the known and tractable experimental errors. Thus the estimate of

	porosity (%)	bulk density (g/cm <sup>3</sup> )	maximum organic liquid saturation (%)	residual organic liquid saturation (%)
all 22 experiments	34.3 ± 1.2	1.741 ± 0.033	84.7 ± 3.4	28.0 ± 3.8
good temp. 13 experiments	33.9 ± 0.6	1.752 ± 0.016	85.1 ± 2.8	27.1 ± 1.7
poor temp. 9 experiments	34.9 ± 1.7	1.724 ± 0.044	84.0 ± 4.1	29.3 ± 5.4

TABLE 5-1. Soltrol residual saturation and other measurements in Sevilleta sand, for three temperature dependent categories (sample mean ± sample standard deviation).

residual saturation,  $S_{or} = 27.1 \pm 1.7 \%$ , taken from these 13 experiments can be considered reliable. This is slightly lower than previously published estimates (Wilson, et al. 1988), which were biased by the temperature fluctuations of the earlier experiments.

According to results from the 13 experiments conducted with good temperature control, twenty-seven percent of the Sevilleta sand pore space is occupied by immobile, discontinuous, blobs of Soltrol. If this estimate is typical for most organic liquids and sandy soils there is a tremendous storage capacity of organic liquid pollutants in the saturated zone. Expressed in terms of volumetric retention (eqn. 2-4), the Sevilleta sand has the capacity to store over 90 liters of Soltrol per cubic meter of soil. For example, a single 10,000 gallon spill of an organic liquid could be absorbed in about 420 m<sup>3</sup> of saturated soil. This volume corresponds to a cube of soil with sides only 7.5 meters in length.

The earlier discussion on mechanisms mentioned capillary trapping was a function of pore structure. Each experiment recorded in Table 5-2 included measurements of porosity and bulk density. Presumably, these measurements give a measure of pore structure as controlled by the density of soil packing. A tendency for increased trapping with decreased porosity has been reported in the petroleum literature (Morrow et al., 1988). This is believed to be related to the fact that as reservoir rocks become more cemented, the percentage of pore throats (from which organic liquid is easily displaced by water) decreases (Chatzis et al., 1983). Low pore connectivity, another attribute of low porosity (heavily cemented) media, is also suspected of contributing to increased trapping (Pathak et al., 1982). To investigate the influence of porosity on residual or maximum organic liquid saturation data from the 13 good temperature controlled samples in Table 5-2 are presented in Figure 5-2. In these results, there is low correlation between porosity

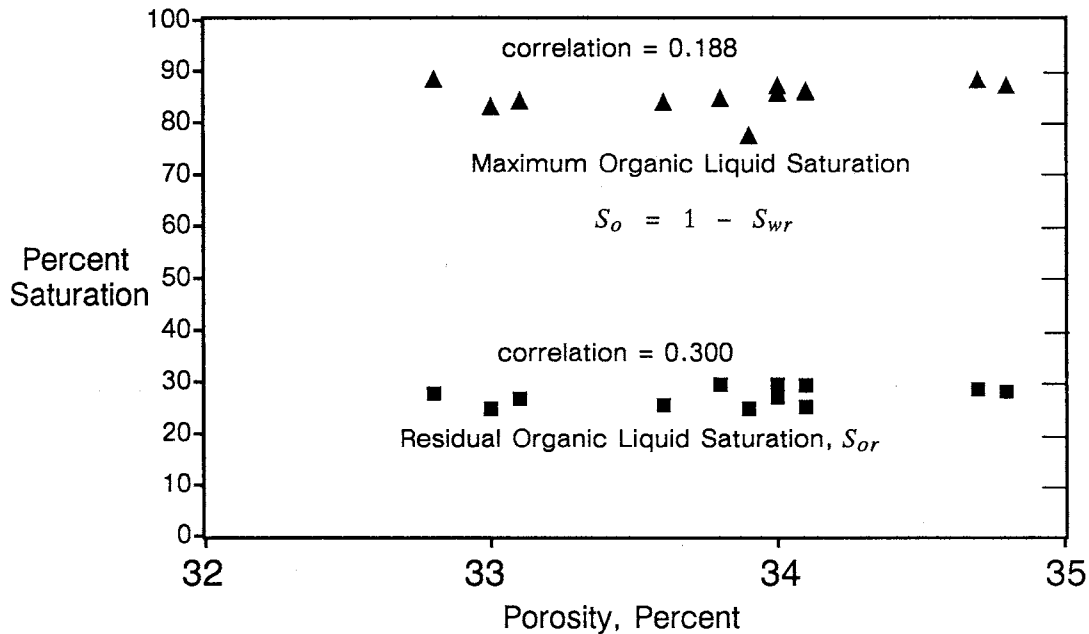


FIGURE 5-2. Correlation of maximum Soltrol saturation (triangles), and residual Soltrol saturation (squares), to porosity in the Sevillaeta sand.

and either the residual or maximum organic liquid saturations. Although the porosities varied from a low of 32.8 to a high of 34.9, this variation did not seem to affect the measurements of saturation in any systematic way. The low correlation between  $S_{or}$  and  $n$  is probably due to the small range of porosity.

In addition to Soltrol, quantitative Sevillaeta sand short column experiments were run with kerosene, gasoline, p-xylene, PCE, and n-decane. The first seven kerosene experiments presented in Table 5-3 are from Conrad (1986) and were run without the benefit of a constant temperature cabinet. The gasoline experiments presented in Table 5-4 were conducted under good temperature control. The six p-xylene tests summarized in Table 5-5 were conducted under a fume hood, but the temperature was fairly well controlled. Although the smaller density difference between water and the p-xylene resulted in greater error propagation for organic liquid saturations, the actual sample standard deviation was relatively small in comparison. The PCE tests described in Table 5-6 were also conducted under a



trial	in box ?	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	organic liquid saturation (%)				temp. range (°C)
						maximum	error	residual	error	
1	no	33.8	0.6	1.754	0.008	84.6	3.5	29.3	1.7	1.0
2	no	36.5	0.5	1.683	0.007	82.2	3.0	32.5	1.5	5.0
3	no	34.0	0.5	1.750	0.007	77.5	3.1	24.6	1.4	1.0
4	no	34.1	0.5	1.747	0.008	85.7	3.5	29.3	1.7	1.0
5	no	33.2	0.6	1.769	0.008	92.7	3.9	34.7	2.0	3.0
6	no	34.8	0.5	1.729	0.007	84.1	3.2	32.7	1.6	2.0
7	no	38.6	0.9	1.626	0.017	78.6	3.7	21.6	1.5	11.0
8	no	34.6	0.5	1.732	0.007	80.2	3.0	37.0	1.7	3.0
9	no	34.6	0.5	1.733	0.008	84.7	3.5	29.3	1.7	2.0
10	no	34.3	0.5	1.741	0.008	87.5	3.6	28.6	1.8	3.0
11	no	34.1	0.6	1.747	0.009	87.0	3.9	26.9	1.8	1.5
12	no	34.1	0.6	1.746	0.009	82.6	3.6	24.3	1.6	2.8
13	no	33.7	0.5	1.756	0.008	83.5	3.3	23.1	1.4	2.8
14	yes	34.9	0.5	1.726	0.007	87.0	3.4	27.9	1.6	0.3
15	yes	34.2	0.6	1.745	0.010	85.8	3.9	25.0	1.7	0.8
16	yes	34.7	0.6	1.730	0.010	88.2	3.9	28.5	1.8	0.4
17	yes	33.7	0.5	1.758	0.006	83.8	3.2	25.4	1.4	0.3
18	yes	34.1	0.6	1.747	0.009	85.6	3.7	27.1	1.7	0.4
19	yes	34.1	0.6	1.746	0.011	86.0	4.0	29.2	1.9	0.9
20	yes	32.8	0.6	1.781	0.010	88.3	4.1	27.6	1.9	1.0
21	yes	33.1	0.6	1.774	0.009	83.0	3.7	24.6	1.7	1.0
22	yes	33.2	0.5	1.771	0.007	84.1	3.4	26.6	1.7	1.1

TABLE 5-2. Summary of Soltrol / Sevilleta sand saturated zone results.

fume hood with relatively good temperature control. The n-decane experiments shown in Table 5-7 were conducted within the constant temperature cabinet. A tabulation of the raw data from all these experiments can be found in Appendix H.

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. range (°C)
					maximum	error	residual	error	
1	33.1	0.4	1.765	0.002	73.3	2.0	28.1	0.9	5.0
2	33.0	0.4	1.769	0.003	52.8	1.6	28.3	0.9	4.0
3	33.7	0.4	1.751	0.003	78.9	1.6	27.3	0.9	3.0
4	33.2	0.5	1.765	0.003	70.1	2.0	25.3	0.8	3.0
5	33.8	0.5	1.747	0.003	73.8	2.1	23.8	0.8	3.0
6	33.7	0.4	1.750	0.002	73.1	2.0	23.3	3.2	5.0
7	33.3	0.3	1.760	0.001	80.1	2.1	25.4	0.8	2.0
8	35.0	0.5	1.721	0.008	80.9	2.8	29.0	1.5	7.0
Avg.*	33.6	0.6*	1.754	0.014*	72.9	9.0*	26.3	2.1*	—

\* Average = sample mean  $\pm$  standard deviation

**TABLE 5-3. Summary of kerosene / Sevilleta sand saturated zone results.**

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. range (°C)
					maximum	error	residual	error	
1	34.3	0.7	1.742	0.011	75.2	6.0	26.9	2.6	0.8
2	33.1	0.6	1.772	0.008	80.9	6.2	29.3	2.8	1.3
3	32.6	0.6	1.786	0.008	83.1	6.3	31.0	2.9	0.6
4	32.1	0.6	1.799	0.009	84.5	6.5	26.9	2.6	1.1
5	33.5	0.6	1.762	0.009	81.2	6.2	28.8	2.7	0.4
Avg.*	33.1	0.8*	1.772	0.022*	81.0	3.6*	28.5	1.7*	----

\* Average = sample mean ± standard deviation

**TABLE 5-4. Summary of gasoline / Sevilleta sand saturated zone results.**

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. Range (°C)
					maximum	error	residual	error	
1	34.1	0.6	1.747	0.009	62.8	8.1	24.3	4.0	2.6
2	33.8	0.6	1.755	0.011	79.6	11.1	25.7	5.2	1.1
3	32.8	0.6	1.781	0.009	75.4	9.8	21.3	3.9	1.5
4	32.6	0.6	1.786	0.009	78.2	10.0	20.1	3.6	2.1
5	34.0	0.5	1.748	0.008	78.2	9.7	26.5	4.2	1.3
6	33.8	0.5	1.754	0.008	78.6	9.7	21.9	3.7	0.6
Avg.*	33.5	0.6*	1.762	0.017*	75.5	6.4*	23.3	2.6*	---

\* Average = sample mean ± standard deviation

**TABLE 5-5. Summary of p-xylene / Sevilleta sand saturated zone results.**

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. range (°C)
					maximum	error	residual	error	
1	32.5	0.6	1.788	0.008	69.5	3.1	27.5	1.4	0.5
2	33.0	0.6	1.776	0.009	85.0	3.9	25.7	1.4	1.7
3	32.2	0.6	1.796	0.010	78.9	3.8	26.1	1.5	0.9
4	32.4	0.6	1.791	0.010	86.2	4.2	28.8	1.5	1.3
Avg.*	33.1	0.3*	1.788	0.009*	79.9	7.6*	27.0	1.4*	---

\* Average = sample mean ± standard deviation

**TABLE 5-6. Summary of PCE / Sevilleta sand saturated zone results.**

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. Range (°C)
					maximum	error	residual	error	
1	34.7	0.6	1.732	0.010	77.0	3.6	28.6	1.8	2.6
2	33.2	0.6	1.776	0.010	72.3	3.6	24.6	1.8	1.1
3	34.2	0.6	1.743	0.010	78.8	3.9	25.1	1.9	1.5
4	32.2	0.6	1.797	0.010	82.4	4.1	26.7	1.8	2.1
5	33.5	0.6	1.763	0.010	82.5	3.9	24.6	1.6	2.0
Avg.*	33.6	1.0*	1.762	0.026*	78.6	4.2*	25.9	1.7*	---

\* Average = sample mean ± standard deviation

**TABLE 5-7. Summary of n-decane / Sevilleta sand saturated zone results.**

## Discussion of Results

A summary of the experiments is given in Table 5-8. From this table it is apparent the soil packing was very consistent from the tests of one liquid to those of another. The soil dependent properties, porosity and bulk density, remained nearly constant over most of the experiments. The porosities for the PCE experiments, however, were slightly lower than all the other experiments because the top endcap on the column was screwed down a little tighter as an added precaution against leakage. This slightly lower soil porosity appeared to have no influence on the results.

Fluid	porosity (%)	bulk density (g/cm <sup>3</sup> )	maximum organic liquid saturation (%)	residual organic liquid saturation (%)
Soltrol (13 trials)	33.9 ± 0.6	1.752 ± 0.016	85.1 ± 2.8	27.1 ± 1.7
kerosene (8 trials)	33.6 ± 0.6	1.754 ± 0.014	72.9 ± 9.0	26.3 ± 2.2
gasoline (5 trials)	33.1 ± 0.8	1.772 ± 0.022	81.0 ± 3.6	28.5 ± 1.7
p-xylene (6 trials)	33.5 ± 0.6	1.762 ± 0.017	75.5 ± 6.4	23.3 ± 2.6
PCE (4 trials)	32.5 ± 0.3	1.788 ± 0.009	79.9 ± 7.6	27.0 ± 1.4
n-decane (5 trials)	33.6 ± 1.0	1.762 ± 0.026	78.6 ± 4.2	25.9 ± 1.7
all liquids	33.5 ± 0.8	1.761 ± 0.020	79.5 ± 7.1	26.4 ± 2.4

Average = sample mean ± standard deviation

TABLE 5-8. Average values for different organic liquids in the Sevilleta sand saturated zone experiments.

There was some concern over the variability in the maximum organic liquid saturations, and whether this variability would substantially affect the residual saturation results. To lessen the possibility of exceeding the breakthrough pressure of the bottom water-wet filter, caution was used in applying high pressure to the organic liquid. As a consequence, it was not always certain that the water had been completely reduced to its so-called irreducible saturation and that the maximum organic saturation possible had been achieved. A plot of maximum organic liquid saturation versus residual saturation for all the experiments is shown in Figure 5-3. Visual inspection of the scatter plot does not reveal much correlation between maximum organic saturation and residual saturation, but least-squares regression analysis reveals a slight positive correlation.

The relationship between residual saturation and the type organic liquid is graphically displayed in Figure 5-4. The average residual organic liquid saturation,  $S_{or}$ , was relatively constant, varying from a low value of 23.3% for p-xylene to a

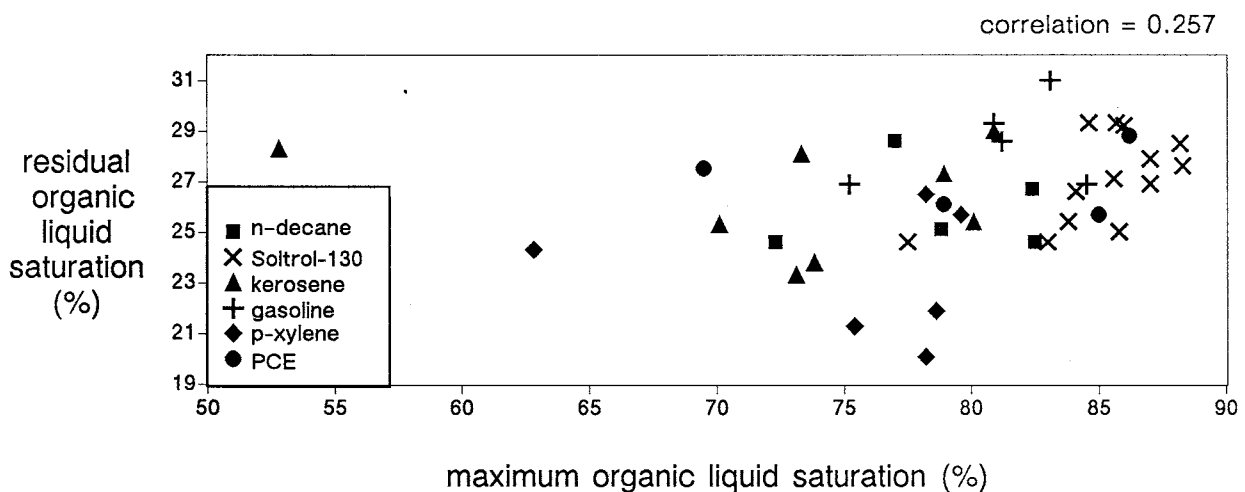


FIGURE 5-3. Residual organic liquid saturation as a function of the maximum organic liquid saturation.

high value of 28.5% for gasoline. The average residual saturation of all the fluids was 26.4%. All the fluids were tested against one another for a statistically significant difference in the sample means using the student's t-test. Although the differences in residual saturations between the fluids appear to be small, the p-xylene results were found to be statistically different from each of the other fluids at the 95% confidence interval ( $\alpha = 0.05$ ). P-xylene had an average residual saturation two and one-half percentage points lower than the next lowest liquid (decane). The low residual saturation may be accounted for by its relatively high solubility in water. It was the most soluble of the organic liquids tested (-0.20 g/l). In each experiment, at least six pore volumes, or about 250 ml of water were flushed through the column to reach residual saturation. If it is assumed the water was flooded slowly enough for the effluent water to reach equilibrium with the xylene, then as much as 0.05 g of xylene could have been removed from the column by dissolution, resulting in an underestimation of the residual saturation by as much as 1.0%. The reduction of xylene's residual saturation by dissolution may account for the significant difference in residual saturation between it and the other fluids tested.

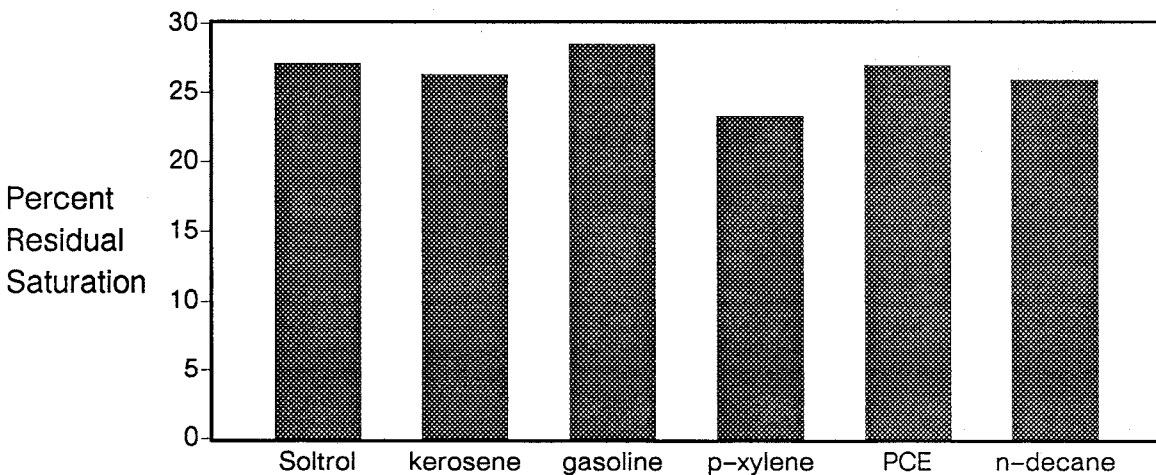


FIGURE 5-4. Residual organic saturation for tested organic liquids in the Sevilleta sand.

The residual saturations of kerosene and gasoline, and decane and gasoline, were also found to have statistically different sample means at the 95% confidence interval ( $\alpha = 0.05$ ). None of the remaining combinations showed significant differences in residual saturations between fluids at the 95% confidence interval. Calculations associated with the t-test are presented in Appendix F.

The organic liquid residual saturation results are again plotted in Figure 5-5, as a function of the interfacial tension (IFT) between water and the organic liquid (see Chapter 4 for IFT data). There appears to be no discernible correlation between IFT and  $S_{or}$ . The capillary forces (proportional to the IFT) so outweigh the other forces which may act to reduce trapping (buoyancy and viscous forces) that halving the interfacial tension — from an IFT of 47.8 for Soltrol to only 22.9 for gasoline — has no effect on the amount of organic liquid trapped. At typical aquifer flow rates IFTs may have to be reduced by at least an order of magnitude or more before any reduction in trapping occurs.

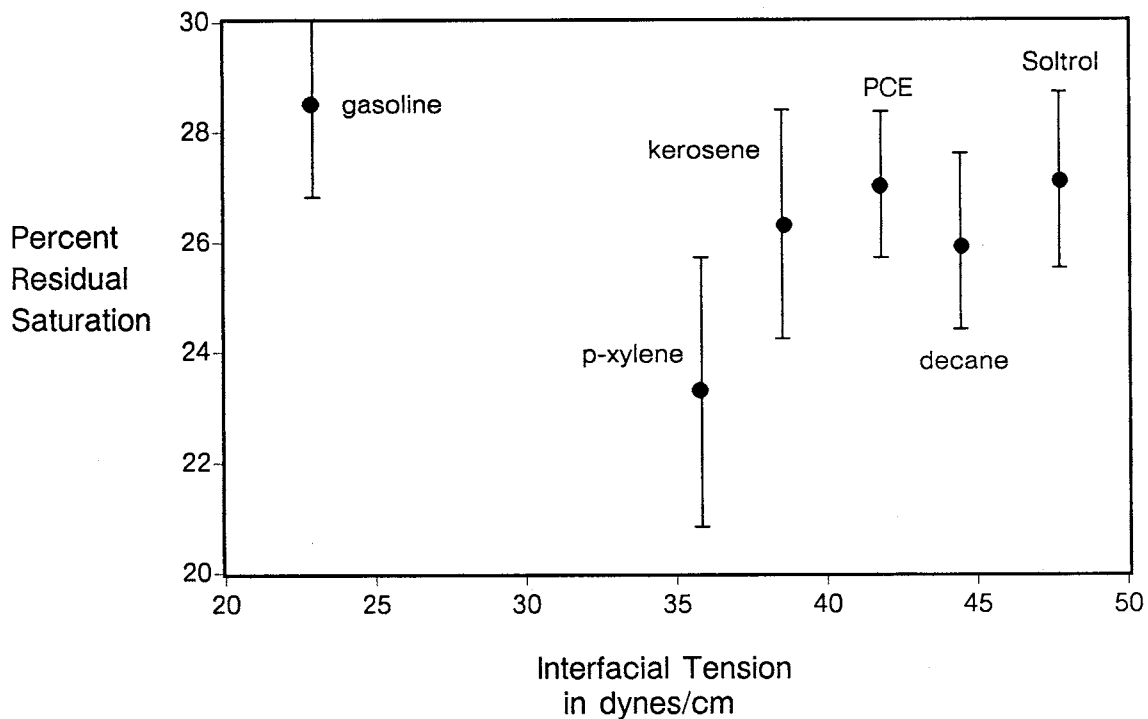


FIGURE 5-5. Residual organic saturation as a function of interfacial tension (IFT). The error bars represent the sample standard deviations taken from Table 5-8.



