
Methods for Determining Inputs to Environmental Petroleum Hydrocarbon Mobility and Recovery Models

Regulatory and Scientific Affairs

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1.0 Introduction

This manual describes methods used to obtain input parameters for models that evaluate the mobility and potential recovery of petroleum liquids in unconsolidated granular porous media. These models are valuable tools for improving system design because, unfortunately, the presence of petroleum liquids in a well is not itself a reliable indicator of the feasibility of free-product recovery or the need to continue recovery operations.

The feasibility and appropriate endpoint for free-product recovery can be addressed by evaluating the mobility of product in the sediment in which it is encountered. If the mobility of product is high, there is a potential for future adverse product migration. In addition, it is likely that properly designed recovery systems can effectively deplete a significant fraction of the mobile product. Conversely, if the mobility of the product is low, the risk associated with future migration is low, and efforts to deplete mobile product will be ineffective.

The intent of this document is to provide a reference for parties needing methods for determining inputs to product mobility, and volume models. The need for such data (in particular at large sites such as refineries) has increased dramatically in recent years. In large part this has been driven by broader use of multiphase flow models (e.g., Parker *et al.*, 1994) and spreadsheet tools for analysis of product mobility (e.g., Charbeneau *et al.*, 1999). Secondly, it is recognized that for small sites the resources needed to conduct site specific mobility investigations may not be available. As such, it would be useful to generate a data base of study results (obtained using consistent methods) that can be used at these sites.

Standardization of methods is the ideal; unfortunately, it may not be possible in all cases. A number of factors frustrate rigid standardization. First, significant differences exist between sites. A direct consequence is that the best methods for many analyses are different for different sites. Secondly, only a few specialized laboratories conduct a number of the analyses (e.g., capillary pressure vs. saturation and relative permeability vs. saturation). The equipment and methods used by these laboratories are highly specialized and frequently different. As such, it may not be possible to have all sites conduct measurements using a single method. Reflecting these challenges, this document provides options as opposed to rigid standards.

The first section introduces nomenclature and parameters of concern. Individuals familiar with multiphase flow in porous media can skip this section. The second section addresses determination of fluid properties. The third section describes methods for analysis of porous media properties at a laboratory (column) scale. The fourth section addresses measurement of porous media properties at a field scale. Lastly, suggestions for reporting results are presented.

Throughout this document practices are described that involve the handling of potentially hazardous materials. This document does not address health, safety, and regulatory compliance issues. It is the responsibility of the user of this document to establish appropriate health and safety practices and to comply with relevant regulations.

2.0 Nomenclature and Parameters of Interest

A general conceptual model for petroleum hydrocarbon in granular porous media is presented in Figure 1. In this example, a surface release of product has percolated through the unsaturated zone. Below the capillary fringe an interval has formed in which product occurs as a continuous **non-wetting phase** in the porous media. The term non-wetting reflects product occupying the largest pore space and not directly contacting the porous media. The porous media is surrounded by a continuous water phase referred to as the **wetting phase**. Immediately above the capillary fringe, product forms a continuous **intermediate wetting phase** between the water (wetting phase) and the air (non-wetting phase). The critical feature to recognize is that two or three separate fluid phases (including product) coexist in the pore space where product is present.

Product that forms a continuous phase within the porous media is referred to as **potentially mobile product** or **mobile product**. The qualifier “potentially” is included because movement is contingent on the presence of a driving force. Product that is not present as a continuous phase is referred to as **residual** or **immobile product**. A significant feature of residual product is that it is typically immobile under the typical range of driving forces associated with natural or induced groundwater flow.

The volumetric flux of product q_o (L^3/L^2-T) at any point in the continuous product interval can be described as:

$$q_o = -\frac{kk_{ro}}{\mu_o} \left(\frac{dP_o}{dx} + \rho_o g \frac{dz}{dx} \right) \quad (1)$$

where:

k (L^2)	Intrinsic Permeability	a property of the porous media that describes its capacity to transmit a single fluid that fully saturates the porous media (saturation equal to 1).
k_{ro} (Dimensionless)	Relative Permeability to Product	a ratio of permeability to product at a pore saturation less than 1 to the permeability at a pore saturation of 1. This describes reduced permeability associated with product occupying only a fraction of the total pore space.
μ_o (M/LT)	Dynamic Viscosity	a measure of a fluid's resistance to shear.
P_o (F/L ²)	Pressure	force per unit area in the product phase in the product or oil.
x (L)	Distance	in the direction of flow.
ρ_o (M/L ³)	Density	mass per unit volume of oil.
g (L/T ²)	Gravitational Constant	acceleration imposed by gravity.
z (L)	Elevation	position above a given datum.

