

**An Investigation on the Influence of Wettability on the Recovery of
Entrapped LNAPLs via Surfactant Flushing**

by

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**A thesis submitted to the Faculty of Graduate Studies and Postdoctoral
Affairs in partial fulfillment of the requirements**

for the degree of

Master of Applied Science

in

Environmental Engineering

Carleton University

Ottawa-Carleton Institute of Civil and Environmental Engineering

Ottawa, Ontario

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ISBN: 978-0-494-87803-3

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ISBN: 978-0-494-87803-3

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ABSTRACT

Light non – aqueous phase liquids (LNAPLs) released into the subsurface constitute long term sources of contamination. Pump and treat systems do not effectively remove residual and entrapped LNAPLs. Wettability has been found to be essential in contaminant transport and soil remediation where non-ideal or mixed wettability conditions may exist. This study investigated the influence of wettability on the recovery of entrapped LNAPLs via surfactant flushing. Wettability, capillary pressure-saturation, and column tests were performed using a lab-grade fluid (heptane) and a field LNAPL. Wettability and column tests conducted on the field LNAPL showed evidence of non-ideal conditions. Overall results indicated that fluid entrapment was independent of fluid type, wettability and contact time. Entrapped LNAPL removal by mobilization occurred as a result of interfacial tension reduction at a surfactant concentration of 0.5 g/L. Entrapped NAPL removal from fractionally-wet columns was higher in comparison to water-wet columns and increased with contact time.

Keywords: Wettability, LNAPLs, fluid entrapment, surfactant flush, column tests.

ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my friends, colleagues, and family who have helped me during my master's thesis journey. I sincerely thank my supervisor, Dr. Paul Van Geel, for sharing his knowledge, time, and effort and supporting my graduate studies. I also thank my colleagues and the staff at Carleton University, especially, Michelle Roberge, Mostafa Said, Dr. Marie Tudoret Chow, Stanley Conley, Pierre Trudel, and Jason Arnott for their continuous advice and technical assistance.

I would also like to thank Dr. Dennis O'Carroll and Stephanie Drake for their help and for allowing me to perform tests at the University of Western Ontario.

I express my gratitude to the Organization of American States Scholarship Program for their financial aid and support. I also deeply appreciate the help provided by the Colombian Petroleum Institute which allowed me to link my research to real-world problems in my home country. This was possible thanks to the great efforts of Engineers Mauricio Cardeñosa Mendoza and Adriana Serrano Santiago.

Finally, I would like to thank those who have borne with me and provided their warmest affection: my sister Beatriz Amparo, my husband, and my parents. Thank-you Kristian, for encouraging me to be a better human being and excel. This thesis would not have been possible without the support and encouragement of my parents, Oscar and Luz Amparo, my education and professional development has always been a priority in their lives and so I dedicate this thesis to them.

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LIST OF NOMENCLATURE AND ABBREVIATIONS

NAPL:	non-aqueous phase liquid
LNAPL:	light non-aqueous phase liquid
P_c	capillary pressure
P_c -S	capillary pressure-saturation
IFT:	interfacial tension
CMC:	critical micelle concentration
C.I.:	confidence interval
SDBS:	sodium dodecylbenzenesulfonate
S_w^{eff} :	effective water saturation
α, n, m, η :	fitting parameters
S_{wr}	residual water saturation
S_{wf}	final water saturation after imbibition
S_{nr}	residual and/or entrapped NAPL saturation
$\overline{S_{nr}^{wf}}$	mean entrapped saturation after the water-flood
$\overline{S_{nr}^{sf}}$	mean entrapped saturation after the surfactant-flood
$R - S_{nr}$	enhanced removed entrapped saturation
R_{LNAPL}	% removed LNAPL

1. INTRODUCTION

1.1 Problem definition

Non-aqueous phase liquids (NAPLs) constitute a major source of soil and groundwater contamination. Light NAPLs (LNAPLs) derived from petroleum are common sources of contamination at industrial sites, distribution pipelines, gas stations, among others. In the US alone, almost 495,000 releases of petroleum from federally regulated underground storage tanks have been reported to the Environmental Protection Agency (EPA) as of September 2010. EPA estimates that 93,000 site cleanups remain (EPA publication 542-F-11-008 2011). In China, one of the world's fastest growing economies, it is estimated that 1,600 environmental accidents related to petroleum spills occur each year, an average of 4 per day (Dong and Fu as cited by Liu et al. 2010).

In Canada and the US, sites where development has been restricted due to subsurface contamination are called "Brownfield sites". EPA is extensively investing in remediation of Brownfield sites. According to EPA reports, on average, \$17.39 is leveraged for each EPA Brownfields dollar spent at a Brownfield site from Assessment, Cleanup, and Revolving Loan Fund cooperative agreements; 72,250 jobs have been leveraged as of September 2011; and nearby property values have increased between 2 to 3% after site redevelopments since the beginning of the EPA Brownfield's program (EPA Brownfields Benefits postcard 2011). Canada has also been actively implementing strategies to redevelop these Brownfield sites. It is estimated that the province of Ontario alone has 40% of all contaminated properties in Canada (ECO Canada, "Who will do the Cleanup?" 2007) and every dollar spent in

Canada on Brownfields redevelopment generates \$3.8 worth of spending on related activities (Ministry of Municipal Affairs and Housing 2004). Taking into account that many sites require remediation and that nations still rely on fuel-oils to drive their economies, substantial efforts on soil and groundwater remediation are and will be required in future years. One important strategy to improve remediation efforts is to conduct fundamental and applied research to better understand the mechanisms that affect the removal of NAPL contaminants from soil and groundwater.

To date, research performed on soil wettability has revealed how variations in wettability may impact NAPL source zone distribution and remediation. There is sufficient evidence that suggests that the porous medium can change from water-wet (ideal condition) to NAPL-wet due to the accidental introduction of NAPLs in subsurface systems. These alterations in wettability have been observed at the pore scale (Aggelopoulos and Tsakiroglou 2008; Al-Raoush 2009; Masalmeh 2002) and at the representative elementary volume (REV) scale through changes in capillary pressure-saturation relationships as well as in relative permeability relationships (Aggelopoulos and Tsakiroglou 2008; Bradford and Leij 1995; Bradford et al. 1997; Dwarakanath et al. 2002; O'Carroll et al. 2004; O'Carroll et al. 2005; Molnar et al. 2011). However, multiphase flow models often operate under the assumption that the porous medium is water-wet and capillary pressure and relative permeability data are normally fed into the models without taking into account the presence of NAPL-wet media. On the other hand, some researchers have attempted to develop and validate models that incorporate changes in wettability (Bradford et al. 1997; O'Carroll et al. 2004; O'Carroll et al. 2005; Bradford and Leij 1995). Wettability alterations may account for larger NAPL accumulations than those predicted by traditional models.

This phenomenon was observed on capillary pressure-saturation tests and column test experiments performed on field soil and NAPL-wet media (Said 2010; Hugaboom and Powers 2002). Hence, wettability, which is directly related to capillary phenomena governing the transport of NAPLs in porous media, plays an essential role in soil remediation.

A few studies have been performed on soil wettability alterations by using lab-grade NAPLs and clean silica sand. Yet, it is necessary to conduct research on wettability incorporating field NAPLs and field soils to gain more insight on real situations occurring at field sites, improving remediation efforts. This is particularly important because “non-ideal wettability” conditions may exist. Moreover, very few studies have evaluated the influence of wettability on the recovery of NAPLs with the use of conventional remediation technologies, e.g. surfactant flushing. This research provides new insight on soil remediation by investigating the behaviour of non-ideal or fractional wettability during a surfactant flush. To the author’s knowledge, this constitutes one the first attempts to understand the implications of wettability while surfactants are used to remove field LNAPLs in fractionally-wet soils. Thus, any NAPL remedial technology should be evaluated under “non-ideal wettability” conditions because changing wettability conditions may exist at contaminated sites.

1.2 Objectives

The general objective of this research was to investigate the influence of soil wettability on the recovery of entrapped LNAPLs after applying a surfactant flush to remobilize LNAPLs. Accordingly, the specific objectives were:

- To characterize “non-ideal wettability” by conducting visual observation tests, interfacial tension measurements, contact angle measurements and capillary pressure-saturation tests on porous media.
- To investigate the behavior of “non-ideally wet” or fractionally-wet media when surfactants solutions are used to re-mobilize entrapped LNAPLs by performing column test experiments.

1.3 Scope of research

The present research was planned in order to study the influence of wettability on the recovery of residual and entrapped LNAPLs incorporating real field samples. Field LNAPL and field soil samples were collected and sent to Carleton University from a Refinery in Colombia (South America) in collaboration with the Colombian Petroleum Institute (ICP – ECOPETROL S.A.). The contaminated site has been exposed to several spills of various refined products mainly: gasoline, kerosene, jet-fuel, and diesel. The field LNAPL was collected from remediation wells where free-phase LNAPL is being recovered using selective oil phase recovery pumps. Contaminated field soil was also collected at the same location during the construction of a remediation trench. The site’s geology is characterized by the presence of three layers of soil: a clay or sandy clay loam (layer 1), followed by a silty sand (layer 2), followed by a loamy or silty sand (layer 3). It is assumed that LNAPLs are travelling preferentially on the third (higher permeability) layer which lies approximately 5 to 6 meters below ground. During the soil sampling, the samples were collected around 4 meters below ground. Unfortunately, these samples were unsuitable for this research because their combined clay and silt content was greater

than 65%, failing to represent the probable route for contaminant transport. Consequently, clean silica sand was purchased and incorporated into the experimental plan.

In order to address the issue of “non-ideal wettability” and represent probable conditions at the field site, the purchased clean silica sand was treated to become NAPL-wet and further mixed with clean sand (non-treated) to create a mixed medium of fractional wettability. From this point forward, fractional wettability will be used to refer to the mixed medium representing non-ideal wettability. Also, heptane was used as the reference lab-grade or “ideal LNAPL” to allow comparison with the field LNAPL. Two-phase (water-LNAPL) capillary pressure-saturation tests and surfactant flush tests in 1-D columns were performed on the following combination of experiments:

- Clean sand and heptane, ideal scenario (water-wet sand and lab-grade LNAPL).
- Clean sand and field LNAPL, non-ideal field LNAPL (water-wet sand and field LNAPL from field site).
- 50% NAPL-wet + 50% water-wet sand and heptane, introducing non-ideal soil wettability (fractionally-wet soil and lab-grade LNAPL).
- 50% NAPL-wet + 50% water-wet sand and field LNAPL, “non-ideal wettability” scenario (fractionally-wet soil and field LNAPL from field site).

Surfactants have been widely used to enhance NAPL recovery because they potentially reduce the volume of water that must be introduced to the soil pore space (pore volumes or PV) to mobilize or solubilize the contaminant. There is a growing concern about the implications of soil surfactant flushing. Among these are: toxicity

levels, adsorption on mineral surfaces, reduction in soil permeability due to formation of gels and solids, foam production at site's clean-up, etc. However, applying low concentrations of surfactants in aqueous solutions minimizes the previous concerns and may still provide effective NAPL removal (Chevalier 2003; Flaming et al. 2002). The Colombian Petroleum Institute has developed a surfactant product which they apply at their contaminated sites at low concentrations to remobilize LNAPLs while minimizing foam production. Hence, in order to further provide insight on real field scenarios two surfactants were tested in this study: a commercial anionic surfactant that has been tested in several laboratory experiments (sodium dodecyl benzene sulfonate – SDBS) and the anionic surfactant used at field sites in Colombia (field site surfactant).

2. LITERATURE REVIEW

2.1 Soil and Groundwater Contamination with Non-Aqueous Phase Liquids (NAPLs)

Non-aqueous phase liquids (NAPLs) are hydrocarbon based products of diverse chemical compositions that do not readily dissolve in water. NAPL migration in the subsurface is governed by gravity, buoyancy and capillary forces (Bedient et. al, 1994). NAPLs with densities lower than water float and move on top of the water table; they are often referred as light NAPLs (LNAPLs). Conversely, dense NAPLs (DNAPLs) move downward through the saturated zone because they have densities greater than water. They can travel deeper compared to LNAPLs.

Generally, NAPLs enter the soil and groundwater systems as a result of accidental spills, leaks, and other natural or anthropogenic processes that may result in uncontrolled contaminant discharges. The petroleum industry often deals with LNAPL soil and groundwater contamination from spills of various refined products such as gasoline, diesel, kerosene, jet-fuel and others. This situation poses a significant environmental risk in the unsaturated and saturated zones because these LNAPLs are potential long term sources of contamination compromising public health and safety (Busby et al. 1995; Van Geel and Sykes 1994).

2.2 Multiphase Fluid Systems

When NAPLs are released at the ground surface, the free-phase or mobile NAPL enters the pores of the soil by the hydrostatic pressure of the body of the NAPL. LNAPLs will migrate through the unsaturated zone and distribute near the water

table. They will form “pools” on top of the water table and can migrate laterally in the direction of the groundwater gradient. Different organic chemicals present in NAPLs also migrate in the subsurface as vapors in soil gas, dissolved constituents in soil pore water or as free phase liquids immiscible in water (Brost and Devaull, 2000). An important concept in multiphase systems is saturation. Saturation (S_i) describes the relative abundance of fluid (i) in a porous medium as the volume of the corresponding fluid (V_{fi}) per unit void volume (V_v) (Domenico and Schwartz, 1998):

$$S_i = V_{fi} / V_v \quad (2.1)$$

When the source of contamination is exhausted and LNAPL migration has ceased, LNAPLs in the unsaturated zone may exist as thin films of fluid coating the soil surfaces. This LNAPL portions present as connected or disconnected films are commonly known as the residual phase. Correspondingly, the saturation at which this phenomenon occurs is known as the residual saturation (S_r), and normally ranges from 5% to 20% (Bedient et. al, 1994). LNAPL portions can also be trapped in the saturated zone as a result of water-table fluctuations and saturated flow phenomena along the pore network. The portion of LNAPL trapped in the saturated zone will be referred herein as “entrapped” in contraposition to the residual portions in the unsaturated zone.

2.3 Wettability of Porous Media

The wettability of a fluid in a porous media is defined as the ability of fluid (i) to spread over the surface of the mineral grains in the presence of another immiscible fluid (Francisca et al. 2003). Wettability depends on the interfacial tension, the fluid

viscosity and the soil medium's properties, among others. Interfacial tension (IFT) can be defined as the force per unit length resulting from the attraction between the molecules of two substances, e.g. a liquid in contact with other fluid such as liquid or gas. The interaction between the forces due to surface tension and the forces due to pressure difference cause the interfaces to shrink forming a contact angle (θ) with the solid surface. Interfacial tension (γ) is often determined by measuring the height at which a liquid rises in a capillary tube (Domenico and Schwartz, 1998):

$$\gamma = \frac{\rho h r g}{2 \cos \theta} \quad (2.2)$$

where h is the height of capillary rise, r is the radius of the capillary tube, ρ is the density of the liquid and g , gravity. Equation 2.2 can be derived from the mechanical equilibrium of the forces described above considering the meniscus in the capillary tube as a hemisphere. From equation 2.2, capillary pressure (P_c) is equal to:

$$P_c = \frac{2\gamma \cos \theta}{r} \quad (2.3)$$

Also, the capillary pressure between two immiscible fluids can be calculated as the difference between the pressures of the non-wetting fluid (P_{nw}) and the wetting fluid (P_w):

$$P_c = P_{nw} - P_w \quad (2.4)$$

In multiphase phase systems, water is generally considered the wetting fluid, while NAPLs and air are considered the non-wetting fluid, air being the least wetting fluid. Mineral grains are considered to be water-wet or oil-wet depending on their wetting preferences (Morrow 1990). Wettability strongly influences capillary processes

during multiphase flow (Powers and Tamblin 1995; Donaldson et al. 1969) and it is often assumed that the porous medium is water-wet. Nonetheless, porous medium that has been exposed to NAPLs may undergo wettability changes from water-wet to NAPL-wet or a combination of both, the latter one commonly referred to as intermediate or fractionally-wet (Powers and Tamblin 1995; Abriola and Bradford 1998; Said 2010). Frequently, the term NAPL-wet and oil-wet are used interchangeably. However, oil-wet is more commonly used to describe naturally occurring wettability conditions rather than wettability alterations caused by NAPL contamination.

2.3.1 Water-wet porous medium

Figure 2.1 illustrates a proposed conceptual model of a multiphase fluid system (water-NAPL-air). This model is most certainly adequate for pure soils such as quartz and has been validated by several authors as indicated by Abriola and Bradford (1998). Water is considered the wetting phase, occupying the volume adjacent to large pores and the entire volume of smaller pores. In the saturated zone (figure 2.1a), NAPL tends to form continuous blobs in the center of large pores. In the unsaturated zone (figure 2.1b) water will wet the surface of the mineral grains and will tend to occupy almost the entire space of smaller pores, the residual NAPL will form continuous films along the water-air interface and the center of bigger pores will be occupied only by air (Abriola and Bradford 1998).

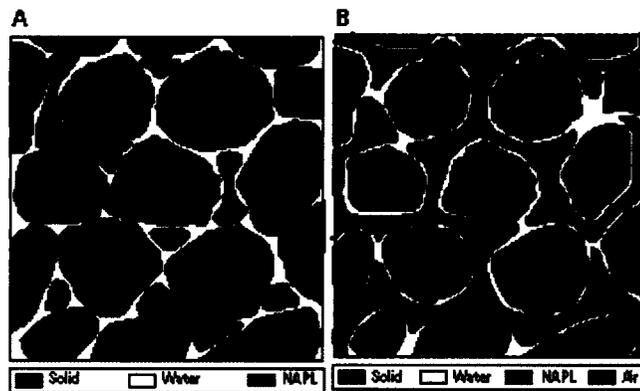


Figure 2.1: Distribution of residual NAPL in the saturated (a) and unsaturated (b) zones when the porous medium is water-wet according to the conceptual model presented by Abriola and Bradford(1998). Reproduced with permission from *Environmental Health Perspectives*.¹

2.3.2 Fractionally-wet porous medium

As mentioned in previous sections, porous medium containing mineral grains of differing wettability is said to be fractionally-wet. This condition can exist in the subsurface due to the interaction of released NAPLs with the mineral grains and/or natural variations in the compositions of the porous matrix; contact with NAPL mixtures which contain different surfactant products can also turn a porous medium from intermediate to NAPL-wet (O'Carroll et al. 2005). Fractional wettability may occur due to spatial and temporal changes in aqueous chemistry, distribution of organic matter, mineralogy, surface roughness, and contaminant degradation (Abriola and Bradford 1998). Figure 2.2 illustrates the conceptual model of residual NAPL distribution in a fractionally-wet porous system with two liquid phases as proposed by Abriola and Bradford (1998). Entrapped NAPL can be found as ganglia (water -wet condition) and as organic films coating the mineral grains (NAPL-wet condition). Gvirtzman and Roberts (1991) state that this behavior will alter NAPL saturation as the organic-water interfacial area will be higher when the NAPL is distributed as a

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film rather than when it is entrapped as ganglia; this subsequently contributes to higher NAPL entrapped saturations. In fact, after conducting a series of capillary pressure-saturation tests, Said (2010) observed higher NAPL entrapment on field soils that had been exposed to diesel spills.

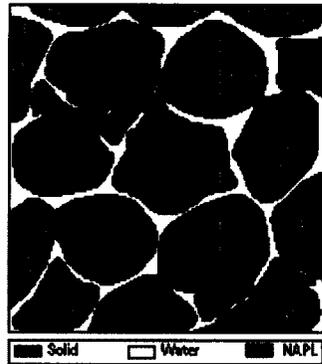


Figure 2.2: Distribution of residual NAPL in the saturated zone when the porous medium has fractional wettability according to the conceptual model presented by Abriola and Bradford(1998). Reproduced with permission from *Environmental Health Perspectives*.²

2.4 Characterizing Wettability

Capillary phenomena govern the transport of NAPLs in a porous medium. One of the properties that strongly influences capillary processes is wettability. Hence, adequate characterization of wettability is vital in order to properly model and predict the impacts and remediation of NAPLs in the subsurface (Powers et al. 1996). Wettability assessment can be performed by using qualitative and quantitative methods. Qualitative methods often give a rapid initial estimation of wettability. These methods include visual observation tests, bottle tests, capillary pressure-saturation and relative permeability curves, and imbibition rate tests(Anderson 1986). Quantitative methods comprise contact angle measurements and capillary pressure-saturation tests accompanied by the calculation of wettability indices. In the next section, qualitative

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methods will be briefly described and further details will be provided in the following sections for the quantitative methods mentioned previously.

2.4.1 Qualitative Methods

Visual Observation tests

This test involves observing the interaction of a specific fluid phase with the porous medium by the naked eye. Frequently, a small soil sample is placed in a container and a drop of fluid is placed on top of the sample. If water is immediately drawn into the pores, it can be concluded the medium is water-wet. On the contrary, if water sits on top of the porous medium and it is eventually drawn into the sample, the soil may be water-wet or intermediate-wet. Accordingly, if a NAPL drop is rapidly drawn into the sample, then the soil is considered to be NAPL-wet. This test help the analyst determine the wetting characteristic of the soil. However, they just provide an initial estimation and further testing is required.