Using arguments which look at pore scale trapping mechanisms, Wardlaw (1982) and Wilson et. al. (1989) have shown that one would expect  $S_{or}$  to be independent of IFT for many common organic pollutants (Table 5-9). Wardlaw (1982), using glass micromodels, showed trapping by snap-off occurred in all fluid pairs studied even though the interfacial tensions ranged from 480 dyne/cm down to 0.1 dyne/cm. For strongly water-wet systems, trapping by snap-off was found to be insensitive to IFT down to 0.1 dyne/cm. Wilson et.al. (1989) demonstrated that to mobilize an organic liquid blob trapped by snap-off in a porous media with characteristics similar to the Sevilleta soil and using a flux rate of  $2.5 \times 10^{-4}$  cm/s, the interfacial tension between the organic and water would have to be less than 0.01 dyne/cm. To prevent trapping in a pore doublet like the one shown in Figure 2-10 due to by-passing, the velocities of the interfaces traveling through each pore would have to be equal. Using values reasonable for the Sevilleta soil and a flux

<u>PRIORITY POLLUTANT</u>	<u>INTERFACIAL TENSION (dyne/cm)</u>
carbon tetrachloride	45.0
PCE	47.5
benzene	35.0
chlorobenzene	37.4
ethylbenzene	38.4
toluene	36.1
phenol	39.3 <sup>A</sup> (40°C)
o-chlorophenol	42.25 <sup>B</sup>
naphthalene	28.8 <sup>B</sup>

A — Lyman et al., 1982  
 B — Weast, 1986

TABLE 5-9. The interfacial tension of some priority pollutants with water at 20°C. The data were obtained from Girifalco and Good (1957) unless otherwise noted.

rate of  $2.5 \times 10^{-4}$  cm/s, Wilson et. al. (1989) calculated that an IFT less than 2 dynes/cm would be needed to avert trapping by by-passing.

Figure 5-6 relates observed residual saturations to non-wetting phase viscosity. At the low flow rates used, residual saturations would be expected to be independent of viscosity and the results corroborate expectations. Some variability in  $S_{or}$  might have been possible had fingering occurred, but since the displacements were conducted with low flow rates and were stable with respect to density, viscous or density instabilities were prevented.

A plot of observed residual saturation versus density is shown in Figure 5-7. There appears to be no overall correlation between density and  $S_{or}$  and none was expected. However, fluids having a larger density difference with water tend to give more accurate results due to the gravimetric method of measuring saturations. A larger density difference increases the buoyancy forces, but in this case the

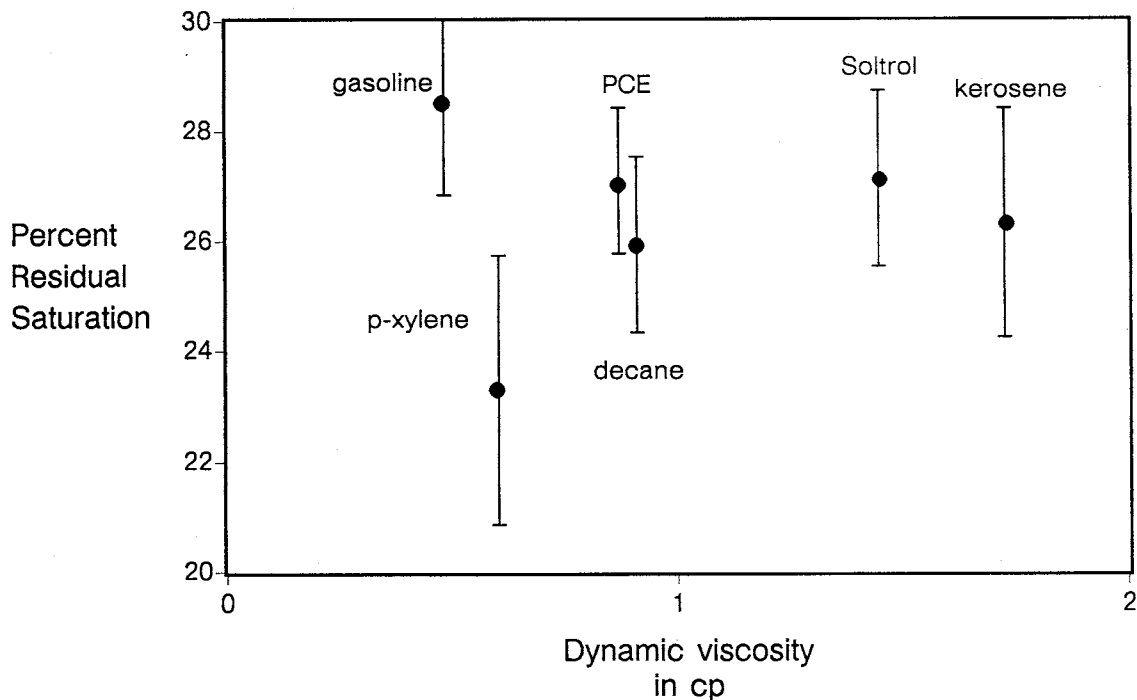


FIGURE 5-6. Residual organic saturation as a function of non-wetting phase viscosity. The error bars represent the sample standard deviations taken from Table 5-8.

system is well below the threshold for gravity induced reduction of trapping. However, had a very coarse soil such as a gravel been used, it may not have been appropriate to disregard buoyancy effects.

For organics lighter than water, the experiments show an apparent decrease in  $S_{or}$  as the density difference between the organic and water approaches zero. This is the opposite effect one would expect had buoyancy played a role. This is probably a coincidental effect of the reduced measurement accuracy as  $\rho_o$  approaches  $\rho_w$ .

PCE was the only organic liquid tested having a density greater than water. Even so, the residual saturation measurements do not appear to have been affected. Although the PCE experiments were run with the column upside down from the other experiments to prevent any density induced instabilities, it is important to realize that on an aquifer scale as a dense organic liquid percolates downward through the saturated zone, density induced fingering may well develop.

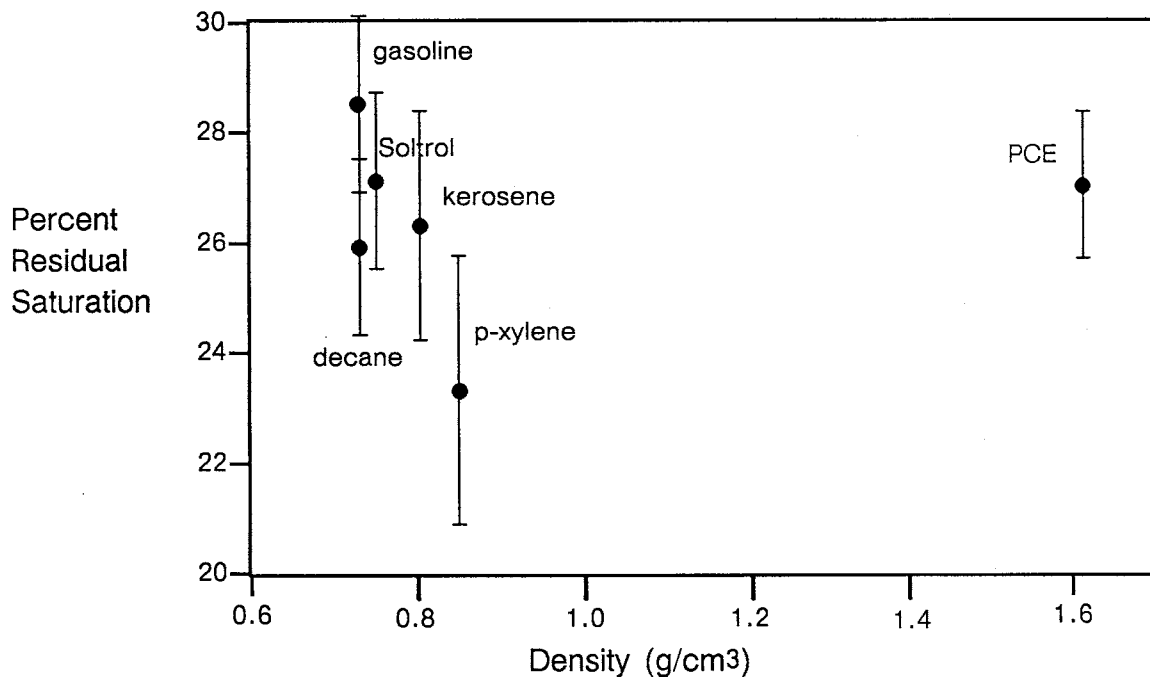


FIGURE 5-7. Residual organic saturation as a function of non-wetting phase density. The error bars represent the sample standard deviations taken from Table 5-8.

## Summary of Sevilleta Results

A total of forty-three experiments, measuring the residual saturations of six organic liquids in Sevilleta sand, under saturated zone conditions, were successfully completed. The average residual saturation over all the liquids was determined to be 26.4%. Residual saturations for each organic liquid varied over a range of about 5%, from 23.3% for p-xylene, to 28.5% for leaded gasoline. The residual saturation was found to be independent of fluid type with respect to fluid properties. No correlation was shown to exist between residual saturation and viscosity, density, or interfacial tension over the range of fluid properties exhibited by the fluids used in these experiments. Variations in these fluid properties were found to have little effect on residual saturation because capillary forces overwhelmingly dominate the forces associated with viscosity and density differences which act to reduce trapping. At least an order of magnitude reduction in interfacial tension is required before any noticeable change in residual saturation can be expected to occur. The lack of correlation between fluid properties suggests residual saturation may be considered independent of fluid type for a variety of immiscible organic liquids. If this is the case, then a relatively nontoxic organic liquid such as Soltrol or n-decane could be substituted for a more hazardous liquid in residual saturation experiments. Only a modest loss in accuracy would be expected to occur if Soltrol (res. sat. = 27.1%) or n-decane (res. sat.= 26.4%) were substituted for PCE (res. sat. = 27.0%) in a residual saturation experiment.

The experimental technique produced the most repeatable results when organic liquids with low water solubilities were used. The average residual saturation for each organic liquid was consistently higher than 25%, except for p-xylene. The most soluble organic liquid in water, p-xylene, displayed the lowest

residual saturation and largest discrepancy from the average residual saturation of all fluids. In fact, the p-xylene residual saturation was more than two and one-half percentage points lower than the next lowest fluid (n-decane - 25.9%). These results imply that small solubility changes may play an important role in determining residual organic liquid saturations.

### PALOUSE LOAM RESULTS

Two quantitative experiments were run with Soltrol and the Palouse Loam soil. In the first trial no Soltrol could be forced into the column even though a head of almost 500 cm H<sub>2</sub>O was placed on the column. In the second trial the maximum Soltrol saturation reached was 11.7%, with an corresponding water saturation of 88.3% (Figure 5-8). The inability to inject an organic phase into the Palouse loam, however, demonstrated that fine-grained, water-wet soils (which do not shrink in the presence of organics) can serve as an effective barrier to organic liquid movement in the subsurface.

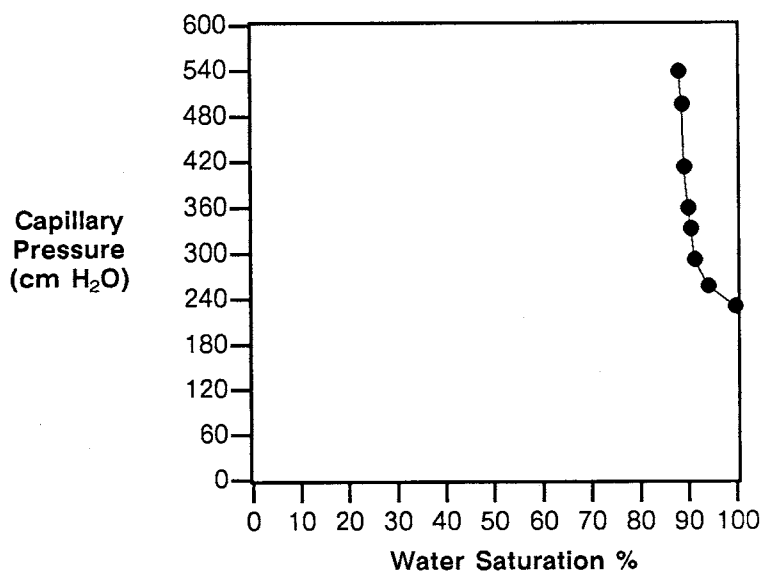


FIGURE 5-8. Water saturation versus capillary pressure for Soltrol in the Palouse loam.

## TRAVERSE CITY SAND RESULTS

The results of four experiments conducted with Traverse City Soil and Soltrol are shown in Table 5-10. All experiments were conducted under good temperature control conditions.

Trial	porosity (%)	error (%)	bulk density (g/cm <sup>3</sup> )	error (g/cm <sup>3</sup> )	Organic liquid saturation (%)				Temp. range (°C)
					maximum	error	residual	error	
1	34.4	0.6	1.738	0.009	85.1	7.3	17.0	2.4	0.7
2	35.7	0.6	1.705	0.010	84.6	6.8	15.8	1.9	1.9
3	36.0	0.6	1.696	0.009	86.6	6.9	19.3	2.2	1.7
4	33.9	0.6	1.753	0.010	88.0	7.2	18.4	2.1	1.1
Avg.*	35.0	1.0*	1.723	0.027*	86.1	1.5*	17.6	1.5*	----

\* Average = sample mean  $\pm$  standard deviation

**TABLE 5-10. Summary of Soltrol / Traverse City soil saturated zone results.**

The average residual saturation of Soltrol in the Traverse City soil was almost 10% lower than in the Sevilleta soil. The lower residual saturation may be caused by the different particle size distributions of the two soils. The Traverse City contains fewer fines and more coarse grains than the Sevilleta soil. The lack of fine grained particles may cause the aspect ratio of the pores to be smaller than in the Sevilleta, thus allowing less organic liquid to be trapped by snap-off. Because both soils are composed predominantly of quartz grains, it seems reasonable to believe any wettability difference between the soils would be minor and not significantly effect the residual saturation. Obviously, more experiments, examining the influence of particle size and wettability, need to be run before the processes responsible for causing the variation in residual saturation between these two very similar soils can be explained.

## CONCLUSIONS

- The average residual saturation calculated from 41 experiments, involving six organic liquids in the Sevilleta soil, under saturated zone conditions, was 26.4%.
- No correlation was found between residual saturation and viscosity, density, or interfacial tension over the range of fluid properties for the organic liquids used in these experiments. This infers that residual saturations may be fluid independent for many organic liquids.
- The small variation in residual saturation from one organic liquid to another suggests that a relatively safe organic liquid may be used to satisfactorily determine the residual saturation of a more toxic organic liquid.
- The experimental technique generally produced the most repeatable results (i.e., smallest standard deviation) when fluids with the following properties were used:
  1. a significant density difference with water;
  2. low solubility in water; and
  3. low volatility.
- The residual saturation of Soltrol ranged from 4% in the Palouse loam, to 27.1% in Sevilleta sand. The Traverse City soil trapped Soltrol in 17.6% of its voids. The wide range of residual saturation values indicates that residual organic liquid saturation is more sensitive to soil properties than organic liquid properties.

## CHAPTER 6

### VADOSE ZONE RESULTS AND DISCUSSION

The portion of the aquifer that includes residual saturation in the vadose zone is depicted in Figure 6-1. Regardless if an organic liquid is more (left) or less (right) dense than water, it leaves behind a zone of capillary trapped residual in the vadose zone as it makes its way downward toward the capillary fringe. The movement of organic liquid through the vadose zone is more complicated, at least

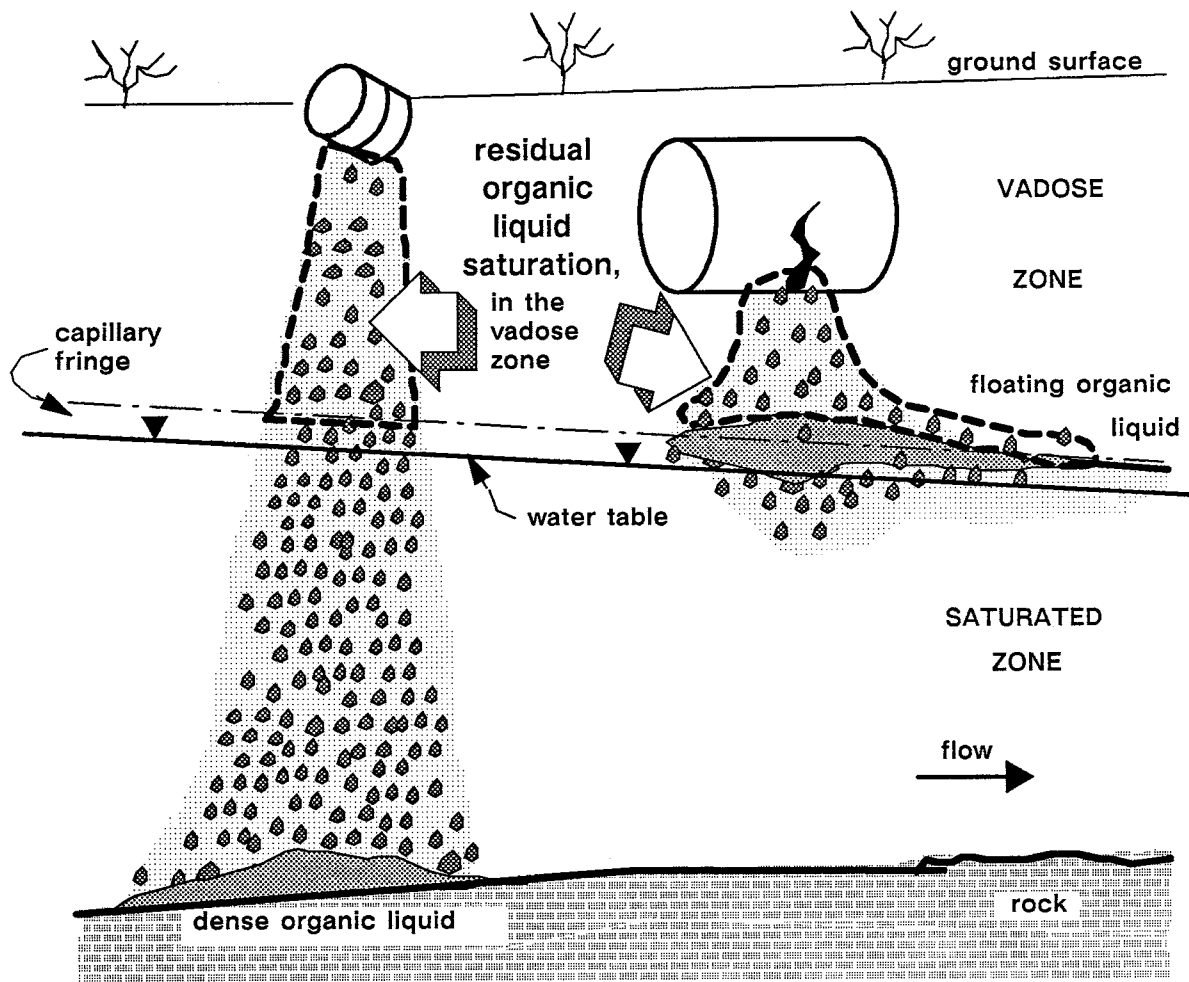


FIGURE 6-1. Schematic of residual organic liquid trapped in the vadose zone (from Wilson et al., 1989)



on a pore scale, than in the saturated zone due to the addition of the air phase. In the vadose zone, a downward percolating organic phase encounters a pore network containing air and water. In a three-phase system of air, water, and organic, the wettability usually follows the order water > organic > air, where the organic is of intermediate wettability. This means the organic is non-wetting relative to water, but wetting relative to air. So the organic phase, depending on whether it encounters air or water, can display either wetting or non-wetting behavior. The wetting behavior in turn determines the size, shape, and quantity of organic liquid trapped. The varied wettability of the organic liquid causes the organic to be trapped in a myriad of ways. Consequently, the distribution of residual organic in the vadose zone is more complex than in the saturated zone below.

In this chapter results of experiments conducted to determine residual organic liquid saturations in the vadose zone are presented. A vertical fluid distribution under equilibrium conditions is shown graphically using experimental data. Residual organic liquid saturations in the vadose zone are compared with saturated zone residual organic liquid saturations. The influence of the interplay between viscous, buoyancy, and capillary forces on residual saturation is examined.

## **EXPERIMENTAL RESULTS**

Quantitative measurements of residual saturation were made in short soil columns, as described in Chapter 3. The vadose zone experiments were designed to investigate the interactions of three phases (air, water and organic liquid) a specified height above the water table. Sixteen experimental trials were successfully completed to determine residual saturations in the vadose zone. All experiments were conducted with Sevilleta soil and Soltrol-130. Briefly, in each experiment an initially water saturated soil column was first drained with air under

an applied suction. The water drainage enabled the soil column to achieve water saturations indicative of moisture conditions commonly found in the unsaturated zone. The magnitude of the applied suction determined the water saturation remaining in the soil. After the water saturation stabilized, Soltrol was flooded into the column, simulating the infiltration of organic pollutants through the vadose zone. After equilibrium conditions were reached, the organic liquid was drained under an applied suction. Once the column equilibrated, the residual organic liquid saturation was measured.

Ten trials of the column experiments were run to measure residual saturations in the vadose zone, representing conditions relatively far above the water table. In these experiments no water was produced from the columns during the organic liquid flood (i.e., the water remains at irreducible saturation over the duration of the experiment). An irreducible water saturation of about 20% was characteristic of these experiments. The air saturation varied from 64.6% to 78.7%, while the organic liquid saturation ranged from 5.5% to 12.2%. A summary of results from the ten Dry Zone experiments is presented in table 6-1.

Six additional vadose zone column experiments were performed to examine the saturation distributions in the Transition Zone between saturated zone and Dry Zone conditions. When water was displaced from the column during the organic liquid flood, indicating mobile water existed and the water saturation was not at irreducible, the results were placed in the Transition Zone category. The largest change in forces acting on the organic liquid occurs in the range of 0-50 cm suction, where the transition from vadose zone to saturated zone conditions is most pronounced. Unfortunately, the procedure used in these experiments is inappropriate for measuring fluid saturations in the region just above the tension

saturated zone. This low suction range is important, particularly for organic liquids lighter than water, because it is the region in which these organic liquids spread laterally, forming a lens on the water table.

Trial	Suction (cm of water) ± 1 cm	Air Saturation (%)	Organic Liquid Saturation (%)	Water Saturation (%)	Temperature Range (°C)
1	60	73.6 + 2.3	8.3 + 0.4	18.1 + 1.9	4.0
2	68	68.2 + 2.9	12.0 + 0.5	19.8 + 1.9	3.6
3	59	67.6 + 2.9	9.7 + 0.6	22.8 + 2.3	5.0
4	61	67.1 + 2.6	11.3 + 0.5	21.6 + 2.1	4.3
5	66	73.8 + 2.5	7.7 + 0.4	18.5 + 2.1	2.3
6	71	71.8 + 2.6	7.9 + 0.5	20.3 + 2.2	4.3
7	70	64.6 + 2.7	12.2 + 0.6	23.2 + 2.2	2.1
8	69	74.7 + 2.9	7.1 + 0.4	18.3 + 2.4	1.9
9	71	71.1 + 4.4	9.1 + 0.7	19.8 + 3.7	2.6
10	75	78.7 + 2.7	5.5 + 0.4	15.8 + 2.4	2.0
Avg.		71.1	9.1	19.8	-
$\sigma_{n-1}$		4.3	2.2	2.3	-

TABLE 6-1. Summary of Soltrol / Sevilleta sand Dry Zone experiments.