(Note: L = length, M = mass, T= time, F= force)

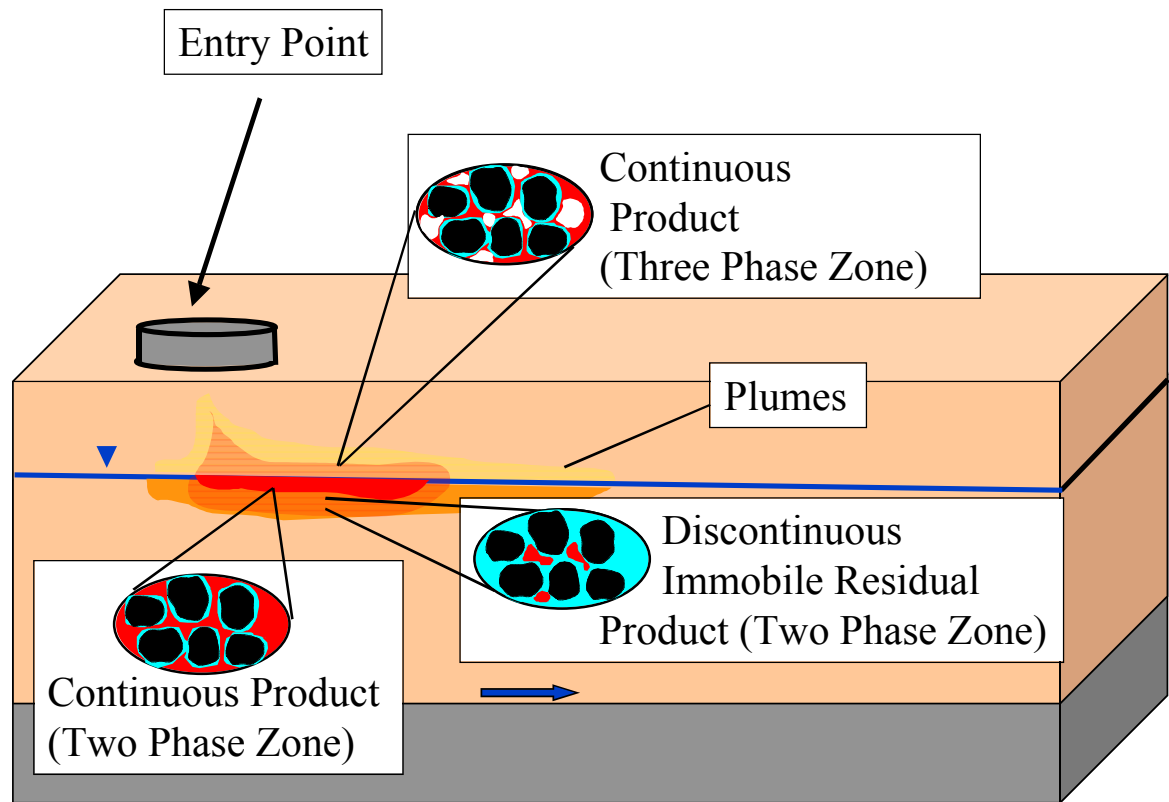


Figure 1 — General Conceptual Model

The **mobility** of the product is defined as:

$$M_o = \frac{k k_{ro}}{\mu_o} \quad (2)$$

Unfortunately, the fraction of pore space filled with product (S_o), and consequently the relative permeability to product (k_{ro}), changes with position. As such, mobility (M_o) is a function of position within the interval of continuous product. Variation in **product saturation** (S_o) reflects locally varying differences in pressure between the non-wetting and wetting phase pressures. This difference is defined as **capillary pressure** (F/L^2)

$$P_c = P_{nw} - P_w \quad (3)$$

Figure 2 illustrates pressure in the air, product, and water phases as a function of vertical position under the condition of no vertical flow. Recalling that pressure is linearly proportional to fluid density ($P = \rho gh$):

- Pressure in the air phase is essentially constant over the interval of concern due to the small density of air.
- With depth, pressure increases fastest in the water phase since water has the greatest density.
- As the product is less dense than water, pressure increases more slowly with depth in the product than in the water,