Bottle tests

Powers et al.(1996) developed a bottle test method to obtain a qualitative indication of wettability based on the method proposed by Dubey and Doe (1993) to determine the wetting properties of crude oils. Soil samples are equilibrated with water and drained to achieve specific aqueous phase saturation. Then, they are equilibrated with the organic phase and excess water is added to promote phase separation (Powers et al. 1996). Subsequently, the bottles are closely observed to determine if the NAPL was effectively separated by gravity or associated with the mineral grains; changes in

color and the presence of NAPL blobs is also observed. This test is suitable to visually observe the relative wettability of a soil medium with unknown wetting behavior.

Relative permeability and capillary pressure curves

Relative permeability accounts for the tendency of fluids to interfere with one another as they flow in a porous medium (Demond and Roberts 1987). As the soil experiences drainage, the hydraulic conductivity (K) of the porous medium decreases progressively from its saturated value (K_{sat}) and becomes a function of the fluid's (i) saturation (S_i). Likewise, during imbibition, hydraulic conductivity progressively increases. Relative permeability (k_r) incorporates this variability as a function of saturation. From Darcy's Law, for one-dimensional flow, the Darcy flow (q_i) is equal to:

$$q_i = -K(S_i) \frac{\partial h}{\partial z} = -k_{ri} K_{sat} \frac{\partial h}{\partial z} \quad (2.5)$$

Methods to measure the relative permeability of a particular fluid (k_{ri}) have been generally developed to determine the wettability of cores in the petroleum industry. Anderson (1986) provides a description of some of the methods that have been developed; hence, he states that these methods can only be used to differentiate between strongly water-wet and strongly oil-wet cores. In a system where water strongly wets the mineral grains, typical k_{ri} curves are obtained, as the one shown in figure 2.3a. Figure 2.3 shows two relative permeability curves in strongly water-wet (2.3a) and oil-wet cores (2.3b), as presented originally by Craig (1971).

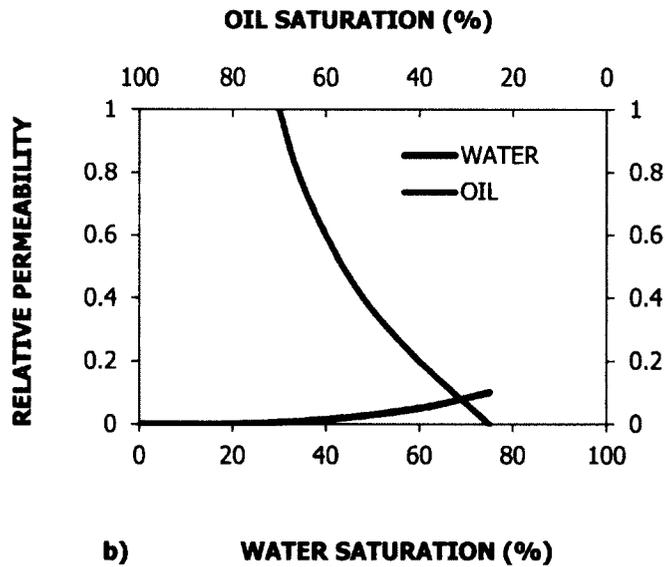
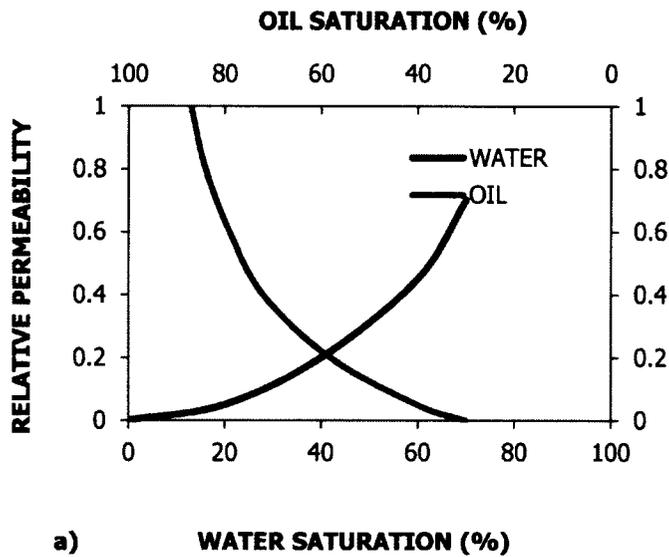


Figure 2.3: Custom water/oil relative permeability curves; a) strongly water-wet media, b) strongly oil-wet media. (Adapted from Craig, 1971).

According to Domenico and Schwartz (1998), there are some key features about relative permeability curves to take into account: the relative permeability of the fluids rarely sum to one; k_r of both the wetting (k_{rw}) and the non-wetting fluid (k_{rn}) approach zero at their respective residual saturations, the fluids become disconnected

across the system of pores and the fluid is no longer mobile; for equivalent saturations, $k_{rn} > k_{rw}$, because the wetting fluid occupies smaller pores that contribute the least to flow; relative permeability curves are also hysteretic relating to the fact that the non-wetting fluid flows along different pathways during drainage and imbibition processes. Capillary pressure curves are also obtained from soil samples to qualitatively describe wettability, further details of their main features will be discussed in Section 2.4.3.

Imbibition rate tests

Imbibition tests are performed to measure the rate at which fluid (i) spontaneously imbibe the soil sample. These tests provide a qualitative interpretation of the soil's wettability because spontaneous imbibition is proportional to the imbibition capillary pressure (Morrow 1990). Depending on the wetting characteristic of the soil, certain fluids will imbibe at a faster rate than others, e.g., if water imbibe faster than a NAPL, the soil is said to be water-wet. Although the imbibition rate test is a fast indicator of the soil's relative wettability, comparisons for diverse samples must be performed carefully since differences in fluid viscosity and interfacial tension play an important role when samples contain different organic phases (Powers and Tamplin 1995). Figure 2.4 shows the typical imbibition rate behavior for different wettability characteristics.

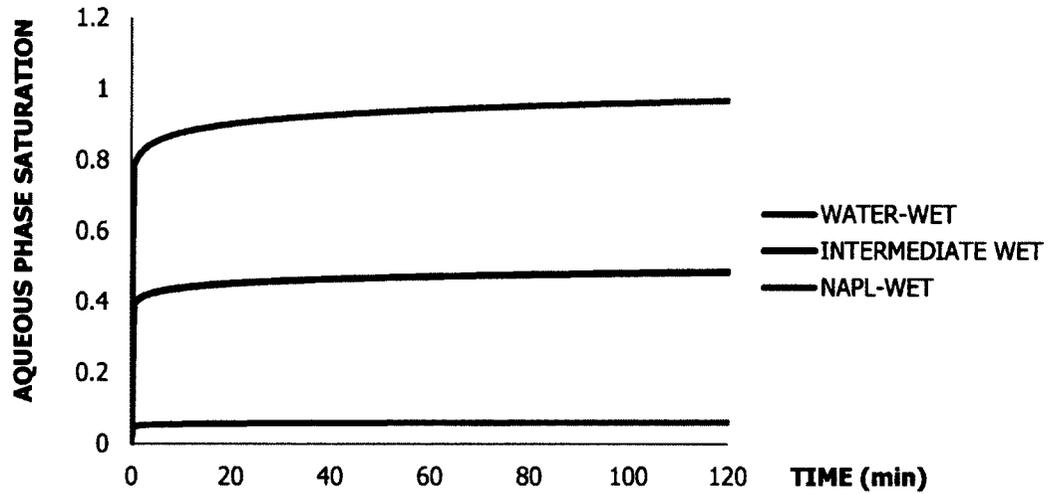


Figure 2.4: Probable imbibition rate behavior of a soil sample as a function of time. (Adapted from Powers and Tamblin, 1995).

2.4.2 Contact angle measurements

Measuring the contact angle of two fluids on a solid surface has been one of the most widely used approaches to measure wettability (Morrow 1990; Powers et al. 1996). Some methods to determine the contact angle include: the tilting plate, sessile drop and sessile bubble (Dullien 1992). Contact angle is normally measured through the water phase and corresponds to the mechanical equilibrium described by Young's equation and illustrated in figure 4.5:

$$\gamma^{os} - \gamma^{ws} = \gamma^{ow} \cos(\theta) \quad (2.6)$$

Contact angles are hysteretic, this means that differences are observed between the advancing (θ_a) and receding (θ_r) angles according to the direction of fluid motion. Advancing and receding angles are representative of drainage and imbibition in capillary pressure-saturation (P_c -S) relationships, respectively. Adamson (as cited by Dullien, 1992) proposes three causes for contact angles hysteresis. First, contamination of either the liquid or solid surface can occur. Second, surface

roughness may account for variations in the contact angle measured macroscopically compared to that at the scale of pore surfaces. Third, the presence of surface active agents can cause surface immobility at the macromolecular scale.

Figure 2.5 describes the wettability characteristic of solid surfaces according to contact angles measurements. Researchers often agree that contact angles around 0° and 180° are indicative of strongly water-wet and NAPL-wet systems, respectively; neutral or intermediate wet conditions apply near 90° contact angles (Powers et al. 1996). The values at which one condition prevails over the other vary among scientists; nonetheless, certain ranges have been proposed (Francisca et al. 2003) as observed in figure 2.5.

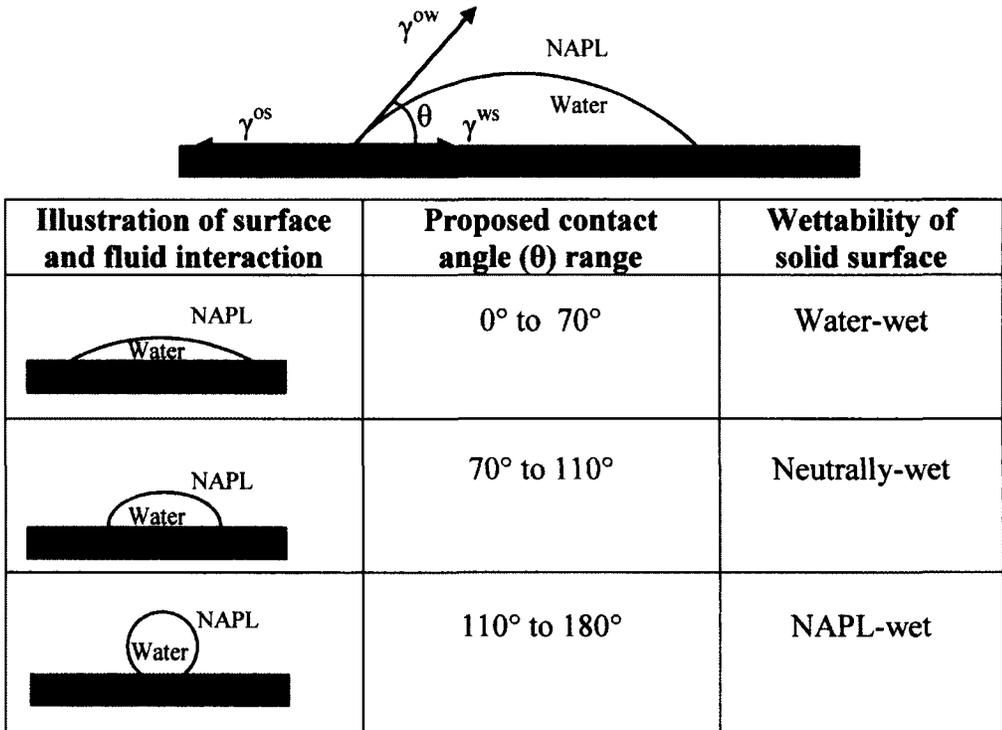


Figure 2.5: Equilibrium at a line of contact (Craig, 1971) and usual ranges for wettability assessment through contact angle measurements (Adapted from Francisca et. al, 2003).

2.4.3 Capillary pressure-saturation tests

Capillary pressure-saturation tests are performed to understand the behavior of the two basic capillary pressure processes: drainage and imbibition, the latter one also referred as wetting. During drainage, the wetting fluid is displaced by the non-wetting fluid and during imbibition, the opposite occurs (Anderson 1987). Capillary pressure relationships are hysteretic, as observed by the differences in the drainage and wetting pathways on the resulting curves for a particular soil sample. The porous medium will have a greater saturation for a given capillary pressure during drainage compared to imbibition. Hysteresis has been attributed to differences in pore geometry and pore surface roughness, and contact angles hysteresis (Morrow 1976; Anderson 1987; Lixia et al. 2007). The impact of pore geometry on drainage and imbibition is often explained as the “ink bottle effect”. When drainage occurs, higher capillary pressures are obtained at a given saturation because the fluid has to percolate through the pore throats (the radius (r) of the idealized capillary tube is very small); in contrast, when imbibition occurs, the pore body (r is larger) dominates the fluid invasion into the pores. As mentioned in the previous section, contact angle displays hysteresis according to the direction of fluid motion, this effect is in turn observed in the capillary pressure curves, contributing to the overall capillary pressure hysteresis.

Figure 2.6 shows a typical hysteretic capillary pressure-saturation relationship (P_c - S). As drainage occurs, the soil sample reduces its saturation until the irreducible wetting phase saturation is achieved (S_{wr}). At this point, increases in capillary pressure will not result in a reduction of the wetting phase saturation. The primary drainage curve depicts the drainage pathway from 100% saturation until S_{wr} is obtained. Likewise, the main imbibition curve represents the wetting pathway from the S_{wr} to the

entrapped non-wetting phase saturation (S_{nwr}) which corresponds to the portion of the non-wetting phase that becomes entrapped in the porous medium. Scanning curves represent different pathways for drainage and imbibition where the S_{wr} is not achieved. As indicated previously, capillary pressure-saturation tests data are used to calculate quantitative indices of wettability. Two methods that were developed for this purpose are the Amott test and the USBM wettability method. The Amott test yields two indices that combined together give the Amott-Harvey wettability index.

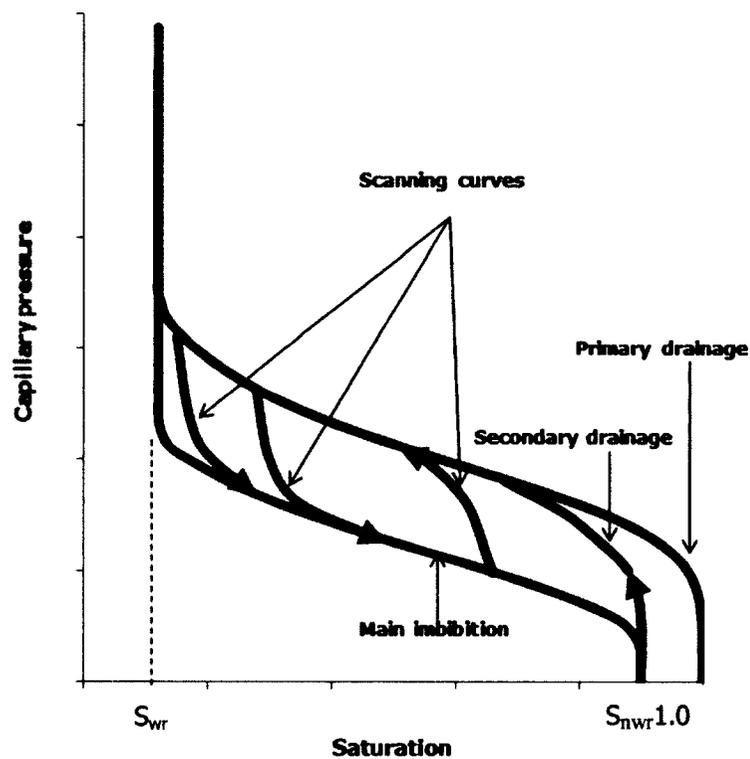


Figure 2.6: Hysteretic capillary pressure-saturation relationship. (Adapted from Chen et. al, 2007).

Amott's test

The original test was developed by Amott in 1959. The amount of fluid that imbibes spontaneously for a period of time (20 hours, originally) is compared to the amount of the same fluid that is displaced under centrifugation or in a viscous

displacement(Dixit et al. 2000). Two indices are normally calculated: the Amott's water index (I_w) and the Amott's oil index (I_o):

$$I_w = \frac{S_w^{Pc=0} - S_{wr}}{1 - S_{wr} - S_{or}} = \frac{\Delta S_{ws}}{\Delta S_{wt}} \quad (2.7)$$

$$I_o = \frac{S_{or} - S_o^{Pc=0}}{1 - S_{wr} - S_{or}} = \frac{\Delta S_{os}}{\Delta S_{wt}} \quad (2.8)$$

where I_w ($\Delta S_{ws}/\Delta S_{wt}$) represents the change in water content due to spontaneous imbibition (S_w at $P_c = 0 - S_{wr}$) to total water imbibition ($1 - S_{wr} - S_{or}$) and I_o ($\Delta S_{os}/\Delta S_{wt}$) is the ratio of spontaneous oil imbibition to total oil imbibition. The Amott-Harvey index (I_{AH}) is calculated as:

$$I_{AH} = I_w - I_o = \frac{\Delta S_{ws} - \Delta S_{os}}{\Delta S_{wt}} \quad (2.9)$$

this index varies from + 1 for a strong water-wet material and – 1 for a strong oil-wet material. A system is considered water-wet when $+0.3 \leq I_{AH} \leq 1$, intermediate wet when $-0.3 < I_{AH} < 0.3$, and oil-wet when $-1 \leq I_{AH} \leq -0.3$ (Anderson 1986; Cuiec 1984).

USBM wettability method/index

The USBM wettability index (I_{USBM}) was developed by Donaldson et al. (1969). The USBM test relates the work done by one fluid to displace the other fluid of interest; its major advantage in comparison to the Amott's test is the sensitivity it shows near neutral wettability but it can only be measured on plug-size samples since the samples must be spun in a centrifuge (Anderson 1986). The I_{USBM} is calculated as the logarithm of the ratio of the areas under the forced oil-drive (A_1 , corresponding to

decreasing water saturation) and forced water-drive (A_2 , corresponding to increasing water saturation) capillary pressure curves (Dixit et al. 2000; Anderson 1986):

$$I_{USBM} = \text{Log} \frac{A_1}{A_2} \quad (2.10)$$

According to the USBM method, the material is considered water-wet when $I_{USBM} > 0$, oil –wet when $I_{USBM} < 0$ and neutrally wet when $I_{USBM} \sim 0.0$.

2.5 Factors affecting wettability

As mentioned in Section 2.3, wettability has been observed to change when NAPLs contact soil systems. To date, the exact mechanisms that cause wettability alterations have not been fully understood. However, several researchers have studied different elements, establishing possible causes for the soil medium's change from water-wet to NAPL-wet. Early insight on this matter comes from studies performed on reservoir rocks. For instance, Buckley (1998) stated that asphaltenes and other crude oil components can alter the mineral surfaces' wettability through one of the following mechanisms: polar interactions between crude oil components and solid mineral surfaces in absence of water, which can establish intermediate or neutral wetting conditions; acid/base interactions when water is present, which in turn affect the surface charge at the oil-water and water-mineral interfaces, and may result in adsorption of compounds; the precipitation of asphaltenes at the interface caused by poor solvent quality of the organic fluid; and ion binding interactions between charged sites and di- or trivalent cations (Buckley 1998; Buckley et al. 1989).

Attempting to provide a review of the most important factors that have been linked to wettability changes, these factors are being grouped by the author into: (1)

precipitation and adsorption of high molecular compounds such as asphaltenes, (2) presence of additives, organic bases and other compounds on field NAPLs, (3) influence of solution chemistry and pH, (4) composition and characteristics of the solid surface and (5) contact order history. It is important to note that this classification attempts to facilitate understanding; yet, most of the factors are interrelated. Following an explanation of these factors, the related research conducted to evaluate their impacts is presented.

2.5.1 Precipitation and adsorption of high molecular weight polar compounds

The adsorption of molecules in their aqueous or organic phases at the solid interface greatly determines the wettability of a soil system (Powers and Tamblin 1995). Reservoir wettability changes occur due to the adsorption of high molecular weight compounds from crude oil through hydrogen-bonding and cation-exchange mechanisms (Dubey and Waxman 1989; Dubey and Waxman 1991). These high molecular weight compounds, asphaltenes, are responsible for reservoir rock wettability changes (Morrow et al. 1986). In fact, Dubey and Waxman (1991) carried out an investigation where sandstone cores were exposed to a 2% by weight solution of tar sand derived asphaltanes in toluene; an asphaltane adsorption level of 0.74 mg/m² was observed and after conducting wettability tests by the USBM method it was found that the cores became less water-wet or neutrally-wet.

Powers et al. (1996) conducted bottle tests to evaluate the wettability of quartz sand exposed to different organic compounds and found that higher molecular weight species had a more significant impact on wettability than low molecular weight

species; the quartz sand became NAPL-wet after a 48-hour exposure to both creosote and coal tar.

Zhenget al. (2001) also investigated the influence of asphaltenes in wettability. A series of asphaltene solutions were prepared by dissolving the asphaltenes in several organic solvents, the solutions were kept at a neutral pH with buffer solutions. Contact angles were measured on quartz sand plates and the surface of the plates was studied by scanning microscopy. When the asphaltene concentration was high (≥ 150 g/L), these compounds could aggregate and precipitate, favoring NAPL-wetting conditions.