Trial	Suction (cm of water) ± 1 cm	Volume of Water Produced (ml)	Air Saturation (%)	Organic Liquid Saturation (%)	Water Saturation (%)	Temperature Range (°C)
1	50	0.8	57.1 + 4.0	10.5 + 2.5	32.4 + 2.5	5.6
2	48	0.1	69.2 + 2.3	4.6 + 0.4	26.2 + 1.9	1.4
3	41	4.2	50.4 + 3.0	9.5 + 1.1	40.1 + 1.9	2.4
4	32	19.4	47.5 + 4.0	21.5 + 1.7	31.0 + 2.2	2.0
5	22	21.7	50.9 + 4.9	22.4 + 2.2	26.6 + 2.8	2.6
6	19	23.5	4.4 + 7.8	79.8 + 4.2	15.8 + 3.6	2.4

TABLE 6-2. Summary of Soltrol / Sevilleta Transition Zone experiments.

## Vertical distribution of fluids

The vertical distribution of fluids is depicted in Figure 6-2. Under equilibrium conditions, the height above the water table (in centimeters) directly corresponds to centimeters of soil suction applied during the experiment. The left curve shows the water saturation versus suction; the right curve shows the total liquid saturation. The difference between the two curves is the residual — or better termed in this case, equilibrium — organic liquid saturation. The saturation versus suction curves are fitted by nonlinear regression (van Genuchten, 1980) to the experimental data (excluding Transition Zone trials 5 and 6).

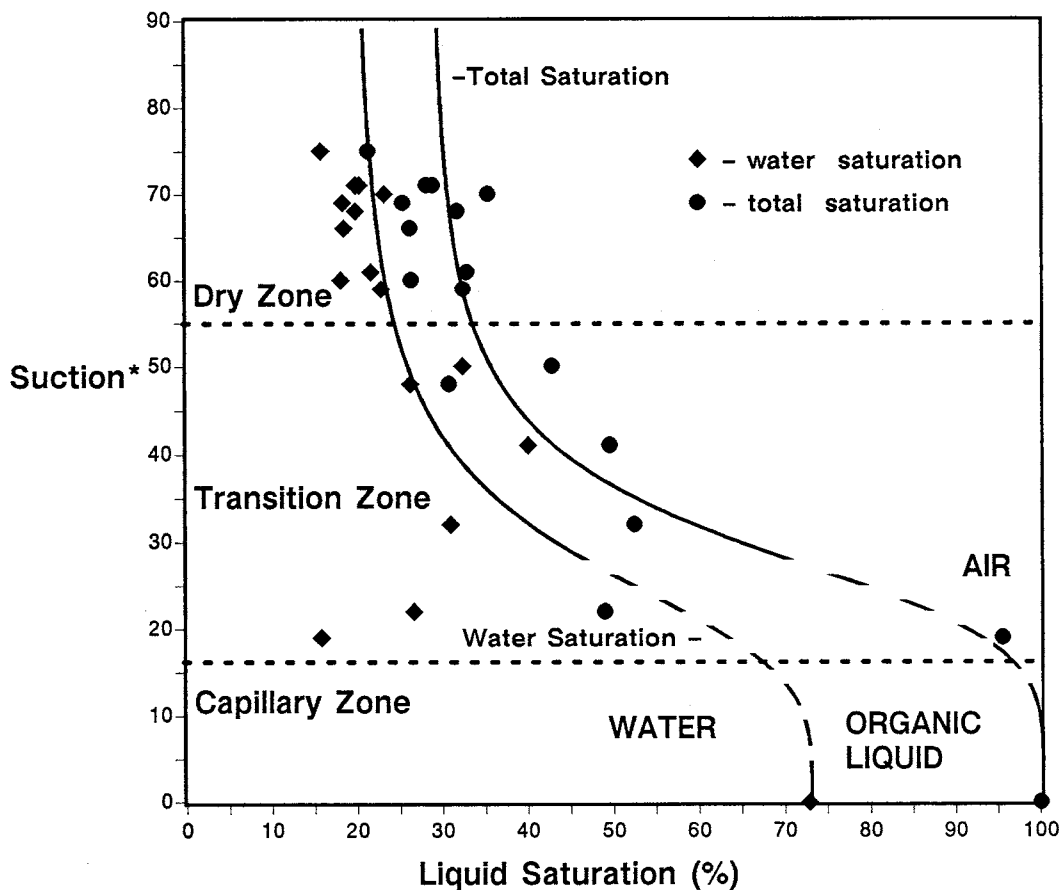


FIGURE 6-2. Vertical distribution of fluids in the vadose zone.

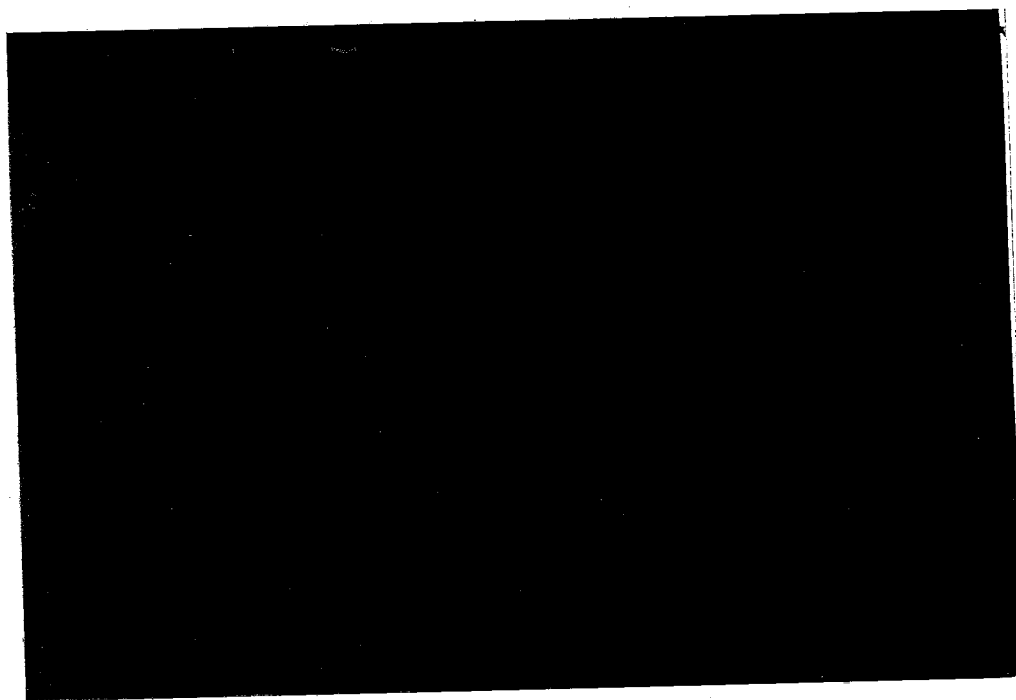
\* cm of water were used during water drainage, cm of Soltrol were used during organic liquid drainage

From Figure 6-2 it appears that the difference between the two curves remains relatively constant at locations higher than 30 cm above the water table. Below 30 cm however, the separation between the curves increases. One would expect the water saturation to increase as the suction decreased, but the data fail to show this trend near the water table. Under low suctions the technique did not allow the water to reimbibe into the soil, causing low water saturations and high organic liquid saturations. The two data points nearest the capillary fringe indicate water saturations below 30% exist near or possibly within the capillary zone. These low values are not indicative of conditions found in natural systems. A Soltrol saturation of nearly 80% was measured in the experiment conducted with the lowest suction. The last two problems serve as examples of the inability of the apparatus to measure residual saturations near the capillary zone.

#### **DISCUSSION OF RESIDUAL ORGANIC LIQUID VARIATION**

Residual organic liquid saturations were found to be much lower in the vadose zone than in the saturated zone. The Dry zone experiments yielded an average value for residual Soltrol saturation (9.1%) approximately one-third as large as the saturated zone residual Soltrol saturation values (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 vadose zone the air-organic fluid pair controls trapping, while in the saturated zone, the water-organic fluid pair controls trapping. The changes in interfacial tensions and fluid densities differences between the important fluid pairs is responsible for the variation in forces, which in turn, determines the residual saturation of the organic liquid.

Three-phase micromodel experiments conducted by Mason et al. (1989) (see also Wilson et al., 1989) showed that the organic liquid can be trapped in several different ways. When the organic liquid is of intermediate wetting (wetting: water > organic liquid > air), it can be trapped as blobs within the water phase, in pore throats, in small pores, and as films within the air phase; and it can form films in between the water and the air phases (Figure 6-3). As an intermediate wetting fluid, the organic liquid will often remain as a continuous phase through films on the water phase. This is a dramatic contrast to the disconnected blobs found in the saturated zone.



**Figure 6-3.** Organic liquid (red) trapped with water (light blue) and air (clear) in a three-phase micromodel (from Mason, 1989).

Because organic liquid is wetting compared to air, as organic liquid is drained from the vadose zone, the largest pores are preferentially emptied and organic liquid is retained in smaller pores. The large density difference (increased buoyancy force) and low interfacial tension (decreased capillary force) between air and organic liquid causes the organic to drain from the larger pores. The water

phase occupies the smallest pores since it is the most strongly wetting fluid. One might think that had no water been present, these smaller water-filled pores may have instead been filled by organic liquid and the vadose-zone residual saturations measured in the column studies would have been larger — roughly equal to the 19% irreducible water saturation, but the Soltrol–air saturation–capillary pressure tests found the irreducible Soltrol saturation to be about 8%. Apparently, even if the smaller pores are filled by organic liquid, the low Soltrol–air surface tension decreases the capillary forces sufficiently to allow the organic liquid to drain from them.

The differences in magnitude and spatial variability of residual organic liquid saturation may be accounted for by an increase in the gravity or buoyancy force with a corresponding decrease in the capillary force. The relation of viscous and buoyancy forces to capillary forces can be accomplished through dimensionless groups used frequently in petroleum engineering studies concerning mobilization of residual reservoir oil (Morrow and Songkran, 1981).

As shown earlier in Chapter 2, nonwetting phase residual saturation decreases as the ratio,  $\frac{F_v + F_b}{F_c}$ , is increased above a critical value. The ratio of viscous and buoyancy forces to capillary forces is often much greater in the vadose zone, causing the critical value to be exceeded at some locations. Most organic liquids have a much greater buoyancy force in the vadose zone (larger  $F_b$ ), due to the larger fluid density difference with air than with water. The interfacial tension between air and organic in the vadose zone is often smaller than the interfacial tension between the organic liquid and water in the saturated zone thus lowering the capillary force (smaller  $F_c$ ). The combination of the larger buoyancy force

Zone	fluid pair	density difference (g/cm <sup>3</sup> )	Interfacial tension (dyne/cm)
Vadose	Soltrol-air	0.75	19.2
Saturated	Soltrol-water	0.25	48.7

TABLE 6-3 Relative density differences and interfacial tensions in the vadose zone and saturated zone.

and a smaller capillary force increases the ratio  $\frac{F_v + F_b}{F_c}$ . For example, Soltrol-130, the organic liquid used in the experiments, has three times the buoyancy forces and 2.5 times less capillary forces in the vadose zone than in the saturated zone (see Table 6-3). Under equivalent conditions ( i.e., same soil and packing)  $\frac{F_v + F_b}{F_c}$  will be much larger in the vadose zone compared to the saturated zone. It is believed that in many cases  $\frac{F_v + F_b}{F_c}$  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 the reduced capillary forces and thereby decrease 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 a maximum.



## CONCLUSIONS

- Equilibrium organic liquid saturations were found to be about 9% in the Sevilleta Soil under vadose zone conditions. This is one-third the amount of organic liquid trapped in the saturated zone.
- Lower residual saturations in the vadose zone are believed to result from the presence of air, a non-wetting phase, and the comparatively larger buoyancy forces and smaller capillary forces in the vadose zone. Therefore, there is less propensity for capillary trapping in the vadose zone.
- The experimental procedure satisfactorily measured residual saturations in the vadose zone well above the capillary fringe. Within the capillary zone, the technique was unable to simulate physical conditions, leading to unrealistic results.

## CHAPTER 7

### SUMMARY OF CONCLUSIONS

#### **Discussion of Project**

The technique used to measure residual saturations in the saturated zone worked very well with soils having a fairly high hydraulic conductivity. However, when a clay-rich organic soil was used in the apparatus, the technique worked less than satisfactorily. The residual saturations of a wide variety of organic liquids were successfully measured in the Sevilleta soil. The vadose zone experiments were able to accurately determine equilibrium three-phase fluid (water, organic liquid, and air) saturations at elevations well above the capillary fringe. Unfortunately, the procedure failed to yield reasonable results in the capillary fringe region just above the water table. Most of the objectives, except for the formation of a complete vertical three-phase fluid distribution in the vadose zone, were achieved.

#### **Saturated Zone Conclusions**

- The average residual saturation calculated from 41 experiments, involving six organic liquids in the Sevilleta soil, under saturated zone conditions, was 26.4%.
- No correlation was found between residual saturation and viscosity, density, or interfacial tension over the range of fluid properties for the organic liquids used in these experiments. This infers that residual saturation may be fluid independent for a variety of organic liquids.
- The small variation in residual saturation from one organic liquid to another suggests that a relatively safe organic liquid may be used to satisfactorily determine the residual saturation of a more toxic organic liquid.

- The amount of Soltrol trapped in a particular soil ranged from 4% in the Palouse loam, to 27% in the Sevilleta sand. The Traverse City sand trapped Soltrol in 18% of its pores. The wide range of residual saturation values indicate that residual organic liquid saturations are more dependent on soil properties than liquid properties.
- The experimental technique gave the most repeatable results when fluids with the following properties were used:
  1. a significant density difference with water;
  2. low solubility with water; and
  3. low volatility.
- The method was able to measure residual saturations of lighter than water and heavier than water organic liquids in soils with fairly high hydraulic conductivities. In soils with low hydraulic conductivity, the technique failed to work properly.

#### **Vadose Zone Conclusions**

- Equilibrium organic liquid saturations were found to be about 9% in the Sevilleta Soil under vadose zone conditions. This is one-third the amount of organic liquid trapped in the same soil in the saturated zone.
- Lower residual saturations in the vadose zone are believed to result from the presence of air, a non-wetting phase, and the comparatively larger buoyancy forces and smaller capillary forces in the vadose zone. Therefore, there is less propensity for capillary trapping in the vadose zone.
- The experimental procedure satisfactorily measured residual saturations in the vadose zone above the capillary fringe. Within the capillary zone, the technique was unable to simulate physical conditions, leading to unrealistic results.

## **Recommendations for Additional Research**

This research study investigated the effect different organic liquid properties had on residual organic liquid saturation. The impact of soil type on residual saturation was not thoroughly examined, but from the results in this paper it appears as if residual saturation is much more sensitive to soil type than it is to organic liquid type. Accordingly, an investigation of the influence soil properties have on residual organic liquid saturation would seem very worthwhile. The determination of residual saturations in a variety of soils would improve our understanding of the influence exerted by a porous media on organic liquid trapping. The effects of wettability on residual saturation need to be investigated more thoroughly. The effect of soil heterogeneities of residual saturation also could easily be investigated using this apparatus.

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**APPENDIX**



## **EXPERIMENTAL PROCEDURES**

## APPENDIX A

### Capillary Pressure–Saturation Test

Soil capillary pressure-saturation relationships were determined using equilibrium methods (Vomocil, 1965). Hanging column type equilibrium stepwise water-air, water-organic, and air-organic displacement experiments were performed under both drainage and imbibition conditions to determine the capillary pressure functions. Standard equilibrium procedures were altered for the water-organic liquid displacement experiments to accommodate conditions involving two liquid phases. Figure 4-2 shows this modified set up. Tubing was used to connect the tops of the burets to seal the system and reduce volatilization. The column was prepared identically to a soil packed, water saturated column, described in the Column Apparatus section. The soil column was attached to burets containing organic liquid (buret A) and water (buret B). The capillary pressure was increased stepwise by lowering buret B and/or raising buret A, thus increasing  $h_2$  or  $h_1$ , respectively. At each step the system was allowed to equilibrate (about 24 hours were required). The capillary pressure was measured as:

$$P_c = \frac{\rho_o h_1 + \rho_w h_2}{\rho_w}$$

where:

$P_c$  = capillary pressure (cm H<sub>2</sub>O)

$h_1$  = height of the fluid in buret A above the center of the column (cm)

$h_2$  = height of the fluid in buret B below the center of the column (cm)

$\rho_o$  = organic liquid density (g/cm<sup>3</sup>)

$\rho_w$  = aqueous fluid density (g/cm<sup>3</sup>)

$$120 \text{ cm H}_2\text{O} \left( \frac{\text{water}}{\text{Soltrol}} \right) \times \left( \frac{\sigma_{\text{wa}}}{\sigma_{\text{wo}}} \right) = 200 \text{ cm H}_2\text{O} \left( \frac{\text{water}}{\text{air}} \right) = 14 \text{ cm Hg}$$

where,

$\sigma_{\text{wa}} = 73.6 \text{ dyne/cm} = \text{water/air interfacial tension}$

$\sigma_{\text{wo}} = 47.8 \text{ dyne/cm} = \text{water/Soltrol interfacial tension}$

The performance standard for this particular air-entry test then, was set at 14 cm Hg.

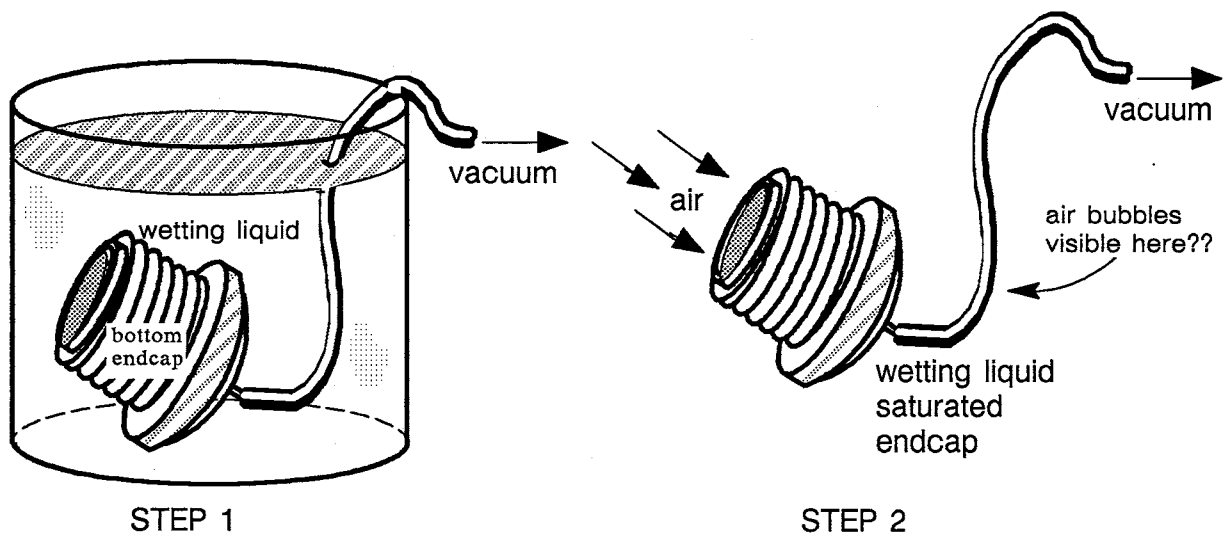


FIGURE B.1 Air entry test for bottom endcap filter and seal

## APPENDIX C

### Wettability Changing Procedure

In the later part of each vadose zone experiment a bottom endcap with an organic liquid wet TFE filter or ceramic disk replaced the water-wet nylon filter. One half bar, high flow ceramic disks, purchased from Soil Moisture Equipment Corporation, having a bubbling pressure of 7-9 psi and a pore size of approximately 6 microns were used in some of the experiments. The ceramic disks originally had a 3" diameter and were 1/4" thick. The disks were initially trimmed to roughly 5 cm in diameter with a hack saw. Final smoothing of the edges into a 5 cm circular shape was accomplished with the aid of a bench grinder. Once the ceramic disk was correctly sized it was cleaned by soaking in a 10% solution of hydrochloric acid for 1 hour, then alternately rinsed and soaked in distilled water for 24 hours. The disk was dried for overnight in an oven set at 85°C.

To change wetting, the disks were first soaked in chlorotrimethylsilane for 2 hours, immersed in toluene for 1/2 hour, and finally rinsed thoroughly in methanol for 1 hour. A similar procedure was used by Lenhard and Parker (1987), and previously by many experimenters in petroleum engineering (see review by Anderson, 1987a).

To accommodate the 1/4" thick ceramic disk, the bottom endcap taper was machined to a 1/4" depth on a lathe. Each revised bottom endcap was fitted with a disk, and the edges of the disk and endcap were sealed with Devcon 2 ton epoxy to prevent any leakage. The epoxy was allowed to dry, the disk was soaked in Soltrol for a day. The ceramic disks were found to maintain their organic-wet properties much better if they were stored in wetting (organic) fluid when not in use.

## APPENDIX D

### Aqueous Fluid Preparation

The aqueous fluid used in all experiments was water with 300 ppm  $\text{CaCl}_2$  added to prevent dispersion of clays. To prepare the aqueous fluid, distilled water was deionized to 18 megaohms using a Barnstead Water-1 deionizer, and discharged into a previously weighed 1000 ml Erlenmeyer flask. After the water was deionized it was boiled to de-air, then sealed with a stopper immediately upon removal from the hotplate. Once cooled, the flask containing the water was weighed to determine the mass of water.  $\text{CaCl}_2$  was added to create a 300 ppm calcium chloride solution. The amount of  $\text{CaCl}_2$  added to the water was calculated in the following fashion:

$$M_w = M_b - M_f$$

$$M_{ca} = 0.00398 \times M_w$$

where,

$$M_w = \text{Mass water (g)}$$

$$M_f = \text{Mass flask empty (g)}$$

$$M_b = \text{Mass flask with boiled water (g)}$$

$$M_{ca} = \text{Mass CaCl}_2 \text{ added to water (g)}$$

The aqueous solution was stored in sealed glass flasks under a vacuum to prevent air from dissolving into the aqueous fluid.

## **EXPERIMENTAL RESULTS**

## APPENDIX E

### Vapor Pressures of Organic Liquids

Compound	Chemical Formula	Solubility in water (gm/l at 25°C)	Vapor Pressure <sup>3</sup> (mm of Hg at 20°C)	Carcinogenic Potency <sup>4</sup>	Noncarcinogenic Toxicity <sup>4</sup>
benzene	C <sub>6</sub> H <sub>6</sub>	1.77 <sup>1</sup>	80	low	
ethylbenzene	C <sub>8</sub> H <sub>10</sub>	0.17 <sup>1</sup>	7.5		low
toluene	C <sub>7</sub> H <sub>8</sub>	0.55 <sup>1</sup>	22		low
n-decane	C <sub>10</sub> H <sub>22</sub>	2.1 x 10 <sup>-5</sup> <sup>1</sup>	1.3		
m-xylene	C <sub>8</sub> H <sub>10</sub>	0.17 <sup>1</sup>	6.0		low
o-xylene	C <sub>8</sub> H <sub>10</sub>	0.17 <sup>1</sup>	6.5		low
p-xylene	C <sub>8</sub> H <sub>10</sub>	0.16 <sup>1</sup>	5.5		low
carbon tet	CCl <sub>4</sub>	0.78 <sup>2</sup>	90	medium	
TCE	C <sub>2</sub> HCl <sub>3</sub>	1.10 <sup>2</sup>	60	low	
PCE	C <sub>2</sub> Cl <sub>4</sub>	.20 <sup>2</sup>	15	low	

1. Average values compiled from Brookman, 1985

2. From Callahan, 1979

3. Compiled using data from Weast, 1981

4. From report by Environ Corp in OTA, 1984

If a value was found for carcinogenic potency of a substance, no search was made for non-carcinogenic toxicity

Unit risk = risk per unit of exposure, where unit of exposure is defined as lifetime average daily intake

MED = Minimum effective dose known to cause adverse impact

Carcinogenic risk levels

High potency = unit risk greater than 5 (mg/kg/day)<sup>-1</sup>

Medium potency = unit risk equal to 0.1-5 (mg/kg/day)<sup>-1</sup>

Low potency = unit risk less than 0.1 (mg/kg/day)<sup>-1</sup>

Non-carcinogenic toxicity levels

High = MED less than 10 mg/kg body weight/day

Moderate = MED 10-100 mg/kg body weight/day

low = MED greater than 100 mg/kg body weight/day

## APPENDIX F

### t-test Calculations

The t-test was used to compare residual organic liquid saturations against one another. A 95% confidence interval was selected as the criteria for determining the samples to be statistically different. A calculated "t" value less than the 95% confidence interval value means that there is a less than one in twenty chance the residual saturations are statistically different. If the "t" value is greater than the 95% confidence interval it means that there is a greater than one in twenty chance the residual saturations are statistically different.

