Quantifying Crude Oil Spill Volume in Homogenous and Layered Porous Media from Product Thickness in Monitoring Wells

by

Khalid Bashir

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

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In

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INFORMATION TO USERS

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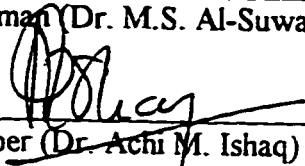
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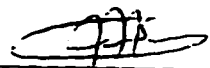
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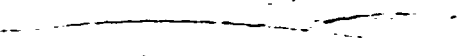
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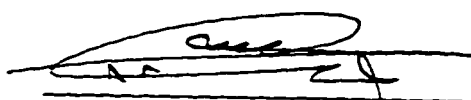
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To my Parents,
and to my teachers.

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Back home, I reserve special thanks and thoughts for my parents, wife Sameena, brother Tariq , Nadia and H. Hooria.

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THESIS ABSTRACT

NAME OF STUDENT
TITLE OF STUDY

MAJOR FIELD
DATE OF DEGREE

Khalid Bashir
Quantifying Crude oil spill volume in homogeneous and layered soils from product thickness in monitoring wells.
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An experimental study was conducted to examine the relation between the hydrocarbon spill volume and its thickness in a fully screened monitoring well in homogeneous and layered soils. Estimates of the spill volume for various hydrocarbon thicknesses were obtained from analytical and empirical models available in literature, using the soil hydraulic parameters estimated from the software SOILPROP.

Comparison of the experimental results and the model predictions shows that the analytical models based on the Brooks-Corey and van-Genuchten equations underpredict the spill volume in all the soils at the relative permeability (k/k_s) ratio of 1% and 0.1%. This ratio significantly affected the model estimates, with estimates at k/k_s of 1% considerably higher than corresponding estimates at k/k_s of 0.1%. The empirical models also consistently underpredicted the spill volume . A modified analytical model approach based on the concept of a hypothetical soil hydrocarbon depth and linearization of the total saturation function (S_t) was developed and it estimated the spill volume very closely.

The study also shows that soil layering can appreciably affect the spill volume-well hydrocarbon thickness relationship, and may result in an increase or decrease in the well hydrocarbon thickness. This effect can be more pronounced in a real life problem. The maximum recovery of the free hydrocarbon in the columns was about 50%, leaving at least 50% of the total spill volume irrecoverable.

Master Of Science Degree
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ملخص البحث

الاسم : خالد بشير

مسمى البحث : تقدير حجم الزيت الخام المسكوب في التربة المتجانسة والطبقية باستخدام سمك الزيت في آبار المراقبة .

التخصص العام : الهندسة المدنية (قسم مصادر المياه والبيئة)

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صممت تجارب معملية لبحث العلاقة بين حجم الزيت الخام المسكوب علــى خــزان جوفي مكشوف وسماكته في آبار المراقبة . شملت هذه الدراسة تربة متجانسة و تربة متعددة الطبقات . قورنت نتائج هذه التجارب بالتقديرات الناتجة من استخدام نماذج تحليلية وتجريبية سبق نشرها في المجلات العلمية . تم تقدير حجم الزيت المسكوب نموذجيا بناءً على سماكته في آبار المراقبة بالإضافة إلى خواصه البيدرولية والتي تم تقديـــرها مـــن خـــلال برنـــامج " SOIL PROP " .

دلـت المقارنـة على أن النمـاذج المـبنيـة على معـادلـتي Brooks-Corey و van Genuchten تعطي تقديرات أقل من الواقع في جميع أنواع التربة المدروسة لكلتا نسبتي النفاذية التي تم مقارنتها . كما طور نموذج معدل مبني على نظرية افتراضية لتوزيع الزيـت في التربة غير المشبعة مما أدى إلى تحسين واضح في تقديرات النماذج التحليلية . بينت هذه الدراسة أن للتركيب الطبقي تأثير واضح على علاقة حجم الزيت المسكوب وسماكته في آبار الاختبار وهذا يزيد من صعوبة المسائل الحقنية . أوضحت هذه الدراسة أن أعنى نسبة أمكـــن استخراجها من الزيت المسكوب لا تتعدى 50% من الحجم المسكوب تاركة جزء كبير مـــن الزيت تحت ضغط سالب .

Chapter 1

INTRODUCTION

Groundwater is the most important source of water for municipal, agricultural, and industrial use, which makes it a lifeline for people around the world. Its primary use is as a self supplied water source for drinking purposes. In addition, groundwater performs many important ecological functions, being a source of fresh water for many fresh water ecosystems and, accordingly it is responsible for their sustenance. The quality of groundwater therefore is of paramount importance. Its quality can be affected by contamination occuring from various sources. Mostly, attention has focused on wastes as a main source of groundwater contamination, however, there are many other sources as well. Some of the prominent sources of contamination are discussed below (Fetter, 1992):

1. Septic tanks and cesspools : These are designed to discharge the domestic wastewater into the soil subsurface. These wastes are predominantly organic, and if they contaminate groundwater, they will be a health hazard.

2. Injection wells : These are mostly used to discharge liquid wastes into soil strata below the water table. The liquid wastes injected include hazardous wastes, brine recovered from oil wells, agricultural runoff, municipal sewage, etc. These wastes can contaminate aquifers through a leak in the well casing or through geological faults around the aquifer.

3. Landfills and open dumps : These facilities store both hazardous and non hazardous wastes which are mostly solids. A major problem associated with landfills is the generation of leachates. The migration of leachates can be prevented by providing a geosynthetic or a clay liner. However, poorly designed liners will allow the leachate to leak and thus contaminate the groundwater.

4. Surface impoundments : Pits, ponds and lagoons are used by industry and municipalities to store or treat hazardous and non-hazardous liquid wastes. These wastes contain a range of contaminants which can contaminate the groundwater .

5. Mining : Surface and underground mining may disrupt natural groundwater flow patterns and expose rocks containing pyrite to oxygenated water, thus producing acidic water. This acidic water can contaminate the groundwater and make it inappropriate for use.

6. Agricultural activities : The use of pesticides and fertilizers in the soil is a major source of contamination. Pesticides applied on the soil are mostly biodegradable; however, their metabolites can migrate through the soil to the water table. Nitrogeneous fertilizers can also leach from the soil through infiltration and contaminate the water table.

7. Radioactive wastes : Unless these wastes are properly buried, there is a potential for radio-nuclides to migrate from the waste into the groundwater. These wastes may not degrade at all in water, making it permanently unfit for use.

1.1. Groundwater Contamination by LNAPLs

Another important type of groundwater contamination is the one resulting from sources designed for storage, transport, and disposal of hazardous substances, i.e.. pipelines, storage tanks. etc. These hazardous substances pose serious health risks and are carcinogenic and bio-magnify even at very low concentrations. The problem is further complicated because many of these compounds are not easily detected during water consumption as they are tasteless and odorless.

Storage tanks can be classified as above ground (AGSTs) and underground (UGSTs). Most often the UGSTs are used to store light non-aqueous phase liquids (LNAPLs) such as gasoline, kerosene, diesel, crude oil, and other organic products. These products are stored at industrial sites and transportation dumps. and are also prominent at gas stations. The number of gas stations is very large and the UGSTs at these stations are a common source of leakage. The leakage may occur through holes in the tank itself or its associated pipeline. These tanks are most often made of steel and this makes them vulnerable to the corrosive effect of the salts in the soil surrounding them. Initially when the leakage starts. the LNAPL will percolate down into the soil and also spread laterally. If the spilled volume is relatively small. it will be held up in the soil as an immobile phase by capillary forces. As the spilled volume increases it will overcome the capillary forces and move further down till it becomes very close to the watertable. It will start spreading laterally forming a pool above the water table. A small part of the LNAPL will dissolve in the water and the plume of contaminated water created will spread with the passage of time

increasing the amount of the water affected. Figure 1.1 illustrates a leaking UGST. and the distribution of the leaking hydrocarbon liquids. Even minute traces of contamination at the parts per billion (ppb) level will seriously undermine the quality of groundwater. Since these problems are taking place underground they are rarely detected early. Discovering the problem and facing it early not only saves vast reserves of the groundwater from contamination but also reduces the associated cost of cleanup.

A precise estimation of the spilled volume is very important to understand the magnitude of the contamination and also for the proper planning of the remediation and restoration of the groundwater quality. Early detection of a leak or a spill is possible using monitoring wells and possibly from hydrocarbon fumes that may emanate from the contaminated zone. If a mobile hydrocarbon fluid appears in the monitoring well, this accumulated hydrocarbon thickness can be a reasonable pointer to the estimation of the volume of the hydrocarbon present in the aquifer. Based on the volume of hydrocarbon estimated. pumps. bore holes. etc. can be designed for the cleanup of the aquifer.

1.2 Problem Definition and Objectives

The primary objective of this laboratory study was to estimate the volume of the crude oil. also referred to as the hydrocarbon resulting from its spill on a sand column. Since direct measurement of the hydrocarbon present in a soil is impossible. the best indicator that can be used to estimate the extent of the contamination of groundwater is the hydrocarbon thickness in monitoring wells. This study focuses on the behavior of the spill volume- hydrocarbon thickness relationship in order to come up with a reliable
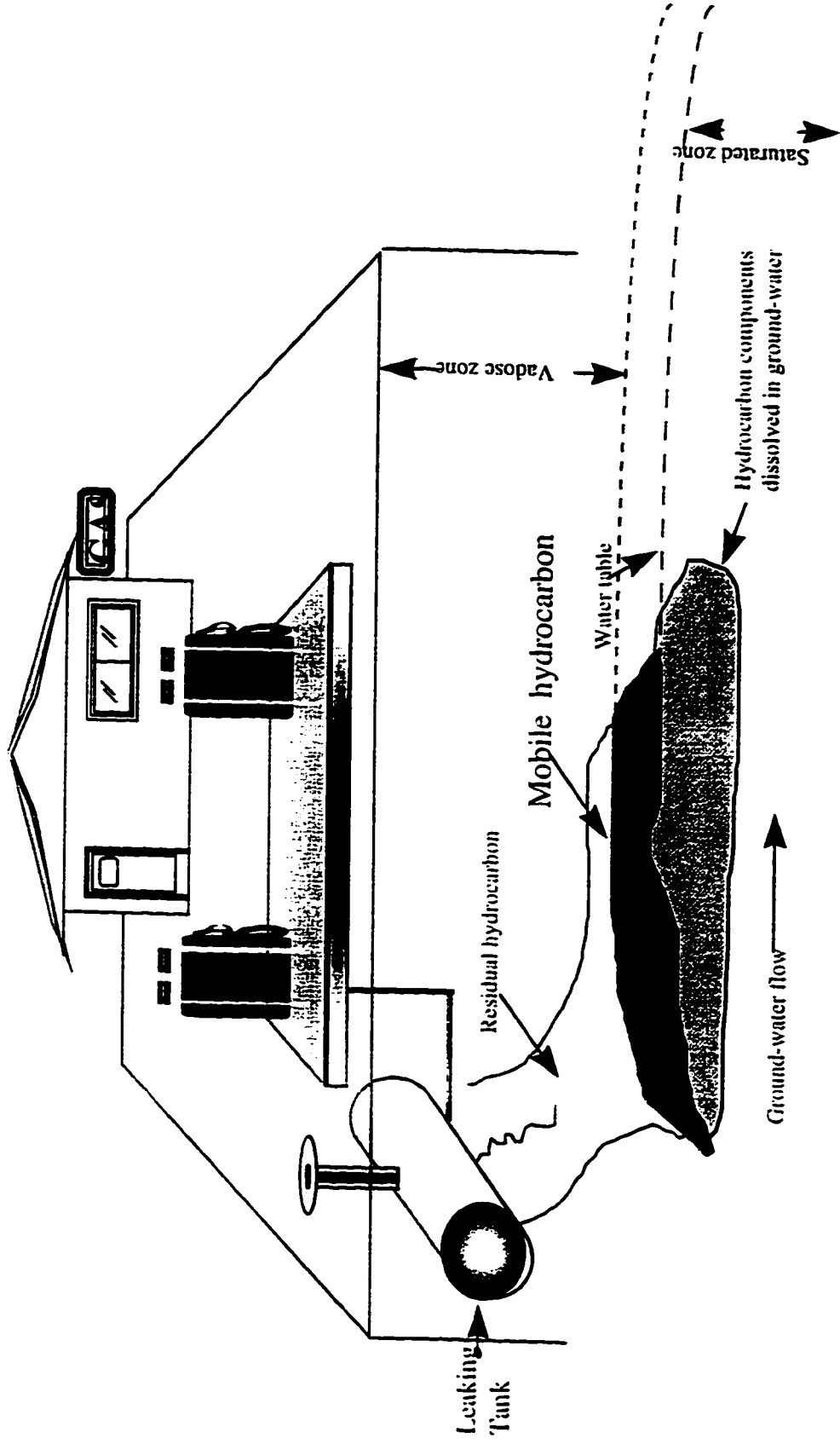
Figure 1.1 : Groundwater contamination by a leaking underground storage tank (UGST).

means of estimating the spill volume from measured values of hydrocarbon thickness. A pair of homogeneous and layered soils were used to broaden the scope of this study.

Analytical and empirical models available to estimate the spill volume were used. The analytical models were based on the saturation-capillary pressure relationships suggested by Brooks-Corey (1964) and van Genuchten (1980). Reliability of these relationships/models was checked by comparing the estimated and the experimental spill volume. More specifically the objectives of the study were as follows :

1. To monitor the appearance of the crude in the monitoring wells and examine the relation between the product thickness in the wells and the total spilled volume for homogeneous and layered soils .

2. To develop a computer model to estimate theoretically the amount of spilled volume using the product thickness in monitoring wells and the soil hydraulic parameters in layered soils by extending the analytical model of Farr et al. (1990) and Lenhard and Parker (1990) to the layered porous media.

3. To compare the estimated and the measured spill volume in the soils. using the developed program and other models available in the literature and check the validity of the models.

4. To compare the predictions based on Brooks-Corey and van Genuchten models.

5. To examine the influence of layering on the volume-thickness relationship .

6. To monitor and examine the changes in the water table position as a result of the spill .

Chapter 2

LITERATURE REVIEW

A simple method to detect a hydrocarbon spill beneath the ground is the installation of monitoring wells. The thickness of the hydrocarbon in a monitoring well may be used to estimate its total volume in the contaminated soil. However the predictions made from the data obtained from monitoring wells can result in significant errors in estimating the volume of contamination as well as in the planning for remediation.

Published studies (Lenhard and Parker. 1990; and Farr et al., 1990) establish that hydraulic properties of the porous media containing the hydrocarbon fluid are important for the understanding and estimation of its volume. These properties, along with the hydrocarbon thickness in monitoring wells. should provide the information necessary for a reliable estimation of the volume.

2.1 Hydrocarbon Thickness in a Monitoring Well

Researchers (Van Dam. 1967; and De Pastrovich et al., 1979) have concluded that the product thickness in a monitoring well is not representative of its actual thickness in the aquifer, which was verified by experimental findings (Ballestero et al., 1993; Abdul et al.. 1989; Hampton and Miller; 1988; and Hall et al., 1984) and a correction factor has to be applied to arrive at the actual thickness. Van Dam (1967) showed that at hydrostatic equilibrium. as the hydrocarbon entered the monitoring well from above the free water

surface. the water level in the well would be lowered approximately a distance of $\gamma_o / (\gamma_w - \gamma_o)$ times its thickness above the water table. where. γ_o is the density of the hydrocarbon and γ_w is the density of water. De Pastrovich et al. (1979) indicated that the thickness of the free product in the formation is about one-fourth its thickness in the monitoring well. Similar results have been reported by Zilliox and Muntzer (1975) and Kramer (1982).

Hall et al. (1984) investigated the relationship between oil thickness in porous media and the thickness of oil in the monitoring well in laboratory scale boxes designed for sandy porous media. After the addition of a critical oil volume which increased as grain size diminished. a 1 : 1 relationship between soil hydrocarbon thickness and well hydrocarbon thickness was observed. Their observations did not agree with the relationships developed by de Pastrovich et al. (1979). They corrected the hydrocarbon thickness in the well by introducing what they called a *formation factor*. This factor depended on the pore size distribution of the porous media as well as the surface tension of the hydrocarbon and is valid only when the hydrocarbon thickness exceeds a certain critical value and ranges from 5 cm to 12.5 cm for different soils.

This is. however. not a reliable rule as proved by the comprehensive experimental study of Hampton and Miller (1988) and Abdul et al. (1989). It has been agreed that correction factors have to be applied which are related to the type of the formation. grain size distribution and the two fluid properties- density and interfacial fluid tension.

Scheigg (1985) developed a theoretical relationship which predicts the actual thickness from the apparent thickness. He corrected the hydrocarbon thickness in monitoring wells

by subtracting twice the capillary height under drainage conditions. This equation was developed using scaling factors based on the Laplace equation for capillarity.

Hampton and Miller (1988) reported, based on their experimental study, the failure of the previous methods to predict the actual hydrocarbon thickness and suggested that layering and packing of the media would determine the distribution of the hydrocarbon. As such, the actual thickness of the product saturated layer is vaguely defined. They proposed to replace the "actual thickness" by a "effective permeable height" defined by Corey (1966). Hughes et al. (1988) also have discouraged the use of hydrocarbon thickness in the monitoring wells as large errors in hydrocarbon thickness can arise due to variation in the grain size distribution and the hydrocarbon density.

Abdul et al. (1989) conducted column experiments to investigate the flow of oil into a well installed in oil contaminated porous media. They found that presence of oil in the monitoring well is an indication of an advanced stage of contamination of the subsurface. Their experimental results also indicated that the ratio of the oil thickness in the well to that in the porous media, defined as "R", is not a constant and that assuming R to be constant can lead to a conservative assessment for remediation purposes. The prediction of R is expected to be more uncertain at the field sites due to the dynamic fluid flow and the spatial variability of the hydrogeologic parameters such as the soil grain size distribution, soil layering, and the water table position.

Farr et al. (1990) also have indicated that there is no simple relation correlating the well hydrocarbon thickness (T) to the actual hydrocarbon volume (V), and the 4:1 rule of thumb proposed by De-Pastrovich et al. (1979) is not reliable. Only in porous media with

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uniform pore sizes is the volume of hydrocarbon in the vadose zone approximately proportional to the thickness of the hydrocarbon in monitoring well(s) and a linear relationship of the form $V = \varphi(1 - Sr)T$ is predicted for soils with large values of the soil parameter λ, where the term $\varphi(1 - Sr)$ is defined as the effective soil porosity (Brooks- and Corey, 1966).

The field experimental results of Huntley et al. (1993) show that the measurement of soil characteristics of an average soil sample is not sufficient to characterise the hydrocarbon thickness within a small area. A greater exaggeration has been reported for fine grained soils, compared to coarser ones, and this can incorrectly encourage the placement of the recovery well in the fine grained material at the site.

Ballestero et al. (1993) also developed an equation to calculate the actual hydrocarbon thickness in a aquifer. This equation was based on the assumption of hydrostatic force equilibrium between the fluids. They calibrated their empirical equation with a physical model, which simulated field conditions. Results of their study were similar to that of Hall et al (1984). The effect of a fluctuating water table was also studied. A rising water table caused a decrease in the well hydrocarbon thickness. while a falling water table caused it to increase. which is attributed to the hysteresis of the saturation curve.

2.2 Theoretical Estimation of Hydrocarbon Volume

A number of theoretical models . both of the analytical and empirical types. have been developed for estimation of the hydrocarbon volume. Besides the availability of data

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on the hydrocarbon thickness in monitoring well(s). the estimation of soil hydraulic parameters is important. The key to the analytical models is the soil saturation-capillary pressure (S-P) characteristic curve. Based on S-P curves for a soil, analytical estimates of the hydrocarbon volume can be obtained. A detailed description of the saturation curves/relationships developed by Brooks and Corey (1966) is presented in the following section.

2.2.1 The Brooks-Corey Saturation-Pressure Relationship

Brooks and Corey (1966) plotted S-P relation curves on a log- log scale for the results of the experiments conducted on homogeneous and isotropic soil samples. Based on these curves they proposed an empirical relation between the effective saturation S_e and the capillary pressure P_c, which is given by.

$$S_e = [P_c/P_d]^{-\lambda} \qquad (P_c \geq P_d)$$

$$S_e = 1 \qquad (P_c \leq P_d)$$

where.

λ is the Brooks-Corey soil parameter. also called the particle size distribution index

P_d is the displacement pressure

Brooks and Corey also defined the effective saturation S_e as follows:

$$S_e = (S- S_r)/(1- S_r)$$

where .

S is the saturation and S_r is the residual saturation taken as a fitting parameter.

A typical Brooks-Corey S-P curve is shown in Figure 2.1. Up to a certain elevation above the water table the soil will remain saturated. Eventually the capillary pressure will become high enough that water begins to drain from the soil. This pressure is called the displacement pressure (P_d). This was experimentally observed in a study conducted later by Corey and Brooks (1975). The capillary behavior of a porous media based on this model can thus be defined on the basis of the constants λ and P_d.

The constant λ for soils is typically around *two*. Soils with well developed structure have a λ less than *one*, sands have λ greater than *two*, sometimes as large as *five*, which theoretically can approach a value of infinity. Brooks and Corey(1975) also called λ an index of pore size distribution. They stated that the media with uniform pore size would have large λ, which theoretically could reach infinity. On the other hand, soils with a very large range of pore sizes should have similar values of λ which theoretically could approach zero.

Another model defining the S-P relation was developed by van Genuchten (1980). Unlike the Brooks and Corey model, it assumes the displacement pressure to be effectively zero. A detailed application of both models for estimating the hydrocarbon volume is presented in the following section.
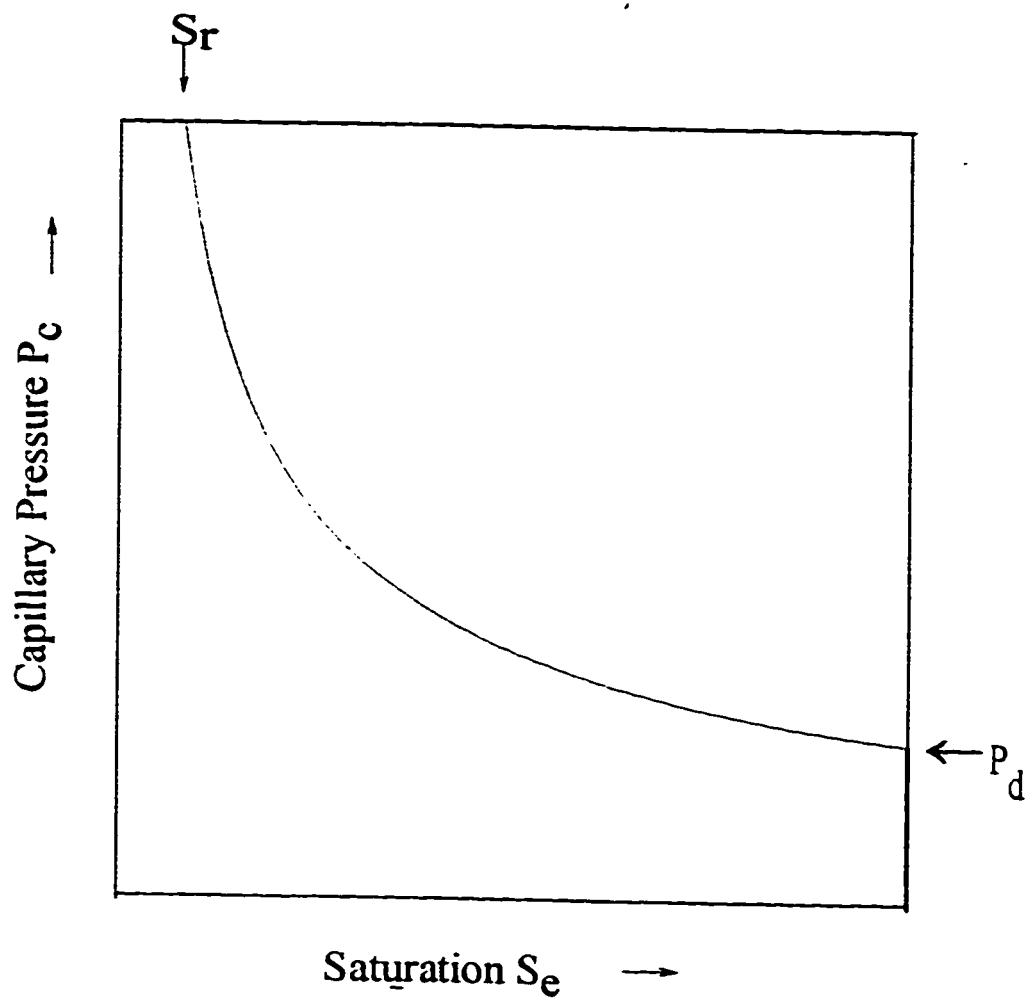
Figure 2.1 : Two phase saturation-capillary pressure curve for Brooks-Corey media.

2.2.2 Analytical Estimation of Volume

Among the spill estimation models, the analytical models of Farr et al. (1990) and Lenhard and Parker (1990) explicitly treat the problem of estimation taking into account the following parameters :

1. Grain -size distribution of the porous media.

2. Saturation characteristics of the fluids/ soils, and

3. Fluid properties, i.e., fluid density and interfacial tension.

These parameters have not been used extensively in the other models, where the relationships are mostly of an empirical nature and do not explain the use of these parameters.

Farr et al. (1990) and Lenhard and Parker (1990) developed a theoretical model to estimate the hydrocarbon volume from its thickness in monitoring wells. This model is based on hydrostatic distribution in fluid pressures and the two phase capillary pressure saturation (S-P) relations of Brooks and Corey (1966) and van Genuchten (1980) which can be extended to the three phase system using scaling coefficients (Lenhard and Parker. 1987). The fluid pressure distribution can be obtained from the fluid levels in a well and this is then used to obtain the saturation profile of the hydrocarbon fluid along the vertical direction of that well. The hydrocarbon fluid volume is obtained from the integration of the saturation profile along the vertical direction.

The key to this model is the knowledge of the moisture retention characteristics of the aquifer media. i.e., the Brooks-Corey hydraulic parameters- pore size distribution

index (λ), displacement pressure (P_d), and residual saturation (S_r) which are uniquely associated with that particular soil. These parameters can be obtained using an experimental saturation - capillary pressure curve . However, such an experiment is time consuming and difficult to perform.

An alternate methodology has been presented by Mishra et al. (1989), wherein they have developed a model which predicts the soil hydraulic parameters using the available particle size distribution of the soil. This model has been copyrighted as SOILPROP and is available commercially. In addition to the calculation of the parameters n and α for the van Genuchten model, it also calculates their equivalents, λ and P_d, for the Brooks- Corey model. The model of Mishra et al. (1989) is based on an earlier model developed by Arya and Paris (1981) in which the soil particle size distribution is transformed into a pore size distribution from which a relation between the cumulative pore volume and a pore radii is obtained. This relation can be converted into one relating the saturation and the capillary pressure. Mishra et al. (1989) calibrated the model using the experimental results on 250 soil samples.

Farr et al. (1990) and Lenhard and Parker (1990) estimated the spilled hydrocarbon volume per unit area, also called the specific volume (cm^3 / cm^2) by integrating the area between the total liquid saturation (S_t) and the water saturation (S_w) in the vertical direction (Figure 2.2). This area is representative of the part of the void space occupied by the hydrocarbon and is applicable for the Brooks-Corey based models, where the
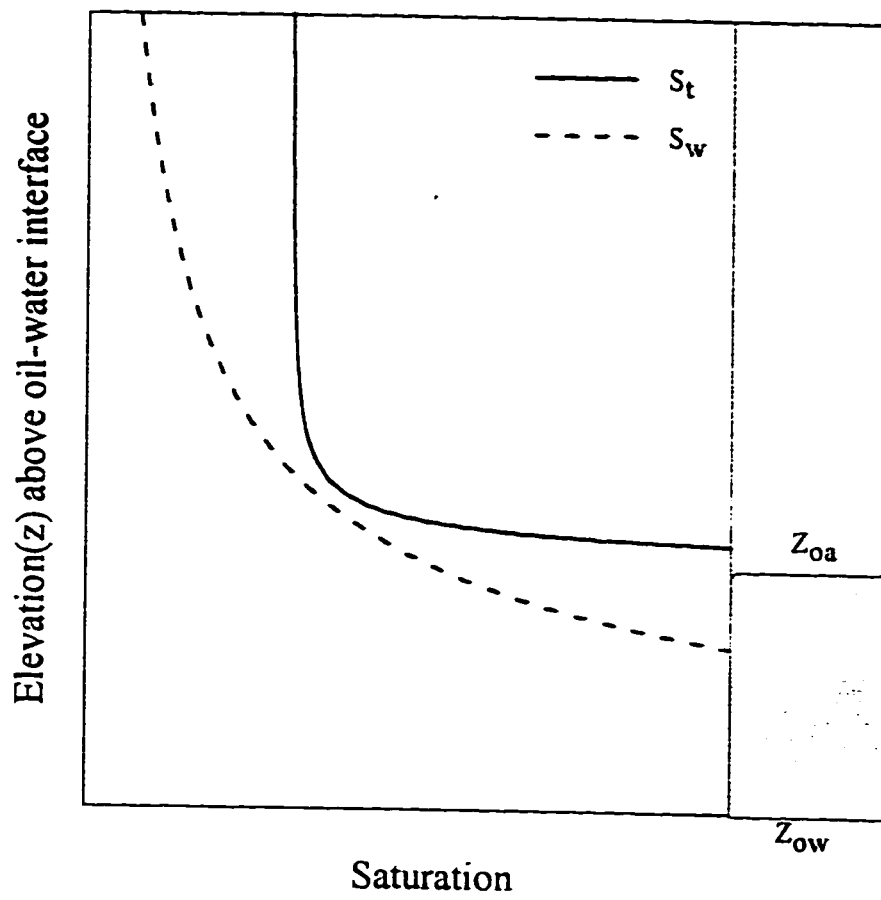
Figure 2.2 : Three phase Brooks-Corey distribution of fluids in a homogeneous soil.

hydrocarbon volume is function of the displacement pressure for the three phase fluid distribution .

