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DEVELOPMENT AND INCORPORATION OF A NAPL RESIDUAL INTO THE LENHARD-PARKER PRESSURE-SATURATION HYSTERETIC MODEL

By

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B Eng.**

**A Thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Master of Engineering ***

**Department of Civil and Environmental Engineering
Carleton University
Ottawa, Ontario
Canada**

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of Ottawa administered by the Ottawa-Carleton Institute for
Civil Engineering**

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NAPL RESIDUAL INTO THE LENHARD-PARKER
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**Submitted by Su-Kim Delores Roy
in partial fulfillment of the requirements for
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**Carleton University
March 4, 1999**

ABSTRACT

The current three-phase hysteretic Lenhard-Parker (LP) pressure-saturation model does not allow for estimates of residual non-aqueous phase liquid (NAPL) saturation terms within multiphase systems. Residual NAPL saturation may be present in significant amounts within the subsurface and may control remediation techniques to be used on NAPL contaminated sites. Thus, some method to include residual NAPL saturation within the current LP model is required.

A number of pressure-saturation experiments were conducted in the laboratory to determine two-phase pressure-saturation parameters required by the LP model, and the factors influencing residual NAPL saturation in three-phase systems.

The three fluids considered were water, heptane, and air, and the porous medium chosen was a well sorted gray silica sand. From the experimental results, three conceptual model equations were developed to estimate residual NAPL saturation within three-phase systems. The conceptual model results were then incorporated into a LP hysteretic pressure-saturation code, and a simple example problem presented.

The importance of including a NAPL residual saturation within the LP model was clearly illustrated by the example problem given. Future work should consider different three-phase fluid / porous medium systems, and verification of the conceptual models presented by comparing simulated data to laboratory / field data.

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NOMENCLATURE

g	Gravitational acceleration constant
h_{cao}	Capillary pressure head across a NAPL-air interface
h_{caw}	Capillary pressure head across a water-air interface
h_{cow}	Capillary pressure head across a water-NAPL interface
K_{hor}	Horizontal saturated hydraulic conductivity
n	Van Genuchten pressure-saturation fitting parameter
N_b	Bond number
N_{bk}	Brownell-Katz number
N_c	Capillary number
P_{cao}	Capillary pressure across a NAPL-air interface
P_{caw}	Capillary pressure across a water-air interface
P_{cow}	Capillary pressure across a water-NAPL interface
P_{cwn}	Capillary pressure for a two-phase wetting / non-wetting fluid pair
P_d	Entry pressure of a non-wetting fluid in a multiphase system
P_{nw}	Pressure in a non-wetting fluid
P_w	Pressure in a wetting fluid
ΔP_{di}^*	Capillary pressure at most recent reversal from drainage to imbibition on preceding imbibition curve
ΔP_{id}^*	Capillary pressure at most recent reversal from imbibition to drainage on preceding drainage curve
∇P	Pressure gradient

R	Land parameter calculated from two-phase entrapment data
r	Radius of a pore body
S*	Drainage / imbibition scanning curve function
$\underline{S}^d$	Apparent saturation on primary drainage pathway
$\underline{S}^{d*}$	Apparent scaled functional for primary drainage curve
$\underline{S}^i$	Apparent saturation on primary imbibition pathway
$\underline{S}^{i*}$	Apparent scaled functional for primary imbibition curve
S_a	Actual air saturation
$\underline{S}_a$	Effective air saturation
$\underline{S}_{af}$	Effective free / continuous effective air saturation
$\underline{S}_{aro}$	Minimum effective entrapped air saturation due to advancing NAPL
$\underline{S}_{arw}$	Minimum effective entrapped air saturation due to advancing water
$\underline{S}_{at}$	Effective entrapped / immobile effective air saturation
$\underline{S}_{ato}$	Effective saturation of air trapped in NAPL
$\underline{S}_{atw}$	Effective saturation of air trapped in water
S_{irr}^{ao}	Actual irreducible saturation from two-phase NAPL-air system
$\underline{S}_{jr}^{jk}$	Maximum effective entrapped saturation based on $\Delta \underline{S}_k^{jk}$ from primary drainage to first imbibition scanning curve
$\underline{S}_{jr}^{i,jk}$	Maximum effective entrapped saturation corresponding to primary imbibition pathway
$\underline{S}_{jt}^{jk}$	Effective entrapped non-wetting phase saturation for two-phase system
$\underline{S}_k^{jk}$	Apparent wetting phase saturation for two-phase system

S_o	Actual NAPL saturation
$\underline{S}_o$	Effective NAPL saturation
$\underline{S}_{of}$	Effective free / continuous effective NAPL saturation
$\underline{S}_{or}$	Maximum effective entrapped NAPL saturation due to a water-NAPL interface
$\underline{S}_{or}^{i\text{ow}}$	Maximum effective entrapped NAPL saturation corresponding to the main imbibition pathway for two-phase water-NAPL system
$\underline{S}_{ot}$	Effective entrapped / immobile effective NAPL saturation
$\underline{S}_{oto}$	Effective entrapped air phase saturation within entrapped NAPL due to a NAPL-air interface
$\underline{S}_{ott}$	Effective total entrapped NAPL saturation
$\underline{S}_{otw}$	Effective entrapped air phase saturation within entrapped NAPL due to a water-air interface
S_{res}	Maximum actual residual heptane saturation for a given S_{wet}
$\underline{S}_{res}$	Effective residual NAPL saturation based on current apparent total liquid saturation $\underline{S}_t$
$S_{res}^{\max}$	Maximum actual residual heptane saturation occurring at 100 % apparent total liquid saturation
$\underline{S}_{res}^{\max}$	Effective maximum residual NAPL saturation based on reversal point $\Delta\Delta \underline{S}_t$
$^D \underline{S}_{res}^{\max}$	Absolute maximum effective residual NAPL saturation for three-phase system
S_t	Total liquid saturation in a multiphase system
$\underline{S}_t$	Effective total liquid saturation in a multiphase system
$\underline{\underline{S}}_t$	Apparent total liquid saturation in a multiphase system
$\underline{\underline{S}}_t^{\min}$	Minimum apparent total liquid saturation in a three-phase system

$\Delta\Delta S_t$	Apparent total liquid saturation reversal point from an imbibition to a drainage scanning curve
S_v	Saturation of fluid v within a porous medium
S_w	Actual wetting phase / water saturation
$\underline{S}_w$	Effective wetting phase / water saturation
$\underline{S}_w$	Apparent wetting phase / water saturation
$\underline{S}_w^{\min}$	Minimum apparent water saturation since NAPL introduction into a three-phase system
S_{wet}	Actual wetting heptane saturation
S_{ws}	Saturated wetting phase / water saturation
$\Delta\underline{S}_w^{aw}$	Minimum effective water saturation in a two-phase water-air system prior to NAPL introduction
$\Delta\underline{S}_w^{aw}$	Minimum apparent water saturation in a two-phase water-air system prior to NAPL introduction
ΔS_{di}^*	Saturation at most recent reversal from drainage to imbibition on preceding imbibition curve
ΔS_{id}^*	Saturation at most recent reversal from imbibition to drainage on preceding drainage curve
$\Delta\underline{S}_k^{jk}$	Initial wetting phase reversal point from primary drainage to first imbibition scanning curve for two-phase wetting (k) / non-wetting (j) system
Z	Coordination number for a porous medium
z	Fitting parameter for exponential residual NAPL saturation conceptual model
α	Van Genuchten pressure-saturation fitting parameter
β_{ao}	Lenhard-Parker scaling factor for NAPL-air two-phase system
β_{aw}	Lenhard-Parker scaling factor for water-air two-phase system
β_{ow}	Lenhard-Parker scaling factor for water-NAPL two-phase system

$\Delta\rho$	Fluid-fluid density difference
λ	Brooks and Corey pressure-saturation fitting parameter
θ	Contact angle between liquid and solid for multiphase system
σ	Interfacial tension between a wetting and a non-wetting fluid pair
σ_{ao}	Interfacial tension between NAPL and air
σ_{aw}	Interfacial tension between water and air
σ_{ow}	Interfacial tension between water and NAPL

CHAPTER 1

1.0 INTRODUCTION

Contamination of subsurface soils by non-aqueous phase liquids (NAPLs) is an environmental concern. These fluids, immiscible in water, can be contained within the subsurface soil for a number of years and, due to their low solubility in water, can contaminate an aquifer for long periods of time. Indeed, the nature of these contaminants often cause remediation efforts either to fail or to be less effective than intended. Primarily for these reasons, research regarding NAPL distribution and contaminant transport within the vadose zone has become increasingly important.

Remediation of contaminated sites often involves efforts to 'remobilize' residual NAPL distributions. In order to do so, it is necessary to obtain knowledge of the NAPL distribution as residual or free product (Van Geel, 1994). Residual NAPL saturation may significantly influence subsurface pressure-saturation relationships and, when considering NAPL contaminated sites, may limit feasible remediation options. Several predictive models governing pressure-saturation relationships for multiphase systems (i.e. air, water and NAPL) exist which measure NAPL distribution within a given system. Models available may contain strictly monotonic systems, although many include effects of fluid entrapment and saturation hysteresis on pressure-saturation relationships (Van Geel, 1994). Unfortunately, these predictive models do not directly account for residual NAPL saturation.

1.1 NON-AQUEOUS PHASE FLUIDS

1.1.1 Light Non-Aqueous Phase Liquids

Light non-aqueous phase liquids (LNAPLs) are immiscible fluids with densities less than water. When spills of LNAPLs occur, contaminants penetrate the soil surface and begin to migrate through the subsurface vadose zone as a result of gravity and capillary pressure forces (see Figure 1.0). As LNAPL moves through the porous medium, a residual saturation is left behind. The amount of residual saturation observed will be dependent on factors such as : NAPL type, whether NAPL is in the saturated or unsaturated zone and porous medium matrix characteristics (Bedient et. al., 1994).

If free phase LNAPL reaches the water table, a pooling of fluid will occur due to the lower density value of the LNAPL. This pool will compress the capillary fringe and may also depress the water table, if a sufficient volume of LNAPL is accumulated. Once this occurs, the free phase LNAPL pool will float on top of the water table as illustrated in Figure 1.0 (Van Geel, 1994).

Transport of LNAPL components in the subsurface can be via many paths. Components of residual or free phase LNAPL may be dissolved into the water phase and carried away by groundwater flow, which creates contaminant 'plumes'. Likewise, LNAPL components may volatilize into air contained within the vadose zone and be carried through soil via advection, dispersion and diffusion mechanisms. Lastly, LNAPL constituents present in the water and / or air phases may partition between these two phases due to liquid-gas mass transfer processes.

Figure 1.0 - LNAPL Transport within Subsurface.

1.1.2 Dense Non-Aqueous Phase Liquids

Dense non-aqueous phase liquids (DNAPLs) are, as indicated by the title, fluids with density values greater than that of water. When a DNAPL release occurs at ground surface (Figure 1.1) the fluid will move under the influence of gravity and capillary pressure forces through the vadose zone. Upon encountering the water table, DNAPL will continue to move downwards, through the saturated zone, until all the DNAPL is trapped as residual or a low permeability lens is encountered (Bedient et. al., 1994). If a lens is encountered, DNAPL pools will form which may eventually 'spill over' to migrate downwards through the subsurface. Conversely, the DNAPL may penetrate the lower permeability lens if the entry pressure of the soil matrix is exceeded during pooling. In addition, DNAPLs may travel through hairline cracks and fissures as depicted in Figure 1.1 (Bedient et. al., 1994).

Transport of DNAPL components is similar to mechanisms transporting LNAPL components. Free phase or residual DNAPL components may dissolve

to generate groundwater plumes, they may volatilize into air contained within the unsaturated zone and, gas-liquid mass transfer processes will cause the components to partition between air and water phases. In spite of these similarities, it has been noted that DNAPL subsurface contamination is usually more problematic than LNAPL contamination. Specifically (Bedient et. al., 1994) :

- DNAPLs can penetrate aquifers to significant distances both vertically and horizontally due to their dense nature and their ability to move through fissures,
- DNAPLs tend to be less biodegradable than their LNAPL counterparts.

As a result, LNAPL contaminated sites are often cited as being more 'amenable' to remediation efforts than DNAPL contaminated sites.

Figure 1.1 - DNAPL Transport within Subsurface.

1.2 RESEARCH OBJECTIVES

A number of researchers have studied hysteresis and modeling of multiphase flow within the subsurface (Brush, 1994; Eckberg and Sunada, 1984; Kaluarachchi and Parker, 1992; Kool and Parker, 1987; Lenhard, 1992; Parker and Lenhard, 1987; Sleep and Sykes, 1993 a and b; and, Van Geel, 1994).

Although a number of the models only consider simple monotonic drainage paths, recent developments have produced models able to consider hysteresis and fluid entrapment influences. In 1980, Van Genuchten introduced a five parameter equation providing a best-fit curve to pressure-saturation data. In 1987, Lenhard and Parker developed a multiphase flow model, including hysteresis and fluid entrapment effects, using Van Genuchten's equation and a scaling factor formulation to extend two-phase data to three-phase systems. Further modifications to the Lenhard-Parker (LP) model have resulted in refinements to fluid entrapment prediction capabilities (Lenhard, 1992). Unfortunately, the current LP model does not consider the effect of a residual non-aqueous phase fluid saturation within a three-phase system. As this may significantly influence fluid distributions within the subsurface, inclusion of residual saturation into the Lenhard-Parker formulation would be beneficial.

The objective of this research was to conduct a number of two and three-phase experiments using a fine silica sand porous medium with air, water and heptane fluids. Henceforth, two-phase refers to any system within the subsurface containing soil and two immiscible fluids. Accordingly, three-phase refers to any system containing soil and three immiscible fluids.

Two-phase pressure-saturation experiments were performed to determine the two-phase system parameters required by the LP model. Three-phase system trials were then performed in order to determine residual saturation effects, and factors influencing residual saturation. Following the experimental work, a conceptual model was proposed to amend the current LP model for residual saturation inclusion. Lastly, a simple example problem was modeled with and without considering residual saturation effects to demonstrate differences.

The remainder of Chapter one of this thesis outlines basic concepts for multiphase systems of immiscible fluids within a porous medium. Chapter two presents macro-scale theory pertaining to hysteresis and the LP model. The third chapter briefly outlines micro-scale theory, particularly factors influencing entrapped saturation in multiphase systems in porous media. Chapter four describes the laboratory experiments that were conducted and results obtained. Chapter five describes the proposed conceptual model for including residual saturation within the LP model and it includes a simple example problem demonstrating the benefits of the modified model. Lastly, conclusions and recommendations for future work are presented in Chapter six.

1.3 MULTIPHASE SYSTEM CONCEPTS

1.3.1 Wettability

When two or more immiscible fluids exist within a porous medium, an interfacial energy exists between fluid-fluid contact surfaces. This energy is

frequently referred to as interfacial tension since it arises as a result of the difference between inward attraction of fluid molecules within each phase and molecules at the adjacent contacting surface (Bear, 1972). Figure 1.2 illustrates a simple schematic of a cross section of a fluid-fluid interface in contact with a circular capillary pore. The interface will be concave with respect to the 'non-wetting' fluid and convex with respect to the 'wetting fluid' as shown (Brush, 1994). The solid-fluid interface angle, also called the contact angle θ , is often employed as a measure of the wettability of a fluid in the system.

Figure 1.2 - Wetting and Non-Wetting Fluid Interface.

Wettability is a relative measure of the tendency for one fluid to preferentially spread over a solid surface in favor of a second fluid (Bedient et. al., 1994). In view of this, fluids with contact angles between 0° and 90° are referred to as *wetting*, and fluids with contact angles between 90° and 180° are classified as *non-wetting*. In a typical three-phase fluid system of water, NAPL and air, water is considered to be the wetting fluid, NAPL is considered to be the intermediate fluid and air the non-wetting fluid. Thus, in order of wettability, most subsurface three-phase systems follow the pattern :

$$\text{Wettability}_{\text{water}} > \text{Wettability}_{\text{NAPL}} > \text{Wettability}_{\text{air}}$$

Theoretically, this order of wettability means that if all three phases are contained within a porous medium, the water will exist closest to the solid surfaces followed by NAPL existing between the air and water phases (Figure 1.3).

Figure 1.3 - Theoretical Three-Phase Fluid System within a Porous Medium.

1.3.2 Capillary Pressure-Saturation Relationships

Capillary pressures will exist in systems containing two or more fluids, one wetting and a number of intermediate and non-wetting liquids. When immiscible fluids are in contact, a discontinuity in pressure across fluid-fluid interfaces may result which may be represented, for a two fluid system, by :

$$P_{cwn} = P_{nw} - P_w \quad (1.0)$$

Where : P_{nw} = pressure in the non-wetting fluid.

P_w = pressure in the wetting fluid.

P_{cwn} = capillary pressure for two-phase wetting/non-wetting fluids.

More specifically, at the pore scale level (Bedient et al., 1994) :

$$P_{cwn} = (2\sigma \cos\theta) / r \quad (1.1)$$

Where : σ = interfacial tension between wetting and non-wetting fluids.

θ = relevant contact angle, measured through the wetting fluid phase and,

r = radius of wetting fluid filled pore.

From this equation it may be inferred that as pore radii decrease, the capillary pressure required to force fluid into or out of a pore increases. It should also be noted that capillary pressure is dependent on : the geometry of the void space within a porous medium (value of r), nature of the liquids and solids involved (in terms of σ and θ) and, the degree of saturation of the fluids present in the system (Bear, 1972).

To perceive how saturation affects capillary pressure it is necessary to envision the subsurface environment at the micro-scale level. Saturation is defined as the volume of voids, or pore space, occupied by a given fluid such that :

$$S_v = \text{Volume of fluid } v / \text{Volume of Voids} \quad (1.2)$$

$$\text{Constrained by, } \sum S_v = 1.0$$

In the case of a two-phase system, one wetting and one non-wetting fluid, the total saturation in the system will be the sum of wetting fluid saturation and non-wetting fluid saturation. From Equation 1.1, it is noted that smaller capillary pressure values will occur across fluid-fluid interfaces existing in larger pores and larger capillary pressure values will occur across interfaces existing within smaller pores. Conceptually, for a two-phase fluid system, three different 'zones' of saturation may exist at different capillary pressure values (Brush, 1994) :

1. *Insular saturation* : At low capillary pressure values, the wetting phase fluid will exist in a continuous state as depicted in Figure 1.4, with most of the fluid contained within larger pore spaces. The non-wetting fluid will exist in an immobile entrapped state that will be present most likely as ganglia 'blobs' within smaller pore volumes.

2. **Funicular saturation** : Over time, as capillary pressure increases, the wetting fluid will drain from the porous medium and be displaced by non-wetting fluid. In this case, both wetting and non-wetting fluids exist in mobile states.
3. **Pendular saturation** : Lastly, at relatively high capillary pressure values, the wetting phase will become immobile, to exist strictly as an 'irreducible saturation' present as thin films coating soil grains and / or pendular rings. In addition to this, the non-wetting fluid saturation will increase within the system.

**Figure 1.4 - Saturation Types Present at Different Capillary Pressures
(Modified from Bear, 1972).**

On the macro-scale, capillary pressure-saturation relationships are usually determined via experimentation on the porous medium / fluid systems of interest (Bear, 1972). Frequently, an apparatus is set-up to measure changes in wetting and non-wetting fluid saturation within a porous medium versus changes in capillary pressure. Figure 1.5 provides a simple example of how primary drainage and imbibition pathways might appear for a two-phase system.

Figure 1.5 - Typical Capillary Pressure - Saturation Curves (Modified from Van Geel, 1994).

At the start of the experiment, soil within the cell would be saturated with a wetting fluid until 100 % saturation was obtained. Following this, the wetting fluid would be forced to drain and non-wetting fluid would be forced to imbibe by increasing the capillary pressure in the experimental cell (Stage 1 in Figure 1.5). It should be noted that no change in wetting saturation would be observed until the entry pressure, P_d , was overcome. Where P_d represents the pressure difference which must be reached before displacement of wetting fluid by the non-wetting fluid may occur (Bear, 1972). After a certain capillary pressure, no decrease in wetting phase saturation would be observed due to the irreducible saturation value being reached.

