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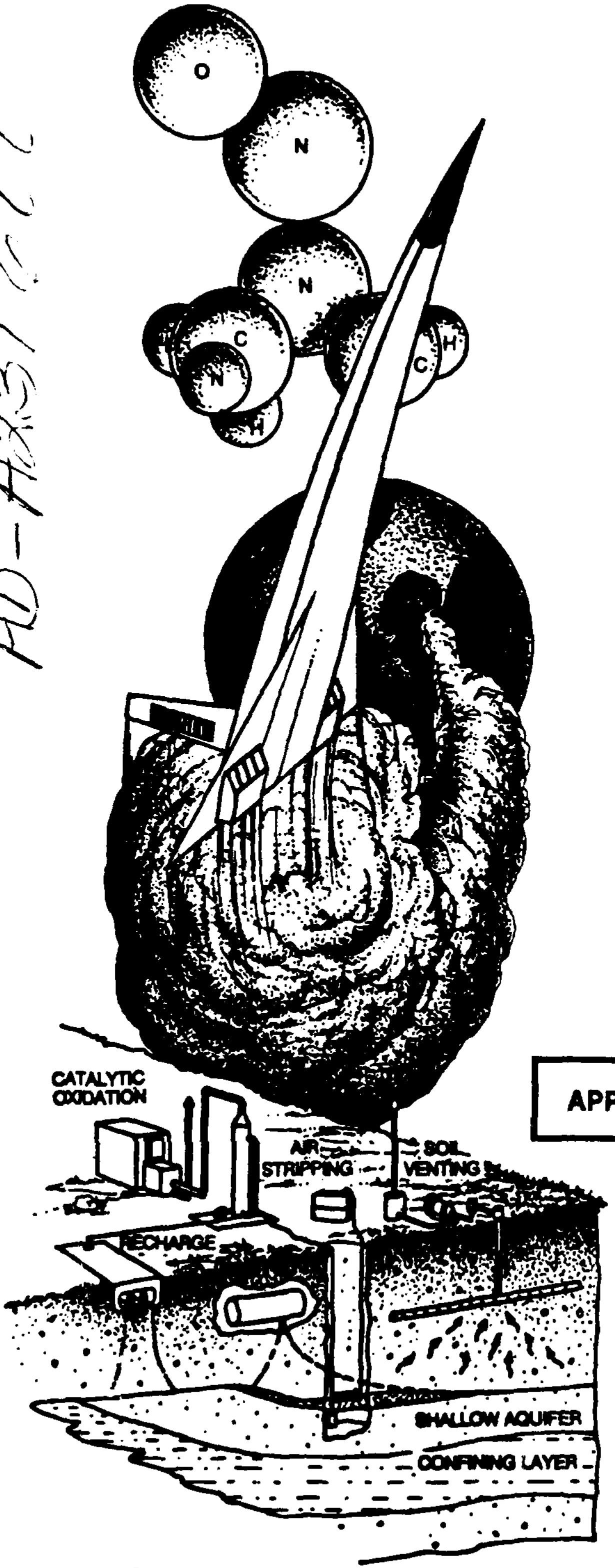

PETROLEUM THICKNESS IN GROUNDWATER - A LABORATORY STUDY

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AIR FORCE ENGINEERING AND
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The objective of the work described in this report was to determine the relationship between the thickness of petroleum product measured in wells and the thickness within the soil foundation. A theory is presented for an equation that predicts soil formation petroleum thickness from well thickness with a fair degree of accuracy. The equation only functions over a narrow range of data because of boundary condition imposed by the physical models used.

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EXECUTIVE SUMMARY

Fuel contamination of the subsurface environment can exist in as many as three phases. One is a residual phase consisting of immobile fuel contained within the pore spaces of the vadose zone above the water table (large volumes of this type of contamination are the most difficult and expensive to mitigate). Another is a free-fuel phase that is a mobile liquid that can spread out over the water table and generally follows its gradient--it is the measurement of this phase's thickness that is the main subject of this update. Finally, there will exist a soluble phase that results from chemical components in the fuel such as benzene, toluene, and xylene dissolving from the other phases into the ground water and becoming transported by it.

The free-fuel phase will flow by gravity. Consequently, it can be induced to flow to wells where it can be pumped to the surface. Once on the surface, its disposal is easily accomplished. The financial efficiency and success of a free-fuel reclamation depends on a properly designed pumping, storage, and ground-surface handling system. The main parameter affecting the proper design is an estimate of the free-fuel volume.

The current technique used to acquire an estimate of free-fuel volume involves the use of observation wells. Depending on the suspected areal extent of contamination, one or more wells will be installed and the thickness of the free-fuel measured in the well. This depth (ft) will be multiplied by the estimated area of free-fuel contamination (ft^2) and a percentage substracted to account for residual fuel to arrive at an estimated volume (ft^3) of free-fuel. This estimate affects the design of the reclamation system. The problem is that <u>fuel thickness measured in observation wells is not the same as the thickness outside the well</u> in the aquifer. This was discovered around 1967 and has been verified more recently by a number of researchers; it is now fairly common knowledge to those working in the cleanup of petroleum-polluted ground water.

The reason for the discrepancy between the fuel thickness in the well (apparent thickness) and the thickness in the aquifer (actual thickness) was speculated to be caused by the water table's capillary fringe. The capillary fringe is the zone above the water table that contains upwardly decreasing percentages of water held by capillary pressures. The thickness of the capillary fringe will vary depending on the soils characteristics, but, in general, the smaller the grain size, the thicker the capillary fringe will be.

The capillary fringe acts as a barrier to the downward movement of free-fuel to the water table. An observation well essentially punches a hole through the capillary fringe. Free-fuel flows off the fringe into the well and accumulates on the water surface in the well until it approaches the elevation of the free-fuel outside the well on top of the capillary fringe (see figure). Because of this phenomenon, fuel thickness in the well (i.e., apparent thickness) may be as much as ten times the actual fuel thickness in the aquifer.

The objectives of this research were to verify the capillary fringe's effect on petroleum thickness measurement and develop a technique to predict actual fuel thickness from apparent fuel thickness.

Laboratory tests were conducted using plexiglas columns filled with varying sizes of sands to simulate aquifer conditions. JP-4 jet fuel was added to the columns and measurements taken of actual and apparent thicknesses. A theory was developed on the relationship between the apparent and actual petroleum thickness based on fundamental properties of the JP-4 and soils. From this theory, an equation is derived that predicts actual fuel thickness from apparent fuel thickness, capillary fringe thickness of water, and capillary fringe thickness of JP-4.

The equation predicts actual thickness with a good degree of accuracy within a limited range of measurements, because of boundary conditions imposed by the physical test model. Additional research is needed to expand the relationship to apply to field conditions.

Persons involved in the review of fuel spill volume estimates should be aware of the apparent versus actual measurement discrepancy and make decisions on contamination cleanup accordingly.

PREFACE

This report was prepared by the Air Force Engineering and Services Center, Engineering and Services Laboratory (HQ AFESC/RDVW), Tyndall Air Force Base FL 32403-6001.

Research documented in this report was performed between May 1987 and March 1989.

This report has been reviewed by the Public Affairs Office (PA) and is releaseable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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g	magnitude of gravity force per unit volume
p	fluid pressure
P_c	capillary pressure
P_d	displacement pressure
P_e	entry pressure
r	radius
s	saturation
S_e	effective saturation
S_r	residual saturation
α	contact angle
Δ	difference
Θ	volumetric water content
λ	empirical exponent used as index of pore size distribution
ρ	fluid density
σ	interfacial tension
ϕ	porosity

SUPERSCRIPTS AND SUBSCRIPTS

o	organic
w	water
a	air

SECTION I

INTRODUCTION

'. OBJECTIVE

At this time, there is no well documented, verified theory for predicting the relationship between well bore hydrocarbon product thickness and the actual thickness of hydrocarbon in the soil formation. The objective of this research was to develop and show applicability of a theory to predict the "actual" thickness of JP-4 in a soil formation from the "apparent" thickness of JP-4 in the well bore. The theory is based on knowledge of fundamental soil properties and pertinent properties of JP-4.

The procedures used to meet the objective stated above were:

1. Develop an appropriate theory to make realistic, but initially simplistic assumptions regarding the soil formation and the properties of JP-4. These assumptions include soil homogeneity and uniformity and static conditions, as well as simplified mathematical representations of the capillary properties of the JP-4-water-air system and time independent properties of JP-4.

2. Measure the properties of JP-4 and the soil parameters needed to develop the theory.

3. Use laboratory column data to demonstrate the validity of the theory.

B. BACKGROUND

1. Fuel Contamination

The contamination of groundwater and vadose zone soils by petroleum products is a widespread problem affecting both civilian and military installations. Civilian problems can range from small gas station spills or leaks to large problems associated with petroleum producers and distributors. Hydrocarbon contamination at military bases generally falls between these extremes and normally involves lighter-than-water fuels such as gasoline or JP-4 jet fuel. The U.S. Air Force has fuel spill sites at nearly every base in the United States. The cleanup of a site requires an estimate of the volume of fuel contamination and the delineation of its location. The volume of contamination can exist in three phases at a site: (1) a soluble phase where chemical components of the fuel, such as benzene, toluene, and xylene dissolve into the groundwater and become transported by it; (2) a residual phase consisting of immobile fuel trapped in the pore spaces of the aquifer vadose zone above the water table; and (3) a free-fuel phase, which is a mobile liquid fuel floating on top of the water table.

The free-fuel phase will flow by gravity; consequently, it is the simplest to clean up because it can be pumped to the surface where it is easy to handle. An accurate estimate of the volume of free-fuel needs to be obtained to properly design the pumping, storage, and aboveground handling systems required in a cleanup effort. A good estimate is also necessary for financial reasons. The cleanup of free-fuel costs approximately $1.00 a gallon. Contractor cleanup fees are based, in part, on the volume estimate of remaining free-fuel; overestimation can result in needless cost, while underestimation could result in an inadequate cleanup or prolonged cleanup from contract renegotiations.

2. Fuel Volume Estimates

Estimation of the total quantity of undissolved petroleum product in the subsurface environment involves (1) an estimation of the total volume retained in the unsaturated zone, and (2) an estimation of the horizontal and vertical accumulation of the free product in the saturated region directly above the groundwater table. Both of these aspects involve immiscible flow processes in the vadose zone.

Free-product volumes are currently estimated by multiplying the thickness of fuel in one or more monitoring wells by the areal extent of contamination and the porosity (100 percent saturation assumed). Unfortunately, it has been discovered that the thickness of fuel in monitoring wells is not indicative of the actual thickness outside of the well. In 1967, J. Van Dam published a paper on the migration of hydrocarbons in a water-bearing stratum (Reference 1). This article provided the fundamental information which led later researchers to discover that the actual fuel thickness differed from apparent monitoring well thickness. One reason for the discrepancy was proposed in 1971 by Williams and Wilder (Reference 2). Their paper described a case history of groundwater contaminated by gasoline. Their contention was that the free-fuel thickness in the well was greater than the free-fuel thickness in the soil formation because the groundwater's capillary fringe created a barrier to the downward movement of fuel to the water table, while the well acted as a conduit. They postulated that the thickness of the fuel in the well was equal to the thickness of the capillary fringe, plus the actual thickness of the fuel outside the well plus the thickness of the water level depression in the well due to the fuel's weight (see Figure 1). Subsequent researchers also confirmed the discrepancy between the "apparent" fuel thickness and the "actual" fuel thickness (References 3, 4, and 5).

In 1984, Yaniga (Reference 6) identified another problem with the measurement of monitoring well fuel thickness. It involved the dynamic hydrological conditions in aquifers. He found that during periods of recharge when the water table is rising, fuel thickness in observation wells can decrease, often to the point of disappearance. Conversely, during periods when the water table is falling, fuel thickness in wells can increase. A study performed in Israel by Kanfi (Reference 7) found a similar relationship in wells contaminated by kerosene. Their measurements produced a negative correlation (-0.95) between water table elevation and kerosene thickness. This phenomenon, which is influenced by each aquifers' physical characteristics, can obviously result in erroneous volume estimates. Yaniga suggested that analysis of soil cores was beneficial in the determination of fuel thickness. However, many aquifers contain predominantly fine- to coarse- grained sands which are, at best, difficult, to capture in any type of coring device available.