The hydrocarbon estimated is composed of two parts: the recoverable hydrocarbon which is under positive pressure and the non-recoverable hydrocarbon which is under negative pressure and the total volume (V_o) can be mathematically expressed as follows :

$$V_o = \int_0^{Tco} \Phi S_o \, dz = \Phi \int_{h_d^{ow}}^{T-h_d^{ao}} (1-S_w) \, dz + \Phi \int_{T+h_d^{ao}}^{Tco} (S_T - S_w) \, dz \qquad (1)$$

where,

h_d^{ow} and h_d^{ao} are the displacement pressures for the oil-water and air-oil phase respectively,

T = well hydrocarbon thickness,

T_{co} = minimum soil hydrocarbon thickness,

ϕ = soil porosity.

The saturation is related to the capillary pressure through the Brooks-Corey equation or the van Genuchten equation. For the Brooks-Corey equation the water saturation curve is given as follows :

$$S_w = (1 - S_r) [P_c^{ow}/P_d^{ow}]^{-\lambda ow} + S_r \qquad (P_c^{ow} \geq P_d^{ow}) \qquad (2a)$$

$$S_w = 1 \qquad (P_c^{ow} \leq P_d^{ow}) \qquad (2b)$$

where,

S_w = water saturation.

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S_r =   residual water saturation.

P_c^{ow} = capillary pressure between water and hydrocarbon.

P_d^{ow} =   displacement pressure between water and hydrocarbon, and

λ_{ow} =   pore size distribution index for hydrocarbon / water system.

The total saturation is assumed to be independent of the water hydrocarbon capillary pressure and depends only on the capillary pressure between the hydrocarbon and air. The total liquid saturation can be expressed as follows :

$$S_o + S_w = (1 - S_r) [P_c^{ao}/P_d^{ao}]^{-\lambda_{ao}} + S_r \qquad (P_c^{ao} \geq P_d^{ao}) \qquad (3a)$$

$$S_o + S_w = 1 \qquad (P_c^{ao} \leq P_d^{ao}) \qquad\qquad (3b)$$

where the variables are the same as defined above except that they apply for the hydrocarbon air system.

Farr et al. (1990) and Lenhard and Parker (1990) assumed that the pore size distribution indices and the residual saturations are properties of the porous media and are independent of fluid properties. The displacement pressures, however, are dependent on the fluid pair in consideration. The three phase parameters can be derived from the two phase parameters using the three phase relationship (Lenhard and Parker 1987):

$$P_d^{ow} / \sigma_{ow} = P_d^{ao} / \sigma_{ao} = P_d^{aw} / \sigma_{aw} \qquad (4)$$

where,

σ_{aw} , σ_{ao} and σ_{ow} are the interfacial tension parameters for an air-water, air-oil, and oil-water interface respectively.

The values of the interfacial tension are available from simple laboratory tests. Knowing the parameter P_d for one of the fluid pairs, this parameter for the other fluid pairs can be readily evaluated from the relationship given in (4).

The capillary pressure heads between the fluid pairs as a function of the elevation z above the water /hydrocarbon interface in the monitoring well are given by the following :

$$P_c^{ow} = (\rho_w - \rho_o) \, gz \qquad (5)$$

$$P_c^{ao} = \rho_o \, g \, (z - T) \qquad (6)$$

where,

ρ_w = water density,

ρ_o = hydrocarbon density, and

g = gravitational acceleration.

The capillary pressure distribution for a three phase fluid distribution is shown in Figure 2.3. Equations 2 to 6 are used in (1) which is integrated to obtain an estimate of the hydrocarbon volume. However, pure static conditions are difficult to achieve in practice and a better approach to the problem would involve a sort of quasi- static approximation of the fluid distribution as indicated by Lenhard and Parker (1990). Fluids tend to take a very long time to achieve static equilibrium because values of relative permeability
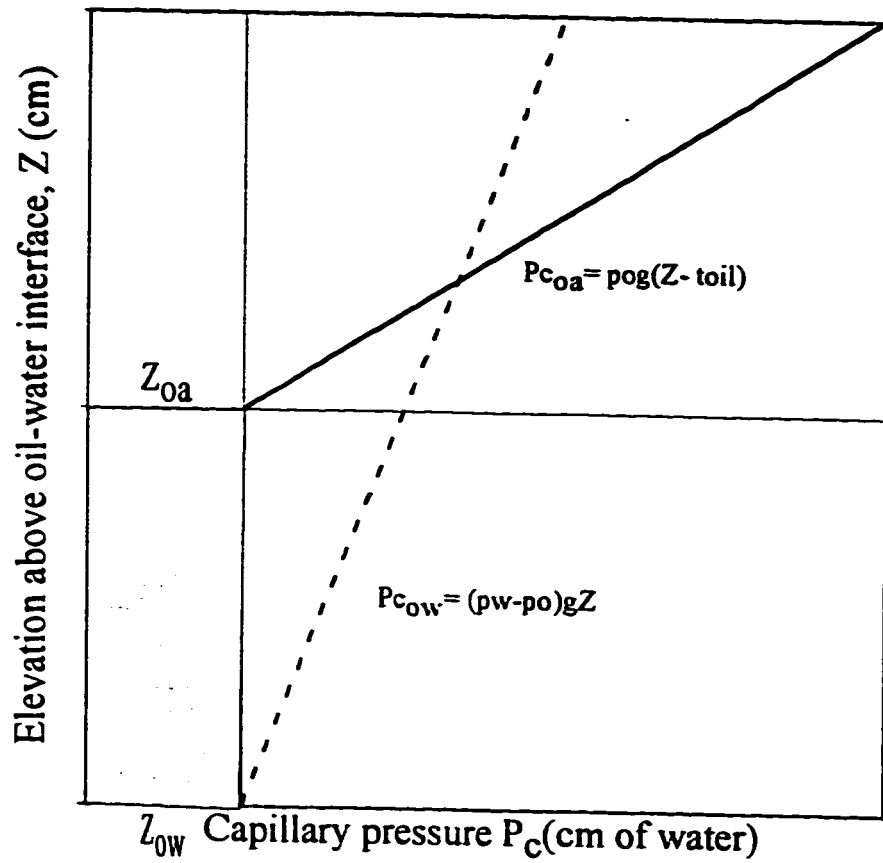
Figure 2.3 : Typical three phase capillary pressure distribution .

The figure shows a plot with:
- Y-axis: Elevation above oil-water interface, Z (cm)
- X-axis: Z_{ow} Capillary pressure P_c(cm of water)
- Z_{oa} marked on the left axis
- Solid line: $Pc_{oa} = pog(Z - toil)$
- Dashed line: $Pc_{ow} = (pw-po)gZ$

decrease rapidly with time. Therefore, a residual saturation is taken such that the relative permeability k_r is very small (say in the range of 0.1% to 1% of the saturated permeability k_s). Equilibrium parameters are obtained by assuming a zero value for the residual water saturation.

Since true equilibrium conditions are difficult to achieve, the fluid saturations may differ from those predicted for ideal hydrostatic conditions. The quasi-static model accommodates the effects of vertical non-equilibrium. The quasi-static residual saturation is determined using the permeability function (Brooks-Corey, 1964):

$$k_w = k_s \, S_w^{\,(2+3\lambda)/\lambda}$$

where,

   k_w = wetting phase permeability,

   k_s = saturated permeability,

   S_w = wetting fluid saturation.

For the van Genuchten equation (1980) the water saturation relationship is expressed as:

$$S_w = (1-S_r)\,(1/(1+(\alpha_{ow}P_c^{ow})^n))^{\,1-1/n} + S_r \qquad (n>1) \qquad (8)$$

where,

   S_w = water saturation,

   S_r = residual water saturation,

P_c^{ow} = capillary pressure between water and hydrocarbon.

α_{ow} = van Genuchten fluid/soil parameter. and

n = van Genuchten soil parameter.

The total saturation is expressed as follows :

$$S_o + S_w = (1-S_r) (1/ (1 + (\alpha_{ao}P_c^{ao})^n)^{1-1/n} + S_r \qquad (n > 1) \qquad (9)$$

where the variables are the same as defined in (8) except that they apply for the hydrocarbon air system.

Unlike the Brooks-Corey equations. the van Genuchten equation does not account for a displacement pressure between the fluids. For the van Genuchten equation, equation (1) can not be integrated to get a closed form solution and numerical integration must be used. The resulting equation for the estimation of volume (V_o) is given by the following :

$$V_o = \phi \{ \ \Sigma \, [1 - S_w(z)]\Delta z + \ \Sigma \, [S_t(z) - S_w(z)]\Delta z \} \qquad (10)$$

Analogous to (4). the van Genuchten three phase parameters can be derived from the two phase parameters using the three phase relationship (Lenhard and Parker, 1987):

$$\alpha_{ow} \ \sigma_{ow} = \alpha_{ao} \ \sigma_{ao} = \alpha_{aw} \ \sigma_{aw} \qquad (11)$$

To accommodate the effects of vertical non-equilibrium and attain a quasi -static model van Genuchten (1980) gave the permeability function :

$$k_w = k_s \, S_w^{1/2} \, (1 - (1 - S_w^{1/m})^m)^2 \qquad (12)$$

where,

k_w = wetting phase permeability.

k_s = saturated permeability.

S_w = wetting fluid saturation, and

m = van Genuchten parameter ($m = 1-1/n$).

Lenhard and Parker (1990) estimated the hydrocarbon volume based on the Brooks-Corey and van Genuchten equations for a pair of hypothetical soils: a well- graded and a uniform soil. These theoretical results were compared with predictions obtained using the models of De Pastrovich et al. (1979) and Hall et al. (1984). These two empirical models predicted the volume without considering the importance of soil pore size distribution. This is considered a serious shortcoming in these models and leads to poor results. The method of Hall et al. (1984) was found to overestimate the hydrocarbon volume for both soils. For the uniform soil. the model of Pastrovich (1979) predicted a larger hydrocarbon volume for small hydrocarbon thicknesses in monitoring wells and vice versa and it consistently underestimated the volume for the well-graded soil. Lenhard and Parker

(1990) subsequently developed a computer program OILEQUIL based on the theory related to these two equations to estimate the hydrocarbon volume.

Farr et al. (1990) have discussed in detail the prediction of the hydrocarbon volume based on the Brooks-Corey and van Genuchten equations. They considered the estimation of gasoline in sands. Their results show that there is a marked difference in the volume estimate based on these equations at low values of the hydrocarbon thickness. The van Genuchten based model shows a single valued volume for the values of hydrocarbon thickness in a monitoring well. However, the Brooks-Corey based model predicts that only at a critical value of hydrocarbon volume in the soil. a thickness $P_d^{ow}/(\rho_w - \rho_o) g$ will be observed in the monitoring well. Below this volume the hydrocarbon will exist at a negative pressure in the porous media and will not be present in the monitoring well. They also studied the sensitivity of hydrocarbon volume estimates to the type of soil and the hydrocarbon properties. They selected porous media ranging from sandstones to silt loams. The density of the hydrocarbons ranged from 0.74 (gasoline) to 0.88 (p - cymene). The theoretical minimum thickness for gasoline in the monitoring wells ranged from 10 cm (unconsolidated sand) to 98 cm for a silt-loam. Their results also showed the estimated hydrocarbon volume to be sensitive to the soil type. For example. large hydrocarbon thicknesses in wells can be associated with very small volumes in an unconsolidated sand.

Durnford et al. (1992) also report the presence of a fairly large hydrocarbon volume in the porous media without being noticed in a monitoring well. Therefore the van Genuchten equation is preferable when a small volume is to be estimated . Note that both of these equations. however are suited for the calculation of large volumes .

Testa and Paczkowski (1989) conducted field studies for the hydrocarbon estimation and recovery. The hydrocarbon thickness in the monitoring well is multiplied by the surface area of the contaminated zone which is calculated by a planimeter. This product multiplied by the porosity of the soil gives the apparent volume of hydrocarbon. This does not take into consideration the specific yield of the formation which is dependent on the flow characteristics of the hydrocarbon and the soil characteristics. The recoverable hydrocarbon is obtained from the relation :

$$V_e = S_y \times V_a$$

where,

V_e = recoverable hydrocarbon volume,

V_a = apparent hydrocarbon volume.

S_y = specific yield of the aquifer.

Waddill and Parker (1997) developed a semi-analytical model to predict the hydrocarbon recovery from unconfined aquifers. Their model predicts the recoverable and residual oil volumes based on the initial distribution of oil-water levels, plus the steady state solution for draw down in an unconfined aquifer. This model is simple in application and requires the soil and fluid properties. and the fluid levels in monitoring wells.

Chapter 3

EXPERIMENTAL WORK

The laboratory scale column experiments are considered the most appropriate laboratory method to study the contamination of ground water. A large number of such studies have been carried to quantify the contamination of unconfined aquifers resulting from spills of crude oil (also called hydrocarbon in this study) beneath the soil surface. Unconfined aquifers are also quite susceptible to contamination from leaking underground fuel storage tanks. The results of such studies can be used to understand and solve actual field problems.

This laboratory study simulates the contamination of different types of unconfined sandy aquifers by a leaking hydrocarbon tank. Sand columns were fabricated for this purpose. Small perforated reservoirs to simulate a leaking storage tank were set at the top of these columns. Crude oil was also used to create the spill in the sand column. An attempt to quantify analytically the extent of contamination resulting from such a leak was made using the hydrocarbon thickness in monitoring wells installed in these columns.

Two sand types, uniform and well-graded, were used during the experiment. The experimental program was conducted in two stages. During the first stage, the spill was generated on a pair of homogeneous sand columns. Likewise during the second stage, the spill was tested on a pair of layered sand columns.

3.1 Materials

The materials used to carry out this work were sand. Plexiglas columns. spill tanks and crude oil.

3.1.1 Sand

The uniform sand was collected from a sand dune near Bagga in Abqaiq area. The effective grain size (D_{10}). Uniformity Coefficient (C_u), and the curvature coefficient (C_c) for the sand are 0.18 mm. 1.7. and 1.4 respectively (Khan,1997), and the soil can be classified as poorly graded (SP) according to the Unified Soil Classification System (USCS). The porosity (ϕ) for this soil is 32%.

The well-graded sand was constructed using a blend of different grain sizes available from three sands. The porosity for this soil is 26%. Grain size in the range of #20 to #40 were sieved from sand obtained from Ras Tanura sand, those in the range of #40 to #80 were sieved from the Bagga sand. The grains in the range of #100 to #200 were sieved using sand available from the KFUPM beach on the outskirts of Aziziyah. Dhahran. The sieving was done in the Soil Engineering laboratory at KFUPM using mechanical shakers. The blended well -graded sand has a D_{10}. C_u. and C_c of 0.14 mm . 6.0 and 1.2 respectively. This soil can be classified as well graded sand (SW) according to USCS. Figure 3.1 shows the grain size distribution curves for the two sands.
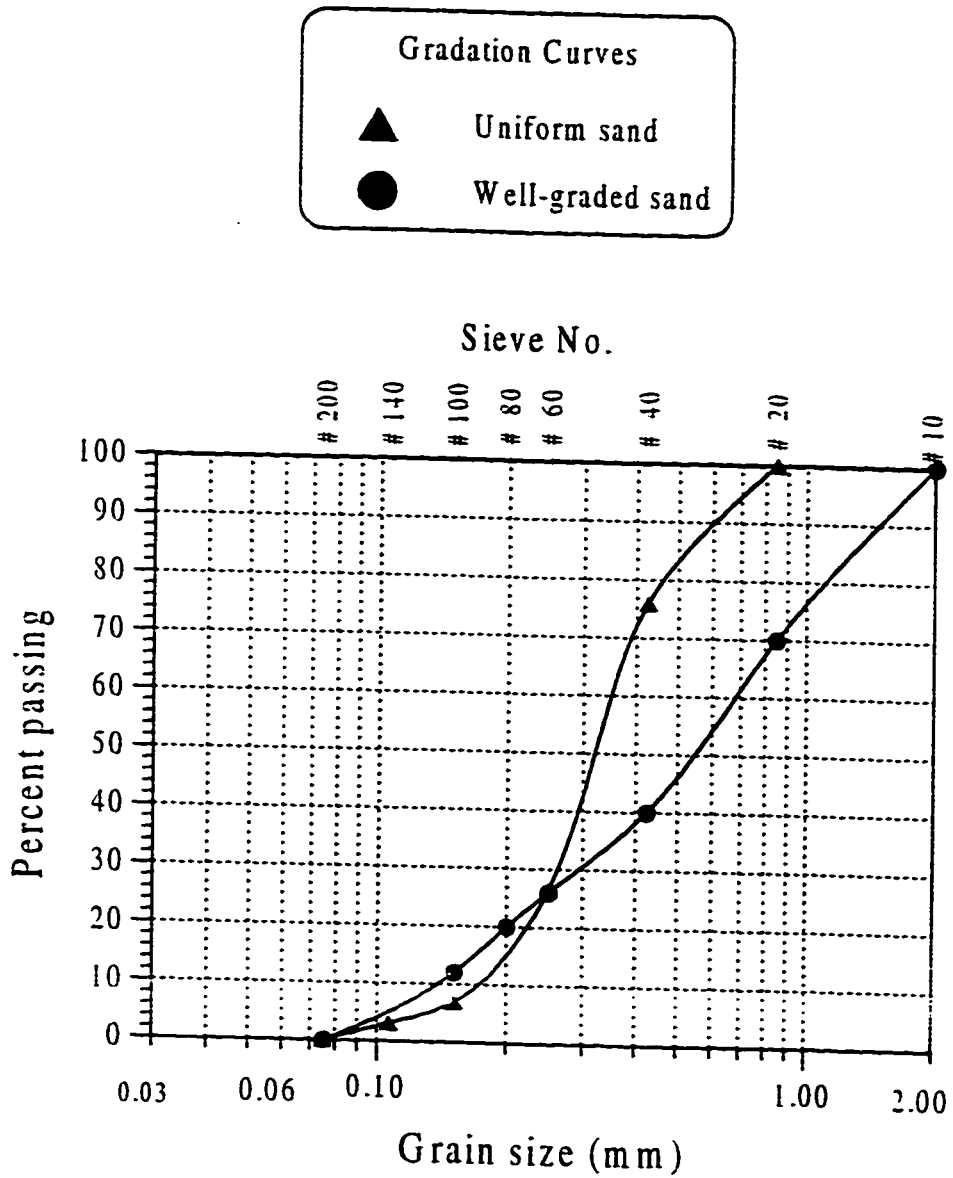
Figure 3.1: Grain size distribution for the uniform and well-graded soil.

3.1.2 Crude oil

The crude oil was provided by Saudi ARAMCO from its refinery at Ras Tanura. The crude oil has a specific gravity of 0.86 and an API number of 31. It can be classified as a medium density hydrocarbon. The interfacial tension of the oil was measured in the Petroleum Engineering Laboratory at KFUPM. The oil-water interfacial tension(σ_{ow}) is 23 dynes/cm, oil-air interfacial tension(σ_{ao}) is 26 dynes/cm, and the air-water interfacial tension(σ_{aw}) is 70.5 dynes/cm.

3.1.3 Column and Spill Tank Fabrication

Three identical Plexiglas columns were fabricated for the experimental setup, in the central workshop at KFUPM. The internal diameter of each of these columns was 290 mm and the height is 1900 mm. Two semi-circular monitoring wells having a diameter of 25 mm were installed inside these columns. These monitoring wells were fully screened by a #100 opening steel mesh . A valve was provided at the base of each column for the inflow or outflow of water through the attached PVC conduit. A piezometer was installed in each column to monitor the water table position. Each column was filled with water and checked to be leakfree. The complete experimental setup is shown in Figure 3.2

A spill tank of internal diameter 240mm and depth 100mm was fabricated for every column. Uniformly spaced perforations were provided at the base of each spill tank to ensure areal distribution of the crude oil inside the sand column. The spill tank was placed at the top of each sand column.

·

290mm

250mm

Spill Tank

100mm

Screened
Monitoring
Well
Semicircular
$\varnothing = 25mm$

1800mm

Water Inlet

Section aa

Base plate

a

a

6 No. holes 2mm dia

Piezometer

Plan
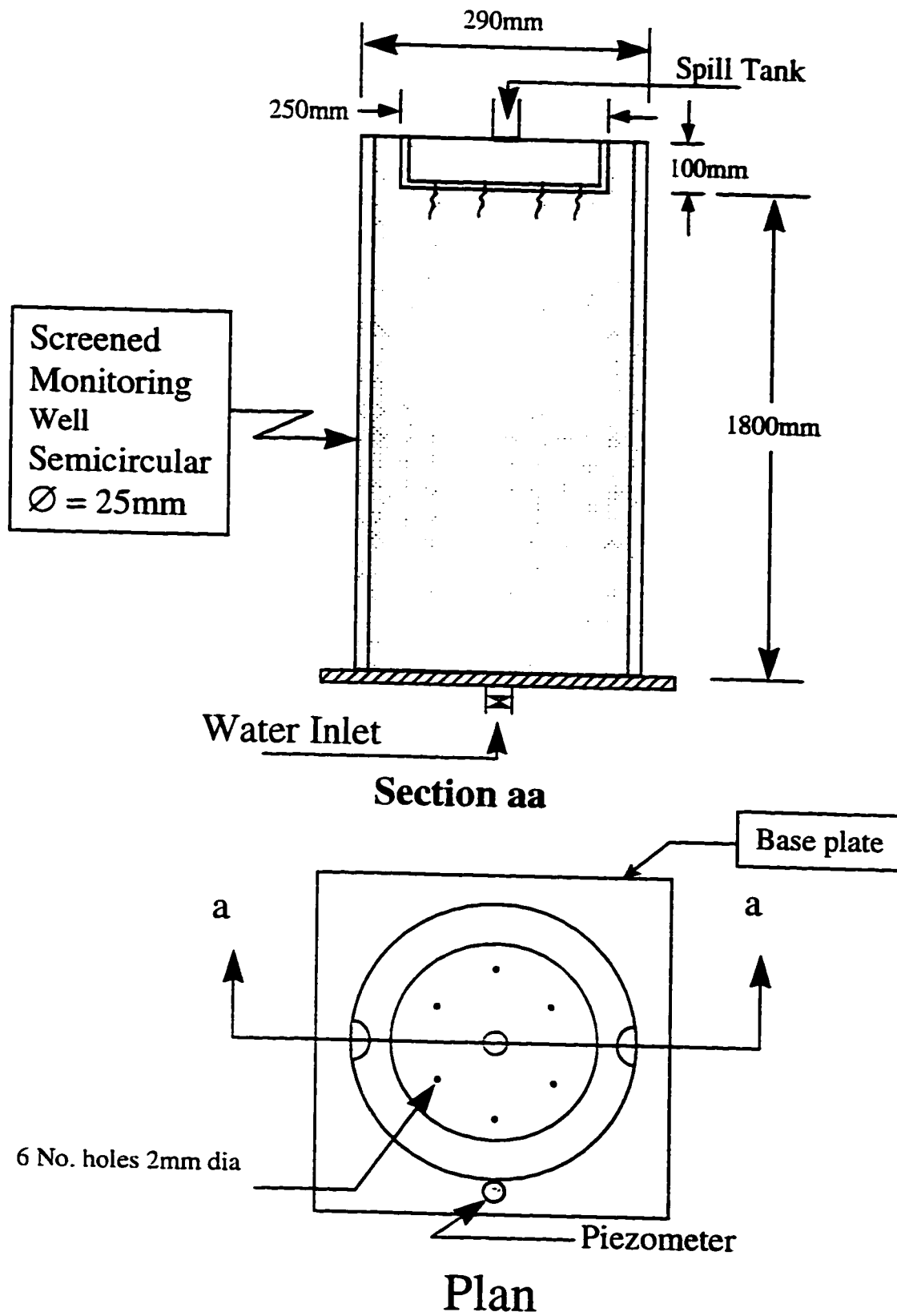
Figure 3.2 : Layout of the experimental sand column setup

3.2 Experimental Procedure

The experimental procedure consisted of a preliminary experimental study and the main column study. The experimental program is detailed below.

3.2.1 Preliminary Experimental Study

The preliminary study was conducted by filling one of the columns with the uniform sand using a pluviation technique. Subsequently, the dry sand was flooded with water. This was done to remove the entrapped air from the sand, and subsequently to maintain a water table 50 cm above the base of the column. Crude oil was released into the sand column after quasi-static moisture distribution in the soil was achieved that took about two weeks.

The specific objectives of this stage of the study were as follows :

1. To monitor the appearance of the hydrocarbon in the monitoring wells and obtain an approximate range of the critical spill volume.

2. To make modifications in the experimental setup if required and avoid any operational problems that could be encountered during the main study.

An operational problem was encountered at the beginning of this experiment. The dry sand leaked into the monitoring wells through its edges while the column was being filled up to an effective height of 180 cm. This was rectified by using an additional layer of silicone sealant on the edges of the monitoring wells in the column. The monitoring wells in the other columns were likewise sealed with an extra layer of the sealant to avoid any

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problem during operation. Subsequent to the rectification process, the sand was flooded up to its top with water flowing through a valve in the base of the column. The valve at the base of the column was later used to drain out the water and desaturate the soil for two weeks.

Crude oil was released into the column at the end of this period at 1500 ml /day for three days for a total of 4500 ml through the spill tank provided at the top of the column. The movement of the hydrocarbon in the column was monitored. A plume was visible from the appearance of scattered black lines along the interface of the sand and the column walls. The plume gradually moved downwards. After about 20 days from the beginning of the spill, the crude oil appeared in one of the monitoring wells and shortly after in the other well. This volume of the crude oil held in the column until it would first appear in the monitoring wells gave a conservative estimate of the *critical volume* below which, the hydrocarbon exists at only a negative pressure in the media and will not be observed in monitoring wells. The oil level in the monitoring wells equilibrated in around two weeks. Since the objectives were met, the main experiment was started.