During Stage 2 of the experiment, wetting fluid would be re-introduced into the cell (Figure 1.5). As the wetting fluid enters the cell, capillary pressure within the system would decrease and non-wetting fluid would be displaced from pore

volumes. At the same time, a fraction of the non-wetting fluid would become entrapped within the advancing wetting fluid front. At capillary pressures of less than or equal to zero, the non-wetting fluid would exist as an entrapped saturation composed most likely of immobile ganglia blobs.

Although laboratory experimentation is required to determine the capillary pressure-saturation relationship for a given system, some 'curve fitting' relationships have been developed. More specifically :

Van Genuchten and Nielsen (1985) found pressure-saturation curves for two immiscible fluid systems could best be fitted using the equations :

$$\begin{aligned} \underline{S}_w &= [1 + (\alpha P_{cwn})^n]^{-m} & \text{for } P_{cwn} > 0 & \quad (1.3) \\ \text{and } \underline{S}_w &= 1 & \text{for } P_{cwn} \leq 0 \end{aligned}$$

Where : $\underline{S}_w$ = effective wetting phase saturation = $(S_w - S_m) / (S_{ws} - S_m)$
 S_w = actual wetting phase saturation,
 S_m = irreducible wetting phase saturation,
 S_{ws} = saturated wetting phase saturation,
 α, n = fitting parameters, and,
 $m = 1 - 1/n$

Similarly, Brooks and Corey (1964) approximated these pressure-saturation relationships by :

$$\begin{aligned} \underline{S}_w &= [P_d / P_{cwn}]^\lambda & \text{for } P_{cwn} > P_d & \quad (1.4) \\ \text{and } \underline{S}_w &= 1 & \text{for } P_{cwn} \leq P_d \end{aligned}$$

Where : λ = fitting parameter, and,
 P_d = air entry pressure.

Although these relationships are frequently used in practice, it should be noted that, as written, they apply only to monotonic drainage and imbibition pathway situations (Brush, 1994).

1.3.3 Hysteresis

Observation of Figure 1.5 illustrates saturation taking on one of two values, for a given capillary pressure, depending on whether drainage or imbibition is occurring. Stated more directly, saturation values will be dependent upon the saturation 'history' of the system. This history dependent phenomena is termed hysteresis and is composed of two separate factors : saturation hysteresis and fluid entrapment (Van Geel, 1994).

Saturation hysteresis results from two distinct influences, namely :

- direction of displacement, also known as the 'rain drop effect' and,
- geometry of the void space, sometimes termed the 'ink bottle effect'.

An illustration of the rain drop effect is given in Figure 1.6. As demonstrated, the contact angle between the fluid-fluid interface and solid will differ depending on whether the interface is advancing or receding into a pore volume. Since capillary pressure is a function of contact angle (see Equation 1.1), and contact angle is dependent on direction of displacement, hysteretic effects will be perceived within porous media-fluid systems.

Figure 1.6 - Rain Drop Effect (Modified from Bear, 1972).

Geometry of pore space also contributes to saturation hysteresis. An example of the 'ink bottle effect' is presented in Figure 1.7. The subsurface pore space is represented by a capillary tube with a larger diameter middle section. The large diameter section models a 'pore body' whereas the thinner tubes symbolize 'pore throats'. Initially, if a saturated tube is allowed to undergo drainage, surface tension forces will hold a portion of the fluid above the wider pore diameter as illustrated. If, conversely, an empty tube is inserted into the fluid basin and allowed to undergo imbibition, surface tension forces will cause the fluid to imbibe to a height less than that obtained during drainage (Van Geel, 1994). In view of this, saturation values obtained during drainage are usually larger than those obtained during imbibition for a given value of capillary pressure.

Figure 1.7 - Ink Bottle Effect (Modified from Corey, 1994).

The last major factor contributing to hysteresis is fluid entrapment. Fluid entrapment will occur within a porous medium when a wetting fluid imbibes into pore space previously occupied by non-wetting fluid. More specifically, as wetting

fluid advances into the void volume, non-wetting fluid will be displaced within some of the pores. In other pore spaces, a proportion of the non-wetting fluid will become 'entrapped' within the wetting fluid (Figure 1.3), and will thus exist as discontinuous ganglia. Because of this, wetting fluid saturation will be less than 100% during imbibition, as part of the pore space will be already occupied by non-wetting fluid.

On the pore scale level, fluid entrapment may be accredited to two mechanisms : (1) snap-off and, (2) bypassing (Chatzis et al., 1983). Figure 1.8 illustrates the differences between the two processes. Snap off will occur within pores of high aspect ratio (pore body diameter / pore throat diameter). As depicted, wetting fluid imbibes into the system via film flow next to the solid phase and flows towards the pore throat. Eventually, as more wetting fluid imbibes, a intrusion will begin to form at the narrow throat which will eventually break up the continuous non-wetting phase contained within adjacent pores. Once this occurs, non-wetting fluid will 'snap-off' into ganglia and hence remain in an entrapped, discontinuous state (Zhou and Orr, 1995).

Bypassing mechanisms tend to occur within pores having low aspect ratios. Within the porous medium, the many different sizes of interconnecting pores tend to promote 'competition' for flow. Wetting fluid undergoing displacement in fast moving pores (R_1) may therefore 'cut off' non-wetting fluid in slow moving pores (R_2). Or, in other words, the non-wetting phase is 'bypassed' by the imbibing wetting fluid. Figure 1.9 summarizes differences and similarities between the different types of hysteresis.

Figure 1.8 - Snap-off vs. Bypass (Modified from Zhou and Orr, 1995)

The solid black curve shown in Figure 1.9 depicts a system with no hysteretic effects included. Observation of this graph reveals no difference

between drainage and imbibition pressure-saturation relationships, as only one saturation value is observed for each capillary pressure. Saturation hysteresis effects are represented by the dashed and crossed imbibition curve in conjunction with the black primary drainage curve. For every value of capillary pressure, two values of saturation are possible depending on whether the system is under going imbibition or drainage. In spite of this, imbibition of the wetting phase will still result in a maximum saturation of 100% as shown. The dashed line imbibition curve illustrates the singular effect of fluid entrapment on wetting phase saturation. As illustrated, fluid entrapment will force the wetting phase saturation to be less than 100% during wetting, as a proportion of pore volume will always be occupied by the non-wetting phase. Lastly, the solid line with circles represents an imbibition curve for a fully hysteretic system, including saturation hysteresis and fluid entrapment. As per the saturation hysteresis depiction, two saturation values exist for a given capillary pressure. In addition to this, fluid entrapment effects are observed as the maximum wetting phase saturation value following imbibition is less than 100%.

1.3.4 Residual Saturation vs. Fluid Entrapment

Fluid entrapment results when pores containing non-wetting fluid undergo displacement processes by imbibing wetting fluid. As noted, entrapment of non-wetting fluid may be due to snap-off and bypass mechanisms. In contrast to this, residual saturation results after a wetting fluid contained within pore voids undergoes drainage and is replaced by a non-wetting fluid. For example, as a

spill of LNAPL moves through the vadose zone in the subsurface, a residual LNAPL phase will remain behind the path of the advancing free phase fluid. This occurs as the LNAPL free phase drains and is replaced by the non-wetting air phase. Currently three-phase models that include hysteresis in the form of saturation hysteresis and fluid entrapment do not provide distinct mechanisms for including a NAPL residual saturation (Van Geel, 1994).

A number of researchers have studied residual saturation under gravity drainage for extended periods of time (Hagoort, 1980 ; Kantzas et al., 1988 ; Pavone, 1989). From these studies it has been observed that gravity drainage of residual will continue over time, but at significantly reduced rates. In addition to these findings, Wilson et al. (1988) observed NAPL which appeared to be entrapped within the air phase during experiments using a Soltrol - 130 / Sevilleta sand system. Currently, a number of hysteretic pressure-saturation models assume that entrapment of one phase in another phase of lesser wettability does not occur. The findings of Wilson et al. (1988) however, seem to contest this assumption, indicating the importance of residual NAPL within the vadose zone. Clearly, further undertakings to incorporate residual saturation effects within multiphase pressure-saturation relationships are required.

CHAPTER 2

2.0 MACRO-SCALE THEORY AND HYSTERESIS

In order to predict NAPL movement within the subsurface, pressure-saturation-relative permeability relationships for coexisting phases need to be considered (Lenhard et al., 1993). As mentioned previously, a number of models have been developed which forecast NAPL behavior within three-phase systems, although relatively few accommodate fully hysteretic relationships. In general, three-phase systems are modeled using data obtained from two-phase relationships, namely : water-air, water-NAPL and NAPL-air. This is mainly due to the difficulty in directly measuring three-phase system values within a laboratory setting (Parker et al., 1987).

Within the last 20 years, advances regarding pressure-saturation-relative permeability (k - S - P) relationship models have been made by a number of researchers. A monotonic parametric model to approximate three-phase k - S - P relationships, based on two-phase data, was introduced by Parker et. al in 1987. Model development incorporated a scaling method presented in an earlier work by Leverett (1941). Following model verification, expansions to include saturation hysteresis and entrapment effects were proposed (Parker and Lenhard, 1987). The following discussion is based on this conceptual model, although some refinements have been introduced since the work in 1987.

2.1 REPRESENTATIVE ELEMENTARY VOLUME

Representative Elementary Volume (REV), is a conceptual measure which signifies the smallest volume of a porous medium over which a given matrix property will remain constant. Stated differently, the REV indicates measurement on the macroscopic / continuum length scale in that pore scale properties are 'lumped' into macroscopic values rather than being directly measured (Brush, 1994).

Depending on the scale of measurement, a number of REV's will exist within a given porous medium. For example, referring to Figure 2.0, at location A, pore scale level measurement of any porous medium property (e.g. porosity, etc.) will provide highly variable results as shown. This is entirely credited to the scale of measurement because at this small level, inclusion or exclusion of a pore within the volume will strongly influence values obtained. At location B, perhaps lab scale samples, property values will remain fairly constant due to pore and non-pore volume influences being 'averaged' out at this larger size. As volume of the sample increases (location C), fluctuation of property values is again noted, perhaps due to heterogeneities (i.e. maybe different soil 'lenses') present at this larger scale. Similar arguments lead to the hypothetical results shown at locations D, E and F. In all cases, as volume increases, disruptive influences are 'averaged' out until new, larger scale influences become included within the volume. Thus, although results of the multiphase models presented below are based on a macroscopic / continuum length scale, it is advisable to

remember that they are actually 'average results' and thus functions of several pore scale properties (Brush, 1994).

Figure 2.0 - Representative Elementary Volume Concept.

2.2 LP HYSTERESIS MODEL

The three-phase LP Hysteretic model was established, as stated, based on two-phase system relationships and a scaling method presented by Leverett in 1941. The model was developed to facilitate prediction of three-phase system parameters from two-phase system relationships (water-air, NAPL-air and water-NAPL), and efforts to accommodate saturation hysteresis and fluid entrapment effects were made. The following discussion is based upon the model initially proposed by Parker and Lenhard (1987).

2.2.1 Three-Phase System Pressure-Saturation Representation

The LP Hysteretic model assumes wettability within a three-phase system to follow the order : water, NAPL, and air. Thus, when all three fluids are present in a system, two interfaces will develop, namely : a water-NAPL interface and a

NAPL-air interface. Capillary pressure values across each interface may be calculated as per Equation 1.0. In addition, the model assumes water saturation to be a function of the water-NAPL capillary pressure only, whereas the total liquid saturation is assumed to be solely a function of the NAPL-air capillary pressure.

Van Genuchten pressure-saturation relations, similar in form to Equation 1.3, may be generated for both the wetting phase saturation and total liquid saturation. Figure 2.1 demonstrates hypothetical pressure-saturation curves for a three-phase system containing water, NAPL and air. S_w and S_t represent water and total liquid saturation values and, P_{cow} and P_{cao} represent capillary pressures values across the water-NAPL and NAPL-air interfaces respectively.

Water saturation is estimated by observation of the water-NAPL interface capillary pressure values. Total liquid saturation is estimated by watching the NAPL-air interface capillary pressures. NAPL saturation may then be estimated as the difference between the two values. S_m represents the irreducible wetting phase saturation for the three-phase system and, as illustrated, is assumed to be the limiting value for both pressure-saturation systems during drainage.

Figure 2.1 - Pressure-Saturation Curves for a Three-Phase System.

2.2.2 Actual, Effective, and Apparent Saturations

For any two or three-phase system containing water, NAPL, and air, effective saturations were defined by Parker and Lenhard (1987) as :

$$\underline{S}_w = (S_w - S_m) / (1 - S_m) \quad (2.0 \text{ a - d})$$

$$\underline{S}_o = S_o / (1 - S_m)$$

$$\underline{S}_a = S_a / (1 - S_m)$$

$$\underline{S}_t = (S_w + S_o - S_m) / (1 - S_m) = \underline{S}_w + \underline{S}_o = 1 - \underline{S}_a$$

Where :
 S_i = actual saturations of water (w), air (a) or NAPL (o),
 $\underline{S}_i$ = effective saturations of water (w), air (a) or NAPL (o),
 $\underline{S}_t$ = effective total liquid saturation, and,
 S_m = irreducible water saturation (assumed independent of system).

Effective saturations were implemented primarily to account for irreducible wetting phase effects, and may also be written to invoke distinctions between free and trapped non-wetting phases as :

$$\underline{S}_o = \underline{S}_{of} + \underline{S}_{ot} \quad (2.1 \text{ a - c})$$

$$\underline{S}_a = \underline{S}_{af} + \underline{S}_{at}$$

$$\underline{S}_{at} = \underline{S}_{atw} + \underline{S}_{ato}$$

Where : $\underline{S}_{of}$ and $\underline{S}_{ot}$ = free (continuous) and trapped (immobile) effective NAPL saturation,
 $\underline{S}_{af}$ and $\underline{S}_{at}$ = free and trapped effective air saturation, and,
 $\underline{S}_{atw}$ and $\underline{S}_{ato}$ = effective saturation of air trapped in water and air trapped in NAPL respectively.

Apparent saturations to include entrapment effects within corresponding fluids were subsequently introduced (Parker and Lenhard, 1987) :

$$\underline{S}_w = \underline{S}_w + \underline{S}_{ot} + \underline{S}_{atw} \quad (2.2 \text{ a and b})$$

$$\underline{S}_t = \underline{S}_w + \underline{S}_o + \underline{S}_{at}$$

Where : $\underline{S}_w$ = apparent water saturation,
 $\underline{S}_t$ = apparent total liquid saturation

Noting that an inherent assumption of the model prevents wetting fluid from becoming occluded within non-wetting fluid (i.e. water in NAPL). It is apparent saturation values which are utilized in the LP Hysteretic model described below.

Figure 2.2 illustrates the differences between actual, effective and apparent saturation values for a general, hypothetical capillary pressure-saturation relationship. From Figure 2.2, it may be observed that actual saturation values include the effects of both irreducible wetting phase saturation and non-wetting fluid entrapment. The second graph presented demonstrates effective saturation values. As expected, irreducible wetting phase saturation effects have been removed although fluid entrapment clearly remains. The last curve contained within Figure 2.2 illustrates apparent saturation. Clearly, both

irreducible saturation and fluid entrapment effects have been removed and accounted for elsewhere, in accordance with the Lenhard-Parker formulation.

Figure 2.2 - Actual, Effective and Apparent Saturation Values.

2.2.3 Scaled Hysteretic LP Function

In order to accommodate fluid entrapment effects, the LP hysteretic model was developed to utilize apparent saturation values, rather than actual or effective values, as defined by Equations 2.2 a and b. In addition to this, saturation hysteresis effects were taken into account by treating the pressure-saturation function of Van Genuchten (Equation 1.3) as a 'history dependent functional' such that (Van Geel, 1994) :

$$\begin{aligned} i\bar{S} &= [1 + (\alpha_i P_{cwn})^n]^{-m} \quad \text{and,} & (2.3 \text{ a and b}) \\ d\bar{S} &= [1 + (\alpha_d P_{cwn})^n]^{-m} \end{aligned}$$

Where : $d\bar{S}$ = apparent saturations on the primary drainage pathway, and,
 $i\bar{S}$ = apparent saturations on the primary imbibition pathway.

In addition to history dependent functions being used within the model, scaling factors were introduced in order to account for fluid specific effects and to extend two-phase data to three-phase systems (Parker and Lenhard, 1987). More specifically, Leverett (1941) defined scaling factors based on two-phase system data as follows :

$$\beta_{aw}P_{caw} = \beta_{ow}P_{cow} = \beta_{ao}P_{cao} , \quad (2.4a)$$

Where : $\beta_{aw} = 1.0$, by convention,
 $\beta_{ow} = \sigma_{aw} / \sigma_{ow}$,
 $\beta_{ao} = \sigma_{aw} / \sigma_{ao}$, and,
 σ_{aw} , σ_{ow} , σ_{ao} = the interfacial tensions for water-air, water-NAPL and NAPL-air interfaces respectively.

Similarly, if data exists for each two-phase pressure-saturation relationship, β_{ij} values may be calculated using α_d values as follows :

$$\beta_{aw}P_{caw} = \beta_{ow}P_{cow} = \beta_{ao}P_{cao} , \quad (2.4b)$$

Where : $\beta_{aw} = \alpha_{daw} / \alpha_{daw} = 1.0$,
 $\beta_{ow} = \alpha_{dow} / \alpha_{daw}$,
 $\beta_{ao} = \alpha_{dao} / \alpha_{daw}$, and,
 α_{dij} = alpha values for each two-phase system primary drainage curve.

Thus Equation 2.3 may be expanded for a three-phase system :

$$^iS_w = [1 + (\alpha_i \beta_{ow} P_{cow})^n]^{-m} \quad (2.5 \text{ a and b})$$

$$^dS_w = [1 + (\alpha_d \beta_{ow} P_{cow})^n]^{-m}$$

For $P_{cow} > 0$ and,

$$^{i \text{ or } d}S_w = 1, \quad \text{for } P_{cow} \leq 0,$$

when considering water-NAPL interface main drainage / imbibition curves, and,

$$^iS_t = [1 + (\alpha_i \beta_{ao} P_{cao})^n]^{-m} \quad (2.5 \text{ c and d})$$

$$^dS_t = [1 + (\alpha_d \beta_{ao} P_{cao})^n]^{-m}$$

For $P_{cao} > 0$ and,

$$^{i \text{ or } d}S_t = 1, \quad \text{for } P_{cao} \leq 0,$$

when considering NAPL-air interface main drainage / imbibition curves.

More concisely, Equations 2.5 a - d may be represented in compact form as follows :

$$^iS^*(P^*) = [1 + (\alpha_i P^*)^n]^{-m} \quad (2.6 \text{ a and b})$$

$$^dS^*(P^*) = [1 + (\alpha_d P^*)^n]^{-m}$$

For $P^* > 0$ and,

$$^iS^*(P^*) = ^dS^*(P^*) = 1, \quad \text{for } P^* \leq 0,$$

Where : $^xS^*(P^*)$ = apparent scaled functional for drainage / imbibition curves.

P^* = scaled capillary pressure value for system under consideration.

Realizing that $\underline{S}_t = \underline{S}_w = S^*(P^*)$ due to the scaling relationships defined in Equation 2.4. It is these scaled, history dependent functions which are employed in the progressive model development described below.

2.2.4 Hysteretic Scanning Curve Interpolation

Main drainage and imbibition pathways within a given system define only the 'extreme' situations which may occur. Main drainage, for example, represents displacement of fluid from an actual saturation value of 100 % to an irreducible wetting phase value. On the other hand, primary imbibition depicts the addition of wetting fluid from the irreducible saturation to a maximum value, which will be dependent on entrapment mechanisms. There are many instances however, where the saturation path does not follow the primary drainage or imbibition pathways. A system may switch from drainage to imbibition before the irreducible value is reached or, conversely, from imbibition to drainage before the maximum saturation is reached (Figure 2.3).