2.5.2 Presence of additives, organic bases and other polar compounds on field NAPLs

Field NAPLs, some of which are manufactured as fuel hydrocarbons, often contain a range of different products to enhance their performance. Gasoline, for example, contains a wide range of additives such as octane-enhancing chemicals, anti-oxidants, surfactants, corrosion inhibitors, dyes, and others. These additives are presumed to alter the mineral grain's wettability. Most of these species are polar and have the potential to adsorb onto surfaces. Powers and Tamblin (1995) performed an investigation on the resulting wetting conditions of sand exposed to synthetic gasoline with an emphasis on the additives traditionally found in gasoline. Isooctane was used as the base of the synthetic gasoline and four different compounds were considered as typical additives: o-tuluidine, 2-butoxyethanol, dodecylamine (DDA) and polybutene amine (PBA). After evaluating the wettability, all experiments performed on samples

with DDA concentrations ranging from 500 – 1000 ppm and PBA at the producer's recommended dose (< 0.22% by weight) showed a transition from water-wet to neutral-wet or weakly NAPL-wet. It was also observed that NAPL-wetting conditions were more likely to be established when air-dry sand was first contacted by the organic phase; this phenomenon was also observed by Ryder and Demond (2008) and will be discussed later.

Zheng and Powers (1999) conducted research on wettability impacts due to organic bases present in NAPLs. The presence of weak organic bases was identified in most NAPLs studied (three different gasoline samples, gasoline – oil mixture, fuel-oil, crude oil, creosote and coal tar) where the creosote showed the most appreciable concentration of bases. It was found that at neutral pH, the effect of these NAPLs on wettability was not important; at a lower pH, though, there was a strong correlation between base number and wettability. NAPLs with a base number³ greater than 2mg/g imparted NAPL-wetting conditions on the quartz sand. Their findings suggest that organic bases could affect interfacial phenomena only if the conditions are such that equilibrium is established towards low pH values. Zheng and Powers (2003) also studied the effects of polar compounds in coal derived NAPLs. The correlation between interfacial tension and the acid and base numbers of coal tar and creosote NAPL mixtures was studied. They found that the acid and base numbers relate directly to wettability alteration at the neutral pH range; creosote samples had higher acid and base numbers (10.73 and 35.02 mg KOH/g, respectively), this corresponded with lower IFT values and consequently the prevalence of non-water wetting conditions.

³Zheng and Powers (1999) define base number as “the quantity of acid, expressed as an equivalent mass mg of potassium hydroxide, required to neutralize the basic constituents in one gram of sample.”

Dwarakanath et al. (2002) studied the wettability of five NAPLs recovered from contaminated alluvial aquifers. Density, viscosity and IFT were determined, and wettability indexes were calculated (Amott, Amott – Harvey, and USBM). The IFT values obtained for the field NAPLs were significantly lower compared to their corresponding laboratory grade hydrocarbons. Of the various NAPLs tested, the weathered fuel hydrocarbon had a negative USBM index, indicating mixed to NAPL-wet conditions; the calculated Amott – Harvey index for the weathered gasoline on Ottawa sand indicated water-wet conditions, contrary to the same index on alluvium from the site which indicated mixed to water-wet conditions. These results highlighted the importance of testing field NAPLs and field soil to properly assess wettability (Dwarakanath et al. 2002).

2.5.3 Influence of solution chemistry and pH

Two important mechanisms that might impact the interfacial properties of subsurface systems are: “(1) the pH sensitivity of aqueous speciation of surface-active co-contaminants; and (2) pH-induced changes in the physicochemical nature of mineral surfaces”(Lord et al. 2000p.80). Lord et al. (1997a and 1997b) researched the influence of solution chemistry on surface tension, interfacial tension, wettability and the capillary- pressure saturation curves. In the first part of the study, the effects on an organic acid (octanoic acid) were studied in two systems: air-water and water-o-Xylene. The surface tension for the air -water system was measured at three different pH values: 3, 6.5 and 10 using a Du Noy ring tensiometer. The surface tension and interfacial tension for the water-o-Xylene system was also measured at three different pH values: 2.9 ± 0.2 , 6.5 ± 0.2 and 8.6 ± 0.2 using the Axisymmetric Drop Shape Analysis (ADSA). Their results indicated that a maximum reduction of the surface

tension was achieved at low pH for air -water systems containing low concentrations of organic acids; in contrast, for the water -o-Xylene system, the maximum reduction in IFT was obtained at neutral or high pH. Overall, their results suggest that the observed variations in surface and IFT were large enough to affect the rate of advance of a solute or an organic liquid (Lord et al. 1997b).

The second part of the study correlated previous findings with changes observed in primary drainage capillary-pressure saturation curves. For the air -water system, P_c -S curves were measured for several octanoic acid concentrations and pH values on quartz sand. For this system, results indicate an appreciable reduction in the air-entry pressure (from 50 to 17 cm of H₂O) near the neutral pH at high octanoic acid concentration (0.1 M); this occurred given the fact that the most surface active form of the octanoic acid is the neutral acid form. When the octanoic acid concentration was constant (0.003 M) lowering the pH resulted in a decrease in the displacement pressure (from 45 to 25 cm of H₂O) because lowering the pH caused the octanoic acid to shift to the neutral acid form. The water-o-Xylene system was also evaluated at different pH concentrations where decreases in displacement pressure were observed for all cases except for the low pH value. The main feature about this system was that the octanoic acid could partition into the organic phase having little to no impact on the interfacial properties; although the octanoic acid remained in the anionic form around neutral to high pH, it impacted the P_c -S curve to a greater extent because it remained in the aqueous phase contrary to the low pH conditions where it partitioned to the organic phase. Contact angle measurements did not show differences attributed to the octanoic acid presence for both systems studied. In general, these findings confirmed that solution chemistry and speciation impacted surface and interfacial

tension only and that these impacts can be observed directly on the P_c -S curves (Lord et al. 1997a).

Lord et al.(2000) studied the impact of pH on surface tension, IFT, wettability and the P_c -S curves on systems containing dodecylamine (DDA). The research was conducted using a similar approach as Lord et al. (1997a) and Lord et al. (1997b); the systems studied were air-water and o-Xylene-water with quartz sand. Similar to previous findings, pH was observed to affect all the aforementioned properties by three mechanisms: speciation, partitioning and sorption of the solute. For the air-water-quartz systems, greater surface tension reductions were observed when adjusting the pH to favor the formation of the neutral specie or dimer complex (neutral to low pH); however, compared to the organic acid, the base was observed to sorb on to the solid surface which effectively impacted the wettability (receding contact angles were observed to be higher when cationic species sorbed onto the negatively charged quartz sand) (Lord et al. 2000). On the other hand, pH adjustments of the water-o-Xylene-quartz system to favor the neutral species caused the base to partition to the organic phase and no effect in surface activity was noticed.

2.5.4 Composition and characteristics of the solid surface

Contaminant hydrogeology investigations are commonly conducted on sand given the fact that sandy layers provide the easiest pathway for field contaminants to flow in the subsurface, i.e., pores are larger and permeability is higher. One of the main minerals found in sand is quartz which is essentially silica or silicon dioxide (SiO_2). Quartz sand or silica sand is frequently used for experimental investigations. Nevertheless,

silica is not the only compound found in aquifers. Depending on the aquifer, soil samples may contain different compounds such as humic acid and a wide variety of minerals such as: feldspar, mica, calcite, dolomite, gypsum, graphite, talc, among others (Anderson 1987; Ryder and Demond 2008; Spangle and Handy 1992). Silica and carbonates are naturally hydrophilic; however, studies have shown that wettability heterogeneity can occur at the pore-scale where some areas are hydrophobic instead of hydrophilic, which in turn could increase the areas where NAPLs are retained (Combes et al.1998; Bauters et al. 2000;O'Carroll et al. 2004).

Ryder and Demond (2008) analyzed wettability on ten solid surfaces: Teflon (PTFE), Ann Arbor II soil, Lachine shale, Garfield shale, Waynesburg coal, graphite, talc, dolomite, calcite and silica. Tetrachloroethylene (PCE) was used as the organic liquid phase. Bottle tests and contact angles measurements were performed on flat slides. Bottle tests were conducted over a period of 48 hours (24 hour-equilibrium time and 24-hour contact time with PCE); wettability was then visually assessed. The shales, coal and graphite were found to be completely PCE-wet, water was clearly observed on top of the soil surface. Some PCE was identified in talc, calcite and dolomite pores. The silica sand and Ann Arbor II soil remained completely water-wet. Most of the carbonaceous materials (shales and coal) showed NAPL-wet conditions. Further findings of this study will be discussed in Section 2.5.5.

Molnar et al.(2011) conducted a study on the DNAPL/surfactant wettability of quartz and iron-oxide coated sands containing DDA as an organic base. The study evaluated: (1) the effect of pH on contact angle measurements performed using the ADSA

system; (2) the P_c -S tests behavior in the presence of DDA at low and neutral pH using the multistep outflow approach described by O'Carroll et al. (2005); and (3) the impact of pH on the migration of PCE and DDA in a two-dimensional flow cell. According to the results from the contact angle measurements, the iron oxide surfaces remained hydrophilic in the low to neutral pH range (3.5 to 7.5) and the quartz surface was hydrophilic at low pH but became hydrophobic at almost neutral pH; both surfaces showed contact angle hysteresis. Hysteresis was more significant for iron-oxide surfaces at neutral pH and both the P_c -S tests and flow cell experiment results were in accordance with the previous findings; the investigation results suggest that water drainage may be different for quartz sand and iron-oxide coated sands but imbibition may have a similar behavior (Molnar et al. 2011). This study highlighted the importance of re-evaluating the traditional assumption which considers the soil system as mainly hydrophilic when modelling field site contamination and remediation. Real soils could have a homogeneous distribution of fractionally-wet mineral grains or individual layers of different wettability; thus, the study concluded that the soil's minerals and the aqueous pH are of great importance to DNAPL source zone architecture (Molnar et al. 2011).

2.5.5 Contact order theory

Ryder and Demond (2008) also observed that the wettability of some solid surfaces changed depending on the fluid that contacted the surface first. This phenomenon was termed "wettability hysteresis" where materials can be water-wet or NAPL-wet depending on the wetting history. Shale, coal, PTFE, graphite and talc were observed to be PCE-wet if contacted first by the NAPL but water-wet if contacted first by water. The researchers defined this behavior as "conditional wettability". The study's

findings suggest that the saturated zone is anticipated to be water-wet but the unsaturated zone will contain variable fluid saturations where conditionally NAPL-wet materials can behave as NAPL-wet (Ryder and Demond 2008).

2.6 Other studies conducted on wettability

Extensive research has also been conducted on the interactions of wettability and multiphase flow. As mentioned in Section 2.3, wettability will determine the flow of fluids in contaminated porous media. Some researchers have studied the effects of wettability and fractional wettability on the capillary pressure-saturation relationships, relative permeability relationships and the constitutive models that will best suit multiphase flow. Several scales have been used to understand these effects: pore scale, representative elementary volume scale (REV) and field scale.

Bradford and Leij (1995) studied fractional wettability effects on two and three-fluid capillary pressure-saturation relationships. Blasting sand was rendered NAPL-wet by using octadecyltrichlorosilane (OTS), a procedure that has been extensively used to render mineral grains hydrophobic (O'Carroll et al. 2004; Bradford and Leij 1995; Sah et al. 2004; Hwang et al. 2006; Ahmed and Van Geel 2009). Primary drainage and imbibition curves were obtained for air-water, NAPL-water and air-water-NAPL systems containing different percentages of OTS treated sand mixed thoroughly with the clean sand; Soltrol 220 was used as the reference NAPL. The study confirmed a decrease in the NAPL-water pressure (P_{ow}) and negative capillary pressure during water imbibition as the NAPL-wet sand fraction was increased in two-fluid systems. In three fluid systems, a dependency of P_c on fluid saturation was detected and

attributed to the inexistence of a non-continuous intermediate phase (water was not likely forming a continuous layer over the air-oil interface) (Bradford and Leij 1995). Bradford et al. (1997) developed a modified version of the Burdine pore-size distribution model⁴ to estimate two and three fluid relative permeability saturation relationships (k_r -S) in NAPL-wet media. Hwanget al. (2006) used experimental k_r -S data for the primary drainage pathway of a NAPL (Soltrol 220)-water system with fractionally-wet media to verify the model proposed by Bradford et al. (1997) and compare it to a Mualem⁵ modified model. The models predicted smaller variability in the k_r -S curves compared to that observed through the experiments, not successfully representing the system. (Hwang et al. 2006).

Masalmeh (2002) also studied the effects of wettability on capillary pressure and relative permeability using cores of heterogeneous wettability. Results confirmed that only the pore space that comes into direct contact with the crude oil changes wettability both at the pore and core scale; the wettability heterogeneity had an important impact on the shape of the P_c -S and K_r curves where the NAPL relative permeability progressively changed while the NAPL moved from the NAPL-wet to the water-wet regions of the core (Masalmeh 2002).

O'Carroll et al. (2004) investigated the effects of PCE infiltration in a system with variable spatial wettability. P_c -S tests were conducted using pressure cells based on the design of Salehzadeh and Demond (1999) as well as a sand box experiment where some regions were packed with OTS treated sand to observe the behavior of the

⁴ Refer to Bradford et al. (1997) for further details.

⁵ Refer to Hwang et al. (2006) for further details.

DNAPL through the NAPL-wet areas. P_c -S data were fitted to modified versions of the Van Genuchten and Brooks and Corey equations. DNAPL migration in the sand box was modelled using a modified multiphase flow simulator as well as modified relative permeability models (modified Burdine and Mualem models). All these models were modified to account for the presence of NAPL-wet media. The modelling results indicated that the modified models could predict DNAPL drainage pathways but could not mirror the behavior and DNAPL infiltration on the NAPL-wet sands (O'Carroll et al. 2004).

O'Carroll et al. (2005) proposed a new model for predicting two-phase P_c -S relationships using an extension of the Leverett scaling theory. This model is referred to as the Leverett-Casie model (after Leverett and Casie, as cited by O'Carroll et al. 2005) and introduces the use of an operative contact angle different from contact angles measured on flat plates in order to represent more accurately the displacement of fluids in subsurface systems (O'Carroll et al. 2005). The model was able to predict the data obtained for PCE-water systems as well as the data measured by Bradford and Leij (1995) on simple fractionally-wet systems.

Aggelopoulos and Tsakiroglou (2008) studied the micro-scale heterogeneity effects on capillary pressure and relative permeability curves induced by broad pore-size distribution. Micro-scale heterogeneities can be understood, for example, as regions of low or high permeability in a medium considered of high and low permeability, respectively. These regions can be associated with the presence of different minerals in soils and varying degrees of wettability. The irreducible wetting phase saturation or residual wetting phase saturation (S_{wr}) was found to increase as the micro-heterogeneity increases. The effective permeability of the non-wetting fluid at the S_{wr}

was higher in comparison to narrow grain size distribution soils because “*the hydraulic conductivity (K) is dominated by the conductivity of a critical path, which also acts as a preferential path for the non-wetting fluid (oil)*” (Aggelopoulos and Tsakiroglou 2008p. 34).

Al-Raoush (2009) investigated the impact of wettability on the characteristics of residual NAPLs at the pore scale. Several three-dimensional images of fractionally-wet fine sand systems were obtained using Microtomography Imaging and residual NAPLs were characterized by using image processing algorithms. This study’s results showed that residual NAPL blobs are greater in magnitude in water-wet media as a result of entrapment in pore bodies; also, as the NAPL-wet areas increase, NAPL-water interfacial areas also increase; finally, residual NAPL saturations were smaller in fractionally-wet systems and were augmented if the systems transitioned to more water-wet or NAPL-wet conditions (Al-Raoush 2009).

2.7 Altering porous media wettability

As mentioned in Section 2.6, several studies have focused their attention on fractionally-wet porous media. Attempting to understand the interactions of mineral grains of different wettability in a particular system, scientists have been using chemical components to alter material wettability from hydrophilic to hydrophobic; i.e, from water-wet to NAPL-wet.

One mechanism to render solids hydrophobic is the in-situ hydrolysis and condensation of alkoxide precursors with hydrophobic side groups, such as

organosilanes, creating a hydrophobic layer on the solid's surface (Sah et al. 2004). Organosilanes are organic compounds which contain an organic silicon bond. Octadecyltrichlorosilane ($\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$) or OTS has been extensively used in fractional wettability studies (O'Carroll et al. 2004; Bradford and Leij 1995; Hwang et al. 2006; Ahmed and Van Geel 2009). This compound is amphiphilic (term used to describe compounds that have both hydrophilic and lipophilic properties) composed by a polar group (SiCl_3 -) and an alkyl group ($\text{C}_{18}\text{H}_{37}$) which is hydrophobic (Ahmed and Van Geel 2009). When organosilanes, such as OTS, are diluted in organic solvents, e.g., toluene or ethanol, the newly formed compound's derivative polar group reacts with the hydrophilic solids forming a thin hydrophobic monolayer on the surface (Sah et al. 2004; Ahmed and Van Geel 2009). This process is commonly known as anhydrous silylation (Yoshida et al. 2001).

Ahmed and Van Geel (2009) studied the use of OTS in rendering soils and porous ceramics hydrophobic. The OTS was catalyzed in ethanol to form the OTS's derivative ($\text{CH}_3(\text{CH}_2)_{17}\text{Si}(\text{OC}_2\text{H}_5)_3$); the polar head ($\text{Si}(\text{OC}_2\text{H}_5)_3$) reacts with the hydrophilic sand turning the medium to NAPL-wet. The OTS treatment procedures followed were analogous to previous studies (O'Carroll et al. 2004; Bradford and Leij 1995; Hwang et al. 2006; Ahmed and Van Geel 2009). However, unusual behavior was noticed on some tests performed with the NAPL-wet sands which led to the suspicion that the OTS treated sands had an excess amount of unbounded OTS (OTS derivative). Further tests confirmed this hypothesis and a new procedure was implemented to eliminate the excess OTS on the porous media. In the traditional treatment, a 5% by volume OTS solution in ethanol was prepared. Then, the sand was saturated in this solution for 24 hours and subsequently washed in ethanol five times.

To remove the excess unbounded OTS several organic solvents were tested: hexane, heptane and decane. The researchers recommend an enhanced – washed OTS procedure where OTS treated materials are washed in hexane for 24 hours in a soxhlet extractor; in addition, the materials (soil or ceramic plates) should be washed in the soxhlet extractor with the NAPL that will be used in subsequent experiments (Ahmed and Van Geel 2009).

2.8 NAPL recovery by surfactant flushing

Surfactants or surface active agents have been broadly used to enhance the recovery of NAPLs in the soil matrix. They have a distinct molecular structure that consists of two structural groups. When found in aqueous solutions, one structural group has little attraction for water (hydrophobic group) and the other has a strong attraction for water (hydrophilic group).

2.8.1 Types of surfactants

According to the nature of the hydrophilic group, surfactants may be non-ionic, ionic (anionic or cationic) or zwitterionic where both positive and negative charges are present. They are commonly used as: detergents (alkyl chains C12 – C18), to prevent precipitation of lime soaps, wetting and dispersing agents, fabric softeners, anticaking agents, corrosion inhibitors, dispersants, flotation agents, foam control agents and for stabilization of oil-water emulsions. In soil remediation, anionic and non-ionic surfactants are employed. Some researchers have explored mixed blends of the previous to enhance NAPL recovery. Table 2.1 presents a summary of some important surfactant characteristics based on Rosen (1989) and Holmberg et al. (2003)

and a list of surfactants that have been used for remediation of soils contaminated with NAPLs as well as other compounds such as PAHs (polycyclic aromatic hydrocarbons) in both field and laboratory experiments.

Type of surfactant: polar group	Characteristics	Product used in soil remediation
Anionic: carboxylate, sulfate, sulfonate, phosphate	<p>Largest surfactant class</p> <p>Easy to manufacture, low cost</p> <p>Sensitive to hard water</p> <p>Physicochemical properties are strongly affected by electrolytes</p>	<p>SDBS - Sodium dodecylbenzenesulfonate (Flaming et al. 2002; Guo et al. 2009; Zhang and Zhu 2010; Yang et al. 2006; Goudar et al. 1999; Rouse et al. 1993)</p> <p>SDS - sodium dodecyl sulfate (Goudar et al. 1999)</p> <p>Sodium DioctylSulfosuccinate (Bettahar et al. 1999)</p> <p>Sodium Dihexylsulfosuccinate (Dwarakanath et al. 1999)</p> <p>HOSTAPUR® SAS 60 (Martel et al. 1998)</p>
Cationic: nitrogen atom carrying the cationic charge	<p>Usually not compatible with anionics</p> <p>Adsorb strongly to most surfaces</p> <p>Hydrolytically stable products show higher aquatic toxicity</p>	<p>None to the author's knowledge, probably due to their tendency to adsorb strongly at the soil surfaces (i.e. cationics will exhibit strong adsorption to sand surfaces composed of electronegative silica/quartz).</p>
Non-ionic: polyether or polyhydroxyl	<p>Second largest surfactant class</p> <p>Compatible with other surfactants</p> <p>Physicochemical properties are not greatly affected by electrolytes</p> <p>Some are temperature dependent (less water soluble as temperature increases)</p>	<p>TWEEN 80 (Guo et al. 2009; Abriola et al. 2002)</p> <p>TRITRON X - 100 (Yang et al. 2006; Mohan et al. 2006)</p> <p>T-maz-80 - POE (20) sorbitanmonoleate (Goudar et al. 1999 ; Penellet al. 1993)</p> <p>CA-620 -Octylphenolpolyethanol (Goudar et al. 1999)</p>

Type of surfactant: polar group	Characteristics	Product used in soil remediation
	Foam generation is smaller	AG 625, LAA 54, LAE 25, LAE 91 – GlucoPON® Alkyl Polyglycoside surfactants (Chevalier 2003) Simple green (Tsai et al. 2009)
Zwitterionic: ammonium (positive charge) and typically carboxylate (negative charge)	Costly, less common and compatible with other surfactant types Stable in acids and bases Low eye and skin irritation	None to the author’s knowledge.