The formula used to calculate the t values was;

$$t = \frac{X_1 - X_2}{S_e} \quad (\text{F-1})$$

where,

$X_i$  = Mean residual saturation of liquid  $i$

$$S_e = S_p \sqrt{\frac{1}{n_1} + \frac{1}{n_2}} \quad (\text{F-2})$$

$$S_p = \frac{(n_1 - 1) S_1^2 + (n_2 - 1) S_2^2}{n_1 + n_2 - 2} \quad (\text{F-3})$$

$S_i$  = Standard deviation of liquid  $i$

$n_i$  = number of samples of  $i$

According to Davis (1986), three assumptions are necessary to perform this test.

The assumptions of the t-test are:

1. both samples are selected at random;
2. populations from which samples are chosen are normally distributed;
3. the variances of the two populations are equal.



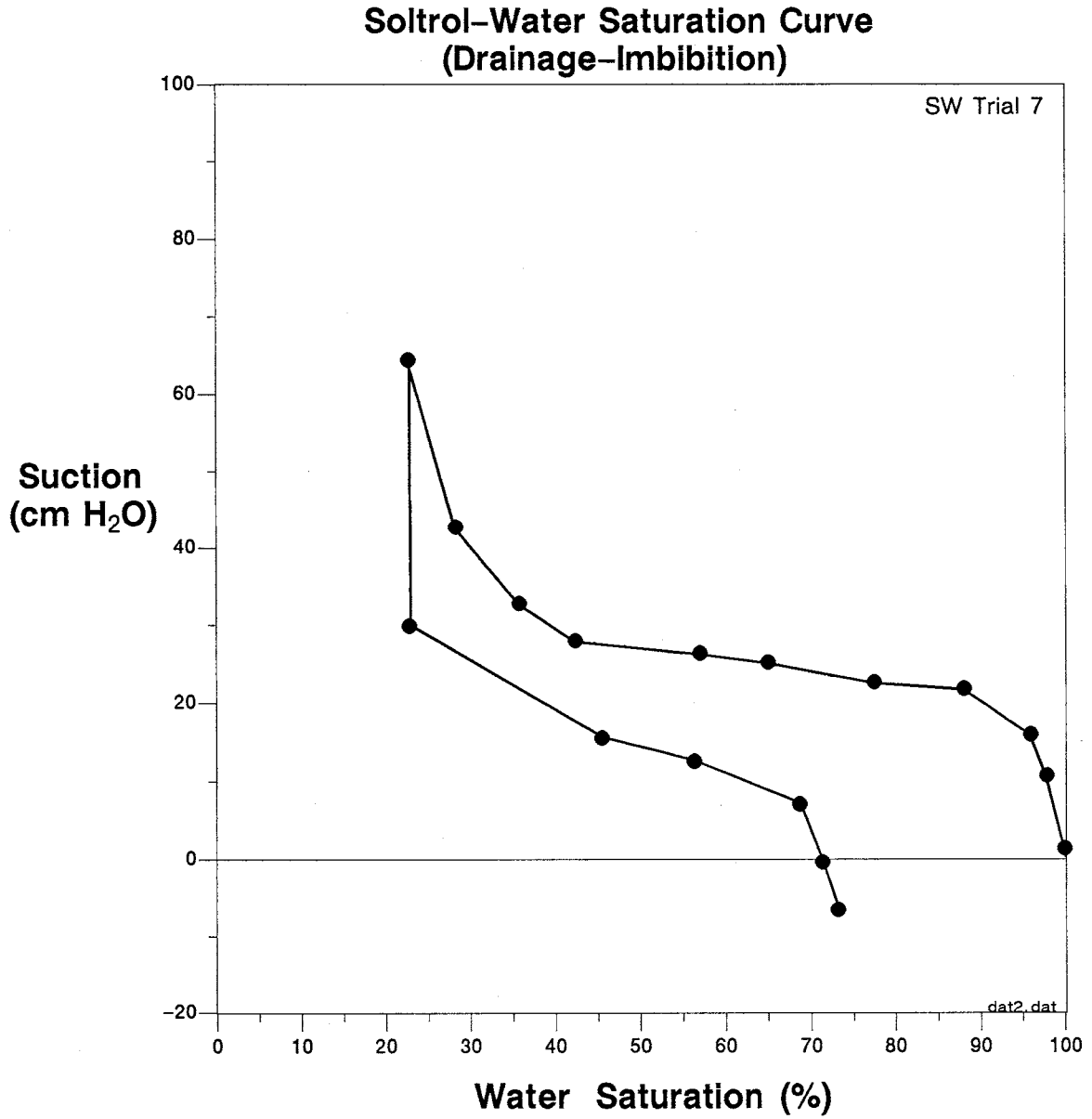
Assumptions 1. and 2. were assumed to be true. The third assumption was validated using the F-test described in Davis (1986)

liquid pair	calculated t-value	95% confidence interval	statistically different
Soltrol-kerosene	0.910	1.729	no
Soltrol-gasoline	1.497	1.746	no
Soltrol-PCE	0.101	1.753	no
Soltrol-decane	1.344	1.497	no
Soltrol-xylene	3.499	1.740	yes
PCE-gasoline	1.416	1.895	no
PCE-kerosene	0.573	1.812	no
PCE-xylene	2.575	1.860	yes
PCE-decane	1.039	1.895	no
xylene-gasoline	3.826	1.833	yes
xylene-kerosene	2.338	1.782	yes
xylene-decane	1.913	1.833	yes
decane-gasoline	2.419	1.860	yes
decane-kerosene	0.345	1.782	no
gasoline-kerosene	1.960	1.782	yes

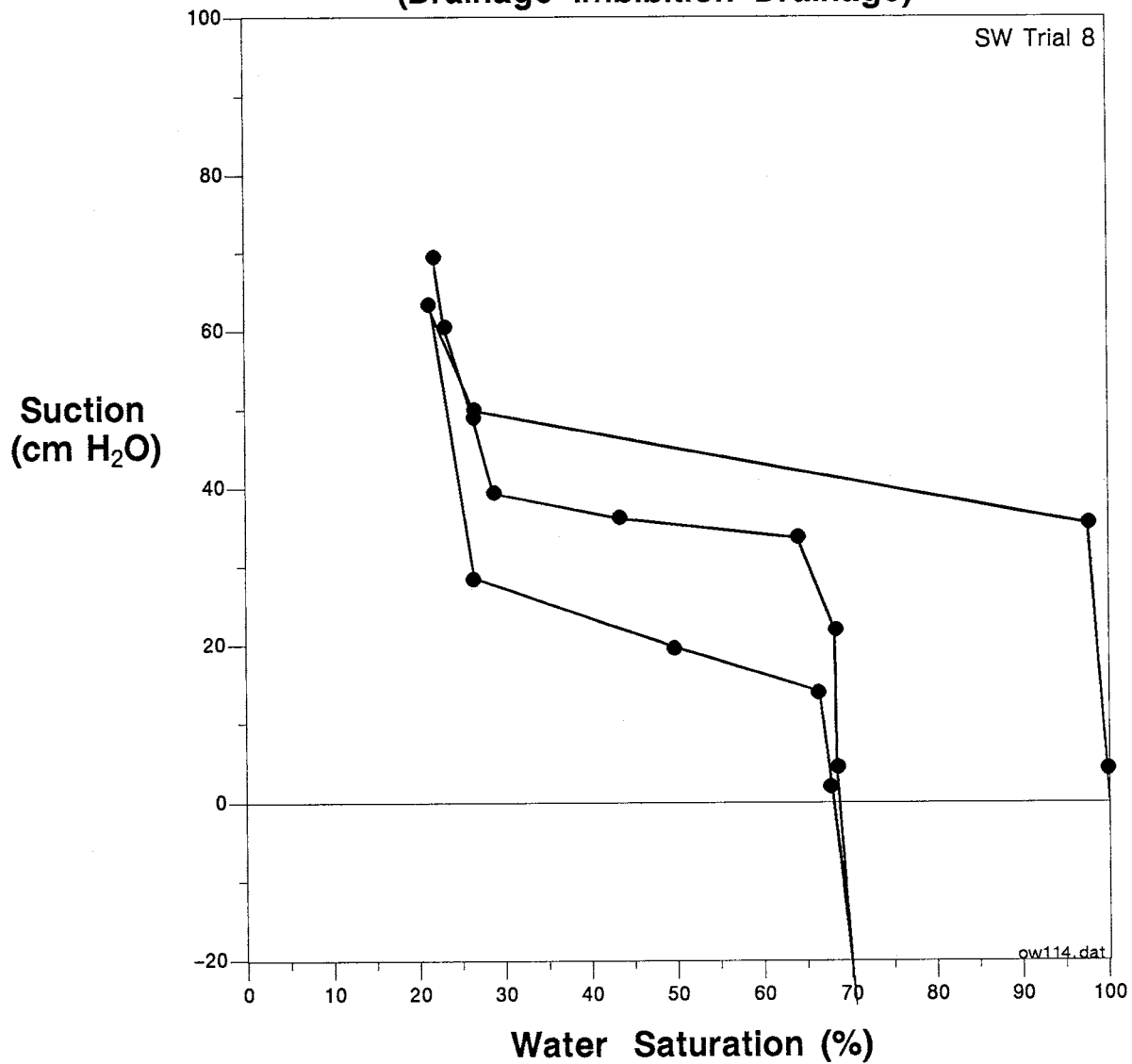
**Table F-1. t-test results**

APPENDIX G

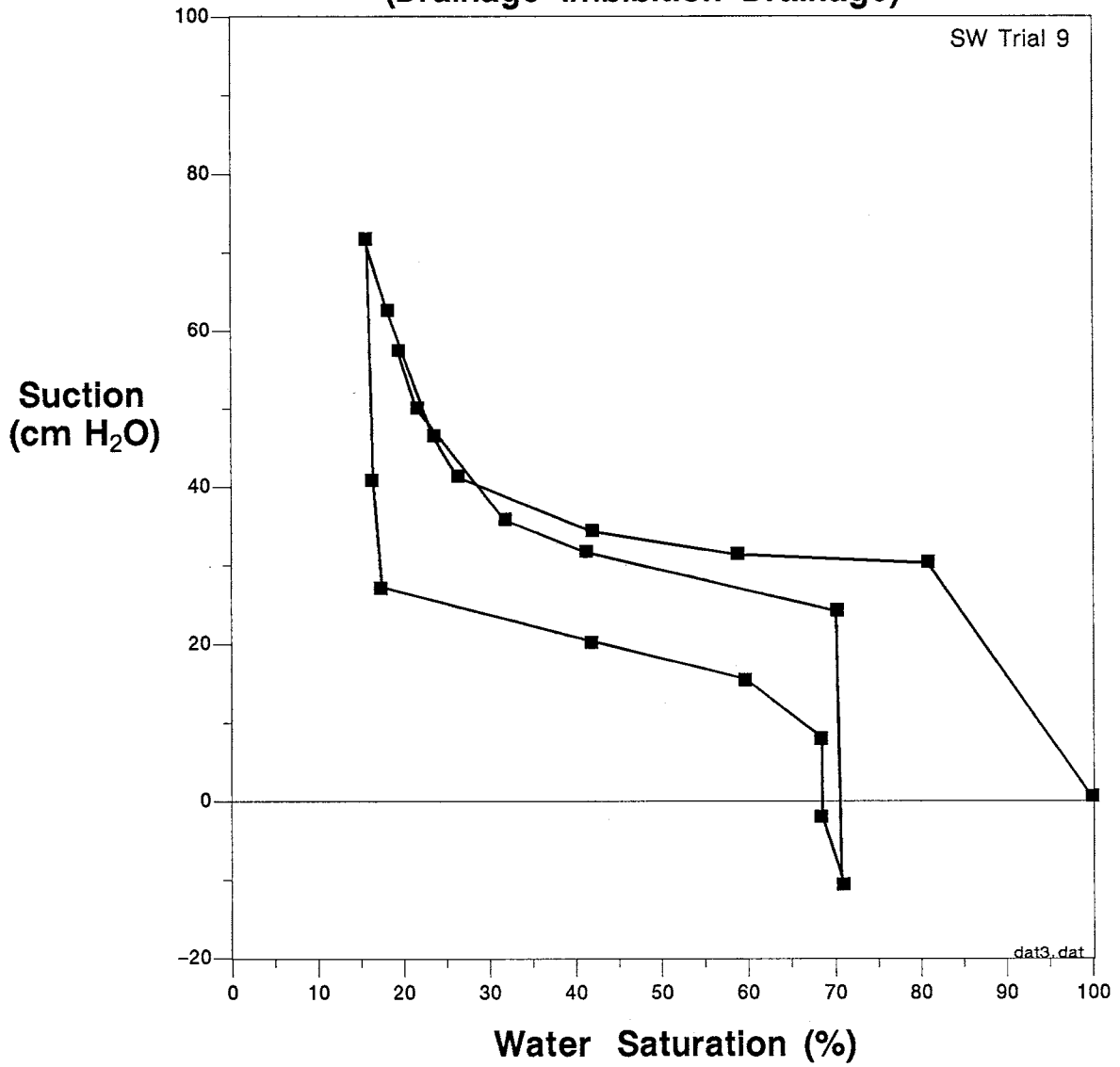
Saturation-Capillary Pressure Curves for Sevilleta Sand Experiments



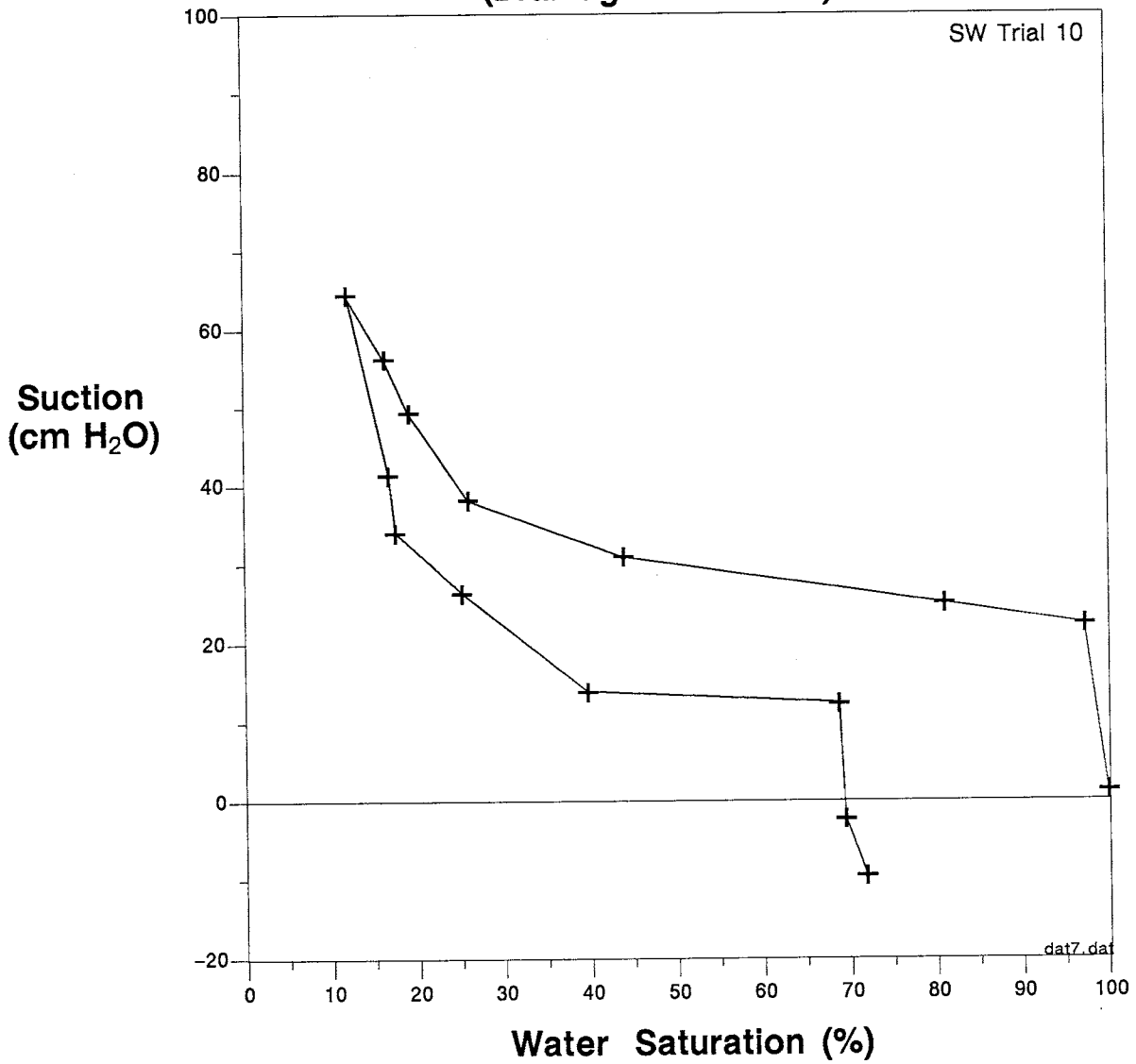
### Soltrol-Water Saturation Curve (Drainage-Imbibition-Drainage)



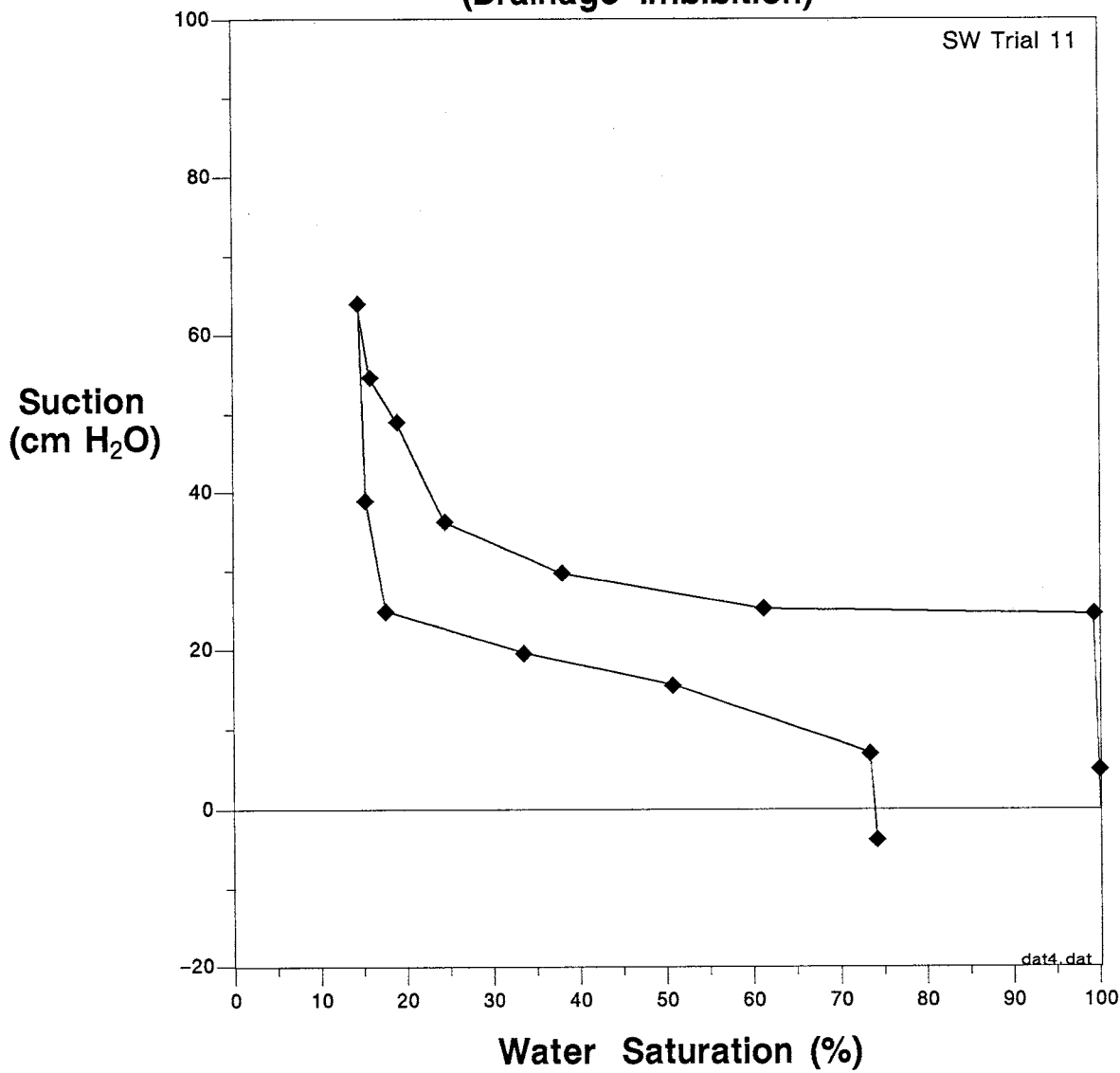
### Soltrol-Water Saturation Curve (Drainage-Imbibition-Drainage)