3.2.2 Main Experimental Study

This was carried out in two stages. Stage 1 involved initiating a spill on a pair of homogeneous soils, namely the uniformly graded sand and the well graded sand (Figure 3.3). The uniform sand column experiment is labelled as S1U and the well-graded sand column experiment as S1W. The effective height of these sand columns was 180 cm and a quasi- static water table of 50 cm above the column base was maintained.
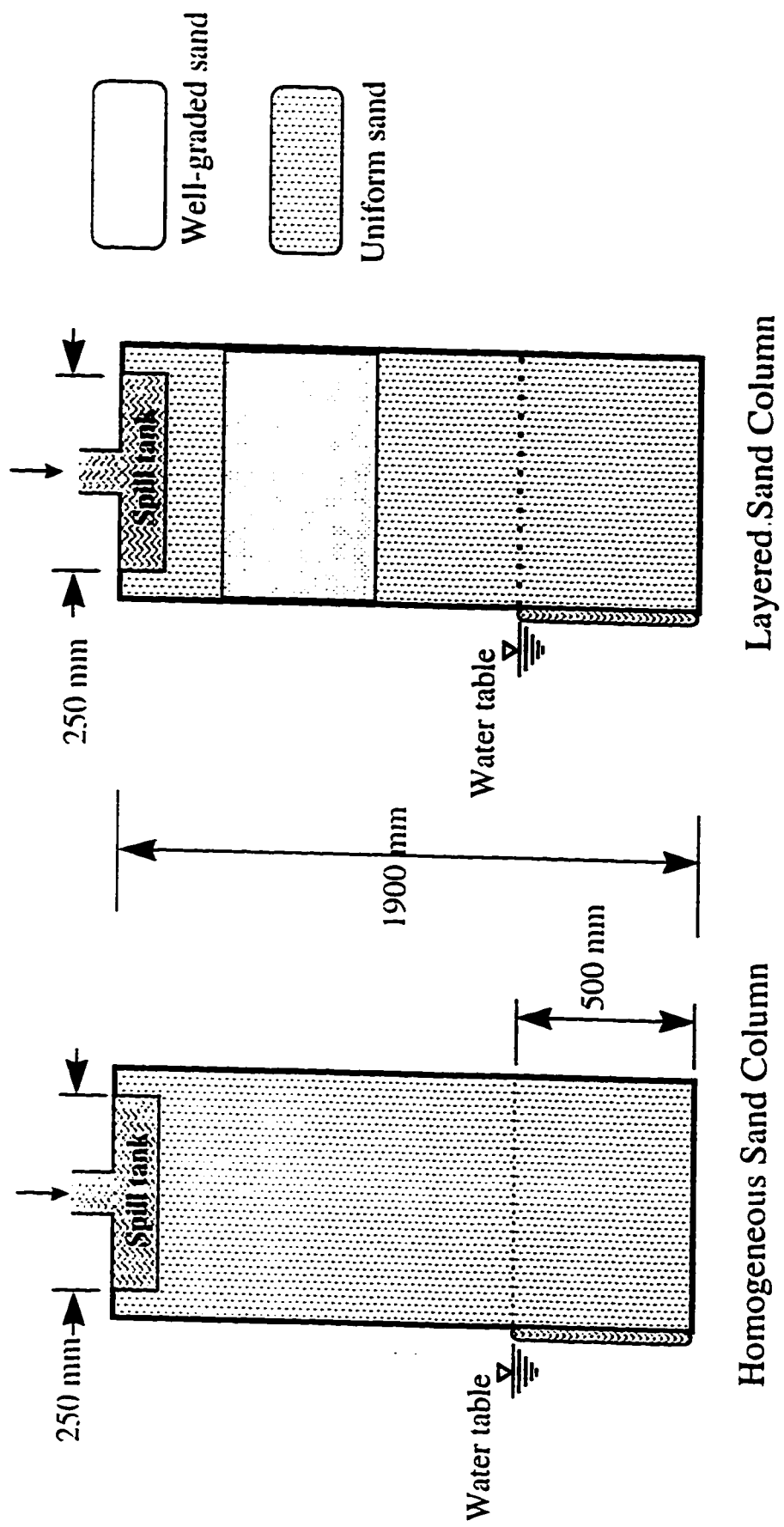
Figure 3.3 : Layout of sand columns

Well-graded sand

Uniform sand

Layered Sand Column

Homogeneous Sand Column

250 mm

1900 mm

500 mm

Water table

Spill tank

33

Stage II involved a methodology essentially similar to stage I on a pair of layered soils (Figure 3.3). The column labelled S2UL had three layers: a bottom layer 140 cm and a top layer 10 cm thick of uniformly graded sand, and a middle layer 30 cm thick of well graded sand. The column labelled S2WL also had three layers: a bottom layer 140 cm and top layer 10 cm thick of the well graded sand and a middle layer 30 cm thick of uniformly graded sand. The water table level was maintained at 50 cm above the column base. A brief summary of the methodology is documented in the next section.

3.2.3 Methodology

The operational methodology is the same for all the columns. After a column had been filled with sand, it was fully saturated with water flowing in an upward manner through a valve at the base of the column. Subsequently, the water was drained from the sand column to a height 50 cm above the column base for two weeks.

Once quasi-static equilibrium had been reached, an oil spill was initiated in the column. On the basis of the trends available from the preliminary work and engineering logic, a judgmental guess was made on the initial oil volume to be released into the sand column. The system was then allowed to equilibrate for around 2 to 3 weeks. During this period, the crude oil displaced laterally and also moved downward. If at any time during the initial spill the hydrocarbon appeared in the monitoring well(s), a value for the *critical volume* would have been obtained. This volume forms an important factor in viewing the limitations of the Brooks-Corey model. However, if the critical volume was not achieved

at the end of this period. an additional 500 ml of crude would be spilled periodically every two weeks to achieve the critical volume.

Once the critical volume had been achieved, the system was allowed to equilibrate for two weeks. Subsequently oil was released incrementally every two weeks and the changes in the well hydrocarbon thickness and the water table were monitored on a daily basis. Six to seven observation points were generated for the spill volume and the corresponding hydrocarbon thickness in monitoring wells in each column. Each column run lasted from 120-150 days which is the time from saturating the soil to the last hydrocarbon thickness measurement in the wells. The results for the four tested columns are discussed in chapter 4.

3.2.4 Hydrocarbon Recovery

An additional objective defined during the main program was the recovery of hydrocarbon from the contaminated soil. The purpose was to ascertain the volume of hydrocarbon that can be actually recovered from an aquifer as a first step towards its remediation. This cleanup process was started at the end of the final hydrocarbon thickness measurement in each column and lasted about three weeks.

Chapter 4

RESULTS AND ANALYSIS

The experimental program was conducted in two stages. The first stage tested a pair of of homogeneous sand columns S1U and S1W and the second stage tested a pair of layered sand columns. S2UL and S2WL. The results from these four experimental columns are detailed below.

4.1 Uniform Sand Column (S1U)

Initially, a volume of 3.000 ml of crude oil was released into the column over a span of 24 hours and the system was allowed to approach a state of quasi-static equilibrium over about two weeks. An additional volume of 500 ml was released at the end of two weeks and before any crude oil had appeared in one of the monitoring wells. Shortly afterward the hydrocarbon was observed in the other monitoring well. Thus, a total spill volume in the range of 3.000 ml to 3.500 ml corresponded to the critical spill volume below which no free product would appear in the monitoring wells. This was expected from the Brooks-Corey model predictions.

Additional crude oil was released incrementally and the well hydrocarbon thicknesses. or the free product hydrocarbon thicknesses corresponding to different spill volumes were measured once the system reached quasi-static equilibrium. A total of six observation points defining the relation between the spill volume and its thickness in a

monitoring well were generated and the results inferred from that are discussed in the following sections.

4.1.1 Hydrocarbon Levels in Monitoring Wells

The free product thickness in the monitoring wells as a function of the spill volume is given in Figure 4.1. For the critical spill volume, the free product thickness in one of the wells reached 18.5 cm, which was temporary, and as the hydrocarbon started accumulating in the other well, the levels in both wells stabilized at 14.2 cm at quasi-static equilibrum. From the figure its observed that as more crude oil was released into the system the hydrocarbon thickness in the wells increased, however levels in both wells were different which could be due to spatial heterogeneity within the soil.

The curves in Figure 4.1 can be divided into two segments- a straight line segment with flatter slope that relates low values of the spill volume with low values of free product thickness and a steeper slope segment that relates a higher spill volume with higher values of free product thickness. At higher spill volume it was found from visual observation that the free product thickness increased at an equal rate in the monitoring wells and above the capillary fringe in the porous media. Similar results have been reported also in an earlier study by Ballestero et al.(1993).

4.1.2 Water Table Change.

Changes in the water table were noticeable within two days after the initial spill of crude oil into the column. These changes occur because of replacement of the water from the soils pore space by the oil. At a total spill volume of 3,500 ml the oil manifested itself
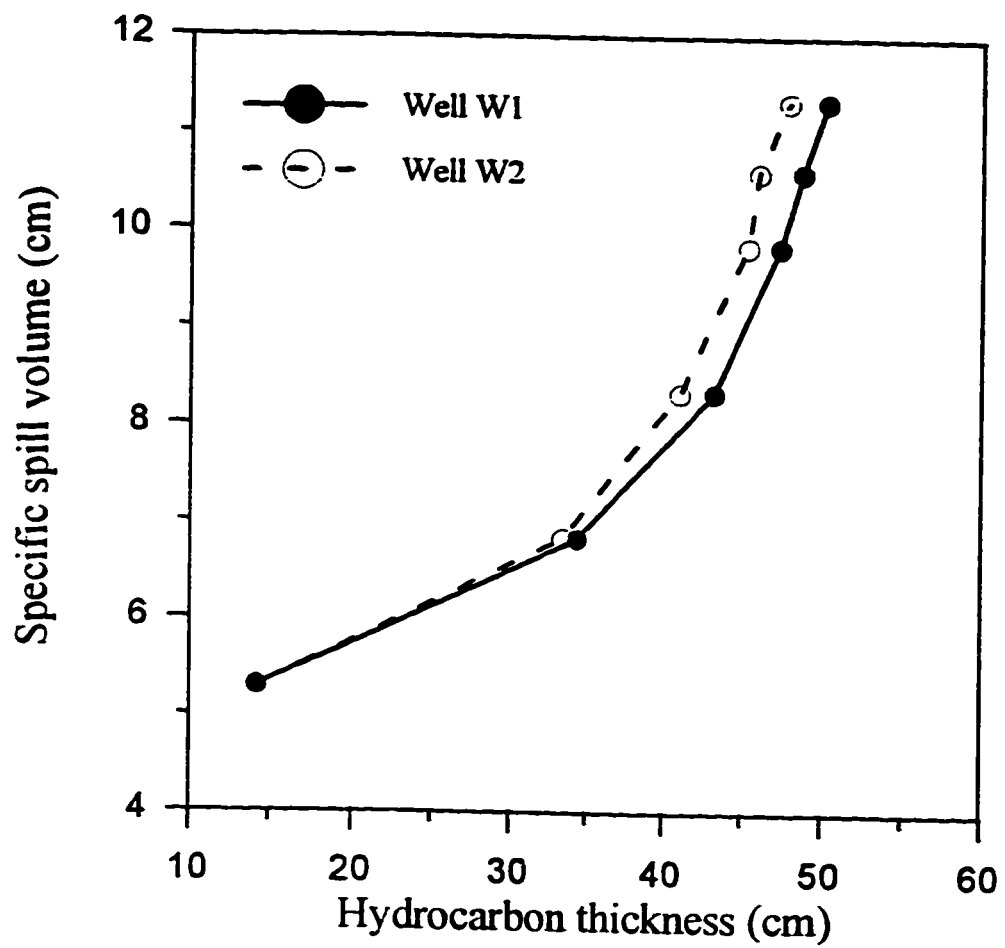
Figure 4.1 : Free product thickness and spill volume relationship for experiment on uniform soil column S1U.

in the monitoring wells. This depressed the water levels in the monitoring wells causing the oil-water interface to fall and simultaneously increase the water table level in the piezometer. Thus the change in water table is attributed to the additional weight coming from the mobile (free) hydrocarbon. A water table change of 13.5 cm was recorded for the critical spill volume at quasi-static equilibrium.

Subsequently more crude oil was released incrementally into the column every 12-14 days until a total spill volume of 7,500 ml had been released into the column. The total water table change for this experiment was 32.6 cm when the last free product thickness measurement was taken. A curve illustrating the change in the water table as a function of the spill volume is shown in Figure 4.2. The slope of the curve is flatter at lower spill volumes, however it becomes steeper for higher spill volumes. The shape of this curve is similar to the curves shown for the spill voume-free product thickness relationship for this soil (Figure 4.1).

The water table change throughout the experiment is shown in Figure 4.3. the flatter regions of this figure indicate that quasi-static equilibrium is obtained at the various stages of oil release. Figure 4.4 shows a curve relating the free product thickness to the change in water table. For the accumulated free product thickness of 50 cm. the water table level change was 32.6 cm. An increase in the free product thickness is directly associated with a corresponding water table change.
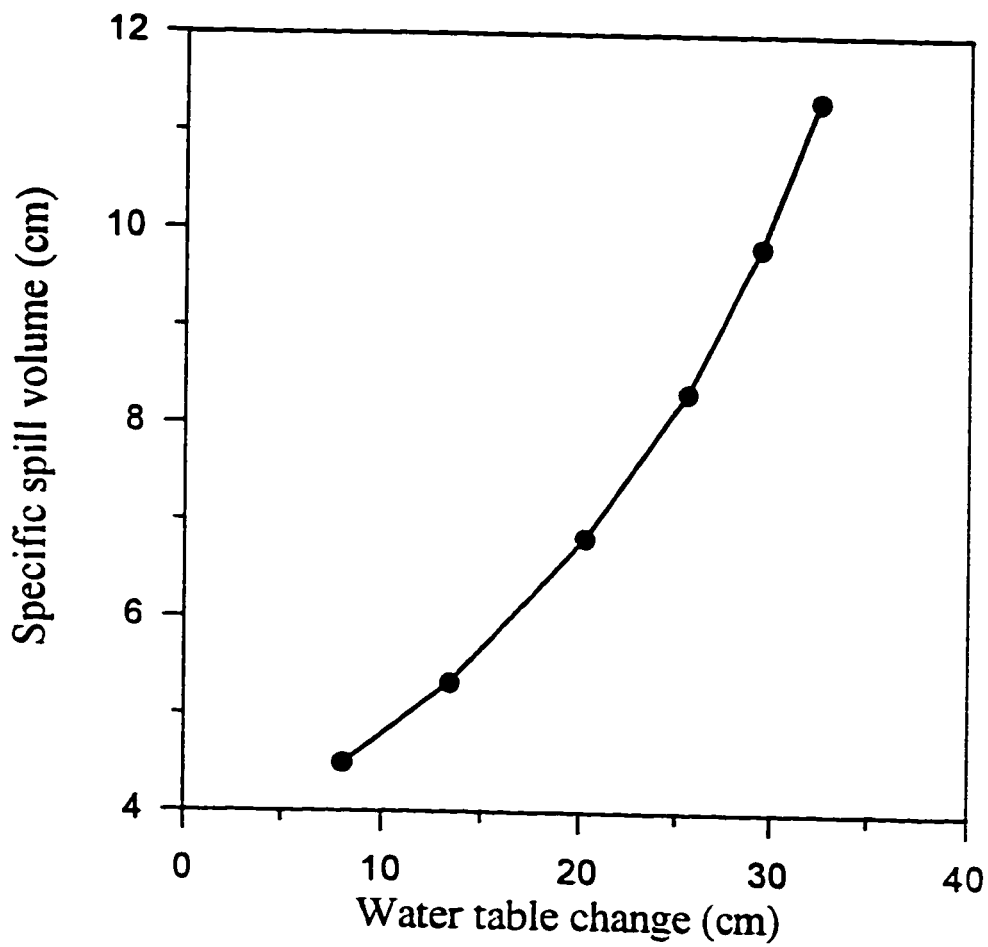
Figure 4.2 : Water table change-spill volume relationship for experiment on uniform soil column S1U.
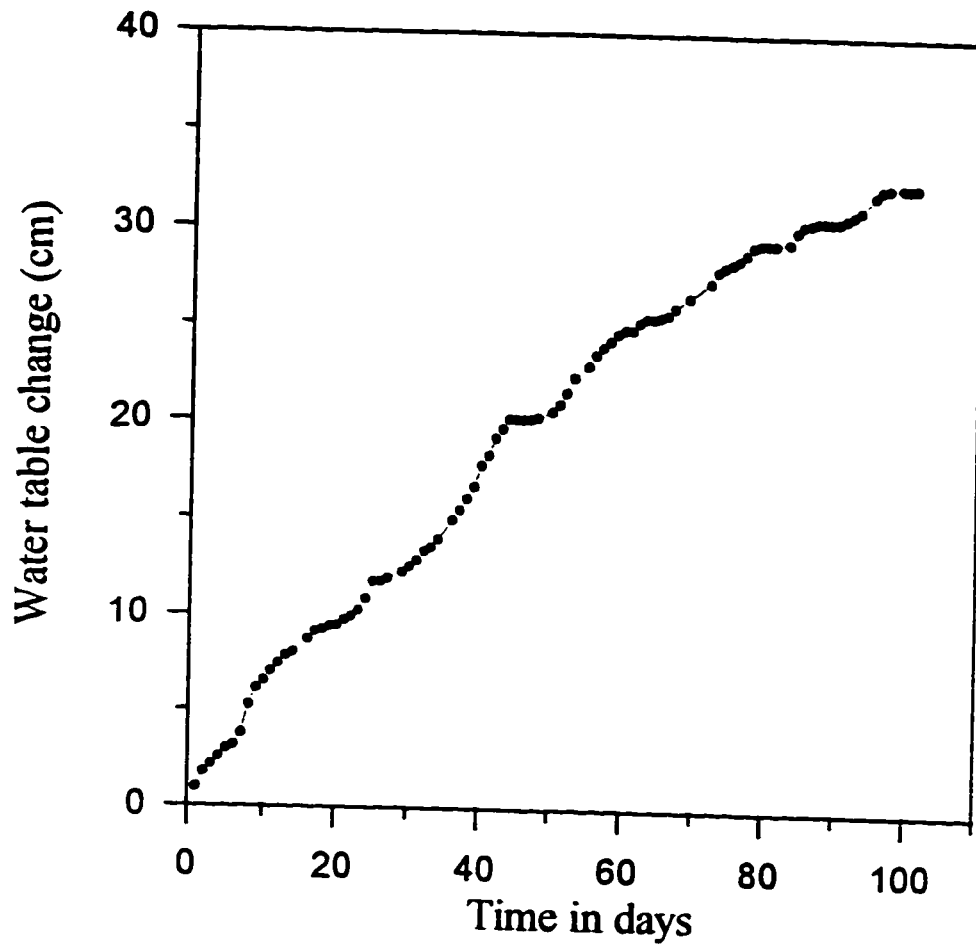
Figure 4.3 : Water table change for experiment on uniform soil column S1U
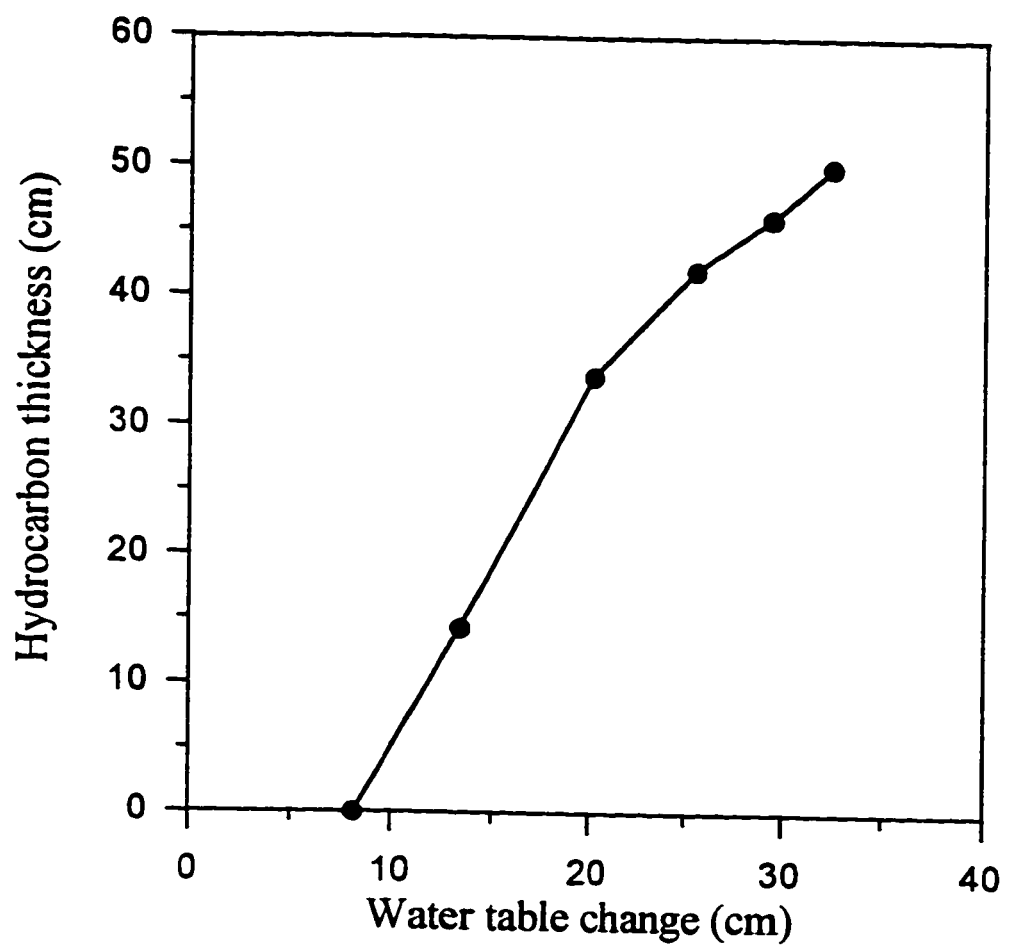
Figure 4.4 : Water table-free product thickness relationship for experiment
on uniform soil column S1U.

4.1.3 Analytical and Empirical Estimates of Spill Volume.

Various empirical and analytical models available to estimate the spill volume using the free product thickness were verified using the results from the experimental model. The analytical models verified were those proposed by Lenhard and Parker (1990) and Farr et al.(1990). These models, which are essentially similar, are developed based on the saturation-capillary pressure models given by Brooks-Corey (1964) and van Genuchten (1980). Empirical models of Hall et al. (1984) and De Pastrovich et al. (1979) were also verified. The estimates of all these models were calculated at a residual soil moisture content θ_r of 0.11 (S_r of 35%) and 0.06 (S_r of 18%). These values of θ_r are based on the assumption of quasi-static moisture content in the soil, and are obtained by substituting a relative permeability (k/k_s) value of 1% and 0.1% in the permeability function (Brooks-Corey, 1964).

The software SOILPROP produced by Environmental Systems & Technologies, Inc. USA was used to obtain other soil parameters for the analytical models, and those are summarised in Table 4.1. The estimates of the analytical and the empirical models at a k/k_s of 1% are summarized in Table 4.2. Both analytical models under predict the spill volume. For the different free product thicknesses generated, the Brooks-Corey based model underestimates the spill volume by about 28% to 35% , while the van Genuchten based model underestimates it in a range of 18% to 21%. The model of Hall et al under estimates the spill volume by about 30% to 93% while the estimates of De Pastrovich et al. are the lowest and under predictions of volume range from 77% to 86%. A comparison between all the model estimates at k/k_s of 1% is given in Figure 4.5. The model based on

Table 4.1: Soil hydraulic parameters for the uniform sand ($\phi = 32\%$)

k/k$_s$	θ_r	α (1/cm)	n	h$_f$ (cm)	λ
0	0	.0528	3.61	13.3	1.61
1%	0.11	.064	4.64	11.6	2.14
0.1%	0.06	.058	4.34	12.6	2.0

Table 4.2 : Estimates of spill volume (cm^3/cm^2) for experiment on uniform soil column STU at a k/k_s of 1%

Soil thickness*	Hydrocarbon	Spill volume	van Genuchten	Brooks-Corey	Hall et al.	Pastrovich
(cm)	thickness (cm)	(cm^3/cm^2)				et al.
116.8	14.2	5.3	4.22		0.36	0.75
101.2	33.8	6.83	5.58	4.47	4.47	1.77
95	42	8.3	6.86	6.1	6.2	2.21
93	46	9.83	8.13	7.33	7.04	2.42
92.2	47.8	10.6	8.38	7.56	7.42	2.51
90	50	11.33	8.99	8.18	7.8	2.63

* above the oil table.
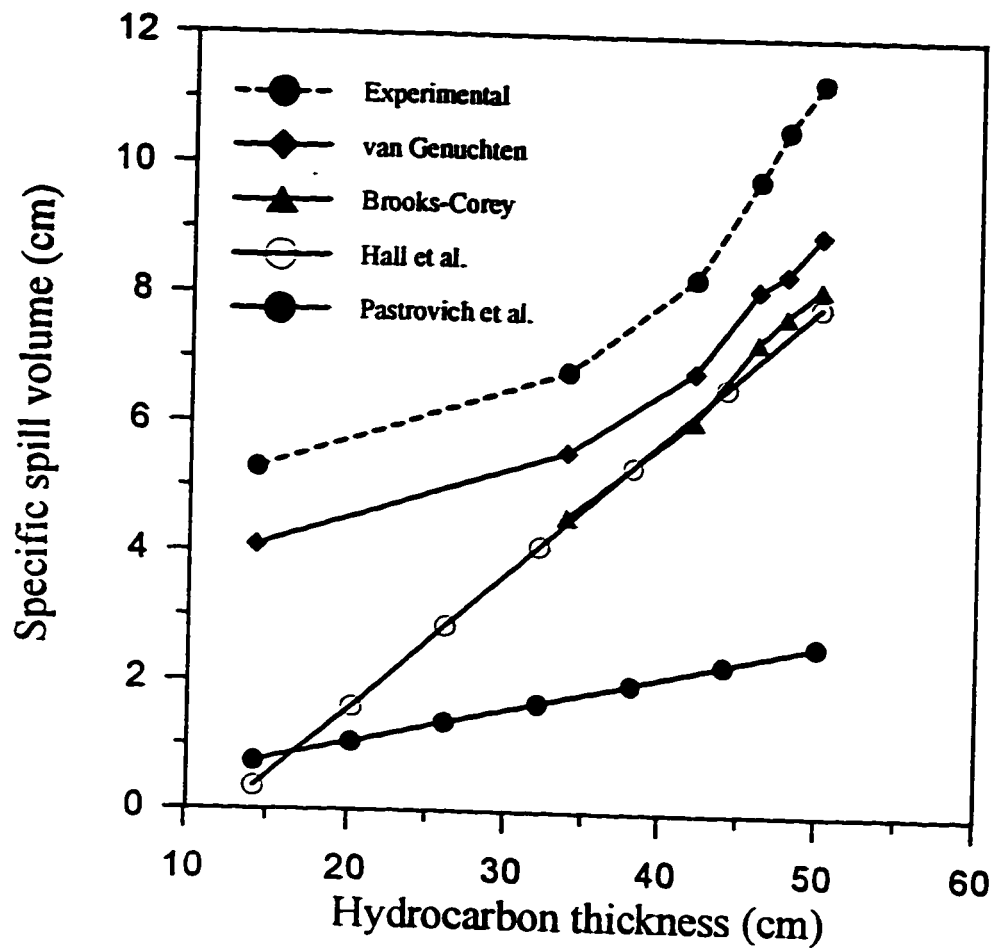
Figure 4.5 : Estimates of spill volume for experiment on uniform soil column S1U at k/k$_S$ of 1%.

the van Genuchten equations is the closest in estimating the spill volume while the estimates of the Brooks-Corey model, though slightly lower, are similar for a spill volume of 6.83 cm and higher. The agreement between the empirical models of Hall et al. and De Pastrovich et al. and the actual spill volume is poor. The model of De Pastrovich et al. estimates a considerably lower spill volume than all other models. From the figure it can also be seen that the van Genuchten model estimates for a spill volume of 5.3 cm are higher than those of all other models .

Table 4.3   shows the estimates of the spill volume predicted by the analytical models at a k/k_s of 0.1% . The Brooks-Corey model underestimates the spill volume by 61% to 81% while the van Genuchten model underestimates it by about 52% to 77% for different values of free product thickness generated. Since the estimates of the empirical models are directly related to the effective soil porosity (ϕ -θr),   higher estimates will be predicted for these models. The model of Hall et al. underestimated the spill volume by 14 % to 92% while the model of De Pastrovich et al. underestimated it by 71% to 82%.

Figure 4.6 shows a comparison of all the model predictions at a k/k_s of 0.1%. The empirical model of Hall et al. comes closest to estimating the spill volume. Its estimates for a spill volume of 6.83 cm and higher are fairly close; however, it underestimates a spill volume of 5.3 cm considerably. The estimates of the analytical models are much lower than those at a k/k_s of 1%. Estimates of the model of De Pastrovich et al. are very low compared to all other models.

Table 4.3 : Estimates of spill volume (cm^3/cm^2) for experiment on uniform soil column SIU at a k/k_s of 0.1%

Soil thickness*	Hydrocarbon	Spill volume	van Genuchten	Brooks- Corey	Hall et al.	Pastrovich
(cm)	thickness (cm)	(cm^3/cm^2)				et al.
116.8	14.2	5.3	1.21		0.44	0.93
101.2	33.8	6.83	2.4	1.28	5.54	2.2
95	42	8.3	3.66	2.65	7.67	2.73
93	46	9.83	4.6	3.58	8.71	2.99
92.2	47.8	10.6	4.83	3.99	9.18	3.11
90	50	11.33	5.43	4.46	9.75	3.25

* above the oil table.
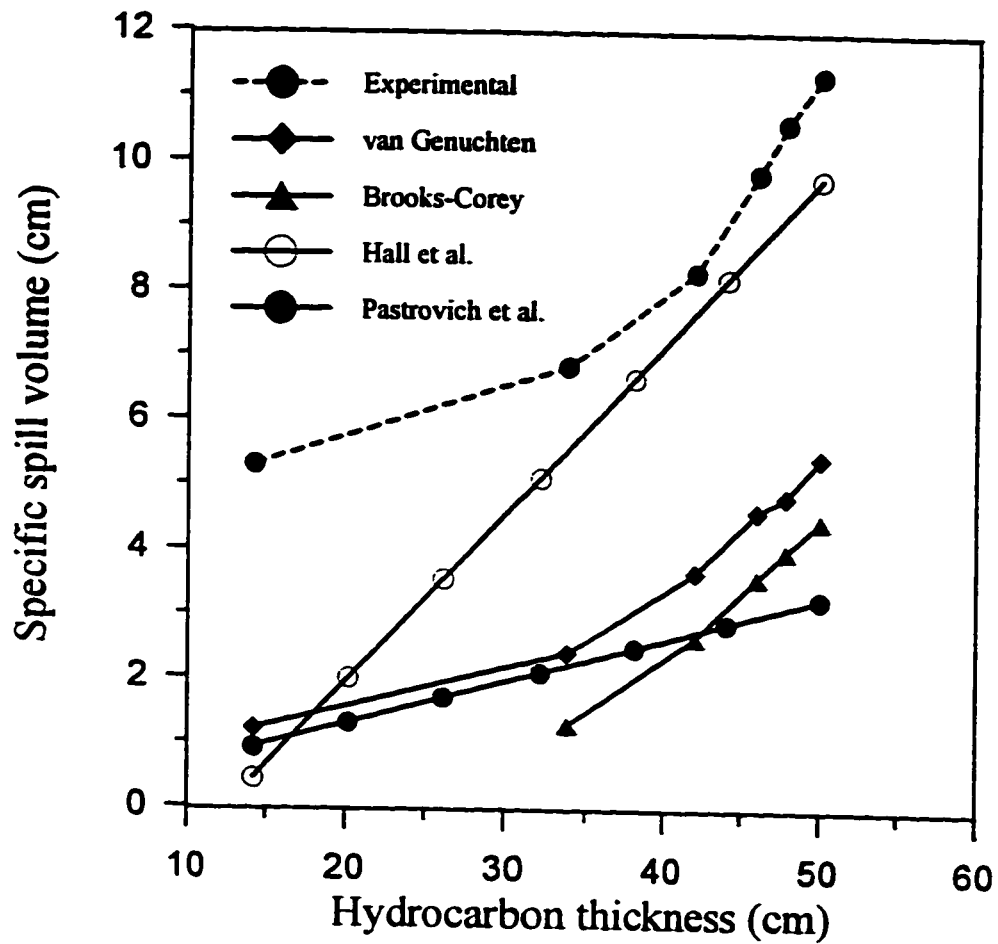
Figure 4.6 : Estimates of spill volume for experiment on uniform soil
column S1U at k/k_s of 0.1%.