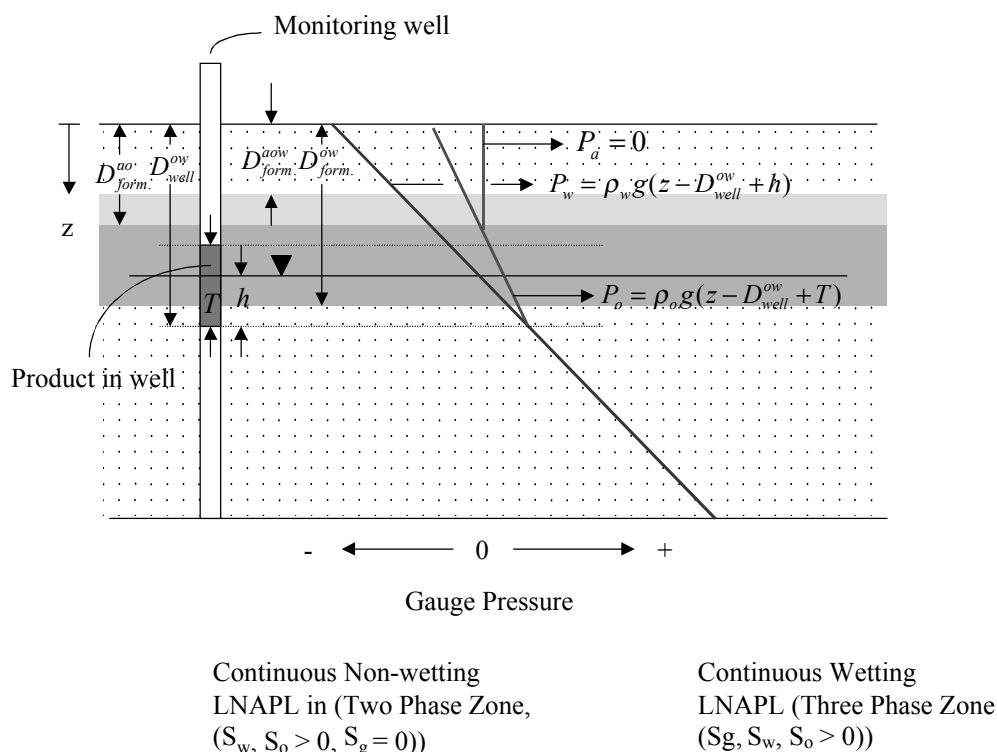


Figure 2 — Hydrostatic pressure in air, product, and aqueous phases (after Farr *et al.*, [1990], ao = air-oil, form. = formation, ow = oil-water, well = well, aow = air-oil-water, a = air, w = water, o = oil).

Building on the conditions defined in Figure 2, one can calculate both the volume and mobility of the continuous product present in the formation. Following Farr *et al.* (1990) and Lenhardt and Parker (1990), this process begins by using fluid levels in wells to characterize static pressures in the air, product, and aqueous phases (see Figure 2). Capillary pressures can be determined from the static pressures. Next, either the Brooks-Corey (1964) or van Genuchten (1980) models are used to estimate product saturation and relative permeability as a function of capillary pressure. These computations can be readily conducted using the spreadsheet model provided by Charbeneau *et al.* (1999).

As an introduction to the remaining parameters of interest, the following describes the Brooks-Corey and van Genuchten models. Both of these models are algebraic equations used to fit capillary pressure versus saturation data obtained from laboratory studies. For simplicity, the definition of physical parameters employed in describing both the models follows that used in Brooks and Corey (1964). Fitting parameters follow the definition presented in Brooks and Corey (1964) and van Genuchten (1980).

A typical capillary pressure-saturation relationship is presented in Figure 3. Procedures used to estimate fitting parameters from the capillary pressure data are described in Corey and Brooks (1999) and van Genuchten (1980). Alternatively, model parameters can be obtained by fitting the models to relative permeability versus saturation data obtained from laboratory studies. A typical relative permeability-saturation relationship is presented in Figure 4.