Intermediate pathways may be represented by hysteretic scanning curves interpolated from main drainage and imbibition functions. As noted, primary drainage and imbibition functions, for $\underline{S}_w$ and $\underline{S}_t$, may be represented by Equations 2.6 a and b in the interests of eliminating factors specific to fluid pair systems. Consequently, the total fluid saturation-pressure relationship (i.e. NAPL-air interface) and the wetting fluid saturation-pressure relationship (i.e. water-NAPL interface) may both be represented by the scaled functions. Considering an arbitrary reversal from the primary drainage curve, a scanning imbibition pathway may be represented by (Parker and Lenhard , 1987) :

$$S^*(P^*) = \frac{[{}^iS^*(P^*) - {}^iS^*(\Delta P_{id}^*)]}{[{}^iS^*(\Delta P_{di}^*) - {}^iS^*(\Delta P_{id}^*)]} \times [\Delta S_{di}^* - \Delta S_{id}^*] + \Delta S_{id}^* \quad (2.7)$$

Where : $S^*(P^*)$ = imbibition scanning curve function,
 ${}^iS^*(P^*)$ = primary imbibition function,
 ΔP_{id}^* = capillary pressure at most recent reversal from imbibition to drainage on preceding drainage curve,
 ΔP_{di}^* = capillary pressure at most recent reversal from drainage to imbibition,
 ${}^iS^*(\Delta P_{id}^*)$ = value of the ${}^iS^*(P^*)$ function at ΔP_{id}^* ,
 ${}^iS^*(\Delta P_{di}^*)$ = value of the ${}^iS^*(P^*)$ function at ΔP_{di}^* ,
 ΔS_{di}^* = saturation at most recent reversal from drainage to imbibition, and,
 ΔS_{id}^* = saturation at most recent reversal from imbibition to drainage on preceding drainage curve.

Similar considerations will lead to an interpolation function for a drainage scanning curve (Parker and Lenhard, 1987) :

$$S^*(P^*) = \frac{[{}^dS^*(P^*) - {}^dS^*(\Delta P_{di}^*)]}{[{}^dS^*(\Delta P_{id}^*) - {}^dS^*(\Delta P_{di}^*)]} \times [\Delta S_{id}^* - \Delta S_{di}^*] + \Delta S_{di}^* \quad (2.8)$$

Where : $S^*(P^*)$ = drainage scanning curve function,
 ${}^dS^*(P^*)$ = primary drainage function,
 ΔP_{di}^* = capillary pressure at most recent reversal from drainage to imbibition on preceding imbibition curve,
 ΔP_{id}^* = capillary pressure at most recent reversal from imbibition to drainage,
 ${}^dS^*(\Delta P_{id}^*)$ = value of the ${}^dS^*(P^*)$ function at ΔP_{id}^* ,
 ${}^dS^*(\Delta P_{di}^*)$ = value of the ${}^dS^*(P^*)$ function at ΔP_{di}^* ,
 ΔS_{id}^* = saturation at most recent reversal from imbibition to drainage, and,
 ΔS_{di}^* = saturation at most recent reversal from drainage to imbibition on preceding imbibition curve.

The graphs below demonstrate hypothetical imbibition and drainage scanning curves interpolated from the scaled primary functions.

Figure 2.3 illustrates a system undergoing a number of drainage and imbibition reversals. From point 1 to 2, drainage from an initially saturated state takes place and saturation follows the main drainage path. At point 2, a reversal from drainage to imbibition is implemented until point 3, resulting in the imbibition scanning curve shown. Lastly, at point 3, a reversal from imbibition to drainage occurs until point 4, resulting in the primary drainage scanning curve illustrated. Terms introduced in Equations 2.7 and 2.8 are also illustrated in Figure 2.3.

The interpolation formulas presented in Equations 2.7 and 2.8 are of identical form and thus may be easily implemented into numerical code. Parker and Lenhard (1987) proposed the following notation :

$$S^*(P^*) = \frac{[{}^pS^*(P^*) - {}^pS^*(\Delta P_{L-1}^*)]}{[{}^pS^*(\Delta P_L^*) - {}^pS^*(\Delta P_{L-1}^*)]} \times [\Delta S_L^* - \Delta S_{L-1}^*] + \Delta S_{L-1}^* \quad (2.9)$$

Where : p = index denoting drainage or imbibition scanning curve, and,
 $(\Delta S_{L \text{ or } L-1}^*, \Delta P_{L \text{ or } L-1}^*)$ = most recent and preceding reversal points.

All scanning pathways, including any number of reversals from drainage to imbibition to drainage and etc., can be described through successive use of Equation 2.9. The p index term may be set equal to d for odd L values and i for even L values to keep track of whether drainage or imbibition is occurring. Lastly, it should be noted that L must be decremented by two following closure of a given scanning curve, as the $S^*(P^*)$ function would then resume its previous path, regardless of whether drainage or imbibition was being undertaken (Parker and Lenhard, 1987).

2.2.5 Fluid Entrapment

In addition to the scanning paths defined by Equations 2.7 and 2.8, functions to calculate volume of entrapped fluid were presented in order to complete the LP model. Specifically, it was determined that the volume of any entrapped phase may be scaled between zero and the maximum entrapment value, based on location of the saturation reversal point from the primary drainage curve (White and Lenhard, 1993). Assuming an empirical relationship based on the work of Land (1968), Parker and Lenhard (1987) defined a maximum entrapped effective saturation based on the initial drainage-imbibition reversal point as :

$$\underline{S}_{jr}^{jk} = \frac{(1 - \Delta \underline{S}_k^{jk})}{1 + R_{jk}(1 - \Delta \underline{S}_k^{jk})} \quad \text{With } R_{jk} = \frac{1}{\underline{S}_{jr}^{jk}} - 1 \quad (2.10)$$

Where :
 j = non-wetting fluid within the applicable two-phase system,
 k = wetting fluid within the applicable two-phase system,
 $\underline{S}_{jr}^{jk}$ = maximum effective entrapped saturation based on $\Delta \underline{S}_k^{jk}$,
 $\Delta \underline{S}_k^{jk}$ = initial wetting phase reversal point, from primary drainage to first imbibition scanning curve, and,
 $\underline{S}_{jr}^{jk}$ = maximum effective entrapped saturation corresponding to the main imbibition pathway.

Furthermore noting that the prediction of fluid entrapment assumes three-phase system mechanisms may be determined from two-phase system relationships.

Examples of the terms used in Equation 2.10 are illustrated in Figure 2.4.

Figure 2.4 - Hypothetical Two-Phase Curves showing Terms defined in Equation 2.10 (Modified from Parker and Lenhard, 1987).

From observation of Figure 2.4 it may be noted that the entrapped non-wetting phase saturation will vary along the primary imbibition scanning curve

from zero at the reversal point, to $\underline{S}_{ir}^{jk}$ when the apparent wetting phase saturation $\underline{S}_k^{jk}$ equals 1.0. In order to estimate intermediate entrapped saturation values between these two extremes, an interpolation formula was proposed whereby entrapped saturation was assumed to vary linearly with the apparent wetting phase saturation according to (Lenhard, 1992):

$$\underline{S}_{it}^{jk} = \frac{\underline{S}_{ir}^{jk} (\underline{S}_k^{jk} - \Delta \underline{S}_k^{jk})}{1 - \Delta \underline{S}_k^{jk}} \quad \text{and} \quad \underline{S}_k^{jk} > \Delta \underline{S}_k^{jk} \quad (2.11)$$

Where : $\underline{S}_k^{jk}$ = apparent wetting phase saturation, and,
 $\underline{S}_{it}^{jk}$ = entrapped non-wetting phase saturation.

Lastly, it should be noted that once $\underline{S}_k^{jk}$ decreases to $\Delta \underline{S}_k^{jk}$ during drainage, the saturation pathway will return to main drainage and $\underline{S}_{it}^{jk}$ will return to zero.

Furthermore, higher order imbibition scanning curves are assumed to follow the same linearity as their primary imbibition scanning path. Thus, higher order imbibition scanning paths are also linked to the drainage-imbibition reversal point on the main drainage pathway (White and Lenhard, 1993).

Equations 2.10 and 2.11 may be applied to a number of different entrapment scenarios occurring within either two or three-phase systems. More specifically, air may become entrapped by NAPL, water, or both, and NAPL may become entrapped by water. Furthermore, NAPL containing entrapped air may itself become occluded within the water phase. Air and NAPL entrapment are assumed to be controlled by NAPL-air and water-NAPL interfaces which approach, in the limit, two-phase system behavior (Parker and Lenhard, 1987). The following sections will consider the equations formulated for NAPL

entrapment within water, air entrapment within NAPL and water and, air entrapment within NAPL occluded within water. All equations contained hereafter were obtained from either Parker and Lenhard (1987) or Lenhard (1992).

(a) NAPL Entrapment

NAPL entrapment is assumed to be controlled by the position of the water-NAPL interface within the porous medium. Maximum entrapped NAPL saturation for a three-phase system may be estimated from two-phase water-NAPL data and Equation 2.10 :

$$\underline{S}_{or} = \frac{(1 - \underline{S}_w^{\min})}{1 + R_{ow} (1 - \underline{S}_w^{\min})} \quad \text{With } R_{ow} = \frac{1}{\underline{S}_{or}^{ow}} - 1 \quad (2.12)$$

Where : $\underline{S}_{or}$ = maximum effective entrapped NAPL saturation due to NAPL-water interface,
 $\underline{S}_w^{\min}$ = minimum apparent water saturation (since NAPL introduction) and,
 $\underline{S}_{or}^{ow}$ = maximum effective entrapped NAPL saturation corresponding to the main imbibition pathway for a two-phase water-NAPL system.

In conjunction with this, the analog of Equation 2.11 is employed to estimate an effective entrapped NAPL saturation for any given apparent water saturation :

$$\underline{S}_{ott} = \min \left[\frac{\underline{S}_{or} (\underline{S}_w - \underline{S}_w^{\min})}{(1 - \underline{S}_w^{\min})}, \underline{S}_o \right] \quad (2.13)$$

Where : $\underline{S}_{ott}$ = effective total entrapped NAPL saturation = $\underline{S}_{ot} + \underline{S}_{otw} + \underline{S}_{oto}$,
 $\underline{S}_{ot}$ = effective entrapped NAPL saturation,
 $\underline{S}_{otw}$ = effective entrapped air phase saturation within entrapped NAPL due to a water-air interface, and,
 $\underline{S}_{oto}$ = effective entrapped air phase saturation within entrapped NAPL due to a NAPL-air interface.

Noting that the second condition in Equation 2.13 ensures that no more NAPL may become entrapped than is present. In conjunction with this, if no air is entrapped within the system (i.e. $\underline{S}_{otw} = \underline{S}_{oto} = 0$), $\underline{S}_{ott}$ will reduce to $\underline{S}_{ot}$.

(b) Air Entrapment

Analysis of air entrapment is similar to that for NAPL, noting however that air may become entrapped within NAPL, water, or within NAPL entrapped within water. The volume of entrapped air prior to the arrival of NAPL will be dependent on the minimum effective water saturation prior to NAPL arrival, $\Delta \underline{S}_w^{aw}$, and the current apparent water saturation $\underline{S}_w$. Following NAPL introduction, air entrapped by the NAPL-air interface will be dependent on the minimum apparent total liquid saturation $\underline{S}_t^{\min}$ and the current total liquid saturation $\underline{S}_t$ (Van Geel, 1994).

Possible air entrapment scenarios, with appropriate equations and conditions are (Lenhard, 1992) :

(2.14 a - e)

$$\text{For } \underline{S}_t^{\min} > \Delta \underline{S}_w^{aw} : \quad \underline{S}_{at} = \underline{S}_{arw} \left[\frac{(\underline{S}_t^{\min} - \Delta \underline{S}_w^{aw})}{(1 - \Delta \underline{S}_w^{aw})} \right] + \underline{S}_{aro} \left[\frac{(\underline{S}_t - \underline{S}_t^{\min})}{(1 - \underline{S}_t^{\min})} \right]$$

$$\text{For } \underline{S}_w \geq \underline{S}_t^{\min} : \quad \underline{S}_{atw} = \underline{S}_{arw} \left[\frac{(\underline{S}_t^{\min} - \Delta \underline{S}_w^{aw})}{(1 - \Delta \underline{S}_w^{aw})} \right] + \underline{S}_{aro} \left[\frac{(\underline{S}_w - \underline{S}_t^{\min})}{(1 - \underline{S}_t^{\min})} \right]$$

$$\text{For } \underline{S}_t^{\min} > \underline{S}_w > \Delta \underline{S}_w^{aw} : \quad \underline{S}_{atw} = \underline{S}_{arw} \left[\frac{(\underline{S}_w - \Delta \underline{S}_w^{aw})}{(1 - \Delta \underline{S}_w^{aw})} \right]$$

$$\text{For } \underline{S}_w \leq \Delta \underline{S}_w^{aw} : \quad \underline{S}_{atw} = 0$$

$$\text{and,} \quad \underline{S}_{ato} = \underline{S}_{at} - \underline{S}_{atw}$$

Where : $\underline{S}_{arw}$ = maximum entrapped air saturation due to advancing water,
 $\underline{S}_{aro}$ = maximum entrapped air saturation due to advancing NAPL

Likewise :

(2.15 a - d)

$$\text{For } \underline{S}_t^{\min} \leq \Delta \underline{S}_w^{aw} : \quad \underline{S}_{at} = \underline{S}_{aro} \left[\frac{(\underline{S}_t - \underline{S}_t^{\min})}{(1 - \underline{S}_t^{\min})} \right]$$

$$\text{For } \underline{S}_w > \underline{S}_t^{\min} : \quad \underline{S}_{atw} = \underline{S}_{aro} \left[\frac{(\underline{S}_w - \underline{S}_t^{\min})}{(1 - \underline{S}_t^{\min})} \right]$$

$$\text{For } \underline{S}_w \leq \underline{S}_t^{\min} : \quad \underline{S}_{atw} = 0$$

and, $\underline{S}_{ato} = \underline{S}_{at} - \underline{S}_{atw}$

Entrapped air phase saturations within entrapped NAPL may be estimated by the following set of equations :

(2.16 a - c)

$$\text{For } \underline{S}_w > \underline{S}_t^{\min} \text{ and } \underline{S}_t^{\min} > \Delta \underline{S}_w^{aw} : \quad \underline{S}_{oto} = \left[\frac{\underline{S}_{aro} \underline{S}_{or} (\underline{S}_w - \underline{S}_t^{\min})}{[(1 - \underline{S}_w^{\min})(1 - \underline{S}_t^{\min})]} \right]$$

$$\text{For } \underline{S}_w^{\min} > \Delta \underline{S}_w^{aw} : \quad \underline{S}_{otw} = \left[\frac{\underline{S}_{arw} \underline{S}_{or} (\underline{S}_t^{\min} - \underline{S}_w^{\min})}{[(1 - \underline{S}_w^{\min})(1 - \Delta \underline{S}_w^{aw})]} \right]$$

$$\text{For } \underline{S}_w^{\min} \leq \Delta \underline{S}_w^{aw} : \quad \underline{S}_{otw} = \left[\frac{\underline{S}_{arw} \underline{S}_{or} (\underline{S}_t^{\min} - \Delta \underline{S}_w^{aw})}{[(1 - \underline{S}_w^{\min})(1 - \Delta \underline{S}_w^{aw})]} \right]$$

Where : $\Delta \underline{S}_w^{aw}$ = minimum apparent water saturation prior to NAPL introduction.

Similar to Equations 2.16 a - c :

(2.17 a - c)

For $\underline{S}_w \leq \underline{S}_t^{\min}$ and $\underline{S}_t^{\min} > \Delta \underline{S}_w^{aw}$:

$$\underline{S}_{oto} = 0$$

For $\underline{S}_w^{\min} > \Delta \underline{S}_w^{aw}$:

$$\underline{S}_{otw} = \frac{[\underline{S}_{arw} \underline{S}_{or} (\underline{S}_w - \underline{S}_w^{\min})]}{[(1 - \underline{S}_w^{\min})(1 - \Delta \underline{S}_w^{aw})]}$$

For $\underline{S}_w^{\min} \leq \Delta \underline{S}_w^{aw}$:

$$\underline{S}_{otw} = \frac{[\underline{S}_{arw} \underline{S}_{or} (\underline{S}_w - \Delta \underline{S}_w^{aw})]}{[(1 - \underline{S}_w^{\min})(1 - \Delta \underline{S}_w^{aw})]}$$

Correspondingly :

(2.18 a and b)

For $\underline{S}_w > \underline{S}_t^{\min}$ and $\underline{S}_t^{\min} < \Delta \underline{S}_w^{aw}$:

$$\underline{S}_{oto} = \frac{[\underline{S}_{aro} \underline{S}_{or} (\underline{S}_w - \underline{S}_t^{\min})]}{[(1 - \underline{S}_w^{\min})(1 - \underline{S}_t^{\min})]}$$

$$\underline{S}_{otw} = 0$$

Lastly :

(2.19 a and b)

For $\underline{S}_w \leq \underline{S}_t^{\min}$ and $\underline{S}_t^{\min} \leq \Delta \underline{S}_w^{aw}$:

$$\underline{S}_{oto} = 0, \text{ and,}$$

$$\underline{S}_{otw} = 0$$

It should be noted that saturation histories (in terms of $\Delta \underline{S}_w^{aw}$, $\underline{S}_w^{\min}$ and $\underline{S}_t^{\min}$) must be known in order to calculate volumes of free and entrapped air and NAPL via Equations 2.12 to 2.19 (Van Geel, 1994).

The linear interpolation equation presented previously (Equation 2.11) was noted by Parker and Kaluarachchi (1992) to introduce numerical problems

when the LP model was included in a multiphase flow code. To overcome these difficulties, Equation 2.11 may be altered giving :

$$\underline{S}_{it}^{jk} = \left[\frac{(1 - \Delta \underline{S}_k^{jk})}{1 + R_{jk}(1 - \Delta \underline{S}_k^{jk})} - \frac{(1 - \underline{S}_k^{jk})}{1 + R_{jk}(1 - \underline{S}_k^{jk})} \right] \quad (2.20)$$

Thus, all entrapment equations presented previously may be modified, to circumvent modeling problems, if required.

2.2.6 Residual Saturation and the LP Hysteretic Model

The LP model presented in Sections 2.2.1 through 2.2.5 allows saturation hysteresis and fluid entrapment effects to be incorporated into three-phase flow systems. However, erroneous predictions may result if the effects of a residual NAPL saturation are neglected. Van Geel (1994) found that incorporation of a residual saturation into the LP Hysteretic model significantly changed predicted subsurface NAPL distributions during a numerical simulation of a LNAPL (heptane) spill in silica sand. Similarly, Sleep and Sykes (1993b) attempted to incorporate a residual NAPL during three-phase flow and contaminant transport simulations generated by a compositional simulator developed previously (Sleep and Sykes, 1993a). Van Geel (1994) and Sleep and Sykes (1993b) forced a residual NAPL saturation to remain during their model simulations by reducing the NAPL permeability to zero once a fixed minimum NAPL saturation was reached during drainage. Eckberg and Sunada (1984), noted a significant residual NAPL phase remaining following a laboratory NAPL spill in an experimental column. Likewise, other researchers (Brush, 1994) have found that

simulations which force a residual NAPL saturation to remain following drainage (by reducing NAPL permeability) are better able to represent actual observed NAPL subsurface distributions. Unfortunately, over simplification problems have been noted with this method, as only a constant residual value, independent of the saturation pathway, may be represented (Brush, 1994). To date, little has been done to incorporate the effects of residual non-wetting phase saturation into three-phase fluid systems. Hence, the need for the research and conceptual model presented in this thesis.