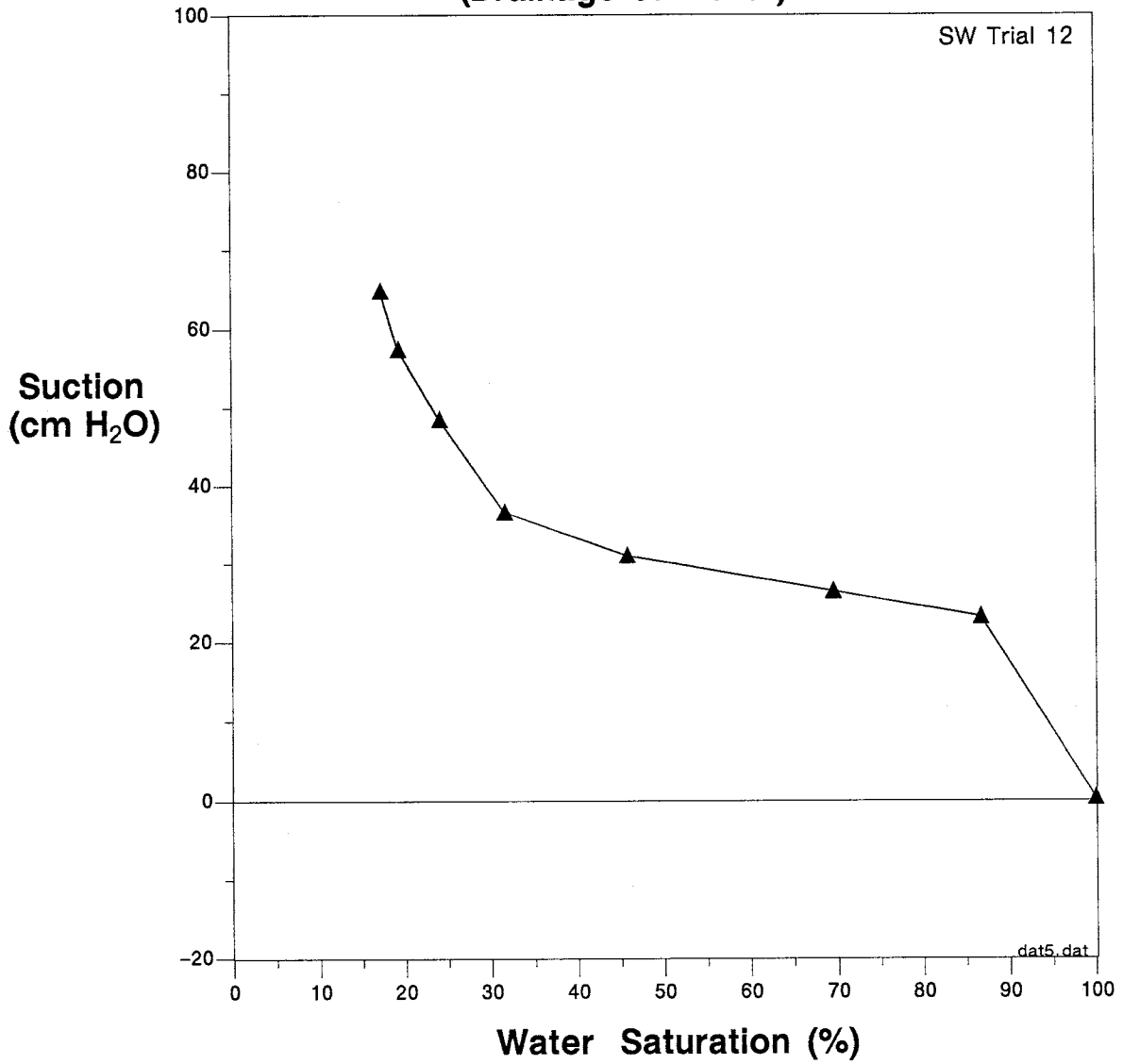
### Soltrol-Water Saturation Curve (Drainage-Imbibition)



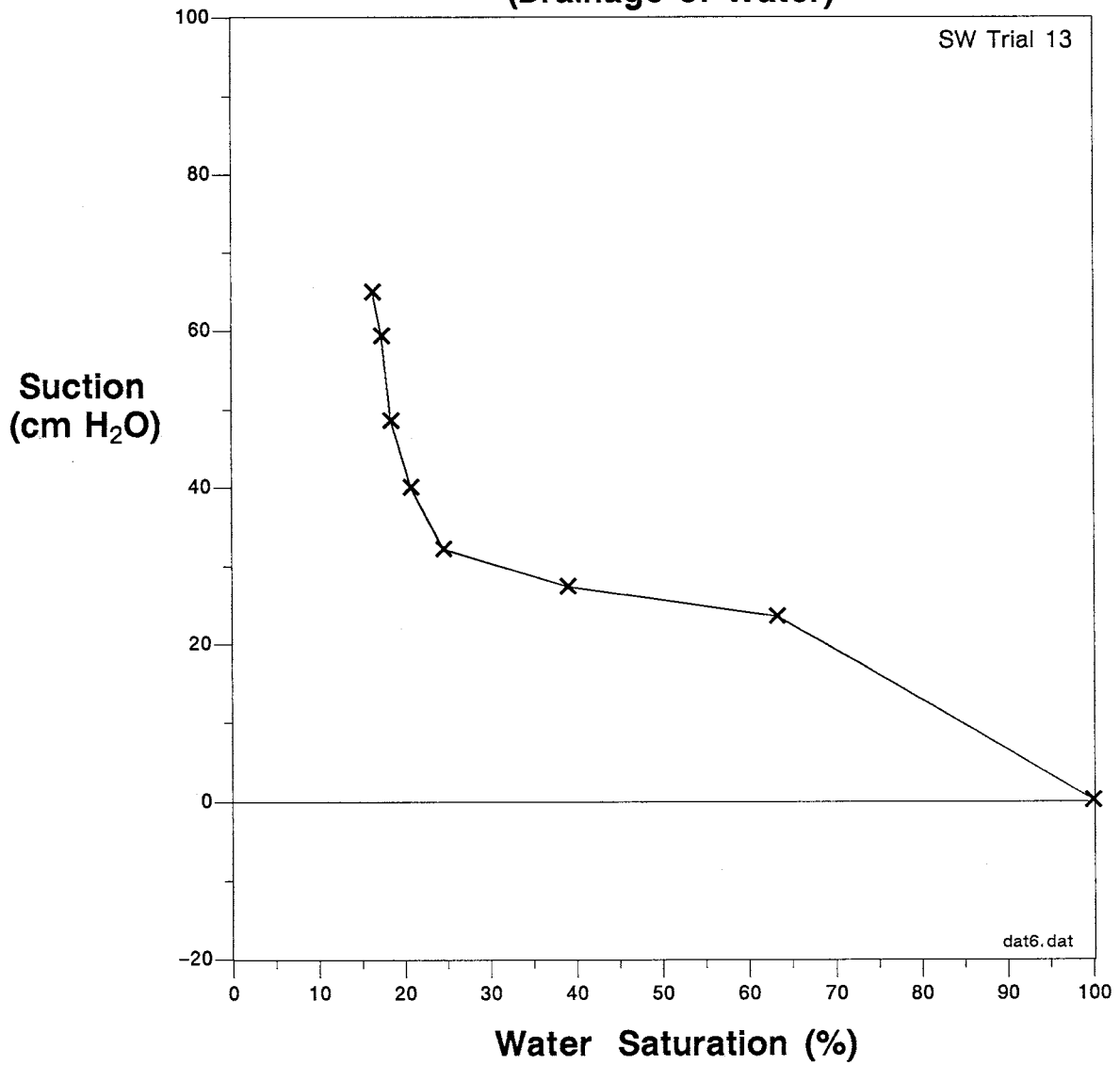
### Soltrol-Water Saturation Curve (Drainage-Imbibition)



### Soltrol-Water Saturation Curve (Drainage of Water)

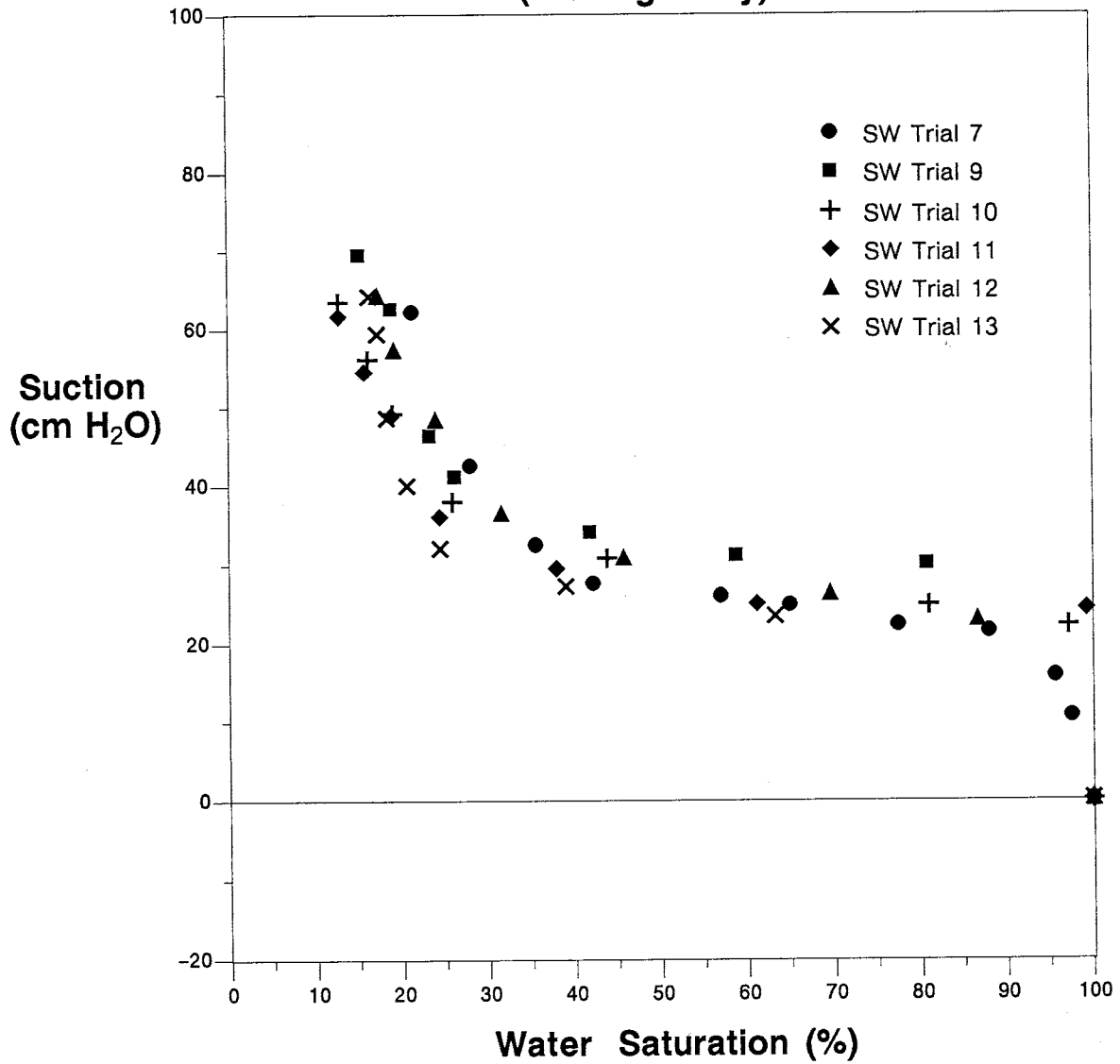


### Soltrol-Water Saturation Curve (Drainage of Water)

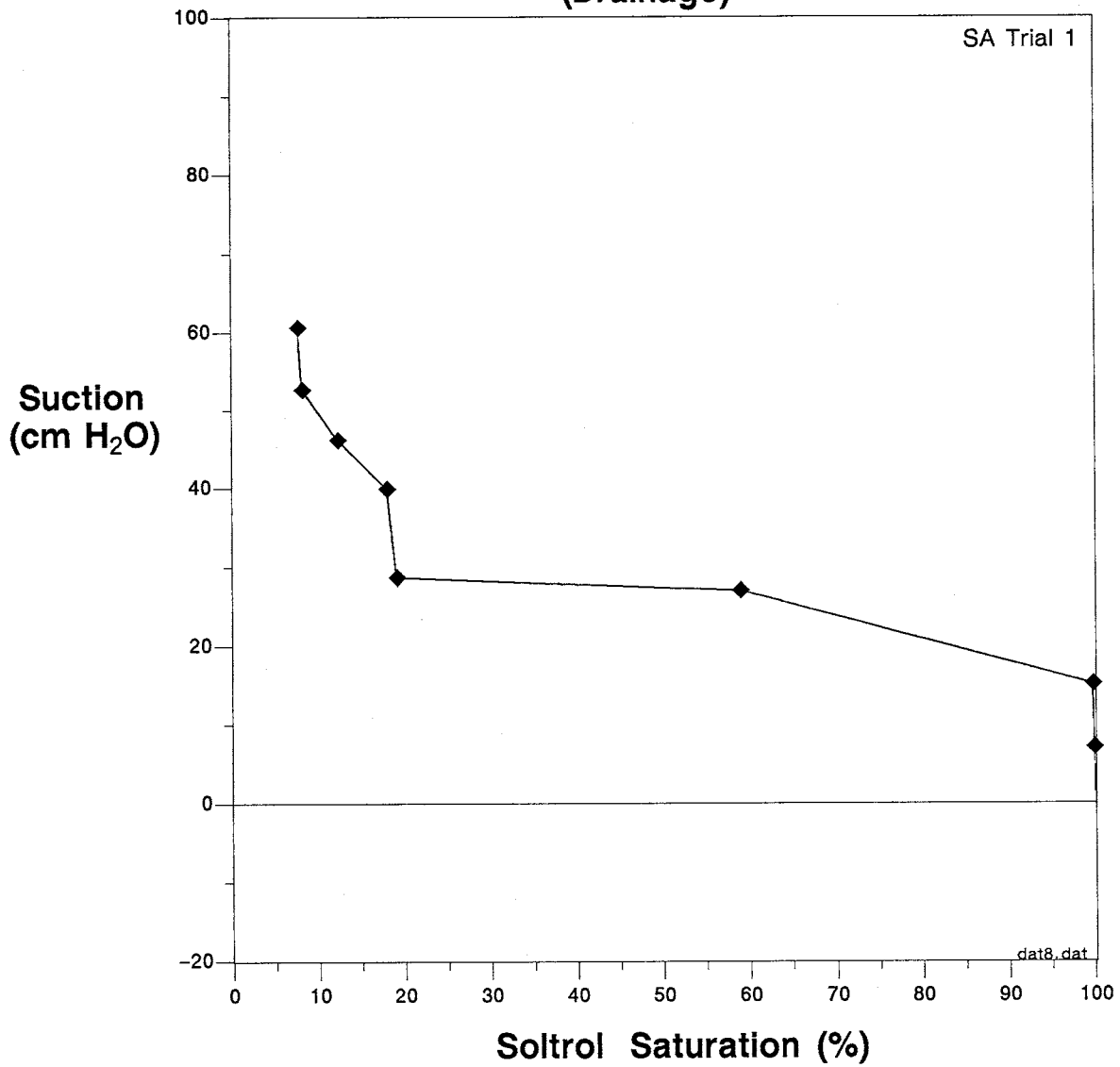




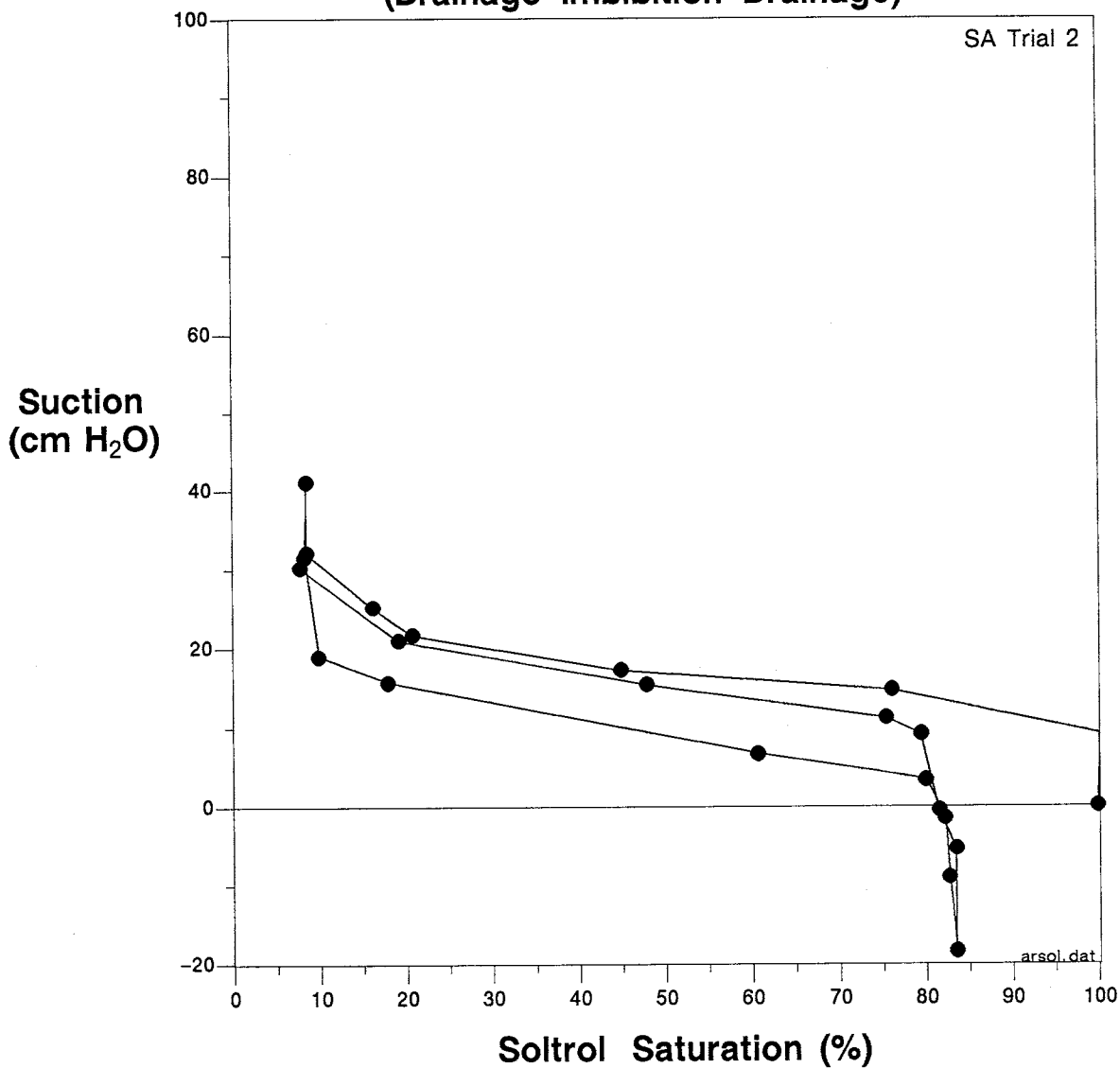
### Soltrol-Water Saturation Curves (Drainage only)



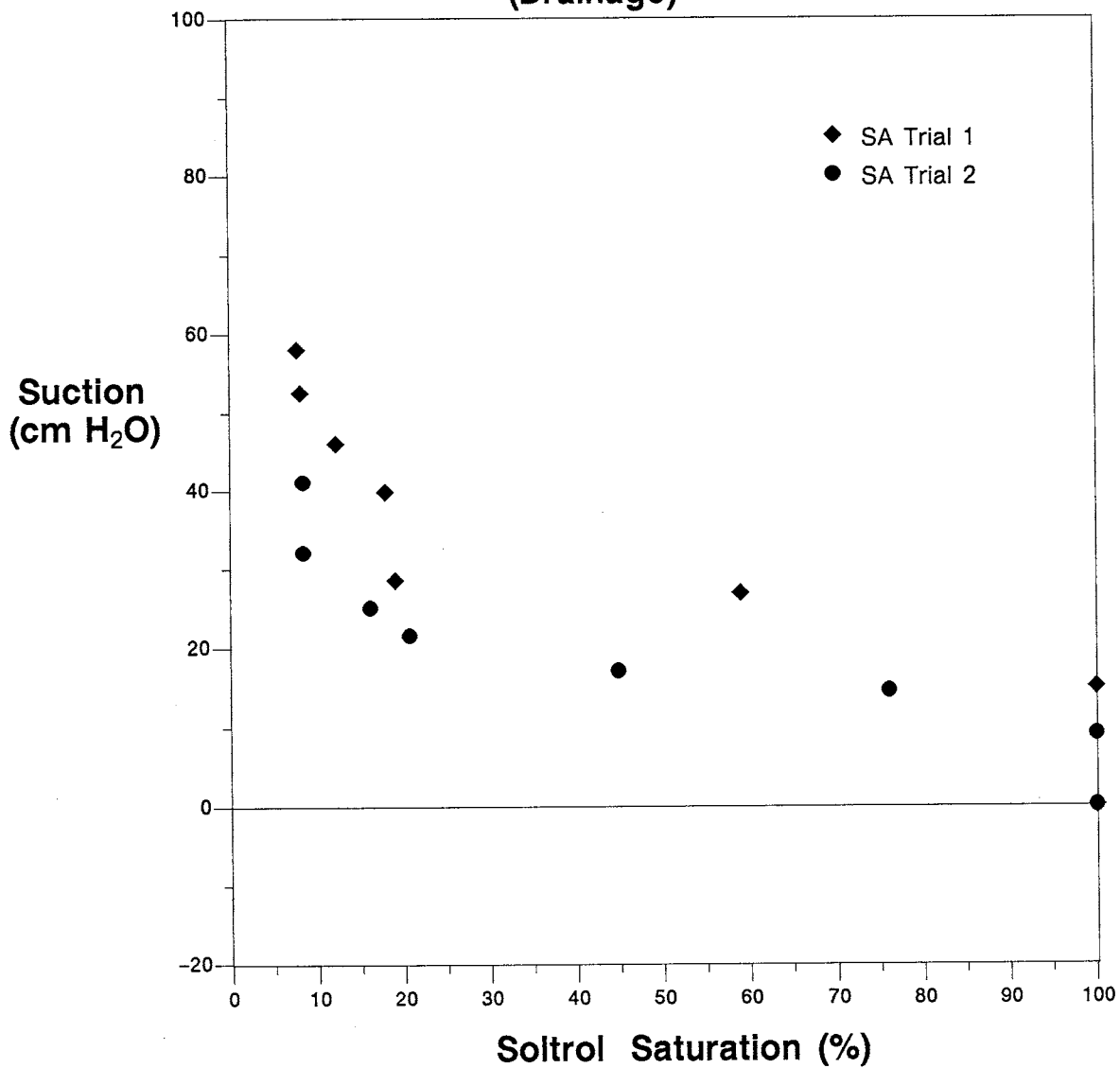
### Soltrol-Air Saturation Curve (Drainage)