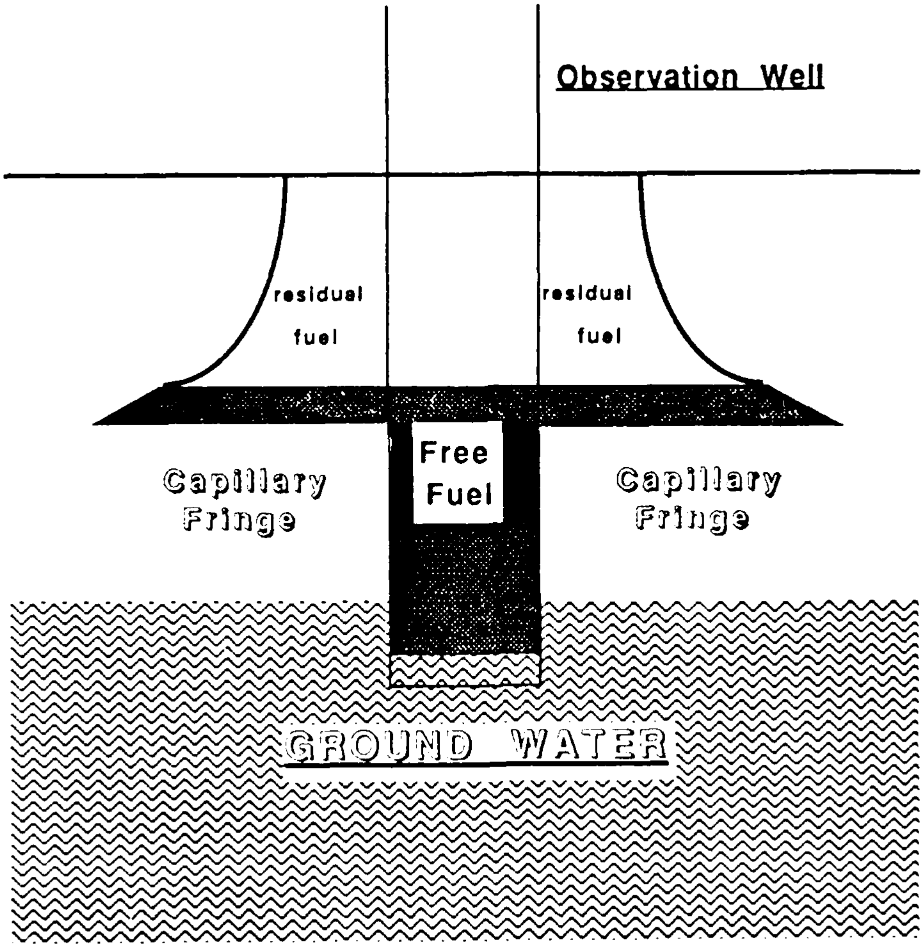

Figure 1. Profile of Petroleum Contaminated Aquifer.

3. Predictive Relationships

The above discussion, shows that the accurate determination of free-fuel thickness in groundwater through the use of monitoring wells is inhibited by hydrological changes in the aquifer and the capillary fringe phenomena. The latter of these problems has been investigated by several researchers who have tried to establish a predictive relationship between the "apparent" fuel thickness in monitoring wells and the "actual" fuel thickness in the adjacent formation. For example, in 1979, CONCAVE, a European study group for the conservation of clean air and water published a report (Reference 8) which presented a rule-of-thumb technique for estimating actual hydrocarbon product thickness in soil formations. They contended that because of certain capillary pressure relationships, the apparent hydrocarbon thickness may be as much as four times the actual thickness and the volumes determined from measurements taken in bore holes should be adjusted accordingly. Yaniga and Warburton (Reference 9) postulated an apparent capillary product accumulation model which relied on calculations of interfacial tensions, capillary pore pressures and displacement pressures to quantify the actual fuel thickness. However, the details of their technique were never presented for verification.

Another pair of researchers, Blake and Hall (Reference 10), performed a laboratory study of the capillary fringe phenomena. Using columns filled with different uniform sands, they studied the relationship between the apparent and actual thickness of hydrocarbons with different specific gravities. From this work, they developed an equation for the estimation of actual thickness as follows:

$$ACT = APT - (D_{wt} + H_m) \qquad (1)$$

where: ACT = actual thickness of fuel

APT = apparent thickness of fuel

D_{wt} = depth of fuel in monitoring well below the water table

H_m = distance from the water table to the bottom of the mobile fuel level

There are problems associated with determining H_m (capillary fringe thickness) which limit the usefulness of this relationship in field application.

In a more mathematically rigorous examination of the apparent versus actual petroleum thickness phenomena, H. O. Schiegg (Reference 11) developed an equation for the average thickness of a petroleum layer parallel to the groundwater table. His equation,

$$\bar{H} \sim H_T - 2(h_c) \qquad (2)$$

where: $\bar{H}$ = the average actual fuel thickness

H_T = the apparent fuel thickness

$h_{\bar{c}}$ = the mean capillary height

is based on the saturation curves of the three nonmixing fluids;, water, fuel, and air. Schiegg's equation was developed from laboratory experiments. The value of $h_{\bar{c}}$ must be determined in the same manner for no valid formula exists for its determination. The limitations imposed by the determination of $h_{\bar{c}}$ in the field make its practical use limited. Consequently, this equation has not been verified with field data. In a comprehensive study to evaluate the above techniques, Hampton (Reference 12) performed laboratory experiments with a sand-filled Plexiglas box. Using a dyed hydrocarbon that could be visually observed through the wall of the box, he compared measurements of what he judged to be the "actual" hydrocarbon thickness to values determined with the above techniques. His findings indicate that all of the above equations and methods lacked predictive power for estimating actual hydrocarbon thickness.

C. SCOPE

If equilibrium and homogeneous conditions are assumed, the relationship between the "apparent" thickness of JP-4 in an observation well and the volume of JP-4 in the soil formation can be determined. The link between the two quantities is given by relating equilibrium pressures determined from the well bore data to the equilibrium volumetric quantities of water, JP-4, and air in the soil that corresponds to these pressures.

The basic data required to determine the relationship between well bore and soil formation JP-4 are:

a. ρ_w: density of the soil water

b. ρ_o: density of the JP-4

c. ρ_a: density of air (assumed zero)

d. ϕ : porosity

e. $\frac{Pc(S)}{\rho g}$: capillary pressure-saturation curves for an air/organic system and for an organic/water system

A capillary pressure-saturation curve is developed from data obtained in the laboratory using standard pressure cell extraction techniques. The curve plots the relationship between percent saturation and capillary pressure. Examples are presented in Figures 3 and 4. After obtaining the required basic data from laboratory measurements, the capillary pressure curves are fit to an appropriate empirical equation. This allows integration of a mathematical function rather than numerical integration of a data curve. The Brooks-Corey equation (References 13 and 14) was used for this study. However, there is some discussion as to its appropriateness for this application (Farr, Houghtalen, and McWhorter, Reference 15). In any case, the basic procedure does not depend on the particular curve fitting equation used. No hysteresis and no air entrapment is assumed. Further, it was assumed that the organic occurs throughout the entire soil profile from the ground surface to the saturated water region. This assumption allows an air/organic capillary pressure curve to represent the capillary relationships between the air and the organic from the ground surface to the organic-water interface even when water is present in the profile. The assumption means that there are no water-air menisci in the profile. This is not an appropriate assumption if the organic has migrated horizontally from a spill or leakage site and migrated upward toward the soil surface without reaching the surface. However, this case only changes the limits of integration for the procedure. The solution process would be the same. This approach assumes independence of the two two-phase systems with separate solutions determined for each system before combining results.

SECTION II

THEORY

In general, the procedure used to estimate a spill volume first requires an estimate of the combined volume of petroleum product and air in the soil profile. This is obtained by subtracting the total water in the profile from the total volume of the voids. The total water content is determined by integrating from the ground surface to the depth of water/organic interface the water/organic capillary curve. Second, total air in the profile is estimated by integrating the difference between porosity and organic content from the ground surface to the depth of air/organic interface. In this case, the air/organic capillary pressure curve is used. The difference of the two volumes obtained by integration and the porosity is an estimate of the volume of organic in the soil profile. The procedure is illustrated in the following section using the Brooks-Corey relationship to develop the capillary-pressure curves. This equation is an empirical representation of capillary pressure as a function of saturation given by $Se = \frac{(Pd)}{(Pc)}^{\lambda}$ where Pd is the displacement pressure (capillary pressure at which one fluid completely displaces another) and λ is called the pore size distribution factor. Se is an effective saturation defined by $Se = \frac{s - s_r}{1 - s}$. It is assumed that entry and displacement pressures (as defined by Brooks and Corey) are approximately the same.

After a petroleum spill, equilibrium conditions are assumed, as illustrated in Figure 2.

Where:

D_w^{ow} = Depth from ground surface to organic-water interface in well

D_w^{ao} = Depth from ground surface to air-organic interface in well

D = Thickness of organic in well

D_a^{ao} = Depth from ground surface to air-organic interface in soil formation

D_a^{ow} = Depth from ground surface to organic-water interface in soil formation

A = Thickness of organic capillary rise

B = Thickness of water capillary rise

If the capillarity between the organic and the water is not influenced by the presence of air, we can use the capillary pressure curve for a water/organic system to estimate the total volume of organic and air in the soil

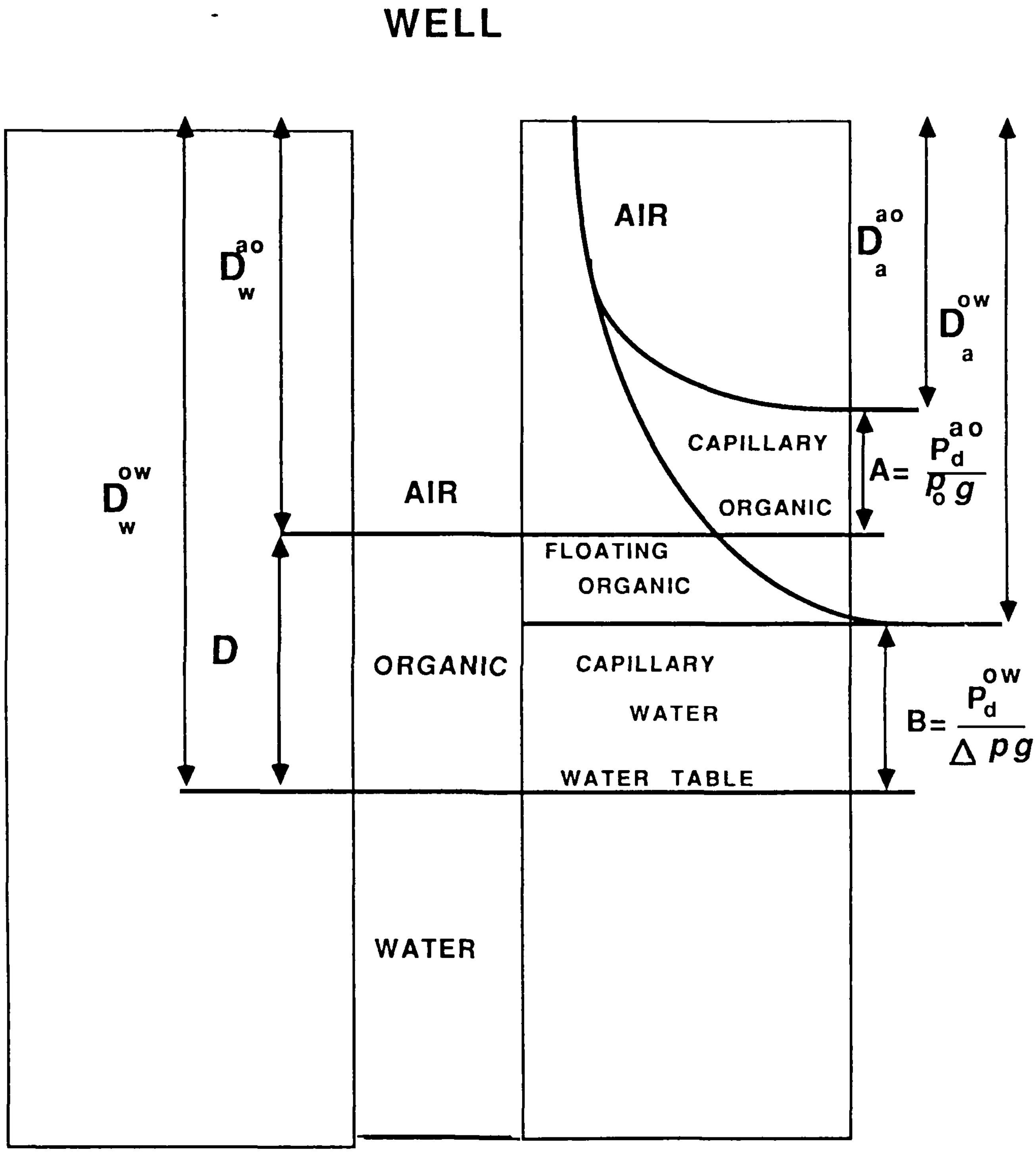

Figure 2. Notation Used for Equilibrium Conditions.

