LABORATORY EVALUATION OF \textit{IN SITU} STEAM FLUSHING FOR NAPL REMOVAL FROM SOIL

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Civil Engineering
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LABORATORY EVALUATION OF IN SITU STEAM FLUSHING FOR NAPL REMOVAL FROM SOIL

Doctor of Philosophy, 1997
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ABSTRACT

The widespread problem of contamination of soil and groundwater by petroleum hydrocarbons and chlorinated solvents is the result of accidental chemical spills, underground tank leakage, and uncontained direct disposal. Organic pollutants can exist as separate non-aqueous phase liquids (NAPLs) and may dissolve in groundwater, adsorb to soil grains, and partition into the soil gas phase.

This research focuses on assessing the feasibility of remediation of groundwater contamination by in situ steam flushing. Steam flushing experiments were conducted in a two-dimensional chamber containing silica sand. The system was equipped with pressure transducers, thermocouples, time domain reflectometry probes, and fluid sampling ports. A computer controlled data acquisition system was used to control a steam generator and to record and monitor the pressure, temperature, and water saturation data. Nonane and PCE were spilled into the chamber under saturated and partially saturated conditions. Complete removal of PCE and nonane from the area swept by steam was achieved. Vertical wells were
more efficient than horizontal wells for steam injection and NAPL extraction. Some steam override occurred in the experiments.

Laboratory measurements of air-water-silica and PCE-water-silica drainage and imbibition capillary pressure-water saturation curves at various temperatures showed that the capillary pressures decreased significantly when temperature was increased from 20 to 80 °C. For the PCE-water-silica system, the residual water saturation increased and the residual PCE saturation decreased when temperature was raised, while there were no clear trends for these parameters for the air-water-silica system. The capillary hysteresis between the drainage and imbibition curves decreased for both the air-water-silica and PCE-water-silica systems when temperature was increased. A model accounting for the decrease of capillary pressures with increasing temperature was developed and fitted to the experimental data. Application of the Laplace equation suggests that the changes in capillary pressures can not be explained only by the changes in interfacial tensions and contact angles.

A steam flushing numerical model was tested against the laboratory experiments. The predictions of the model matched experimental results reasonably well.
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DEDICATION

This work is dedicated to my wife Jing, whose love has been shown with patience, understanding, and inspiration, and to my son Kevin.
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Chapter 1. Introduction

CHAPTER 1 INTRODUCTION

1.1 Background

The contamination of soil and groundwater by petroleum hydrocarbons and chlorinated solvents is a widespread problem facing the world today. Contamination is the result of accidental chemical spills, underground tank leakage, and uncontained direct disposal. Organic chemical pollutants can exist as separate non-aqueous phase liquids (NAPLs) which may dissolve in groundwater, adsorb to soil grains and partition into the gas phase.

When an organic chemical spill percolates downward through the vadose zone, it is trapped and immobilized by capillary forces as blobs and ganglia and retained by low-permeability layers or scattered fine-grained lenses. When enough chemical is present it will reach the water table. If the chemical is lighter than water (referred to as light non-aqueous phase liquid or LNAPL), it will pool on the water table, and move laterally along the water table. If the chemical is denser than water (referred to as dense non-aqueous phase liquid or DNAPL), it will move downward past the water table until it pools on fine-grained lenses and layers. The trapped and retained DNAPL in the saturated zone below the water table is immobilized by capillary and buoyancy forces (Kueper, 1989; van Geel, 1994).

1.2 In Situ Remediation Methods

Over the past decade, many in situ biological, chemical and physical methods have been developed for groundwater remediation. Biological methods such as bioventing stimulate the local biological community to use the organic contaminants as sources of carbon and energy. Chemical methods include processes such as surfactant flushing which reduces the water-NAPL interfacial tension and increases aqueous phase solubility, making the removal of trapped blobs and ganglia easier. Physical methods such as soil vapor extraction (SVE), air
sparging, and aqueous pump-and-treat use hydraulic gradients to remove contaminants from the subsurface.

Physical remediation methods have been the most widely used to date. SVE and aqueous pump-and-treat have been applied in soil and groundwater remediation for many years. The SVE technique involves applying a vacuum to an extraction well to recover the gaseous phase in the vadose zone. Volatile contaminants with high vapor pressures and high Henry's law constants, are removed preferentially due to high concentrations in the gaseous phase. Less volatile contaminants are removed slowly due to low concentrations in the gaseous phase (She et al., 1995; Pedersen and Curtis, 1991).