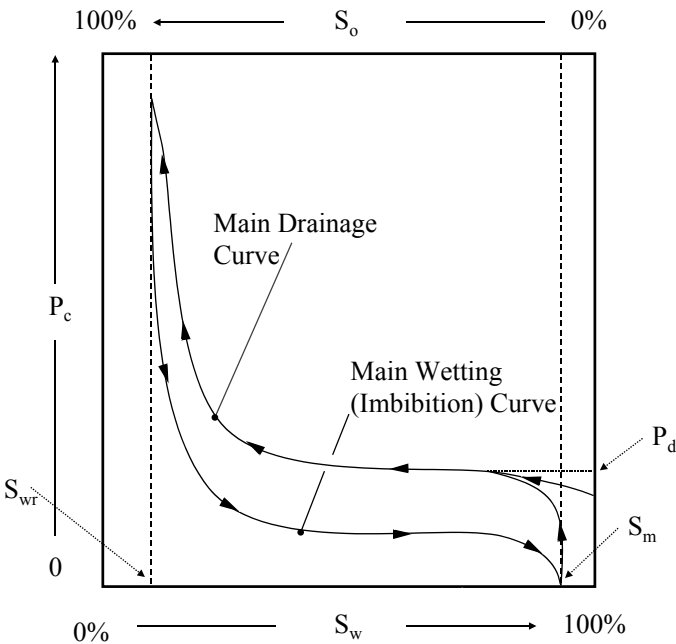


Figure 3 — Capillary pressure - saturation relationship for two-fluid system in porous media

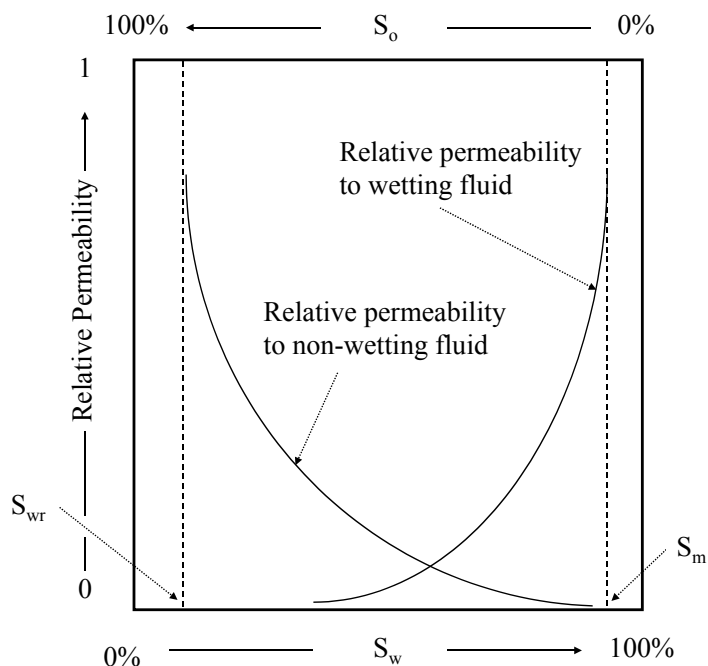


Figure 4 — Typical relationship between relative permeability and fluid saturation for a two-phase system under drainage.

The Brooks-Corey model is described in Equations (4) through (6).

$$S_e = \frac{S_w - S_{wr}}{1 - S_{wr}} = \left(\frac{P_d}{P_c} \right)^\lambda \quad \text{for } P_c \geq P_d \quad (4)$$

$$k_{ro} = \left[1 - \frac{S_w - S_{wr}}{1 - S_{wr}} \right]^2 \left[1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{\frac{\lambda+2}{\lambda}} \right] \quad (5)$$

$$k_{rw} = \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{\frac{2+3\lambda}{\lambda}} \quad (6)$$

where:

S_e (Dimensionless)	Effective Wetting Phase Saturation	wetting phase saturation as defined in (4)
S_w (Dimensionless)	Wetting Phase Saturation	fraction of the pore space filled with wetting phase.
S_{wr} (Dimensionless)	Irreducible Wetting Phase Saturation	model fitting parameter. Roughly equal to the minimum wetting phase saturation at large capillary pressure (maximum product saturation).
P_d (F/L ²)	Displacement Pressure	model fitting parameter. Roughly equal to the minimum capillary pressure at which the non-wetting phase is present as continuous phase in the porous media. Brooks and Corey (1964) also refer to this parameter as bubbling pressure.
λ (Dimensionless)	Lambda	model fitting parameter. Generally a function of grain size distribution.
k_{ro} (Dimensionless)	Relative Permeability to the non-wetting phase	a ratio of permeability to the non-wetting phase at pore saturation less than 1 to the permeability at a pore saturation of 1.
k_{rw} (Dimensionless)	Relative Permeability to the wetting phase	a ratio of permeability to wetting phase at a pore saturation less than 1 to the permeability at a pore saturation of 1.