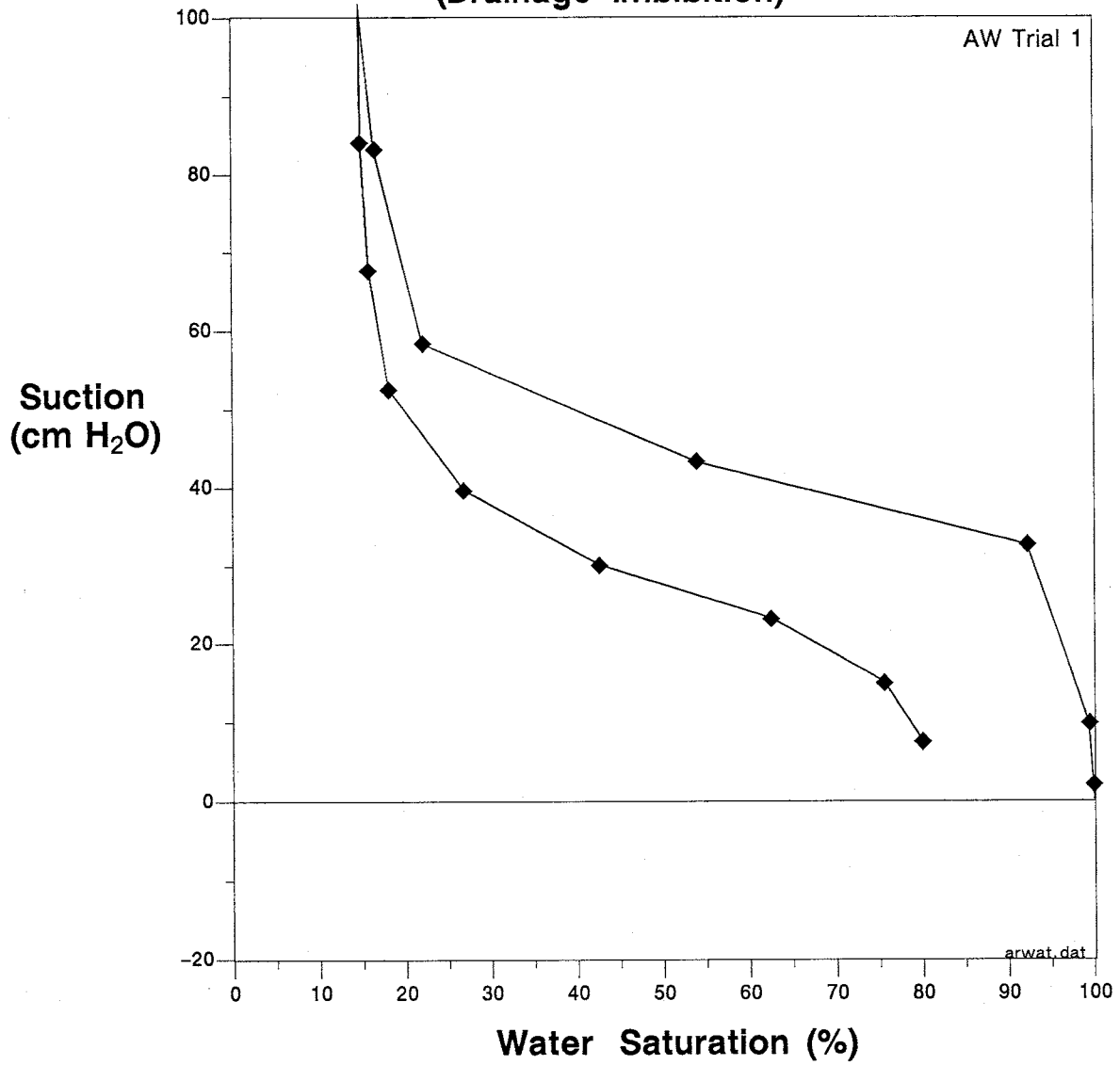
### Soltrol-Air Saturation Curve (Drainage-Imbibition-Drainage)



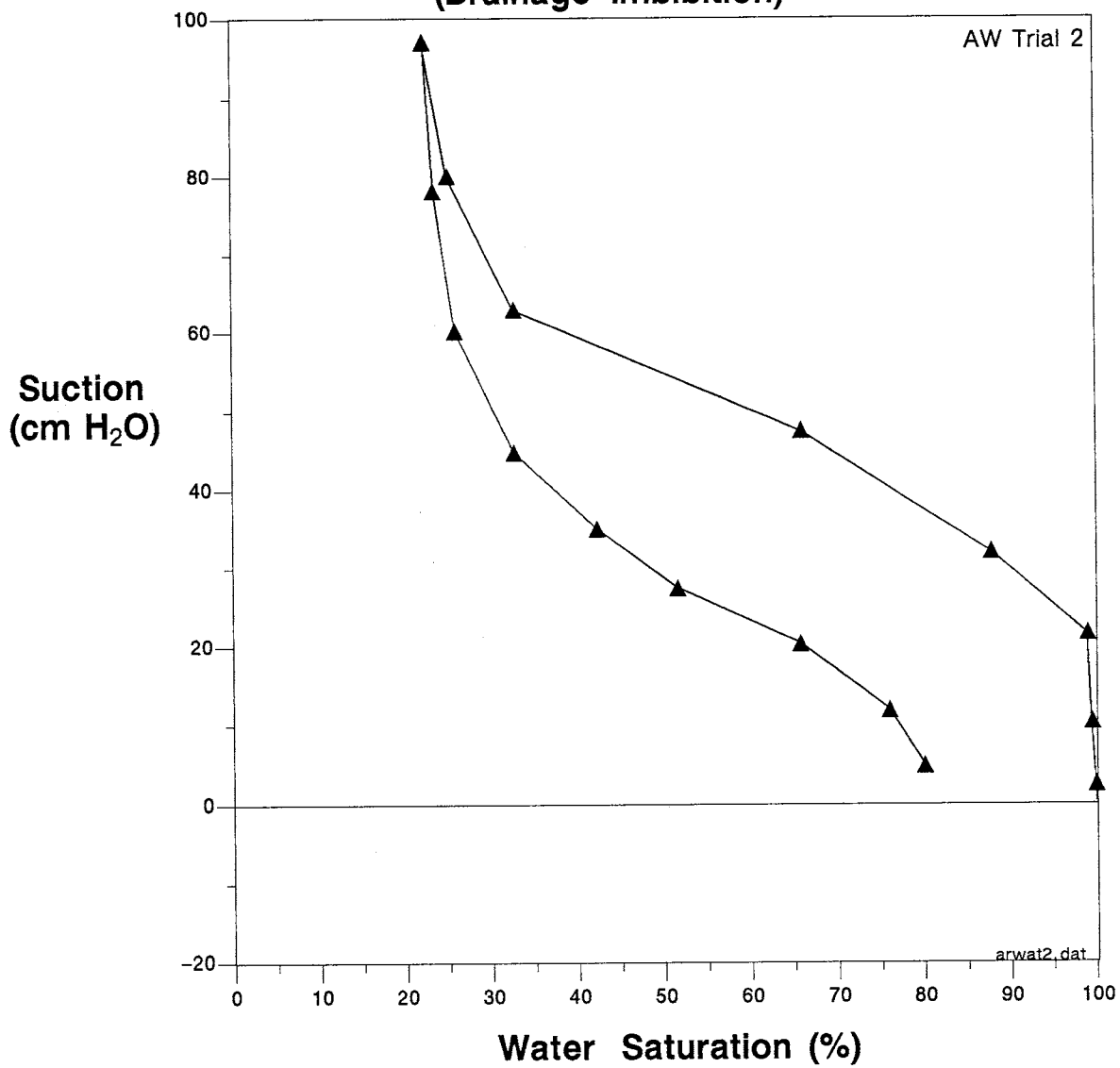
### Soltrol-Air Saturation Data (Drainage)



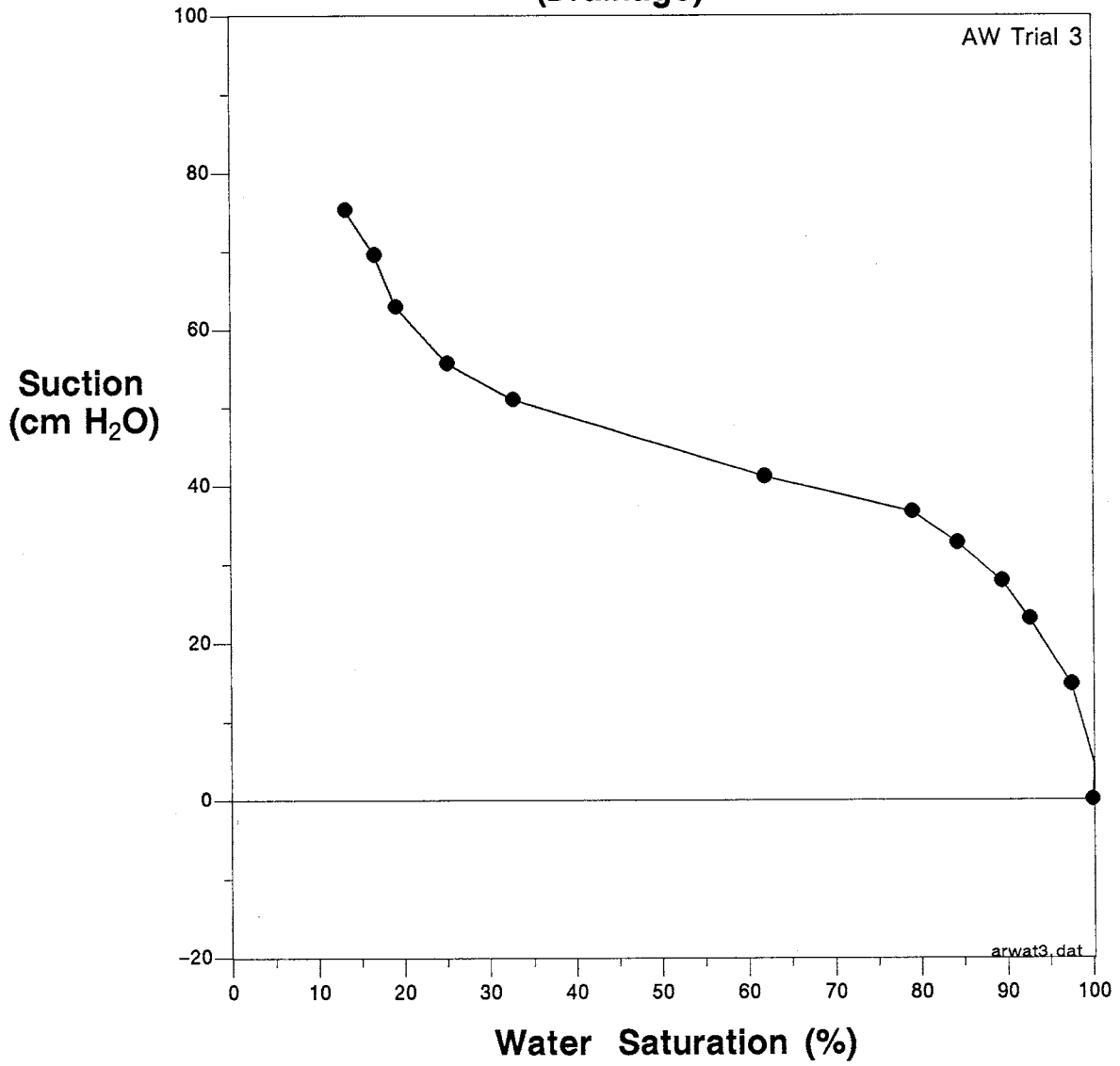
### Air-Water Saturation Curve (Drainage-Imbibition)



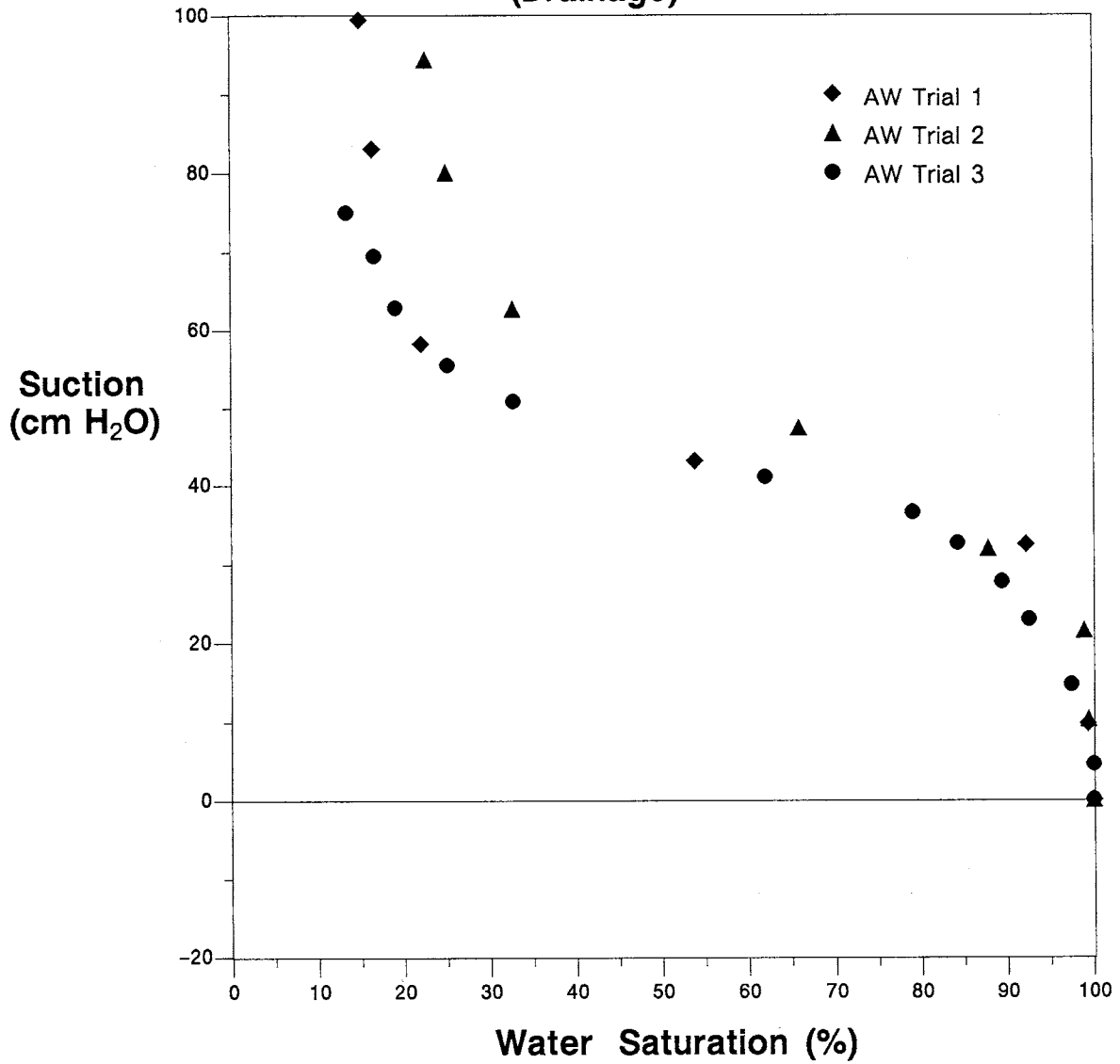
### Air-Water Saturation Curve (Drainage-Imbibition)



### Air-Water Saturation Curve (Drainage)



### Air-Water Saturation Data (Drainage)





The following data was used in the formation of the previous saturation-capillary curves. Saturations are given in percent of void volume. The capillary pressures are in equivalent cm of water, and the temperature is in °C at time of measurement.

SW Trial 7			SW Trial 8		
<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	26.5	100	0	22
97.6	10.5	26	97.6	35.1	24
95.7	15.7	25	26.5	49.6	24.5
88	21.5	24	22	60.9	24
77.5	22.3	23	-- Primary Imbibition --		
65	24.8	24	26.7	28.6	24.5
57	26	24.5	49.9	19.8	23
42.3	27.6	25	66.6	14	27
35.6	32.5	27	68	1.9	28
28	42.5	28.5	69.3	-10.6	26
23	62.1	31	-- Secondary Drainage --		
-- Primary Imbibition --			68.3	4.3	21.5
23.1	30	31	68.1	21.8	20.5
45.6	15.7	31	63.9	33.3	20
56.4	12.7	28.5	43.5	35.8	20
68.9	7.2	18.5	28.7	39.1	18.3
71.6	-0.4	19	26.3	28.8	20
73.2	-5.7	20	23	60.4	23
			22	67.4	21.5

SW Trial 9

SW Trial 10

<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	24	100	0	23
80.8	30	24.5	97.2	22.2	23.2
58.8	31.1	25.5	81	24.8	20.5
41.9	34.1	24	43.9	30.8	21.5
26.2	41.1	24.5	25.9	38	20.5
23.3	46.3	20	19	49.1	21.8
18	62.5	24	16.2	56.1	21.3
16	69.5	24.5	12.3	63.4	21.8
-- Primary Imbibition --			-- Primary Imbibition --		
16.6	40.8	25.5	16.8	41.3	21.8
17.6	27.3	23	17.6	34.1	20.8
41.9	20.5	27	25.2	26.4	23
59.8	15.6	28	39.7	13.9	20
68.7	8	22	68.8	12.4	22
68.7	-2	22.5	69.5	-2.4	22.5
70.6	-8.6	21.5	71.8	-9.3	19.5
-- Secondary Drainage --					
70	24	20.5			
41.2	31.4	20			
31.7	35.6	20			
21.4	49.8	18			
19.5	56.4	20			
15.7	66.5	20.5			

SW Trial 11

SW Trial 12

<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	23.2	100	0	24.5
99.3	24.3	21.6	86.7	23	24.5
61.2	25	20.5	69.6	26.3	26.8
38	29.5	21.5	45.8	30.9	25.8
24.4	36.1	20.5	31.6	36.5	26.4
18.9	48.8	21.8	24	48.4	24.8
15.8	54.5	21.3	19.2	57.3	27.6
14.7	61.6	21.7	17.3	64.3	25.6
-- Primary Imbibition --					
15.4	38.9	21.8			
17.7	24.9	20.8			
33.6	19.6	23			
50.8	15.6	20			
73.5	7	22			
74.2	-2.1	22.5			

SW Trial 13

SA Trial 1

<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	24.5	100	0	23
63.3	23.4	26.8	99.7	15	21.5
39.1	27.2	25.8	59	26.8	22.4
24.5	32	26.4	19	28.5	22.8
20.7	40	24.8	17.9	39.8	22
18.4	48.5	27.6	12.2	46	22
17.3	59.3	25.6	8.1	52.5	22.6
16.4	64.1	28.2	7.8	58	22

SA Trial 2

AW Trial 1

<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	21.3	100	0	26.9
100	9	21.8	99.3	9.7	23.3
76.1	14.5	21.2	92.2	32.5	25
44.9	17	22	53.9	43.1	25
20.7	21.5	22.2	22	58.2	24
16.1	25	22.2	16.4	83.1	18.4
8.4	32	22	14.9	99	16.8
8.4	41	22	-- Primary Imbibition --		
-- Primary Imbibition --			15	84	15.6
8.4	31.5	22	15.9	67.6	18.6
10	19	22	18.2	52.5	24.2
17.9	15.7	22	26.9	39.7	24.6
60.7	6.7	22	42.7	30.2	26.2
80.1	3.4	22	62.6	23.2	26.8
82.3	-1.5	22.6	75.7	14.9	22.2
82.8	-9.1	22	80	7.7	21
83.4	-15.5	22.5			
-- Secondary Drainage --					
83.4	-5.5	22.8			
81.4	-0.6	22.9			
79.4	9	22.7			
75.4	11	23			
47.9	15.2	23			
19.1	20.8	23.5			
7.8	30	22.5			

AW Trial 2

AW Trial 3

<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>	<u>Saturation</u>	<u>Capillary Pressure</u>	<u>Temperature</u>
-- Primary Drainage --			-- Primary Drainage --		
100	0	27	100	0	24.9
99.4	10.2	23.3	100	4.5	24.3
98.9	21.5	24	97.4	14.7	24
87.8	31.9	25	92.6	22.9	25.1
65.9	47.3	25	89.4	27.7	24.6
32.7	62.7	18.4	84.3	32.6	24
25	80	16.8	79.1	36.5	27
22.6	94.4	15.6	62	41	24.6
-- Primary Imbibition --			-- Primary Imbibition --		
23.6	78.1	18.6	32.8	50.8	24.4
26	60.1	24.2	25.1	55.5	24.4
32.8	44.8	24.6	19.1	62.8	26.1
42.4	35.1	26.2	16.6	69.5	26
51.7	27.5	26.8	13.4	75	22.9
65.8	20.4	22.2			
76.1	11.9	21			
80.1	5	20			