Figure 4.7 illustrates the estimates of the analytical models at a k/k_s of 1% and 0.1%. Although the van Genuchten model gives slightly higher estimates at both the values of k/k_s used. both models arrive at nearly the same estimate of the hydrocarbon in the porous media for a free product thickness of 33.8 cm and higher. The figure also shows a significant difference between the predictions of the two models. The Brooks-Corey model does not predict any volume at a well hydrocarbon thickness of 14.2 cm or less since it is far below the critical thickness of 31 cm that this model proposes for this soil. In essence it means that this model may not quantify a significant volume of the hydrocarbon present in the soil.

4.2 Well-Graded Sand Column (S1W)

Following a methodology similar to that adopted for S1U. crude oil volume in the range of 2.250 ml to 2.750 ml was released in this soil column, before it was observed in the monitoring wells. The critical volume for this soil is lower than that for S1U (3,000 ml to 3.500 ml) and could primarily be ascribed to the lower porosity (26%) of this soil. In addition. the grain size or the pore size distribution can also influence the critical volume for a soil. This shows that the critical volume is a porous media dependent property.

Additional crude oil was released incrementally every 12-14 days and the free product hydrocarbon thickness corresponding to different spill volumes at quasi-static equilibrium in the system was measured. A total of seven observation points defining the relation between the spill volume and its thickness in a monitoring well were generated
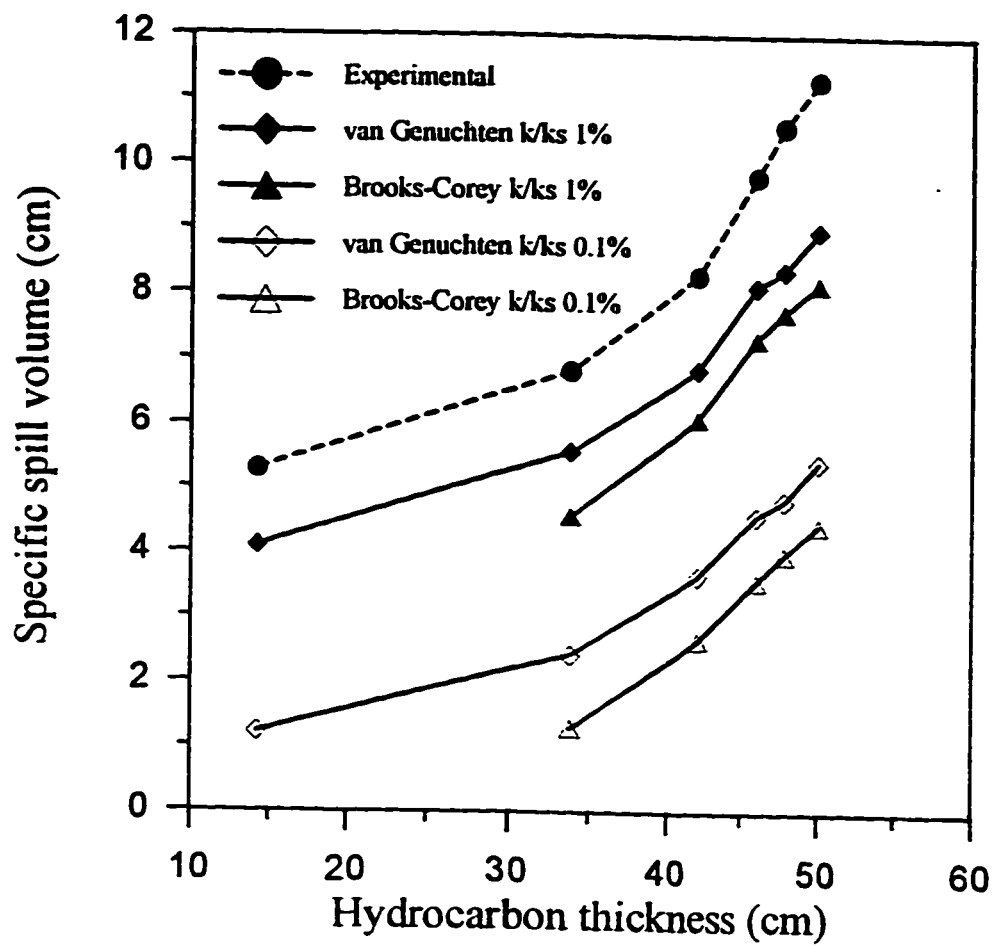
Figure 4.7 : Effect of k/k_s on analytical estimates for experiment on uniform soil column S1U.

experimentally for this column. The last observation point was generated at a total spill volume of 9,000 ml. The visually observed free product thickness above the capillary fringe, for this soil column, was much higher than that for a similar observation of column S1U. This is mainly because the free product thickness in a soil is a function of the pore size of the soil; the smaller the pore size, higher the free product thickness value will be (Ballestero et al. 1993).

4.2.1 Hydrocarbon Levels in Monitoring Wells

Figure 4.8 shows curves representing the free product thickness in the monitoring wells as a function of the spill volume. It is observed from the data that the levels in the monitoring wells equilibrated closely throughout. At a release volume of 2,750 ml, the free product thickness initially reached 10 cm in one of the monitoring wells while in the other it was only 2 cm. However this was temporary, and as the oil started accumulating in the other well, the levels in the wells stabilized at 18.2 cm. As more crude oil was released into the system the hydrocarbon thickness in the wells increased, and they were similar (Figure 4.8). The general shape of the curves of Figure 4.8 is similar to the curves presented earlier for S1U. Like those curves, they too can be approximated into two segments- a straight line segment with a flatter slope for low values of the free product thickness, and a part with a steeper slope for higher values of the free product thickness. This indicated that curves of a similar nature should be expected for different types of homogeneous soils. The explanation of the relation between the spill volume and the free product thickness of these curves is similar to that discussed in sec. 4.1.1.
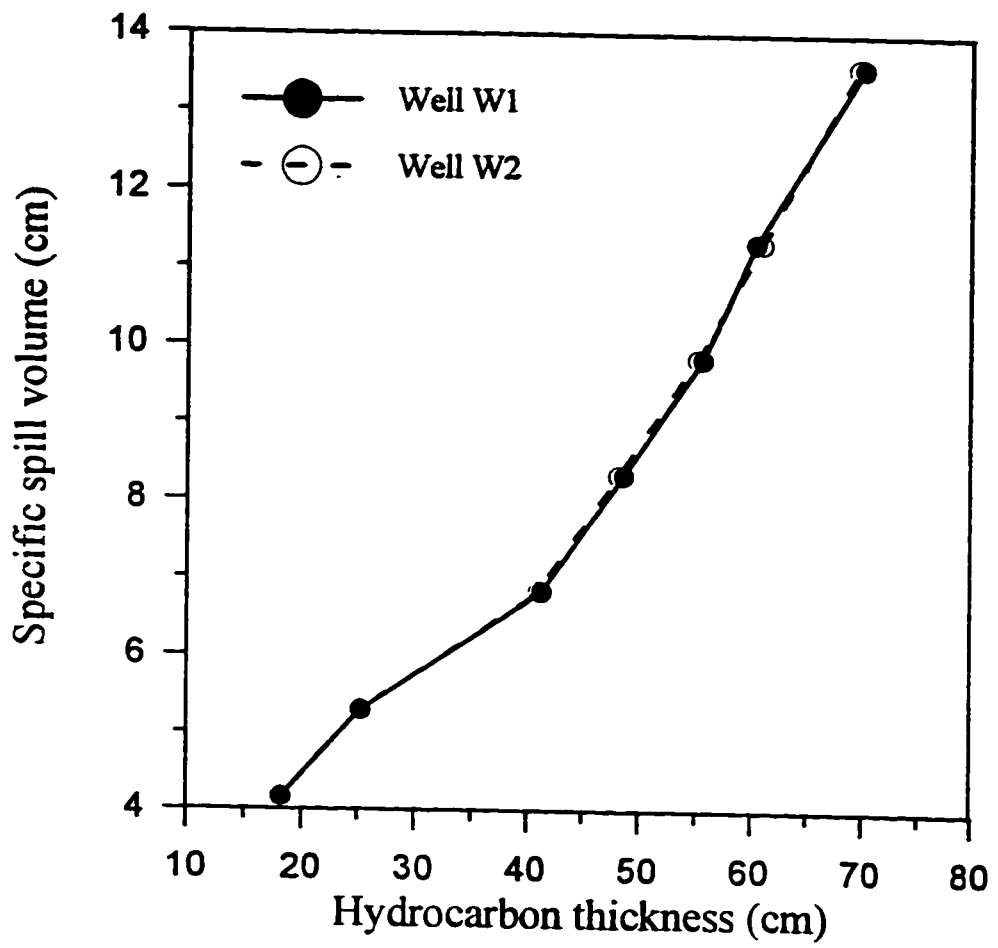
Figure 4.8 : Free product thickness and spill volume relationship for experiment on well-graded soil column S1W.

A comparison of the spill volume and the free product thickness relationships for S1U and S1W columns also shows that the criterion of a "high" or "low" free product thickness is not predefined but is essentially dependent on the properties of the porous media (Ballestero et al., 1993) and what is a low thickness for one soil could represent a higher thickness for another soil at a lower spill volume (Farr et al., 1990).

4.2.2 Water Table Change

Changes in the water table were noticeable a couple of days after the initial volume of 2,250 ml of crude oil was released in the sand column. At a total spill of 2,750 ml in the column, a thin layer of the free product started accumulating on the capillary fringe before flowing into the wells. A water table change of 14.8 cm was recorded at quasi-static equilibrium for this critical spill volume. As more crude oil was released incrementally every two weeks, the water table level rose further due to reasons discussed earlier in sec. 4.1.2. Figure 4.9 depicts the variation of the spill volume with the change in water table. This curve, very closely, matches a straight line. The water table change is significantly higher for this experiment, which can be attributed to a lower soil porosity and displacement of a higher volume of water from the vadose zone of the soil column. Figure 4.10 shows the changes in the water table as a function of time. The flatter regions within the figure signify attainment of quasi-static equilibrium in the system after an increment of crude oil had been released in the column. A curve relating the free product thickness to the change in water table is shown in Figure 4.11. Corresponding to the final

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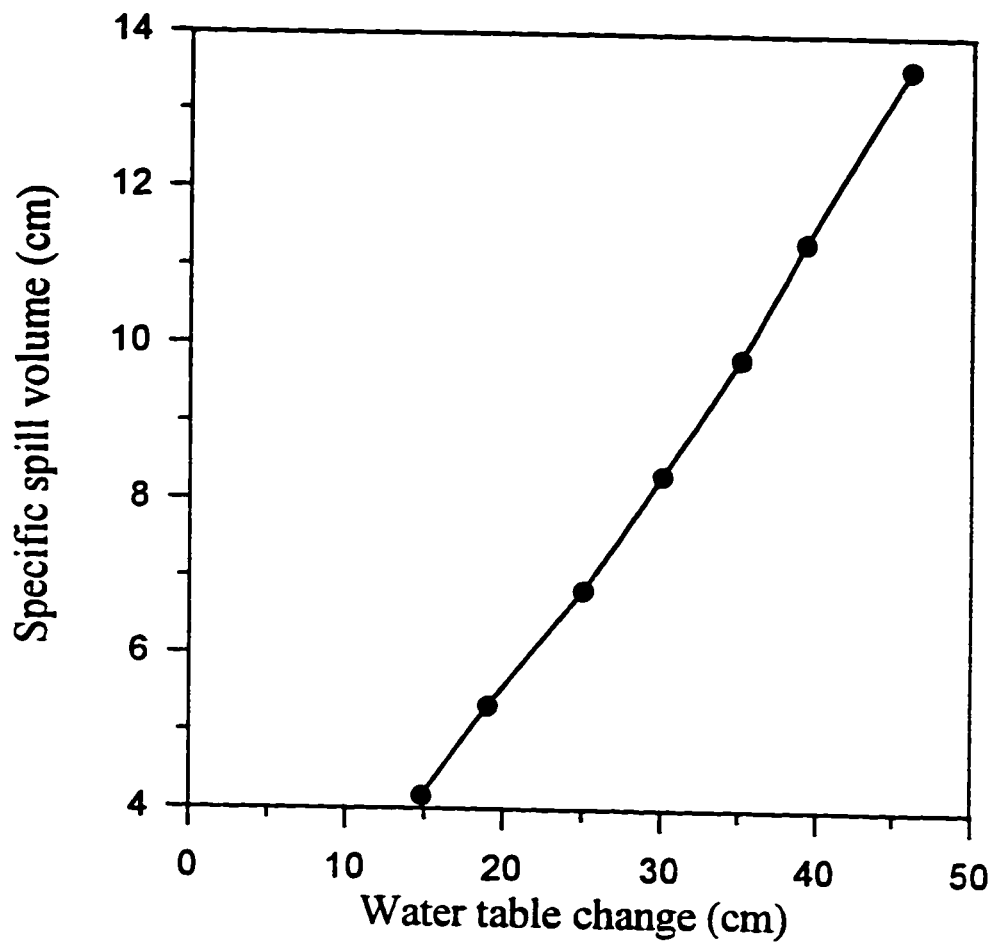
Figure 4.9 : Water table change-spill volume relationship for experiment on well-graded soil column S1W.
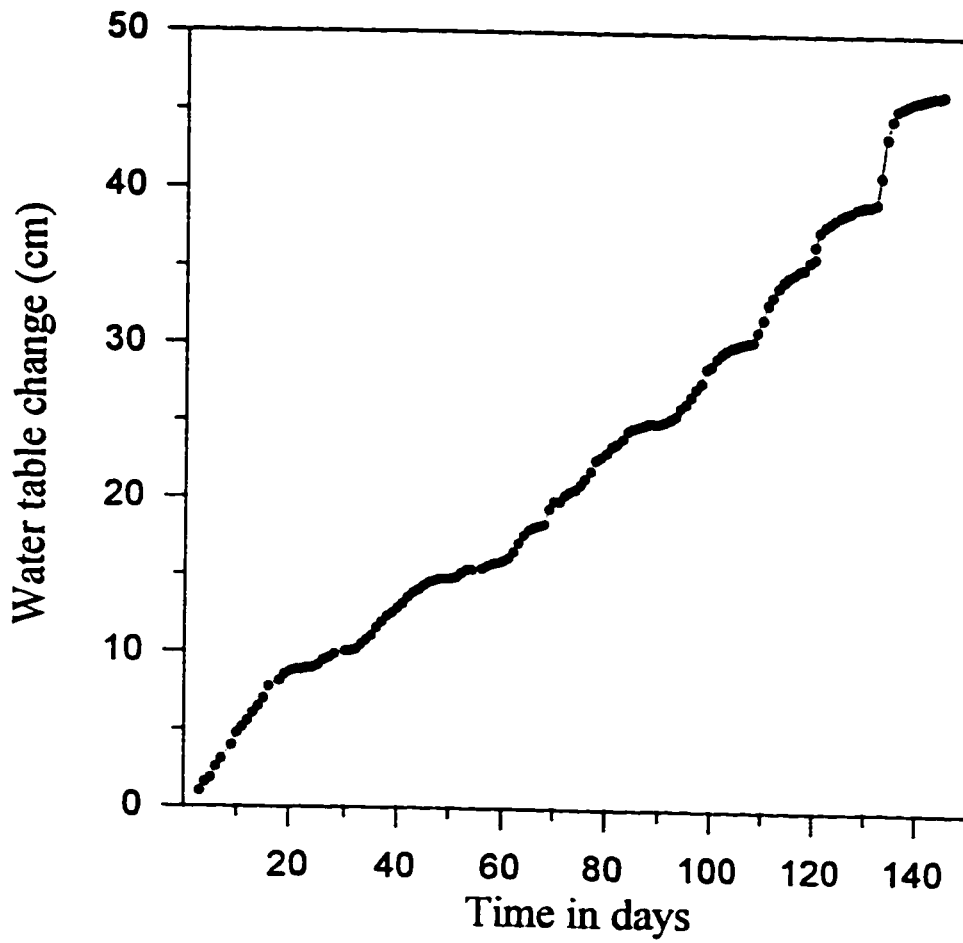
Figure 4.10 : Water table change for experiment on well-graded soil column S1W.
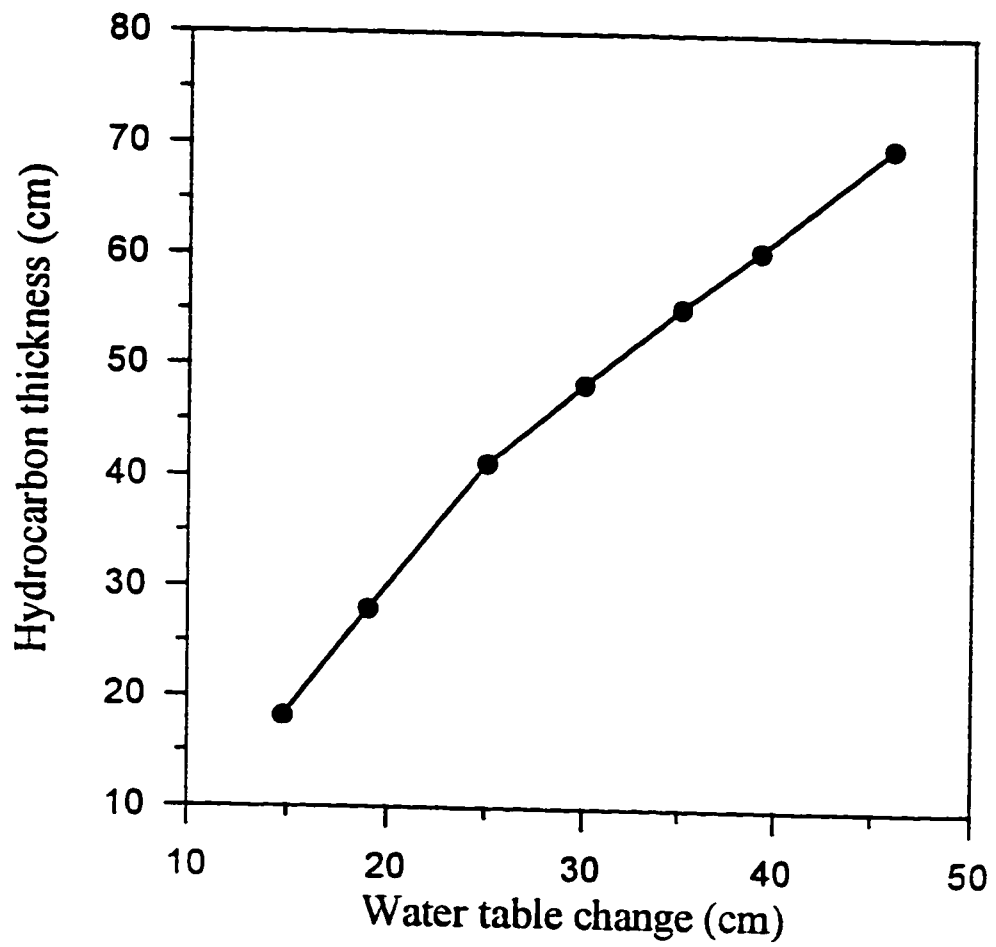
Figure 4.11 : Water table -free product thickness relationship for experiment on well-graded soil column S1W.

free product thickness measurement of 70 cm , the water table change for this experiment was 46 cm.

4.2.3 Analytical and Empirical Estimates of Spill Volume

Corresponding to the relative permeability (k/k_s) values of 1% and 0.1% , a residual soil moisture content. θ_r, of 0.12 (S_r of 46%) and 0.09 (S_r of 35%) respectively were obtained for this soil. The other soil parameters for the analytical models which were estimated from the software SOILPROP are summarized in Table 4.4 . The estimates of the analytical and empirical models for this soil at a k/k_s of 1% are summarized in Table 4.5. The analytical models underestimate the spill volume; however, their estimates are almost close enough to be called similar. The Brooks-Corey model underestimates the spill volume by 30% to 40%. The corresponding van Genuchten underestimate in volume ranges from 31% to 38%. The empirical models also underestimate the spill volume. The model of Hall et al. underestimates it by 36% to 64%, while the model of De Pastrovich et al. underestimates it in a higher range of 81% to 85%.

Figure 4.12 illustrates the estimates of all these models at a k/k_s of 1%. The estimates of analytical models match closely. Among the empirical models, the model of Hall et al. estimates the highest volumes, which are nonetheless lower than those of the analytical models. The De Pastrovich et al. model estimates of volume are very low. The estimates of this model were also low for the experiment (S1U column) reported earlier. The 1 : 4 conversion principle of this model appears to fail badly. Lenhard and Parker (1990) have also reported the limitations of this model in an earlier study.

Table 4.4 : Soil hydraulic parameters for the well-graded soil ($\phi = 26\%$)

k/k$_s$	θ_r	α (1/cm)	n	h$_d$ (cm)	λ
0	0	.0923	1.79	6.78	.623
1%	0.12	0.11	3.63	6.41	1.62
0.1%	0.09	0.1	2.96	6.66	1.27

Table 4.5 : Estimates of spill volume (cm³/cm²) for experiment on well-graded soil column STW at a k/k_s of 1%

Soil thickness*	Hydrocarbon	Spill volume	van Genuchten	Brooks-Corey	Hull et al.	Pastrovich et al.
(cm)	thickness(cm)	(cm³/cm²)				
113.8	18.2	4.17	2.58	2.51	1.5	0.64
107	28	5.3	3.65	3.44	2.87	0.98
95.8	41.2	6.83	5.07	5.21	4.72	1.44
90.6	48.4	8.3	6.32	6.41	5.73	1.7
84.6	55.4	9.83	7.3	7.39	6.71	1.94
80.4	60.6	11.33	8.03	8.08	7.43	2.10
72	70.0	13.58	9.4	9.47	8.75	2.45

* above the oil table.
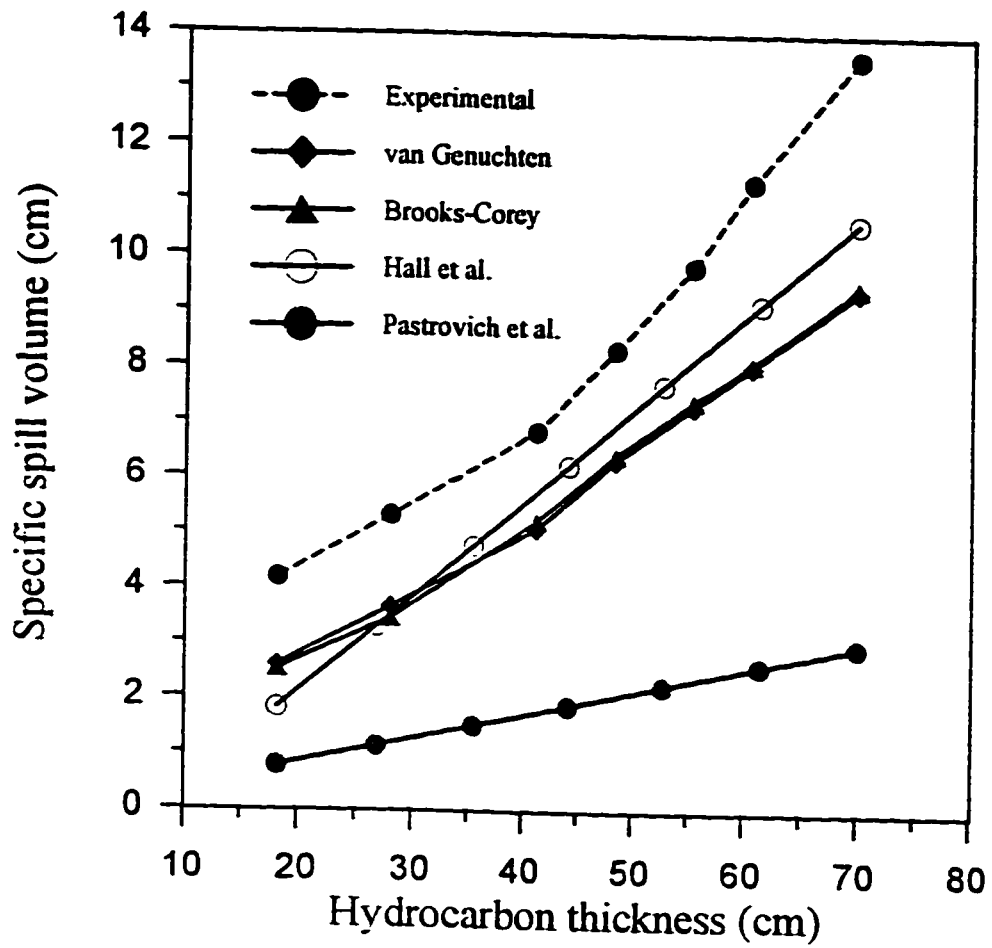
Figure 4.12 : Estimates of spill volume for experiment on well-graded soil column S1W at k/k_s of 1%.

Table 4.6 shows the estimates of the spill volume predicted by all models at a k/k_s of 0.1%. All the models underestimate the spill volume. The analytical models predict a lower volume than that predicted at a k/ks of 1%. While the Brooks-Corey model underestimates the volume by 44% to 83%, the van Genuchten model underestimates it in a range of 45% to 77%. At a k/k_s of 0.1%, the empirical models predicted higher spill volume than that predicted by them at a k/k_s of 1%. Hall et al. underestimates the volume by 22% to 56% while De Pastrovich et al. underestimates it by 78% to 82%. Figure 4.13 shows a comparison of the model estimates at a k/k_s of 0.1%. The estimates of Hall et al. are closest to the actual spill volume. However, the analytical models predict almost similar estimates and the estimates of De Pastrovich et al. are the lowest.

Figure 4.14 gives a comparison of the estimates of the analytical models at a k/k_s of 1% and 0.1%. The estimates are lowered at a k/k_s of 0.1%. Both models arrive at nearly the same estimate of the spill volume in the porous media. The minimum theoretical Brooks-Corey free product thickness for this soil is 15.9 cm, hence the Brooks-Corey model can not estimate a spill volume corresponding to a free product thickness of 15.9 cm or lower.