Table 2.1: Summary of surfactant types, characteristics and uses.

2.8.2 Reduction of surface and interfacial tension by surfactants

In surface active agents, the presence of the hydrophobic group might cause a distortion of the liquid structure, increasing the energy of the system. As a result, less work is needed to bring the surfactant molecule to the surface, reducing surface tension. The hydrophilic group will be oriented towards the surface and the hydrophobic group away from it (Rosen, 1989). Interfacial tension between immiscible fluids is reduced in a similar way. Since interfacial tension can be understood as a measure of the similarity of two fluids, where similar fluid pairs will have low interfacial tension, introducing surfactants to promote fluid displacement is of great significance. When the fluid pairs are immiscible, the surface active agent at the interface will ideally have the hydrophobic group oriented towards the non-polar fluid (i.e. heptane or other NAPL) and the hydrophilic group towards the water, as shown in figure 2.8 and proposed by Rosen (1989). When this condition is met, the tension between the interfaces is effectively reduced as similar fluid pairs are in contact (e.g. the non-polar fluid and the hydrophobic group of the surfactant).

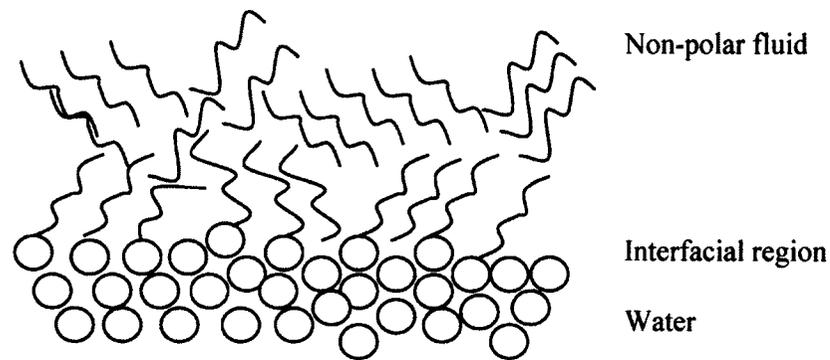


Figure 2.7: Schematic of non-polar fluid and water interface with surfactant adsorbed at the interface. (Adapted from Rosen, 1989)

2.8.3 Mechanisms responsible for surfactant enhanced remediation of NAPLs

Surfactants promote the recovery of NAPLs by two mechanisms: mobilization and solubilization of the NAPLs on the micellar structure of the surfactant solution. Mobilization occurs because the reduction in the interfacial tension between the NAPL and the aqueous solution facilitates the transport of the NAPL as the solution moves along the pores of the soil. This could be an important mechanism if the distribution of the NAPL is mostly at the center of the pores, as presented previously in figure 2.1. Some studies have attributed NAPL removal from the soil to mobilization. For example, 80% of PCE (perchloroethylene), TCE (trichloroethylene) and a field DNAPL were recovered from surfactant soil column experiments by mobilization of the free phase with a solution composed of sodium dihexylsulfosuccinate (4 – 8% by weight) and secondary butyl alcohol (4% by weight) in combination with electrolytes (0.5% by weight NaCl or CaCl₂) (Dwarakanath et al. 1999). In a similar way, 60% of the residual NAPL (decane) was removed as free phase in column experiments with a surfactant mixture of 2% Hynic PE and 2% Witconate 93-S by weight (Chevalier 2003).

Surfactants are very soluble in water, as their concentration increases, a change in the internal structure of the solution occurs. A solution containing single surfactant molecules or ions (unimers) changes to a solution where the surfactant is present in a self-assembled or self-aggregated state (Holmberg et al. 2003). These aggregates are called micelles and the concentration at which they appear is called the critical micelle concentration or CMC. Hydrophobic compounds are soluble in surfactant aqueous solutions that contain micelles. Thus, the solubilization of these compounds is very low below the CMC and increases as surfactant concentration increases. NAPLs in turn are removed from contaminated soil by enhanced solubilization when flushing occurs with surfactant solutions at or above the CMC. However, this has several implications:

- The surfactant mass to be dissolved increases, increasing remediation costs.
- Certain surfactants show toxic levels at high concentrations which implies that further soil and water contamination might occur.
- Adsorption of surfactants at the surface of mineral grains can occur preventing the removal of the target contaminant.
- Foam production increases, especially with anionic surfactants; this is undesirable in the field because it contributes to visual pollution. If the site clean-up is conducted in non-industrial property, property owners perceive foam production as an additional contamination issue.

As mentioned in the previous section, the interfacial tension between the immiscible fluids has to be effectively reduced in order to achieve NAPL displacement. This can occur from low interfacial tensions (i.e. < 5 dynes/cm) to ultralow interfacial tensions.

Rosen (1989) defines the ultralow interfacial tension as $< 10^{-3}$ dynes/cm. This value of ultralow interfacial tension is generally achieved only at values greater than the CMC. Anionic surfactants are normally combined with electrolytes to reduce the value of the CMC and effectively reach the ultralow interfacial tension threshold. Several studies have then tested surfactants at values above the CMC (Goudar et al. 1999; Bettahar et al. 1999; Martel et al. 1998; Tsai et al. 2009). In contraposition to these studies, 40% to 50% reductions in water and NAPL residual saturations, respectively, were achieved in soil column experiments with SDBS at submicellar concentrations (surfactant concentrations where less than 0.4 g/L) with no added electrolytes (Flaming et al. 2002). Chevalier (2000) also presented results where NAPL saturations were reduced by 20% using a dual blend of surfactants each at a concentration of 1 g/L.

2.9 Summary

As presented throughout Section 2, most of the research on wettability has been performed on characterization and identification of wettability alteration factors. Likewise, extensive research has been conducted on incorporating fractional wettability in multiphase flow models. Despite these great efforts, few studies have been performed on actual field soils and field NAPLs. Also, to the author's knowledge, none of these studies have investigated non-ideal wettability during soil remediation via surfactant flushing. It is necessary to link wettability alterations to actual remediation technologies, to predict field site behavior and actual remediation efficiency. Hence, this study will provide new understanding on the influence of wettability on the recovery of entrapped LNAPLs when surfactants are used to remobilize entrapped LNAPLs.

3. MATERIALS AND METHODS

Two types of soil media were used for this research: clean sand (silica test sand ASTM C-778), i.e. as purchased with no chemical treatment, and a mixture of this clean sand with sand treated to become NAPL-wet. The sand was homogeneous, medium to coarse grained, with a hydraulic conductivity of 0.3 cm/s and a median grain size (d_{50}) of 0.073 cm. To obtain the NAPL-wet medium, the silica test sand (naturally water-wet) was treated with OTS (obtained from Sigma Aldrich) following the enhanced OTS procedure proposed by Ahmed and Van Geel (2009). Two different LNAPLs were used in the experiments: heptane (lab-grade LNAPL purchased from Fisher Scientific) and the field LNAPL, recovered from a contaminated refinery site and provided by the Colombian Petroleum Institute. Distilled water was used in all experiments as the water phase.

3.1 OTS treatment to produce NAPL-wet sand

To modify the wettability of the silica test sand, a 5% by volume OTS solution in ethanol (100%) was prepared. The sand was saturated with this solution and stirred for 24 hours. Subsequently, the sand was rinsed in ethanol at least five times to remove the excess OTS. After air drying, the sand was washed in hexane for 24 hours in a soxhlet extractor to remove any excess unbounded OTS. Afterward, the sand was removed from the soxhlet apparatus and air-dried. Visual wettability tests were conducted on the OTS-treated sand to ensure that its wettability was successfully changed from water-wet to NAPL-wet. These tests were performed by releasing a

water droplet on top of a small amount of sand and further observing the behavior of the droplet; water-wet sand will draw the water in while NAPL-wet sand will not.

3.2 Interfacial tension and contact angle measurements

Interfacial tension (IFT) and contact angle measurements for heptane and the field LNAPL were performed using the ADSA method (Axisymmetric Drop Shape Analysis method). This system fits the Young-Laplace equation to a drop shape obtained from high resolution photographs of LNAPL drops in water, either floating from a j-shaped needle (to obtain IFT) or against a quartz plate (to obtain contact angle) (Drake 2011). Figure 3.1 shows an example of a drop shape image to measure IFT and contact angle. Interfacial tension was measured for the LNAPL-water systems and the LNAPL-surfactant solutions: 0.02, 0.1 and 0.5 g/L. Both advancing and receding contact angles were measured.

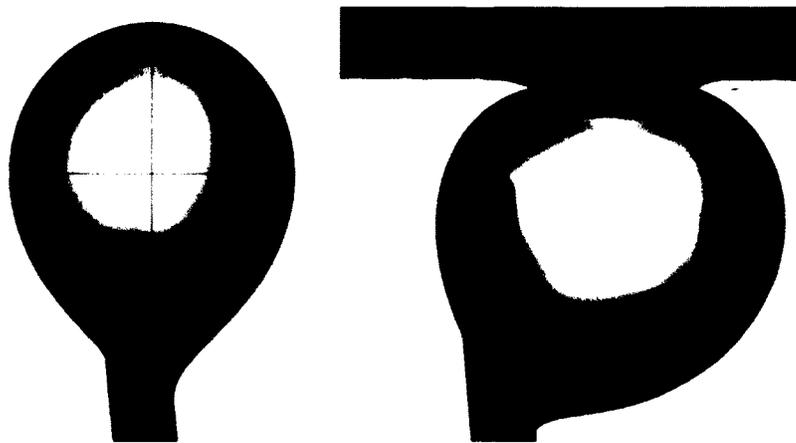


Figure 3.1: Drop shape images to measure IFT (left) and contact angle (right).

For IFT tension measurements, heptane and the field LNAPL were equilibrated with water and the surfactant solutions for 72 hours in glass vials. After equilibration, IFT was measured and recorded. Each individual measurement corresponds to a drop introduced into the water by a syringe. To measure contact angle, the LNAPLs were equilibrated with both water and the quartz plate in a 30 ml beaker. In this case, an inverted vial containing the LNAPL was introduced into the beaker allowing equilibration between the three phases while preventing LNAPL from contacting the plate. After equilibrium, the contact angles were measured by injecting LNAPL drops against the quartz plate. The needle was kept static during NAPL injection. As the NAPL exit the needle, the drop increased its size and advanced on the quartz plate. Advancing angles were measured after allowing the drop to equilibrate with the quartz plate for 1 hour. Receding contact angles were measured instantly. A total of 10 IFT measurements were recorded both for each LNAPL and for advancing contact angles. A minimum of three readings were recorded for receding contact angles. For each set of measurements, the mean was calculated with its corresponding standard deviation and 95% confidence intervals.

3.3 Capillary pressure-saturation tests

Capillary pressure - saturation tests (water-heptane and water-field LNAPL) were performed on clean sand and a 50/50 percent by weight sand mixture (50% OTS treated + 50% clean sand) using pressure cells. The pressure cells were designed after Salehzadeh and Demond (1999) and the procedures are analogous to Said (2010). Figure 3.2 shows the components of the pressure cells. Each pressure cell consisted of three main components: upper and lower caps (2 cm in height) which connect to a cylindrical soil chamber (height = 2 cm, diameter = 5 cm).Stainless steel porous plates

were fitted to the upper and lower sections and hydrophobic and hydrophilic porous membranes were placed between the soil sample and the upper and lower sections, respectively.

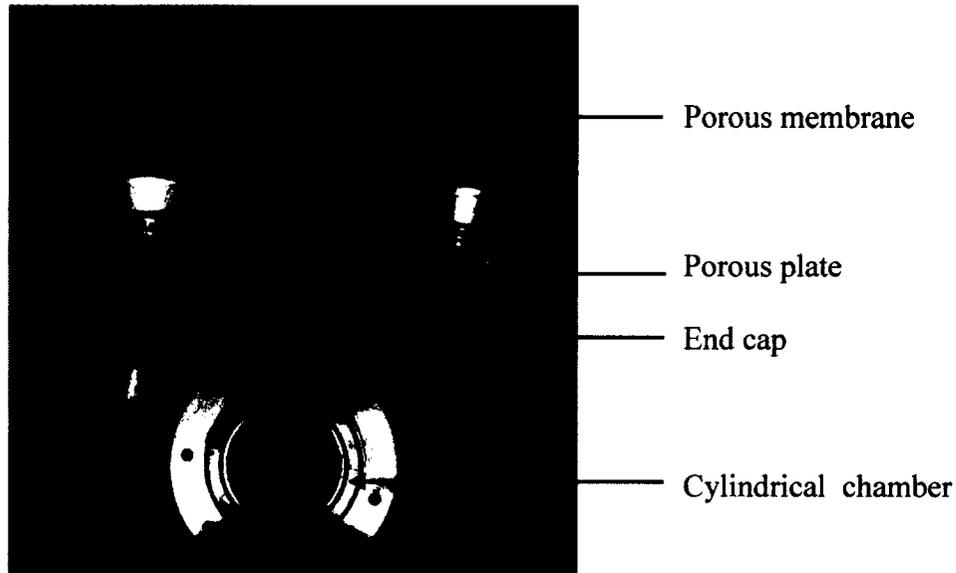


Figure 3.2: Pressure cell components for the P_c -S experiments.

During the set-up of a P_c -S test, the bottom section of the pressure cell was assembled and the soil sample was placed inside the chamber. The weight of the cell, before and after being filled with soil, was recorded to obtain the mass of dry soil deposited inside the soil chamber. Dry density (ρ_d) and porosity (n) were calculated for each P_c -S experiment using the pressure cell as:

$$\rho_d = \frac{\text{mass of dry soil in cell}}{\text{Volume of cell}} \quad (3.1)$$

$$n = 1 - \frac{\rho_d}{G_s} \quad (3.2)$$

where G_s is the specific gravity of silica sand (2.65). After, the pressure cell was assembled and the soil was flushed with CO_2 for 15 minutes. Then, the water tubing

was connected to the bottom of the cell and the soil was flushed with 50 pore volumes (PV) of distilled water to ensure saturation. After saturation, the top section of the cell was replaced. A hydrophobic membrane was placed to allow flow of the LNAPL into the chamber and the LNAPL tubing was connected to the top section of the cell. Subsequently, the drainage experiment proceeded (by lowering the water burette) and the capillary height (h_w for water and h_n for the LNAPLs) and change in fluid volume were measured on the fluid burettes which are connected to the pressure cell with Tygon® tubing. Chemical resistant Tygon® tubing was used for the LNAPLs. When drainage ceased, the direction of fluid flow was reversed (by raising the water burette) and imbibition occurred. For the 50/50 sand mixture (fractionally-wet medium), the soil was flushed under positive water pressure (100 cm of water) to try to achieve 100% saturation. Figure 3.3 shows a schematic diagram of the P_c -S experiment.

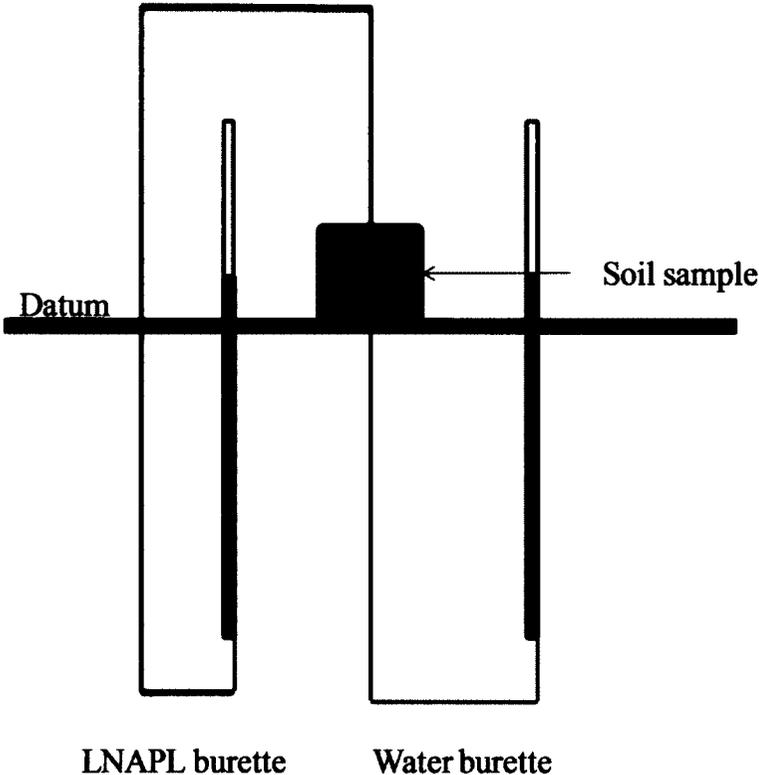


Figure 3.3: Diagram representing the set-up for a P_c -S experiment.

P_c-S tests were performed on the following combination of experiments:

- Clean sand and heptane, ideal scenario
- Clean sand and field LNAPL, non-ideal field LNAPL
- 50% NAPL-wet + 50% water-wet sand and heptane, non-ideal soil wettability
- 50% NAPL-wet + 50% water-wet sand and field LNAPL, non-ideal wettability scenario

After data collection, capillary pressure was calculated as the difference between the NAPL pressure (P_n) and the water pressure (P_w). Water was considered as the wetting fluid and the LNAPLs were considered as the least or non-wetting fluids. Accordingly, capillary pressure height (h_c in cm of H₂O) resulted in:

$$h_c = \rho_N h_n - h_w \quad (3.3)$$

where ρ_n corresponds to the density of the LNAPL. Water saturation for each step (i) during drainage was calculated according to:

$$S_{wi}(\%) = \left(1 - \frac{V_{out}}{n}\right) * 100 \quad (3.4)$$

where V_{out} corresponds to the volume of water that had exit the pressure cell as recorded from the water burette and n is the porosity. Water saturation during imbibition was calculated as:

$$S_{wi}(\%) = S_{wr} + \left(\frac{V_{in}}{n}\right) * 100 \quad (3.5)$$

where V_{in} corresponds to the volume of water that had entered the cell or re-wetted the soil. Volume recorded in the water and LNAPL burettes was corrected for evaporation. Evaporation was monitored in separate water and LNAPL burettes.

3.4 Column experiments

Column experiments were set up in clear 1.5 in diameter PVC pipes with top and bottom end caps. Bottom and top caps were connected through tubing to a collection reservoir and a peristaltic pump, respectively, as observed in figure 3.4. The dimensions of the columns and other details are included in table 3.1. Each column consisted of a bed of pebbles followed by a geo-synthetic (to prevent the migration of fines) on top of which the sand column sat.

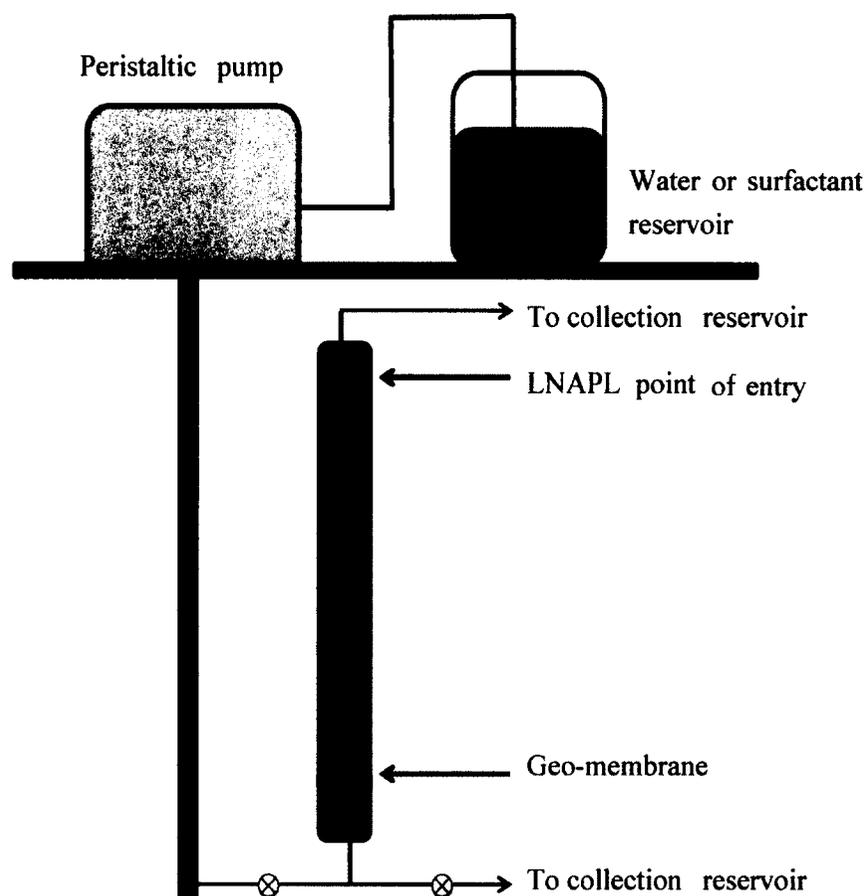


Figure 3.4: Set-up for column experiments.