TeKrony et al. (1995) investigated the use of thermal venting to increase SVE efficiency. In thermal venting hot air is injected to raise subsurface temperatures. As temperatures are increased the vapor pressures of the organic species are increased and removal rates may be increased. However, the energy carried into the soil is quickly dissipated due to the low heat capacity of air relative to that of water and soil. Therefore, no significant improvement of SVE efficiency will be made by hot air injection (TeKrony et al. 1995).

Recently, there has been interest in applying steam flushing to remove volatile and semi-volatile organic compounds from soils (Hadim et al., 1993; Falta et al., 1992; Hunt et al., 1988a; Sleep, 1995). Steamflooding methods have been used successfully in the petroleum industry for several decades, primarily as a tertiary oil recovery method. Steam is injected through vertical and horizontal wells to raise the temperature of heavy oil in order to reduce its viscosity dramatically. Heated oil is then pushed by the steam to several production wells which are usually around the injection well. Special attention has been given to heavy oil and bitumen since the large reduction of viscosity of heavy oil and bitumen makes the ratio of oil viscosity to water (steam condensate) viscosity closer to unity, reducing the risk of viscous fingering and making the displacement more efficient.
Several field demonstration projects related to in situ soil remediation by steam flushing techniques have been conducted in the past few years (DePercin, 1991; Noonan et al., 1993; Hadim et al., 1993; and TeKrony et al., 1995). DePercin (1991) reported that more than 85% of the volatile organic compounds (VOCs) and as much as 55% of the semi-volatile organic compounds (SVOCs) were removed by the steam and hot air flushing technique from a field demonstration project performed by the U.S. EPA under the Superfund Innovative Technology Evaluation (SITE) program. In a pilot-scale field study of a site contaminated by acetone, 2-butanone, chlorinated solvents, BTEX (benzene, toluene, ethyl benzene, and xylenes) Noonan et al. (1993) reported that the initial soil concentration of 2000 mg/kg was reduced to a final soil concentration of 12 mg/kg in 140 hours by steam injection. TeKrony et al. (1995) reported the results of a pilot-scale study of in situ steam extraction and SVE for the recovery of DNAPLs from the vadose zone. They found that the two columns charged with saturated steam at 7.5 psig (528 cm H₂O) yielded 71% and 97% recoveries of the initial chloroform volume after the addition of less than one pore volume of steam, compared with an average recovery of 15% achieved by SVE in one pore volume at the same site.

Steam flushing may be combined with other in situ remediation methods to improve NAPL clean up efficiency and overall removal. The natural aerobic bioremediation of some NAPLs in the subsurface may be enhanced by injecting a certain amount of steam to maintain the soil temperature between 20 and 40 °C for the optimal growth of local microorganisms (especially attractive in the winter time). It is also possible that heating of soil for prolonged time may have adverse effects on the local microorganisms and the soil. The groundwater sterilization of the local biological community may be avoided if warm water instead of steam is injected. The efficiency of pump-and-treat systems may be improved by injecting warm water instead of ambient temperature water into the subsurface for the free phase NAPL recovery due to the increase of NAPL solubilities in the groundwater and the decrease of residual NAPL saturations in the soil. Soil vapor extraction may be combined with steam flushing to enhance the removal of NAPL vapors in the soil gas phase and minimize the risk of steam breakthrough at the ground surface.
Even though the steam flushing method has good potential for remediating NAPL concentrations in the subsurface, further studies have to be undertaken since the NAPL remediation process differs from petroleum recovery processes in many ways (Sleep, 1995). These differences include different initial petroleum/NAPL saturations, chemical species and properties, final removal goals, and operational risks. The initial petroleum saturations in petroleum reservoirs can be as high as 100% while the initial NAPL saturations in contaminated aquifers are usually at residual levels (10 - 40%, Wilson and Corad, 1984). The petroleum species are mainly hydrocarbons while NAPLs can be any toxic or hazardous chemical such as halogenated (mainly chlorinated) solvents, BTEX, PCBs, as well as petroleum hydrocarbons. The production of petroleum is stopped once the operation is no longer economical while the NAPL remediation operation has to continue until the NAPL concentrations reach the regulated level. There are greater operational risks involved in NAPL remediation than oil production since the contaminated site may be underneath a building or factory while oil fields are almost always located in less populated areas.