profile. Figure 3 shows a typical capillary pressure-saturation curve when an organic displaces water. The curve represents the relationship between capillary pressure head (in cm of water) and saturation values of water if water is the wetting phase and the organic is the nonwetting phase in a two-phase system. Recall saturation is the ratio of volumetric water content and porosity so a saturation of 1.0 implies that all pores are filled with water. Similarly, a saturation of 0.4 on this curve indicates that at the corresponding capillary pressure head, 40 percent of the pores are filled with water and 60 percent of the void space is occupied by organic. The pressures in these two fluids are not equal because of the surface tension along the meniscus between the two fluids in the pores. However, the pressures are related by the equation

$$P_c = P_o - P_w \tag{3}$$

where P_c is capillary pressure, P_o is the pressure in the organic phase, and P_w is the pressure in the water phase. Expressed as pressure heads in cm of water

$$\frac{P_c}{\rho g} = \frac{P_o}{\rho g} - \frac{P_w}{\rho g} \tag{4}$$

Further, if hysteresis is ignored and equilibrium is assumed, $\frac{(P_d)^{ow}}{\rho_w g}$ is approximately the distance of a column of water above the water table to the organic-water interface. The distance D_a^{ow} from the ground surface in Figure 2 can also be determined from Figure 3.

Using the Brooks-Corey relationship, the volume of soil voids occupied by air and organic per unit area can be estimated by:

$$V_a + V_o = \int_0^{Da^{ow}} \left(\phi - \Theta_w^{ow}\right) dz = \phi \int_0^{Da^{ow}} \left(1 - s_w^{ow}\right) dz \tag{5}$$

where: ϕ = porosity

Θ = volumetric water content

$$= \phi \int_0^{Da^{ow}} \left[1 - 1 + \frac{\Delta\rho g z}{P_d^{ow}}^{-\lambda^{ow}}\right] dz \tag{6}$$

since $s_w^{ow} = \frac{P_c^{ow}}{P_d^{ow}}^{-\lambda^{ow}}$ (the Brooks Corey equation with residual water saturation)

and $P_c^{ow} = P_d^{ow} + \Delta\rho g$

Integrating Equation (6) gives:

$$V_a + V_o = \phi D_a^{ow} - \phi B \left[\frac{1 + \frac{D_a^{ow}}{B}^{-\lambda^{ow}+1}}{-\lambda^{ow} + 1} - \frac{1}{-\lambda^{ow} + 1} \right] \qquad (7)$$

where $B = \frac{P_d^{ow}}{\Delta\rho g}$

Since, the equation describes volumes of air and organic per unit horizontal area, units on V_a and V_o are length. Other notation is given in the list of symbols. In addition, we have assumed that the residual water saturation is zero.

Using a similar procedure, the volume of air per unit area in the profile after a spill is estimated from the air/organic capillary pressure curves. Notation is given in Figure 4. Again, the assumption is made that the organic is in contact with air throughout the profile and the presence of water in the profile does not affect the capillarity between the organic and air. With this assumption:

$$V_a = \phi \int_o^{D_a} (1-s_o^{ao})\, dz = \phi \int_o^{D_a^{ao}} \left[1 - \left(1 + \frac{\rho_o gz}{P_d^{ao}} \right)^{-\lambda^{ao}} \right] dz \qquad (8)$$

where $s_o^{ao} = {\frac{P_c^{ao}}{P_d^{ao}}}^{-\lambda^{ao}}$

and $P_c^{ao} = P_d^{ao} + \rho_o gz$

Integrating equation 8 gives:

$$V_a = \phi D_a^{ao} - \phi A \left[\left(\frac{\frac{1+D_a^{ao}}{A}}{-\lambda^{ao}+1} \right)^{-\lambda^{ao}+1} - \frac{1}{\lambda^{ao}+1} \right] \qquad (9)$$

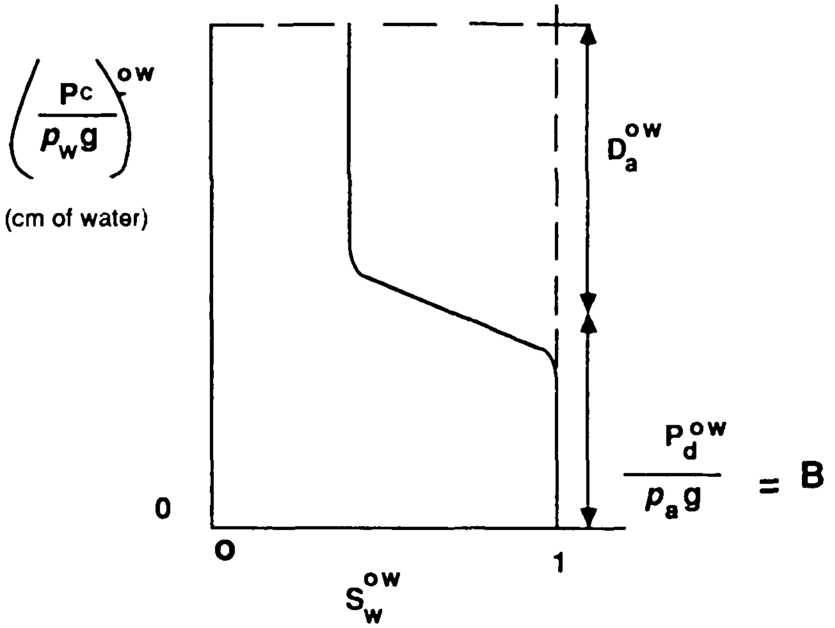

Figure 3. Capillary Pressure-Water Saturation Curve for an Organic/Water two Phase System.

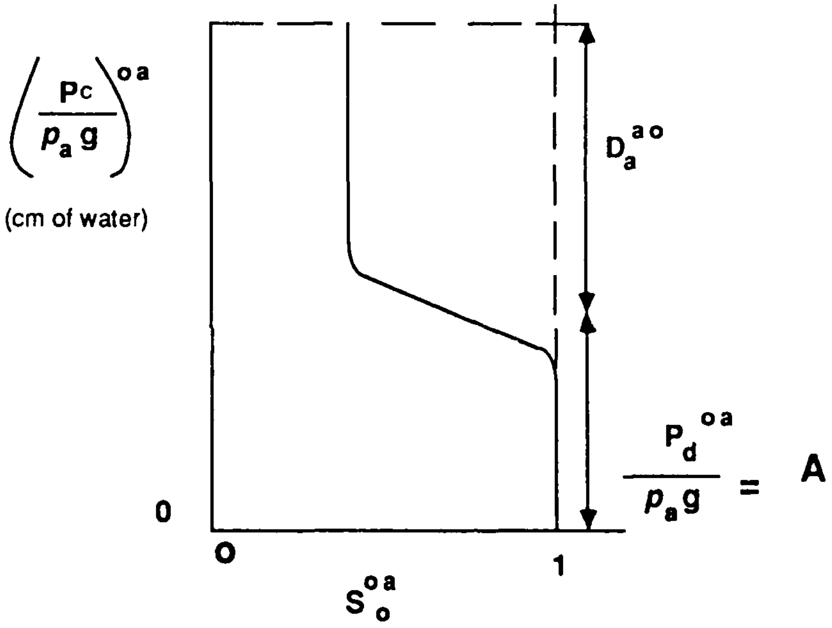

Figure 4. Capillary Pressure-Organic Saturation Curve for an Organic/Air two Phase System.

where $A = \frac{P_d^{ao}}{\rho_o g}$

If the total change in water in the aquifer before and after the spill is zero and it is further assumed that $\lambda^{ao} = \lambda^{ow}$, then the volume of organic per unit area can be estimated by subtracting Equation 9 from Equation 7, so that:

$$V_o = \phi \left(D_a^{ow} - D_a^{ao}\right) - \frac{(A-B)}{-\lambda+1}\phi + \frac{A\phi}{-\lambda+1}\left(1 + \frac{D_a^{ao}}{A}\right)^{-\lambda+1}$$

$$- \frac{B\phi}{-\lambda+1}\left(1 + \frac{D_a^{ow}}{B}\right)^{-\lambda+1} \qquad (10)$$

Equation 10 relates the volume of organic (V_o) in the soil to the capillary pressure curve parameters as defined by the Brooks-Corey relationship (A, B, and λ) and the depths to the organic water interface (D_a^{ow}) and the air organic interface (D_a^{ao}) as delineated by the location of the displacement pressures in the Brooks-Corey relationship. It still remains to relate the volume of organic to the measureable depth of organic in the well bore. The following relationships that are defined in Figure 2 are used to establish the relationship:

$$D + A - B = D_a^{ow} - D_a^{ao} \qquad (11)$$

$$D_w^{ow} - D - A = D_a^{ao} \qquad (12)$$

$$D_w^{ow} - B = D_a^{ow} \qquad (13)$$

and $D_w^{ow} - D = D_w^{ao}$ (14)

$$V_o = \phi\,(D + A - B) + \frac{A\phi}{-\lambda+1}\left[\left(\frac{D_w^{ao}}{A}\right)^{-\lambda+1} - 1\right] - \frac{B\phi}{-\lambda+1}\left[\left(\frac{D_w^{ow}}{B}\right)^{-\lambda+1} - 1\right] \qquad (15)$$

The value of Φ (D + A - B) equals the volume of free petroleum product in the soil formation. Subtracting ≈'80 percent of this value from Vo leaves the volume of the fuel residual in the soil formation per unit area (typically, 20 percent of saturated free product is residual). Note that if the organic does not extend to the ground surface, the limits of integration are changed in the above equations. Otherwise, the procedure is the same. The units on V_o are again length; that is, V_o is the volume of organic per unit area. If both sides of the equation are divided by porosity, the equation is in terms of an equivalent depth of organic.

SECTION III

LABORATORY COLUMN STUDIES

A. METHODOLOGY

To test the theoretical relationships presented above, laboratory studies were conducted using columns constructed of clear Plexiglas. Each column measured 29 cm in diameter and 76 cm high, with a total volume of 202 L^3. A standpipe was attached to the side of the column open to its bottom to allow the observation of water levels. An inlet/drain was also installed within the bottom 5 cm to facilitate draining and allow the addition of water to the bottom of the column. Along the inside of the column from bottom to top was attached a slotted polyvinyl chloride (PVC) well screen, 5 cm in diameter, split longitudinally to allow viewing of the inside of the well.

The columns were packed, with vibration, using commercially obtained quartz filter sand with mean diameters of 0.25 mm, 0.5 mm, 0.6 mm, 0.8 mm, and 1.0 mm (± 50%), to a depth of approximately 60 cm in the columns. Water was slowly introduced near the bottom of the column to allow capillary rise to precede the free water level, which was stabilized approximately 40 cm from the bottom of the column. After the columns were hydrologically stabilized (capillary wetting ceased), JP-4 jet fuel was added through a glass tube at the top of the capillary fringe in 100 mL increments every 24 hours for approximately 30 days.

The fuel thickness in the well (apparent thickness) and the height of the water table were measured each day before the addition of fuel. The "actual" fuel thickness outside the well bore would normally be difficult to measure because the water/fuel interface at the top of the capillary fringe is not readily discernible due to the similarity of the two fluids' colors. However, fluorescing agents have been shown to fully partition into oil (Reference 16). For this study, it was also discovered that they would preferentially be retained in JP-4 when water was present. Consequently, a mixture of two fluorescing agents, Uvitek OB® (Ceiba-Geigy Corp.) and Yellow 131SC® (Morton Chemical Co.) was added to the JP-4 prior to its introduction into the columns. With illumination by long-wave ultraviolet irradiation, vivid fluorescence of the fuel through the column wall made the actual fuel thickness visible and, consequently, measureable. Measurements of actual petroleum thickness were then made with the same frequency as the apparent thickness and water height. The elevation of the bottom of the actual thickness was also recorded.