4.3 Layered Sand Column S2UL

Sand column S2UL, as discussed earlier in sec. 3.1.2, is similar to the sand column S1U, except that a 30 cm layer of well-graded sand was placed 10 cm below the soil surface to study the effect of layering. The crude oil volume of 3,000 ml released at the start in this column was observed in the monitoring wells at the end of two weeks. This

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Table 4.6 : Estimates of spill volume (cm^3/cm^2) for experiment on well-graded soil column S1V at a k/k$_s$ of 0.1%

Soil thickness* (cm)	Hydrocarbon thickness (cm)	Spill volume	van Genuchten	Brooks- Corey	Hall et al.	Pastrovich et al.
113.8	18.2	4.17	0.95	0.69	1.82	0.77
107	28	5.3	1.86	1.58	3.49	1.19
95.8	41.2	6.83	3.3	3.13	5.72	1.75
90.6	48.4	8.3	4.35	4.31	6.95	2.06
84.6	55.4	9.83	5.37	5.47	8.14	2.29
80.4	60.6	11.33	6.19	6.32	9.03	2.48
72	70	13.58	7.48	7.60	10.63	2.93

* above the oil table.
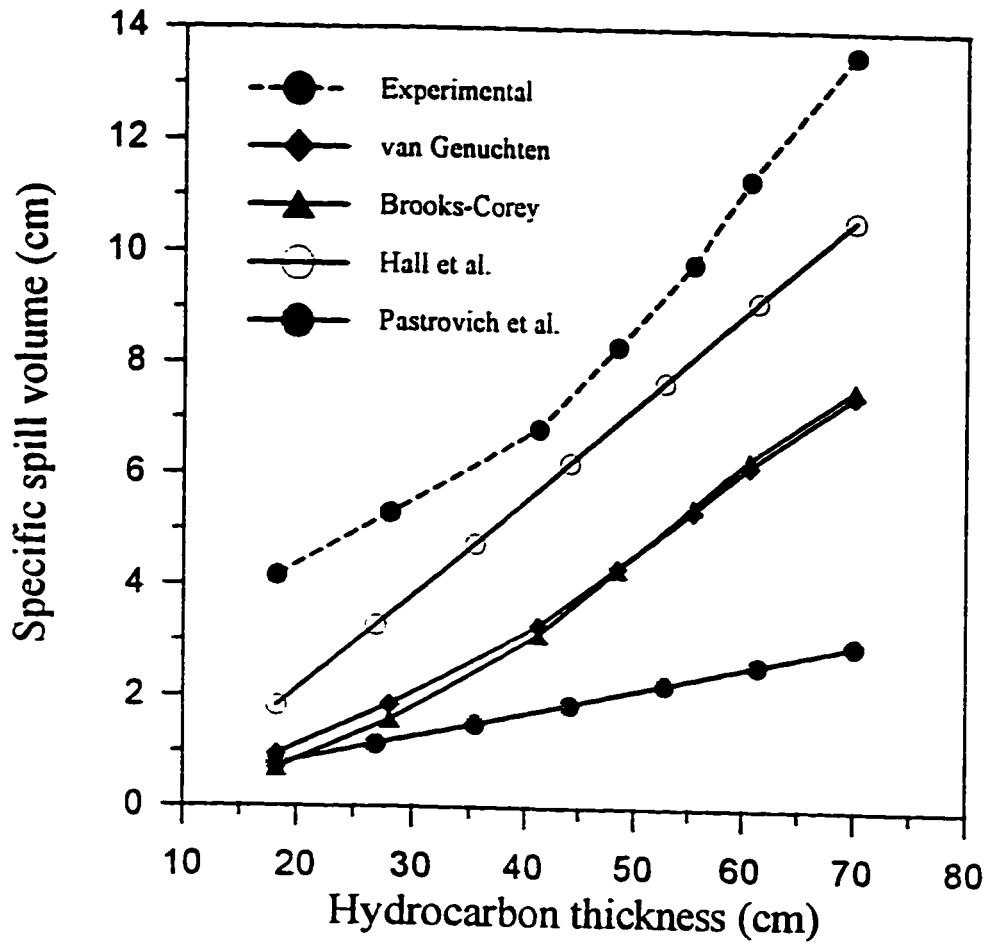
Figure 4.13 : Estimates of spill volume for experiment on well-graded soil
column S1W at k/k$_s$ of 0.1%.
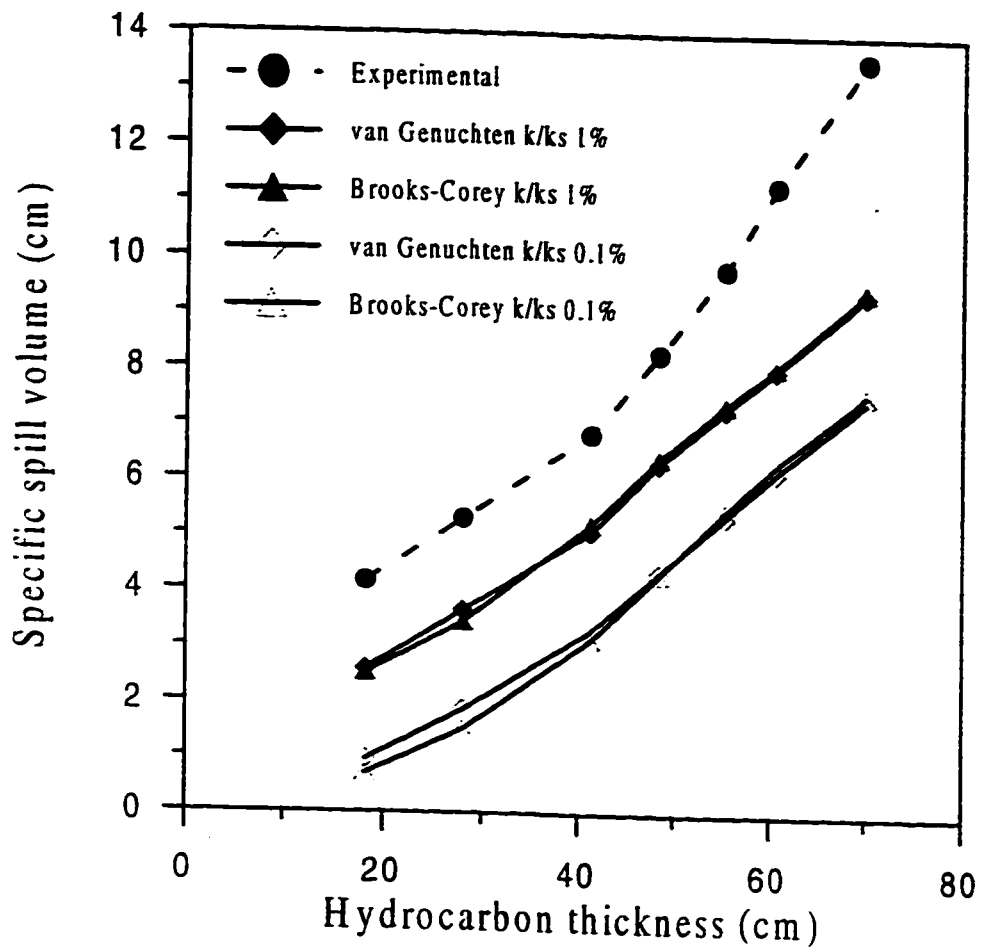
Figure 4.14 : Effect of k/k$_s$ on analytical estimates for experiment on well-graded soil column S1W.

volume corresponds to the critical value for this soil. Additional crude oil was released incrementally every two weeks in the column till a total of 7,500 ml of crude oil had been spilled into the column. A total of six observation points defining the relationship between the spill volume and its thickness in a monitoring well were generated.

4.3.1 Hydrocarbon Levels in Monitoring Wells

For the critical volume, the hydrocarbon levels in the monitoring wells were 24.7 cm and 23.9 cm at equilibrium. As more crude oil was spilled in the column, the hydrocarbon levels in the wells became very close. This can be seen from Figure 4.15 which relates the spill volume and the hydrocarbon thickness for this experiment. The curves of this figure can be approximated into two segments- a straight line segment with flatter slope for values of free product thickness in the range of 24.4 cm to 46 cm and another segment with a steep slope for higher free product thickness in the range of 46 to 55 cm. A comparison of these curves with similar curves for experiment S1U given in Figure 4.16 shows that layering had a significant effect on the experimental results. At similar values of the crude oil release in these columns, a free product thickness higher by about 4 cm. was consistently observed for experiment S2UL.
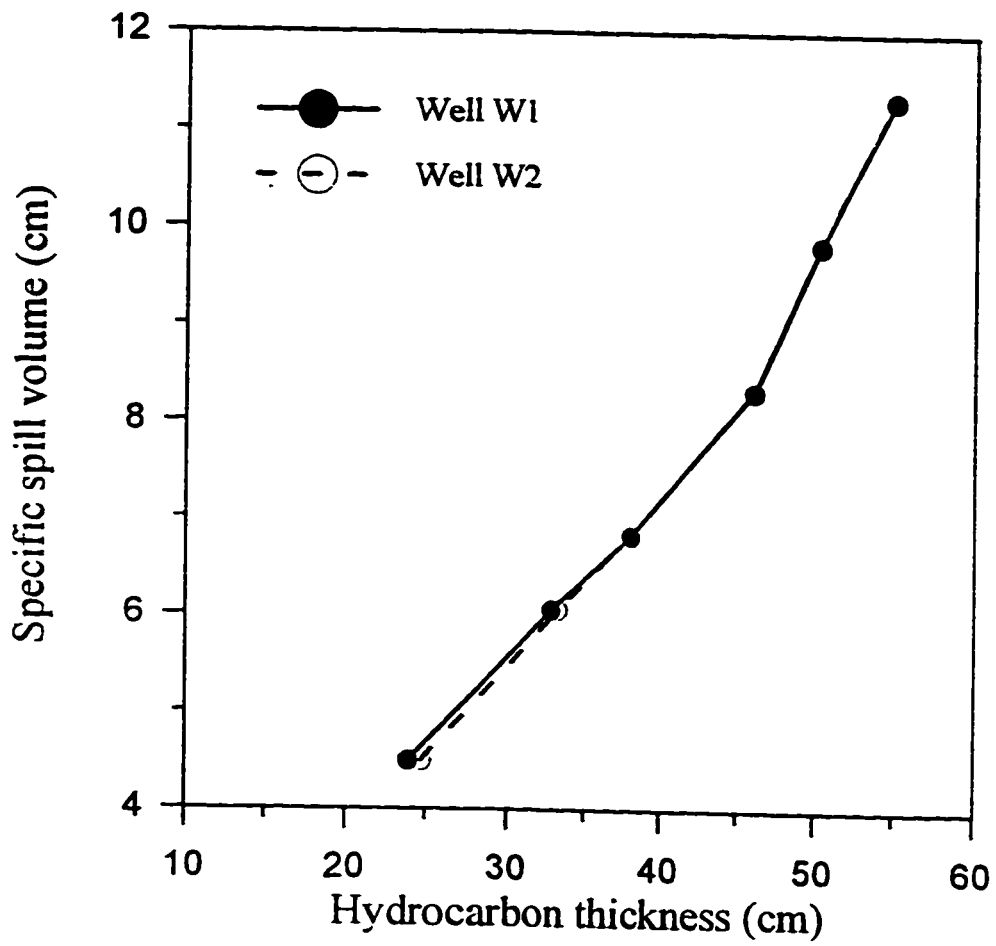
Figure 4.15 : Free product thickness and spill volume relationship for experiment on layered soil column S2UL.
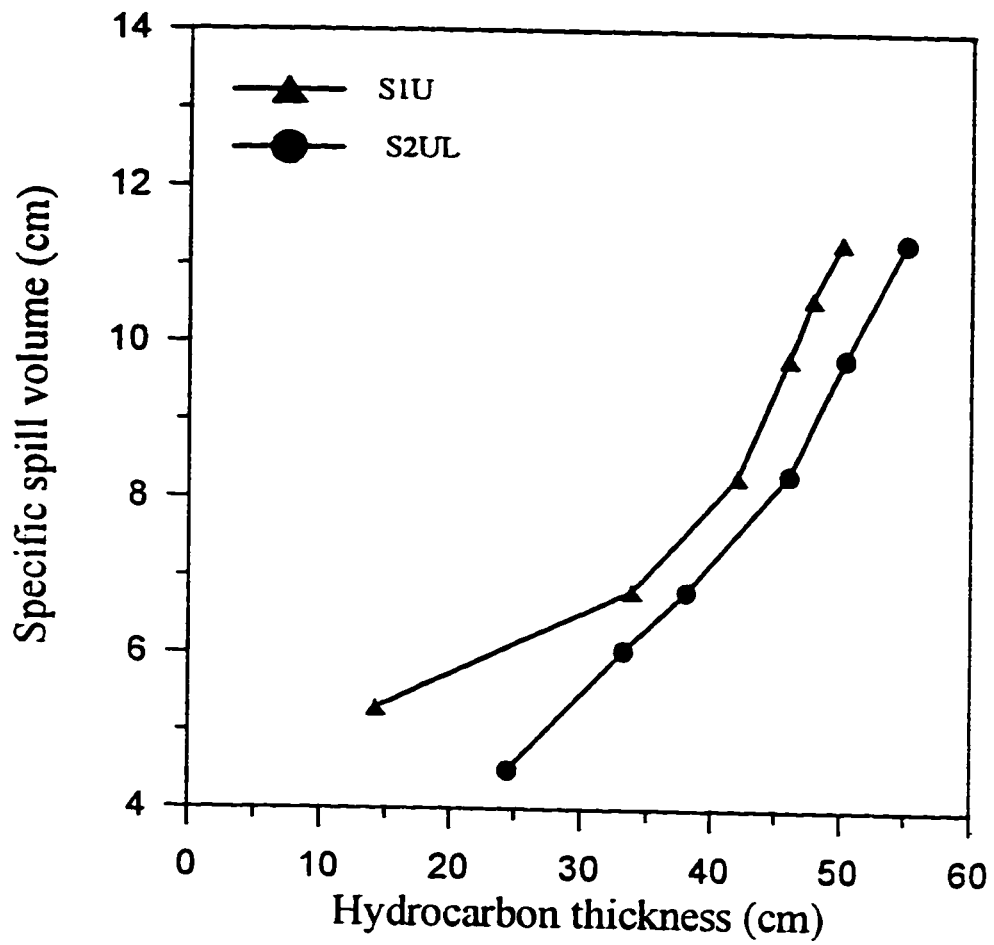
Figure 4.16 : Comparison of free product thickness and spill volume relationships for experiments on uniform soil column S1U and layered soil column S2UL.

4.3.2 Water Table Change

The water table rise at quasi-static equilibrium in this soil column was 10.2 cm for the initial spill volume of 3.000 ml. As more crude oil was released into the column incrementally, the water table rose further. The total water table change for this experiment was 29.6 cm at a total spill of 7.500 ml. The reasons for the water table change are the same as explained previously in sec. 4.1.2. A curve relating the spill volume and the change in water table is shown in Figure 4.17. This curve closely approximates to a straight line and is very similar to the spill volume-hydrocarbon thickness curve generated for this experiment. Figure 4.18 depicts the changes in the water table throughout the experiment, the flatter regions of the plot show the water table approaching a quasi-static equilibrium after an increment of oil had been released. Figure 4.19 shows a curve relating the free product thickness to the change in water table. For a total free product thickness of 55 cm, the water table change is 29.6 cm.

4.3.3 Analytical Estimates of Spill Volume

The analytical models of Farr et al. (1990) and Lenhard and Parker (1990) were extended to the layered soils using a methodology similar to that adopted for the homogeneous soils. The detailed explanation of the extended model is presented in chapter 5. This model is compiled in a FORTRAN code. the flowchart for which is given in appendix 1.

The predictions of the analytical models were compared with the results of the experimental model. The empirical models were not used. however. because they do not
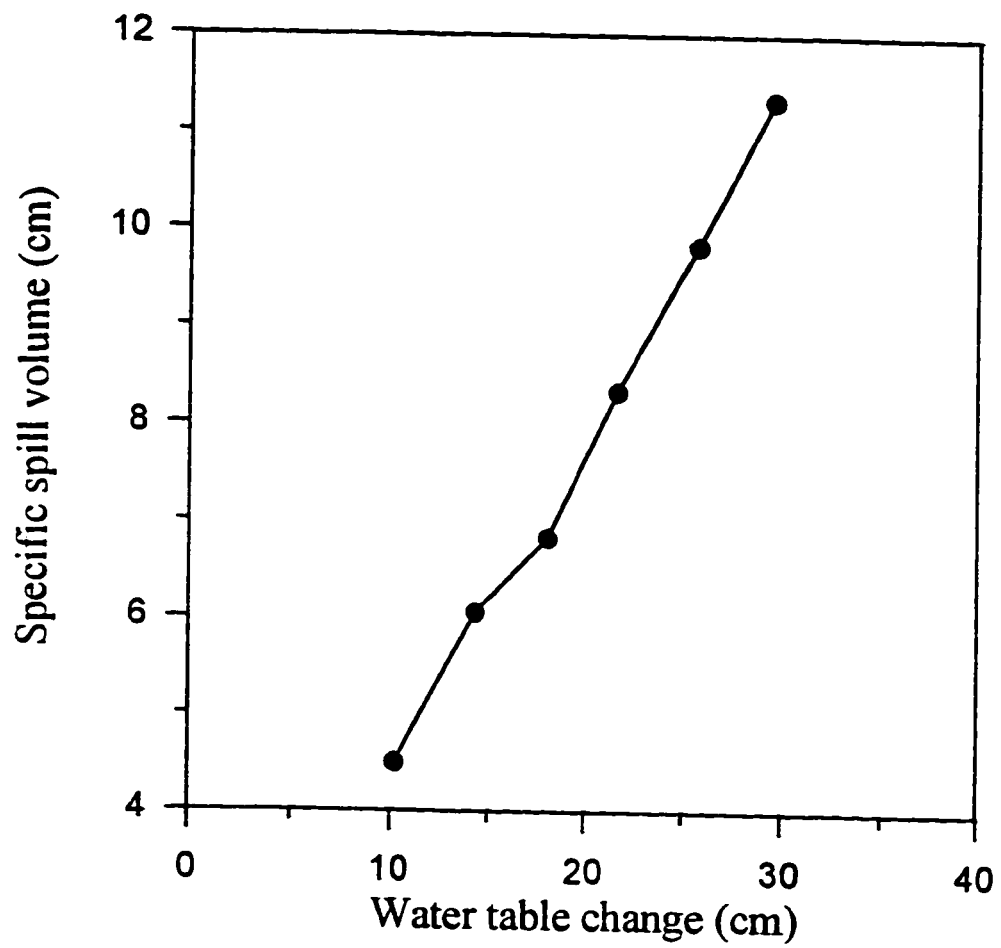
Figure 4.17 : Water table change-spill volume relationship for experiment on layered soil column S2UL.
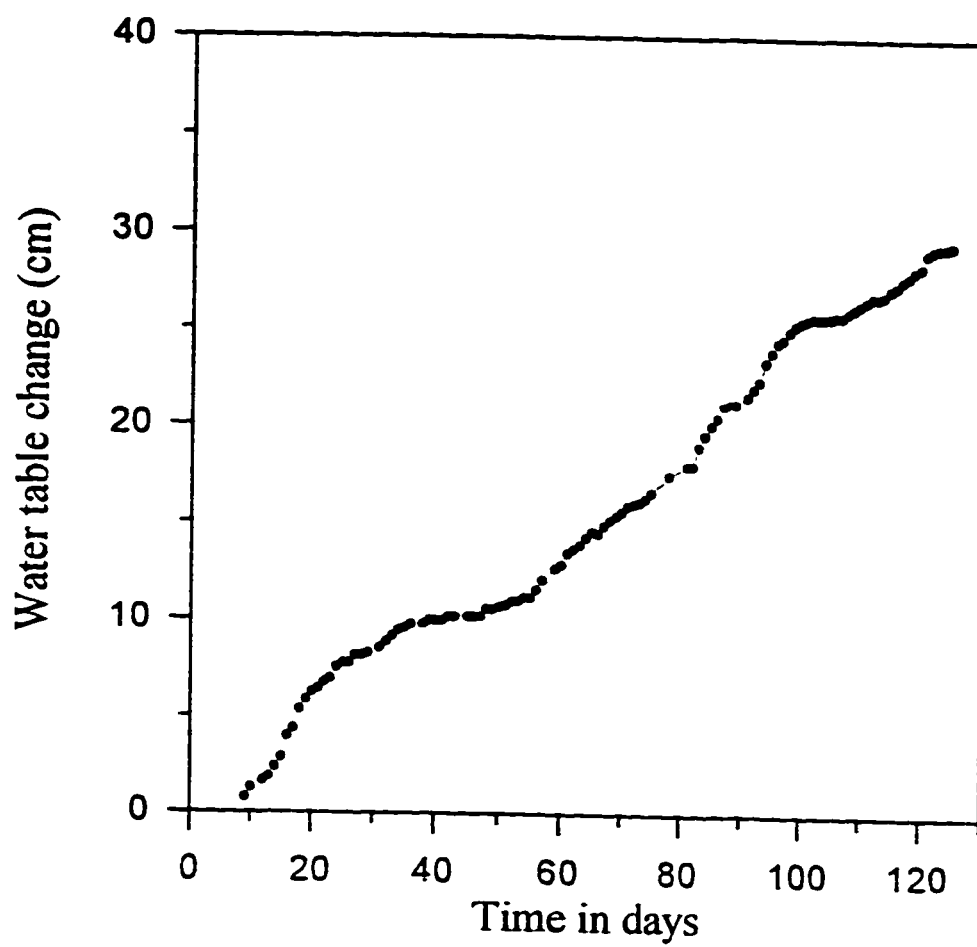
Figure 4.18 : Water table change for experiment on layered soil column S2UL.
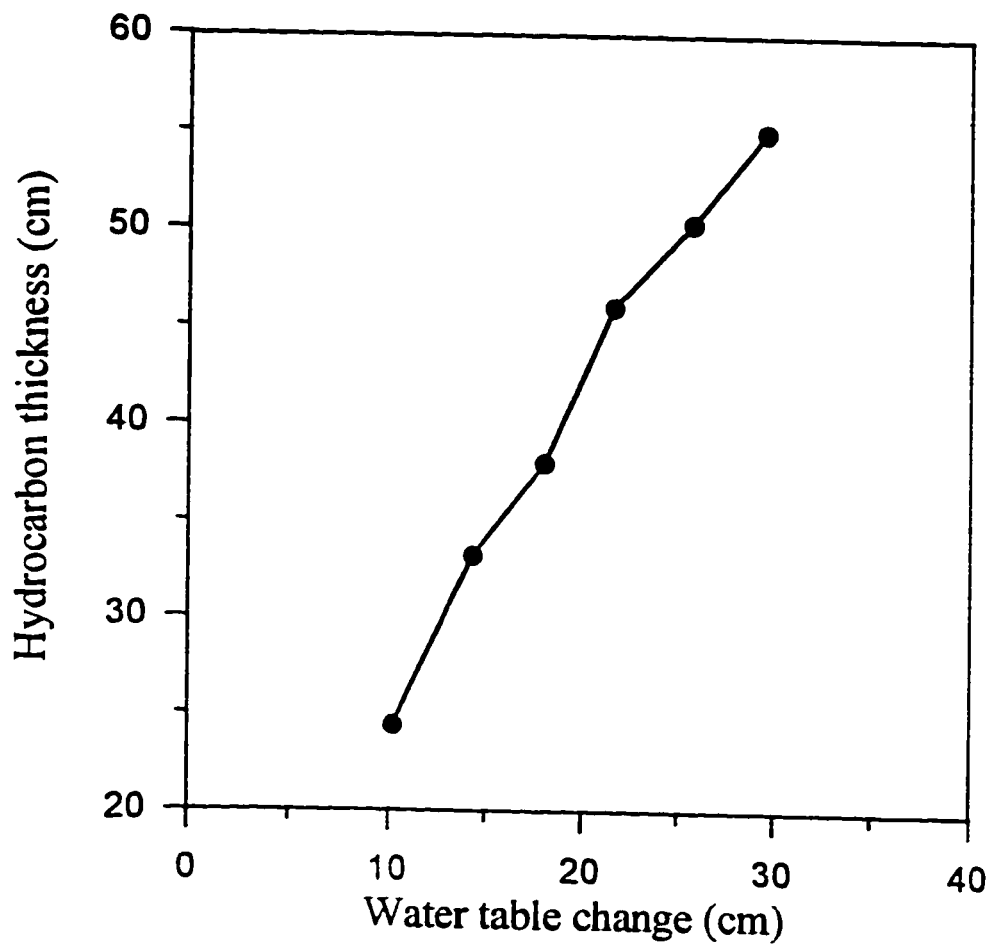
Figure 4.19 : Water table-free product thickness relationship for experiment on layered soil column S2UL.

provide methodology for the spill estimates in a layered soil. The soil parameters estimated earlier at a k/k_s value of 1% and 0.1% for the soils of the S1U and S1W columns are applicable, and are shown in Table(s) 1 and 3 in sec. 4.1.3 and 4.2.3. respectively.

The estimates of the analytical models at a k/k_s value of 1% are summarized in Table 4.7. For the different values of the free product thickness. the Brooks-Corey model underestimates the volume by 19% to 32% while the van Genuchten model underestimates it by 13% to 15%. Table 4.8 shows the estimates of the spill volume calculated by the analytical models at a k/k_s of 0.1% . The Brooks-Corey model underestimates the volume by 49% to 78% while the van Genuchten model underestimates volume by 43% to 77% .

Figure 4.20 illustrates the spill volume calculated by the analytical models at k/k_s values of 1% and 0.1% respectively. The estimates are very sensitive to the k/k_s value used. The spill volume estimates are much higher at a k/k_s of 1%. At both values of k/k_s, the van Genuchten model consistently estimates a slightly higher volume than the Brooks-Corey model for all values of the free product thickness. At a free product thickness of 24.4 cm , the Brooks-Corey model does not estimate the spill volume since the given thickness is below the estimated theoretical thickness of 31 cm for this soil.

4.4 Layered Sand Column S2WL

This sand column as described in sec. 3.2.2 is essentially similar to the sand column S1W. except that a 30 cm layer of uniform sand was placed 10 cm below the surface to observe the effect of layering on the free product thickness. The hydrocarbon was observed in the monitoring wells about three weeks after a volume of 2,750 ml of crude oil

Table 4.7: Estimates of spill volume (cm³/cm²) for experiment on layered soil column S2UL at k/k_s of 1%

Soil thickness*	Hydrocarbon thickness (cm)	Spill volume	van Genuchten	Brooks- Corey
(cm)		(cm³/cm²)		
105.6	24.4	4.5	4.92	
106.8	33.2	6.06	4.8	4.13
107	38	6.83	5.94	5.29
104	46	8.33	7.87	7.34
99.7	50.3	9.83	8.71	8.15
96	55	11.33	9.82	9.23

* above the oil table.

Table 4.7: Estimates of spill volume (cm³/cm²) for experiment on layered soil column S2UL at k/k_s of 1%

Soil thickness*	Hydrocarbon thickness (cm)	Spill volume	van Genuchten	Brooks- Corey
(cm)		(cm³/cm²)		
105.6	24.4	4.5	4.92	
106.8	33.2	6.06	4.8	4.13
107	38	6.83	5.94	5.29
104	46	8.33	7.87	7.34
99.7	50.3	9.83	8.71	8.15
96	55	11.33	9.82	9.23

* above the oil table.

Table 4.8 : Estimates of the spill volume (cm³/cm²) for experiment on layered soil column S2UL at k/k$_s$ of 0.1%

Soil thickness* (cm)	Hydrocarbon thickness (cm)	Spill volume (cm³/cm²)	van Genuchten	Brooks- Corey
105.6	24.4	4.5	1.03	
106.8	33.2	6.06	2.05	1.34
107	38	6.83	2.89	2.13
104	46	8.33	4.46	3.73
99.7	50.3	9.83	5.28	4.61
96	55	11.33	6.45	5.8

* above the oil table.
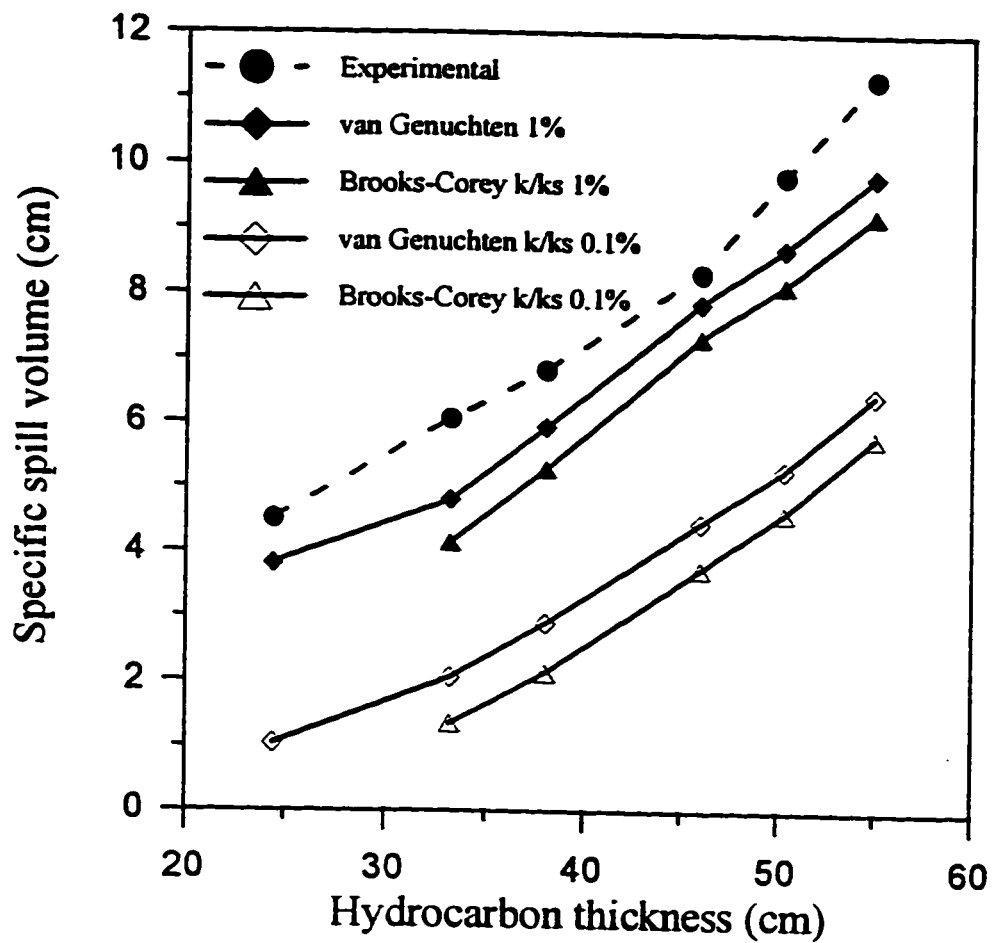
Figure 4.20 : Effect of k/k_s on analytical estimates for experiment on layered soil column S2UL.

had been released into the column. The total volume of 2,750 ml corresponds to the Brooks-Corey critical spill volume for this soil.