1.3 Research Objectives and Thesis Organization

This thesis focuses primarily on the following three major objectives:

1. To study the feasibility of the remediation of volatile and semi-volatile organic chemical contaminated soil and groundwater by in situ steam flushing in a two-dimensional system
2. To investigate the effect of temperature on the air-water-silica and PCE-water-silica capillary pressure-water saturation curves
3. To test an existing steam flushing numerical model

This thesis consists of seven chapters which are organized as follows:
Chapter 1. Introduction

- **Chapter 1**, the current chapter, briefly introduces the problem of soil and groundwater contamination and relevant *in situ* remediation methods. This chapter explains why steam flushing, as a potentially very good alternative method of soil and groundwater remediation, should be studied further.

- **Chapter 2** presents a literature review of steam flushing both in petroleum reservoir engineering and in remediation. The lack of multi-dimensional studies of steam flushing in groundwater remediation literature motivates this thesis research. Steam flushing removal mechanisms are examined in detail and their relative importance is discussed.

- **Chapter 3** deals with measurements of the impact of temperature on the capillary pressure-water saturation curves for the fluid pairs of air-water and NAPL-water in unconsolidated silica sand at different temperatures. The experimental methods are described and results presented. A model accounting for the change of capillary pressure with temperature, based on the previous research results reported in the literature, is developed and fitted to the experimental results. The measured data and model parameters provide insight and understanding of the effect of temperature on organic contaminant removal in soil and groundwater during steam flushing. The possible factors affecting the change of capillary pressure with temperature are discussed.

- **Chapter 4** describes the steam flushing system. The tensiometers, time domain reflectometry probes, fluid sampling ports, chemical spill distributor, wells, two-dimensional sand packer, steam generator, condenser, and chemical/water separator are the key devices and apparatuses designed and constructed. The apparatuses described in this chapter provide very important tools to study the steam flushing.

- **Chapter 5** presents and discusses the results of the steam flushing experiments and demonstrates that the first objective is satisfactorily accomplished. Contour plots of organic concentrations, water saturations, water pressures, and soil temperatures for
different well orientations and water saturation conditions in the two-dimensional sand chamber show how the steam flushing technique works and illustrate why steam flushing may be effective for the clean up of groundwater contamination.

- **Chapter 6** presents and discusses the computer simulation of the steam flushing experiments obtained with COMPSIM described in Appendix D. The complex numerical model, once tested against the experimental measurements, could be used to predict the outcome of a site remediation by steam flushing without actual operation for the purpose of feasibility evaluation.

- **Chapter 7** contains conclusions derived from the capillary pressure-water saturation experiments, steam flushing experiments, and numerical simulations. Recommendations for future research are also made.
CHAPTER 2 STEAM FLUSHING THEORY

2.1 Literature Review

2.1.1 Petroleum Reservoir Engineering

Since steam injection techniques were first used in 1933 (White and Moss, 1983), approximately 80% of all tertiary oil produced worldwide has been recovered by thermal methods, primarily steam injection (Ahner and Sufi, 1994). Steam injection techniques have been used to enhance oil recovery for both light and heavy oil reservoirs after secondary enhanced oil recovery (usually water-flooding). The steam injection still leaves behind 10 - 40% of the oil found in the steam zones even when economical limits are reached (White and Moss, 1983). The principle oil recovery mechanisms are steam distillation for light oil and oil viscosity reduction for heavy oil. Other factors include thermal oil expansion and solvent-extraction effects (Willman et al., 1961; Stewart and Udell, 1988; White and Moss, 1983).

Steamflooding, cyclic stimulation, and steam assisted gravity drainage are the three main modes of steam injection (Sleep, 1995). In steamflooding, steam is usually injected in a central well to drive heated oil to four evenly spaced wells around the injection well (five-spot well pattern). As shown by the top graph of Figure 2.1 (White and Moss, 1983), the temperatures drop sharply at the steam condensation front, where latent heat is released raising the system temperature. The bottom curve shows oil being displaced by cold water in zone 3, followed by hot water and steam in zone 2 and steam in zone 1.

This saturation distribution illustrates that both steam and hot water can displace oil efficiently because oil viscosity decreases at elevated temperatures. However, steam displacement has many advantages over hot water displacement. Higher in situ temperatures can be achieved with steam injection than with hot water flooding, allowing greater
reductions in viscosity and density. The most significant advantage is steam distillation (Stewart and Udell, 1988).

Figure 2.1 Temperature and saturation profiles of steam injection processes between injection and production well.