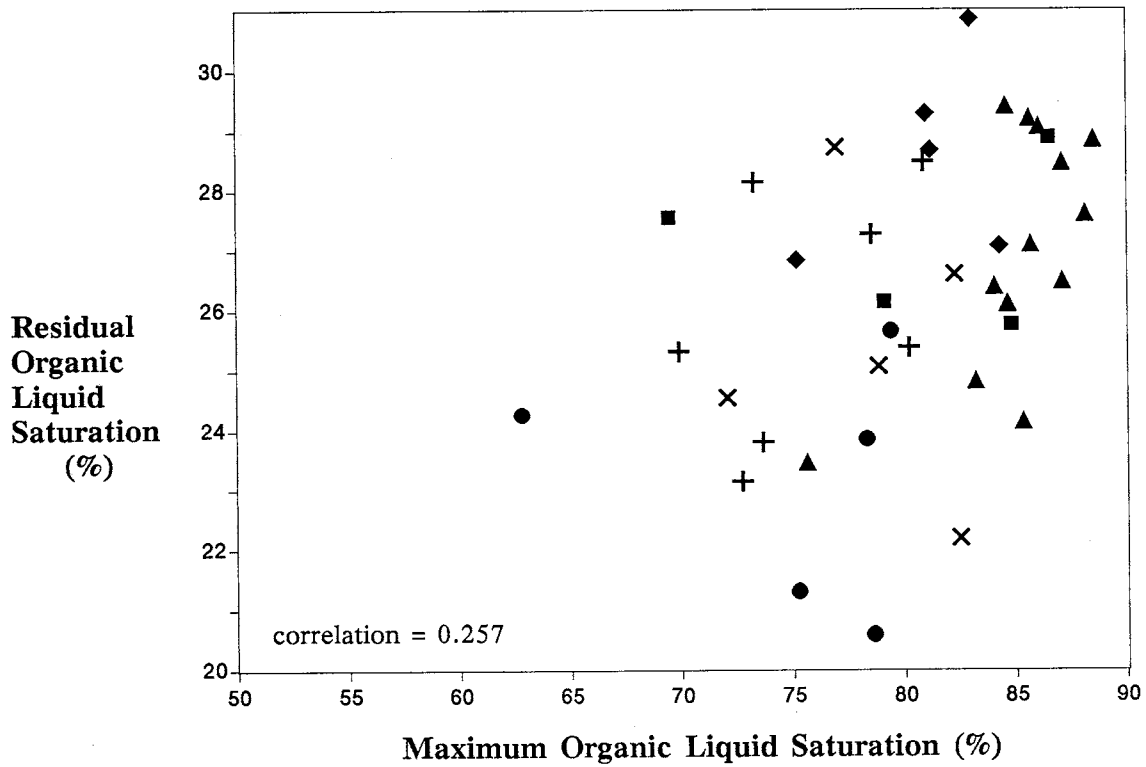
# APPENDIX H

## Residual Saturation

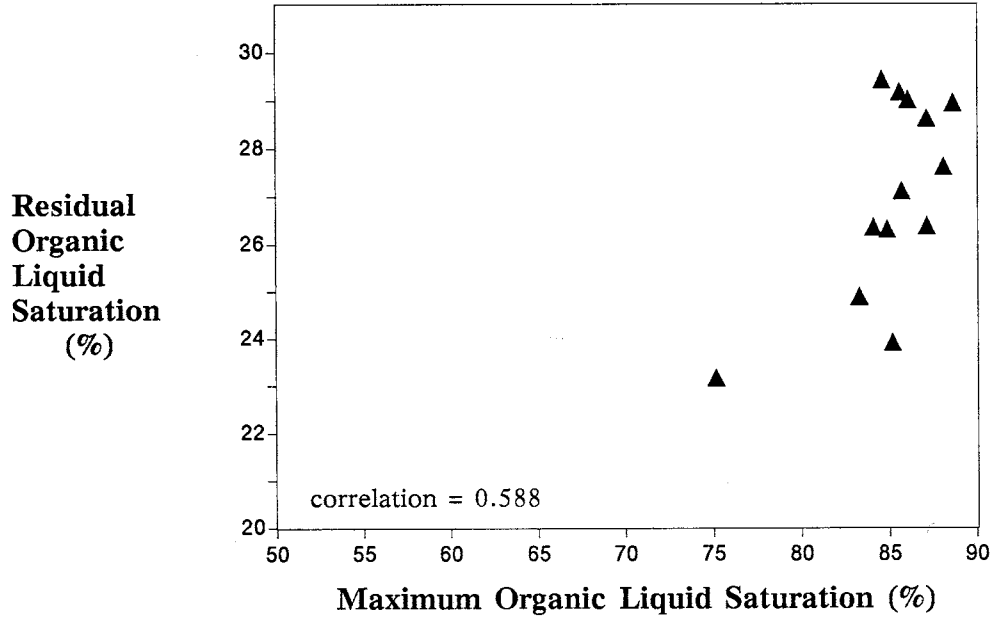
vs

## Maximum Organic Liquid Saturation

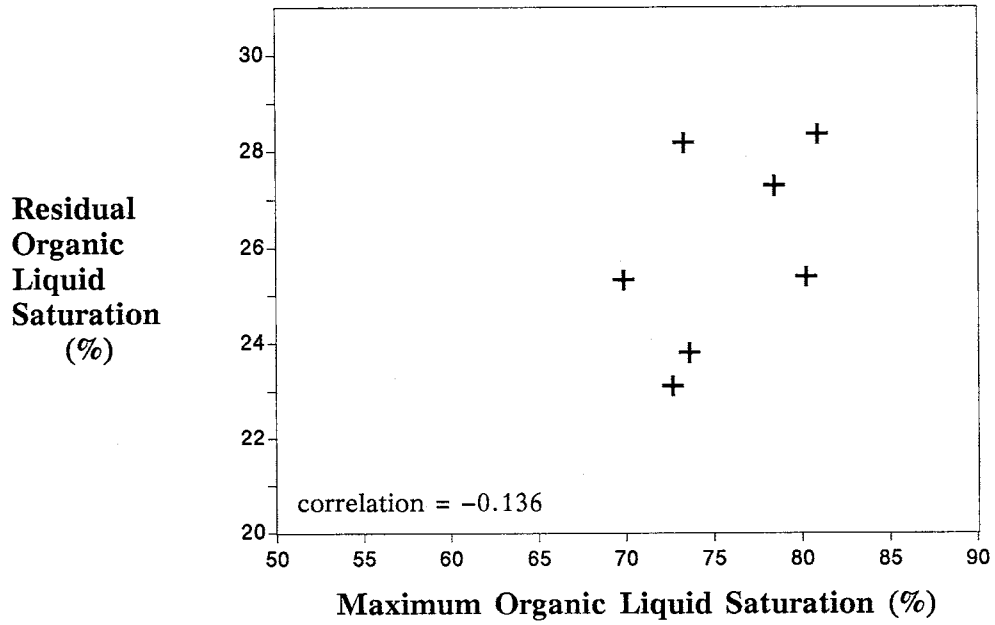
All experiments

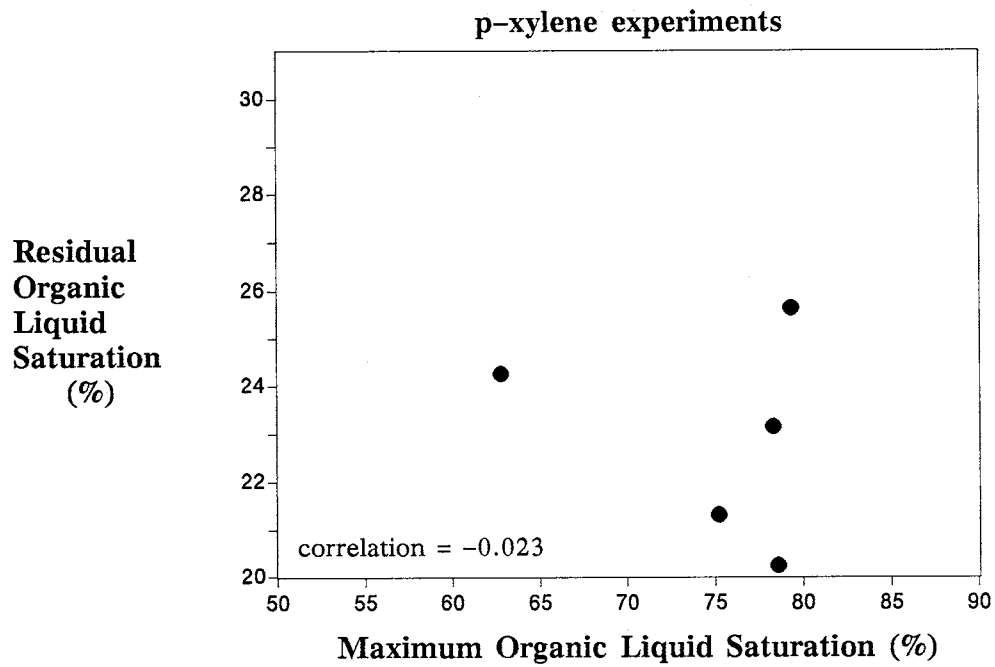
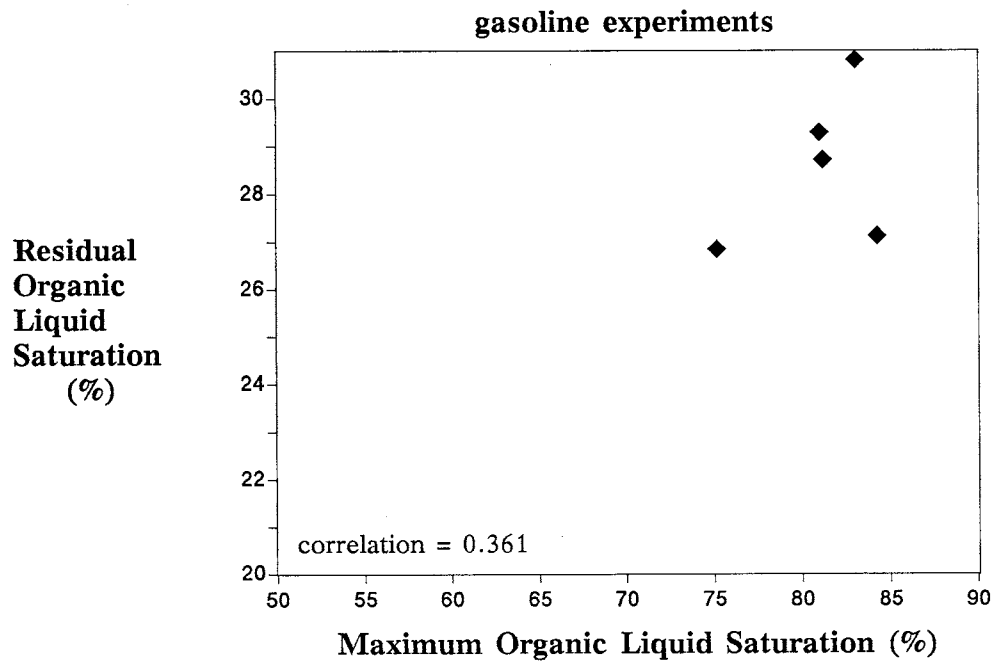


### Soltrol experiments



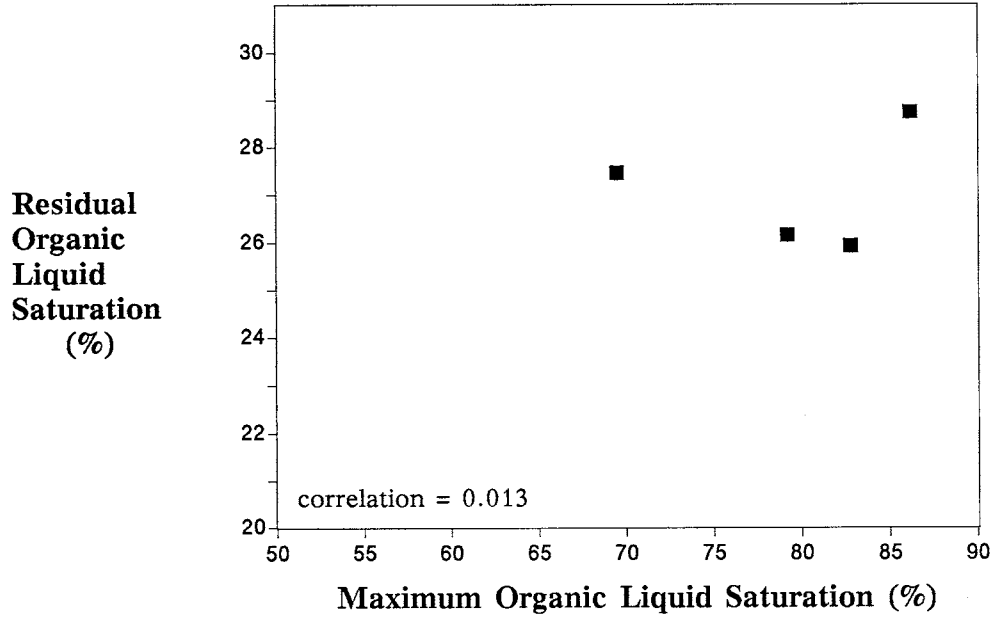
### kerosene experiments



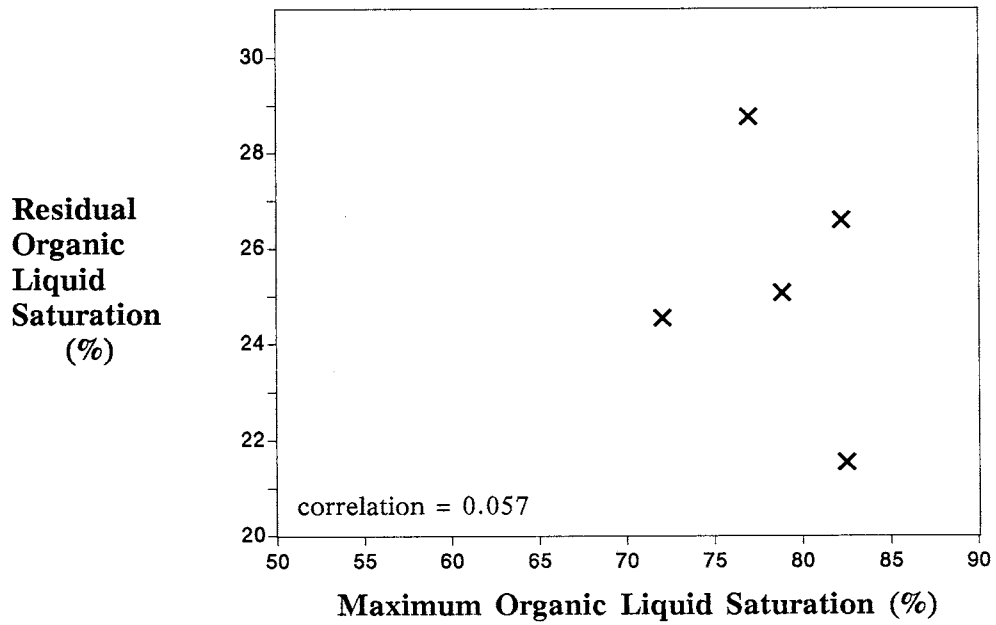




### PCE experiments



### n-decane experiments



**APPENDIX I**  
**COMPUTER PROGRAMS**

**Program used to calculate two-phase residual saturations**

```
C THIS PROGRAM CALCULATES 2 PHASE RESIDUAL SATURATIONS AND OTHER
C RELEVANT VALUES AND ASSOCIATED ERRORS.
C NAMED BLOB2.FOR ON HYDROVAX
c CORRECT VERSION AS OF FEB 1, 1989
c PROGRAM INPUT - READS FROM A DATA FILE
C PROGRAM OUTPUT - TO FILE OF YOUR CHOICE
C WRITTEN BY ED HAGAN
C
c      DENSITY OF SILICON GLUE =1.04
C      DENSITY OF CLEAR GLUE= 1.10
C      DENSITY OF WHITE GLUE = 1.84
C      DENG=DENSITY OF GLUE USED TO GLUE FILTERS ON TOP ENDCAP
c      ERDENG = ERROR IN GLUE DENSITY MEASUREMENT
c
c *****
c      CHARACTER FILNAM*10,OUTNAM*10
c      REAL Me,Mw,Mglue,msand,Msat,Mos,Msor
C
C      ENTER DENSITY OF GLUE USED ON TOP ENDCAP
C
C      WRITE(6,*)'DENSITY OF GLUE USED ON TOP ENDCAP, error'
C      READ(5,*)DENG,ERDENG
C
C *** CHECK IF SCRIMS ARE USED ON TOP ENDCAP ***
C
C      VSCRM=VOLUME OF TWO POLYPROPYLENE SCRIMS
C
C      WRITE(6,*)' WERE SCRIMS USED ON TOP ENDCAP,YES=1,NO=2'
C      READ(5,*)Z2
C      IF (Z2 .EQ. 1) GO TO 888
C      VSCRM=0.0
C      ERSCRM=0.0
C      GO TO 787
888      VSCRM=0.34
C      EVSCRM=0.02
C
```

```

787 WRITE(6,*)'ENTER INPUT FILE NAME'
    READ(5,901) FILNAM
    OPEN(UNIT=98,FILE=FILNAM,STATUS='OLD',READONLY)
c
    WRITE(6,*)'ENTER OUTPUT FILE NAME'
    READ(5,901) OUTNAM
    OPEN(UNIT=89,FILE=OUTNAM,STATUS='NEW')
901 FORMAT(A)
902 FORMAT(/6X,'INPUT FILE = ',A,4X,'OUTPUT FILE = ',A/)
    WRITE(89,902)FILNAM,OUTNAM
    WRITE(6,902)FILNAM,OUTNAM
C
C
C DATA VARIABLES READ FROM INPUT FILE
C
c VGROV= measured groove volume in top endcap,error
    READ(98,*)VGROV,EVGROV
    WRITE(89,11)VGROV,EVGROV
C Me=Mass of column empty,error
    READ(98,*)ME,ERME
    WRITE(89,11)ME,ERME
c MW=Mass of column water saturated,error
    READ(98,*)MW,ERMW
    WRITE(89,11)MW,ERMW
c Mglue=mass of glue on top endcap
    READ(98,*)MGLUE,ERGLUE
    WRITE(89,11)MGLUE,ERGLUE
c Pdens=particle density of soil,error
    READ(98,*)PDENS,EPDENS
    WRITE(89,11)PDENS,EPDENS
c dens=density difference of liquids,error
    READ(98,*)DENS,ERDENS
    WRITE(89,11)DENS,ERDENS
c Pstmrk=distance shy of alignment mark,error
    READ(98,*)PSTMRK,EPSTMK
    WRITE(89,11)PSTMRK,EPSTMK
c Msand=mass of sand
    READ(98,*)MSAND,ERSAND
    WRITE(89,11)MSAND,ERSAND
c Msat=mass of soil column de-aired,error
    READ(98,*)MSAT,ERMSAT
    WRITE(89,11)MSAT,ERMSAT

```

```

c Mos=mass of column at max oil saturation,error
  READ(98,*)MOS,ERMOS
  WRITE(89,11)MOS,ERMOS
c Msor=mass of column at residual oil,error
  READ(98,*)MSOR,ERMSOR
  WRITE(89,11)MSOR,ERMSOR
11  FORMAT(2X,F8.3,4X,F6.3)
C
C ONE TURN DECREASES VOLUME BY 8.25 +/- 0.72 CM3 PG 26 STEVE'S BOOK3
C or one cm short of mark increases volume by .42+/-0.05 ml avg. of 3 columns
c
c      watden = density of water
      watden=1.000
c      erwat = error in water density measurement
      erwat=0.002
      VOL2=0.42*PSTMRK
      ERVOL=(EPSTMK/PSTMRK+.05/.42)*VOL2
      VPAP=.34
      ERVPAP=.02
C
c*****  CALCULATE THE VOLUME OF GLUE *****
      Vglue=Mglue/DENG
      ergluv=(erglue/mglue+erdeng/deng)*Vglue
c  *****  CALCULATE TOTAL VOLUME (VT)
      VT= (Mw-Me)/(watden)-Vglue-VGROV-VPAP-VSCRM+VOL2
      ErVT1=((Erme+ErMw)/(Mw-Me)+(erwat/watden))*((Mw-Me)/watden)
      ERVT=ERVT1+ergluv+EVGROV+ErVPAP+EvSCRM+ERVOL
C *****  CALCULATE VOID VOLUME (VV) *****
      VV=VT-(Msand/PDENS)
      ErVV=ErVT+(Ersand/msand+(EPDENS/PDENS))*(msand/PDENS)
C*****  CALCULATE POROSITY (POR) *****
      X1=(PDENS*VT)
      POR=1-Msand/X1
      X3=(EPDENS/PDENS+ErVT/VT)*X1
      ErPor=(X3/X1+Ersand/msand)*(msand/x1)
C *****  CALCULATE BULK DENSITY *****
      BULK=MSAND/VT
      ERBULK=BULK*(ERSAND/MSAND+ERVT/VT)
C *****  CALCULATE OIL SATURATION (SOIL) *****
      X4=Dens*VV
      SOIL=(Msat-Mos)/X4
      X5=(Erdens/dens+ErVV/VV)*X4

```

```

Ersoil=((Ermsat+Ermos)/(Msat-Mos)+X5/X4)*soil
C *****      CALCULATE RESIDUAL OIL (SOR)      *****
SOR=(Msat-Msor)/x4
ErSOR=(((ErMsat+ErMsor)/(Msat-Msor))+X5/X4)*SOR
write(89,5)VT,ERV
write(6,5)VT,ERV
5  FORMAT(/2X,'TOTAL VOLUME = ',F7.3,4X,'ERROR = ',F6.4)
WRITE(89,6)VV,ERVV
WRITE(6,6)VV,ERVV
6  FORMAT(/2X,'VOID VOLUME = ',F7.3,4X,'ERROR = ',F6.4)
WRITE(6,7)POR,ERP
WRITE(89,7)POR,ERP
7  FORMAT(/2X,'POROSITY = ',F7.3,4X,'ERROR = ',f6.4)
10 FORMAT(/2X,'BULK DENSITY = ',F7.3,6X,'ERROR = ',F6.4//)
WRITE(6,8)SOIL,ERSOIL
WRITE(89,8)SOIL,ERSOIL
8  FORMAT(/2X,'OIL SATURATION = ',F7.3,4X,'ERROR = ',F6.4)
WRITE(6,9)SOR,ERSOR
WRITE(89,9)SOR,ERSOR
9  FORMAT(/2X,'RESIDUAL OIL = ',F7.3,4X,'ERROR = ',F6.4)
write(89,10)bulk,erbulk
write(6,10)bulk,erbulk
STOP
END

```

### Program used to calculate Three-phase equilibrium saturations

```

C *****
C This program calculates 3 phase residual saturations and associated
c errors.
c Named blob3.for on Hydrovax computer
c updated Feb. 7, 1989
c program input - reads from a data file, or from the screen
c program output - to file of your choice
c written by Ed Hagan
C
c density of silican glue = 1.04
c density of clear glue = 1.10
c density of white glue = 1.84
c deng = density of glue used on top endcap
c erdeng = error in glue density measurement
c
c*****

```

```

C      CHARACTER FILNAM*10, outnam*10
      REAL Me,Mw,Mglue,msand,Msat,M1,M2,M3,M4,M2P,VWP,m3p
c
      write(6,*)' Enter density of glue used on top endcap, error'
      read(5,*)deng,erdeng
c
      write(6,*)' Does top endcap have scrims?, yes=1,no=2'
      read(5,*)Z2
      if(z2 .eq. 1) go to 888
      vscrm=0.0
      evscrm=0.00
      go to 887
888    vscrm=0.34
      evscrm=0.02
c
887    WRITE(6,*)'READ FROM A DATA FILE YES=1,NO=2'
      READ(5,*)ZX
      IF(ZX .EQ. 1) GO TO 101
c
      write(6,*)'ENTER VOLUME OF GROOVES IN TOP ENDCAP,ERROR'
      READ(5,*)VGROV,EVGROV
C
      write(6,*)'ENTER MASS OF COLUMN EMPTY,ERROR'
      READ(5,*)ME,ERME
C
      write(6,*)'ENTER MASS OF COLUMN WITH WATER,ERROR'
      READ(5,*)MW,ERMW
C
      write(6,*)'ENTER MASS OF GLUE ON TOP ENDCAP,ERROR'
      READ(5,*)MGLUE,ERGLUE
c
      write(6,*)'ENTER PARTICLE DENSITY OF SOIL,ERROR'
      READ(5,*)PDENS,EPDENS
c
      write(6,*)'ENTER DENSITY DIFFERENCE OF LIQUIDS,ERROR'
      READ(5,*)DENS,ERDENS
C
      write(6,*)'ENTER LENGTH IN CM SHORT OF MARK,ERROR'
      read(5,*)PSTMRK,EPSTMK
C
      write(6,*)'ENTER MASS OF SAND IN COLUMN,ERROR'

```

```

READ(5,*)MSAND,ERSAND
C
write(6,*)'ENTER MASS OF COLUMN SATURATED,ERROR'
READ(5,*)MSAT,ERMSAT
C
write(6,*)' MASS OF COLUMN AFTER H2O SUCTION m2,ERROR'
READ(5,*)M2,ERM2
C
write(6,*)'MASS OF COLUMN ENDCAP CHANGE m2p,ERROR'
READ(5,*)M2P,ERM2P
C
WRITE(6,*)'MASS AFTER OIL FLOOD m3,ERROR'
READ(5,*)M3,ERM3
C
WRITE(6,*)'VOLUME OF WATER PRODUCED vwp,ERROR'
READ(5,*)VWP,ERVWP
C
WRITE(6,*)'COLUMN END MASS m4,ERROR'
READ(5,*)M4,ERM4
c
GO TO 102
101 WRITE(6,*)'ENTER INPUT FILENAME'
READ(5,901)FILNAM
OPEN(UNIT=98,FILE=FILNAM,STATUS='OLD',READONLY)
901 FORMAT(A)
WRITE(6,*)' ENTER OUTPUT FILENAME'
READ(5,901)OUTNAM
OPEN(UNIT=89,FILE=OUTNAM,STATUS='NEW')
write(89,902)FILNAM,OUTNAM
902 FORMAT(/6X,'INPUT FILE = ',A,4X,'OUTPUT FILE = ',A/)
C
READ(98,*)VGROV,EVGROV
READ(98,*)ME,ERME
READ(98,*)MW,ERMW
READ(98,*)MGLUE,ERGLUE
READ(98,*)PDENS,EPDENS
READ(98,*)DENS,ERDENS
READ(98,*)PSTMRK,EPSTMK
READ(98,*)MSAND,ERSAND
READ(98,*)MSAT,ERMSAT
READ(98,*)M2,ERM2
READ(98,*)M2P,ERM2P