Additional crude oil was released in increments every 10-14 days and the well hydrocarbon thickness or the free product hydrocarbon thickness corresponding to different spill volumes was measured at quasi-static equilibrium in the system. A total of seven data points were generated for the spill volume-free product thickness relationship for this experiment. The last free product thickness measurement was taken at a total spill volume of 9,000 ml.

4.4.1 Hydrocarbon Levels in Monitoring Wells

The hydrocarbon thickness in the monitoring wells as a function of the spill volume is illustrated in Figure 4.21. For the critical spill volume, the hydrocarbon levels in both monitoring wells was 11.0 cm at equilibrium. As more crude oil was released, the hydrocarbon levels in the monitoring wells increased but matched very closely, as can be observed in Figure 4.21. The curves of this figure show a smooth transition from a flatter slope at lower spill volumes to a steeper slope for higher spill volumes. This trend is similar to the corresponding curves generated for other soil columns and supports the conclusion that such curves should be divided into two segments- a segment of flatter slope for low spill volumes and a segment with steeper slope for high spill volumes. Comparing the spill volume-free product thickness curves for soil columns S1W and S2WL (Figure 4.22), a thickness higher by about 5 cm is consistently observed for column
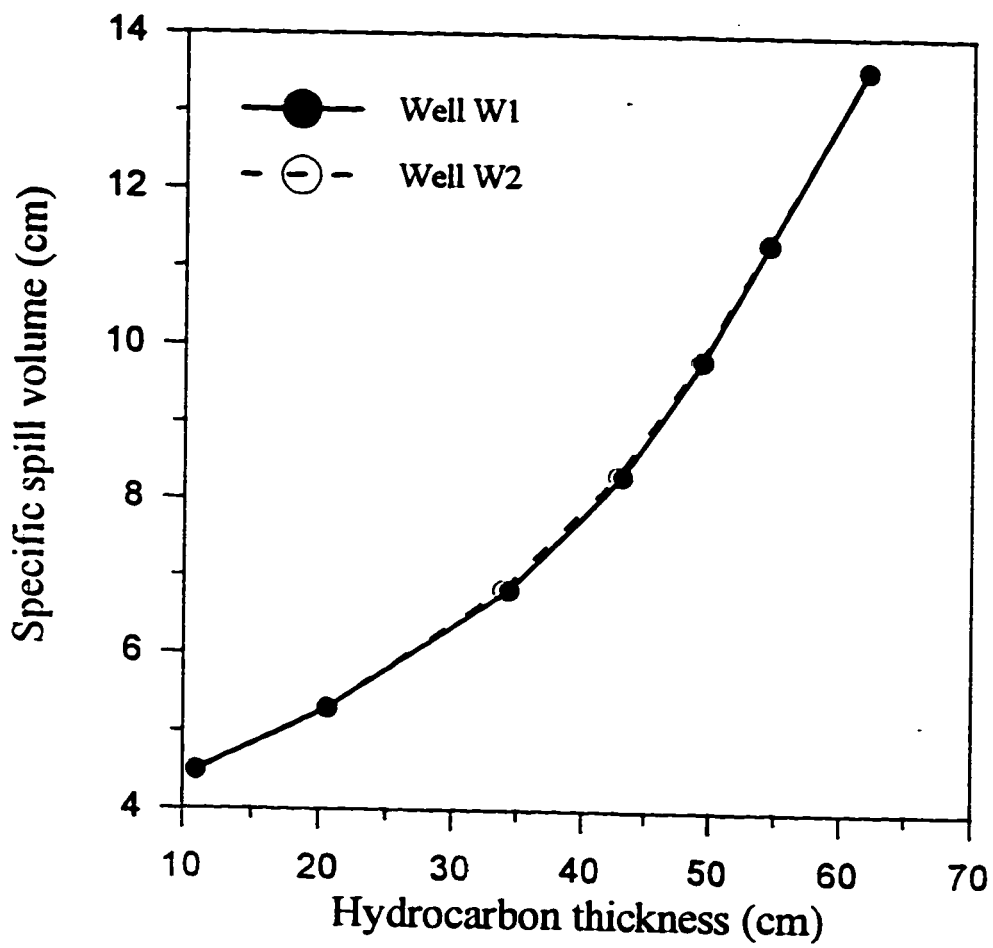
Figure 4.21 : Free product thickness and spill volume relationship for experiment on layered soil column S2WL.
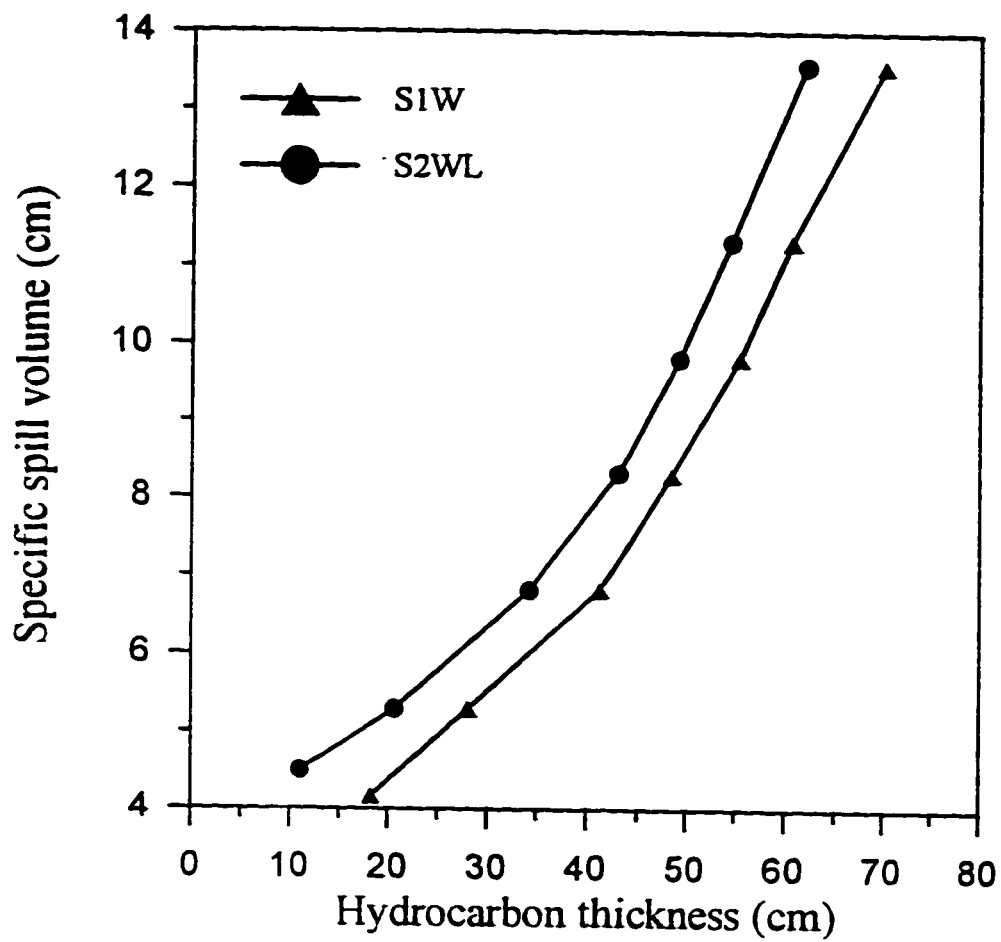
Figure 4.22 : Comparison of free product thickness-spill volume relationships for experiments on well-graded soil column S1W and layered soil column S2WL.

S1W. Corresponding curves (Figure 4.16) for the soil columns S1U and S2UL show that there was a increase in the free product thickness after layering. Therefore quantifying the spill volume without assessing the possible effect of layering could lead to significant deviations in the estimates which could either result in estimates that are either too high or too low.

4.4.2 Water Table Change

The changes in the water table level were noticeable a day after the initial volume of 2,750 ml of crude oil had been released into the column. A water table change of 13.9 cm was recorded for the critical spill volume at quasi-static equilibrium. As more crude oil was released incrementally in the column, the water table level rose further. The reasons for the changes in the water table have been explained earlier in sec. 4.1.2 . At a total spill volume of 7,500 ml, the water table level change was 42 cm which is higher than that for the soil column S2UL. This is expected, since similar results were obtained for the soil column S1W which was given characteristics essentially similar to this soil column. Figure 4.23 shows the changes in the water table with the spill volume. The day to day water table level changes are plotted in Figure 4.24. The flatter regions within the curve signify attainment of quasi-static conditions in the system at different times after the crude oil had been released. A curve relating the free product thickness to the change in water table is shown in Figure 4.25. For a total free product thickness of 61 cm, a water table change of 42 cm was observed at the end of the experiment.
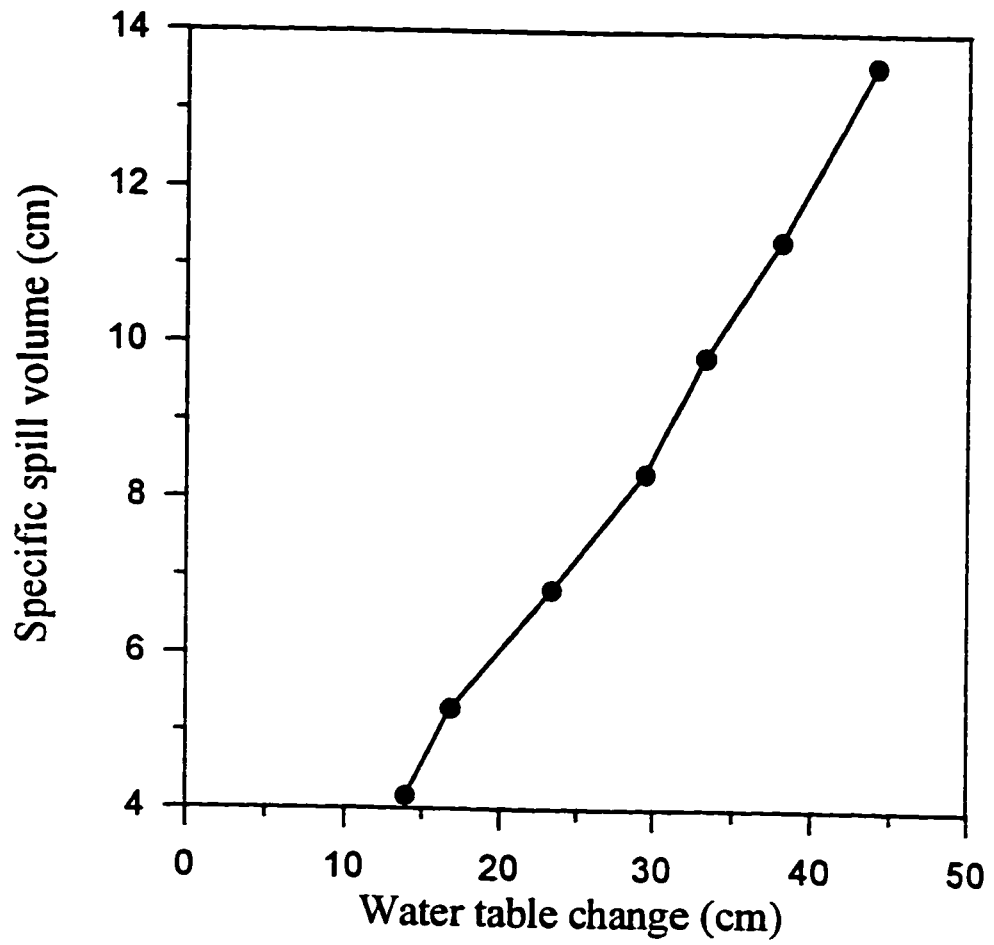
Figure 4.23 : Water table change-spill volume relationship for experiment on layered soil column S2WL.
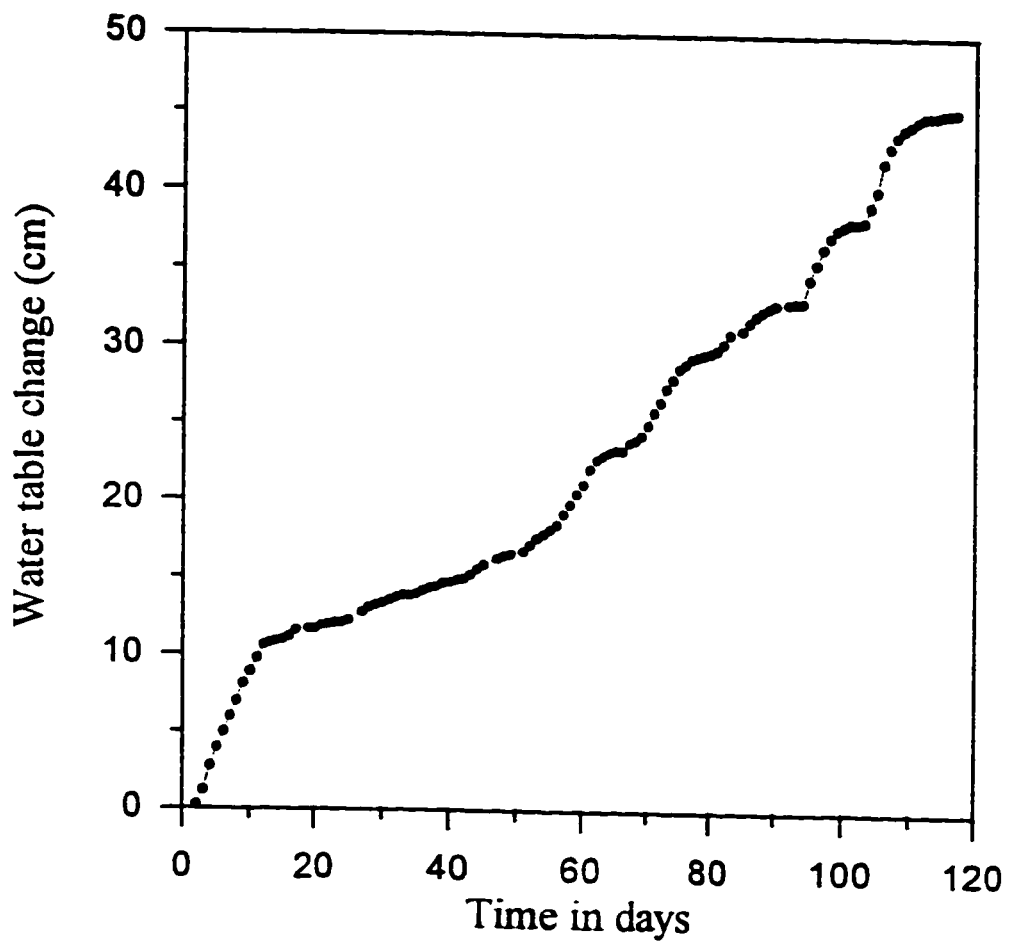
Figure 4.24 : Water table change for experiment on layered soil column S2WL.
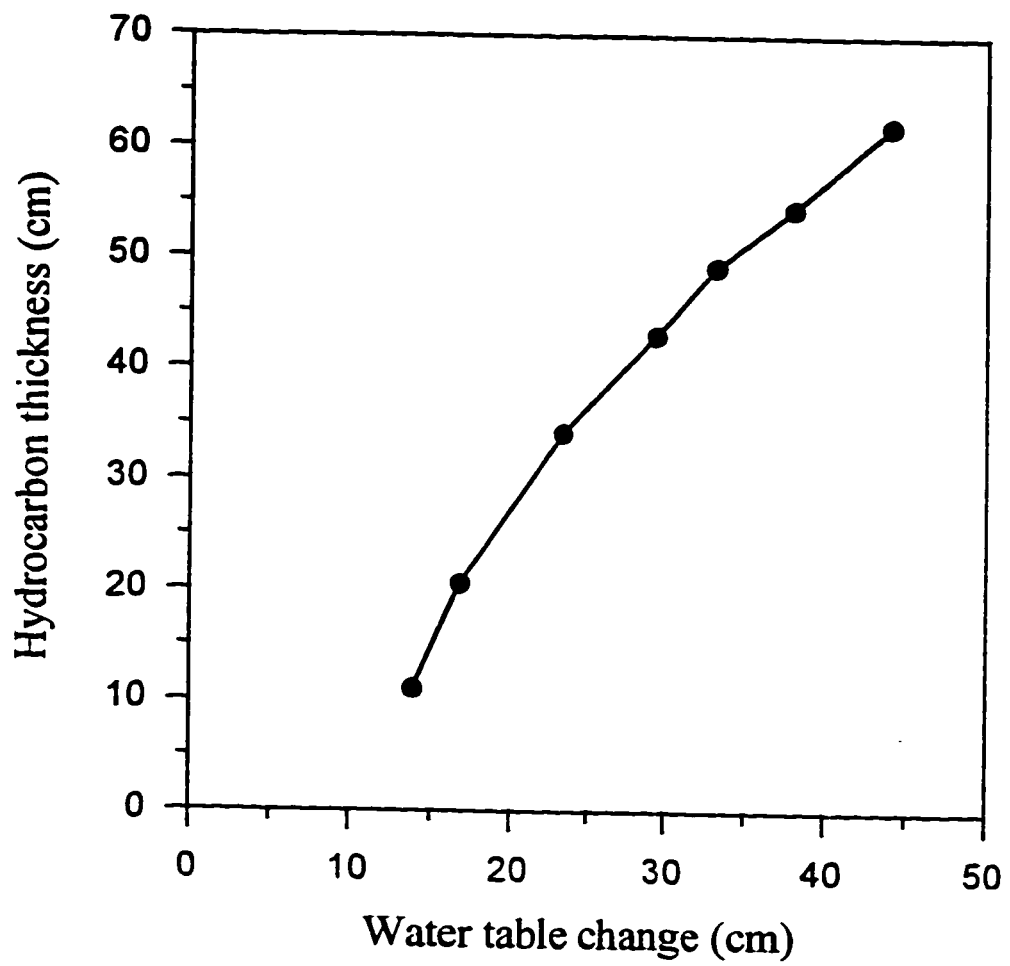
Figure 4.25 : Water table-free product thickness relationship for experiment on layered soil column S2WL.

4.4.3 Analytical Estimates of Spill Volume

The estimates at a k/k_s value of 1% are summarised in Table 4.9 and it is clear that both models underestimate the spill volume. The Brooks- Corey model underestimates the spill volume by 28% to 31% for the different values of the free product thickness, while the van Genuchten model underestimates it by 24% to 26%. At a k/k_s value of 0.1 % ,the estimates of both the models are reduced. Table 4.10 shows the estimates of the spill volume predicted by the analytical models at a k/ks of 0.1% . The Brooks-Corey model underestimates the spill by 54% to 81% while the van Genuchten model underestimates it by 49% to 76%.

Figure 4.26 shows the spill volume estimated by the analytical models at a k/k_s of 1% and 0.1%. The van Genuchten model gives slightly higher estimates than the Brooks-Corey model; however, both the models arrive at nearly the same estimates for a experimental volume of 5.3 cm and higher. A significant difference between these models can be observed at a free product thickness of 11 cm. The van Genuchten model estimates the volume corresponding to this free product thickness. however the Brooks-Corey model can not quantify a spill volume for this thickness. since it is below the estimated theoretical critical thickness of 15.9 cm for this soil.

4.5 Modified Analytical Estimates of Spill Volume

Since the analytical and empirical models presented in this study consistently underestimated the spill volume. an alternate approach was used to estimate the spill

Table 4.9: Estimates of spill volume (cm³/cm³) for experiment on layered soil column S2WL at k/k_s of 1%

Soil thickness*	Hydrocarbon thickness (cm)	spill volume (cm³/cm²)	van Genuchten	Brooks-Corey
(cm)				
119	11.0	4.5	3.4	
114.4	20.6	5.3	3.84	3.64
101.8	34.2	6.83	5.40	5.02
96	43	8.3	6.81	6.43
90.8	49.2	9.83	7.78	7.40
85.5	54.5	11.33	8.44	8.14
80	61	13.58	9.23	8.9

* above the oil table.

Table 4.10 : Estimates of spill volume (cm³/cm²) for experiment on layered soil column S2VL at k/k$_s$ of 0.1%

Soil thickness*	Hydrocarbon	Spill volume	van Genuchten	Brooks-Corey
(cm)	thickness (cm)	(cm³/cm²)		
119	11.0	4.5	1.08	1.03
114.4	20.6	5.3	1.75	2.39
101.8	34.2	6.83	3.03	2.39
96	43	8.3	4.24	3.69
90.8	49.2	9.83	5.32	4.67
85.5	54.5	11.33	5.83	5.26
80	61	13.58	6.78	6.23

* above the oil table.

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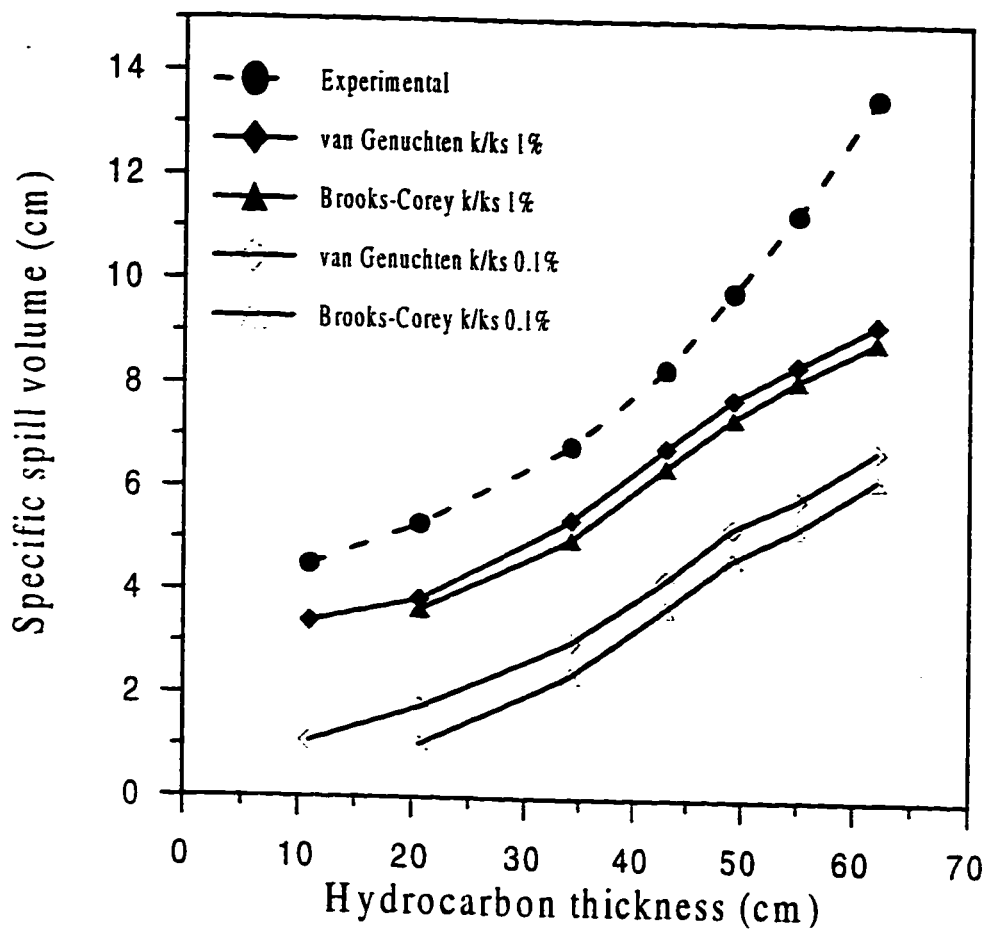
Figure 4.26 : Effect of k/ks on analytical estimates for experiment on layered soil column S2WL.

volume more accurately. In the modified approach, the total moisture retention function, S_T, for these models has been redefined as a linear function. This is done by interpolating the function for both the models linearly from a value of ϕ (the soil porosity) at the top of the oil table in the monitoring well to a value of S_r, at some elevation (z) above the oil table. This elevation (z) represents a hypothetical depth of the hydrocarbon in the media above the oil table and is based on the assumption that an insignificant volume of hydrocarbon is present above this elevation. Based on this approach, estimates were calculated for a range of depths varying from 30-60 cm. At a z value of 50 cm estimated spill volume came close to the actual spill volume. The estimates obtained for the various experiments for a depth of 50 cm are discussed in the following sections.