Initially, the columns were packed in 5 cm lifts and compacted each time. After being assembled, the columns were flushed with CO₂ for 15 minutes. Afterward, 10 PV of distilled water were injected at a rate of 1 ml/min which corresponds approximately to

a Darcy velocity of 5 cm/h. Once fully saturated, 60 ml of the corresponding LNAPL (heptane or field LNAPL) were spilled instantaneously and allowed to percolate downward through the entire length of the column by gradually lowering the water table. The LNAPL was allowed to remain in the columns for a period of 2 hours. After, soil flushing was performed (10 PV) at a rate of 1 ml/min from bottom to top. The free-phase LNAPL was collected directly in separating funnels and the volume of recovered free phase LNAPL was quantified.

Column features	Parameter
Length of soil in column (cm)	25.5
Column diameter (cm)	3.61
Volume of soil (cm ³)	291
Soil pore volume(ml)	105

Table 3.1: Column dimensions and features.

Preliminary tests were performed to identify an appropriate approach to determine free phase entrapped LNAPLs removed by the surfactant solution. Surfactants have been shown to be more efficient when used for primary recovery (Chevalier 2000), i.e. applied directly to the contaminated soil with no prior water-flood. Preliminary tests confirmed that free phase LNAPL removal was very small and difficult to quantify if a water-flood took place before the surfactant-flood. As a result, the enhanced removal due to the addition of surfactants was assessed by comparing the entrapped NAPL saturations that remained when the NAPL source was displaced and flushed with 10 PV of water to the entrapped NAPL saturation that remained when the NAPL source was displaced and flushed with 10 PV of the surfactant solution.

The difference between the remaining entrapped NAPL saturation will be referred to as the enhanced entrapped NAPL removal expressed as a percentage of the entrapped NAPL saturation after the water-flood.

SDBS/sodium dodecylbenzenesulfonate (technical grade, purchased from Sigma – Aldrich) and the field site surfactant were applied at a concentration of 0.5 g/l. For SDBS, this concentration is thought to be under the CMC which has been reported to be around values of 1.4 g/L (Rouse et al. 1993), 0.7 g/L (Flamming et al. 2003), and 0.75 g/L (estimated from methodology presented by Rosen 1989 chapter 2). This implies that the dominant mechanism for LNAPL removal should be mobilization via interfacial tension reduction.

For columns flushed with SDBS, five replicates were performed on each combination of experiments (4 combinations), as detailed in the previous section, both for the surfactant-flood and water-flood, for a total of 40 (5x4x2) column experiments with a contact period of 2 hours (i.e. the released LNAPL remained in the columns for 2 hours before a water or surfactant flood). To further investigate the effects of contact time on wettability and entrapment, a second round of experiments was conducted where LNAPL remained in the columns for 5 days prior to a water or surfactant flood. These experiments were performed in duplicate; 16 column experiments in total (2x4x2). The field surfactant was tested in the same fashion, in duplicate, 16 (2x2x2) experiments for a 2-hour contact period and 16 (2x2x2) experiments for a 5-day contact period. A mean entrapped saturation was calculated from the replicates of each set of experiments. Statistical significance tests were performed on the first

round of experiments with SDBS (2-hour contact period) comparing the water-flood to surfactant-flood saturations for each combination of experiments. Four column experiments were performed simultaneously to ensure that experimental procedures and environmental conditions were the same for the group of experiments to be compared. This means, for example, that clean sand columns being exposed to the field LNAPL and flushed with SDBS were set up at the same time, 2 for the water-flood, and 2 for the surfactant-flood.

As mentioned previously, the primary mechanism for LNAPL removal that was targeted during this study was mobilization. In order to confirm that no significant solubilization was occurring, GC (gas chromatography) analyses were performed by an external laboratory on the following samples:

1. Field LNAPL: to obtain the GC chromatogram and identify the range of hydrocarbon compounds present in the LNAPL sample.
2. Water equilibrated with the field LNAPL: to obtain the solubility limit of the field LNAPL in water.
3. SDBS solution after being flushed through the column: to estimate if LNAPL solubilization was occurring.
4. Field site surfactant solution after being flushed through the column: to estimate if LNAPL solubilization was occurring.

For samples 2, 3 and 4, the GC chromatogram was also obtained. GC analyses were performed only on the field LNAPL as this is the NAPL of interest for site remediation. Samples 3 and 4 were collected from the separating funnels after performing two column experiments with clean sand.

4. RESULTS AND DISCUSSION

4.1 Visual wettability tests

Visual wettability tests were performed to have an initial estimation of the wetting behavior of the clean sand, the OTS-treated sand and the clean sand exposed to the field LNAPL for a period of 24 hours. Figure 4.1 shows the results of these tests. The OTS-treated sand was found to be NAPL-wet, as shown in figure 4.1a, where the water droplet sat on top of the sand. The wettability of the clean sand was successfully changed from water-wet (as shown in figure 4.1.b) to NAPL-wet through the OTS treatment. Also, when the clean sand was exposed to the field LNAPL for 24 hours, the wettability appeared to be changed to NAPL-wet, as observed in (c). However, after one minute, the water was drawn into the soil suggesting that the sand may have a “non-ideal” wettability behavior after its exposure to the field LNAPL.

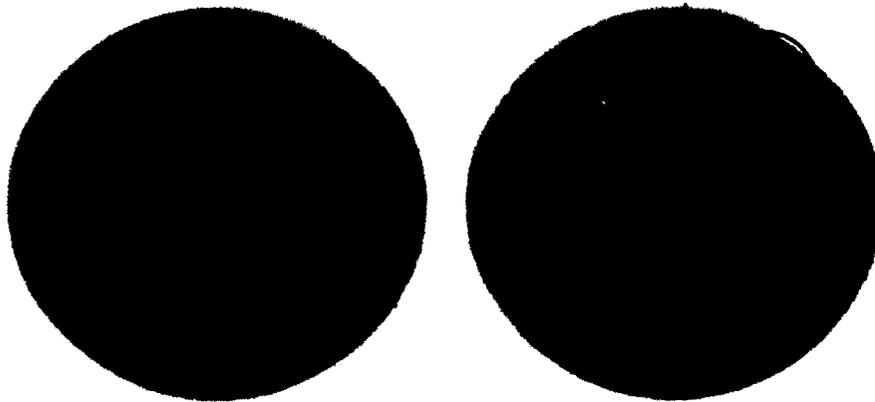


Figure 4.1: Visual wettability tests. a. OTS-treated sand, NAPL-wet. b. Clean sand, water-wet. c. Clean sand exposed to field LNAPL, initially NAPL-wet. d. Clean sand exposed to field LNAPL after 1 minute.

4.2 Interfacial tension and contact angle measurements

4.2.1 Interfacial tension

The results for the interfacial tension measurements with heptane as the NAPL phase are shown in table 4.1 and figure 4.2. Table 4.1 shows the calculated mean and its corresponding standard deviation and 95% confidence interval (95% C.I.).

Surfactant	Concentration (mg/L)	IFT	Standard deviation	95% C.I.
SDBS	0	44.0	1.91	1.36
	20	28.6	2.25	1.61
	100	9.8	0.58	0.42
	500	3.1	0.49	0.35
Field surfactant	0	44.0	1.91	1.36
	20	4.6	0.03	0.02
	100	3.6	0.09	0.07
	500	2.5	0.10	0.07

Table 4.1: IFT results for heptane.

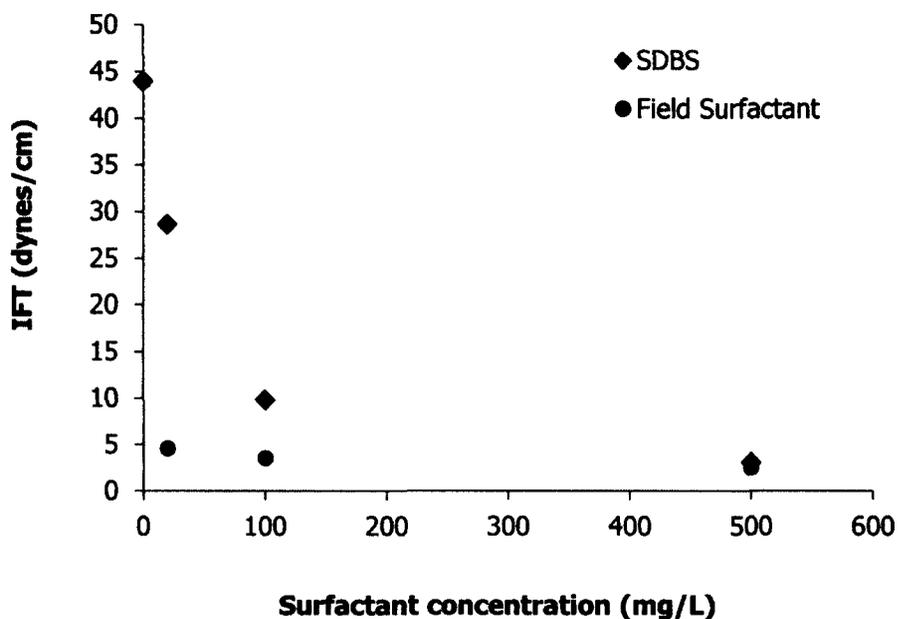


Figure 4.2: IFT tension results for heptane.

An increase in the concentration of SDBS resulted in a gradual decrease of the IFT between heptane and the surfactant solution. On the other hand, an increase in the field surfactant concentration resulted in a more drastic decrease of the IFT. At a concentration of 500 mg/L both surfactants were able to reduce the IFT to values smaller than 5 dynes/cm.

Table 4.2 and figure 4.3 show the results for IFT with the field LNAPL as the NAPL phase. The value of IFT against water (34.6 dynes/cm) is smaller than for heptane (44 dynes/cm). The field surfactant, as observed previously, appears to reduce the IFT more effectively even at lower concentrations.

Surfactant	Concentration (mg/L)	IFT	Standard deviation	95% C.I.
SDBS	0	34.6	1.07	0.77
	20	20.8	0.61	0.44
	100	13.8	0.69	0.49
	500	4.9	0.31	0.22
Field surfactant	0	34.6	1.07	0.77
	20	2.6	0.08	0.05
	100	1.4	0.07	0.05
	500	1.9	0.04	0.03

Table 4.2: IFT results for the field LNAPL.

SDBS and the field surfactant showed a similar reduction of the IFT at a concentration of 500 mg/L. For the soil flushing, they were used at this concentration allowing comparison of their ability to remove the field LNAPL as a result of mobilization. Also, as observed by the IFT plots and found in the literature (Rouse et al. 1993; Flammig et al. 2003; Rosen 1989), it can be inferred that a concentration of

500 mg/L (0.5 g/L) is near to but below the CMC for SDBS. This condition suggested that NAPL removal by enhanced solubilization would be negligible.

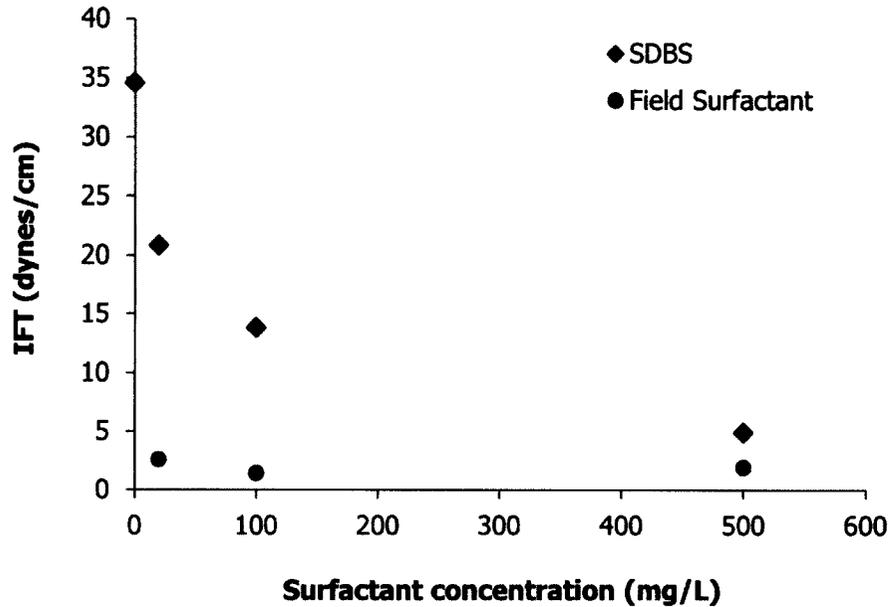


Figure 4.3: IFT results for the field LNAPL.

4.2.2 Contact angle measurements

Table 4.3 shows the results for the contact angle measurements; values are reported through the water phase. Heptane showed advancing and receding contact angles indicative of water-wet conditions (24.3°) to less water-wet during recession (57.4°). On the other hand, the field LNAPL showed advancing and receding contact angles indicative of water-wet conditions (26.2°) to NAPL-wet during recession (111.4°). It is interesting to note that the field LNAPL's receding angle suggests a wettability reversal for the imbibition phase of the P_c -S relationship. During imbibition, NAPL recedes through the pores while allowing water to re-wet the soil. These results indicate that water may difficulty re-wet the pores that previously had been in contact

with this particular field LNAPL. Similar findings have been observed in P_c -S relationships for other field LNAPLs where lower P_c pressures were required for water to successfully re-wet the pores (Said 2010; Drake 2011).

LNAPL	Contact angle	Standard deviation	95% CI	Type
Heptane	24.3	1.56	1.11	Advancing
	57.4	1.63	2.02	Receding
Field LNAPL	26.2	1.37	0.98	Advancing
	111.4	9.61	15.29	Receding

Table 4.3: Contact angle results.

Figure 4.4 and 4.5 show sample images for the measurement of contact angle. In figure 4.4a, heptane was injected through the syringe from the right hand side of the figure to the left (as indicated by the arrow); the drop advanced through the quartz plate in this direction and the advancing contact angle was measured. Likewise, the receding contact angle was measured as the drop was removed from the plate in the opposite direction (from left to right as observed in figure 4.4b).

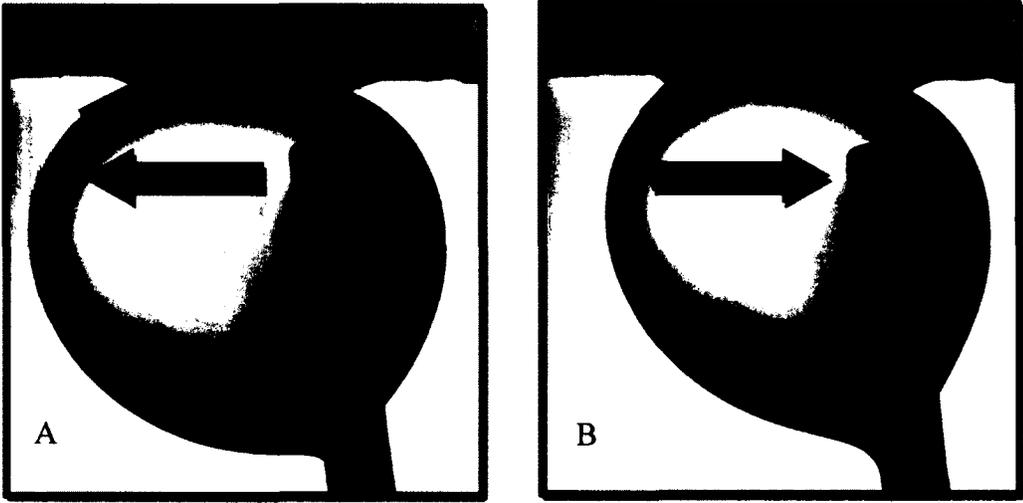


Figure 4.4: Heptane’s advancing (a) and receding (b) contact angle images.

In the case of the field LNAPL, notice the marked difference in the shape of the receding drop. In this set of images, the drop was injected originally from the left side (figure 4.5a) and the recession movement occurred from right to left (as observed in figure 4.5b). The receding drop “pinned” as it receded along the plate.

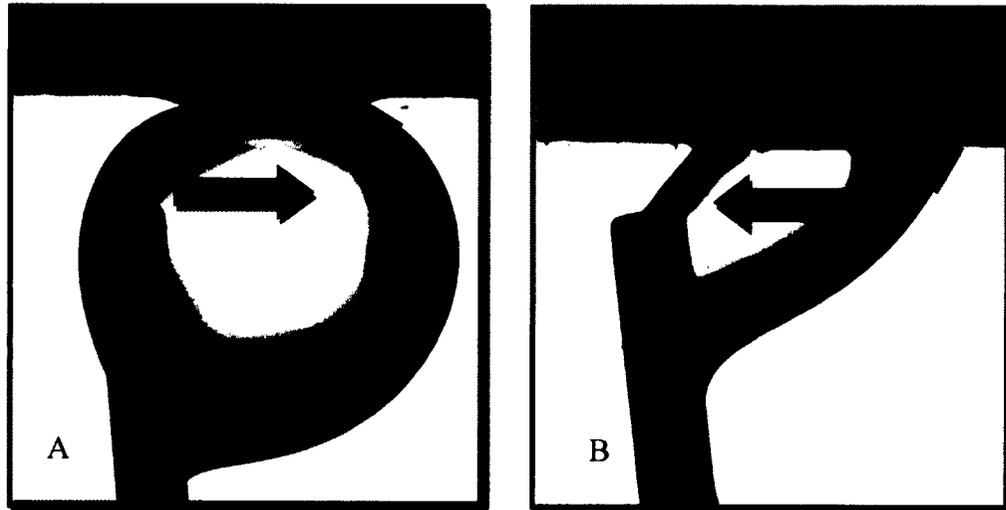


Figure 4.5: Field LNAPL's advancing (a) and receding (b) contact angle images.

This “pinning” phenomenon could be attributed to the heterogeneous nature of the field LNAPL which is composed by diverse refined oil products and most likely contains additives and surfactants. This may contribute to the differences observed in comparison to heptane which behaves as the ideal, lab-grade NAPL. The value obtained for the receding contact angle as well as the “pinning behaviour” of the field LNAPL are indications of the effects of non-ideal wettability.

4.3 Capillary pressure-saturation tests

As mentioned in Section 3.3, dry density and porosity were calculated for each P_c -S experiment. Table 4.4 includes the mean \pm standard deviation for these parameters. 10 measurements were recorded for each soil medium. A two-sample t-test (unequal

variance) was performed to established statistical significance (significant if t-value > t-critical with 95% confidence). It was found that there is statistical difference between the dry density and porosity of the clean sand and the 50/50 medium. Thus, in laboratory procedures and engineering calculations, these differences are virtually inexistent.

Parameter	Clean silica sand	50/50 sand	t-value	t-critical
ρ_d (g/cm ³)	1.68 ± 1.10E-02	1.70 ± 2.39E-02	3.07	2.16
n []	0.37 ± 4.17E-03	0.36 ± 9.03E-03	3.07	2.16

Table 4.4 Dry density and porosity for soil media used in the experiments

Capillary pressure-saturation test results are shown in figures 4.5 to 4.8. Each figure shows the results of five P_c -S experiments performed for each combination of tests as described in Section 3.3. The resulting data were fitted according to the van Genuchten model (van Genuchten 1980) and to a modified version of the van Genuchten model (Bradford and Leij 1995; Drake 2011). The van Genuchten model was used to fit the drainage data for all experiments according to the empirical equation:

$$S_w^{eff} = (1 + (\alpha P_c)^n)^{-m} \quad (4.1)$$

where S_w^{eff} is the effective water saturation and α, n, m are fitting parameters. m is often assumed as $(1 - 1/n)$. An optimization process or “least square fitting method” was carried out in order to obtain adequate values for the fitting parameters. Initially, S_w^{eff} was calculated from the experimental data (S_w^{eff} experimental) as:

$$S_w^{eff} \text{ experimental} = \frac{S_w - S_{wr}}{1 - S_{wr}} \quad (4.2)$$

and also from equation 4.1 (S_w^{eff} equation) assigning initial arbitrary fitting parameters.

Imbibition experimental results were fitted to the modified van Genuchten model. This model allows the fitting of both negative and positive capillary pressure data. Accordingly, this model incorporates fluid entrapment and is able to fit the changes in the shape of the wetting P_c - S curves due to non-ideal wettability. The empirical equation includes a shifting parameter (η) where:

$$S_w^{eff} = (1 + (\alpha(P_c + \eta))^n)^{-m} \quad (4.3)$$

The imbibition data were fitted using the same optimization approach as described before by changing the values of α , n , and η . The condition $P_c + \eta \geq 0$ must be satisfied for all values of P_c (Bradford and Leij 1996; Drake 2011).