```

```

READ(98,*)M3,ERM3
READ(98,*)VWP,ERVWP
READ(98,*)M4,ERM4
C
C **** WATER AND SOLTROL DENSITIES ****
102    Pw=1.000
        Erpw=0.002
        Po=0.753
        Erpo=0.002
C
c    ONE TURN DECREASES VOLUME BY 8.25 +/- .72 CM3 PG 26 STEVE'S BOOK 3
c    or one cn short of mark increases volume by 0.42+/-0.05 ml
c    determined from average of 3 columns
c
        vol2=0.42*pstmrk
        ervol=(epstmk/pstmrk+0.05/0.42)*vol2
        VPAP=.34
        EVPAP=.02
C
c***** CALCULATE THE VOLUME OF GLUE *****
C
        Vglue=Mglue/deng
        ergluv=(erglue/mglue+erdeng/deng)*Vglue
C
c ***** CALCULATE TOTAL VOLUME (VT)
C
        VT=(MW-ME)/pw-VGLUE-VGROV-VPAP-VSCRM+VOL2
        ErVT1=((Erme+ErMw)/(Mw-Me)+(erpw/pw))*((Mw-Me)/pw)
        ERVT=ERV1+ergluv+EVGROV+EVPAP+EvSCRM+ERVOL
C
C ***** CALCULATE VOID VOLUME (VV) *****
C
        VV=VT-(MSAND/PDENS)
        ERVV=ERV1+(ERSAND/MSAND+(EPDENS/PDENS))*(MSAND/PDENS)
C
C***** CALCULATE POROSITY (POR) *****
C
        X1=(PDENS*VT)
        POR=1-MSAND/X1
        X3=(EPDENS/PDENS+ERV1/VT)*X1
        ERPOR=(X3/X1+ERSAND/MSAND)*(msand/x1)
C

```



```

C ***** CALCULATE BULK DENSITY (BULK) *****
C
      BULK=MSAND/VT
      ERBULK=BULK*(ERSAND/MSAND+ERVV/VT)
C
C***** 2 PHASE STUFF *****
C *****CALCULATE OIL SATURATION (SOIL) ***** *
c      X4=DENS*VV *
c      SOIL=(MSAT-MOS)/X4 *
C      X5=(ERDENS/DENS+ERVV/VV)*X4 *
C      ERSOIL=((ERMSAT+ERMOS)/(MSAT-MOS)+X5/X4)*SOIL *
C ***** CALCULATE RESIDUAL OIL (SOR) ***** *
C      SOR=(MSAT-MSOR)/X4 *
C      ERSOR=((ERMSAT-ERMOS)/(MSAT-MSOR)+X5/X4)*SOR *
C*****
C
C *****CALCULATE AIR SATURATION AFTER WATER SUCTION *****
C
      M1=MSAT-VGROV
      write(6,*)m1,m2
20  format(2x,f7.3,3x,f7.3)
      ERM1=ERMSAT+EVGROV
      SA=(M1-M2)/(PW*VV)
      ERVPW=(ERPW/PW+ERVV/VV)*(VV*PW)
      ERSA=((ERM1+ERM2)/(M1-M2)+ERVPW/(pw*vv))*SA
C
C ** CALCULATE INITIAL WATER SATURATION AFTER WATER SUCTION **
C
      SWI=1-SA
      ERSWI=ERSA
C
C*** CALCULATE WATER SAT AFTER OIL FLOOD *****
C
      SW=SWI-VWP/VV
c
c***** IF NO WATER IS PRODUCED SET VOX = 0.0 *****
c
      if(vwp .eq. 0.0) go to 505
      vox=ervwp/vwp
      go to 506
505  vox=0.0
506  ERSW=(VWP/VV)*((vox)+ERVV/VV)+ERSA

```

```

c
C** CALCULATE OIL SAT. AFTER OIL FLOOD *****
c
M3P=M3-VGROV*PO
ERM3P=ERM3+(VGROV*PO)*(EVGROV/VGROV+ERPO/PO)
SO=(M3P-M2P+(PW*VWP))/(PO*VV)
ERVPO=(ERPO/PO+ERVV/VV)*(PO*VV)
PWVWP=PW*VWP
POVV=PO*VV
ervpw=(erpw/pw+vox)*pwwwp
ERSx=((erm3p+erm2p+ervpw)/(m3p-m2p+(pwwwp)))
erso=(ersx+ervpo/povv)*so
c
C *** CALCULATE AIR SAT. AFTER OIL FLOOD *****
c
SA2=1-SO-SW
ERSA2=ERSO+ERSW
c
C ** CALCULATE RESIDUAL OIL SAT. AFTER OIL SUCTION ****
c
SOR=(M4-M2P+PWVWP)/POVV
erdx=(erm4+erm2p+ervpw)/(m4-m2p+(pwwwp))
ersor=(erdx+ervpo/povv)*sor
c
c ** CALCULATE FINAL AIR SATURATION *****
c
FAS=1-SOR-SW
ERFAS=ERSOR+ERSW
c
c ***** SET UP OUTPUT FORMAT *****
C
write(6,5)VT,ERVV
write(89,5)VT,ERVV
5 FORMAT(/2X,'TOTAL VOLUME = ',F7.3,4X,'ERROR = ',F6.4)
write(6,6)VV,ERVV
WRITE(89,6)VV,ERVV
6 FORMAT(/2X,'VOID VOLUME = ',F7.3,7X,'ERROR = ',F6.4)
write(6,7)POR,ERPOR
WRITE(89,7)POR,ERPOR
7 FORMAT(/2X,'POROSITY = ',F7.3,10X,'ERROR = ',f6.4)
write(6,10)bulk,erbulk
write(89,10)bulk,erbulk

```

```

10      format(/2x,'BULK DENSITY = ',F7.3,6X,'ERROR = ',F6.4)
C      write(6,8) SA,ERSA
      WRITE(89,8)SA,ERSA
8      FORMAT(/2X,'AIR SATURATION = ',F7.3,4X,'ERROR = ',F6.4)
      WRITE(89,9)SWI,ERSWI
C      write(6,9)SWI,ERSWI
9      FORMAT(/2X,'INITIAL WATER SAT. = ',F7.3,6X,'ERROR = ',F6.4)
      WRITE(89,11)SW,ERSW
C      WRITE(6,11)SW,ERSW
11     FORMAT(/2X,'WATER SAT./OIL FLOOD = ',F7.3,4X,'ERROR= ',F6.4)
      WRITE(89,12)SO,ERSO
C      WRITE(6,12)SO,ERSO
12     FORMAT(/2X,'OIL SAT.AFTER OIL FLOOD= ',F7.3,4X,'ERROR= ',F6.4)
      WRITE(89,13)SA2,ERSA2
C      WRITE(6,13)SA2,ERSA2
13     FORMAT(/2X,'AIR SAT. OIL FLOOD = ',F7.3,4X,'ERROR=',F6.4)
      WRITE(89,15)SOR,ERSOR
C      WRITE(6,15)SOR,ERSOR
15     FORMAT(/2X,'RESIDUAL OIL SAT = ',F7.3,4X,'ERROR= ',F6.4)
      WRITE(89,14)FAS,ERFAS
C      WRITE(6,14)FAS,ERFAS
14     FORMAT(/2X,'AIR SAT.AFTER OIL SUCTION= ',F7.3,4X,'ERROR= ',F6.4)
      STOP
      END

```

## APPENDIX J

### Raw Data From Two-Phase Experiments

TWO-PHASE COREFLOOD DATA

INPUT DATA

trial #	in box?	from:	to:	soil	organic	aqueous	FLUIDS	organic	aqueous	DENSITIES	organic	aqueous	particle	empty	COLUMN MASS	organic	aqueous	sol	mass
1	no	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
2	no	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
3	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
4	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
5	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
6	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
7	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
8	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
9	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166
10	yes	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166	166

trial #	glue mass	glue dens	filter vol	TO FIND CORE VOLUME	groove vol	shy of mk	EXPERIMENTAL MASSES	at start	at stop	EXTRAS	temp range	I-TEMP
1	166	166	166	166	166	166	166	166	166	166	166	166
2	166	166	166	166	166	166	166	166	166	166	166	166
3	166	166	166	166	166	166	166	166	166	166	166	166
4	166	166	166	166	166	166	166	166	166	166	166	166
5	166	166	166	166	166	166	166	166	166	166	166	166
6	166	166	166	166	166	166	166	166	166	166	166	166
7	166	166	166	166	166	166	166	166	166	166	166	166
8	166	166	166	166	166	166	166	166	166	166	166	166
9	166	166	166	166	166	166	166	166	166	166	166	166
10	166	166	166	166	166	166	166	166	166	166	166	166

COLUMN VOLUME

trial #	total vol	void vol	porosity	b. dens	maximum	Residual	time(days)
1	166	166	166	166	166	166	166
2	166	166	166	166	166	166	166
3	166	166	166	166	166	166	166
4	166	166	166	166	166	166	166
5	166	166	166	166	166	166	166
6	166	166	166	166	166	166	166
7	166	166	166	166	166	166	166
8	166	166	166	166	166	166	166
9	166	166	166	166	166	166	166
10	166	166	166	166	166	166	166

=====  
TWO-PHASE COREFLOOD DATA  
=====

INPUT DATA

trial #	in box?	from:	to:	soil	FLUIDS	organic	aqueous	aqueous	DENSITIES (g/cc)	partic	empty	COLUMN MASS (g)	soil mass (g)
1	no	0-May-88	01-Jun-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12
2	no	10-Jul-88	14-Jul-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12
3	no	20-Jul-88	17-Aug-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12
4	no	03-Aug-88	06-Sep-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12
5	no	03-Aug-88	06-Sep-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12
6	no	03-Aug-88	06-Sep-88	sevilleta	organic	0.860	0.000	1.000	0.000	2.655	888.29	166.56	132.12

trial #	glue mass (g)	glue dens (g/cc)	filter vol (cc)	TO FIND CORE VOLUME	groove vol (cc)	shy of mk (cm)	EXPERIMENTAL MASSES (g)	at Sr	at Sr	TEMP (C)
1	0.39	1.10	0.01	0.68	0.04	0.00	1090.94	1090.94	1090.94	22.2
2	0.29	1.04	0.03	0.34	0.04	0.00	1090.94	1090.94	1090.94	22.2
3	0.29	1.04	0.03	0.34	0.04	0.00	1090.94	1090.94	1090.94	22.2
4	0.29	1.04	0.03	0.34	0.04	0.00	1090.94	1090.94	1090.94	22.2
5	0.29	1.04	0.03	0.34	0.04	0.00	1090.94	1090.94	1090.94	22.2
6	0.29	1.04	0.03	0.34	0.04	0.00	1090.94	1090.94	1090.94	22.2

COLUMN VOLUME

trial #	total vol (cc)	void vol (cc)	porosity	b dens (g/cc)	maximum	residual	time(days)	temp.range (C)
1	81.56	0.44	0.005	1.745	0.528	0.243	15	1.5
2	81.56	0.44	0.005	1.745	0.528	0.243	15	1.5
3	80.57	0.45	0.006	1.786	0.782	0.201	228	1.16
4	88.68	0.38	0.003	1.748	0.782	0.215	228	2.0

ORGANIC LIQUID SATURATIONS

EXTRAS

TWO-PHASE COREFLOOD DATA

INPUT DATA

trial #	in box?	from:	to:	soil	organic	aqueous	densities (g/cc)	particle	empty	COLUMN MASS (g)	soil mass (g)	+/-
1	yes	26-Aug-88	26-Sep-88	sevilleta	gasoline	CaCl2	1.000	2.55	866.29	988.73	156.43	0.04
2	yes	26-Aug-88	10-Sep-88	sevilleta	gasoline	CaCl2	1.000	2.55	864.34	974.26	109.92	0.04
3	yes	10-Sep-88	18-Oct-88	sevilleta	gasoline	CaCl2	1.000	2.55	859.33	982.93	123.60	0.04
4	yes	07-Sep-88	19-Nov-88	sevilleta	gasoline	CaCl2	1.000	2.55	916.44	1003.78	87.34	0.04

trial	glue mass (g)	glue dens (g/cc)	filter vol (cc)	groove vol (cc)	shy of bk (cm)	at start	EXPERIMENTAL MASSES (g)	at swi	TEMP (C)
1	0.44	1.10	0.03	0.88	0.26	107.66	1096.67	107.27	22.8
2	0.39	1.10	0.03	0.78	0.04	107.21	1071.00	103.26	23.7
3	0.50	1.10	0.03	0.51	0.04	109.80	1034.83	109.52	22.8
4	0.50	1.10	0.03	0.57	0.04	1106.23	1099.38	1104.07	22.2

trial #	total vol (cc)	void vol (cc)	porosity	b. dens (g/cc)	maximum	residual	time(days)	temp range
1	89.61	26.97	0.30	1.743	0.754	0.269	19	0.9
2	88.61	26.67	0.30	1.773	0.820	0.394	24	1.2
3	87.93	26.67	0.30	1.787	0.852	0.371	69	1.7
4	87.44	26.70	0.30	1.793	0.814	0.266	73	1.6

TWO-PHASE COREFLOOD DATA

INPUT DATA

trial #	in box?	from	to	soil	fluids	aqueous	organic	particle	empty	column mass	soil mass
1	Yes	21-Jan-88	04-Feb-88	sevilleta	organic	1.000	1.320	2.55	87.0	0.03	126.77
2	Yes	21-Aug-88	03-Sep-88	sevilleta	organic	1.000	1.320	2.55	87.0	0.03	126.77
3	Yes	22-Aug-88	03-Sep-88	sevilleta	organic	1.000	1.320	2.55	87.0	0.03	126.77
4	Yes	19-Aug-88	11-Sep-88	sevilleta	organic	1.000	1.620	2.55	89.0	0.03	155.44
5	Yes	19-Aug-88	11-Sep-88	sevilleta	organic	1.000	1.620	2.55	89.0	0.03	155.44

trial #	glue mass (g)	glue dens (g/cc)	filter vol (cc)	TO FIND CORE VOLUME	shy of mk (cm)	at start	EXPERIMENTAL MASSES (g)	TEMP (C)
1	0.41	1.04	0.74	groove vol (cc)	0.00	1086.58	1092.58	19.7
2	0.41	1.04	0.74	cc)	0.00	1086.58	1092.58	19.7
3	0.36	1.04	0.74	cc)	0.50	1087.89	1102.70	23.0
4	0.36	1.04	0.74	cc)	2.20	1097.19	1111.19	23.0
5	0.36	1.04	0.74	cc)	1.00	1069.63	1083.74	22.4

trial #	total vol (cc)	void vol (cc)	porosity	b dens (g/cc)	maximum	residual	time (days)	temp. range (C)
1	88.6	29.19	0.33	1.789	0.326	0.206	17	1.9
2	88.6	29.19	0.33	1.789	0.326	0.206	17	1.9
3	88.6	28.19	0.32	1.777	0.852	0.327	18	0.8
4	88.6	28.19	0.32	1.777	0.852	0.327	18	0.8
5	81.40	26.34	0.324	1.793	0.864	0.289	24	1.3



TWO-PHASE COREFLOOD DATA

INPUT DATA

trial #	in box?	from:	to:	soil	organic	aqueous	organic	aqueous	particle	empty	at Sor	soil mass	+/-
1	Yes	11-Feb-89	24-Feb-89	sevilleta	decane	CaCl2	0.727	0.002	2.65	0.01	897.29	0.03	155.05
2	Yes	11-Feb-89	24-Feb-89	sevilleta	decane	CaCl2	0.727	0.002	2.65	0.01	902.32	0.03	146.08
3	Yes	11-Feb-89	04-Mar-89	sevilleta	decane	CaCl2	0.727	0.002	2.65	0.01	886.90	0.03	157.64
4	Yes	15-Feb-89	14-Apr-89	sevilleta	decane	CaCl2	0.727	0.002	2.65	0.01	902.49	0.03	156.31
5	Yes	17-Feb-89	20-Apr-89	sevilleta	decane	CaCl2	0.727	0.002	2.65	0.01	887.93	0.03	163.00

trial #	glue mass (g)	+/-	glue dens. (g/cc)	+/-	filter vol. (cc)	+/-	groove vol. (cc)	+/-	shy of mk (cm)	+/-	at start	at Swi	at Sor	low	high
1	0.60	0.03	1.84	0.03	0.51	0.04	0.77	0.07	0.50	0.10	1093.78	0.03	1091.36	22.8	23.7
2	0.50	0.03	1.84	0.25	0.51	0.04	0.47	0.04	0.90	0.10	1084.27	0.03	1082.43	22.8	23.7
3	0.59	0.03	1.84	0.25	0.51	0.04	0.52	0.04	1.20	0.10	1085.30	0.03	1083.18	22.6	23.8
4	0.41	0.03	1.10	0.03	0.51	0.04	0.51	0.04	-1.30	0.15	1096.30	0.03	1090.00	22.7	23.9
5	0.38	0.03	1.10	0.03	0.51	0.04	0.68	0.04	1.50	0.15	1091.24	0.03	1084.27	22.2	23.8

COLUMN VOLUME

trial #	total vol. (cc)	+/-	void vol. (cc)	+/-	porosity	+/-	b. dens. (g/cc)	+/-	maximum	+/-	residual	+/-	time(days)	temp.range (C)
1	89.53	0.47	31.02	0.71	0.347	0.006	1.732	0.010	0.770	0.036	0.286	0.018	19	0.9
2	82.52	0.44	27.39	0.66	0.332	0.006	1.770	0.010	0.723	0.036	0.246	0.018	24	0.9
3	90.43	0.47	30.95	0.71	0.342	0.006	1.743	0.010	0.788	0.039	0.251	0.019	46	1.2
4	87.00	0.47	28.02	0.71	0.322	0.006	1.797	0.010	0.824	0.041	0.265	0.018	69	1.2
5	92.46	0.49	30.96	0.73	0.335	0.006	1.763	0.010	0.825	0.039	0.246	0.017	73	1.6

ORGANIC LIQUID SATURATIONS

EXTRAS

Two-phase coreflood data-kerosene

trial	1	2	3	4	5	6	7
temperature range (°C)	18-23	18-22	20-23	20-23	19-22	19-24	19-21
system hydraulic conductivity, K (cm/sec)	2.5E-04	1.4E-04	not determined	2.1E-04	not determined	not determined	3.2E-03
soil mass, M <sub>s</sub> (g)	217.66 ± 0.05	218.50 ± 0.05	215.22 ± 0.05	217.25 ± 0.05	215.64 ± 0.05	215.49 ± 0.05	206.80 ± 0.05
begin column mass (g)	1138.50 ± 0.01	not recorded	1135.97 ± 0.01	1137.43 ± 0.01	1136.38 ± 0.01	1134.38 ± 0.01	1130.49 ± 0.01
stabilized column mass, M <sub>1</sub> (g)	1139.66 ± 0.01	1138.70 ± 0.01	1137.06 ± 0.01	1139.08 ± 0.01	1137.18 ± 0.01	1136.21 ± 0.01	1131.79 ± 0.01
entrapped air removed (cm <sup>3</sup> )	1.16 ± 0.02	not recorded	1.09 ± 0.02	1.65 ± 0.02	.080 ± 0.02	1.83 ± 0.02	1.30 ± 0.02
total column volume, V <sub>t</sub> (cm <sup>3</sup> )	123.30 ± 0.13	123.49 ± 0.15	122.89 ± 0.16	123.12 ± 0.18	123.43 ± 0.18	123.16 ± 0.13	117.48 ± 0.06
soil bulk density, ρ <sub>b</sub> (g/cm <sup>3</sup> )	1.765 ± 0.002	1.769 ± 0.003	1.751 ± 0.003	1.765 ± 0.003	1.747 ± 0.003	1.750 ± 0.002	1.760 ± 0.001
void volume, V <sub>v</sub> (cm <sup>3</sup> )	40.85 ± 0.46	40.72 ± 0.48	41.37 ± 0.49	40.83 ± 0.51	41.75 ± 0.51	41.54 ± 0.49	39.15 ± 0.38
porosity, n (%)	33.1 ± 0.4	33.0 ± 0.4	33.7 ± 0.4	33.2 ± 0.5	33.8 ± 0.5	33.7 ± 0.4	33.3 ± 0.3
step 1 column mass, M <sub>2</sub> (g)	1133.85 ± 0.01	1134.51 ± 0.01	1130.74 ± 0.01	1133.57 ± 0.01	1131.21 ± 0.01	1130.33 ± 0.01	1125.69 ± 0.01
step 1 water saturation, S <sub>w</sub> (%)	26.7 ± 2.0	47.2 ± 1.6	21.1 ± 2.1	29.9 ± 2.0	26.2 ± 2.1	26.9 ± 2.0	19.9 ± 2.1
step 1 organic liquid saturation, S <sub>o</sub> (%)	73.3 ± 2.0	52.8 ± 1.6	78.9 ± 2.1	70.1 ± 2.0	73.8 ± 2.1	73.1 ± 2.0	80.1 ± 2.1
step 2 column mass, M <sub>3</sub> (g)	1137.47 ± 0.01	1136.50 ± 0.01	1134.90 ± 0.01	1137.11 ± 0.01	1135.28 ± 0.01	1134.36 ± 0.01	1129.89 ± 0.01
final water saturation, S <sub>w</sub> (%)	71.9 ± 0.9	71.7 ± 0.9	72.7 ± 0.9	74.7 ± 0.8	76.2 ± 0.8	76.7 ± 0.8	74.6 ± 0.8
residual organic liquid saturation, S <sub>or</sub> (%)	28.1 ± 0.9	28.3 ± 0.9	27.3 ± 0.9	25.3 ± 0.8	23.8 ± 0.8	23.3 ± 0.8	25.4 ± 0.8

TWO-PHASE COREFLOOD DATA

INPUT DATA

trial #	in box?	from:	to:	soil	organic	aqueous	particle	empty	w/H2O	soil mass (g)	+/-
1	Yes	10-Apr-89	30-Apr-89	traverse	CaCl2	0.753	2.65	902.45	0.03	994.48	0.03
2	Yes	20-Apr-89	02-May-89	traverse	CaCl2	0.753	2.65	899.28	0.03	899.19	0.03
3	Yes	22-Apr-89	03-May-89	traverse	CaCl2	0.753	2.65	891.15	0.03	876.60	0.03
4	Yes	23-Apr-89	04-May-89	traverse	CaCl2	0.753	2.65	889.02	0.03	972.41	0.03
5	Yes	24-Apr-89	04-May-89	traverse	CaCl2	0.753	2.65	901.73	0.03	991.33	0.03

trial #	glue mass (g)	+/-	glue dens. (g/cc)	+/-	filter vol. (cc)	+/-	groove vol. (cc)	+/-	shy of mk (cm)	+/-	at start	+/-	at SWI	+/-	at Sor	+/-	TEMP (C)	low	high
1	0.41	0.03	1.10	0.03	0.68	0.04	0.53	0.04	?	0.10	1100.70	0.03	?	0.03	?	0.03	22.0	23.8	
2	0.44	0.03	1.10	0.03	0.51	0.04	0.52	0.04	1.50	0.10	1091.63	0.03	1087.18	0.06	1092.34	0.06	23.2	23.9	
3	0.56	0.03	1.10	0.03	0.51	0.04	0.51	0.04	1.80	0.10	1073.88	0.03	1067.57	0.03	1072.70	0.03	22.0	23.9	
4	0.72	0.06	1.10	0.03	0.72	0.06	0.47	0.04	0.10	0.01	1065.55	0.03	1059.27	0.03	1064.15	0.03	22.3	23.4	
5	0.70	0.06	1.10	0.03	0.74	0.04	0.50	0.03	1.20	0.10	1094.31	0.03	1087.82	0.03	1092.95	0.03	22.9	24.0	

COLUMN VOLUME

trial #	total vol. (cc)	+/-	void vol. (cc)	+/-	porosity	+/-	b. dens. (g/cc)	+/-	maximum	+/-	residual	+/-	time (days)	temp. range (C)
1	89.11	0.46	30.68	0.70	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	15	1.8
2	84.68	0.47	30.19	0.69	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	44	0.7
3	81.59	0.41	29.37	0.52	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	32	1.9
4	88.23	0.47	29.87	0.71	ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	28	1.1
5					ERR	ERR	ERR	ERR	ERR	ERR	ERR	ERR	36	1.1

ORGANIC LIQUID SATURATIONS

EXTRAS