CHAPTER 3

3.0 MICRO-SCALE THEORY

Traditionally, conceptual models describing multiphase flow systems within porous media have been developed on macro / continuum scales (see Section 2.1). While these models are useful in that they predict some measure of fluid distribution within the subsurface, they often cannot adequately describe formation, dissolution and mobilization of entrapped non-wetting fluid (Lowry and Miller, 1995). Stated differently, most models treat the non-wetting entrapped phase saturation as a uniform parameter, neglecting the influence of micro-scale phenomena. To this end, a great deal of research investigating how the effects of micro-scale phenomena should be incorporated into constitutive theory has been under taken. More specifically, a number of conceptual, numerical, and experimental pore scale models have been developed and studied in the past to determine qualitative and quantitative micro-scale factors influencing multiphase flow (Lowry and Miller, 1995 ; Soll et al., 1993 ; Dias and Payatakes, 1986 a and b ; Chatzis et al., 1983 ; Zhou and Orr, 1995).

3.1 PORE SCALE MODELS

Pore scale models are frequently used to study micro-scale parameters and their effect on entrapped saturation. Dullien (1992) defined two basic categories of pore scale models, namely : capillary tube bundles and, network models. The first model category results in a rather simplified depiction of a porous medium structure, whereas the second model class may range from very

simple to very complex. Indeed, over the past three decades, a number of advances have been made with network modeling, resulting in models with fairly accurate quantitative prediction capabilities.

(a) Capillary Tube Bundles

Capillary tube models consist of a bundle of cylindrical capillary tubes of different diameters and equal lengths (Figure 3.0). Each tube has a uniform diameter along the length, L , and capillary pressure for one tube may be calculated via Equation 1.1.

Capillary pressure-saturation drainage relationships, by way of example, may be modeled by first filling the largest tubes with the non-wetting fluid, at a given threshold pressure, and allowing successively smaller tubes to fill as pressure is increased (Dullien, 1992). Unfortunately, the simple nature of the model precludes inclusion of capillary hysteresis, fluid entrapment, residual saturation, and irreducible saturation effects.

Figure 3.0 - Conceptual Capillary Tube Bundle Model.

(b) Network Models

Network models typically consist of some 'idealization' of porous medium void space, in either two or three dimensions (Figure 3.1). Pore space is usually represented by interconnecting pore 'bodies' and 'throats' which may be of equal or differing sizes. Networks may also be regularly or randomly arranged.

Physical representations of networks have been created for experimental purposes and are usually prepared by etching network bodies and throats into thin surfaces. Fluid displacement experiments may be performed by connecting the network to pressure controlled fluid 'reservoirs' and noting saturation changes with increasing or decreasing pressures. Frequently, digital image analysis methods are used to facilitate calculations and provide an increased degree of accuracy (Soll et al., 1993).

Numerical computational network representations are frequently employed in pore scale studies and offer a number of advantages over physical models. More specifically :

- numerical models allow relatively easy analysis of three dimensional configurations which are difficult to represent physically,
- numerical models enable large scale systems to be analyzed (on the order of 8000 pore bodies (Lowry and Miller, 1995), and,
- numerical models allow users to easily change system parameters such as aspect ratios, pore size distributions, etc. An option which is not available with physical models (i.e. a new model must be created to study each change in parameter).

Figure 3.1 - Two vs. Three Dimensional Networks.

3.2 PORE SCALE FACTORS INFLUENCING ENTRAPPED SATURATION

Recent research efforts into micro-scale phenomena have led to an increased understanding of pore scale influences on multiphase flow. Factors affecting entrapped non-wetting phase saturation have garnered particular interest among researchers due to the large number of NAPL contaminated sites currently requiring remediation. A number of pore scale properties have been observed to affect entrapped non-wetting fluid saturation including : Connectivity, pore size distribution, aspect ratio, and gravity and viscous forces.

3.2.1 Connectivity

Connectivity refers to the manner in which pore bodies are connected to pore throats within the void space network representation. The most common measure of connectivity is the coordination number (Z) for a given pore, referring

to the number of 'sites' or pore throats connected to the body. Cruder network models may employ pore bodies with identical Z values, although more advanced models may incorporate coordination number 'distributions' reflecting true subsurface void space conditions with greater accuracy.

Using a complex numerical network model, Lowry and Miller (1995) studied the effect of changing connectivity within a three dimensional network on entrapped non-wetting fluid saturation. Primary drainage and imbibition curves were generated for distributions with average coordination numbers ranging from 7 to 10. In general, it was observed that increasing Z resulted in increased curvature for both the drainage and imbibition curves (refer to Figure 3.2). This was accredited to a greater number of pore throats being accessible at the beginning and end of fluid displacement processes, hereby leading to the increased curvature observed.

In addition to curvature observations, it was noted that entrapped saturation values obtained during imbibition decreased with increasing average Z . It was hypothesized that this decrease was due to a greater probability of maintaining a continuous non-wetting phase in higher connectivity systems (hereby reducing entrapped fluid), as more conduits are available for continuous non-wetting fluid flow (Lowry and Miller, 1995). Stated differently, a greater number of bypass and snap-off events must occur to isolate non-wetting fluid into ganglia for higher connectivity systems.

Lastly, regarding the lower entrapped saturation values observed, it was noted that increasing Z will lead to a larger ratio of total pore throat to total pore

body volume. In addition to this, wetting fluid will tend to remain within pore throats and entrapped non-wetting fluid will prefer to remain within the larger pore bodies (due to wettability characteristics). Taken together, it was concluded that the volume fraction of entrapped non-wetting fluid should tend to decrease with increasing connectivity effects (Lowry and Miller, 1995).

**Figure 3.2 - Drainage and Imbibition Curves Obtained for Different Coordination Numbers.
(Taken from Lowry and Miller, 1995).**

Figure 11. The influence of pore coordination number on p_c - s drainage curves.

Figure 12. The influence of pore coordination number on p_c - s imbibition curves.

3.2.2 Pore Size distribution

Within any porous medium, a wide range of pore throat and pore body sizes are contained within the void volume. Thus, pore size distribution is an important parameter characterizing a medium, and may significantly affect multiphase flow processes (Dias and Payatakes, 1986a). Variability in pore throat and body distributions and the effects of such on pressure-saturation relationships were investigated by Lowry and Miller (1995). Five distributions of pore body and throat sizes were generated, ranging from least variable (11.3 - 13.0) to most variable (4.33-5.00) as shown in Figure 3.3.

Increasing variability was noted to result in increased curvature of both the drainage and imbibition pressure-saturation graphs, similar to the findings discussed above. This observation was credited to the wider pore size distributions resulting in a greater fraction of smaller and larger pores being available for fluid displacement at higher and lower capillary pressures. In conjunction with these results, it was noted that increased variability resulted in greater values of entrapped saturation during imbibition. This finding was credited to the increased tortuosity of wetting phase imbibition paths in highly variable systems, encouraging a greater amount of bypass (Lowry and Miller, 1995).

Figure 3.3 - Drainage and Imbibition Curves Obtained for Increasing Variability (Taken from Lowry and Miller, 1995).

Figure 20. The influence of pore-size variability on p_c - s drainage curves.

Figure 21. The influence of pore-size variability on p_c - s imbibition curves.

3.2.3 Aspect ratio

The aspect ratio of a given pore refers to the ratio of pore body diameter to pore throat diameter, and indicates what entrapment mechanism is most likely to occur on the micro-scale. In general, it has been observed that increasing aspect ratios result in a greater percentage of entrapped non-wetting phase fluid

being retained within pores via 'snap-off', and decreasing aspect ratios result in increased 'bypass' entrapped fractions (Zhou and Orr, 1995).

Lowry and Miller (1995) studied aspect ratio effects on a three dimensional pore volume network by altering average pore throat radii within their numerical model. Four successive simulations were generated, resulting in average aspect ratio values of 1.4, 2.0, 2.6 and 3.7 respectively. As the simulation was done to determine the prevalence of 'snap-off' entrapment during imbibition only, drainage pressure-saturation curves were not generated.

The results of increasing aspect ratio are presented in Figure 3.4. As illustrated, as aspect ratio was increased, entrapped saturation values also increased substantially. This was accredited to a greater number of pore throats becoming amenable to 'snap-off' processes hereby increasing the total amount of entrapped non-wetting phase. In conjunction with this, curvature was noted to increase with increasing aspect ratio. This was also attributed to the increasing prevalence of snap-off within pores.

Figure 3.4 - Imbibition Curve Obtained for Increasing Aspect Ratio (Taken from Lowry and Miller, 1995).

Figure 16. The influence of the aspect ratio on the p_c - s imbibition curve.

3.2.4 Gravity and Viscous Force Influences

Non-wetting entrapped saturation is held within soil pores through the influence of capillary pressure forces. Under natural circumstances, these forces are sufficient to render ganglia immobile. Occasionally however, gravity forces associated with buoyancy / density effects and viscous forces associated with ground water flow may overcome capillary forces and remobilize entrapped fluid (Bedient et al., 1994). Thus, under some circumstances, gravity and viscous forces may significantly affect entrapped saturation and they will need to be considered.

Zhou and Orr (1995), investigated gravity and viscous effects on snap-off and bypass entrapment processes. They defined three parameters to describe physical system properties :

Capillary number : $N_c = k \nabla P / \sigma$, (3.0 a - c)

Bond number : $N_b = \Delta \rho g k / \sigma$, and

Brownell-Katz number : $N_{bk} = N_c + N_b$

Where : k = intrinsic permeability,
 ∇P = pressure gradient,
 σ = interfacial tension,
 $\Delta \rho$ = fluid-fluid density difference, and,
 g = gravitational acceleration constant.

The Capillary number (N_c) being a ratio of viscous force to capillary force, the Bond number (N_b) being a ratio of gravity force to capillary force and, the Brownell-Katz number (N_{bk}) being a combination of the two (Bedient et al., 1994).

During the experiment, immiscible displacements on a vertical sand pack were performed while varying N_c and N_b . It was observed that a significant correlation between the amount of entrapped non-wetting saturation and the Brownell-Katz number existed for the system considered. More directly, entrapped saturation was observed to increase with decreasing N_{bk} . Zhou and Orr (1995) found no direct correlation between N_c and entrapped fluid, although some researchers have observed increasing entrapped saturation values with decreasing capillary number (Bedient et al., 1994).

CHAPTER 4

4.0 LABORATORY STUDY:

Experimental procedures were established to define two-phase parameters required by the current LP model and to determine factors influencing residual NAPL saturation. Basic soil and fluid characteristics were determined by literature review and prevalent laboratory techniques. Following this, two-phase pressure-saturation relationships were generated for water-air, water-heptane, and heptane-air systems. Lastly, three three-phase experiments were performed during which water saturations were held constant as heptane was sequentially imbibed and drained from each experimental apparatus. Experimental procedures, apparatus, and data are described in Sections 4.1 through 4.5.

4.1 SOIL AND FLUID SYSTEM PARAMETERS

The porous medium used throughout all experimental procedures was a grey, silica based sand manufactured by Unimin Canada Ltd. The sand ordered was 7030, being 30% retained on a 70 mesh or coarser. The grain size distributions obtained from two independent sieve analyses are included in Table 4.0 and Figure 4.0. The vertical saturated hydraulic conductivity was determined by performing constant head tests on three independent samples. The average K value was then determined by taking the average of the three hydraulic conductivities obtained. A summary of these results is presented in Table 4.1.

The three immiscible fluids used during all experiments were tap water, ambient air and heptane dyed with Sudan III. The heptane was dyed with Sudan III in order to distinguish the heptane visually from water, as the dye is miscible in heptane and immiscible in water. Values for the density, viscosity and molecular weight of the three fluids at 20 °C are presented in Table 4.2. Vapour pressure and solubility of heptane at 20 °C are 35 mm Hg and 3 mg/L respectively (Van Geel, 1994).

Table 4.0 - Porous Medium Sieve Analysis Results.

Sieve	Diameter (mm)	% Passing	Diameter (mm)	% Passing
20	0.85	100	0.85	100
30	0.6	99.97	0.6	100
40	0.425	91.41	0.425	90.06
60	0.25	29.11	0.25	29.6
70	0.212	20.81	0.212	21.45
120	0.125	8.8	0.125	8.6
200	0.075	3.2	0.075	3.27
pan	N/A	0	N/A	0

Figure 4.0 - Grain Size Distribution Curves Obtained for Silica Sand. **Table 4.1 - Summary of Constant Head K_{vert} Determinations.**

Trial	K_{vert} (cm / sec)	n
1	0.016483	0.403123
2	0.014497	0.395462
3	0.010605	0.382721
Average Values	0.013862	0.393768

Table 4.2 - Fluid Parameter Values (Van Geel, 1994).

Parameter	Water	Air	Heptane
Density (kg/m^3)	998.2	1.2	685.8
Viscosity (cP)	1.002	0.01827	0.409
Molecular Weight (g/mol)	18.016	28.97	100.2

Surface tension values between each two-phase system are (Adamson, 1997):

$$\sigma_{aw} = 72.75 \text{ dynes / cm}$$

$$\sigma_{ow} = 50.20 \text{ dynes / cm}$$

$$\sigma_{ao} = 19.70 \text{ dynes / cm}$$

4.2 PRESSURE TRANSDUCERS AND DATA ACQUISITION SYSTEM

In order to measure fluid pressures during the experimentation, wet / dry transducers manufactured by Sensotec Inc. (model number WD-TJE) were utilized. Initially, the transducer cavities were filled with water and attached to a horizontal manifold. The transducers were attached to the manifold via threaded connectors and Teflon tape to create a water tight seal, and a procedure was followed to ensure that the cavities within the transducers were completely filled with fluid (Van Geel, 1994). The manifold was then slowly filled with water and attached to a water filled burette using flexible C flex tubing. The burette was raised and lowered systematically to create positive and negative pressure heads. Resulting voltage readings were obtained by connecting each transducer to a Sciometric Instruments Inc. System 200 data acquisition system. The transducers were powered by a 10 volt power supply, and the millivolt output signal was recorded by the data acquisition system.

After a number of calibration trials, it was determined that the error for some transducers was unacceptable (ranging from plus or minus 3 to 5 cm). Initially, it was thought this might be due to a poor voltage source which was later determined to be drifting between 9 to 11 volts, rather than remaining at 10 volts as required. The voltage source was replaced with a Hewlett Packard DC power supply (model number E3610A). After replacing the voltage source, the transducers were re-calibrated although errors obtained for some were still deemed unacceptable. Because of this, five of the transducers were sent to the manufacturer for re-calibration, then re-tested. The final calibration results, and

equations generated for each transducer are presented in Table 4.3. Each transducer was tested under three independent trial runs and a best-fit regression line fitted to all data points using Microsoft Excel (Version 5.0). All equations obtained are of the form :

$$\text{Head (cm H}_2\text{O)} = \text{Intercept} + \text{Slope} \times \text{Voltage Reading of Transducer (millivolts)}.$$

Table 4.3 - Results of Transducer Calibration.

Transducer Serial Number	Sent to Manufacturer	Slope of Calibration Equation (cm of H ₂ O head / mVolts)	Intercept of Calibration Equation (cm of H ₂ O head)	Maximum Absolute Error Obtained (cm of H ₂ O head)
331095	No	13982.34	-3.91612	0.53798
331101	No	13784.62	-13.4863	0.56524
331093	No	13602.35	4.5121	0.7609
331098	Yes	13863.86	-1.01123	0.57487
331099	Yes	13944.34	-4.324	0.68486
331103	Yes	13908.94	-4.80547	0.5072
331097	Yes	14046.66	-3.84433	0.57159
331105	No	14223.71	-4.74084	0.9172
331092	No	14254.5	-5.92768	0.9219
331100	No	14163.15	-4.79098	0.8679
331091	Yes	13822.09	-4.13024	0.62477

4.3 EXPERIMENTAL APPARATUS AND TWO-PHASE EXPERIMENTS

In order to determine the two-phase Van Genuchten parameters for water-air, heptane-air, and water-heptane systems, five stainless steel pressure cells were constructed. The cells were designed to accommodate a representative elementary volume of sand between two square plates of stainless steel, contained within a stainless steel cylinder. A simple schematic of an experimental cell is illustrated in Figure 4.1.

The cells were initially filled with sand, as uniformly as possible, then sealed using the bolt connectors. The porosity values for each experiment were determined using the weights of each cell with and without sand. The specific density of the silica sand was assumed to be 2.67 g / cm^3 . The experimental set-up and specific problems encountered for each two-phase study are presented in the following sections.

Figure 4.1 - Schematic of Stainless Steel Experimental Cells.

4.3.1 Water-Air Two-Phase System

The experimental set-up for the two-phase water-air experiment is provided in Figure 4.2. Each cell was initially flushed with CO_2 for five minutes prior to saturating the cells. This was done to eliminate air being entrapped in the water phase during filling, as CO_2 more readily dissolves in water.

To saturate a cell, the top port hole containing a porous cup was removed and a syringe filled with water was pushed to the bottom of the cell. Water was then slowly pushed into the cell, using the syringe, until a saturated state was

obtained. Cells were then left overnight to allow for all the CO₂ to dissolve.

Subsequently, a pressure transducer, attached to a saturated porous cup, was inserted into the empty port hole with Teflon tape used to create a water tight seal. A procedure was used to ensure that the cavity within the transducer and porous cup was completely filled with water, as illustrated in Figure 4.3 (Van Geel, 1994).

Table 4.4 contains parameters calculated for each cell (C1 through C4) and fritted glass funnel (F1 through F3), by weighing the apparatus prior to and after filling with silica sand. Fritted glass funnels were used in conjunction with the stainless steel cells, for reasons outlined in Section 4.3.4.

Table 4.4 - Parameters used to calculate Void Volumes for each Cell and Funnel, Water-Air Two-Phase System.

Cell / Funnel	Mass Sand (g)	Total Volume (V_t) cm³	Volume of Solids (V_s) cm³	Volume of Voids (V_v) cm³	Porosity (n)
C1	397.8	242.9	148.9	93.9	0.386
C2	396.4	242.9	148.5	94.4	0.388
C3	384.7	242.9	144.1	98.8	0.407
C4	395.5	242.9	148.1	94.7	0.390
F1	505.4	307.7	189.3	118.4	0.385
F2	483.4	313.5	181.0	132.5	0.422
F3	514.2	325.1	192.5	132.5	0.408

Figure 4.2 - Two-Phase Water-Air Experimental Apparatus.

Figure 4.3 - Schematic of Transducer and Porous Cup Connection (Taken from Van Geel, 1994).

Initially all porous cups were attached to stainless steel fittings using a 5 minute epoxy mixture. Prior to use in the cells, all porous cups were saturated with water by attaching them to a hose and using a peristaltic pump to push water through the cups for approximately two minutes to ensure the porous cups were saturated. The bottom porous cup (Figure 4.3) was attached to a hose barb connector which was then connected to a water filled burette using flexible C flex Masterflex tubing. The top plug was then removed from each cell, to allow for an air entry point within each system. Lastly, burette water levels were then set to coincide with the top of each cell, to provide initial starting pressure values.

To generate pressure-saturation data points for each cell, the flexible Masterflex tubing joining the cell and burette was fed through a peristaltic pump, which was used to pump water into and out of the cell. To create water-air drainage curves, water was pumped out of each cell, a few millilitres at a time, and voltage readings were taken when an equilibrium condition within the cell was reached. Equilibrium was determined by observing successive voltage readings recorded by each transducer. Four identical readings (taken 30 seconds apart) were deemed to indicate an equilibrium state within the cells. Voltage readings were then converted to pressure values using the calibration equations presented in Section 4.2. Water saturation values in each cell were determined by comparing water levels in the burettes between successive readings.

Once irreducible water saturation values had been obtained, water was pumped into each cell, a few millilitres at a time, and voltage readings recorded

at equilibrium to generate wetting curve data. Irreducible water saturation was determined to be when changes in capillary pressure resulted in no additional change in water saturation. An apparent saturated state was assumed to occur once water could be seen collecting within the air port hole.