In addition to the column data, some of the basic properties of JP-4 and the capillary pressure-saturation curves for the column sands were needed. Capillary pressure curves for three column sands (mean sizes of 0.5, 0.6, and 0.8 mm) arre given in Appendix A. For the approach described previously, only the JP-4/air and H_2O/JP-4 curves are needed. The H_2O/air curves were measured for completeness. Laboratory measurement of surface tension and density for JP-4 are given in Table 1.

TABLE 1. BASIC PROPERTIES OF JP-4

	Fresh JP-4	Aged JP-4[1]
Surface Tension $\frac{\text{dynes}}{\text{cm}}$		
Water/air	75.5	59.0
JP-4/air	25.0	27.3
Water/JP-4[2]	25.0	5.3
Density $\frac{\text{gms}}{\text{cm}^3}$		
JP-4	0.745	0.769

JP-4 obtained from well, Tyndall AFB

Initially 38.4, stablilized at 25.0 after 16 hours

Although only fluid densities are required for the analyses, surface tensions also measured to provide some insight into the accuracy of the capillary pressure curves. For the same porous medium, the three capillary pressure curves are related by the LaPlace equation, which defines the condition of mechanical equilibrium at an interface between two fluids. The LaPlace equation can be written as:

$$P_c = \frac{2\sigma\cos\alpha}{r_m} \qquad (16)$$

where P_c = capillary pressure

σ = surface or interfacial tension

α = contact angle

r_m = mean radius of curvature

Values of the required contact angles were not measured; however, if we assume that the contact angles for all three interface conditions are approximately the same, the LaPlace equation would suggest that the curve for JP-4/air and water/JP-4 using fresh JP-4 would be the same if both were measured in cm of water. Since the values on the JP-4/air curve are measured in cm of JP-4, the ordinates on this curve should be multiplied by $\rho_o \rho w$, or 0.75 (density correction) to compare to the corresponding ordinates on the water/JP-4 curve. Similarly, since the surface tension between water and air is three times that for JP-4 and air and three times that for JP-4 and water, the capillary pressures on the water/air curve should be approximately three times those on the other two curves for the same saturation levels. The capillary pressure curves given in Appendix A show that, although not exact, this relationship generally holds. This relationship would directly influence the height of an average capillary fringe, and the amount of free product.

Surface tensions and density were also measured for an aged sample of JP-4 taken from a monitoring well at Tyndall AFB. Density was found to be only slightly higher than for a fresh JP-4 sample. The surface tension for aged JP-4 in contact with air was also similar to the value measured with fresh JP-4. There was a significant difference was found in the interfacial tension between the contaminated water and aged JP-4 (5.3 dynes/cm) and the fresh JP-4 and clean water (25 dynes/cm). The lower value measured would suggest that this change in surface tension should be further investigated before lab results are extended for field use.

B. DISCUSSION OF COLUMN DATA

By using the values of A and B, as defined by the Brooks-Corey relationship (see Figure 2), to estimate the top and bottom of the saturated JP-4 zone, respectively, it is implied that the displacement pressures in the columns can be visually determined. This is not realistic. Therefore, to illustrate this relationship, an "average capillary pressure" corresponding to an "average saturation" will be used. Of course, these values are subjective. However, they will serve to illustrate the concepts involved. When visual averages are used, A and B will be marked with primes, i.e., A' and B'. Further, since the JP-4 was added at the top of the capillary fringe, (as opposed to the top of the column) full equilibrium profile is not developed in the columns. Therefore, the last two terms in Equation (15) (estimating organic plus air and air pore space volume) are difficult to evaluate. These are related to the "residual" JP-4 measured in the columns. The data for the 0.5 mm sand column test (Table 2), which is typical of other test data, will be used to discuss the trends seen in the column data. For this discussion, a value for JP-4 density of 0.77 will be used.

TABLE 2.: DATA SET 1 FOR 0.5 MM COLUMN TEST

CUMULATIVE JP-ADDED (mls)	APPARENT[1] THICKNESS D (cm)	ACTUAL[2] THICKNESS (cm)	WTE[3] (cm)	BOF[4] (cm)	B' = BOF-WTE (cm)
100	-	-	35.8	-	-
200	-	-	35.6	-	-
300	-	-	35.6	43	7.4
400	4.5	-	32.6	43	10.4
500	19.3	-	20.6	43	22.4
600	26.7	-	15.9	43	27.1
700	28.5	4	14.6	-	-
800	30.3	5	13.4	-	-
900	30.6	5.5	11.9	42.5	30.6

[1] Thickness of JP-4 measured in well

[2] Thickness of JP-4 observed in sand

[3] Water table elevation

[4] Bottom of fuel in sand

The data are discussed in three sections. In the initial period of the tests, all JP-4 added to the column either entered the well bore or was in equilibrium in the soil formation at negative pressures. The second stage begins when enough JP-4 has been added so that the capillary pressure exceeds the entry displacement pressure needed for the JP-4 to enter the positive pressure zone; organic saturation of soil, but no free product. The third stage begins when all the water is at positive pressures and the JP-4 has reached the water table. The soil is saturated with organic and free product exists.

1. Data Set 1: All JP-4 in the formation is at negative pressure. Initially, the JP-4 added to a column enters the well bore and then establishes an equilibrium in the soil at negative pressures, i.e., all JP-4 in the soil is located above the JP-4/air interface in the well bore. The JP-4 will continue to be held in the formation at negative pressures until enough JP-4 is added so that the capillary pressure in the soil at the elevation of zero pressure in the organic is equal to or greater than the organic entry pressure. This is about 7.1 cm of water using the data given on Table 2 for the 0.5 mm soil. Notation is shown in Figure 5.

For the 0.5 mm data used in this illustration, data set one includes the first 900 mLs of fuel added (approximately). A capillary pressure of approximately 7.1 cm of water is needed for entry of the organic into water. An appropriate A' value of 5.5 cm of organic is also indicated from the data. Both the 5.5 cm of organic and 7.1 cm distance to the water table below the JP-4/air interface in the well bore are from the column data. These numbers, however, should also be predictable from the capillary pressure-saturation curves. Again, visual information is difficult to interpret, but an A' = 5.5 cm of organic is a reasonable approximation for the average capillary pressure head in Figure A.2 and 7.1 cm of water is a reasonable value for the average capillary pressure head in Figure A.2. values of A' and B' that will be used in the next section are 5.5 cm and 30.6 cm, respectively, where $\frac{30.6\text{ cm}}{\rho\, g} = \frac{(7.1\text{ cm}}{\Delta\rho g_{w}}$.

2. Data Set 2: JP-4 and water both occupy zones of positive and negative pressures (Figure 6).

After the JP-4 enters the region below the organic/air interface in the well, the JP-4 is at negative pressures above the water table and positive pressures below the water table. The water table can be located by multiplying ρ_o/ρ_w * D and adding this value to the water elevation in the well. The interface between the organic and water in the formation is always at a capillary pressure head equal to the organic entry pressure.

The portion of the data for the 0.5 mm column that falls within this data set represents the cumulative fuel added from about 900 mLs to 3100 mls (Table 3).

TABLE 3: DATA SET 2 FOR 0.5 MM COLUMN TEST

CUMULATIVE JP-4 ADDED (mls)	APPARENT[1] THICKNESS D (cm)	ACTUAL[2] THICKNESS (cm)	WTE[3] (cm)	BOF[4] (cm)	B'=' BOF - WTE (cm)	D + A' -B'[5] (from data) (cm)
900	30.6	5.5	11.9	42.5	30.9	5.5
1900	32.5	8.5	5.9	34.9	29	9
2100	32.5	9	6	34.5	28.5	9.5
2600	34.2	12.5	6.2	31.7	25.5	14.2
3100	38.6	14	7	36	29	15.1

[1] Thickness of JP-4 measured in well

[2] Thickness of JP-4 observed in sand

[3] Water table elevation

[4] Bottom of fuel in sand

[5] Thickness of JP-4 as estimated using Eqn 15

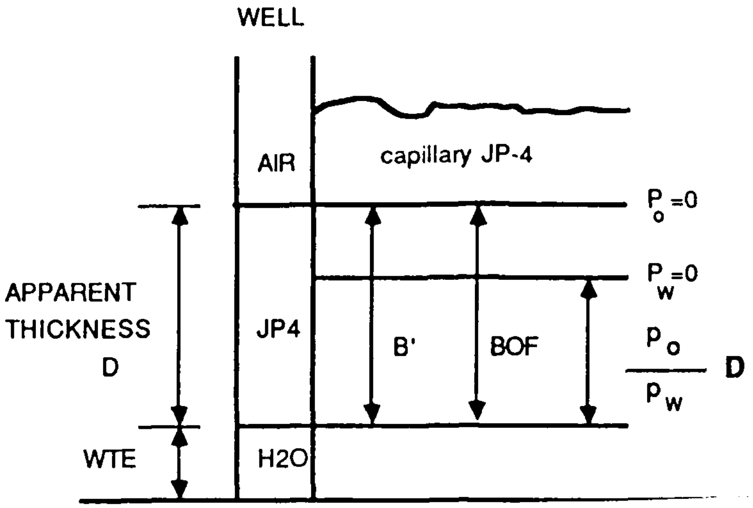

Figure 5. Notation Used When all JP-4 is at Negative Pressure.

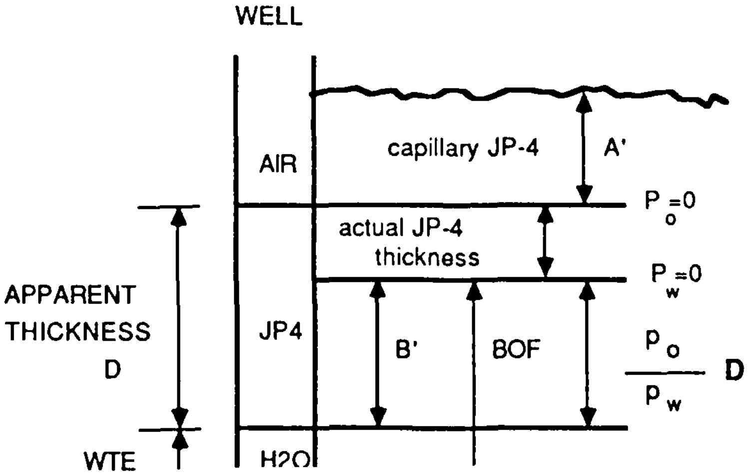

Figure 6. Notation Used When JP-4 is at both Positive and Negative Pressure.

This region demonstrates the revised form of Equation (11) given previously, that relates the predicted (actual) and apparent thicknesses:

$$D + A' - B' = \text{the predicted thickness} \qquad (17)$$

where D equals the apparent thickness in the well. A' equals the capillary thickness of JP-4 in the sand, and B' equals the capillary thickness of water. Using the "average" visual A' and B' values of 5.5 and 30.6 cm obtained from the column data, the predicted and measured values of the actual thickness are plotted in Figure 7. Note that the apparent and predicted thicknesses are linearly related by Equation (17), but the ratio is not a constant. In this data set, the ratio varies from 5.5 to 2.75.

The end of this data set occurs when the JP-4/water interface in the formation is at the water table, i.e., $B = 0.77 * D$.

3. Data Set 3: All water is at positive pressures, JP-4 has reached the water table in the formation.

When the interface between the JP-4 and the water in the formation is at the water table, all water is at positive pressures. In an infinite aquifer, as more JP-4 is added, the water would flow horizontally out of the spill region and the JP-4/water interface would continue to move downward. However, since the columns are a closed system, an increase in JP-4 cannot displace the water that occupies the pores. Therefore, the minimum value of B occurs when the fuel just reaches the water table or $B = 0.77 * D$. Additional fuel added does not relate to a physically feasible field case. If more fuel is added, the water table elevation (WTE) remains constant, the bottom of fuel (BOF) and B values remain constant, and the thickness of the organic in the well and in the formation begins to build up vertically.