4.3.1 P_c - S experiments on clean sand

Figure 4.6 and 4.7 correspond to the P_c - S experiments performed on clean sand for water/heptane and water/field LNAPL, respectively. Both P_c - S relationships show very low NAPL entry pressures and most of the drainage occurred at capillary pressures smaller than 6 cm of water. This behavior was expected and is characteristic of a homogeneous medium to coarse sand. There is a strong similarity between heptane and LNAPL P_c - S relationships which could be attributed to the small difference in their IFT values.

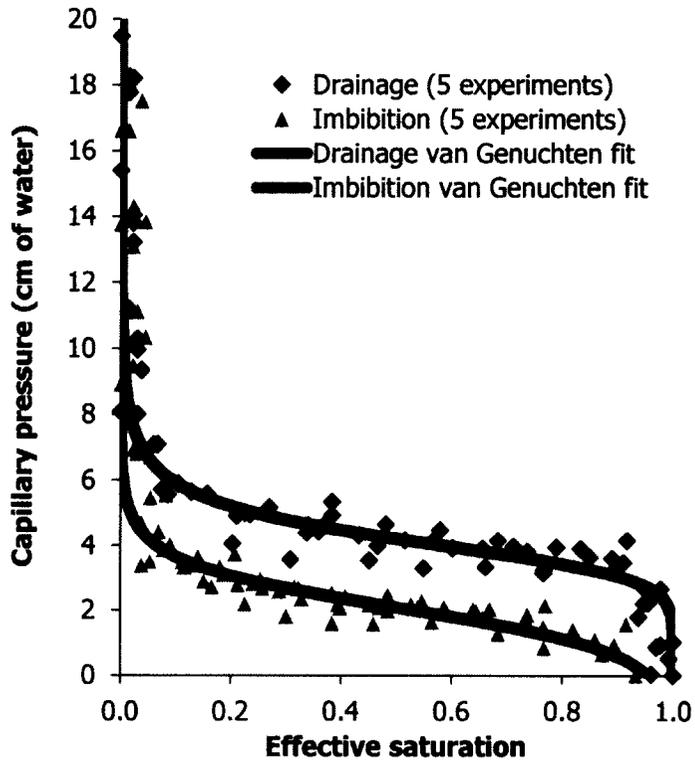


Figure 4.6: P_c - S relationship for clean sand water/heptane.

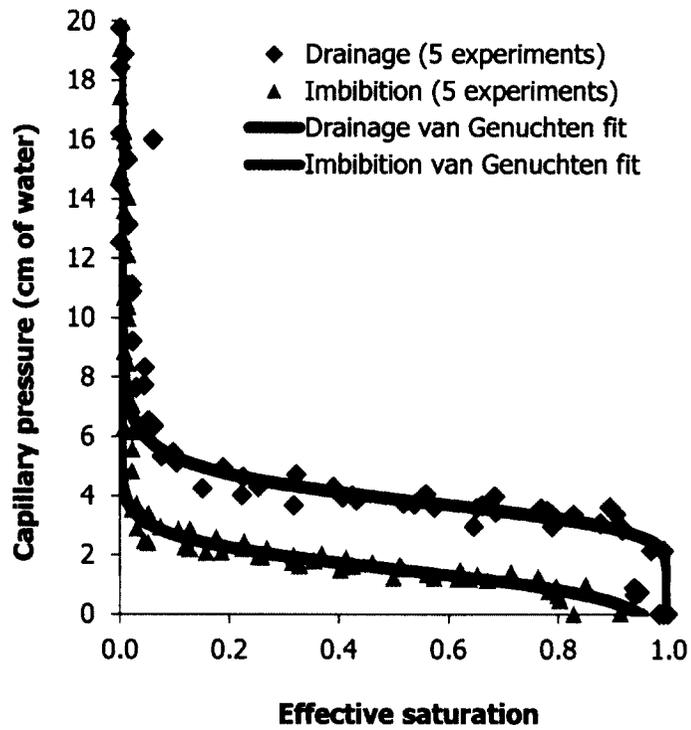


Figure 4.7: P_c - S relationship for clean sand water/field LNAPL.

Table 4.5 includes the mean values for the irreducible water phase saturation (S_{wr}), final water saturation after imbibition (S_{wf}), and entrapped NAPL saturation (S_{nwr}) along with the standard deviation and 95% confidence interval for the previous set of experiments. According to this table, similar irreducible water saturations were achieved for water-heptane (9.2%) and water-field LNAPL (8.7%). In contrast, lower entrapped NAPL saturations were achieved for the field LNAPL, 8.3 % vs. 15.6% for water-heptane.

Parameter	Water –heptane			Water - field LNAPL		
	S_{wr} (%)	S_{wf} (%)	S_{nwr} (%)	S_{wr} (%)	S_{wf} (%)	S_{nwr} (%)
Mean	9.2	84.4	15.6	8.7	91.7	8.3
Standard deviation	1.5	4.6	4.6	2.5	1.4	1.4
95% CI	1.8	5.7	5.7	3.0	1.7	1.7

Table 4.5: Water and NAPL saturations for P_c -S curves on clean sand.

Table 4.6 shows the resulting fitting parameters for the P_c -S curves on clean sand. In terms of goodness of fit, water-heptane data were found to have a correlation coefficient of 0.96 and 0.94 for drainage and imbibition, respectively. Likewise, water-field LNAPL data has a correlation coefficient of 0.98 both for drainage and imbibition.

Fitting parameter	Water-heptane		Water-field LNAPL	
	Drainage	Imbibition	Drainage	Imbibition
n	7.00	46.64	7.62	88.94
m	0.86	0.98	0.87	0.99
α	0.25	0.03	0.26	0.02
η	-	30.31	-	44.32
Correlation coefficient	0.96	0.94	0.98	0.98

Table 4.6: Fitting parameters for P_c -S curves on clean sand.

The van Genuchten and modified van Genuchten models were able to reproduce water-field LNAPL data more easily. In fact, water-field LNAPL data were found to be less variable between the experiments. This can be observed in figure 4.7 where data points follow a smoother curve, i.e. there is less fluctuation of individual points in comparison with the data for water-heptane. Water-heptane P_c -S tests were more sensitive to volumetric fluctuations in the LNAPL burettes as a result of evaporation.

Whenever P_c -S data for field NAPL products are absent, it is possible to scale the P_c -S curves for different fluid pairs by using the ratio of IFT of the fluids of interest, according to the Leverett scaling theory (Leverett 1941) where:

$$P_c^1 = P_c^2 * \frac{\gamma_1}{\gamma_2} \quad (4.5)$$

Equation 4.5 applies for different fluid pairs, i.e. water-heptane (1) and water-field LNAPL (2) when the porous medium remains unchanged. Figure 4.8 includes the P_c -S curves for water-heptane and water-field LNAPL as well as the scaled water-field LNAPL curve from the water-heptane curve according to:

$$P_c^{water-field LNAPL} = P_c^{water-heptane} * \frac{\gamma_{field LNAPL}}{\gamma_{heptane}} \quad (4.6)$$

Figure 4.8 confirms the strong similarity between the ideal fluid (heptane) and the non-ideal fluid (field LNAPL) P_c -S curves. Also, scaling from water-heptane data reproduces the imbibition section of the water-field LNAPL P_c -S curve very accurately as shown by the overlap of the van Genuchten fit and the scaled curve. On the other hand, the drainage curve was not reproduced so accurately; the scaled water-field LNAPL curve is slightly lower than the actual curve.

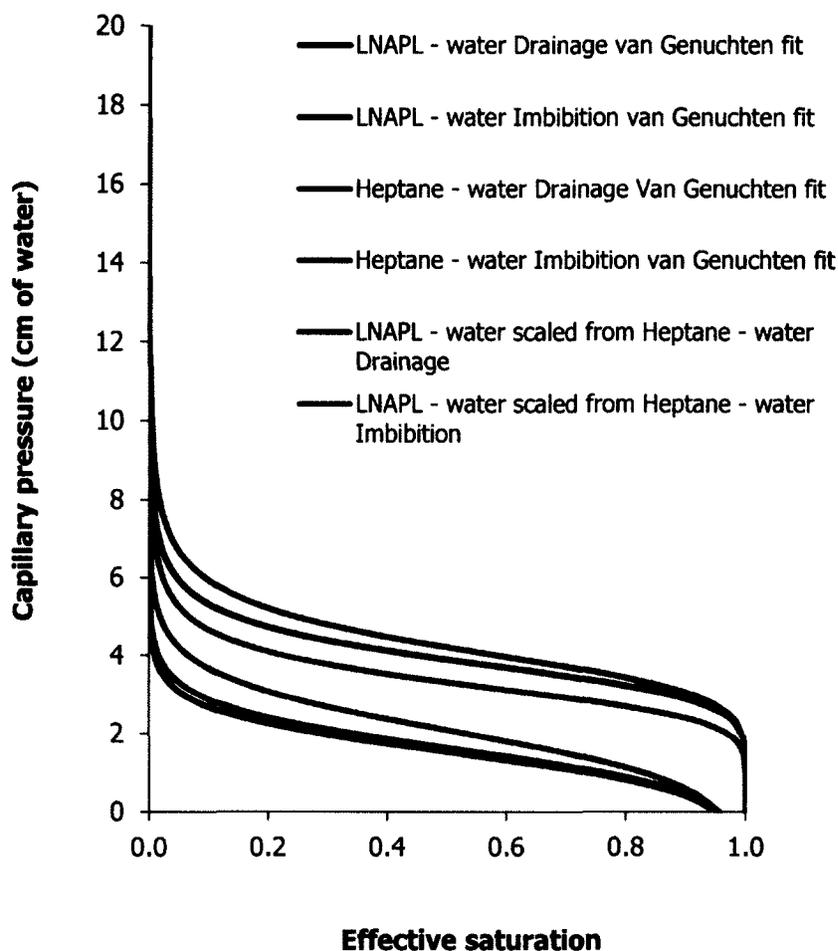


Figure 4.8: Water-heptane and water-field LNAPL fitted P_c -S curves and scaled water-field LNAPL P_c -S curves.

Overall, scaled P_c -S curves from water-heptane systems could be used to predict the behavior of this particular field LNAPL in different soil media. The receding contact angle results from Section 4.2 initially suggested that the field LNAPL had the potential to impart NAPL-wetting conditions on clean silica sand. Nonetheless, this was not observed in the P_c -S experiments. Drainage and imbibition curves for heptane and the field LNAPL are typical of water-wet conditions.

4.3.2 P_c -S experiments on 50% water-wet + 50% NAPL-wet sand

Results of P_c -S experiments on the fractionally-wet system are plotted in figure 4.9 and 4.10 and shown in tables 4.7 and 4.8. Drainage for both fluid pairs progresses in a similar fashion as observed in the previous section for clean sand. Nonetheless, the drainage curves are lower for the 50/50 medium. Imbibition does not follow the typical pathway observed for a water-wet medium. The presence of NAPL-wet grains impacted the wetting portion of the P_c -S curve and the curve appears to be shifted downwards as noted in previous studies (Bradford and Leij 1995; Said 2010; Drake 2011). According to table 4.7, mean irreducible water saturation values are very similar, 10.8 for water-heptane and 11.7 for water-field LNAPL. NAPL saturation at zero capillary pressure is very high for both fluid pairs and mean values are very close to each other, 54% for water-heptane and 55% for field LNAPL. In addition, there seems to be more variability for P_c -S data for the fractionally-wet medium. This is more evident in the water-heptane P_c -S curve. In fact, as observed in table 4.8, the correlation coefficient for water-heptane fitting parameters is very poor, 0.8 for drainage and 0.69 for imbibition.

Parameter	Water – heptane			Water - field LNAPL		
	S_{wr} (%)	S_{wf} (%)	S_{nr} (%)	S_{wr} (%)	S_{wf} (%)	S_{nr} (%)
Mean	10.8	46.2	53.8	11.7	45.2	54.8
Standard deviation	4.2	8.2	8.2	2.2	17.9	17.9
95% CI	5.2	10.1	10.1	2.8	22.2	22.2

Table 4.7: Water and NAPL saturations for P_c -S curves on 50/50 sand.

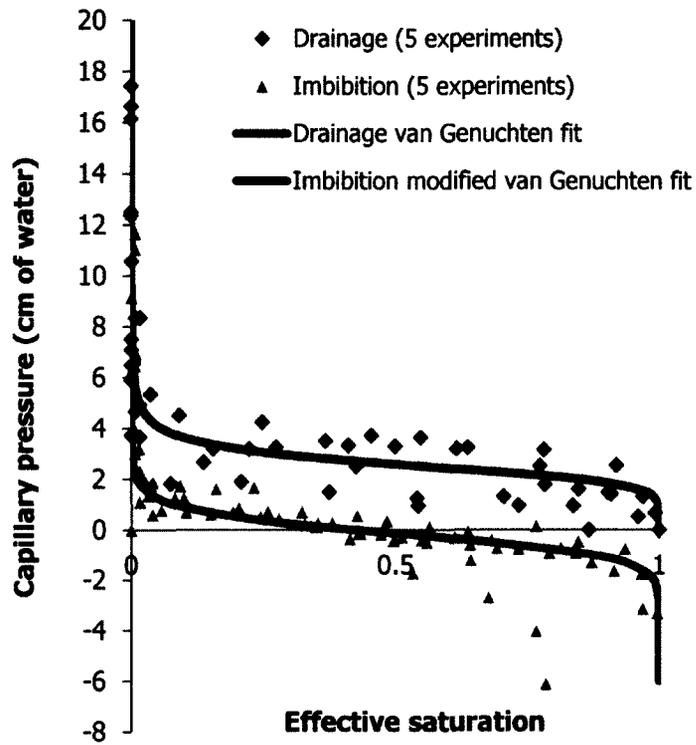


Figure 4.9: P_c - S relationship for 50/50 sand water/heptane.

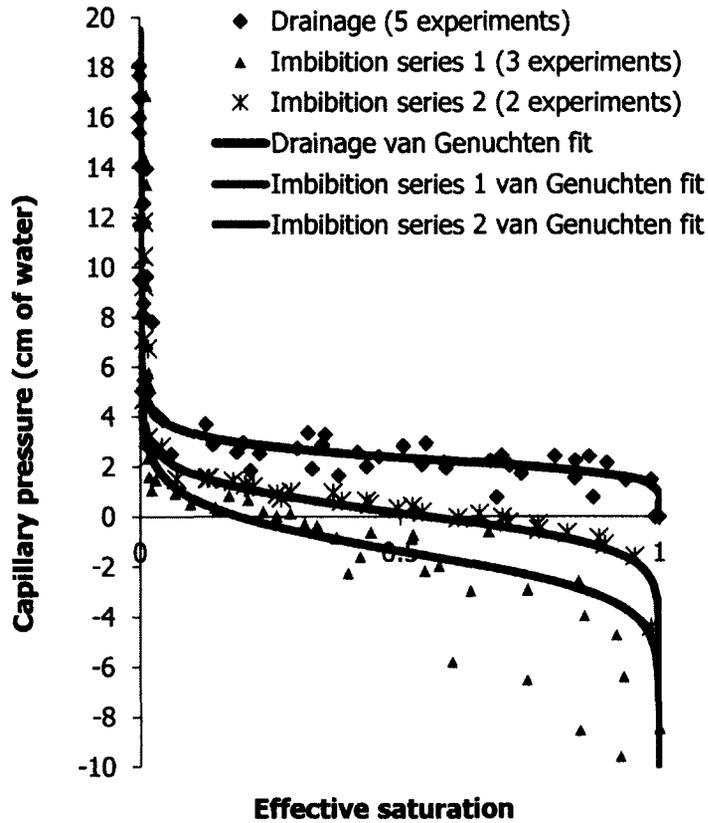


Figure 4.10: P_c - S relationship for 50/50 sand water/field LNAPL.

Fitting parameter	Water-heptane		Water-field LNAPL		
	Drainage	Imbibition	Drainage	Imbibition series 1	Imbibition series 2
n	7.00	30.00	7.00	30.00	42.00
m	0.86	0.97	0.86	0.97	0.98
α	0.4	0.08	0.44	0.04	0.04
η	-	13.50	-	28.44	28.44
Correlation coefficient	0.8	0.69	0.88	0.95	0.99

Table 4.8: Fitting parameters for P_c -S curves on 50/50 sand.

Imbibition P_c -S data for water-field LNAPL were fitted to two different curves as overall data points suggested two probable wetting pathways. However, this was not strongly observed for water-heptane, although there are indeed few points that diverge from the single fitted wetting pathway. For the water/field LNAPL data, the wetting pathway “Imbibition series 1” closely resembles the wetting curve for water/heptane. The second fitted curve, “Imbibition series 2” is even lower compared both to “Imbibition series 1” and to the clean sand medium. In contrast with the water-wet clean sand, the studied fractional system seems to be more difficult to characterize. The variability in P_c -S data might result from differences in pore distribution of NAPL-wet mineral grains even though all experiments contained the same proportion of water to NAPL-wet grains. Also, heptane’s very high volatility impacts the precise calculation of P_c , especially during drainage. Evaporation was monitored throughout the experiments but was found to be variable from one set-up to another in the same period of time.

The introduction of the NAPL-wet media aimed to represent field scenarios where some of the mineral grains might have reversed their initial wettability. These results

confirm that the introduction of NAPL-wet sand fractions (chemically treated) can effectively represent situations of non-ideal wettability as the impacts of the wettability reversal were clearly observed on the P_c -S relationships for both fluids.

4.4 Column experiments

Sections 4.4.1 to 4.4.5 present the results for the column experiments performed to investigate the influence of wettability on the removal of entrapped LNAPLs via surfactant flushing.

4.4.1 Preliminary tests

During preliminary tests, columns were flushed at a rate of approximately 10ml/min. After the LNAPL spill had occurred, 2 PV of water were flushed through the column to remove the bulk free phase LNAPL. After, 10 PV of SDBS solution were flushed to recover entrapped LNAPL. This approach is similar to the technique some researchers refer to as “secondary recovery” (Chevalier 2000). Two replicates were performed for water-diesel and water-heptane. Another column was set up and flushed with 10 PV of water only. Field diesel and heptane were used for these experiments because they were available at the time and general column procedures were being tested. Mean entrapped saturations after the water-flood ($\overline{S_{nr}^{wf}}$) and surfactant-flood ($\overline{S_{nr}^{sf}}$) were calculated. The difference among them was considered as the enhanced removed entrapped saturation ($R - S_{nr}$). The % removed LNAPL (R_{LNAPL}) was also calculated as:

$$R_{LNAPL} = \frac{\text{volume of removed LNAPL}}{\text{volume of entrapped LNAPL after water-flood}} * 100(4.7)$$

R_{LNAPL} is an indication of the amount of free phase product that was removed relative to the amount that was entrapped in the columns after the water-flood. Results of preliminary tests are shown in table 4.9⁶.

Experiment	$\overline{S_{nr}^{wf}}(\%)$	$\overline{S_{nr}^{sf}}(\%)$	$R - S_{nr}(\%)$	$R_{LNAPL}(\%)$
Clean sand water-diesel	18	15	3	17
Clean sand water-heptane	23	18	5	23
Clean sand water-heptane (water-flood only)	26	-	-	-

Table 4.9: Results for preliminary column tests.

As observed in table 4.9, removal of free phase LNAPL was very small, 3 and 5% reduction in LNAPL saturation and 17 and 23% LNAPL removal for diesel and heptane columns, respectively. These results were thought to have been influenced by the velocity at which the flushing proceeded which corresponded to a Darcy velocity of approximately 50cm/h. It is possible that the rate at which the flushing proceeded was too high to allow for adequate interaction between the entrapped NAPL and the surfactant solution; consequently, the mobilization via IFT reduction might not have occurred effectively. Also, these results suggested that secondary recovery might not significantly reduce the amount of entrapped LNAPL. Once the major portion of LNAPL is removed from the soil, the surfactant solution might have more difficulty in targeting areas of reduced LNAPL accumulation since the bulk free phase LNAPL was removed by the water-flood.

⁶Calculated values have been individually rounded to facilitate observation and analysis but calculations were carried out with original values.

According to the previous findings, further column tests with heptane and the field LNAPL were performed at a flow-rate of 1 ml/min. This flow-rate translates into a Darcy velocity of 5 cm/h which is more representative of typical water-flood conditions. Also, the primary recovery approach was followed in order to improve the overall efficiency of the surfactant flush. Nonetheless, the primary objective of this research is to provide understanding on the effects of non-ideal wettability during surfactant flushing regardless of the actual values of LNAPL removal.

4.4.2 Column tests with SDBS (2-hour contact period)

As mentioned in Section 3.4, five replicates of each type of experiment were performed during the first round of column tests with SDBS, for a total of 40 column experiments. This number of replicates was selected in order to obtain a representative mean value of entrapped saturation also allowing the calculation of statistical significance using the two-sample t-test. This t-test compared the mean entrapped saturation of the surfactant-flooded columns with the water-flooded columns (from each type of experiment) to determine if their respective population's mean could actually be the same. In other words, this t-test gives information on the significance of the difference between the samples' mean. Table 4.10 includes the results for the column tests with SDBS with a contact period of 2 hours.