4.3.2 Heptane-Air Two-Phase System

To generate heptane-air pressure-saturation relationships, a methodology similar to that outlined for the water-air experiments was used (Figure 4.3). In order to render the porous cups wetting to heptane and hydrophobic, the porous cups were treated by soaking them for two hours in chlorotrimethylsilane, then rinsing with toluene and methanol (Lenhard and Parker, 1988). As before, the stainless steel cells were filled with sand, and saturated with heptane using the syringe method. Transducers filled with heptane, in turn connected to heptane saturated porous cups, were inserted into the top of each cell. Treated porous cups, epoxied to hose barb fittings, were attached to heptane filled burettes using braided tubing as for the water-air systems. However, a flexible fuel and lubricant Tygon tubing was employed in place of the C flex tubing due to reactivity between the heptane and the C flex. Heptane-air drainage and wetting curves were then generated using peristaltic pumps as described in Section 4.3.1. Table 4.5 contains parameters calculated for each cell. Fritted glass funnel data were not obtained for the two-phase heptane-air system, due to a large amount of evaporation from the funnels.

Table 4.5 - Parameters used to calculate Void Volumes for each Cell, Heptane-Air Two-Phase System.

Cell	Mass Sand (g)	Total Volume (Vt) cm³	Volume of Solids (Vs) cm³	Volume of Voids (Vv) cm³	Porosity (n)
1	386.9	242.9	144.0	97.99	0.403
2	389.0	242.9	146.1	97.20	0.400
3	382.6	242.9	139.7	99.60	0.410

A notable problem observed during heptane-air data generation was evaporation of heptane over time. Trial runs were observed to take a number of days due to the sometimes long periods of time required for equilibrium conditions to be achieved within cells. To help reduce evaporation of heptane from the cells, a silicone skin was utilized and applied within the cracks between the stainless steel plates and cylinder, as well as around all stainless steel fittings. In order to correct for evaporation, a control cell was set-up and weighed every day. In addition to this, air entry portholes were sealed using a silicone plug when the cells were left overnight in the lab. Average evaporation was determined to be 0.25 g / day, or 0.364 ml per day. This evaporation rate was applied to the final saturation values obtained.

4.3.3 Water-Heptane Two-Phase System

The last two-phase relationship generated was for a water-heptane system. Once again, a similar methodology was used, although all four port holes were utilized and the air port hole was attached to a heptane reservoir. In addition to this modification, both water filled and heptane filled transducers were attached to each cell to allow for measurement of both pore fluid pressures.

A simple schematic of the water-heptane experimental set-up is provided in Figure 4.4

Figure 4.4 - Two-Phase Water-Heptane Experimental Apparatus.

Initially the three cells were saturated with water as in the water-air experiments. To generate drainage curves, water was pulled out of each cell incrementally using the pumps, and water and heptane pressures recorded. Once again, wetting curves were generated following irreducible saturation by pushing water into each cell incrementally using the pumps. Table 4.6 lists

parameters calculated for each cell and fritted glass funnel, as outlined in Section 4.3.1.

Table 4.6 - Parameters used to calculate Void Volumes for each Cell and Funnel, Water-Heptane Two-Phase System.

Cell / Funnel	Mass Sand (g)	Total Volume (V_t) cm³	Volume of Solids (V_s) cm³	Volume of Voids (V_v) cm³	Porosity (n)
C1	389.1	242.4	147.5	94.87	0.391
C2	386.6	242.4	146.1	96.25	0.397
C3	395.4	242.4	148.1	94.30	0.389
F1	280.15	176.4	104.9	71.462	0.405
F2	233.3	143.8	87.4	56.4	0.392

One problem noted during the generation of the two-phase water-heptane data, was leakage of heptane into the braided tubing used to draw water out of the cell during drainage. Initially, a substantial amount of leakage was observed, causing results to be discarded. When the cells were dismantled, the epoxy around the hose barb fittings was noted to be 'soft' and easily imprinted. It was hypothesized that the epoxy used previously had perhaps somehow 'reacted' with the heptane in the system, allowing heptane to leak in between the porous cup and stainless steel fitting. New porous cups were obtained and fitted into the hose barbs using a new 24 hour epoxy. In addition to this, a solvent resistant silicone was obtained, and a thin skin applied over the epoxy for further protection. Following these measures, two-phase water-heptane data was regenerated. Although a small amount of heptane leakage was still noted, results obtained were not discarded, rather heptane leaving the system through the braided tubing was accounted for by measuring volumes using an equivalent amount of braided tubing and a graduated cylinder. To generate wetting curve

data for the cells, heptane trapped in braided tubing was removed and replaced with water prior to initiating imbibition.

4.3.4 Fritted Glass Funnel Apparatus

In addition to the two-phase pressure-saturation relationships generated with stainless steel cells, relationships were also obtained using fritted glass funnels (Figure 4.5). The fritted glass funnels were utilized in order to allow for comparison with results obtained from the cells, and also to generate some results while waiting for the cells to be constructed. Water-air two-phase relationships were generated as well as water-heptane data. Heptane-air relationships were not generated, due to excessive evaporation, and time constraints. Two-phase relationships obtained using the cells and the funnels were comparable, and apparent saturation results obtained using both methods are presented in Figure 4.6.

Figure 4.5 - Fritted Glass Apparatus (Taken from Van Geel, 1994).

4.4 TWO-PHASE SYSTEM RESULTS AND LP PARAMETERS

The results obtained from each two-phase experiment are presented in Figure 4.6 and Table 4.7. The first three curves illustrate primary drainage-wetting relationships obtained for water-air, water-heptane and heptane-air systems. The final plot depicts the Lenhard-Parker primary drainage curves, and raw drainage data points, for each two-phase system. Experimental apparent saturation-capillary pressure data points were fit to the Van Genuchten equation using the solver subroutine in Excel (version 5.0), specified to minimize the sum of squares of differences between predicted and experimental values.

Best-fit equations for each two-phase curve (drainage and imbibition) were generated by allowing all Van Genuchten parameters to vary such that n , α_d and α_i , could assume any value required to minimize the sum of squared differences between predicted and observed values. As illustrated in Table 4.7, the best-fit approach resulted in significantly different α_i / α_d ratios for each two-phase system, as well as considerably different n values for each curve.

In order to generate the parameters required for the LP model (α_d , α_i , n , β_{aw} , β_{ow} , and β_{ao}) the n value obtained for the water-air drainage curve was fixed for all subsequent systems and α_d values for the water-heptane and heptane-air drainage curves were regressed. The Lenhard-Parker scaling factors, β_{ij} , were determined by using the ratio of the α_d values for each two-phase system as per Equation 2.4b. The primary imbibition curve for the water-air system was then regressed using the n value obtained from the drainage curve. Lastly, the water-

heptane and heptane-air primary imbibition curves were then scaled from the water-air wetting curve using the β_i values determined previously.

Figure 4.6 - Two-Phase Capillary Pressure-Saturation Data.

Table 4.7 - Best-Fit and LP Two-Phase System Parameters.

Two-Phase System	Path	α_d or α_i	n	α_i/α_d
Water-Air	Drainage - Best Fit	0.02019	6.633	2.063
	Imbibition - Best Fit	0.04166	3.767	
Water-Air	Drainage - LP	0.02019	6.633	1.940
	Imbibition - LP	0.03917	6.633	
Water-Heptane	Drainage - Best Fit	0.04530	4.944	1.365
	Imbibition - Best Fit	0.06182	3.335	
Water-Heptane	Drainage - LP	0.04530	6.633	1.940
	Imbibition - LP	0.08790	6.633	
Heptane-Air	Drainage - Best Fit	0.07490	5.528	1.255
	Imbibition - Best Fit	0.09400	4.554	
Heptane-Air	Drainage - LP	0.07490	6.633	1.940
	Imbibition - LP	0.14530	6.633	

The β_{aw} , β_{ow} , and β_{ao} values obtained from the two-phase experimentation were determined to be 1.0, 2.24 and 3.71 respectively. When these values were compared to the β_{ij} values obtained from the ratios of interfacial tensions (Equation 2.4) some discrepancies were observed. Specifically, β_{ij} scaling factors based on interfacial tension ratios were calculated to be 1.0, 1.45 and 3.69 (Van Geel, 1994).

The α_i / α_d values obtained from the best-fit data sets were 2.063, 1.365 and 1.25 respectively. These values were noted to be quite different from the α_i / α_d value of 1.940 obtained from the Lenhard-Parker water-air data set, but not unreasonable. Kool and Parker (1987), evaluated constrained (LP) and best-fit hysteretic model parameters for eight separate two-phase soil pressure-saturation data sets generated in the laboratory. Constrained fits were determined by only allowing α_i and α_d values to vary, while maintaining equal n

values for both main drainage and main wetting curves. Best-fit parameters were allowed to vary such that n_i and n_d were not set equal for primary wetting and drainage data. Not surprisingly, best-fit data was observed to give considerably less deviation from experimental results than constrained data. In addition to this, Kool and Parker (1987) noted an average α_i / α_d value of 2.08 with a standard deviation of 0.46 from all data obtained, and hence suggested a value of 2.0 be used in situations where no other options are available. Lastly, it was noted that soils with uniform / narrow pore size distributions in the study gave the most deviation from experimental data when implementing constrained fit equations. These soils were observed to have significantly different curves for the constrained and best-fit parameters. From the curves presented in Figure 4.0, the soil used in the present study was noted to have a uniform / narrow grain size distribution. This factor could perhaps explain some of the discrepancy observed between the LP model (constrained) curves generated and the best-fit equations presented in Figure 4.6 and Table 4.7.

Maximum irreducible wetting and entrapped non-wetting fluid saturations for each two-phase system were also determined from the data generated. For the water-air two-phase system, irreducible water saturations were observed to range between approximately 8 - 29% with an average value of 18 %. Similarly, entrapped air saturations were noted to range between approximately 6 - 18 %, with an average value of 13 %. For the water-heptane system, irreducible water saturations ranged from approximately 9 to 28 %, with an average of 17 %. Entrapped heptane saturations were observed to range between approximately

18 and 26 %, with an average value of 22 %. Lastly, for the heptane-air system, irreducible heptane saturations obtained were between 13 and 23 %, with an average of approximately 19 %. Entrapped air saturations were observed to range between approximately 5 and 7 %, with an average value of 5.8 %.

4.5 THREE-PHASE PRESSURE-SATURATION EXPERIMENTS

In order to determine factors influencing NAPL residual for three-phase systems, three sets of experiments were undertaken. For the three experiments, water saturation was held at irreducible saturation, 20 % water saturation, and 40 % water saturation, respectively, while NAPL was introduced and removed from each cell. The following sections describe each experiment performed and the results obtained.

4.5.1 Three-Phase System Held at Irreducible Water Saturation

A simple schematic of the experimental set-up used to perform all three-phase experiments is provided in Figure 4.7. In order to monitor the pressures and volumes of all fluids within a three-phase system, a fifth port was added to each of the stainless steel pressure cells as shown. Two of the port holes were filled with water saturated porous cups : one to measure water pressure using a transducer and a second one to control the flow of water into and out of each cell. Similarly, two additional port holes were filled with treated heptane saturated porous cups, to measure the pressure and control the flow of heptane into and out of each cell. The fifth remaining port hole was used to allow air to freely enter

or exit the system. In all cases, porous cups were attached to fittings using an industrial strength epoxy (Scotch-Weld 2216 B/A Gray) manufactured by 3M Canada. The epoxy was cured in accordance to the manufacturer's instructions, in an effort to minimize the leakage problems noted in prior experiments.

In order to reduce the heptane evaporation rate from each system, a solvent resistant silicone, manufactured by Dow Corning (RTV 730 Sealant) was obtained and applied within the cracks between stainless steel plates and cylinder, as well as around all stainless steel fittings. To correct for evaporation, a control cell was set-up and weighed every day. From the control cell the average evaporation rate using the new silicone was determined to be 0.1 ml / day. This evaporation was applied to all three-phase saturation results obtained. Parameters used to calculate void volumes and porosity values determined for each stainless steel cell are presented in Table 4.8.

Table 4.8 - Parameters used to calculate Void Volumes for each Cell, Water Saturation held at Irreducible.

Cell	Mass Sand (g)	Total Volume (Vt) cm ³	Volume of Solids (Vs) cm ³	Volume of Voids (Vv) cm ³	Porosity (n)
1	396.3	241.9	148.42	93.48	0.386
2	398.3	241.9	149.17	92.73	0.383
3	397.8	241.9	149.0	92.90	0.384
4	403.8	241.9	151.2	90.66	0.375
5	397.7	241.9	148.9	92.95	0.384

Figure 4.7 - Three-Phase Experimental Apparatus.

As for the two-phase water-air experiments, each stainless steel cell was initially saturated with water. From a water saturated state, each cell was drained to irreducible water saturation by applying a suction pressure using Masterflex peristaltic pumps. The irreducible water saturation was determined to occur when no further water drained from a cell in response to increased suction. To inhibit heptane entering the cells during water drainage, the heptane burette stopcocks were closed. After irreducible water saturation conditions were reached in each cell, the water burette stopcocks were closed and the peristaltic pumps removed.

To introduce heptane into each cell, the peristaltic pumps were attached to the heptane-filled fuel and lubricant Tygon tubing connected to the heptane-filled burette. Heptane was slowly pumped into each cell until the desired heptane saturation was reached. The cells were then allowed to reach equilibrium prior to recording water and heptane pressures.

Following heptane imbibition, suction pressure was applied to the heptane porous cups at the bottom of each cell to initiate drainage. Drainage of heptane from each cell was performed until residual heptane conditions had been reached. Residual conditions were deemed to occur when no further heptane was observed to drain from the system in response to increased suction.

A number of heptane wetting saturations were utilized to study the effects of heptane saturation on residual. Initially, 20 millilitres of heptane were introduced into cells 1, 2, 3, 4, and 5. Each cell was then drained of heptane by applying suction pressure to the bottom of each cell until residual conditions were observed. Initially, a problem with heptane leakage into the water tubing was noted. In order to correct for this problem, the water tubing was detached from each cell and volume of heptane within the tubing recorded. To ensure no further fluid could leak from the bottom water porous cups, a solvent resistant silicone was applied around the water hose barb openings to form a seal.

After introducing 20 millilitres of heptane into each cell and draining to residual, 30 millilitres of heptane was introduced into cells 1, 2, and 3. Once again cells 1, 2, and 3 were drained to residual conditions. Following this, cells 1 through 5 were imbibed with 40 millilitres of heptane and drained to residual.

Lastly, all cells were saturated with heptane to a saturated state and drained to residual. Saturation was determined by noting when heptane collected within the air port holes.

One problem noted during draining of heptane from the cells was water leakage into the braided tubing used to introduce heptane into and out of each cell. This was noted to occur for cells 2, 3, 4 and 5, although cell 1 had no noticeable leakage. Changes in water saturation were accounted for by detaching the braided tubing after irreducible conditions had occurred and measuring volumes using a graduated cylinder. The tubing was then filled with heptane prior to initiating the next heptane wetting cycle, and all volumes carefully recorded. Although the cells initially started at irreducible water saturation, the water leakage noted indicates a change in the irreducible water saturation following heptane introduction into the three-phase system. The current LP model assumes a fixed irreducible water saturation (S_m), although the results suggest this may not be a valid assumption. Eckberg and Sunada (1984), observed significant reductions in irreducible water saturations following introduction of NAPL into an experimental soil column containing air and water phases. They accredited this reduction to differences in interfacial tension and contact angles between fluid and solid for the three-phase system as opposed to prior conditions existing for the two-phase water-air system.

Another discrepancy noted during the three-phase experimentation was lower initial irreducible water saturations than expected. Initial irreducible water saturations were recorded to range between 5.1 to 10 %, with an average value

of 7.6 %. From the two-phase water-air system data obtained previously, irreducible water saturations were noted to be between 8 to 29 % with an average value of 18 %. It is thought that this discrepancy could be accredited to some heptane being present in the system, during water drainage, for the three-phase experiments. In other words, perhaps applying suction pressure to the bottom water porous cups induced some heptane to enter into the system through the bottom heptane porous cups / hose systems, in spite of the burette stopcocks being closed. If this was the case, a thin layer of heptane could be present in the system, existing between the air and water phases. Thus, prior to imbibing with heptane, the assumption of only air and water being present in each cell may have been erroneous. In accordance with observations made by Eckberg and Sunada (1993), a small amount of heptane existing within the system during water drainage could have conceivably influenced irreducible water saturation values obtained.

It was also observed that irreducible water saturation values were obtained at significantly lower capillary pressures than the values obtained for the two-phase water-air systems. White and Lenhard (1993) noted that the presence of a thin molecular film of organic compound in a two-phase water-air system resulted in a double meniscus forming at water-air interfaces, which controlled interface geometry. In the presence of a thin layer of organic phase, β_{aw} no longer assumes the value of one, rather becomes a weighted value based on β_{ow} and β_{ao} . More specifically, β_{aw} will become greater than one, according to the formula (White and Lenhard, 1993) : $\beta_{aw}' = (1/\beta_{ow} + 1/\beta_{ao})^{-1}$. From the β_{ij}

values determined from each two-phase system (Section 4.4), the β_{aw}' value would become 1.4 as opposed to 1.0 for β_{aw} previously. Using this modified beta value would give capillary pressures, at irreducible water saturations, comparable to values obtained. Adamson (1997) also noted that two immiscible fluids in contact will result in changes in surface tension for each fluid, due to impurities arising from mutual dissolution of compounds from one fluid into the other, limited by equilibrium processes. This factor could also have contributed to the higher β_{aw} value observed.

Results obtained from the three-phase experiments conducted at irreducible water saturation for cells 1 through 5 are presented in Table 4.9. Water saturation, heptane saturation, and total liquid saturation values obtained for each cell are included in columns 2 through 4. Water pressures, heptane pressures, calculated capillary pressures between the heptane and water (P_{cow}), and heptane and air phases (P_{cao}) follow in columns 5 through 8.

Table 4.9 - Three-Phase Experimental Results at Irreducible Water Saturation.

Cell	Water Saturation	Heptane Saturation	Total Liquid Saturation	Water Pressure (cm of H ₂ O)	Heptane Pressure (cm of H ₂ O)	P _{cow} (cm of H ₂ O)	P _{cao} (cm of H ₂ O)
1	0.066	0	0.066	-89.8	N/A	N/A	N/A
	0.066	0.217	0.283	-68.4	-14.7	43.7	14.7
	0.066	0.092	0.158	-61.4	-18.6	42.8	18.6
	0.066	0.420	0.486	-49.6	-9.2	40.5	9.2
	0.066	0.128	0.194	-60.9	-17.4	43.5	17.4
	0.066	0.558	0.624	-49.4	-9.1	40.3	9.1
	0.066	0.130	0.196	-68.0	-15.2	52.9	15.2
	0.066	0.779	0.846	-55.3	1.8	57.1	-1.8
	0.066	0.134	0.199	-71.7	-15.3	56.4	15.3
2	0.100	0	0.100	-72.9	N/A	N/A	N/A
	0.100	0.217	0.317	-46.8	-13.7	33.1	13.7
	0.059	0.093	0.152	-60.2	-19.2	41.1	19.2
	0.059	0.416	0.475	-48.6	-10.3	38.3	10.3
	0.053	0.133	0.187	-66.4	-19.6	46.7	19.6
	0.053	0.568	0.622	-52.9	-8.6	44.4	8.6
	0.041	0.178	0.218	-65.7	-19.1	46.6	19.1
	0.041	0.817	0.858	-64.5	1.0	65.6	-1.0
	0.041	0.173	0.214	-74.8	-19.3	55.5	19.3
3	0.052	0	0.052	-76.4	N/A	N/A	N/A
	0.052	0.226	0.278	-49.1	-14.0	35.2	14.0
	0.052	0.084	0.136	-59.6	-20.3	39.3	20.3
	0.052	0.408	0.459	-47.0	-10.7	36.4	10.7
	0.041	0.124	0.165	-55.9	-19.2	36.7	19.2
	0.041	0.556	0.597	-43.4	-8.4	34.9	8.4
	0.041	0.113	0.154	-60.4	-20.1	40.3	20.1
	0.041	0.838	0.880	-40.9	0.4	41.3	-0.4
	0.041	0.138	0.179	-61.8	-19.7	42.1	19.7
4	0.064	0	0.064	-67.7	N/A	N/A	N/A
	0.064	0.221	0.284	-46.1	-15.1	31.1	15.1
	0.054	0.127	0.181	-50.0	-18.0	32.1	18.0
	0.054	0.579	0.633	-42.3	-10.6	31.6	10.6
	0.054	0.194	0.248	-50.8	-17.8	33.0	17.8
	0.054	0.794	0.848	-29.6	0.5	30.1	-0.5
	0.054	0.244	0.298	-52.1	-17.2	34.9	17.2
5	0.096	0	0.096	-57.8	N/A	N/A	N/A
	0.096	0.216	0.312	-43.0	-15.0	28.1	15.0
	0.084	0.127	0.212	-46.3	-18.1	28.2	18.1
	0.084	0.568	0.652	-39.2	-10.2	29.1	10.2
	0.084	0.125	0.209	-45.3	-19.0	26.3	19.0
	0.084	0.769	0.853	-24.8	-0.2	24.7	0.2
	0.084	0.174	0.258	-44.9	-20.1	24.8	20.1

For all five cells, introducing approximately 20 millilitres of heptane into the systems resulted in wetting saturations of 21.7, 21.7, 22.6, 22.1, and 21.6 % respectively. Inducing drainage from these primary wetting reversal points resulted in residual saturations of 9.2, 9.3, 8.4, 12.7 and 12.7 %. For cells 1, 2 and 3, 30 millilitres of heptane were introduced for the second wetting cycle, resulting in heptane saturations of approximately 42.0, 41.6 and 40.8 %. Draining the cells to residual resulted in saturations of 12.8, 13.3 and 12.4 %. Cells 1 through 5 were then imbibed with 40 millilitres of heptane, resulting in heptane wetting saturations of 55.8, 56.8, 55.6, 57.9 and 56.8 %. Draining the cells from these saturations produced residual saturations of 13.0, 17.8, 11.3, 19.4 and 12.5 %. Lastly, cells 1 through 5 were saturated with heptane to 100 % apparent total liquid saturation, corresponding to heptane saturations of 77.9, 81.7, 83.8, 79.4, and 76.9 %. The last draining cycle for these cells resulted in residual saturations of 13.4, 17.3, 13.8, 24.4, and 17.4 % respectively.