Cyclic stimulation is more energy efficient than steamflooding. In cyclic stimulation, a well is injected with steam for several days to several weeks, then the heated well is used to produce heated oil. This "huff-and-puff" injection technique requires heating only a small area around the well, while in steam flooding it is necessary to heat up all the reservoir rock between the injection and production wells.
The steam assisted gravity drainage technique was developed to avoid the steam override and channeling problems associated with steamflooding. Steam override occurs because of the density differences between steam and oil. Steam channeling is due to heterogeneity of the formation. Both problems cause steam to bypass the target zone and create an early breakthrough of steam at the production well (Butler et al., 1981; Butler and Stephens, 1981; Joshi and Threlkeld, 1985; Chung and Butler, 1988; Ahner and Sufi, 1994). In steam assisted gravity drainage, steam is injected into a horizontal well just above the horizontal production well. The steam chamber expands upward and sideward while the heated oil and steam condensate flow countercurrently as a thin layer around the steam chamber down to the production well. Foam production should be avoided since foam has a higher viscosity than oil and is hard to break.

2.1.2 Groundwater Remediation

Sleep (1995) presented a detailed review of steam injection technology applied recently for NAPL remediation. He stated that the published applications of steam injection techniques are limited to remediation of LNAPL from the vadose zone of unconsolidated and unfractured media.

Hunt et al. (1988b) conducted laboratory studies of steam injection in a horizontal Ottawa sand column which was equipped with pressure transducers and thermocouples and wrapped with heating tapes to ensure uniform axial flow conditions. The initial average NAPL saturation in the column was 2.5%. Experiments with trichloroethylene (TCE), a benzene-toluene mixture, and a commercial gasoline showed that water flow at rates as high as 15 m/d could not displace these NAPL, while steam injection recovered 94% of the TCE, 50% of the benzene-toluene mixture and 74% of the gasoline.

Hadim et al. (1993) published their bench-scale one-dimensional laboratory experiments of steam injection for in situ remediation of soils contaminated by No. 2 heating oil and jet fuel.
They used four soils with uniform grain sizes of 1.2, 0.6, 0.3, 0.22 mm, and a well-graded soil with a mean grain size of 1.2 mm. The LNAPL saturation established after waterflooding was fixed at 23% for all the experiments except for the well-graded soils, for which it was 48%. The temperature of the steam was 102-110°C and the pressure was 12.4-44.8 kPa (125-451 cm H₂O). The final recovery was 98.2%-99.8%. They concluded that an increase in steam injection pressure and soil grain size resulted in an increase in LNAPL recovery, and the LNAPL residual saturation after steam injection was essentially independent of the starting LNAPL saturation.

More multi-dimensional experiments are needed to evaluate the design of horizontal/vertical well systems and the degree of steam override, steam channeling and unwanted downward remobilization of NAPLs. The difference in removal efficiency between LNAPLs and DNAPLs, between saturated and unsaturated conditions, and between volatile and semi-volatile organic pollutants should be examined in multi-dimensional systems as well.

2.2 Mechanisms

The mechanisms of organic contaminant removal by steam injection include steam distillation of NAPL, steam and hot water drive, solvent drive, and residual NAPL clean up. These are discussed in more detail below.

2.2.1 Steam Distillation of NAPL

The primary mechanism of the removal of volatile and semi-volatile LNAPLs and DNAPLs by steam injection is steam distillation (Hunt et al., 1988; Stewart and Udell, 1988; Willman et al., 1961). The vapor pressures of NAPLs increase when temperature is increased. The variations of PCE, n-nonane, and water vapor pressures with temperature are shown in Figure 2.2 (Lide and Frederikse, 1995).
Chapter 2 Steam Flushing Theory

According to Dalton's law for the summation of partial pressures, the total gaseous phase pressure (Pa), $P_g$, is the sum of the partial pressure (Pa), $P_a$, of the $N$ individual compounds present:

$$P_g = \sum_{\alpha=1}^{N} P_a$$  \hspace{1cm} 2.1

![Figure 2.2 Vapor pressures of PCE, nonane, and water vs. temperature.](image)

The ideal gas law states:

$$P_a V = n_a RT$$  \hspace{1cm} 2.2

where $V$ is the gaseous phase volume (m$^3$), $n_a$ is the number of moles of component $\alpha$, $T$ is the absolute temperature (K), and $R$ is the universal gas constant (0.082 atm-m$^3$/gmol-K). Then we have:

$$\sum_{\alpha=1}^{N} P_a = \left( \sum_{\alpha=1}^{N} n_a \right) \frac{RT}{V}$$  \hspace{1cm} 2.3