C. SUMMARY OF ANALYSIS FORD 0.6 MM AND 0.8 MM COLUMN DATA.

Data sets 1, 2, and 3 were delineated for the 0.6 mm data given in Table 4. Data set 1 ends when B' = D, or just before the JP-4 enters the positive pressure zone. There is some scatter in the data, but B' appears to be about 22.5 cm, which corresponds to $\rho_o = 0.77$ and a value of $(Pc/\rho_w g)^{ow} = 5.2$ cm of water. The corresponding value of A' is about 2 cm of organic. Both of these values appear to be slightly low when compared to the capillary pressure-saturation curves given in Figures A.4 and A.5. From these figures, reasonable values for A' and B' appear to be about 4 cm of organic and 28 cm of water, respectively.

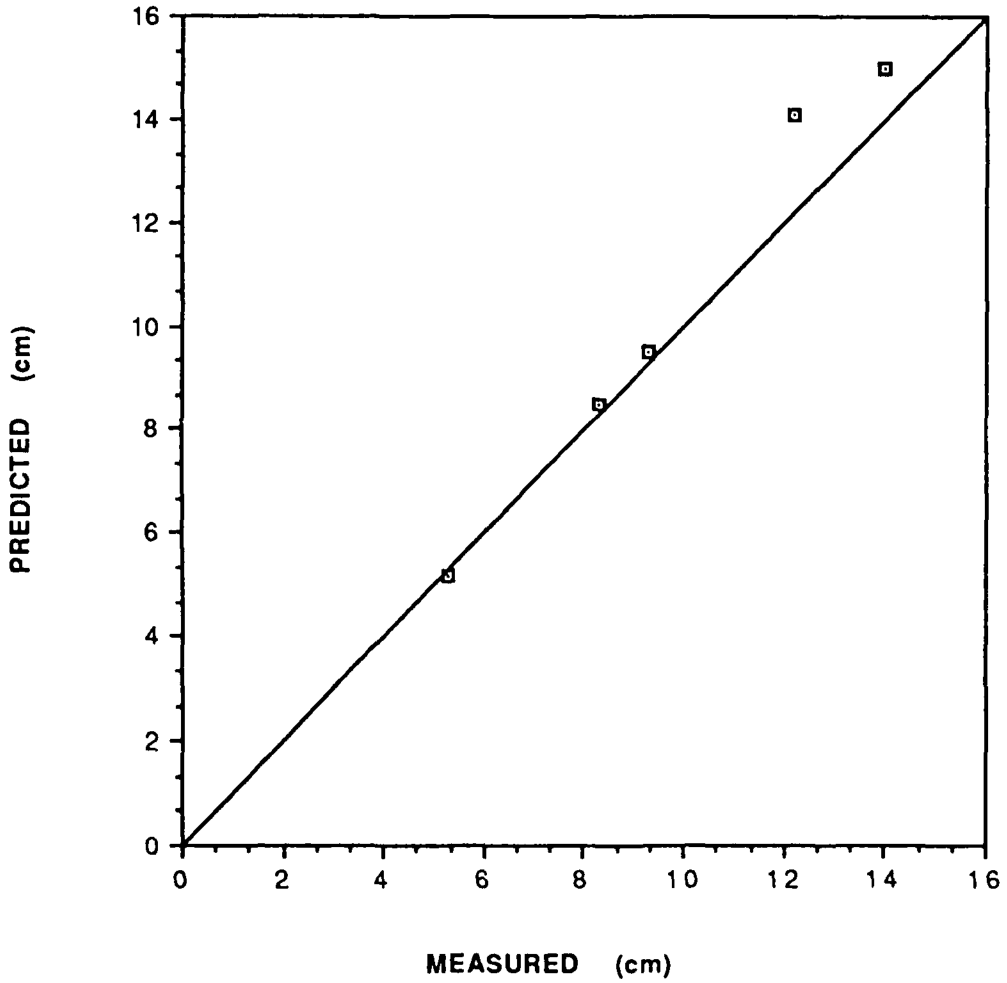

Figure 7. Measured versus Predicted JP-4 Thickness in 0.5mm Sand Column.

TABLE 4: DATA SET FOR 0.6 MM COLUMN DATA

CUMULATIVE FUEL ADDED (mls)	APPARENT THICKNESS D (mls)	ACTUAL THICKNESS (mls)	WTE (cm)	BOF (cm)	B' = BOF - WTE
100	0	0	32.3	38	5.7
200	0	0	32	38	6
300	4.4	0	29	37	8
400	15	0	20.6	37	16.4
500	21	0.8	16.5	38	21.5
600	21.7	1.2	15.7	38	22.3
700	21.7	1.8	15.7	38	22.3
800	22.3	1.8	15	37.5	22.5
900	22.6	2.4	15.1	37.5	22.4
1000	23.6	1.6	13.6	37.5	23.9
1100	24.7	2.9	13.5	37	23.5
1200	25.5	3.6	14.2	36.5	22.3
1300	25.7	3.5	14.1	36.4	22.3
1400	26.2	3.8	14.1	36.4	22.3
1500	26.2	3.9	13.8	36.2	22.4
1600	26.9	4.6	13.8	36	22.2
1700	27.1	4.9	14	36	22
1800	27.5	5.6	14	36	22
1900	27.2	5.8	14.7	36	21.3
2000	26.3	5.5	15	36	21
2100	27.1	6.8	15.2	36	20.8
2200	27.4	6.8	15.2	36	20.8
2300	26.5	7.8	15.1	36	20.9
2400	27.1	7.8	15.3	36.5	21.2
2500	27.8	7.4	15.2	36	20.8
2600	28	7.4	15.2	36	20.8
2700	28.2	7.4	15.1	36	20.9
2800	25	7.3	15.2	36	20.8
2900	25.7	7.5	15.4	36	20.6
3000	26.2	7.4	15.4	36	20.6
3100	26.6	7.4	15.2	35.2	20
3200	27.2	7.4	15.1	35.2	20.1
3300	25	7.2	14.9	35.2	20.3
3400	26.3	8.3	15.1	35.2	20.1
3500	26.8	9.1	15.2	35.2	20
3600	27.2	9.7	15.2	35.2	20
3700	26.9	9.7	15.2	35	19.8
3800	27.6	9.8	15.2	35	19.8
3900	28	10.7	15.2	35	19.8
4000	28.2	11	15.2	35	19.8
4100	28.6	11	15.2	35	19.8
4200	28.6	11.5	15.2	35	19.8
4300	29	11.6	15.2	35	19.8
4400	29.7	12.8	15.2	35	19.8
4500	30	13	15.2	35	19.8

Assuming that A' = 2 cm and B' = 22.5 cm, predicted and measured values of actual thickness are plotted on Figure 8. Note that the predicted values are slightly higher than the measured values As an arbitrary comparison, a better fit is obtained when A' - B' is -22, rather than -20.5. This is also plotted on Figure 8. The difference could be attributed to several factors, including the difficulty of measuring these values to within the accuracy required.

Data set 2 ends when B'(thickness of capillary fringe) equals 0.77 * D, or at about 2100 mls of fuel added. At this point, further additions of JP-4 to the column does not result in meaningful measurements because of the column boundary conditions. Data in the third set does not correspond to a realistic field case because the JP-4 cannot displace the water occupying the saturated zone in the column. Therefore, it will not be considered further except to note that the WTE and B' approach constant values of about 15.2 cm and 20 cm, respectively. At the same time, both D and the actual thickness are increasing, indicating a buildup of organic under positive pressure.

The 0.8 mm column data are more difficult to analyze than the other data sets, partly because this data set has more scatter while increased accuracy is needed because of the greater response to fuel additions. Data Set 1 of the 0.8 mm data appears to include the first 400 mls of fuel added. However, the end of Data Set 2 is not clear because there are several times when B' = 0.77 * D. These are marked with an asterisk on Table 5. However, B', BOF, and WTE appear to stabilize by about 1500 ml so this is used as the end of this data set.

A reasonable value of B' (thickness of saturated capillary zone that JP-4 cannot penetrate) is 15.2 cm. The value of B' in the data stabilizes at about this value and it is also consistent with an organic entry pressure of 3.5 cm of water ($3.5/\Delta\rho g = 15.2$), a reasonable value on Figure A.8. A value of for of 2 cm from Figure A.8, also appears reasonable. Figure 9 plots the predicted and measured JP-4 thickness if A' - B' is assumed to be (-13.2) cm.

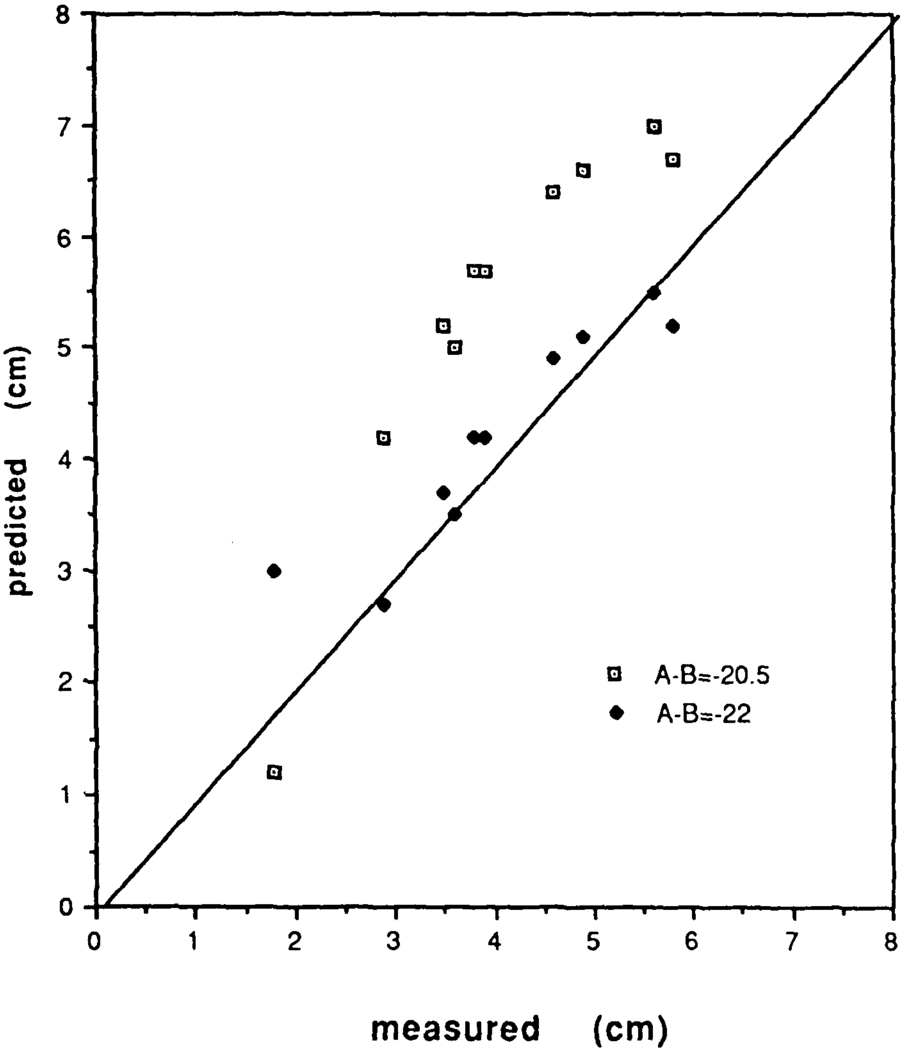

Figure 8. Measured versus Predicted JP-4 Thickness in 0.6mm Sand Column.