As observed in table 4.9 below, $\overline{S_{nr}^{wf}}$ is very similar for all experiments ranging from 17 to 21%. Likewise, $\overline{S_{nr}^{sf}}$ ranges from 13 to 18%. The t-test reveals that the reduction of S_{nr} as a result of the surfactant-flood is only significant for the 50/50 medium exposed to heptane where NAPL removal is close to 40%. In other words, for the rest

of the experiments, these results suggest that the surfactant does not significantly reduce S_{nr} . SDBS was more effective in reducing heptane in the 50/50 medium perhaps due to the absence of additives and other surfactants in comparison to the field LNAPL. In the absence of polar groups, non-polar heptane might more easily come into contact with the non-polar head of the surfactant solution effectively reducing surface tension and promoting mobilization.

Experiment	$\overline{S_{nr}^{wf}}$ (%)	$\overline{S_{nr}^{sf}}$ (%)	$R - S_{nr}$ (%)	R_{LNAPL} (%)	t-value	t-critical value	S ⁷
Clean sand & heptane	17	16	2	9	0.94	2.31	No
Clean sand & field LNAPL	21	18	3	16	0.88	2.45	No
50/50 sand & heptane	21	13	8	38	2.46	2.45	Yes
50/50 sand & field LNAPL	17	15	3	15	1.74	2.30	No

Table 4.10: Results for column tests with SDBS, 2-hour contact period.

In terms of saturation, the 50/50 medium was expected to have higher S_{nr}^{wf} due to the presence of NAPL-wet media. T-tests performed among the fluid pairs (i.e. clean sand and 50/50 sand exposed to heptane) confirm that there is no statistical difference between their $\overline{S_{nr}^{wf}}$ values. Section 4.4.9 will present a conceptual model on the phenomena that might be occurring at the pore scale in an attempt to explain the previous finding.

⁷ S stands for statistical significance.

4.4.3 Column tests with SDBS (5-day contact period)

Columns in contact with LNAPL for 5 days were left undisturbed for this period of time and the water-flooding or surfactant-flooding was performed afterwards. A total of 16 experiments were performed (eight for both water-flood and surfactant-flood conditions). Table 4.11 shows the results for these tests. As detailed in table 4.11, $\overline{S_{nr}^{wf}}$ is very similar for all experiments ranging from 17 to 21%. $\overline{S_{nr}^{sf}}$ ranges from 11 to 15%. Overall, results indicate that LNAPL removal with surfactants was favoured by the increase in contact time. In comparison with the 2-hour contact time experiments, the entrapped field LNAPL was removed more efficiently. However, this removal seems to be independent of the presence of NAPL-wet media. Also, it is of interest to note that the ideal scenario (clean sand and heptane) performs poorly with SDBS independently of contact time.

Experiment	$\overline{S_{nr}^{wf}}$ (%)	$\overline{S_{nr}^{sf}}$ (%)	$R - S_{nr}$ (%)	R_{LNAPL} (%)
Clean sand & heptane	17	15	1	9
Clean sand & field LNAPL	18	11	7	39
50/50 sand & heptane	17	11	6	37
50/50 sand & field LNAPL	21	14	7	33

Table 4.11: Results for column tests with SDBS, 5-day contact period.

4.4.4 Column tests with the field site surfactant (2-hour contact period)

Tests with the field-site surfactant were of particular interest to draw conclusions on both its efficiency and wettability interactions, given the fact that it is being currently used at several contaminated sites in Colombia. Each type of experiment was conducted by duplicate for a total of 16 experiments (8 for water-flood and 8 for surfactant-flood conditions). Table 4.12 includes the results for this particular group

of experiments. Each type of experiment was conducted by duplicate, a total of eight experiments for water-flood and eight experiments for surfactant-flood conditions. $\overline{S_{nr}^{wf}}$ ranges from 13 to 24% and $\overline{S_{nr}^{sf}}$ from 12 to 19%. LNAPL removal seems to be of importance for clean sand exposed to heptane and 50/50 sand exposed to the field LNAPL. Nonetheless, values of $\overline{S_{nr}^{wf}}$ for this set of experiments are more variable in comparison to the previous experiments, with a high of 24% entrapped saturation for clean sand and heptane and a low of 13% for the 50/50 medium exposed to heptane. There is no sufficient evidence to believe that entrapped saturation might vary so greatly among the same type of columns. This in turn suggests that removed LNAPL results might be impacted by this variability, over and underestimating the values for clean sand with heptane and the 50/50 medium with heptane. Overall, LNAPL removal seems to be very small but the efficiency of the field-site surfactant might be underrated given the low $\overline{S_{nr}^{wf}}$ values reported in the table. Section 4.4.6 will present removed LNAPL results based on the average entrapped saturation calculated for all experiments which is thought to be a more reliable comparison approach (refer to section 4.4.6 for more details).

Experiment	$\overline{S_{nr}^{wf}}$ (%)	$\overline{S_{nr}^{sf}}$ (%)	$R - S_{nr}$ (%)	R_{LNAPL} (%)
Clean sand & heptane	24	19	6	24
Clean sand & field LNAPL	15	14	1	9
50/50 sand & heptane	13	12	1	11
50/50 sand & field LNAPL	17	14	3	17

Table 4.12: Results for column tests with the field site surfactant, 2-hour contact period.

4.4.5 Column tests with the field site surfactant (5-day contact period)

Table 4.13 includes the results for the column tests performed with the field site surfactant with a contact time of 5 days. A total of 16 experiments were performed (eight for both water-flood and surfactant-flood conditions). $\overline{S_{nr}^{wf}}$ ranges from 15 to 20% and $\overline{S_{nr}^{sf}}$ from 11 to 16%. Removed LNAPL results are analogous to the ones obtained for SDBS (5 days contact time) where LNAPL removal increased with prolonged contact time. This strongly suggests that for this particular homogeneous medium there is an important mechanism at the pore scale governing LNAPL removal. Nevertheless, for the experiments performed in this study, wettability seems to be of importance for the ideal LNAPL (heptane) but has little influence on the field LNAPL.

Experiment	$\overline{S_{nr}^{wf}}$ (%)	$\overline{S_{nr}^{sf}}$ (%)	$R - S_{nr}$ (%)	R_{LNAPL} (%)
Cleansand&heptane	15	16	0	0
Cleansand&field LNAPL	17	12	5	29
50/50 sand&heptane	20	11	9	46
50/50 sand&field LNAPL	16	11	4	27

Table 4.13: Results for column tests with the field site surfactant, 5-day contact period.

4.4.6 Analysis of entrapped saturation results

According to the previous results, entrapped NAPL saturations after water-flooding seem to be similar and independent of contact time. In an attempt to verify this finding, data for each particular type of column (i.e. clean sand and heptane, clean sand and LNAPL, 50/50 sand and LNAPL, and 50/50 sand and field LNAPL) was combined to calculate $\overline{S_{nr}^{wf}}$. Therefore, data from individual replicates, performed at different moments in time, were combined and treated as a group. In total, 11 readings

were used in the calculations for each experiment type (5 readings from the experiments with SDBS with a 2-hour contact time and 2 readings for the three subsequent experiments, i.e. SDBS5 days, field surfactant 2-hour, field surfactant 5 days). Table 4.14 includes $\overline{S_{nr}^{wf}}$ for this data, as well as the standard deviation and 95% confidence interval.

Type of experiment	Clean sand & heptane	Clean sand & field LNAPL	50/50 sand & heptane	50/50 sand & field LNAPL
Mean	18.91	19.45	19.64	18.36
STD	3.78	3.56	5.73	2.46
95% CI	2.54	2.39	3.85	1.65

Table 4.14: Mean entrapped saturations for column test experiments.

According to table 4.14, $\overline{S_{nr}^{wf}}$ values are almost the same and there is no statistical difference among these values. This was confirmed by performing two-sample t-tests between sample pairs. This fact can also be observed clearly in figure 4.11. In the figure, the mean value has been plotted and the bar extends upwards or downwards representing the \pm 95% confidence interval. In general, data from columns exposed to heptane presents the highest variability. In fact, P_c -S data variability was also very high for experiments performed on heptane, as discussed in Section 4.3.

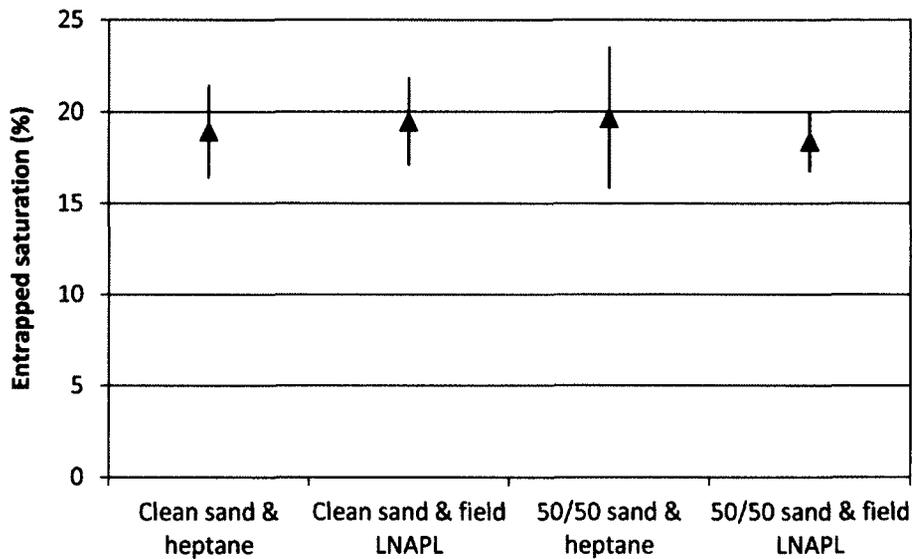


Figure 4.11: Mean entrapped saturation for column tests \pm 95% confidence interval.

For the porous medium being studied, it can be concluded that entrapped saturation is independent both of the type of LNAPL and the wettability conditions under investigation. This finding is of great interest and contrary to expected results for the following reasons:

- The complex nature of the field LNAPL (presence of additives, surfactants, and polar compounds normally found in refined products) was thought to have contributed to the entrapped saturation due to adsorption at the soil surface (Powers and Tamblin 1995; Zheng and Powers 2003) and interactions with the mineral grains (Lord et al. 2000).
- The presence of NAPL-wet media was thought to have favored the entrapment of NAPLs based on the hypothesis that NAPL-wet mineral grains could have become coated with NAPL instead of water after a prolonged exposure. This has been previously indicated by Gvirtzman and Roberts (1991) and Abriola and Bradford (1998). The NAPL then would be able to displace the water film, residing in the

saturated soil both as ganglia and films, increasing the amount of NAPL accumulation.

4.4.7 Results for LNAPL removal

Removed entrapped saturations were recalculated based on the mean entrapped saturations found in table 4.14 for each type of column experiment. This approach is thought to be more reliable and representative of actual removal accomplished by the surfactant solutions. Figure 4.11 shows the corresponding results for the % removed entrapped LNAPL.

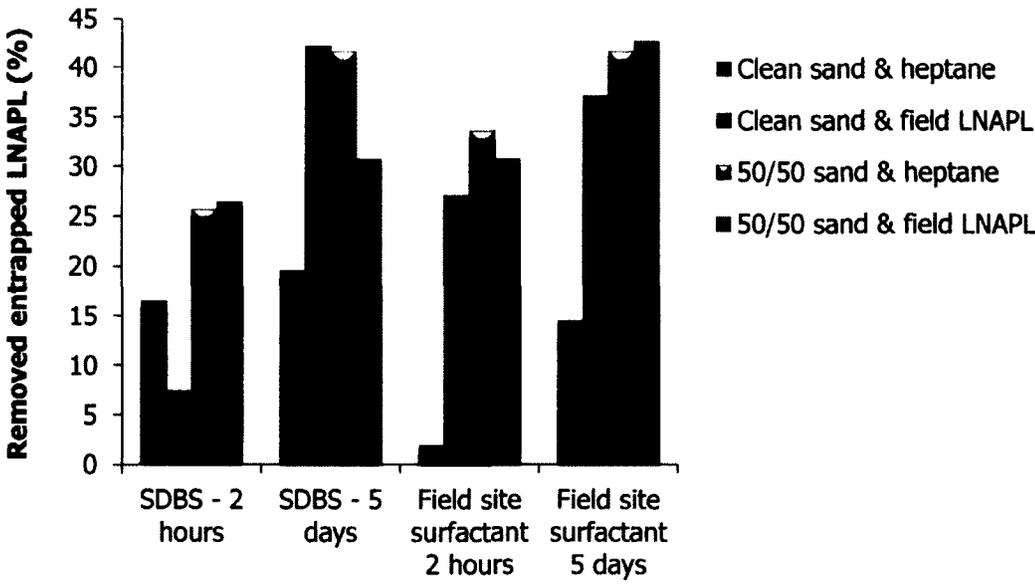


Figure 4.12: Results for LNAPL removal.

According to figure 4.12, for:

- Clean sand and heptane - ideal scenario: removal of entrapped LNAPL by mobilization was always less than 20%. In fact, the ideal scenario seems to be the

worst case scenario for removal with the anionic surfactants being tested. The field site surfactant (2 hour contact period) was the least efficient.

- Clean sand and field LNAPL: entrapped field LNAPL removal was greater than 25%, except when the flushing was performed with SDBS and contact time was 2 hours. In comparison with the ideal scenario, field LNAPL was removed more efficiently. Taking into account that entrapment for heptane and the field LNAPL was virtually the same, the complex nature of the field LNAPL might have surprisingly contributed to the enhanced removal as a result of LNAPL-surfactant solution interactions.
- 50% NAPL-wet + 50% water-wet sand and heptane: entrapped heptane removal was greater than 25% for all scenarios, with a high of 40% when the surfactants were flushed after 5 days. NAPL-wet media seems to have positively contributed to NAPL removal.
- 50% NAPL-wet + 50% water-wet sand and field LNAPL -non-ideal wettability: entrapped LNAPL removal was greater than 25% for all scenarios. The highest removal was obtained with the field site surfactant after 5 days.

Hugaboom and Powers (2002) performed similar column test experiments with a DNAPL as the contaminant source. Their results showed that fractionally-wet to water-wet systems had the lowest remaining NAPL saturations but the highest NAPL recovery efficiencies after a water-flood. In comparison to this study, entrapped NAPL saturations after the water-flood between the water-wet and the fractionally-wet systems are not statistically different but the highest recovery efficiencies after the surfactant-flood were indeed achieved in the fractionally-wet systems.

4.4.8 Gas chromatography analyses

Results for the GC analyses performed on liquid samples are included in table 4.15. For the field LNAPL, the GC chromatogram was obtained. The chromatogram (included in Appendix B) revealed that the field LNAPL mostly contains hydrocarbons chains between C5 and C10. This is evident by the intensity of the peaks in this particular range. Some larger chains from C10 – C16 might be present in smaller quantities. This leads to the conclusion that the field LNAPL sample might correspond to a gasoline. Gasoline typically contains hydrocarbon chains ranging from C5 to C12.

As shown in table 4.15, both surfactant samples report hydrocarbon concentrations very similar to the solubility limit of the field LNAPL in water. The solubility of the field LNAPL was found to be 27300 µg/L. As seen in the table, most of the mass corresponds to the C6 – C10 range which is consistent with previous observations in the field LNAPL chromatogram. The surfactant solution with SDBS and the field site surfactant reported dissolved hydrocarbons (C6 to C16) up to a value of 25600 µg/L and 27900 µg/L, respectively. The surfactant solutions reported detectable values for the ranges C10 – C16 and C16 – C34. Previous to the GC analyses, the samples were treated to eliminate the polar compounds associated with the surfactants. However, small remnants of the surfactants might have been present in the liquid matrix and further appeared in the C10 – C34 range. SDBS for instance, is composed by C12 hydrocarbon chains ($\text{CH}_3(\text{CH}_2)_{11}\text{C}_6\text{H}_4\text{SO}_3\text{Na}$). In general, these results confirm that LNAPL removal by enhanced solubilization was negligible.

Parameter	Units	MDL ⁸	Sample		
			Water Equilibrated with Field LNAPL	SDBS + Dissolved LNAPL	Field Surfactant + Dissolved LNAPL
<i>Hydrocarbons</i>					
F1 PHCs (C6-C10)	µg/L	25	27000	25600	26600
F2 PHCs (C10-C16)	µg/L	100	339	940	1260
F3 PHCs (C16-C34)	µg/L	100	ND ⁹ (100)	940	1260
F4 PHCs (C34-C50)	µg/L	100	ND (100)	ND (100)	ND (100)
F1 + F2 PHCs	µg/L	1350	27300	26500	27900
F3 + F4 PHCs	µg/L	200	ND (200)	940	1260

Table 4.15: Results for GC analyses performed on liquid samples.

4.4.9 Summary and significance of results and conceptual model

This section presents a summary of the main findings obtained from the column test experiments and attempts to provide a hypothesis to explain the observed results. Accordingly, column experiments described in Section 4.4 indicated the following main points:

- *Heptane and field LNAPL entrapment in soil columns was similar and independent of fluid type, initial wettability conditions and contact time:* in order to explain this phenomenon, two hypothesis are presented:

Hypothesis 1: NAPL resided in the pore space as ganglia in both the clean and fractionally-wet systems: observations during column experiments strongly suggest that this might have occurred due to two important factors: contact order theory and NAPL distribution in the pore space. In fact, contact order might be a determinant factor in NAPL distribution for the homogeneous medium being studied. Since the

⁸ MDL = minimum detectable limit

⁹ ND = non-detectable

soil medium was homogeneous, entrapped LNAPL was more likely to be found as blobs or ganglia inside the pore space. This condition might prevail for water-wet media where films of water coat the soil grains (Abriola and Bradford 1998). The 50/50 medium contained NAPL-wet grains that were expected to impact fluid entrapment. Nonetheless, the fractionally-wet medium might have behaved as water-wet too because it was flushed with CO₂ followed by 10 pore volumes of water to ensure 100% water saturation prior to the introduction of LNAPL. This saturation process is thought to have reversed the wettability of the medium to water-wet. Ryder and Demond (2008) observed the same phenomena in their studies and used the term “wettability hysteresis”. During this study’s procedures, water-wet columns were saturated homogeneously throughout and the water front advanced continuously wetting the entire pore space as shown in figure 4.13, column A. On the other hand, in the fractionally-wet columns, water advanced by-passing the NAPL-wet mineral grains, as shown in figure 4.13, column B. However, after 2 to 3 PV, the entire pore space was gradually saturated by water, as shown in figure 4.13, column C. Since the water eventually coated all the mineral grains, even the original NAPL-wet grains, the entire medium behaved as water-wet and as a result the NAPL must have resided as ganglia in the center of pores as originally described by Abriola and Bradford (1998) and shown in figure 2.1 in Section 2.3.2. As a consequence, entrapped NAPL saturations were very similar. This hypothesis also explains why contact time had no further influence on entrapment. Similarities in density and IFT between the field LNAPL and heptane might have also contributed to this occurrence.

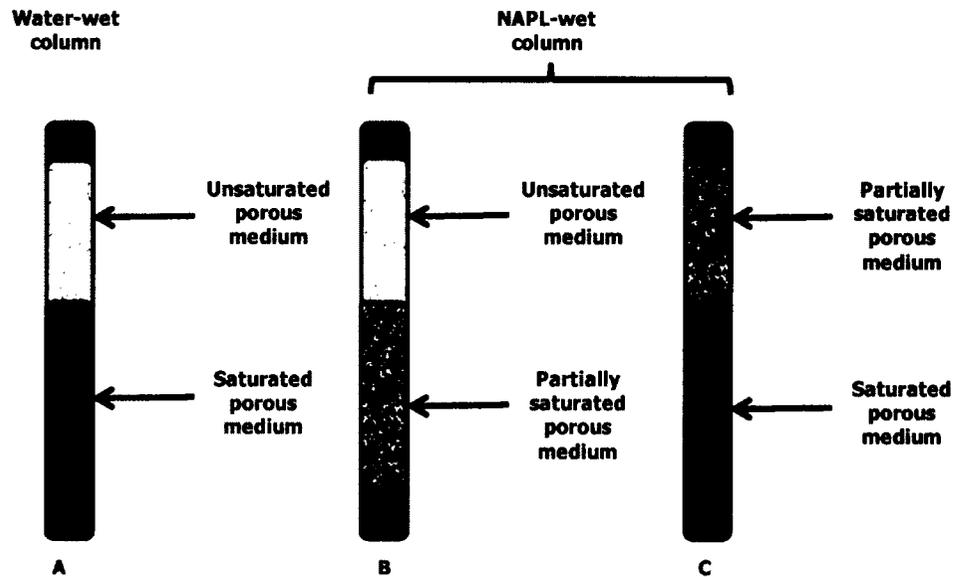


Figure 4.13: Schematic of column test during saturation.