For all cells used, increases in heptane saturation resulted in increased residual saturations being obtained. The lowest residual saturation values were observed to occur during the first wetting / drainage cycles and ranged from 8.4 to 12.7 %. The highest residual saturation values, occurring during the last drainage cycle following an apparent total liquid saturation of 100%, ranged from 13.4 to 24.4 % (Table 4.9).

4.5.2 Three-Phase System Held at Irreducible : Results

In order to compare results, wetting heptane saturation values versus the corresponding residual heptane saturations were plotted for each cell in Figure 4.8. In the following discussion, wetting heptane saturation refers to the heptane saturation present in each cell prior to initiating drainage to residual saturation. For all cases, an increasing wetting heptane saturation resulted in increasing residual heptane. In addition to these observations, it was noted that some of the experimental cells exhibited an almost logarithmic asymptotic shape (cells 1, 2, and 3) whereas other cells (4 and 5) seemed to indicate perhaps a more linear relationship between wetting heptane saturation and resultant residual saturation. These two separate trends may be seen more clearly in Figure 4.9. To compare results between cells, data was normalized by calculating the percent maximum residual obtained, for each wetting heptane saturation, for each cell. This was done in an attempt to eliminate variation between data sets, as each cell reached a different maximum residual saturation value following the last wetting / drainage cycles imposed.

As illustrated, most of the raw data points generated fall within an envelope bounded by linear and logarithmic relationships. Due to these observations, both forms were considered when developing the conceptual model outlined in Chapter five.

Figure 4.8 - Wetting Heptane Saturation vs. Residual Heptane Saturation for Cells 1-5, Water Saturation Held at Irreducible.

Figure 4.9 - Wetting Heptane vs. % Maximum Residual for Linear, and Asymptotic Exponential Equations, Water Saturation Held at Irreducible.

4.5.3 Three-Phase System Held at 20% Water Saturation

A similar methodology was employed for performing experiments at 20 % water saturation as for the three-phase experiments held at irreducible water saturation. All five cells were filled with sand, saturated with water and drained until approximately 20 % water saturation had been obtained. As for prior experiments, the heptane burette stopcocks were closed to inhibit heptane flow into the stainless steel cells. Following water drainage, the peristaltic pumps were transferred to the heptane tubing, and wetting and drainage cycles initiated as before.

The results obtained for the second three-phase experiment are presented in Table 4.11. Table 4.10 includes parameters used to calculate void volumes, and porosity values determined for each stainless steel cell.

Table 4.10 - Parameters used to calculate Void Volumes for each Cell, Water Saturation held at 20 %.

Cell	Mass Sand (g)	Total Volume (Vt) cm ³	Volume of Solids (Vs) cm ³	Volume of Voids (Vv) cm ³	Porosity (n)
1	400.5	241.9	150.0	91.90	0.380
2	392.9	241.9	147.2	94.70	0.391
3	397.6	241.9	148.9	93.00	0.384
4	388.3	241.9	145.4	96.50	0.399
5	394.5	241.9	147.8	94.1	0.389

**Table 4.11 - Three-Phase Experimental Results at 20 %
Water Saturation.**

Cell	Water Saturation	Heptane Saturation	Total Liquid Saturation	Water Pressure (cm of H₂O)	Heptane Pressure (cm of H₂O)	P_{cow} (cm of H₂O)	P_{cao} (cm of H₂O)
1	0.208	0	0.208	-50.2	N/A	N/A	N/A
	0.208	0.219	0.427	-33.6	-11.9	21.6	11.9
	0.136	0.076	0.212	-47.0	-18.9	28.1	18.9
	0.136	0.404	0.540	-35.4	-11.0	24.4	11.0
	0.102	0.110	0.212	-46.9	-17.6	29.3	17.6
	0.102	0.545	0.647	-38.3	-9.7	28.5	9.7
	0.089	0.147	0.236	-48.7	-18.2	30.5	18.2
	0.089	0.799	0.888	-30.4	0.4	30.8	-0.4
	0.079	0.168	0.247	-53.9	-19.9	34.0	19.9
2	0.194	0	0.194	-50.9	N/A	N/A	N/A
	0.194	0.212	0.406	-35.8	-11.1	24.6	11.1
	0.148	0.091	0.239	-48.3	-17.5	30.8	17.5
	0.148	0.407	0.556	-37.0	-9.2	27.7	9.2
	0.135	0.129	0.264	-48.9	-17.0	31.9	17.0
	0.135	0.551	0.686	-38.4	-8.1	30.4	8.1
	0.129	0.135	0.263	-51.4	-18.0	33.4	18.0
	0.129	0.783	0.912	-31.4	0.7	32.1	-0.7
	0.113	0.131	0.244	-55.2	-18.5	36.7	18.5
3	0.207	0	0.207	-48.9	N/A	N/A	N/A
	0.207	0.215	0.422	-32.8	-11.7	21.1	11.7
	0.207	0.102	0.310	-35.0	-15.6	19.4	15.6
	0.207	0.538	0.745	-26.4	-8.6	17.8	8.6
	0.160	0.130	0.290	-37.1	-15.2	21.9	15.2
	0.160	0.711	0.871	-18.8	1.5	20.2	-1.5
	0.149	0.161	0.311	-36.3	-15.5	20.9	15.5
4	0.198	0	0.198	-57.7	N/A	N/A	N/A
	0.198	0.212	0.410	-39.3	-13.5	25.8	13.5
	0.159	0.093	0.253	-48.6	-19.4	29.2	19.4
	0.159	0.408	0.568	-38.3	-11.1	27.3	11.1
	0.132	0.123	0.256	-51.2	-18.6	32.6	18.6
	0.132	0.540	0.672	-40.2	-8.8	31.4	8.8
	0.110	0.134	0.243	-52.3	-18.8	33.6	18.8
	0.110	0.677	0.786	-32.7	1.2	33.9	-1.2
	0.095	0.148	0.243	-53.4	-19.3	34.1	19.3
5	0.207	0	0.207	-48.2	N/A	N/A	N/A
	0.207	0.217	0.423	-38.8	-12.6	26.3	12.6
	0.207	0.089	0.296	-40.0	-15.5	24.5	15.5
	0.207	0.515	0.722	-30.3	6.1	36.4	-6.1
	0.143	0.135	0.278	-45.1	-17.9	27.1	17.9
	0.143	0.669	0.812	-31.9	1.3	33.1	-1.3
	0.128	0.202	0.330	-43.2	-17.2	26.0	17.2

As with the prior three-phase experiments, increasing wetting phase heptane saturations were observed to result in increased residual saturations. Introducing approximately 20 millilitres of heptane into the cells during the first wetting cycle resulted in heptane saturations of 21.9, 21.2, 21.5, 21.2, and 21.7 %. Inducing drainage from these wetting reversal points yielded residual heptane saturations of 7.6, 9.1, 10.2, 9.3 and 8.9 % respectively. For the second wetting cycle, cells 1, 2 and 4 were saturated with heptane to saturations of 40.4, 40.7 and 40.8 %. Drainage from these states resulted in residual heptane saturations of 11.0, 12.9 and 12.3 %. Following this stage, cells 1 through 5 were saturated to 54.5, 55.1, 53.8, 54.0 and 51.5 % heptane saturation, and drained to residual values of 14.7, 13.5, 13.0, 13.4, and 13.5 %. Lastly, cells 1 through 5 were wetted with heptane until 100 % apparent total liquid saturation conditions were observed at heptane saturations of 79.9, 78.3, 71.1, 67.7, and 66.9 %. Drainage from these conditions yielded residual saturation values of 16.8, 13.1, 16.1, 14.8, and 20.2 %.

For all cells used, increases in wetting heptane saturation resulted in increased corresponding residual saturations. The lowest residual saturation values were observed to occur during the first wetting / drainage cycles and ranged from 7.6 to 10.2 %. The highest residual saturation values, occurring during the last drainage cycle following an apparent total liquid saturation of 100%, ranged from 13.1 to 20.2 % (Table 4.11).

As illustrated in Table 4.11, significant changes in water saturation within each cell were noted to occur over time. Although this change was observed and

measured in the lab, the cells did not remain at 20 % as intended and a significant reduction in cell water saturations resulted. Once again, this water leakage was credited to perhaps an improper seal between the porous cups and connectors resulting from epoxy deterioration. In addition to this, after performing the experiment, cells were disassembled and the porous cups used to introduce and remove heptane from the cells tested. Each porous cup hose barb connector was attached to a piece of tubing which was further filled with heptane. The tubing was then fed through a peristaltic pump, and the tip of the porous cup submerged in a water reservoir. The end of the tubing was placed in an empty beaker to allow for fluid collection. The peristaltic pump was then set on a drainage setting, in an attempt to pull water through the actual porous cup, excluding the epoxy-filled space between cup and fitting (which was not submerged in the water reservoir). A small amount of water was observed to collect in the empty beaker for all but one of the treated porous cups. As only the tips of the porous cups were submerged, it was concluded that some of the water leakage could be credited to water passing through the actual porous cups in addition to the spaces between the cups and stainless steel fittings. Thus, the entry pressure for water entering treated porous cups was exceeded. In spite of these findings, results from the three-phase experiments were not discarded. Further experiments were not conducted due to time constraints. Future work should consider these observations, and methods to prevent water passage through the treated porous cups further researched.

4.5.4 Three-Phase System Held at 20% : Results

Wetting heptane saturation values versus residual heptane saturations are plotted for each cell in Figure 4.10. As for the cells held at irreducible water saturation, some of the data seemed to indicate a logarithmic asymptotic relationship between the wetting heptane and resultant residual saturation, whereas other cells seemed to indicate a more linear relationship. As before, to compare results between cells, data was normalized by calculating the percent of maximum residual saturation obtained for each cell for each corresponding wetting heptane saturation value (Figure 4.11). As shown, most of the raw data points were noted to fall within an envelope bound by linear and logarithmic relationships.

4.5.5 Three-Phase System Held at 40% Water Saturation

The methodology employed for performing experiments at 40 % water saturation was identical to the three-phase experiments held at 20 % and irreducible water saturations. The five cells were filled with sand, water saturated and drained to approximately 40 % water saturation. During water drainage, heptane burette stopcocks were closed to inhibit heptane flow into the stainless steel cells. Following this, the peristaltic pumps were transferred to heptane tubing, and wetting and drainage cycles initiated.

The results obtained for the third three-phase experiment are presented in Table 4.13. Table 4.12 includes parameters used to calculate void volumes, and porosity values determined, for the stainless steel cells.

Table 4.12 - Parameters used to calculate Void Volumes for each Cell, Water Saturation held at 40 %.

Cell	Mass Sand (g)	Total Volume (Vt) cm³	Volume of Solids (Vs) cm³	Volume of Voids (Vv) cm³	Porosity (n)
1	395	241.9	147.9	93.96	0.388
2	391.2	241.9	146.5	95.38	0.394
3	390.8	241.9	146.4	95.54	0.395
4	395.2	241.9	148.0	93.89	0.388
5	388.1	241.9	145.4	96.54	0.399

**Table 4.13 - Three-Phase Experimental Results at 40 %
Water Saturation.**

Cell	Water Saturation	Heptane Saturation	Total Liquid Saturation	Water Pressure (cm of H₂O)	Heptane Pressure (cm of H₂O)	P_{cow} (cm of H₂O)	P_{cao} (cm of H₂O)
1	0.414	0	0.414	-36.6	N/A	N/A	N/A
	0.414	0.214	0.628	-24.2	-9.3	14.9	9.3
	0.116	0.091	0.206	-49.6	-25.3	24.3	25.3
	0.116	0.516	0.632	-37.1	-9.5	27.6	9.5
	0.087	0.119	0.206	-53.5	-19.4	34.1	19.4
	0.087	0.773	0.860	-30.2	0.9	31.1	-0.9
	0.075	0.141	0.216	-56.0	-19.7	36.3	19.7
2	0.400	0	0.400	-34.6	N/A	N/A	N/A
	0.400	0.210	0.609	-25.8	-8.1	17.6	8.1
	0.144	0.076	0.219	-46.8	-17.8	29.0	17.8
	0.144	0.496	0.639	-37.4	-8.7	28.7	8.7
	0.104	0.099	0.202	-52.1	-14.7	37.4	14.7
	0.104	0.749	0.852	-31.7	2.5	34.2	-2.5
	0.090	0.120	0.210	-52.3	-16.4	35.8	16.4
3	0.411	0	0.411	-36.1	N/A	N/A	N/A
	0.411	0.211	0.622	-24.9	-9.6	15.2	9.6
	0.327	0.107	0.434	-32.2	-18.4	13.9	18.4
	0.327	0.421	0.748	-25.2	-8.3	16.8	8.3
	0.139	0.171	0.309	-42.9	-16.1	26.8	16.1
	0.139	0.711	0.849	-26.8	0.4	27.3	-0.4
	0.111	0.190	0.301	-45.9	-17.3	28.6	17.3
4	0.413	0	0.413	-39.3	N/A	N/A	N/A
	0.413	0.213	0.626	-27.5	-3.7	23.7	3.7
	0.398	0.110	0.508	-31.0	-3.8	27.2	3.8
	0.398	0.424	0.822	-23.0	-3.8	19.2	3.8
	0.375	0.182	0.557	-31.0	-3.9	27.1	3.9
	0.375	0.504	0.879	-17.6	-0.7	17.0	0.7
	0.362	0.215	0.557	-31.3	-4.2	27.1	4.2
5	0.397	0	0.397	-36.1	N/A	N/A	N/A
	0.397	0.208	0.605	-26.9	-9.6	17.3	9.6
	0.387	0.072	0.458	-31.4	-20.5	10.9	20.5
	0.387	0.482	0.868	-16.8	0.1	17.0	-0.1
	0.373	0.163	0.536	-30.7	-16.2	14.5	16.2

As expected, increasing wetting phase heptane saturations were observed to correspond with increased residual saturations. Introducing 20 millilitres of heptane into the cells during the first wetting cycle resulted in heptane saturations of 21.4, 21.0, 21.1, 21.3, and 20.8 %. Drainage from these wetting reversal points yielded residual saturations of 9.1, 7.6, 10.7, 11.0, and 7.2 %. During the second wetting cycle, cells 1, 2, 3, 4 and 5 were imbibed with heptane to saturations of 51.6, 49.6, 42.1, 42.4 and 48.2 %. At this point, heptane was observed to collect in the air porthole of cell 5, indicating an apparent saturation of 100 %. Subsequent drainage resulted in residual saturations of 11.9, 9.9, 17.1, 18.2 and 16.3 %. Following this stage, cells 1, 2, 3 and 4 were saturated to apparent saturations of 100 %, corresponding to actual heptane saturations of 77.3, 74.9, 71.1 and 50.4 %. Resulting residual values obtained were 14.1, 11.9, 19.0 and 21.5 %.

As with prior experiments, increases in wetting heptane saturations were observed to correspond to increased heptane residual saturations. Lowest residual values were noted during the first wetting / drainage cycles and ranged from 7.2 to 11.0 %. The highest residual saturation values, obtained during the last drainage cycles, ranged from 12.0 to 21.5 % (Table 4.13).

As noted with prior three-phase experiments, significant water drainage from some cells (1, 2, and 3) was observed. Unfortunately, the water saturation in these cells did not remain at 40 % as intended, and reached substantially lower values of 7.5, 9.0 and 11.1 % at the conclusion of the experiment. Due to

this factor, no new information regarding water saturation influence on residual heptane could be obtained.

Cells 4 and 5 were noted to remain at water saturation levels close to 40 %, and thus are more amenable to comparisons with prior three-phase results. Unfortunately, two single samples may not be representative of the three-phase system, and repeat experimentation was not possible due to factors mentioned previously. In addition to this, heptane capillary pressure head values for cell 4 were inexplicably observed to remain at relatively similar values throughout the entire experiment (Table 4.13). In spite of this, irreducible heptane saturation values were deemed to occur when further suction pressures resulted in no further heptane drainage from the cell. When cell 4 was disassembled at the end of the experiment, the transducer heptane porous cup tip was noted to be broken, negating any of the pressure readings obtained.

4.5.6 Three-Phase System Held at 40% : Results

Wetting heptane saturation values versus corresponding residual heptane saturations for each cell are depicted in Figure 4.12. Cells 1, 2, and 3 seem to indicate a logarithmic asymptotic relationship between wetting heptane saturation and corresponding residual saturation, whereas cells 4 and 5 appear to indicate a more linear relationship. As before, to compare results between cells, data was normalized as illustrated in Figure 4.13. Most of the raw data points were again noted to fall within an envelope bound by linear and logarithmic relationships.

Figure 4.12 - Wetting Heptane Saturation vs. Heptane Residual Saturation for Cells 1 -5, Water Saturation Held at 40%.

Figure 4.13 - Wetting Heptane vs. % Maximum Residual, for Linear and Asymptotic Exponential Equations, Water Saturation held at 40 %.

CHAPTER 5

5.0 CONCEPTUAL MODEL DEVELOPMENT

From the data obtained during the three-phase system experiments, three different conceptual models for the residual heptane saturation were proposed. Specifically, a linear model, an exponential model and a modified Land model were compared to the raw data obtained during the laboratory study. These models, which estimate the apparent maximum residual heptane saturation obtained following a given apparent wetting heptane saturation, were then incorporated into the hysteretic LP model.

5.0.1 Analysis of Three-Phase Results : Irreducible Water Saturation

The simplest proposed relationship between maximum residual heptane saturation and wetting heptane saturation was linear. Noting that residual saturation must necessarily be equal to zero when wetting heptane saturation equals zero (no residual will occur if no heptane is present in the system), the linear relationship assumes the form :

$$S_{res} = b \cdot S_{wet} \quad (5.0)$$

Where S_{res} is the maximum residual heptane saturation obtained for the given wetting heptane saturation, S_{wet} is the wetting heptane saturation achieved, and b is the slope of the line relating the two variables, with intercept (0,0).

The next relationship considered was the exponential equation which assumes the form :

$$S_{res} = [1 - \exp^{-z \cdot S_{wet}}] \cdot S_{res}^{max} \quad (5.1)$$

Where S_{res} and S_{wet} are defined as for the linear relationship, S_{res}^{max} is the maximum residual saturation value occurring at 100 % apparent total liquid saturation, and z is a fitting parameter of the model.