4.5.1 Modified Analytical Estimates for Uniform Sand Column S1U

The results at a k/k_s of 0.1% and 1% are summarized in Table 4.11. The estimates at both values of k/k_s are similar, and the Brooks-Corey model projects slightly higher estimates at both values of k/k_s. The estimates at a k/k_s of 1% are illustrated in Figure 4.27. The Brooks-Corey model consistently overestimates the spill volume by 6% to 19% for the different values of free product thickness quantified by this model. The van Genuchten model, on the other hand underestimates the spill volume at the lower end significantly. Its estimates at higher values of volume, however, are fairly close to the actual spill volume. The results at a k/k_s of 0.1% are illustrated in Figure 4.28. The Brooks-Corey model overestimates the spill volume by 11% at the lower end, however it predicts higher values of the volume very closely, while the van Genuchten model

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Table 4.11: Modified estimates of spill volume (cm³/cm²) for experiment on uniform soil column SI1I

Soil thickness*	Hydrocarbon	Spill volume	van Genuchten		Brooks-Corey	
(cm)	thickness (cm)	(cm³/cm²)	k/k, 1%	k/k, 0.1%	k/k, 1%	k/k, 0.1%
116.8	14.2	5.3	2.59	2.08		
101.2	33.8	6.83	7.14	6.52	8.13	7.59
95	42	8.3	9.21	8.55	9.99	9.27
93	46	9.83	10.36	9.71	11.1	10.39
92.2	47.8	10.6	10.72	10.05	11.79	10.99
90	50	11.33	11.39	10.71	12.03	11.32

* above the oil table.
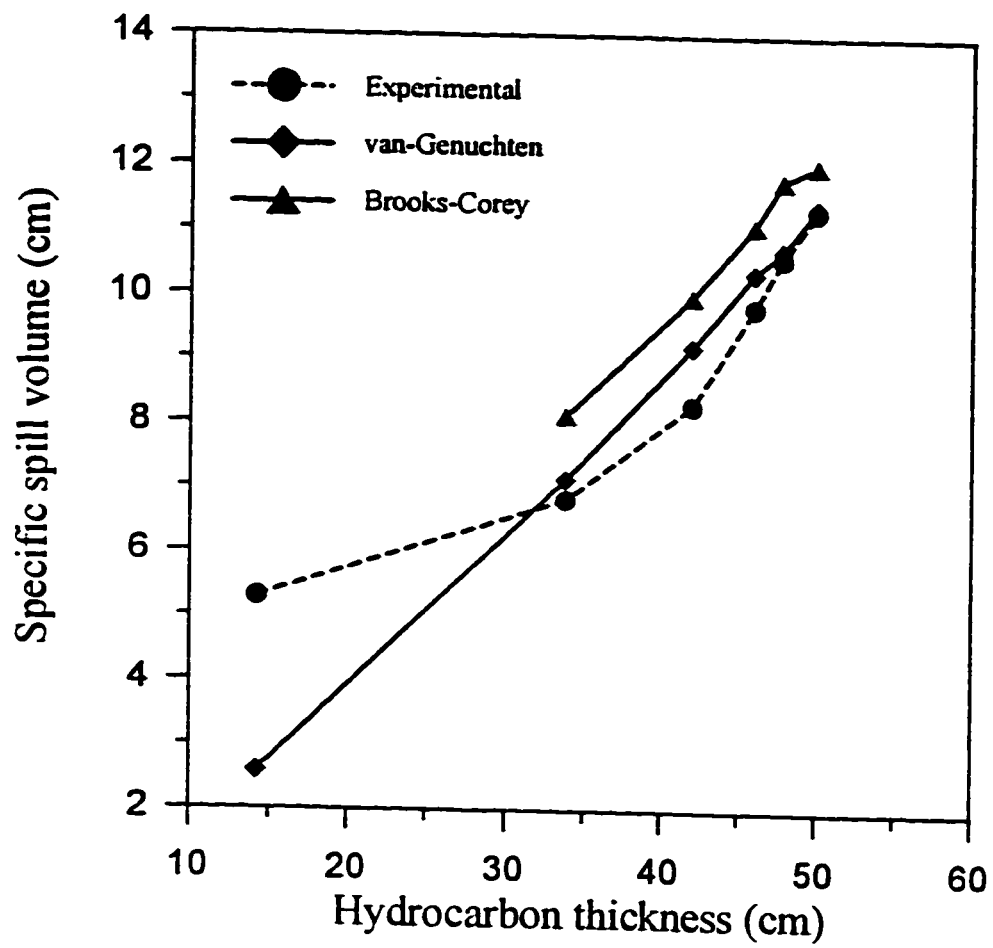
Figure 4.27 : Modified analytical estimates for experiment on uniform soil column S1U at k/k$_s$ of 1%.
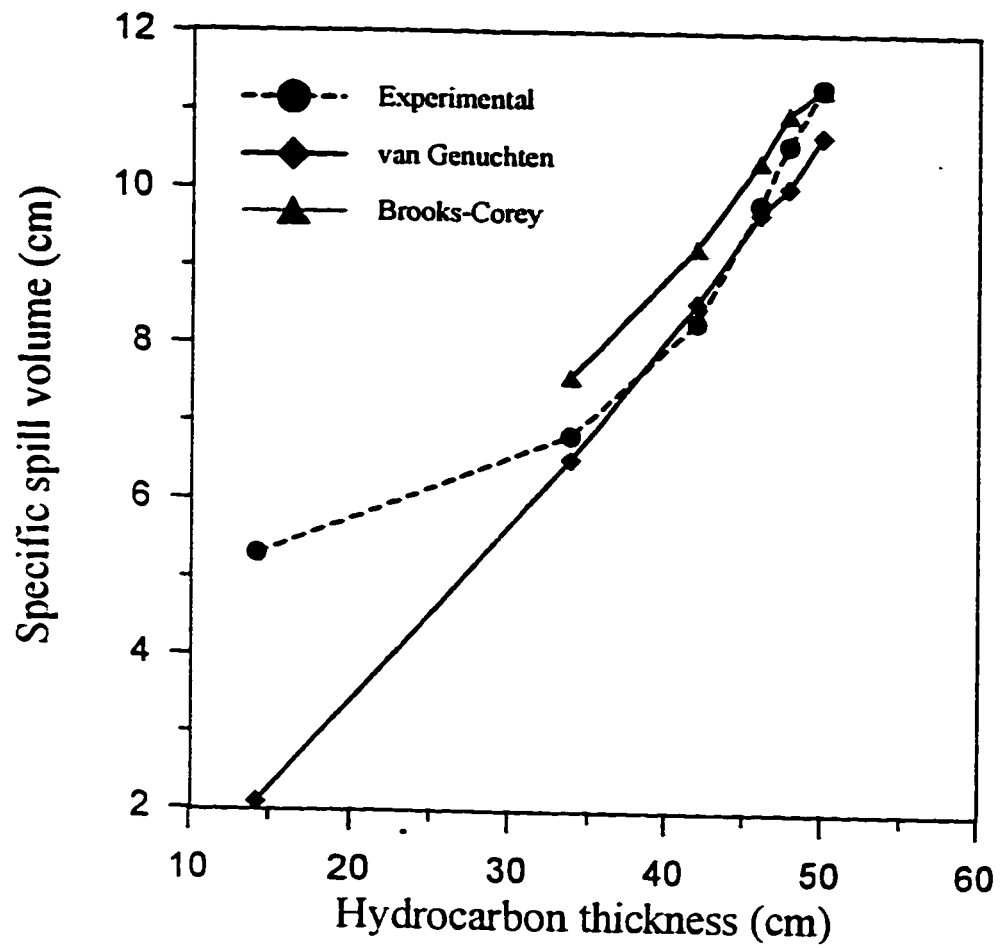
Figure 4.28 : Modified analytical estimates for experiment on uniform soil column S1U at k/k$_s$ of 0.1%.

underestimates the spill at the lower end by 61%, but estimates intermediate values of the spill volume between the lower end and the higher end very closely.

4.5.2 Modified Analytical Estimates for Well-Graded Sand Column S1W

Estimates of spill volume predicted by the models at k/k_s of 1% and 0.1% are similar, and are summarised in Table 4.12. The estimates at a k/k_s of 1% are illustrated in Figure 4.29, for the different values of free product thickness generated, both models predict the volume closely. The Brooks-Corey estimates are slightly higher than the van Genuchten estimates; however, both models estimate the spill volume for the range of 4.17 cm to 11.33 cm very closely. The spill volume is estimated more closely at a k/k_s of 0.1% as shown in Figure 4.30. At both values of k/k_s, the Brooks-Corey estimates of the spill volume are slightly higher than the corresponding van Genuchten estimates; however, both models underestimate a spill volume of 13.58 cm at the higher end.

4.5.3 Modified Analytical Estimates for Layered Sand Column S2UL

Table 4.13 and Figure 4.31 show the estimates of the modified models at a k/k_s of 1%. At a k/k_s of 1% the Brooks-Corey model overestimates the spill volume by 19% to 35%, while the predictions of the van Genuchten model are similar but the volume is overestimated by 9% to 29%. Comparing the two models, the Brooks-Corey estimates are higher for a spill volume of 6.06 cm and higher.

Table 4.12 : Modified estimates of spill volume (cm³/cm³) for experiment on well-graded soil column S1W

| Soil thickness* (cm)	Hydrocarbon thickness (cm)	Spill volume (cm³/cm³)	van Genuchten		Brooks-Corey	
			k/k_s 1%	k/k_s 0.1%	k/k_s 1%	k/k_s 0.1%
113.8	18.2	4.17	4.05	3.73	4.45	4.03
107	28	5.3	5.61	5.27	5.89	5.53
95.8	41.2	6.83	7.48	7.10	7.95	7.45
90.6	48.4	8.3	8.76	8.36	9.15	8.72
84.6	55.4	9.83	9.85	9.41	10.24	9.76
80.4	60.6	11.33	10.62	10.16	11.0	10.54
72	70	13.58	12.15	11.63	12.43	11.89

* above the oil table.

Figure 4.29 : Modified analytical estimates for experiment on well-graded soil column S1W at k/k$_s$ of 1% .

Figure 4.30 : Modified analytical estimates for experiment on well-graded
soil column S1W at k/k$_S$ of 0.1%.

Table 4.13 : Modified estimates of spill volume (cm³/cm²) for experiment on layered soil column S2U1.

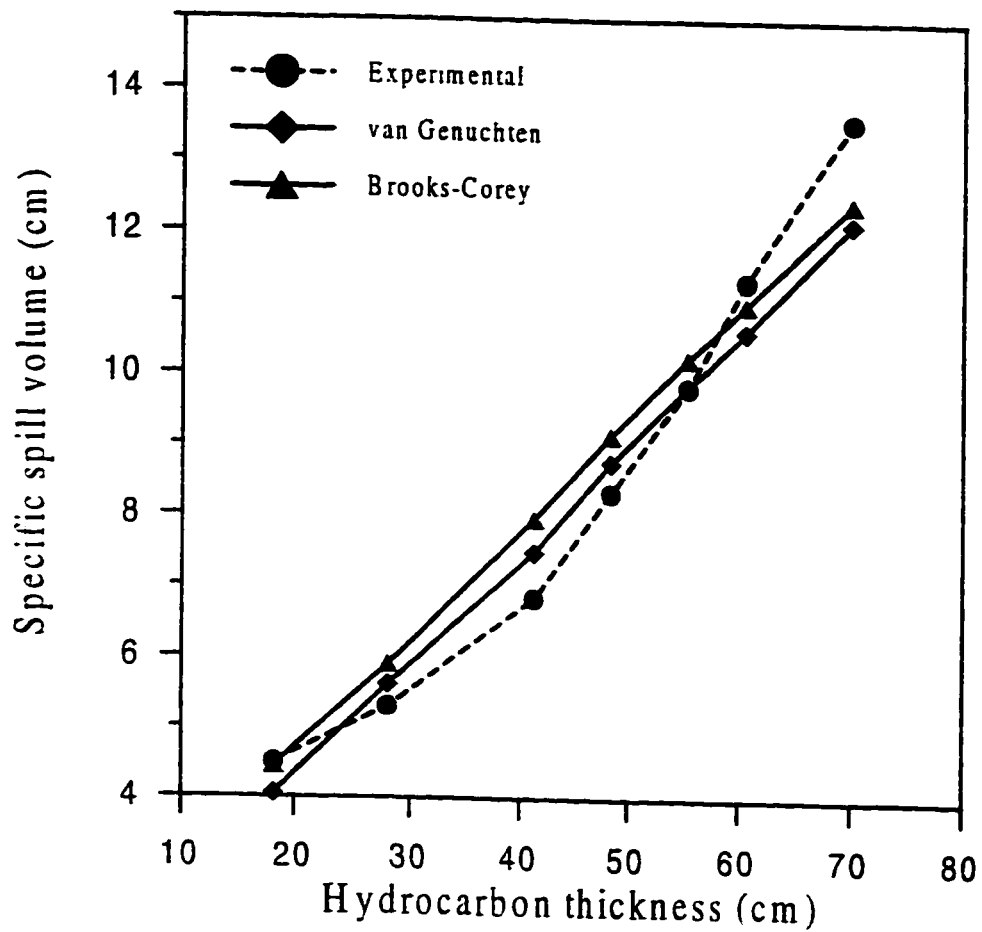| Soil thickness*	Hydrocarbon	Spill volume	van Genuchten		Brooks-Corey	
(cm)	thickness (cm)	(cm³/cm²)	k/k$_s$ 1%	k/k$_s$ 0.1%	k/k$_s$ 1%	k/k$_s$ 0.1%
105.6	24.4	4.5	4.92	4.28		
106.8	33.2	6.06	6.98	6.43	8.2	7.54
107	38	6.83	8.46	7.89	9.31	8.68
104	46	8.33	10.8	10.04	11.35	10.71
99.7	50.3	9.83	11.71	11.1	12.56	11.81
96	55	11.33	13	12.34	13.56	12.86

* above the oil table.
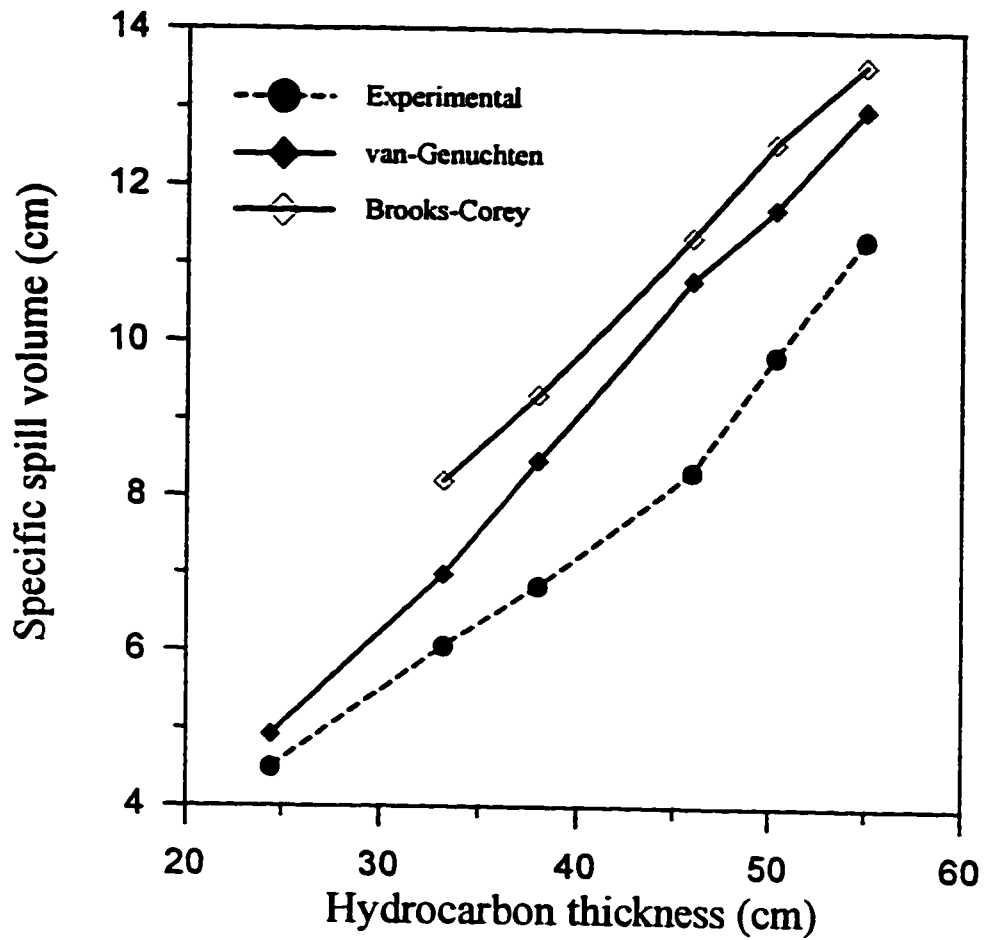
Figure 4.31 : Modified analytical estimates for experiment on layered soil column S2UL at k/k$_s$ of 1%.

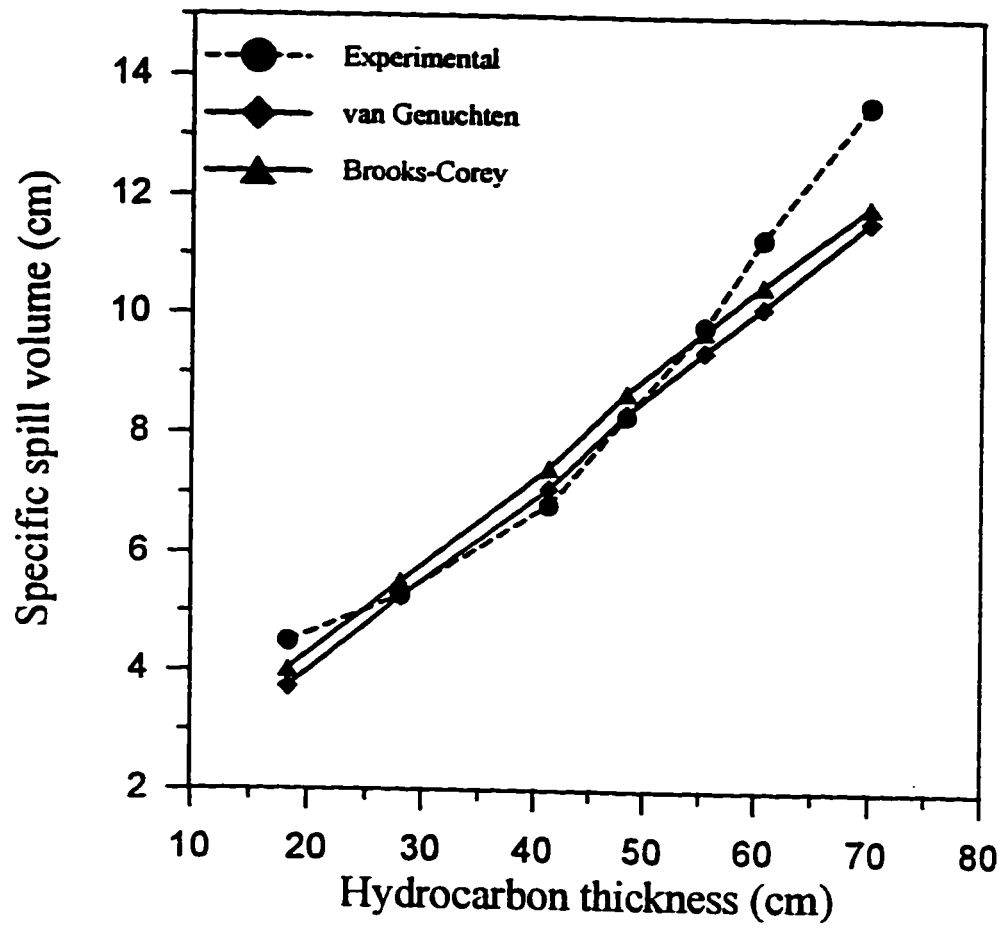Figure 4.32 : Modified analytical estimates for experiment on layered
soil column S2UL at k/k_s of 0.1% .

overestimates higher volumes by 6% to 19%. Comparing the two models, the van Genuchten model estimates the spill volume more closely.

4.5.4 Modified Analytical Estimates of Spill Volume for Layered Sand Column S2WL

The spill volume. though underestimated. is estimated closely by both models at the values of k/k_s. The estimates are similar at the values of k/k_s used. The estimates at a k/k_s of 1% are summarised in Table 4.14 and illustrated in Figure 4.33. At a k/k_s of 1% the Brooks-Corey model estimates the spill volume very closely; only a spill of 13.58 cm at the higher end is underestimated considerably. As seen from the figure the van Genuchten model also underestimates the volume at the upper and lower end of the curve considerably: however. its predictions of intermediate range of volumes is fairly close. The Brooks-Corey model predicts the spill volume more closely.

The estimates at a k/k_s of 0.1% are shown in Figure 4.34, and are similar to those at a k/k_s value of 1%. Thus. the relative permeability (k/k_s) may not have any major influence on the modified estimates of spill volume. The Brooks-Corey model estimates the volume very closely. the estimates of van Genuchten model, though slightly lower, are similar. A spill volume in the range of 11.33cm to 13.58 cm at the higher end of the curve appears to be underestimated considerably by both models.

Table 4.14 : Modified estimates of spill volume (cm³/cm²) for experiment on layered soil column S2WL

| Soil thickness* | Hydrocarbon | Spill volume | van Genuchten | | Brooks-Corey | |
(cm)	thickness (cm)	(cm³/cm²)	k/k_s 1%	k/k_s 0.1%	k/k_s 1%	k/k_s 0.1%
119	11	4.5	3.16	2.86		
114.4	20.6	5.3	4.45	4.12	4.84	4.51
101.8	34.2	6.83	6.43	6.08	6.9	6.50
96	43	8.33	7.97	7.59	8.25	7.96
90.8	49.2	9.83	8.82	8.42	9.3	8.78
85.5	54.5	11.33	9.69	9.26	10.08	9.62
80	62	13.58	11.05	10.46	11.26	10.90

* above the oil table.
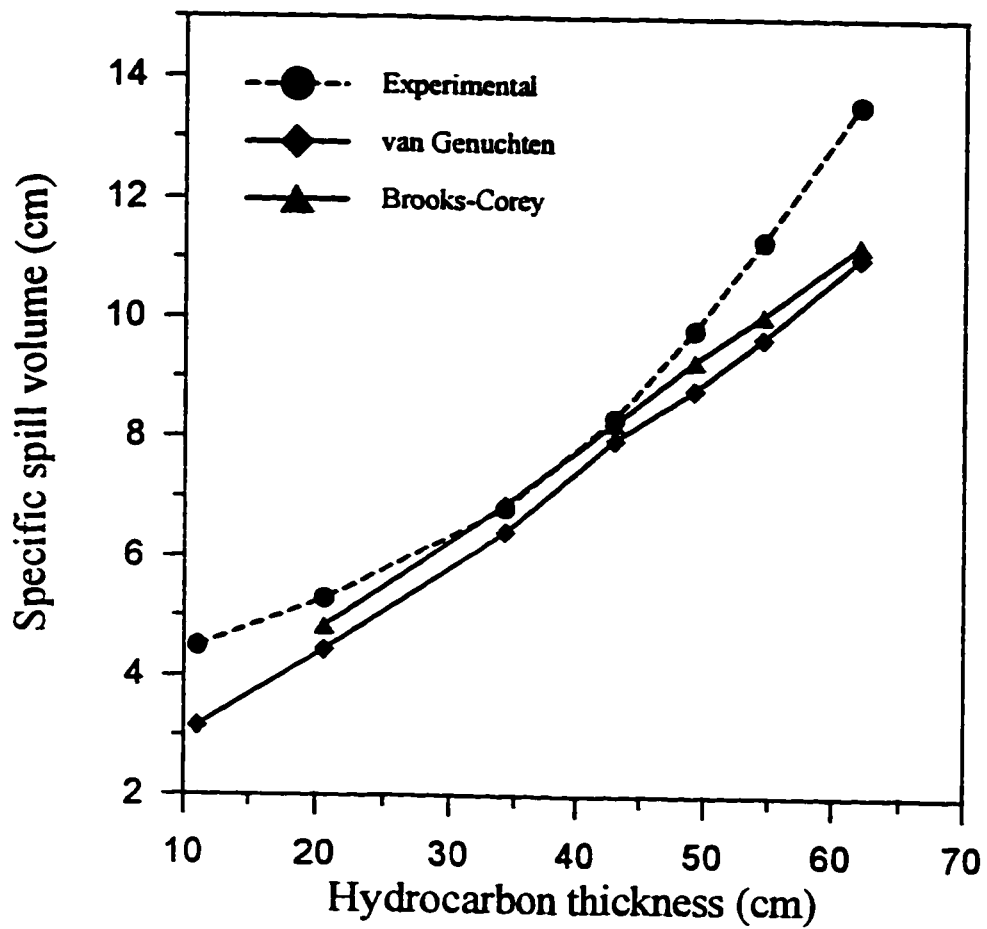
Figure 4.33 : Modified analytical estimates for experiment on layered
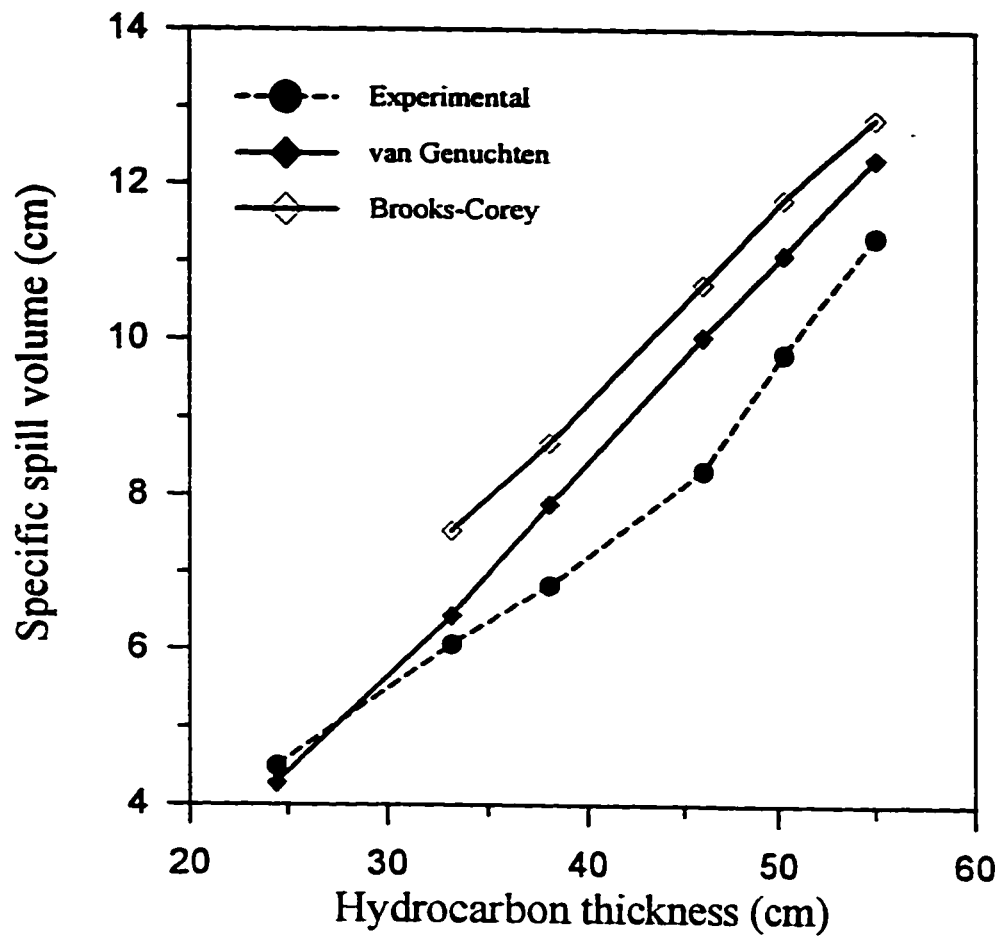soil column S2WL at k/k_s of 1%.
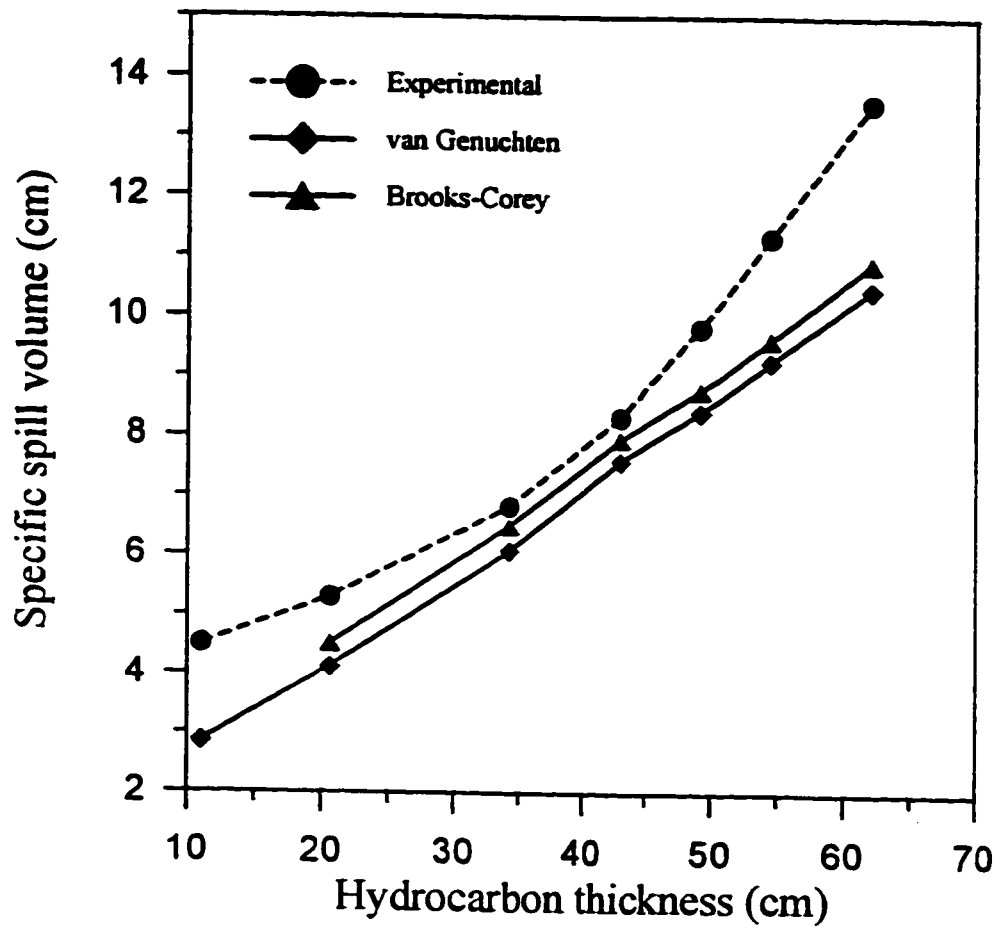
Figure 4.34 : Modified analytical estimates for experiment on layered
soil column S2WL at k/k$_s$ of 0.1%.

4.6 Hydrocarbon Recovery from the Sand Columns

Hydrocarbon recovery was started two weeks after the last spill had been introduced into the column. A first step for the remediation of the aquifer was done by recovering the free product from the monitoring wells using a Cole Parmer pump of rating 3KVA. This pump can be operated at variable speeds up to 3,200 rpm. For consistency, it was operated at a speed of 2,560 rpm during the cleanup operation in all the sand columns.

The cleanup process was conducted for a period of three to four weeks for each sand column. In all the columns, about 80 to 85% of the total hydrocarbon recovery took place during the first 5 to 7 days. During this period the hydrocarbon was pumped out from the monitoring wells three times in a period of twelve hours. The hydrocarbon level in the wells was allowed to stabilize overnight (for a period of twelve hours) before the recovery operation was repeated the next day. With passage of time, the recoverable hydrocarbon in the monitoring wells decreased, and therefore the pumping was reduced to two times in a period of twelve hours. Progressively the free product thickness decreased and hydrocarbon recovery was done once every day. During the later stages, the recovery of the hydrocarbon was carried out once every 2 to 3 days. Recovery was then insignificant. The results of the hydrocarbon recovery in the various soil columns is discussed in the following sections.

4.6.1 Hydrocarbon Recovery from Uniform Sand Column S1U

For a total spill volume of 11.33 cm^3/cm^2. around 40% of the hydrocarbon was recovered from this column. The result of the hydrocarbon recovery is shown in Figure 4.35 as a function of time. The steep region of the total recovery curve indicates the high rate of recovery. About 90% of the hydrocarbon recovery took place during the first 7 to 10 days of pumping. after which the continuing recovery. as shown by the flatness of the curve was insignificant. Theoretically a volume of the hydrocarbon greater than 40% should be recoverable: however that is not possible because hydrocarbon recovery is associated with a readjustment of the hydrocarbon-water interface in the soil. This can also be confirmed from the results of a field study conducted by Testa et al. (1993) where a recovery of the order of 30 to 50% of the total estimated spill volumes at various contaminated sites was reported.