Hypothesis 2: Entrapped NAPL saturations were similar but NAPL redistribution occurred in the fractionally-wet columns: Abriola and Bradford (1998) postulated that NAPL-wet mineral grains in a fractionally-wet saturated medium could become coated by NAPL. This would occur after continuous exposure to NAPLs where pore scale interactions could promote the displacement of the water film that coats the grains. These interactions could arise for instance due to changes in aqueous chemistry as a result of contaminant dissolution, presence of additives, bases, and polar compounds (Powers et al. 1996), composition of the solid surface (Ryder and Demond 1998), and pore-scale heterogeneities (Aggelopoulos and Tsakiroglou2008), among others. For the column tests conducted, it is possible that NAPL-wet grains were originally coated by water but displacement of the water film occurred and entrapped NAPL was redistributed, residing both as ganglia and films. If NAPL resided both as ganglia and films, NAPL interfacial area increases. When columns were water-flooded, water was then able to mobilize similar amounts of NAPL in both systems resulting in similar entrapped saturations after the water-flood.

In fact, Al-Raoush (2009) observed that fractionally-wet systems had actually less NAPL entrapment than water-wet systems. For this homogeneous system, it is also possible that NAPL residing as films around NAPL-wet grains increases the overall saturation in the same range of variation as the entrapped saturation. According to table 4.14, this range lies between 2.5 to 6%.

▪ ***Entrapped LNAPL removal was higher in fractionally-wet media:*** this phenomenon can be explained by recalling the mechanisms that promote mobilization as a result of interfacial tension reduction. According to the second hypothesis presented above, when NAPL is distributed both as ganglia at the center of pores and films (around NAPL-wet grains) in fractionally-wet systems, NAPL interfacial area is higher. Recall, that IFT reduction is a surface phenomenon that occurs when fluid surfaces come into effective contact. Because fractionally-wet systems may contain higher NAPL interfacial area (Al-Raoush 2009; Gvirtzman and Roberts 1991), the surfactant solution encounters more available surfaces for an effective IFT reduction. In other words, the phenomenon described by Rosen (1989) where hydrophobic or non-polar surfaces must come into contact to reduce IFT is favored by the increase in NAPL-surfactant solution interfacial area, contributing to LNAPL mobilization.

▪ ***Entrapped LNAPL removal was higher after 5 days of contact time:*** contact time was expected to increase fluid entrapment causing the surfactant flush efficiency to be enhanced. Fluid entrapment did not increase but the surfactant solution was able to reduce entrapment more noticeably in columns that were exposed to the NAPL for 5 days. If NAPL redistribution in a saturated medium due to pore scale interactions is considered as a time-dependant process, as time increases, NAPL could potentially

continue to redistribute itself around NAPL-wet grains and consequently NAPL-solution interfacial area increases, enhancing LNAPL mobilization.

- *Fractional wettability is believed to have a greater impact on surfactant flushed columns previously exposed to heptane:* for the “ideal lab-grade NAPL”, fractionally-wet columns reported the highest removal in all the scenarios studied. In contrast, field LNAPL removal in the fractionally-wet system was appreciably higher only for SDBS and 2 hours of contact time. It could be hypothesized that NAPL redistribution also occurred for clean sand columns exposed to the field LNAPL. Recall, that visual wettability tests and contact angle measurements indicated that the field LNAPL was able to impart NAPL-wetting conditions on clean silica sand. Hence, if fractionally-wet conditions were established, the surfactant flushing would yield similar NAPL recovery results for the field NAPL in clean and fractionally-wet columns. In any case, there might be other factors to be studied that might be responsible for this phenomenon.

In summary, for the column tests performed, NAPL distribution in the pore space was likely a critical factor for the removal of entrapped NAPL. Based on the author’s knowledge, observations, and findings, the hypothesis of NAPL redistribution provides a feasible explanation for the column test findings. Nonetheless, pore scale studies should be performed to confirm and provide more insight on this matter. In addition to pore scale studies, it is of critical importance to test field soils and field LNAPLs to more accurately predict wettability effects on entrapped NAPL recovery by surfactant flushing.

5. CONCLUSIONS

5.1 Conclusions

Visual wettability tests were initially able to indicate that the field LNAPL could impart non-ideal wetting behavior on dry clean silica sand. Furthermore, contact angle measurements indicated the possibility of a “wetting reversal” where the test sand could behave as NAPL-wet during imbibition. Overall, these results strongly suggest that non-ideal wettability may be present when dealing with complex field NAPL products.

The interfacial tension between heptane and the field LNAPL with water was effectively reduced by a quantity greater than 30 dynes/cm with a surfactant concentration of 0.5 g/L. SDBS and the field site surfactant were found to have similar IFT reduction potential for both LNAPLs. Hence, comparison among them was possible in further stages of the investigation.

P_c -S experiments for both LNAPLs on clean sand were characteristic of water-wet conditions. Even though contact angle measurements had suggested a possible wettability reversal for the field LNAPL, this was not confirmed by the P_c -S tests. However, although the field LNAPL itself was not able to impart NAPL-wet conditions, this can't be generalized for other types of media or for field soils. The porous media used for this study was homogeneous and contained only sand particles. The presence of other minerals and/or soil fractions as well as pore structure heterogeneity (e.g. clay, silt, etc.) may contribute to wettability alterations (Combes et al. 1998; Bauters et al. 2000; O'Carroll et al. 2004). Hence, non-ideal wettability may

result from a combination of factors including pore structure heterogeneity, fluid characteristics, contact time and contact order. Non-ideal wettability can be represented by introducing NAPL-treated soil fractions. Results of P_c -S experiments on the mixed wettability medium showed consistent findings with previous studies (Said 2010, Drake 2011). Non-ideal wettability was observed to impact the wetting section of the P_c -S curves.

Column test experiments indicated that fluid entrapment was consistent and independent of fluid type, contact time and the wettability conditions studied. Nonetheless, this is true for the silica sand being studied and is thought to be different for heterogeneous media with more complex pore structure. Also, contact order might be an important factor for fluid entrapment causing “wettability hysteresis” and changes in entrapped saturations. Despite fluid entrapment, tests on fractionally-wet columns resulted in higher LNAPL removal. It is hypothesized that the presence of NAPL-wet mineral grains favours pore scale interactions causing NAPL redistribution and increasing NAPL-surfactant solution interfacial areas. This in turn might benefit the overall mechanisms of IFT reduction. Also, contact time was found to contribute to LNAPL removal, especially for the field LNAPL. Overall, non-ideal wettability played a positive role in LNAPL removal for the fractionally-wet homogeneous medium under study.

A fraction of the entrapped LNAPL was successfully removed by mobilization. LNAPL removal for non-ideal scenarios was very important considering that surfactant concentrations were very low and that entrapped LNAPL is difficult to

remove by traditional technologies. The removal of the entrapped “ideal lab-grade” fluid from fractionally-wet columns was enhanced when using the surfactant solutions. The removal of entrapped field LNAPL was enhanced by the use of surfactants in both the water-wet and the fractionally-wet media. Even though the field LNAPL is complex in nature, there is high prospective for its removal using surfactants. The field-site surfactant was found to have a superior performance in comparison to SDBS. This suggests a great potential for field site remediation applications.

In general, results for the “non-ideal wettability” scenario suggest that increasing complexity, i.e. the introduction of fractional wettability and the field LNAPL, contributed positively to entrapped NAPL removal. Nevertheless, to assess the effectiveness of entrapped NAPL re-mobilization by surfactant flushing, field soils and field NAPLs should be tested in combination.

This research provides an important reference for future work on the influence of non-ideal wettability during soil remediation. Considering that surfactants are widely used to remove LNAPLs and perform site clean-up, it is very important to continue to investigate the role that wettability plays during LNAPL removal. This is of key significance because there is wide range of field LNAPLs and field soils to be remediated and numerous surfactant products are available.

5.2 Recommendations

Heptane was found to be useful as the lab-grade LNAPL. It is a good substitute for common field LNAPLs such as gasoline or diesel. Nonetheless, it is very volatile and must be carefully monitored during experiments. Thus, other lab-grade LNAPLs could be used as base case products (e.g. decane, dodecane, etc.) provided that they adequately represent the conditions of study.

To further investigate “wettability hysteresis” and a possible “wettability reversal”, contact angles could be measured on NAPL-treated quartz plates. Also, P_c -S tests should be performed directly on field soil. If the field soil is not available, P_c -S experiments could be performed on clean lab-grade soil exposed initially to the particular field NAPL. This could be done by saturating the dry clean soil in the NAPL, air drying, and posteriorly performing P_c -S tests on this soil. This would be beneficial to observe to what extent does the actual field NAPL alter wettability and changes the soil’s P_c -S relationship. In addition, scanning curves should be obtained to identify cycles of wettability reversal on water imbibition as observed by Drake (2011).

It is necessary to further investigate the effect of contact order and contact time. For this purpose, supplementary studies should investigate different saturation approaches, incorporate soil that has been previously contacted by LNAPLs, and include field soil and/or heterogeneous media. Also, long-term column tests could be performed simulating seasonal groundwater table fluctuations and monitoring its effects on entrapment.

In order to further remove entrapped LNAPL, higher concentrations of surfactants could be tested in combination with other compounds (e.g. electrolytes, alcohols, etc.) to reduce IFT even more and reach the ultra-low IFT threshold. At ultra-low IFT values, removal is dominated by enhanced solubilization and higher entrapped NAPL removal is possible. However, the impacts of the introduction of higher surfactant concentrations in the soil must be considered. At contaminated field sites, the environmental professional must decide which approach to follow to minimize further contamination and dissolution.

As mentioned previously, research on soil and groundwater contamination should be performed on field soils and field LNAPLs. This can only be achieved by integrating industry and academia and establishing multilateral collaborations. Whenever this convergence is possible, real-world environmental problems can have an effective and optimal solution.

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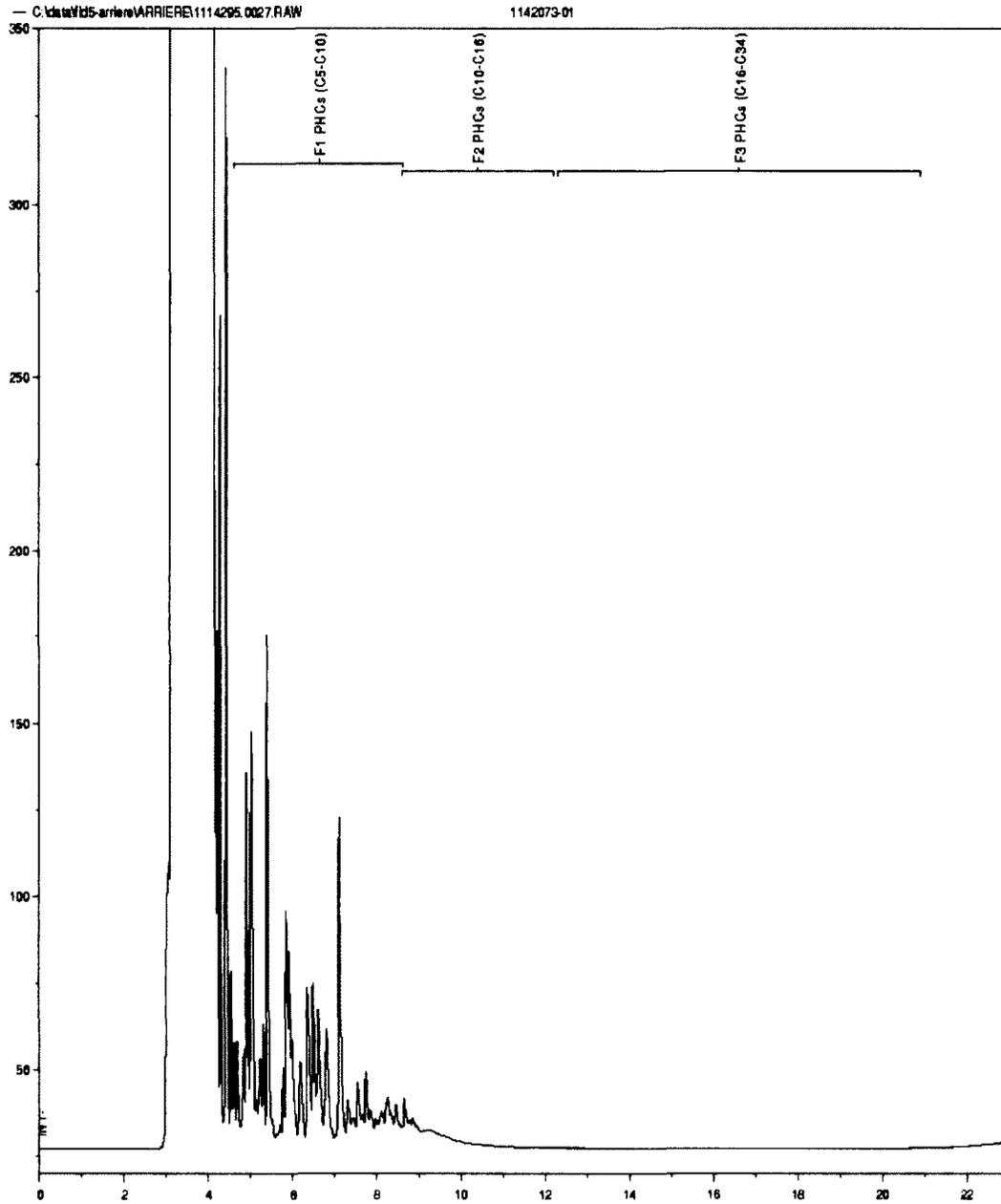
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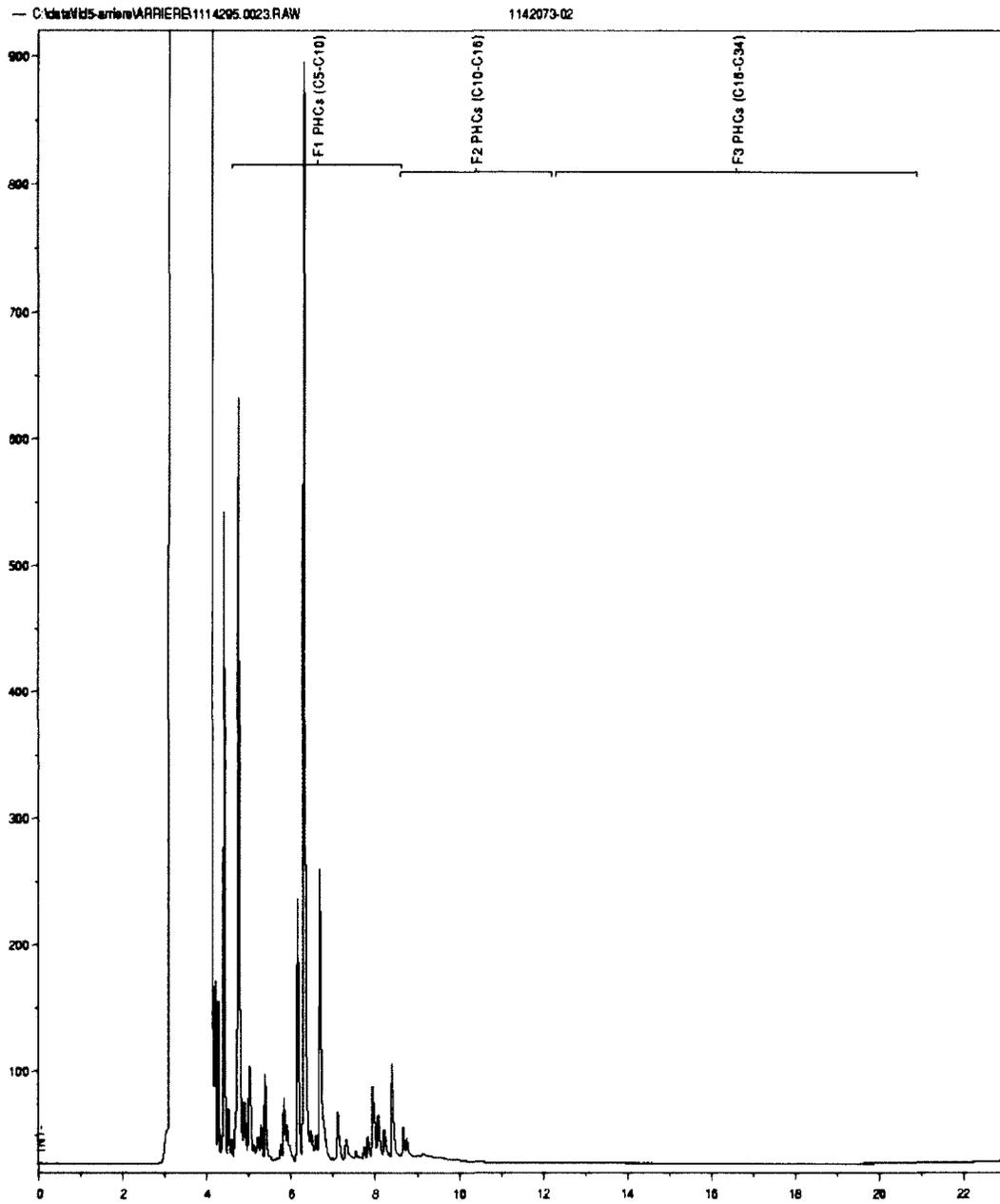
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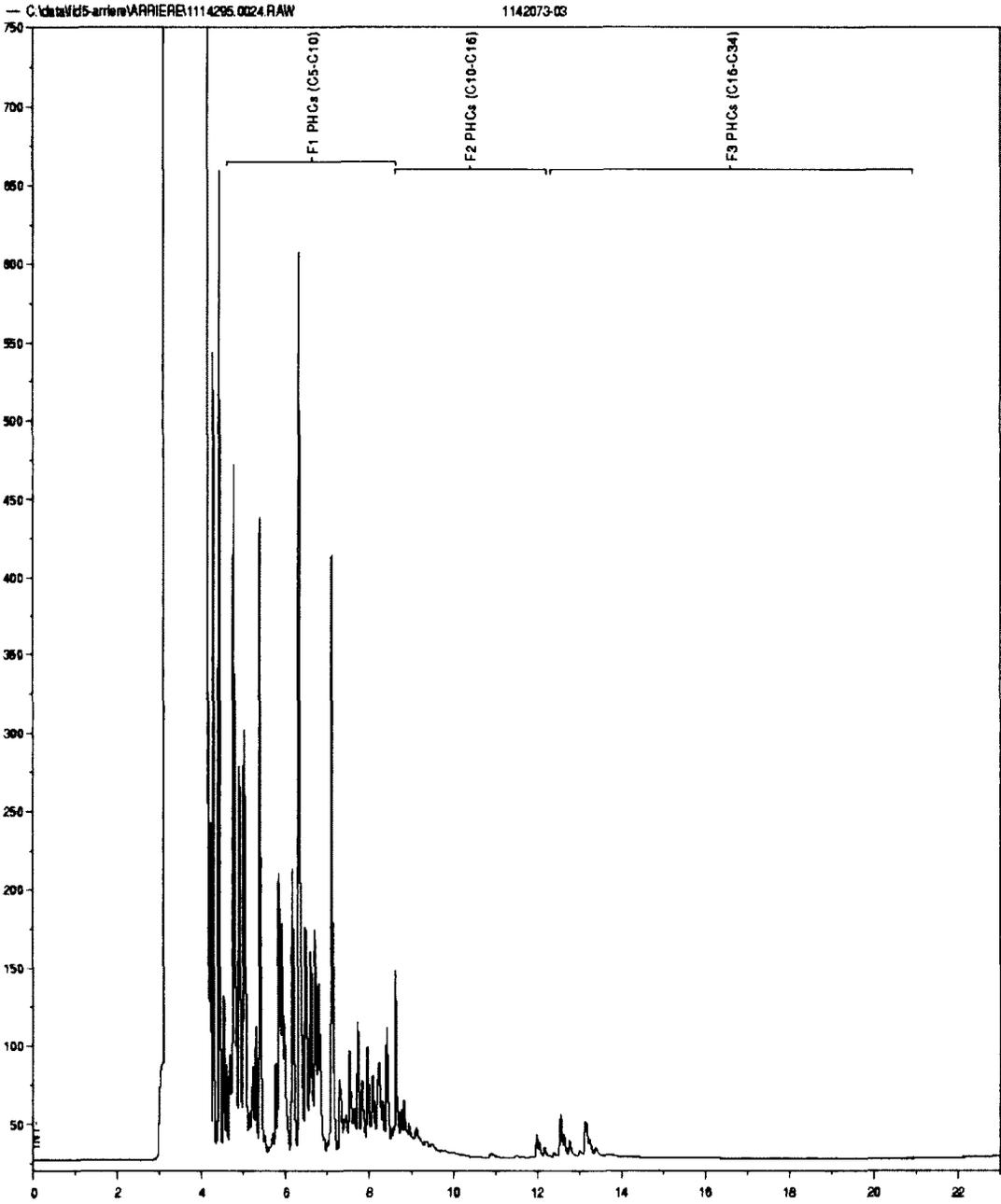
Field LNAPL chromatogram



Water equilibrated with field LNAPL chromatogram



SDBS with dissolved field LNAPL chromatogram



Field site surfactant with dissolved field LNAPL