The last relationship considered to estimate residual heptane saturation was an adaptation of the Land formula (Equation 2.10) used to estimate maximum entrapped non-wetting fluid saturation based on two-phase system data and saturation reversal points. This form was considered for a number of reasons. First, the Land formulation depends on parameters readily available from two-phase system data and current or historic saturation values with no need for a 'fitting' parameter (b or z in the previous relationships) which requires that an actual data set be generated. Secondly, Land (1968) found a similar increasing asymptotic relationship between initial non-wetting fluid saturation and entrapped non-wetting fluid saturation when he analysed data from a number of different sources. The proposed modified Land equation for estimating maximum residual heptane, based on a given wetting heptane saturation was :

$$S_{res} = S_{wet} / (1 + R * S_{wet}), \quad R = 1 / S_{res}^{max} - 1 \quad (5.2)$$

Where S_{res} , S_{wet} and S_{res}^{max} are defined as for the prior two relationships.

Data from each cell, for three-phase experiments performed at irreducible water saturation, were compared to the linear, exponential and Land formulations. Linear relationships were found by performing a regression analysis on each data set, using Microsoft Excel version 5.0, specifying an intercept of (0,0). Exponential relationships were generated by minimizing the sum of the squared differences, between actual values and predicted values, by

changing the z fitting parameter. Land relationships were determined by calculating R values, using the maximum residual saturation values observed following 100 % apparent total liquid saturation conditions. Parameters determined for each cell, and sum of the squared differences obtained are presented in Table 5.0. Figure 5.0 illustrates each relationship along with the raw data values for cells 1 through 5.

Table 5.0 - Parameters Generated for Linear, Exponential and Land Models, Water Held at Irreducible Saturation.

Cell	S_{res}^{max}	z	b	R	$\Sigma Sq.Dif$ Linear	$\Sigma Sq.Dif$ Exp.	$\Sigma Sq.Dif$ Land
1	0.1337	5.867	0.2195	6.476	0.0047	6.017×10^{-5}	0.00036
2	0.1736	4.053	0.2631	4.759	0.00436	6.519×10^{-4}	0.00088
3	0.1377	4.308	0.2010	6.259	0.00417	0.00262	0.00031
4	0.2439	3.301	0.3290	3.099	0.00332	0.000495	0.00038
5	0.1739	4.624	0.2410	4.749	0.00595	0.00167	0.00134

Figure 5.0 - Linear, Exponential and Land Relationships for Experimental Cells, Water Held at Irreducible.

Following individual cell analysis all data sets were taken together and analysed. The best-fit linear equation was determined by specifying the best-fit line with intercept (0,0) as before. The best-fit exponential relationship was obtained by minimizing the sum of squared differences between predicted and experimental cell values, for all data points. Lastly, the Land formulation was determined by calculating the average R value (based on each maximum residual saturation obtained for each cell) and proceeding as before.

Table 5.1 and Figure 5.1 illustrate the results obtained for the combined analysis of all data sets. As depicted in Figure 5.1, the Land formulation was able to mimic the best-fit exponential equation, and sum of squared differences values were observed to be almost identical (Table 5.1). The sum of squared differences value obtained for the linear equation was noted to be approximately twice the values obtained for both the exponential and Land formulations.

Table 5.1 - Parameters Generated for Composite Data Linear, Exponential and Land Models, Water Held at Irreducible Saturation.

Model	Composite b	Composite z	Composite R	Σ Sq. Dif Linear	Σ Sq. Dif Exp.	Σ Sq. Dif Land
Linear	0.249	N/A	N/A	0.0332	N/A	N/A
Exp.	N/A	3.881	N/A	N/A	0.0156	N/A
Land	N/A	N/A	4.794	N/A	N/A	0.0154

5.0.2 Analysis of Three-Phase Results : 20 % Water Saturation

Data from the three-phase experiments performed at 20 % water saturation were analysed in a manner similar to results from the irreducible water saturation data. Individual cells were compared to the linear, exponential and Land formulations, as shown in Figure 5.2 and Table 5.2.

As before, model equations were compared using the sum of squared differences between values predicted by equations and raw data values observed. In general, the exponential model seemed to give the best-fit to the data, followed by the Land formulation and then the linear relationships. However, for cell 5, the linear equation was observed to give the best-fit to the raw data, and cell 4 observed a better fit to the data for the linear formulation than for the Land formulation.

Table 5.2 - Parameters Generated for Linear, Exponential and Land Models, Water Held at 20 % Saturation.

Cell	S_{res}^{max}	z	b	R	$\Sigma Sq.Dif$ Linear	$\Sigma Sq.Dif$ Exp.	$\Sigma Sq.Dif$ Land
1	0.1675	3.120	0.2399	4.967	0.00157	0.00043	0.00146
2	0.1308	6.403	0.2202	6.641	0.00537	0.00016	0.000648
3	0.1613	4.216	0.2457	5.199	0.00261	0.00031	0.000232
4	0.1482	4.614	0.2523	5.746	0.00250	5.362×10^{-5}	0.00908
5	0.2018	2.864	0.2945	3.955	0.00095	0.00133	0.00229

Figure 5.2 - Linear, Exponential and Land Relationships for Experimental Cells, Water Held at 20 % Saturation.

Following individual cell analysis, data sets were combined together, and analysed in a similar manner to the data obtained for the irreducible water saturation experiments.

Table 5.3 and Figure 5.3 demonstrate the results obtained for the combined analysis of all data. As shown in Figure 5.3, the Land formulation was once again able to approximate the best-fit exponential equation and sum of squared differences values were comparable (Table 5.3). In addition to this, the sum of squared difference obtained for the linear equation was significantly higher than either of the two values obtained for the other formulations.

Table 5.3 - Parameters Generated for Composite Data Linear, Exponential and Land Models, Water Held at 20 % Saturation.

Model	Composite b	Composite z	Composite R	Σ Sq. Dif Linear	Σ Sq. Dif Exp.	Σ Sq. Dif Land
Linear	0.247	N/A	N/A	0.0156	N/A	N/A
Exp.	N/A	3.795	N/A	N/A	0.00454	N/A
Land	N/A	N/A	5.174	N/A	N/A	0.00538

5.0.3 Analysis of Three-Phase Results : 40 % Water Saturation

Data from the three-phase experiments performed at 40 % water saturation were analysed in the same manner as results from the 20 % and irreducible water saturation data. Single cells were compared to the linear, exponential and Land equations, as illustrated in Figure 5.4 and Table 5.4.

Model equations were compared using the sum of squared differences between values predicted and raw data values observed. For cells 1, 2, and 3, the exponential model appeared to give the best-fit to raw data, followed by the Land then the linear equations. Cells 4 and 5 were observed to give the least amount of error for the linear formulation, followed by exponential then Land.

Table 5.4 - Parameters Generated for Linear, Exponential and Land Models, Water Held at 40 % Saturation.

Cell	S_{res}^{max}	z	b	R	$\Sigma Sq.Dif$ Linear	$\Sigma Sq.Dif$ Exp.	$\Sigma Sq.Dif$ Land
1	0.1405	4.507	0.208	6.12	0.00265	8.76×10^{-5}	6.07×10^{-5}
2	0.1195	4.395	0.181	7.37	0.00174	8.77×10^{-5}	0.00013
3	0.1895	4.530	0.315	4.28	0.00426	0.000240	0.00615
4	0.2151	4.273	0.436	3.65	0.00031	0.000985	0.00176
5	0.1626	3.928	0.338	5.15	1.165×10^{-6}	0.000976	0.00143

Figure 5.4 - Linear, Exponential and Land Relationships for Experimental Cells, Water Held at 40 % Saturation.

As for prior experiments, data sets were combined together, and analysed as a composite. Table 5.5 and Figure 5.5 demonstrate the results for the combined analysis of all data. As expected, the Land formulation was able to approximate the best-fit exponential equation with some degree of accuracy (Figure 5.5). Once again the sum of squared differences were also comparable between the exponential and Land formulations. In addition to this, although the sum of squared difference obtained for the linear equation was higher than the two values obtained for the other formulations, it should be noted that the values for all three approximations were of the same magnitude.

Table 5.5 - Parameters Generated for Composite Data Linear, Exponential and Land Models, Water Held at 40 % Saturation.

Model	Composite b	Composite z	Composite R	Σ Sq. Dif Linear	Σ Sq. Dif Exp.	Σ Sq. Dif Land
Linear	0.27	N/A	N/A	0.0351	N/A	N/A
Exp.	N/A	4.47	N/A	N/A	0.0153	N/A
Land	N/A	N/A	5.04	N/A	N/A	0.0164

5.1 INCORPORATION OF CONCEPTUAL MODEL INTO LP MODEL

In order to incorporate the conceptual model for residual NAPL saturation into the LP model, effective and apparent saturations need to be considered. Raw data values obtained from three-phase experiments allowed for comparisons using actual heptane saturation values. As outlined in Section 2.2.2 however, apparent saturations are required in the LP model to simplify computational requirements and also to facilitate scaling of scanning curves when required. The following sub sections outline steps taken to modify the conceptual model, introduced in Section 5.0, into an appropriate LP form for inclusion into the LP model.

5.1.1 Absolute Maximum NAPL Residual ($D_{S_{res}}^{max}$)

The first step in developing an expression for use in the LP model was to evaluate a way to estimate the absolute maximum NAPL residual saturation for the three-phase system. The absolute maximum NAPL residual would occur after complete drainage from a state of 100 % apparent total liquid saturation. It should also be noted that a three-phase system must exist for a residual NAPL saturation to have any meaning.

In accordance with the LP model's reliance on two-phase data, it was assumed that the absolute maximum residual NAPL saturation for a three-phase system could be estimated from two-phase NAPL-air data. Specifically, for the three-phase system studied here, the average irreducible heptane saturation following primary drainage for two-phase heptane-air systems was determined to be approximately 19 %. Average maximum residual heptane values for the

three-phase experiments were determined to range between 16 and 17 %.

Lastly, to put the absolute maximum residual NAPL saturation into terms used by the LP model, actual saturations must be converted to effective and apparent saturations. Thus, from two-phase system data, the maximum residual NAPL saturation for the three-phase system may be estimated by :

$$^D S_{res}^{max} = S_{irr}^{ao} / (1 - S_m) \quad (5.3)$$

Where : $^D S_{res}^{max}$ = Absolute maximum effective residual saturation for three-phase system,
 S_{irr}^{ao} = Actual irreducible saturation from NAPL-air system, and,
 S_m = Irreducible water saturation, assumed constant.

Accordingly, $^D S_{res}^{max}$ corresponds to the effective NAPL saturation which would remain in a three-phase system that had reached 100 % apparent total liquid saturation and subsequently drained to the minimum total liquid saturation possible. That is, the water saturation would be at irreducible, and, likewise the NAPL saturation would be at its irreducible or minimum saturation (residual NAPL saturation). Further conceptual model development, to estimate irreducible NAPL saturations based on reversals from wetting to drainage, are presented in the following section.

5.1.2 Maximum NAPL Residual ($^D S_{res}^{max}$) Based on S_t Reversal

The next step in developing an appropriate equation was to estimate an effective maximum residual NAPL saturation based on the reversal point from the primary wetting curve to a drainage scanning curve on the apparent total liquid saturation path. In order to do so, relationships introduced in Section 5.0. were used. Specifically, from experiments performed, irreducible heptane

saturation was observed to be dependent on wetting heptane saturation.

Furthermore, it was determined the relationship could be approximated using linear, exponential or Land equations. It was assumed these relationships could be employed for total effective and apparent liquid saturation values, as the NAPL saturation is assumed to be controlled by the position of the NAPL-air interface in a three-phase system.

In order to incorporate the equations introduced in Section 5.0 into the conceptual model, a new parameter was introduced. Defining $\Delta\Delta S_t$ as the apparent total liquid saturation at the reversal point from the primary wetting curve to a drainage scanning curve, the linear, exponential and Land formulations become :

$$\text{Linear : } \underline{S}_{res}^{max} = \Delta\Delta S_t * {}^D\underline{S}_{res}^{max} \quad (5.4 - 5.6)$$

$$\text{Exponential : } \underline{S}_{res}^{max} = [1 - \exp^{-z * \Delta\Delta S_t}] * {}^D\underline{S}_{res}^{max}$$

$$\text{Land : } \underline{S}_{res}^{max} = \frac{\Delta\Delta S_t}{[1 + {}^D R * \Delta\Delta S_t]}$$

Where : $\underline{S}_{res}^{max}$ = Effective maximum residual NAPL saturation based on total saturation reversal point,
 ${}^D R = 1 / {}^D\underline{S}_{res}^{max} - 1$,
 z = Fitting parameter for best-fit exponential equation, and,
 ${}^D\underline{S}_{res}^{max}$ is as defined previously.

Equations 5.4 - 5.6 maintain the same form as Equations 5.0 - 5.1 introduced in Section 5.0. Maximum effective residual NAPL saturation ($\underline{S}_{res}^{max}$) is calculated using expressions dependent the on apparent wetting total liquid saturation reversal point ($\Delta\Delta S_t$) and the absolute maximum effective residual NAPL saturation (${}^D\underline{S}_{res}^{max}$). The linear expression however, no longer requires a best-fit

slope parameter (b) as for prior developments. The linear form was refined by noting that the apparent total liquid saturation, by definition, varies between 0 and 1. This being the case, if $\Delta\Delta S_t$ is equal to zero, zero maximum residual NAPL saturation will result. If $\Delta\Delta S_t$ is equal to one, the maximum residual NAPL saturation possible, $^D S_{res}^{max}$, will occur. Noting that these values correspond to the reversal points for zero and absolute maximum residual NAPL saturation, respectively. For $\Delta\Delta S_t$ values between 0 and 1, maximum possible residual NAPL saturations will be scaled accordingly through use of Equation 5.4. The exponential and Land forms remain identical to those introduced in Section 5.0, noting however that the $\Delta\Delta S_t$ term replaces the S_{wet} term shown in Equations 5.1 and 5.2.

To demonstrate use of Equations 5.4 - 5.6, raw data obtained from the three-phase experiment performed at irreducible water saturation was manipulated to generate effective and apparent total liquid saturations. To compare Equations 5.4 - 5.6 with the raw data, $^D S_{res}^{max}$ was estimated from two-phase heptane-air data generated previously. S_{res}^{max} was then calculated using the estimated $^D S_{res}^{max}$ value and $\Delta\Delta S_t$ values generated. The estimated S_{res}^{max} values were compared to observed values, and error estimates calculated by determining the sum of squared differences between predicted and actual saturation values for each equation used. The irreducible water saturation value, S_m , used in determining $^D S_{res}^{max}$ was estimated by taking the average of irreducible values obtained during the three-phase experiments, rather than using values observed during two-phase water-air experiments. This was done

due to problems mentioned previously with small amounts of heptane being present in each cell during water drainage for the three-phase experiments.

Table 5.6 and Figure 5.6 illustrate the comparisons between observed and predicted maximum heptane residuals, based on apparent total liquid saturation reversal points.

Table 5.6 - Parameters Generated from Comparing Observed to Actual Data, Water held at Irreducible.

Model	z	$\Sigma \text{Sq. Diff.}$	$\bar{S}_{\text{res}}^{\text{max}}$	$\bar{R}$
Linear	N/A	0.0365	0.201	N/A
Exponential	2.413	0.0173	0.201	N/A
Land	N/A	0.0276	0.201	3.962

As illustrated in Figure 5.6, each model was observed to give a reasonable fit to the manipulated raw data. The best-fit exponential model was noted to give the least amount of error (Table 5.6) in terms of sum of squared differences, although the Land and linear equations produced errors of the same magnitude. Due to these observations, and a number of other considerations, the exponential model may not be the most practical form for use in the LP model. More specifically, the exponential model still requires that a fitting parameter, in terms of z , be generated from raw data analysis. Thus, in order to use the model, three-phase experiments, similar to those presented previously, would need to be performed. In comparison to this, the linear and Land models do not require any fitting parameters and thus may be used directly if two-phase NAPL-air data (in terms of D_{res}^{max}) and apparent total liquid saturation reversal points ($\Delta\Delta S_t$) are known. A primary consideration in the LP model is to reduce experimental requirements by estimating three-phase systems from two-phase data. Thus, in this regard, it was concluded that the exponential model is impractical.

Another difficulty in using the exponential model is that the best-fit equation does not necessarily predict the maximum heptane residual obtained at 100 % apparent total liquid saturation. From observing Figure 5.6, the linear and Land models start at the ordinate (0,0) and end at the effective absolute maximum residual NAPL saturation obtained experimentally from two-phase NAPL-air data. In comparison to this, the exponential best-fit equation ends at an absolute residual NAPL saturation value somewhat less than the estimated

maximum, due to the fitting procedure used. The linear and Land models allow for lower and upper 'estimates' in predicting maximum heptane residual saturations from apparent total liquid saturations. This being the case, under field conditions, attempting to define parameters to use in the exponential model becomes not only difficult, but superfluous as well.

The three-phase experiments, performed at 20 and 40 % water saturation, were not manipulated to compare results with Equations 5.4 - 5.6. This was primarily due to difficulties in determining irreducible water saturation values to be used when estimating the $^D S_{res}^{max}$ value required by Equations 5.4 - 5.6. Ideally in the LP model, S_m is assumed to be equal to the irreducible water saturation obtained after drainage in a two-phase water-air system. However, due to problems with heptane being present in small amounts during water drainage for all three-phase experiments, S_m was actually observed to be somewhat less than the value obtained for the two-phase experiments. For the three-phase experiments held at irreducible water saturation, reasonable approximations for S_m could be obtained. For the experiments held at 20 and 40 % water saturation however, irreducible values were not easily estimated. Obviously S_m values obtained from two-phase data would be too high and, conversely S_m values obtained from the experiment held at irreducible water would most likely be too low. This is because the three-phase experiment held at irreducible water saturation would be expected to have the greatest amount of heptane introduced during water drainage, due to the higher suction pressures applied to the cells. This would presumably result in the lowest S_m values for the

three-phase systems. For the experiments performed at 20 and 40 % saturation, higher S_m values, ranging between those obtained for the two-phase system and those obtained for the three-phase irreducible system, would be expected. As Equations 5.4 - 5.6 are very sensitive to estimates of S_m , data obtained at 20 and 40 % are not easily manipulated for comparison purposes.

5.1.3 NAPL Residual ($\underline{S}_{res}$) Based on Current $\underline{S}_t$

The last step in developing the conceptual formulation to be used in the LP model, was to consider an equation for estimating intermediate residual NAPL saturation values. Theoretically, for apparent total liquid saturation values ($\underline{S}_t$) equal to the saturation reversal point $\Delta\Delta\underline{S}_t$, a residual NAPL saturation of zero would be expected. Conversely, for three-phase systems at irreducible water saturation, when $\underline{S}_t$ was equal to zero, the maximum residual NAPL saturation, $\underline{S}_{res}^{max}$, would be expected to occur. For $\underline{S}_t$ values between $\Delta\Delta\underline{S}_t$ and zero, some proportion of $\underline{S}_{res}^{max}$ would transpire. Thus, with these stipulations, the following development for estimating intermediate residual NAPL saturations was proposed. Three cases were considered : constant water phase saturation ($\underline{S}_w$) as $\underline{S}_t$ decreases, increasing $\underline{S}_w$ as $\underline{S}_t$ decreases and, decreasing $\underline{S}_w$ as $\underline{S}_t$ decreases.