TABLE 5: DATA SET FOR 0.8 MM COLUMN DATA

CUMULATIVE FUEL ADDED (mls)	APPARENT[1] THICKNESS D (cm)	ACTUAL[2] THICKNESS (cm)	WTE[3] (cm)	BOF[4] (cm)	B[5], = BOF - WTE (cm)	(0.77*D)[6] (cm)
100	0	0	30.5	34.5	4	0
200	1.6	0	29.4	34.5	5.1	1.232
300	8.9	0	24.1	34.5	10.4	6.853
400	11.8	0	22.4	34.5	12.1	9.086
500	13.5	0	21.5	34.5	13	10.395
600	14.1	2	20.9	34.5	13.6	10.857
700	14.8	3.8	21	34	13	11.396
800	16.1	2.8	20	34	14	12.397
900	16.9	3.4	19.7	34	14.3	13.013
1000	17.5	4.1	19.4	33.5	14.1	13.475
1100	18.1	3.8	18.4	33	14.6	13.937
1200	18.9	4.3	18.4	33	14.6	14.553*
1300	19.4	4.8	18.4	33	14.6	14.938
1400	19.6	4.9	18.2	33	14.8	15.092
1500	19.8	5.1	17.8	33	15.2	15.246*
1600	20.5	6	18	33	15	15.785
1700	20.6	6.5	18	33	15	15.862
1800	21.2	6.5	17.7	33	15.3	16.324
1900	21.6	6.3	17.5	33	15.5	16.632
2000	18.5	8.2	18	33	15	14.245
2100	19.6	10.2	17.9	33	15.1	15.092*
2200	20.1	10.5	17.8	33	15.2	15.477
2300	20.6	10.5	17.5	33	15.5	15.862
2400	21	10.5	17.3	33	15.7	16.17
2520	20.9	10.5	17.4	33	15.6	16.093
2600	20.6	10.5	17.7	33	15.3	15.862
2700	21.6	10.5	17.5	33	15.5	16.632
2800	22.1	10.5	17.4	33	15.6	17.017
2900	22.4	10.5	17.3	33	15.7	17.248
3000	21.8	10.5	17.7	33	15.3	16.786
3100	22.8	10.5	17.5	33	15.5	17.556

Possible end points for data set 2 when B = 0.77 * D

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[1] Thickness of JP-4 measured in well

[2] Thickness of JP-4 observed in sand

[3] Water table elevation

[4] Bottom of fuel in sand

[5] Thickness of JP-4 as estimated using Eqn 15

[6] Thickness of saturated capillary zone

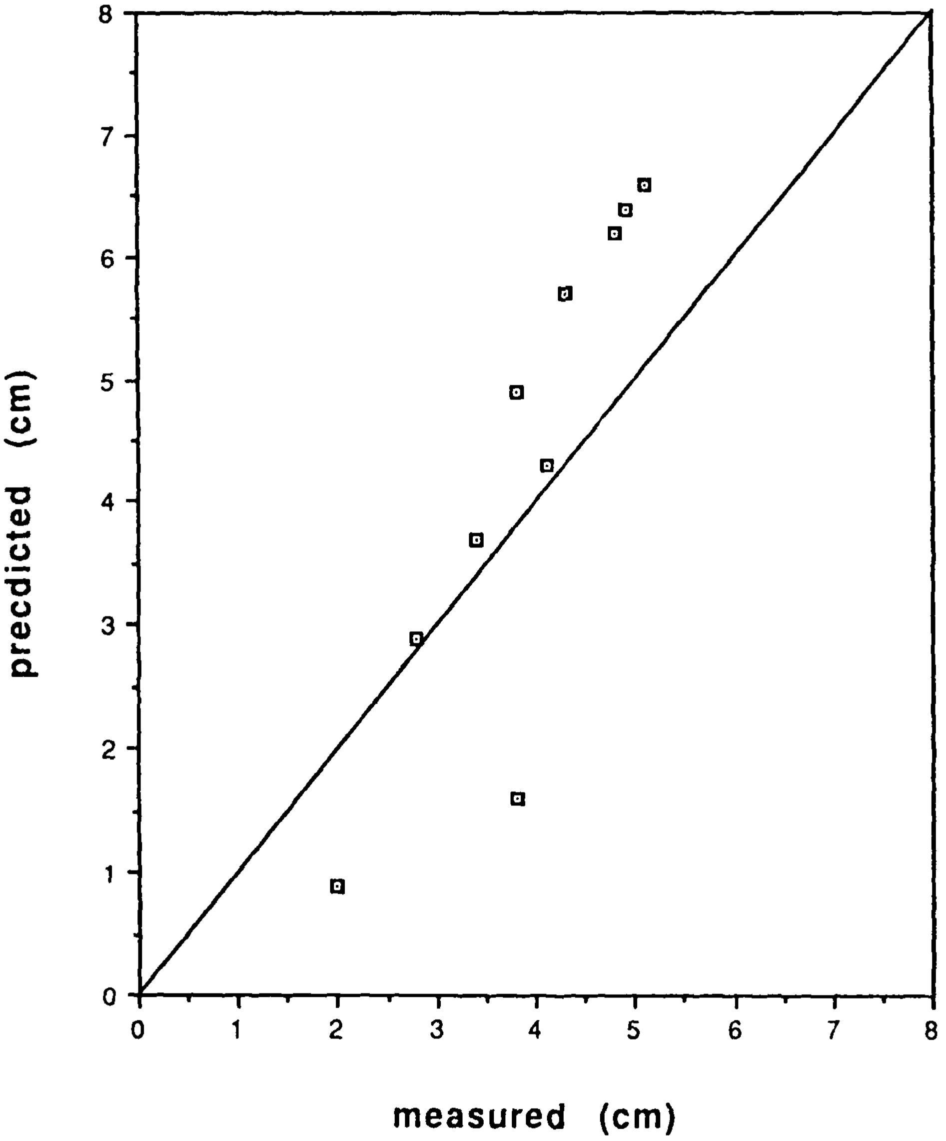

Figure 9. Measured versus Predicted JP-4 Thickness in 0.8mm Sand Column.

SECTION IV

CONCLUSIONS

Based on previously estalished relationships for estimating immisible fluid volumes in porous media, an equation was derived for estimating "actual" petroleum thickness in a soil formation from the "apparent" thickness in a monitoring well. The equation requires the thickness of petroleum in a well, the capillary thickness of water, and the capillary thickness of petroleum in the soil formation as input variables. The latter two variables cannot be measured directly in the field and must be determined from the interrelationship of capillary-pressure-saturation curves of air/organic and organic/water systems determined in the laboratory. The equation gave a good match, however, between predicted JP-4 thickness and the thickness measured in laboratory columns. Because of the physical boundary conditions imposed by the columns, it was only possible to evaluate the equation over a narrow range of conditions. In addition, it was tested only under equilibrium conditions; additional experiments would need to be performed to address these limitations.

It also needs to be restated that the findings of this study confirm what previous researchers have speculated; that capillary thickness, which is a function of particle size, affects the relationship between apparent and actual petroleum thickness. A "rule-of-thumb" is that the coarser the aquifer material, the more reliable the fuel volume estimates will be based on observation well data with finer aquifer material the discrepancy between actual and apparent thickness increases. It would be prudent to keep this in mind when evaluating fuel thickness estimates.

SECTION V

RECOMMENDATIONS

The following recommendations are offered in this area:

1. The column studies provide valuable intermediate verification of theory; therefore, they should be continued and expanded. Some possible considerations are:

    a. Tensiometers need to be designed that can measure negative organic and negative water pressures for instrumentation of the columns.

    b. When initially applied during data set 1, the JP-4 was at

    simulates a field case where wells are in place before and during a spill. If the equilibrium location of the JP-4 is in the negative pressure zone only, none of the JP-4 will enter wells that are installed after a spill. Another series of column tests needs to be designed to simulate this second field case.

    c. The columns should be modified so that free outflow of water can occur in response to the addition of JP-4.

2. An extension of the column studies to two dimensions should be performed using a laboratory sand tank. Instrumentation of the column is important in order to verify theory. Concepts of apparent and actual thickness can be extended directly to two dimensions. In addition, prediction of the horizontal extent of a spill, if the total quantity of leakage is known (or vice versa), would be an important interesting application.

3. A number of aspects of the capillary pressure-saturation curve determinations should be further pursued. Some of these are:

    a. measurement of the contact angles required and comparison of the three curves for each sand to see if the LaPlace equation accurately relates the curves. This verification would require the measurement of only one curve.

    b. A further investigation of the differences found between the new and aged JP-4 properties and an evaluation of the effects of these differences when extending laboratory data to field application.

    c. Develop faster and simpler methods of capillary pressure curve determination.

APPENDIX A

CAPILLARY PRESSURE CURVES

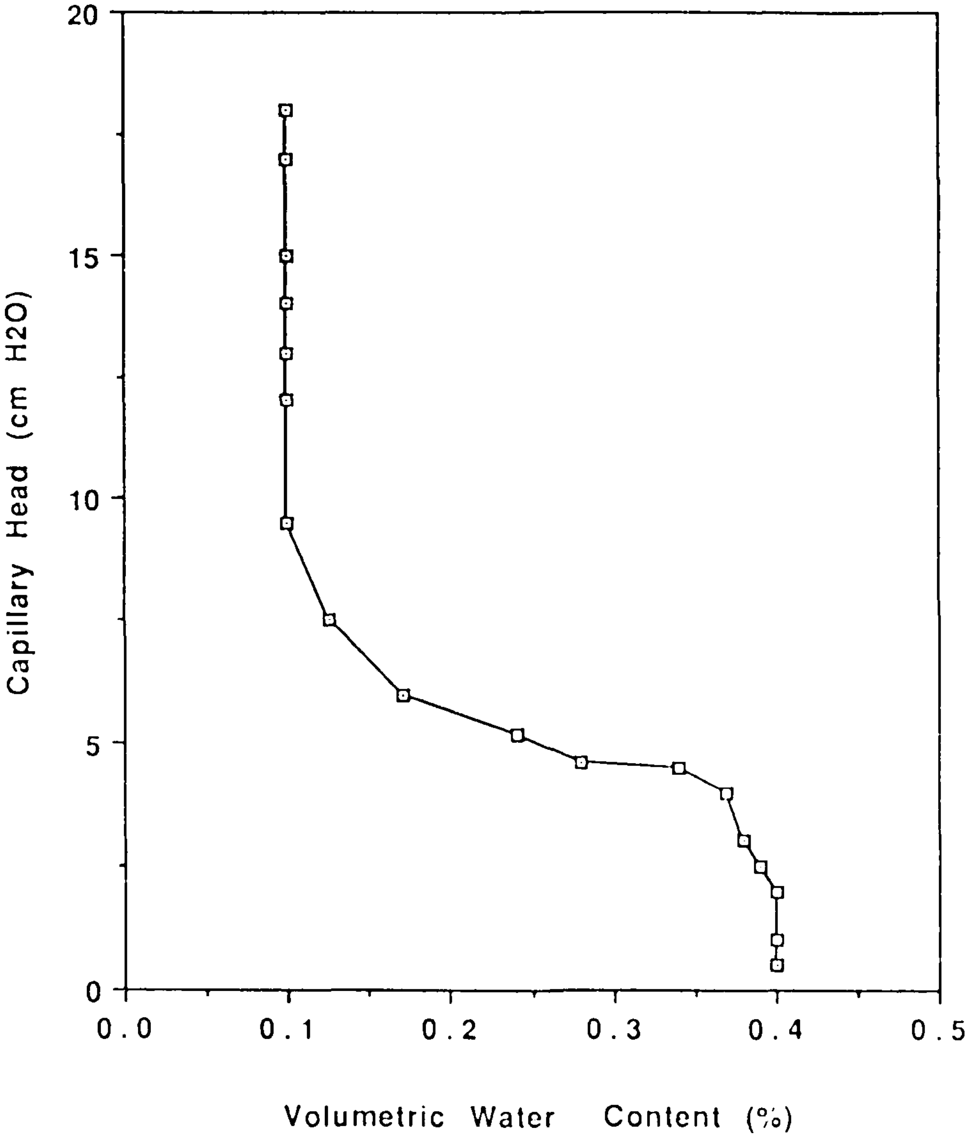

Figure A-1. Capillary Pressure-Volumetric Organic Content for JP-4/Air System (0.5mm Sand).