Following Parker *et al.*, (1987) and Charbeneau *et al.*, (1999), the van Genuchten model is described in Equations (7) through (9). Note the van Genuchten model parameter (N) is not included in Equations (7) through (9). This reflects the substitution $N = 1/(1 - M)$ proposed by van Genuchten (1980) when using Mualem's model for relative permeability (Mualem, 1976).

$$S_e \int \frac{S_w - S_{wr}}{1 - S_{wr}} = \left(\frac{1}{1 + (\alpha P_c)^{\frac{1}{1-M}}} \right)^M \quad \text{for } P_c \geq 0 \quad (7)$$

$$k_{ro} = \left(\frac{S_o}{1 - S_{wr}} \right)^{\frac{1}{2}} \left\{ \left[1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{\frac{1}{M}} \right]^M - \left[1 - \left(\frac{S_w + S_o - S_{wr}}{1 - S_{wr}} \right)^{\frac{1}{M}} \right]^M \right\}^2 \quad (8)$$

$$k_{rw} = \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{\frac{1}{2}} \left\{ 1 - \left[1 - \left(\frac{S_w - S_{wr}}{1 - S_{wr}} \right)^{1/M} \right]^M \right\}^2 \quad (9)$$

where:

M (Dimensionless)
 α (L^2/F)

M
Alpha

van Genuchten fitting parameter.
van Genuchten fitting parameter.

Lastly, the parameters of concern are not always measured using site water and product. In some cases air or mercury are used in laboratory studies. To correct back to the fluids of concern, it is necessary to obtain estimates of air-product interfacial tension (σ_{ao}), air-water interfacial tension (σ_{aw}), and product-water surface tension (σ_{ow}). The units of interfacial and surface tension are force per unit area (F/L).

3.0 Fluid Properties

3.1 Sample Collection

Analysis of product properties begins with obtaining representative product samples. Typically this is accomplished by bailing free product from monitoring wells or collecting samples from active free-product recovery systems. Samples should be collected from a sufficient number of points to characterize the product present. Spatial variations in product properties commonly occur due to releases of different products and/or differential *in situ* weathering. A minimum volume of 250 mL of product (free of water) should be collected. Samples should be stored in brown glass containers with minimal head space and kept cool. No preservatives are required.

In all cases the *in situ* temperature of the product should be determined. This reflects the dependence of fluid properties on temperature. In the case of bailed product samples, temperature should be measured immediately after collection. In the case of active recovery systems, the temperature should be measured in fluids that are “fresh” from the well (as opposed to stagnant fluids from piping or tanks). A third option is to lower a thermometer in a secure housing down a well to the water table. In all cases the thermometer should have a minimum accuracy of 1-degree Celsius.

After sources of representative product samples have been identified, additional product and water samples should be collected for laboratory core studies. The volume of water and product needed to conduct core studies should be determined by asking the laboratory. Again, samples should be stored in brown glass containers with minimal head space and kept cool.

3.2 Density (ρ_o)

Table 1 presents methods for determining the density of petroleum liquids. The order reflects common to uncommon use. Results can be reported in terms of density (M/L³) or as °API gravity. Calculations typically require results to be expressed in terms of density. The conversion from API gravity to density is:

$$\rho_o = \frac{141.5}{^{\circ}\text{API} + 131.5} \rho_w \quad (10)$$

In general, the density of site water should also be measured. This reflects the fact that both dissolved organic and inorganic compounds can effect water density. The density of water is significant in that capillary pressure is a function of the difference in density between water and product. Ideally, measurements should be made using liquids at their *in situ* temperature. Sensitivity to temperature is illustrated by considering fuel oil which varies in density by 2 percent over the range of 0 to 25 degrees Celsius (Charbeneau *et al.*, 1999).