Case I : Constant $\underline{S}_w$, decreasing $\underline{S}_t$

The first case considered corresponds to a scenario during which the apparent water saturation remains constant, at an irreducible value or greater. Defining $\underline{S}_{res}$ as the effective residual NAPL saturation at a given apparent total liquid saturation $\underline{S}_t$, two scaling factors would require consideration. Figure 5.7

demonstrates terms used in the following development. For simplicity, irreducible water saturation conditions are depicted in Figure 5.7 such that $\underline{S}_t$ assumes a value of zero at high capillary pressures. Point 1, $\Delta\Delta\underline{S}_t$, corresponds to a saturation reversal point from the primary wetting curve to a drainage scanning curve. $\underline{S}_{res}^{max}$ may be calculated using one of the equations introduced in Section 5.1.2, $\Delta\Delta\underline{S}_t$, and ${}^D\underline{S}_{res}^{max}$ obtained from two-phase data. This value would be the maximum residual NAPL saturation possible for reversal occurring at point 1, assuming drainage occurred from this point to a total liquid saturation ($\underline{S}_t$) of zero at point 2. Or, stated differently, if $\underline{S}_t$ were to equal zero, $\underline{S}_{res}$ would assume the value of $\underline{S}_{res}^{max}$ for given reversal point $\Delta\Delta\underline{S}_t$. If however, drainage only occurs to an intermediate value of $\underline{S}_t$ (point 3), $\underline{S}_{res}$ would assume a value between zero and $\underline{S}_{res}^{max}$, dependent on $\underline{S}_w$ and distance between $\underline{S}_t$ and $\Delta\Delta\underline{S}_t$.

Figure 5.7 - Residual Saturation Based on Reversal Point.

To calculate $\underline{S}_{res}$ at intermediate point 3, the following expression to scale between values of zero and the maximum ($\underline{S}_{res}^{max}$) was proposed :

$$\underline{S}_{res} = \frac{(\Delta\Delta \underline{S}_t - \underline{S}_w)}{\Delta\Delta \underline{S}_t} \times \frac{(\Delta\Delta \underline{S}_t - \underline{S}_t)}{(\Delta\Delta \underline{S}_t - \underline{S}_w)} \times \underline{S}_{res}^{max} \quad (5.7)$$

Where all parameters are as defined previously. The first term in Equation 5.7 was introduced as a scaling factor to account for the possibility of water saturation being at a value greater than irreducible. If the three-phase system is held at irreducible water, $\underline{S}_w$ is equal to zero, and the first scaling factor becomes equal to one, having no reducing effect on the maximum possible residual NAPL saturation of $\underline{S}_{res}^{max}$, and correspondingly $\underline{S}_{res}$. If however, water saturation is held at a value greater than irreducible, the first term in Equation 5.7 becomes less than one, reducing $\underline{S}_{res}^{max}$ accordingly. Ideally, as water saturation increases, residual saturation will decrease, due to a greater number of pore spaces being occupied by water, precluding occupation by NAPL. Thus, as $\underline{S}_w$ increases, the first term in Equation 5.7 decreases, reducing $\underline{S}_{res}$ as required.

The second scaling term in Equation 5.7 was applied to account for the position of actual apparent total liquid saturation, $\underline{S}_t$, from reversal point, $\Delta\Delta \underline{S}_t$. The denominator of the second term represents the allowable change in $\underline{S}_t$ that may occur within the three-phase system. In other words, $\underline{S}_t$ may be equal to any value between $\Delta\Delta \underline{S}_t$ and $\underline{S}_w$. For example, if irreducible water saturation conditions exist, $\underline{S}_t$ may assume any value between zero and $\Delta\Delta \underline{S}_t$. The numerator of the second term allows $\underline{S}_{res}^{max}$ to be scaled accordingly, depending

on the position of $\underline{S}_t$, relative to $\Delta\Delta\underline{S}_t$. If $\underline{S}_t$ equals $\Delta\Delta\underline{S}_t$, then $\underline{S}_{res}$ will equal zero, as expected (no residual saturation will occur, as system is not undergoing drainage). If however, $\underline{S}_t$ equals $\underline{S}_w$, then the second term in Equation 5.7 will equal one, and the residual saturation will only be dependent on scaling by the first term. In the special case of constant irreducible water saturation conditions, if $\underline{S}_t$ equals zero, the first and second terms will both be equal to one and $\underline{S}_{res}$ will equal $\underline{S}_{res}^{max}$, as expected.

Further inspection of Equation 5.7 reveals possible simplification. Noting that the nominator of the first term is equal to the denominator of the second term, cancellation gives :

$$\underline{S}_{res} = \frac{(\Delta\Delta\underline{S}_t - \underline{S}_t)}{\Delta\Delta\underline{S}_t} \times \underline{S}_{res}^{max} \quad (5.8)$$

At first glance, Equation 5.8 seems to indicate an independence of the $\underline{S}_{res}$ term from $\underline{S}_w$, for case I. It should be remembered however that possible values of $\underline{S}_t$ are inherently dependent on $\underline{S}_w$. For example if the system is at irreducible, $\underline{S}_w$ will equal zero and $\underline{S}_t$ will be equal to any value between zero and $\Delta\Delta\underline{S}_t$. Thus $\underline{S}_{res}$ will be equal to any value between $\underline{S}_{res}^{max}$ and zero, respectively. If $\underline{S}_w$ is greater than zero, $\underline{S}_t$ may assume any value between $\underline{S}_w$ and $\Delta\Delta\underline{S}_t$. In this case, $\underline{S}_{res}$ will always be less than $\underline{S}_{res}^{max}$, dependent on the value of $\underline{S}_w$.

Case II : Increasing $\underline{S}_w$, decreasing $\underline{S}_t$

The second case considered is when water saturation increases while total liquid saturation decreases. This might occur when water would be imbibing into a three-phase system at a slower rate than NAPL would be draining from the

same. Equation 5.7 may be employed in this situation, providing NAPL entrapment, due to the advancing water front, was also accounted for, as is the case with the LP model. Specifically, as water saturation increased, the first term in Equation 5.7 would decrease, reducing the total S_{res} term as required. This decrease would be observed in the physical system as a result of a larger proportion of pore space being occupied by water, precluding further residual NAPL saturation as a result of drainage. However, as the water saturation increased, a portion of the NAPL would be entrapped by the advancing water front as outlined in Section 1.2.3. The effect of decreasing NAPL saturation would manifest itself in the second term of Equation 5.7, as S_t would decrease accordingly.

Case III: Decreasing S_w , decreasing S_t

The last case considered is when both S_w and S_t are decreasing, either at the same or different rates. This case would occur when water or both water and NAPL are draining from the soil in a three-phase system. In the first instance, ΔS_w would be equal to ΔS_t . In the second instance, ΔS_w would be different from ΔS_t . Considering Equation 5.7 once again, as S_w decreased, the first term would increase, allowing for a greater potential residual value. Similarly, as S_t decreased, the second term in Equation 5.7 would increase and again the residual NAPL saturation would increase as drainage occurs. Logically, these observations seem sound. If water drains from the system, a greater proportion of pore space will be available for a residual NAPL saturation. Similarly, as NAPL drains from the system a greater volume of NAPL will exist as residual, rather

than as a free phase. Thus, Equation 5.7 also serves to estimate residual NAPL during case III conditions.

5.2 APPLICATION OF CONCEPTUAL MODEL

To illustrate use of the modified LP model a simple example is presented below. A multiphase, hysteretic, LP pressure-saturation code developed by Van Geel (1994) was modified to include the residual saturation equations introduced in Section 5.1. It was assumed that constant irreducible water saturation circumstances prevailed (case I in Section 5.1) throughout each simulation, as results could only be compared to observations obtained under these conditions.

Variables entered into the code are presented in Table 5.7 and include the required LP model parameters with the addition of the absolute maximum residual NAPL saturation $^D S_{res}^{max}$, and the exponential model's fitting parameter z . To compare predicted values with actual values, S_{res}^{max} terms (averaged over all cells) were calculated from the three-phase experiments performed at irreducible water saturation. Sequential pressure-saturation reversal points in the modified code were then selected to correspond to the saturation values measured during the laboratory experiments, as demonstrated in Figure 5.8. Simulations were run to illustrate the application of the linear, exponential, and Land NAPL residual models. Although all residual values (S_{res}) were calculated by the code, only end point saturations (i.e. S_{res}^{max}) were comparable to experimental data, as only these were measured in the laboratory. Table 5.8 presents experimental 'cell averaged' $^{\Delta\Delta} S_i$ and S_{res}^{max} and the predicted S_{res}^{max}

values obtained from the model simulations. Figure 5.9 compares experimental average S_{res}^{max} values to those calculated using the modified code.

Table 5.7 - Input Parameters for the Modified LP Code.

Parameter	Value
n	6.63
$m = 1 - 1/n$ (Constrained)	0.849
Water-Air α_d	0.02019
Water-Air α_i	0.03917
Water-Heptane α_d	0.0453
Water-Heptane α_i	0.0879
Heptane-Air α_d	0.0749
Heptane-Air α_i	0.1453
Water-Air (Entrapped Air)	0.13
Water-Heptane (Entrapped Heptane)	0.22
Heptane-Air (Entrapped Air)	0.058
Irreducible Water S_m	0.18
Heptane-Air S_{res}^{max}	0.20
z fitting parameter (exponential)	2.413

Figure 5.8 - Wetting Reversal Points Used in Modified LP Code Simulation.

Table 5.8 - Experimental average $\Delta\Delta S_t$ and Simulated S_{res}^{max} Values.

Calculated Average $\Delta\Delta S_t$	Calculated Average S_{res}^{max}	Simulated Linear S_{res}^{max}	Simulated Exponential S_{res}^{max}	Simulated Land S_{res}^{max}
0	0	0	0	0
0.28	0.11	0.057	0.099	0.132
0.55	0.13	0.109	0.146	0.17
0.72	0.167	0.144	0.164	0.185
1.0	0.183	0.20	0.181	0.20

Figure 5.9 - Observed vs. Simulated S_{res}^{max} based on Observed Reversal Points $\Delta\Delta S_t$.

Table 5.8 and Figure 5.9 indicate reasonable agreement between observed S_{res}^{max} values and those predicted by the conceptual model equations presented previously. Although the exponential estimates seem to provide the closest approximations to actual observed values, it should be noted that most of

the actual values lie in between those predicted by the linear and Land formulations. This observation would seem to indicate a preference for using the linear and Land equations to provide upper and lower 'estimates' for the residual NAPL saturation. Although the exponential model provides the most accurate estimates, the difficulty in obtaining the z fitting parameter for the model precludes its practical widespread usage.

To demonstrate the influence of the residual NAPL saturation on the three-phase pressure-saturation relationships, simulation data for each run (linear, exponential, Land, and no residual) were plotted for each wetting / drainage cycle shown in Figure 5.8. During the simulations it was assumed that each of the four cycles occurred in a sequential manner (i.e. drainage to wetting to drainage, etc.), and constant irreducible water saturation conditions prevailed. Parameters used for each simulation were presented previously (Table 5.7).

Figures 5.10 through 5.13 depict pressure-saturation pathways for each conceptual formulation (i.e. linear, exponential and Land) corresponding to each wetting cycle. The first wetting cycle (Figure 5.10) occurs with the introduction of heptane into a system at irreducible water saturation ($h_{ca0} = 30$ cm). Heptane is allowed to incrementally imbibe until an apparent total liquid saturation of approximately 28 % is achieved, which corresponds to a NAPL-air capillary head of 8.25 cm. From this point, heptane is incrementally drained until capillary pressure head equals 30 cm once again.

Residual saturation effects are included in each figure by adding calculated residual saturation values (for each equation) to calculated apparent

total liquid saturation values. As shown in Figure 5.10, the effects of neglecting residual results in drainage from the reversal point to zero total liquid saturation, as expected. The effects of including residual are observed to 'shift' the drainage curves to the right, such that the loops no longer close to zero saturation, but rather to maximum residual values obtained for the first saturation reversal point (S_{res}^{max1}). In addition to this, in agreement with observations in Table 5.8, the Land simulation results in the greatest residual predictions, followed by the exponential and linear model predictions.

Figure 5.10 - Simulated Pressure-Saturation Relationships for First Reversal Point.

For the second cycle, heptane is again incrementally imbibed into the system until an apparent total liquid saturation of 55 % is achieved (Figure 5.11). At this time, the capillary pressure head is equal to 6.9 cm. From this reversal point, heptane is again incrementally drained to a capillary pressure head value

of 30 cm. As for the first wetting cycle, no residual inclusion results in closure of the wetting 'loop' to zero apparent total liquid saturation. In addition to this, residual effects are again manifested by shifting the secondary drainage curves to the right, such that closure occurs at S_{res}^{max2} (for the second reversal point). It should be noted however, that imbibition for the second wetting cycle no longer starts from the zero saturation point. Instead, wetting is initiated from the S_{res}^{max1} values obtained previously, following drainage during the first wetting cycle. As before, the Land equation generates the greatest predictions for residual, followed by the exponential and linear model predictions.

Figure 5.11 - Simulated Pressure-Saturation Relationships for Second Reversal Point.

The third wetting cycle simulations were implemented in an identical manner to the first and second cycles. Heptane was imbibed into the system until

apparent total liquid saturations of 72 %, and capillary head values of 6.11 cm were obtained. From this point, drainage of heptane was initiated until capillary pressure head values of 30 cm were again achieved. Similar results were obtained as with prior wetting cycles. Again, excluding residual effects resulted in closure to zero saturation. For all other simulations, saturation pathways were observed to start at S_{res}^{max2} values (as a result of the second wetting cycle) and close at S_{res}^{max3} , the maximum residuals obtained based on the current reversal point. As expected, the Land equation was noted to give the highest residual values followed by the exponential and linear models.

Figure 5.12 - Simulated Pressure-Saturation Relationships for Third Reversal Point.

For the last wetting cycle initiated, heptane was imbibed into the system until an apparent total liquid saturation value of 100 % ($h_{cao} = 0.01$ cm) was

observed. Following this, heptane was allowed to drain from the system to residual saturations at capillary pressure heads of 30 cm. As before, exclusion of a residual term resulted in closure of the fourth cycle to zero apparent total liquid saturation. A similar 'shifting' to the right of the fourth drainage curves was also observed as a result of including residual terms. In addition to this, wetting cycles for each residual included simulation were noted to start at $\underline{S}_{res}^{max3}$ values obtained during drainage from the third reversal point previously, as expected.

One difference, from prior wetting cycles, was noted for the last simulation. Prior results predicted the greatest residual estimates to occur for the Land formula, followed by the exponential and then the linear equations. In the fourth wetting cycle, the Land and linear predictions close to the same $\underline{S}_{res}^{max4}$ value (in fact equal to $^D\underline{S}_{res}^{max}$), as expected (see Figure 5.9). The exponential formula in this case was observed to predict the lowest residual saturation values.

Figure 5.13 - Simulated Pressure-Saturation Relationships for Fourth Reversal Point.

CHAPTER 6

6.0 CONCLUSIONS AND RECOMMENDATIONS

The LP model provides a means of estimating multiphase pressure-saturation relationships. The model allows for the inclusion of hysteretic effects and it also makes provisions for estimating various entrapped non-wetting phase saturations. It is these factors which allow the code to approximate real systems with relative accuracy. In addition to these benefits, the LP model allows three-phase system behavior to be predicted from two-phase system parameters, thus reducing computational and experimental requirements.

In spite of the mentioned benefits, the LP model has made no allowance in the past for inclusion of a residual NAPL saturation when modeling three-phase systems. Residual saturations may affect pressure-saturation relationships considerably and must be included when modeling real systems. In terms of NAPL contaminated sites, the presence of a residual phase may influence methods to be used in remediation efforts. To this end, the preceding research was undertaken in an attempt to modify the LP pressure-saturation model to include residual NAPL saturations under three-phase conditions.

A number of two-phase experiments were performed by the researcher to characterize system parameters required by the current LP model. Primary drainage and wetting curves for water-air, water-heptane and heptane-air systems were generated, from which α_d , α_i , n , m , S_m , β_{aw} , β_{ow} , β_{ao} , and maximum entrapped saturations were determined. For LP parameters,

constraints were imposed such that the α_d / α_i ratios were set equal for each two-phase system and n (and hence m) was not allowed to vary from the value determined for the water-air drainage system. Unconstrained best-fit parameters were also generated by allowing all previous terms to vary. The LP system parameters were observed to provide reasonable estimates of the water-air and water-heptane pressure-saturation relationships. For the two-phase heptane-air system however, LP approximations were noted to significantly underestimate the capillary pressure head values observed. An inherent assumption of the LP model is that total liquid saturation for a three-phase system is controlled by heptane-air interfaces. Thus, for the system considered, using the two-phase LP parameters rather than the best-fit parameters may result in a loss of accuracy. In spite of these observations, LP parameters were used in all subsequent model simulations as the primary goal of the preceding study was not to critique the LP model, but rather to modify the model to include a residual NAPL saturation.

Following the two-phase system experiments, a number of three-phase experiments were undertaken. Various wetting and drying heptane saturation cycles were initiated for cells held at irreducible, 20 %, and 40 % water saturation. In all cases observed, residual heptane saturation increased as wetting heptane saturation increased. From the data obtained, three separate equations for estimating residual NAPL saturation from actual wetting NAPL saturation were generated. Specifically, a linear, an exponential, and an equation similar in form to that brought forth by Land (1968) were proposed for further consideration in conceptual model development.

A number of problems were encountered by the researcher through the course of generating data during the three-phase system experiments. Prior to introducing heptane into experimental cells, it was noted that irreducible water saturation values obtained were significantly lower than those observed for the two-phase water-air systems. It was concluded that this discrepancy may be accredited to a small amount of heptane being present in each cell during water drainage, which would likely effect water-air interfaces directly. Similar observations were reported by White and Lenhard in 1993.

Another discrepancy noted was that irreducible water saturation values were observed to decrease following heptane introduction into each experimental cell. Currently, S_m is assumed to remain constant in the LP model although other researchers (Eckberg and Sunada, 1984) have also observed changes in irreducible water following NAPL introduction into a water-air system. The effects of including a modified β_{aw} , and changing S_m , on the LP model were not considered, as they were deemed to be outside the scope of the preceding research.

To modify the LP code, a conceptual model based on the three-phase experimental data was proposed. It was assumed that an absolute maximum effective residual saturation ($^D\underline{S}_{res}^{max}$) could be estimated from NAPL-air data, in accordance with the LP model's reliance on two-phase system parameters. Linear, exponential and Land equations were generated to estimate the maximum residual NAPL saturation ($\underline{S}_{res}^{max}$) based on the total liquid saturation reversal point ($^{\Delta\Delta}\underline{S}_t$). To estimate residual values ($\underline{S}_{res}$) at current total liquid

saturations (S_t) in the LP model, a linear interpolation formula, dependent on S_{res}^{max} , was proposed. At this point the modified LP model was considered complete and simple simulations were run using the altered code for illustration purposes.

Four simulations were run considering linear, exponential, Land and no residual calculation. Each simulation included four wetting / drainage cycles and irreducible constant water saturation conditions were assumed throughout. Simulations were observed to provide reasonable estimates of the S_{res}^{max} values obtained from the three-phase experiments. In addition to this, S_{res} values generated between all wetting / drainage reversal points, were observed to significantly effect three-phase pressure-saturation relationships. In all cases, inclusion of a residual saturation was observed to shift drainage curves to the right, such that closure was no longer to zero apparent total liquid saturation.

Simulations using the linear conceptual model underestimated the residual saturation measured in the laboratory. In comparison, simulations using the Land and exponential models provided a better estimate of the residual. The Land conceptual model generally overestimated the residual NAPL saturation, however the exponential model was considered impractical for widespread usage, as a fitting parameter (z) based on three-phase system data must be generated prior to use.

Although the preceding study has produced a method whereby residual saturation effects may be included in the LP model, much more remains to be done. The results obtained, and thereby conclusions drawn, were only for the

particular system under consideration and thus it is not known whether the developed equations would apply under differing circumstances. In light of this, future efforts might include three-phase system experiments (similar to those performed for this study) considering a variety of NAPLs and porous media. Only through this verification can the proposed conceptual equations be utilized in widespread application.

Other future endeavors should also include verification of the proposed equations through field and / or laboratory multiphase flow studies. This could be achieved by perhaps observing actual fluid distributions within a porous medium matrix (in terms of free, entrapped and residual) which could then be compared to calculated distributions obtained using the modified LP code. In this way a better understanding of the limitations and advantages of the modified code could be realized.

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