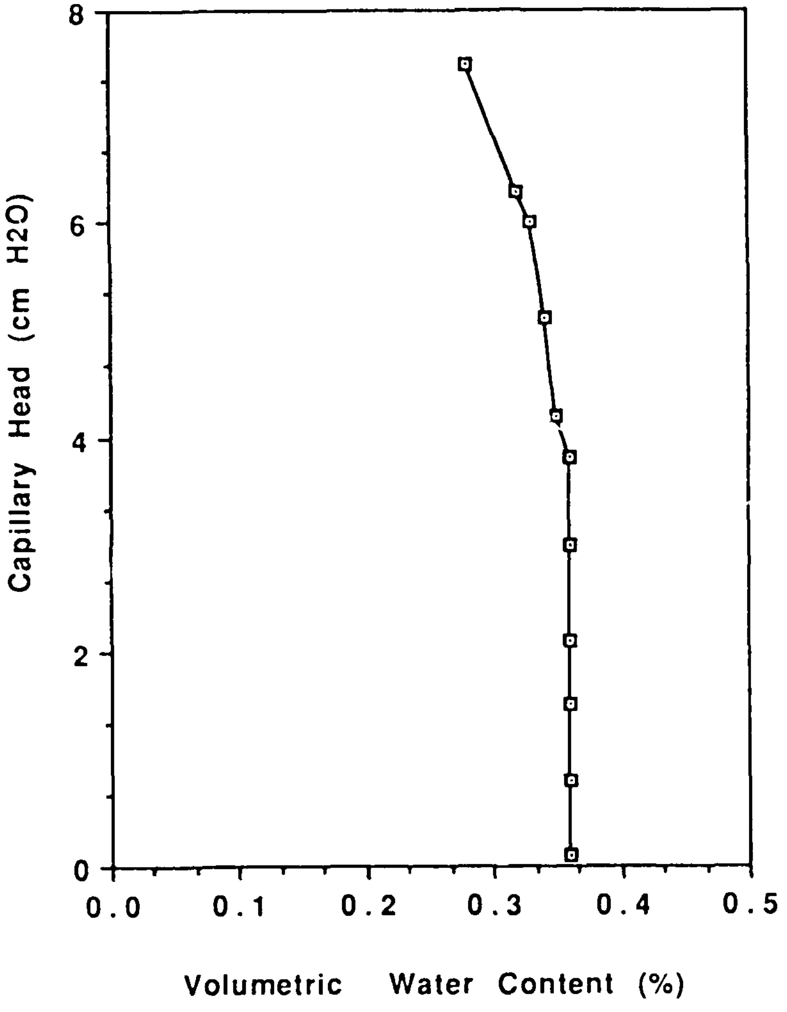

Figure A-2. Capillary Pressure-Volumetric Water Content for JP-4/Water System (0.5mm Sand).

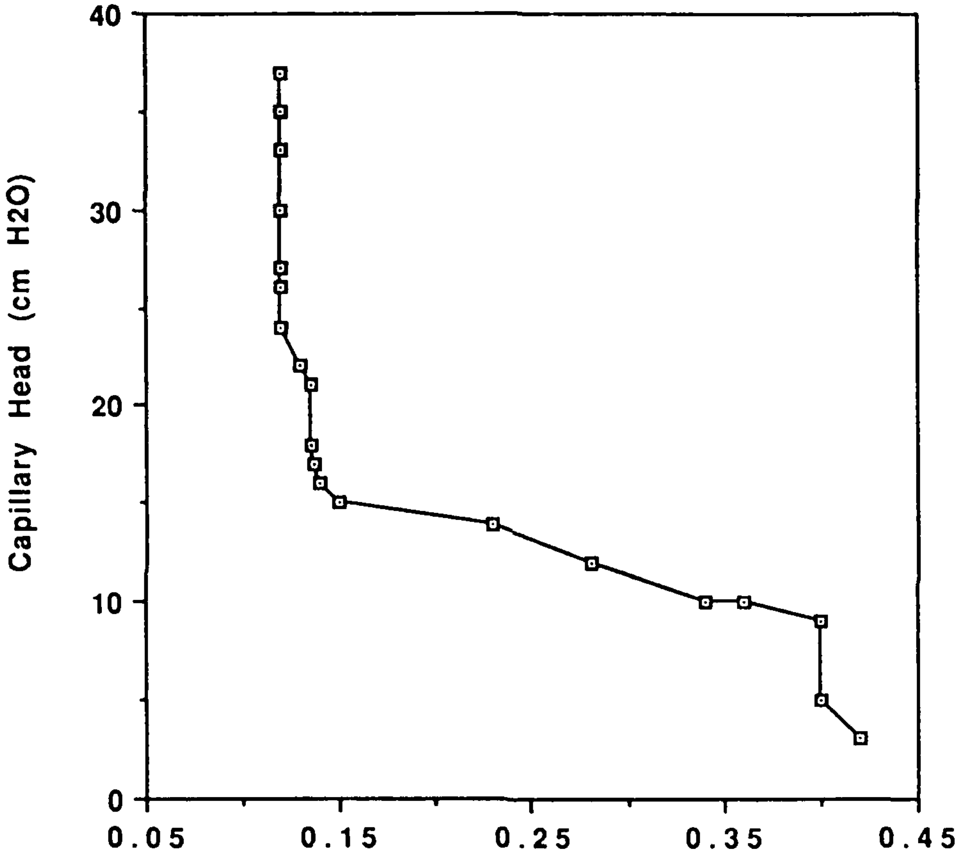

Figure A-3. Capillary Pressure-Volumetric Water Content for Air/Water System (0.5mm Sand).

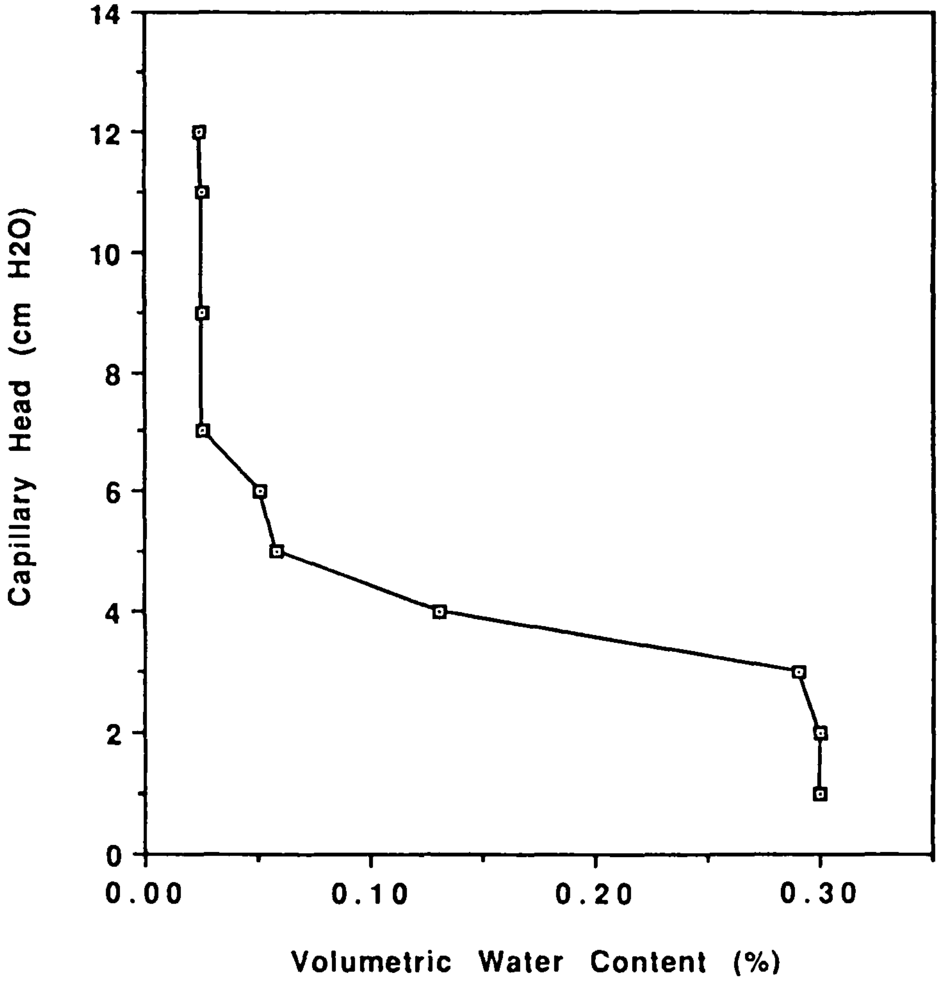

Figure A-4. Capillary Pressure-Volumetric Organic Content for JP-4/Air System (0.6mm Sand).

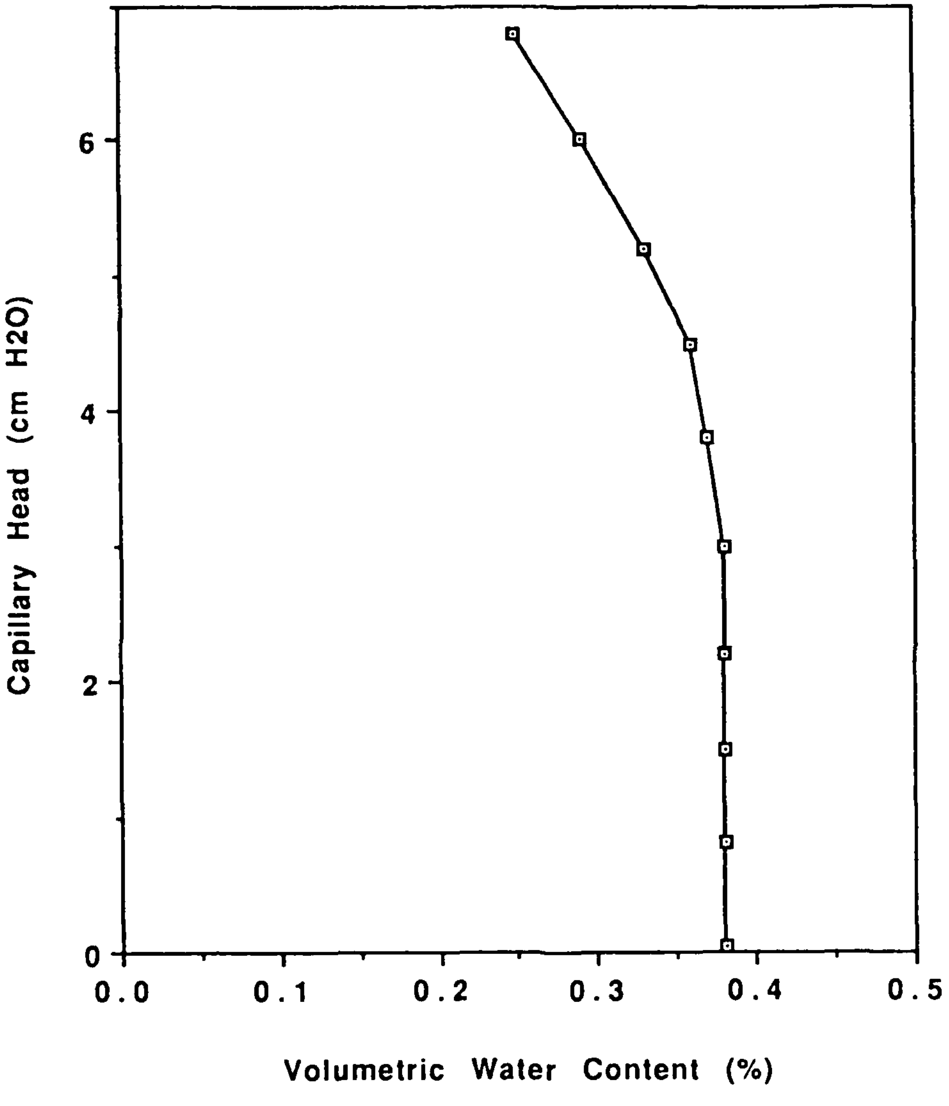

Figure A-5. Capillary Pressure-Volumetric Water Content for JP-4/Water System (0.6mm Sand).