Table 1 — Product density methods (ρ_o)

Method	Description	Comments
ASTM D1298-99 or ASTM D-287	Standard Practice for Density, Relative Density (Specific Gravity), or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method	Suitable for field determination of density. Hydrometers can be purchased for a small cost. Accuracy (typically 0.0035 to 0.007 gm/cm ³) is dependent on the range of the hydrometer used. Method requires ~ 200 mL sample.
ASTM D1217-93(1998)	Standard Test Method for Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer	Best for distillates that boil between 90 and 110°C. Precision is ~0.00001 gm/cm ³ .
ASTM D1481-93(1997)	Standard Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Lipkin Bicapillary Pycnometer	Oils more viscous than 15 cSt at 20°C (mm /s), and of viscous oils and melted waxes at elevated temperatures.
ASTM D1480-93(1997)	Standard Test Method for Density and Relative Density (Specific Gravity) of Viscous Materials by Bingham Pycnometer	Less accurate than ASTM D1217-93. Precision is ~0.00005 gm/cm ³ .
ASTM D4052-96	Standard Test Method for Density and Relative Density of Liquids by Digital Density Meter	Suitable for materials that are liquids at 15-35°C. Liquids should be translucent. Precision is ~0.0001 gm/cm ³ .
ASTM D5002-99	Standard Test Method for Density and Relative Density of Crude Oils by Digital Density Analyzer	Appropriate for low vapor pressure crude oils.
ASTM D3505-96	Standard Test Method for Density or Relative Density of Pure Liquid Chemicals	Requires accurate knowledge of temperature expansion functions.

Further details regarding ASTM methods may found in Appendix A - Short Abstracts of Relevant ASTM Methods.

3.3 Viscosity (μ_o)

Table 2 presents methods used to determine the viscosity of petroleum liquids. The order reflects common to uncommon use. Measurements should be made at *in situ* temperatures. Illustrating sensitivity to temperature, the viscosity of kerosene varies by 54% over the range of 0 to 25 degrees Celsius (Charbeneau *et al.*, 1999). Whenever possible, measurements should be made using liquids collected from the site of concern. Prolonged exposure of petroleum liquids to soil and water can have contact significant effects on the viscosity of petroleum liquids.

Table 2 — Viscosity methods (μ_o)

Method	Description	Comments
ASTM D445-97	Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (the Calculation of Dynamic Viscosity).	Common wet chemistry technique.
Brookfield, Pfann, or Rotational Viscometer	Principle of rotational viscosity measurement employs a spindle immersed in the fluid sample to sense torque resistance when running at constant speed.	Common instrument technique.
ASTM D4486-91 (1996)e1	Standard Test Method for Kinematic Viscosity of Volatile and Reactive Liquids.	Best for volatile and reactive liquids.

3.4 Surface Tension and Interfacial Tension (σ_{ao} , σ_{ow} , and σ_{aw})

Table 3 presents methods used to measure surface and interfacial tension. Key parameters of concern are air-oil interfacial tension, air-water surface tension, and oil-water surface tension. The order reflects common to uncommon use. Measurements should be made at temperatures close to *in situ* conditions. As with viscosity and density, measurements should be made using liquids from the site of concern. Prolonged interactions between water, petroleum liquids and soil can have significant effects on fluid properties.

Table 3 — Surface tension and interfacial tension methods (σ_{ao} , σ_{ow} , and σ_{aw})

Method	Description	Comments
ASTM D971-99a (e.g., DuNouy Tensiometer)	Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method	(Gas-Liquid & Liquid-Liquid) ± 0.1 mN/m.
Spinning Drop Tensiometer	Relies on centripetal forces which replace gravity in other types of tensiometers	(Gas-Liquid & Liquid-Liquid) 0.005 mN/m ~ 500 mN/m, measuring range good for crude oil, surfactant solutions.
ASTM D3825-90(1995)	Standard Test Method for Dynamic Surface Tension by the Fast-Bubble Technique	(Gas-Liquid) Suitable for liquids with viscosity less than 4 centipoise, not suitable for opaque DNAPL.
ASTM D1331-89(1995)	Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface-Active Agents	(Liquid-Liquid) Suitable to surface-active agents. Also applicable to nonaqueous solutions and mixed solvent solutions.
ASTM D2285-99 (Pendant Drop)	Standard Test Method for Interfacial Tension of Electrical Insulating Oils of Petroleum Origin Against Water by the Drop-Weight Method	Applicable to viscous solutions.

4.0 Porous Media Properties – Laboratory-Scale

The following outlines procedures for determining physical properties of porous media that relate to product mobility. In general, the methods described reflect decades of research in the fields of petroleum, soil science, and groundwater hydrology.