4.6.2 Hydrocarbon Recovery from Well-Graded Sand Column S1W

Hydrocarbon recovery of about 48% of the total spill volume of 13.58 cm^3/cm^2 took place during the first seven days. After this period the recovery decreased appreciably. At the end of three weeks the total recovery was about 52%, a higher percentage of the hydrocarbon (48%) being unrecoverable due to reasons discussed earlier in sec. 4.6.1. The hydrocarbon recovery curves (daily and total recovery) for this sand column are shown in Figure 4.36. these are similar to corresponding curves for column S1U.
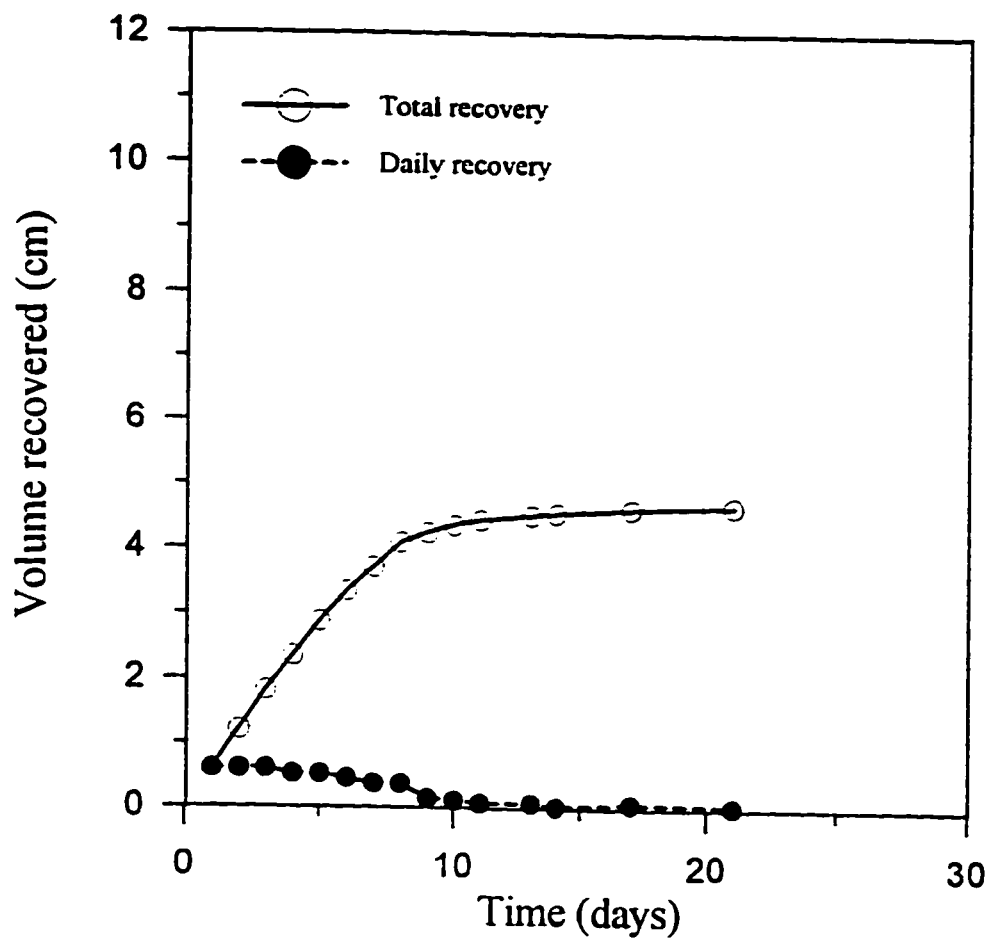
Figure 4.35 : Hydrocarbon recovery from uniform sand column S1U.
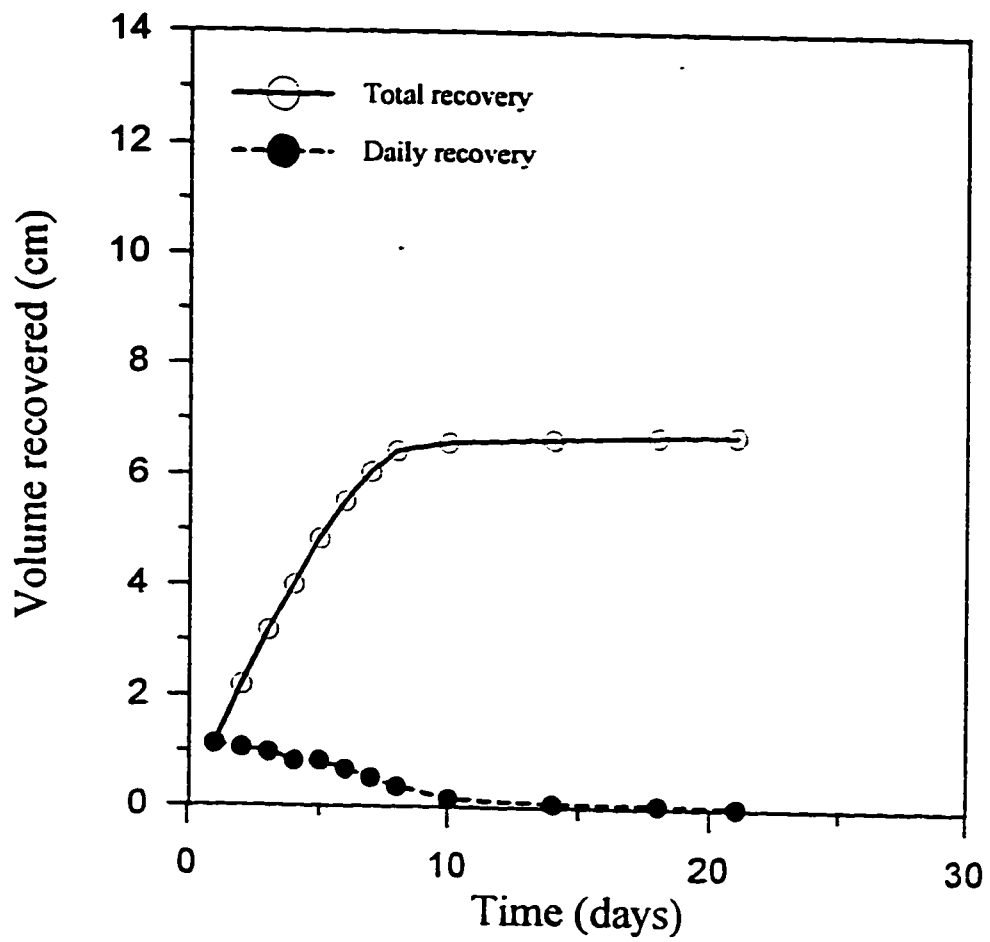
Figure 4.36 : Hydrocarbon recovery from well-graded sand column S1W.

4.6.3 Hydrocarbon Recovery from Layered Sand Column S2UL

About 46% of the total spill volume of 11.33 cm³/cm² was recovered from this column. For this experiment, pumping operations were carried out for a fourth week. As seen from the total recovery curve shown in Figure 4.37, there was not any significant accretion to the total recovery after the high rate of recovery achieved during the early stages of recovery. Similar to the recovery rates for the other experiments, most recovery took place during the first ten days, and beyond that period the recovery was insignificant.

4.6.4 Hydrocarbon Recovery from Layered Sand Column S2WL

About 42% of the total spill volume of 13.58 cm³/cm² was recovered from this column. Similar to the recovery operations for other experiments, most hydrocarbon recovery took place during early stages of the experiment (Figure 4.38). Though recovery was continued into the seventh week also, late stage recovery was minimal. The recovery curves are similar to curves of this type generated for other experiments.
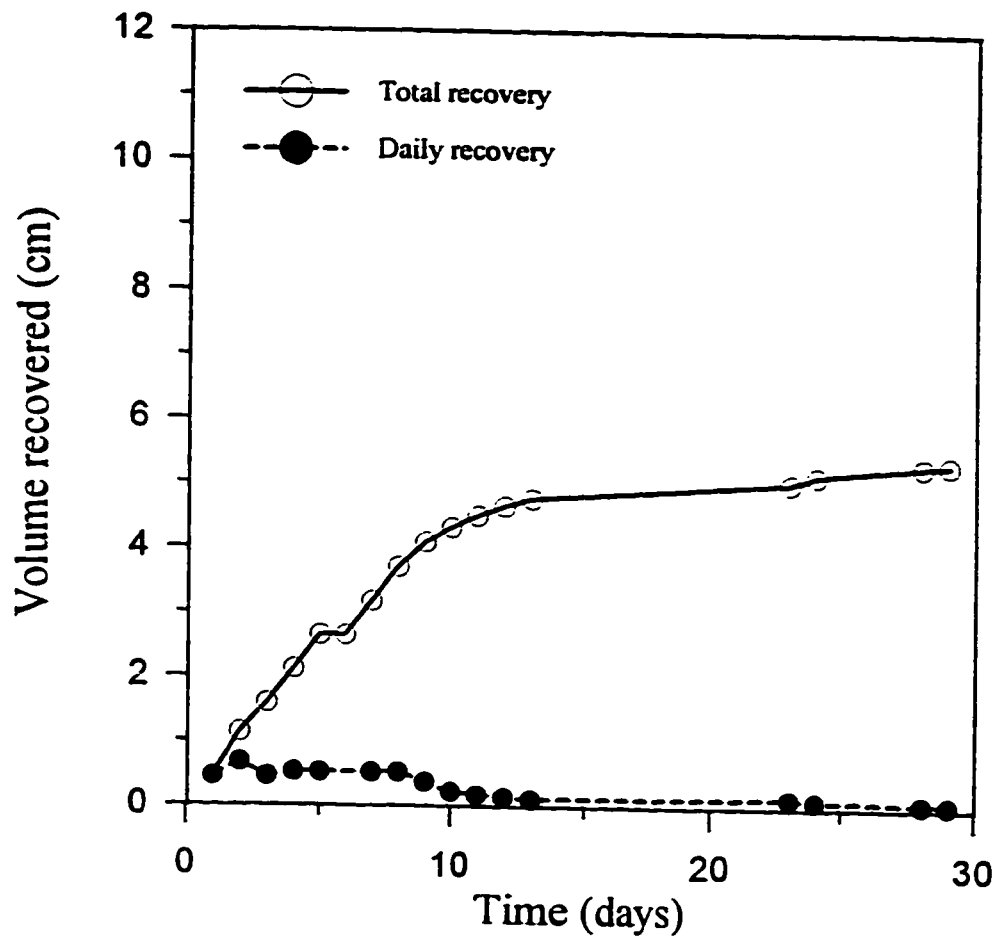
Figure 4.37 : Hydrocarbon recovery from layered sand column S2UL .
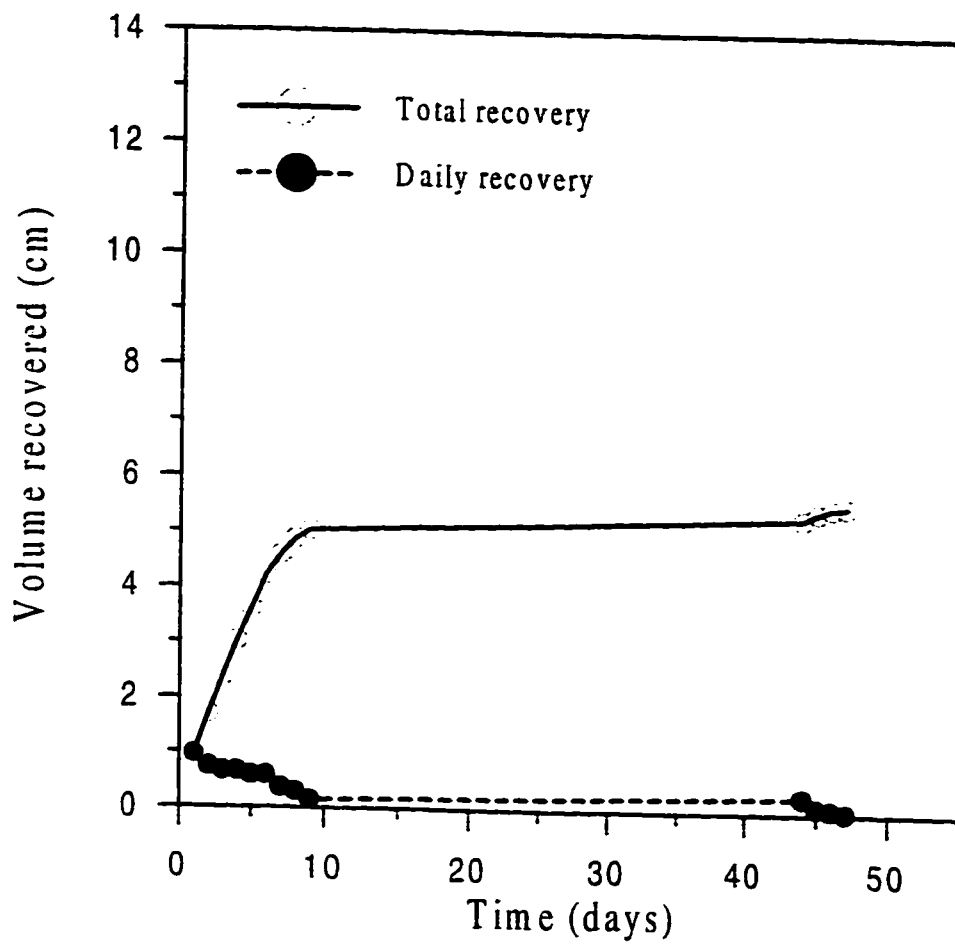
Figure 4.38 : Hydrocarbon recovery from layered sand column S2WL .

Chapter 5

ANALYTICAL MODEL FOR LAYERED SOILS

Based on the Brooks-Corey (1966) and van Genuchten (1980) saturation-capillary pressure relationships discussed earlier in chapter 2, the model proposed by Lenhard and Parker (1990) and Farr et al. (1990) for estimating the spill on homogeneous soils was extended to the layered soil system. This model is similar in principle to the model used for the homogeneous soils, the only difference being the use of the saturation value which will be different for each soil type. The saturation profile will be discontinuous at the interface of two soils.

Figure 5.1 is a quantitative depiction of a static Brooks-Corey distribution of fluids for the layered soil S2UL. The area between the S_t and S_w curves represents the volume of the hydrocarbon in each layer of the soil . The volume (V_i) of hydrocarbon in a soil layer is expressed by the relation :

$$V_i = \phi\{\Sigma(1 - S_w)\Delta z + \Sigma(S_t - S_w)\Delta z\} \qquad (a)$$

The first term on the right side of the relationship gives the recoverable part of the hydrocarbon while the second term gives the residual part of the hydrocarbon. The terms S_w and S_t are the water saturation and total saturation functions respectively and are uniquely associated with the soil. Based on these functions, the hydrocarbon in a soil can
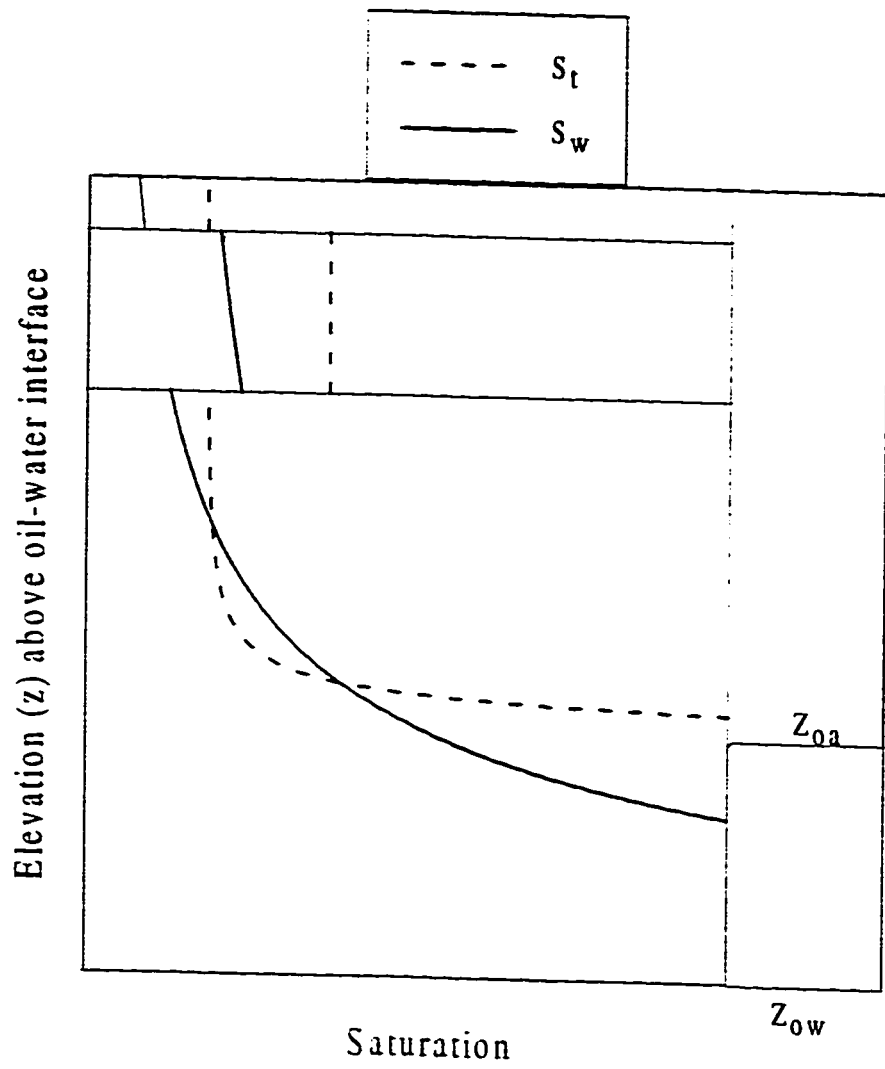
Figure 5.1 : Three phase Brooks-Corey distribution of fluids in a layered soil.

be estimated. The saturation functions can be expressed using the Brooks-Corey equation (1964) as follows :

$$S_w = (1- S_r) [P_c^{ow} / P_d^{ow}]^{-\lambda ow} + S_r$$

$$S_t = (1- S_r) [P_c^{ao} / P_d^{ao}]^{-\lambda ao} + S_r$$

For an alternate methodology proposed by van Genuchten (1980) these functions are expressed as follows :

$$S_w = (1-S_r) (1/ (1 + (\alpha_{ow} P_c^{ow})^n)^{1-1/n} + S_r$$

$$S_t = (1-S_r) (1/ (1 + (\alpha_{ao} P_c^{ao})^n)^{1-1/n} + S_r$$

Based on the values of S_w and S_t for each layer and the associated fluid distribution (Figure 5.1), the total hydrocarbon volume (V_t) in the layered soil can be calculated by numerical integration of equation (a), which is expressed by the following :

$$V_t = V_1 + V_2 + V_3$$

where,

V_1 the total hydrocarbon in layer 1,

V_2 the total hydrocarbon in layer 2, and

V_3 the total hydrocarbon in layer 3.

This methodology for the estimation of the hydrocarbon volume in the layered soil (and homogeneous soils) has been compiled in a FORTRAN code. the flow chart for which is provided in appendix 1. This code has the option to compute the estimates based on the Brooks-Corey (1964) or the van Genuchten (1980) equations.

Chapter 6

SUMMARY AND CONCLUSIONS

6.1 Summary

The objectives of this experimental program were to estimate the extent of groundwater contamination resulting from a hydrocarbon spill in an unconfined aquifer. Quantification was made possible by relating the measured hydrocarbon thickness in a monitoring well to the hydrocarbon volume spilled into a sand column using the various volume estimation models available. An important objective of the research program was to study the effect of soil gradation and layering on the estimates of the hydrocarbon volume. During stage I, the experimental program was conducted on a pair of homogeneous sand columns using a uniform and a well graded sand. Layering was incorporated into a pair of sand columns for use during stage II of the program. The uniform sand was locally available from Abqaiq, while the well graded sand was obtained by blending three different sands in proportions corresponding to the intended grain-size distribution of the soil. The results of these two stages are summarized as follows.

The analytical models based on the Brooks-Corey and van Genuchten equations arrived at nearly the same estimates of higher spill volumes. The Brooks-Corey model failed to quantify low values of the spill volume (about 35% to 45% of total spill volume). The analytical models underestimated the spill volume in homogeneous soils in a range of 18% to 40% and 45% to 83% at a k/k_s of 1% and 0.1% respectively. The empirical models

of Hall et al. (1984) and De Pastrovich et al. (1979) also underestimated the spill volume. Comparing the two models. the model of Hall et al. predicted the volume more closely, while the model of De Pastrovich et al. predicted a very low spill volume . The analytical models underestimated the spill volume in the layered soils. and the underestimates ranged from 13% to 32% and 43% to 78% at a k/k_s of 1% and 0.1% respectively.

The modified analytical models gave very close estimates of the spill volume at both the values of k/k_s used. The spill volumes for columns S1U. S1W and S2WL were underestimated with an error of 5% to 10%. while for column S2UL the spill volume was overestimated in a range of 9% to 35%.

Layering affected the free product thickness in a soil column. Comparing the results of columns S1U and S2UL. a higher free product thickness (4 cm to 5 cm) was observed for S2UL. For columns S1W and S2WL. a free product thickness consistently higher by about 5 cm to 7 cm was observed for S1W..

6.2 Conclusions

On the basis of the results of this study following specific conclusions can be drawn :
1) The analytical models based on the Brooks-Corey and van Genuchten equations underestimate the volume significantly in all the soils. The predictions of both models for higher spill volumes match closely. Low spill volumes can not be quantified by the Brooks-Corey model.

2) The empirical models underestimate the spill volume. The model of Hall et al. (1984) estimated a much higher volume than the model of De Pastrovich et al. (1979) .

3) The permeability ratio (k/k$_s$) had a major influence on the analytical estimates. The estimates at a k/k$_s$ of 1% were much higher than those corresponding to a k/k$_s$ of 0.1%. However, this ratio had very little effect on the analytical estimates generated from the modified models.

4) The analytical models estimated the spill volume closely on modification of the saturation function, S$_T$, and assumption of a hypothetical soil hydrocarbon depth.

5) Soil layering had a significant effect on the spill volume-free product relationship. This study shows that any attempt to use the free product levels to quantify the extent of contamination must account for layering. This effect could be even more pronounced in a field problem and can lead to significant errors in estimates if not considered.

) The spill volume-free product thickness relationship can be simplified into two parts- a part with a flatter slope for low values of the free product thickness, and another with steeper slope for high values of the free product thickness.

7) The critical volume and free product thickness in a soil are highly sensitive to the soil hydraulic properties such as grain size distribution and porosity.

Chapter 7

RECOMMENDATIONS

On the basis of the observations made during this study the following specific recommendations are made for future work:

1) the scope of this study may be extended to a larger class of soils to examine the reliability of the modified analytical models for estimating a spill volume.

2) Effects of layering on quantification of volume should be studied in greater detail.

3) Since water table levels in an aquifer are mostly dynamic, the effect of water table fluctuations on the hydrocarbon distribution should be incorporated.

4) Hydrocarbons of different range (densities) should be used to evaluate their effect on the spill volume-free product thickness relationship and the estimates of spill volume.

5) A field study should be undertaken so as to correlate the results of the laboratory study with those of an actual real life condition. Unlike the laboratory studies which were conducted under controlled conditions. a field study will ensure that the spill will closely model real life conditions and the migration of the contaminant will not be restricted. The estimates of the spill volume generated from a field study will help in calibration and possible validation of the modified model suggested for the laboratory study. The effects of soil overburden and soil heterogeneity on the spill volume-free product thickness relationship should also be studied in greater detail.

APPENDIX

```
                    ┌──────────────────┐
                    │      READ        │
                    │  ZOBASE,TOIL.NL  │
                    │   . MOD.CODE     │
                    └──────────────────┘
                              │
                    ┌──────────────────┐
                    │     50 II=       │
                    │     1,NL         │
                    └──────────────────┘
         Modcode = 1                    Modcode = 2
```

```
┌──────────────────┐              ┌──────────────────┐
│  READ relevant   │              │  READ relevant   │
│   Brooks-Corey   │              │  van Genuchten   │
│   parameters     │              │   Parameters     │
└──────────────────┘              └──────────────────┘
```

Yes ◇ TOIL.LT.HDOW   No   Yes

II = 1   No

Stop

```
        5,IR
        =1,JR
┌──────────────────────┐
│     CALCULATE        │
│     THEW(IR)         │
│  S(IR) = PHI-THEW(IR)│
└──────────────────────┘

     Continue 5

       9,IR =
       1,JR
┌──────────────────┐
│    CALCULATE     │
│      UR,EC       │
└──────────────────┘

     Continue 9

       10, I = 1,J
┌──────────────────┐
│    CALCULATE     │
│  thew(I),thet(i )│
└──────────────────┘

     Continue 10

     Continue 50

      Stop
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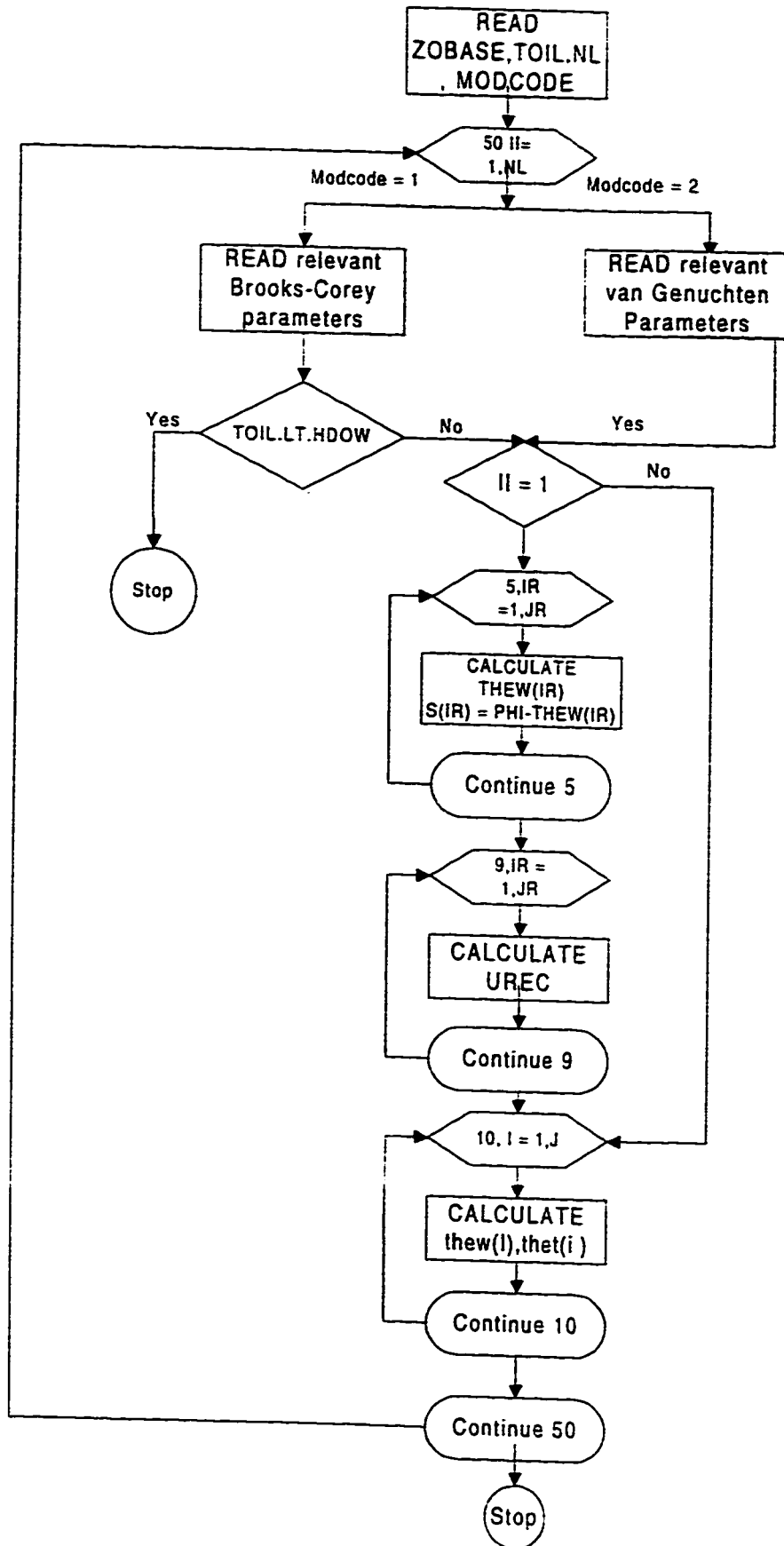
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