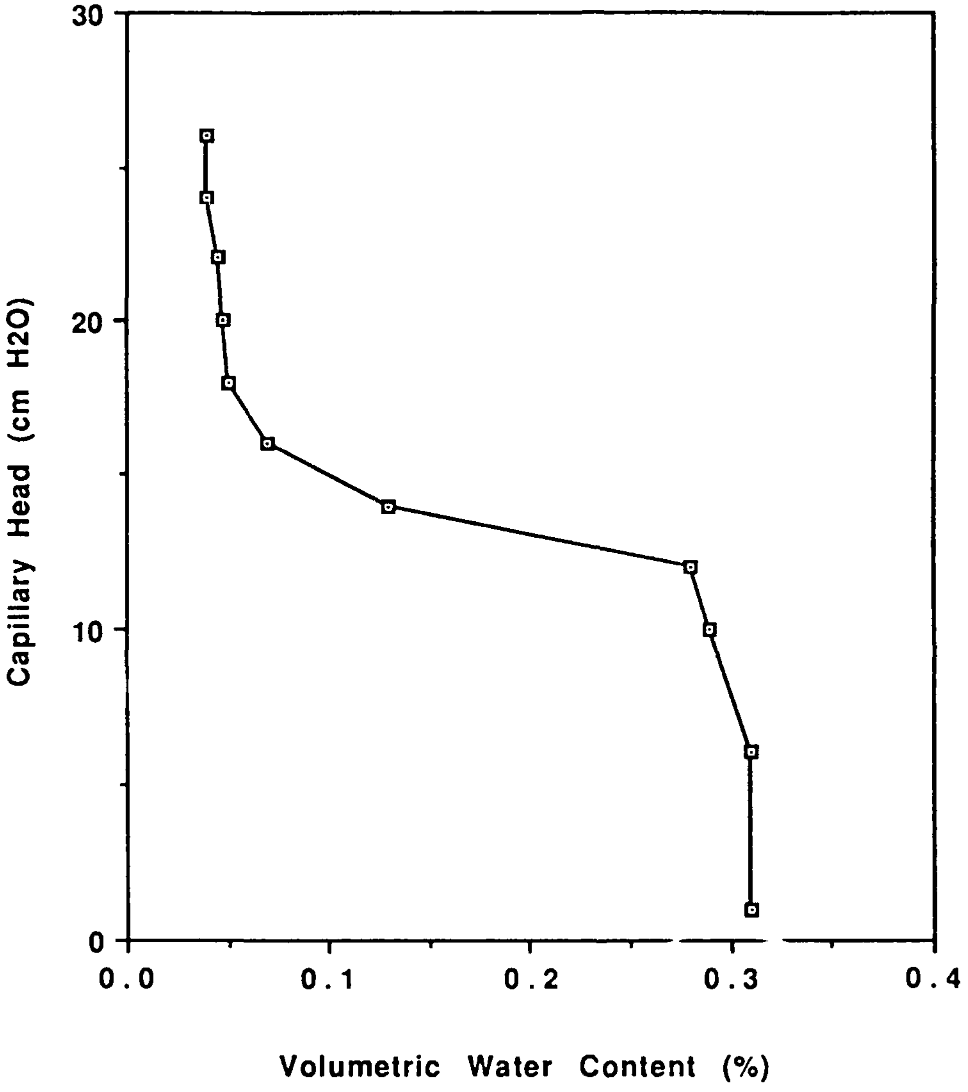

Figure A-6. Capillary Pressure-Volumetric Water Content for Air/Water System (0.6mm Sand).

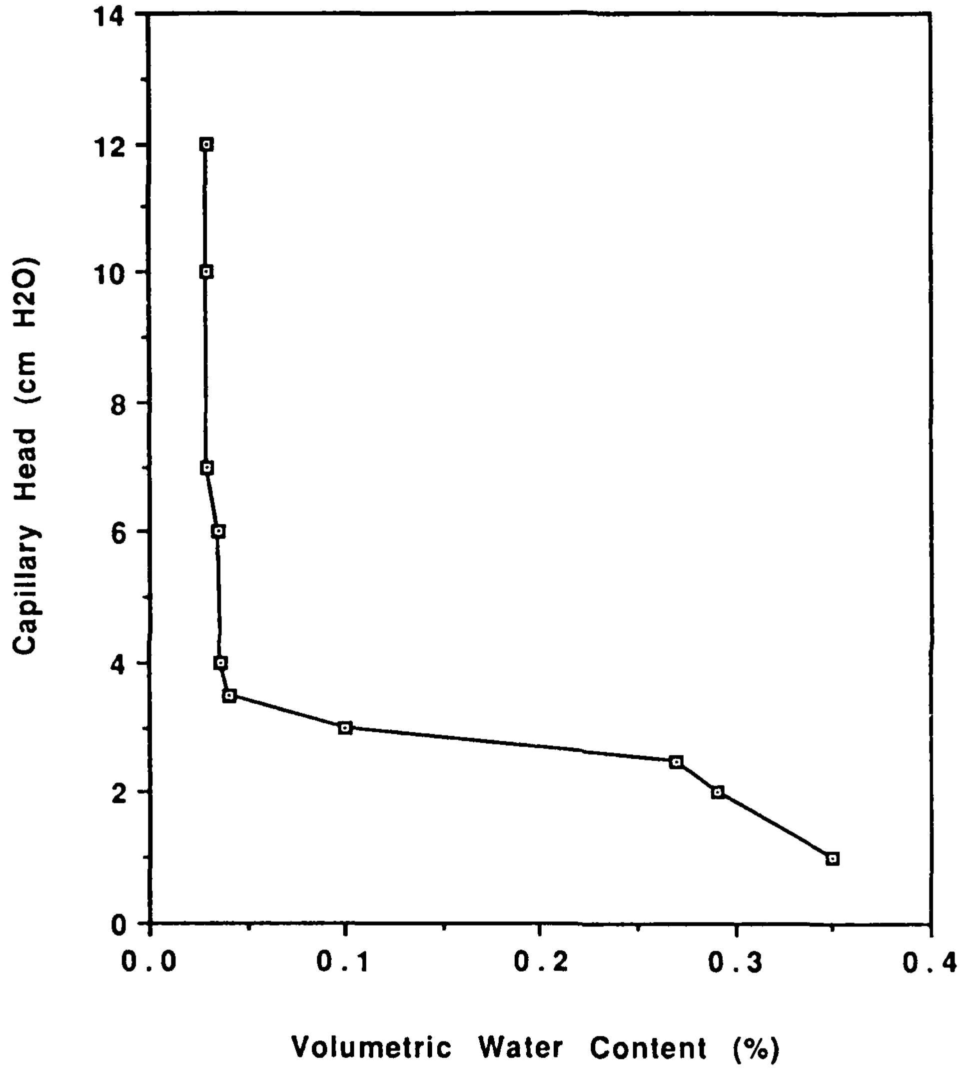

Figure A-7. Capillary Pressure-Volumetric Organic Content for JP-4/Water System (0.8mm Sand).

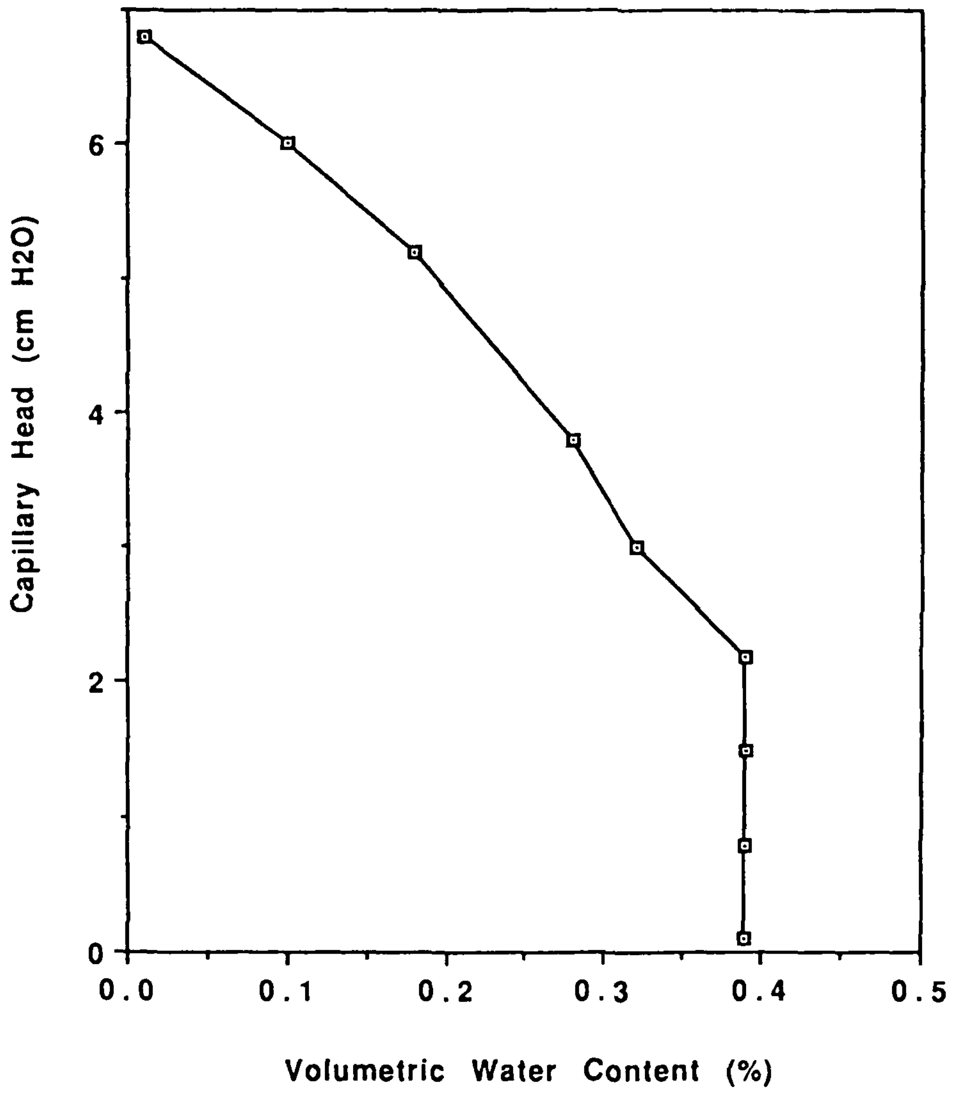

Figure A-8. Capillary Pressure-Volumetric Water Content for JP-4/Water System (0.8mm Sand).

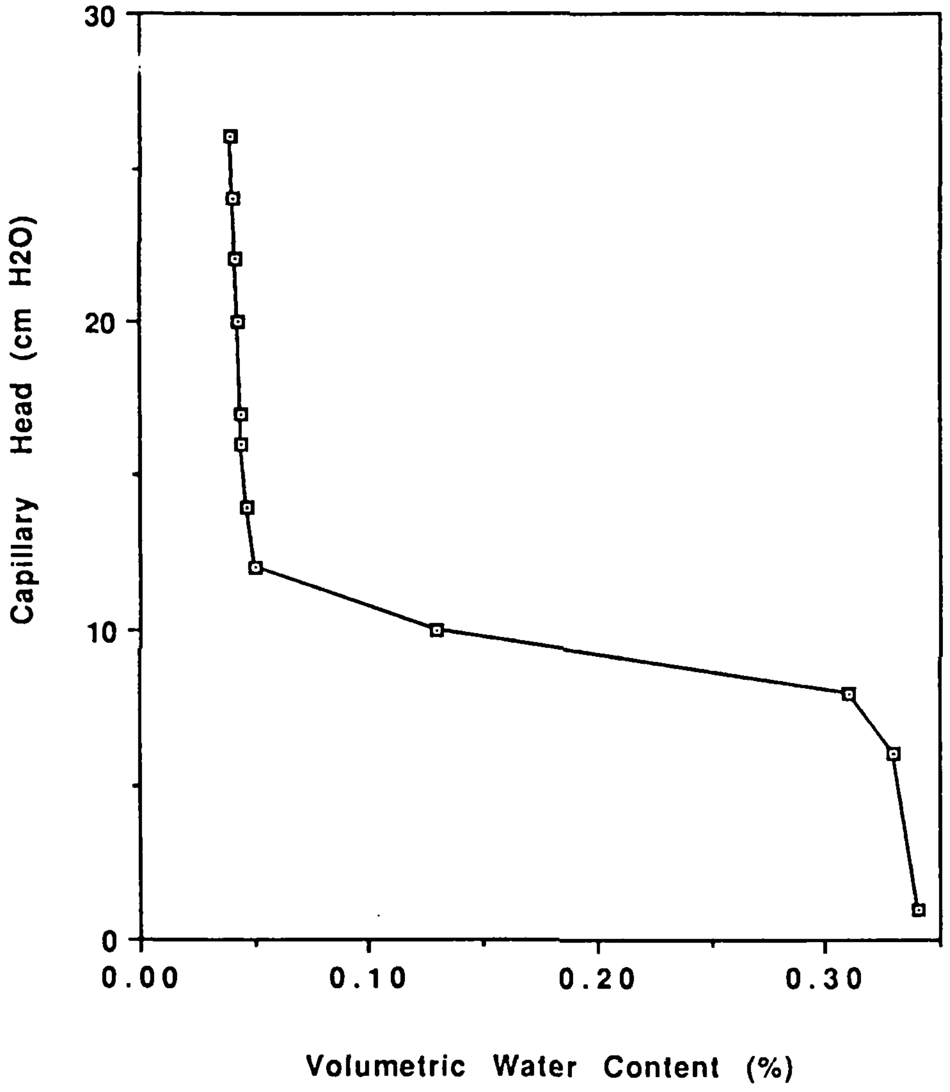

Figure A-9. Capillary Pressure-Volumetric Water Content for JP-4/Water System (0.8mm Sand).

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