4.1 Sample Collection

Sediments - Analysis of soil properties at a laboratory scale begins with obtaining representative soil samples. Ideally, soil samples should be undisturbed. This reflects the fact that parameters of interest are dependent on the geometry of pore bodies and throats. Preservation of these features or reproducing these features represents a significant challenge.

At one extreme, soil samples can be recovered using hollow stem auger and split spoon sampling equipment [see ASTM D1586-99 or ASTM D1452-80(1995)e1]. After extraction of product, samples can be dried and sieved to remove larger materials (e.g., gravel) that would block flow in a standard core holder (diameters of a few centimeters). Lastly, samples can be placed in coreholders with confining pressure similar to the *in situ* overburden pressure. The assumption associated with this approach is that the procedure will result in pore bodies and throats representative of the *in situ* conditions. In general, this approach should be avoided when possible due to potential biases associated with disturbing the architecture of the sediments.

Alternatively, soil samples can be collected in liners. This can be accomplished using hollow stem auger drilling systems equipped with continuous sampling systems or using direct push drilling systems (see ASTM D6282-98) or thin-walled sampling tubes (see ASTM D1587-94). The liners serve as core preservation systems. Immediately after recovery the core should be frozen on site. This has been accomplished using liquid nitrogen or dry ice. Assuming the pore space is fully saturated with water (worst case), this will effect an approximate 5 percent expansion of the pore space. This may fracture the plastic sleeve. Even if this occurs, it is hoped that the general geometry of the particles will be preserved. Note: further complication is added by the fact that petroleum liquids shrink at reduced temperatures. The primary assumption with this approach is that compaction during sample collection and freeze-thaw do not impose significant biases.

Beyond the above, options are limited. Within the crude oil production industry, a number of special coring systems have been developed, including pressure retaining cores, sponge-lined coring systems, full-closure coring systems, rubber sleeve core barrels, and side wall coring systems [see API (1998)]. Unfortunately, these systems are generally not available for collection of shallow unconsolidated soils. Notable exceptions are described by:

- Durnford *et al.*, (1991) – A prototype sampler is described that cools soil at the bottom end of a sampler to near freezing. Cooling is achieved by allowing compressed carbon dioxide to expand to atmospheric pressure *in situ* at the bottom end of the sampler. The principle benefit is retention of liquids in the soil core. Samples are frozen upon retrieval to the surface.
- McElwee *et al.*, (1991) – A prototype sampler that closes *in situ* is described. Nitrogen gas is used to inflate a bladder located in the drive shoe of the sampler. The primary advantage noted is improved recovery of sands and gravels.

- Murdoch *et al.*, (2000). – A sampling tool is described that collects horizontal sidewall soil core up to 15 centimeters in length and 4 cm in diameter. A hydraulic pushing mechanism advances and retracts a sidewall sample tube. Promising aspects include direct collection of horizontal soil cores (potentially less disturbed) and collection of short samples which are less prone to drainage of interstitial liquids. A difficulty is that direct observation of the sample may not be possible prior to testing due to the sample tube.

The user should determine the commercial availability of the above three techniques.

Residual Liquids – Often it is desirable to obtain measurements of product and water saturation from cores. In such instances it is necessary to address the issue of whether the residual fluids present in samples after collection are representative of liquid saturations present *in situ*. Using conventional split spoon or direct push techniques, significant biases can be introduced, including:

- Driving sampling equipment through sediments may compress the samples and displace fluids.
- Fluids that accumulate in sampling devices above the sample (e.g., water in portions of the sampler above the sample) will drain through the sample as it is brought to the surface. As this occurs, water and product saturations within the sample may be altered significantly.
- As the sample is brought to the surface, air can invade the pore space. If this occurs, product and/or water will drain out.

The severity of the above problems will increase with the hydraulic conductivity of the sediments and the length of the sample collected.

Methods outlined by Durnford *et al.*, (1991) or Murdoch *et al.*, (2000) hold promise to overcome the noted biases. Unfortunately, their availability and effectiveness is not well documented. Alternatively, using conventional equipment, samples should not be collected from below the water table as this limits fluid flushing through the sample. In addition, core lengths should be less than the height of capillary rise in the soil of interest. This will limit drainage of liquids from the samples as they are collected. McWhorter (1996) describes an empirical approach to estimating air-water displacement pressure. Using this method and the assumption that only water liquid is present in the pore space, estimates of capillary rise (maximum sample height) as a function of sediment hydraulic conductivity can be obtained (See Figure 5).