Therefore, the individual compound mole fraction $x_{\alpha g} = n_{\alpha}/\Sigma n_{\alpha}$ in the gaseous phase can be derived from Equation 2.1, 2.2, and 2.3 as the following:
Mole fractions of various NAPL in air or steam (water vapor) are calculated and shown in Table 2.1. It is assumed that only two components, either air-NAPL or steam-NAPL, exist in the system when the mole fractions are calculated.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vapor Pressure (cm H₂O)</th>
<th>( x_{aq} ) (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pure phase (20°C)</td>
<td>Pure phase (100°C)</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>244.9</td>
<td>3478.1</td>
</tr>
<tr>
<td>TCE</td>
<td>78.0</td>
<td>1475.3</td>
</tr>
<tr>
<td>PCE</td>
<td>18.7</td>
<td>544.7</td>
</tr>
<tr>
<td>nonane</td>
<td>4.3</td>
<td>211.9</td>
</tr>
<tr>
<td>Anthracence</td>
<td>0.0017</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 2.1 Chemical component mole fractions in air and steam.

When steam is first injected into the subsurface, it condenses immediately and the heat is transferred to the soil and pore fluids to raise their temperature. The vapor pressures of water and LNAPL increase when steam is injected above the water table, which makes more LNAPL partition into gaseous phase. If the steam is injected below the water table, a vapor phase is formed at a particular location when the sum of the vapor pressures of the liquid phases present (water and DNAPL) exceeds the in situ liquid pressure. The composition of the vapor phase formed will be a function of temperature and of the fluids present. That is, compounds which have higher vapor pressures at steam temperatures will have higher mole fractions in the vapor phase and will be preferentially removed from the DNAPL.
2.2.2 Steam Drive

2.2.2.1 NAPL in the Vadose Zone

When steam is injected continuously from several injection wells covering the contaminated region in the vadose zone, the steam zone expands toward the extraction well in the center. A typical scenario is postulated in Figure 2.3.

Fig 2.3 LNAPL and DNAPL steam flushing.
As steam enters the subsurface, it gives up latent heat to the soil, air, water, and LNAPL to raise the temperature. The higher temperature results in higher LNAPL and water vapor pressures which makes more LNAPL partition into the gaseous phase. The organic and water vapors in the gaseous phase condense at the steam front where the temperature is lower than the steam temperature. This condensate forms a LNAPL bank followed by a hot water bank ahead of the steam front. These LNAPL and water banks have higher LNAPL saturation and water saturation, respectively, than was originally present. Therefore, the LNAPL bank, which is mobile, is displaced by hot water and followed by steam to the extraction well. Complete clean-up of LNAPL is possible for lower boiling point organic compounds. The LNAPL and water banks are shown conceptually in Figure 2.4.

![Diagram showing steam, LNAPL bank, water bank, and saturation levels](image)

Figure 2.4 LNAPL and Water Banks.

2.2.2.2 DNAPL Below Ground Water Table

When steam is injected continuously below the water table, it also condenses and releases heat to raise the soil, water, and DNAPL temperatures. A gaseous phase forms when the
Chapter 2 Steam Flushing Theory

total vapor pressure of water and DNAPL exceeds the total \textit{in situ} liquid phase pressure. The immobile residual DNAPL is vaporized and then condensed at a propagating steam front where it forms a DNAPL bank (Figure 2.5). The steam phase expands and drives the DNAPL bank toward the extraction well (Figure 2.3).

![Diagram of DNAPL Bank](image)

**Figure 2.5** DNAPL Bank.

When the DNAPL is perched on an aquitard it may be mobile if enough DNAPL was leaked, spilled, or dumped. This mobile DNAPL is displaced by water first and then distilled by steam to join the DNAPL bank at the steam front. The risk of contaminating the aquitard and underlying aquifers with the DNAPL is possible since increasing temperature causes a decrease of water-DNAPL interfacial tension which reduces the DNAPL entry pressure into the aquitard (see Figure 3.7). Steam may also desaturate the aquitard so that DNAPL can displace the gaseous phase. One way to reduce the risk is to inject steam below the aquitard so that the DNAPL is pushed upwards.
Chapter 2 Steam Flushing Theory

For both LNAPL and DNAPL cases, steam override due to the density difference between steam and the liquid (water, NAPL) can be a significant problem.

2.2.3 Solvent Drive

As seen in Table 2.1, different organic compounds have different vapor pressures and mole fractions in the vapor phase at steam temperature. The more volatile compounds (e.g. PCE) are stripped first from the trapped blobs and ganglia by steam. These more volatile compounds condense at the steam front to form a NAPL bank. The NAPL bank dissolves less volatile compounds, making their removal more efficient. This mechanism is not considered as a major one.

2.2.4 Residual NAPL Removal

Blobs and ganglia of organic contaminants present at residual saturations in soil pores are trapped by capillary forces. In order to mobilize a trapped blob or ganglion, the interfacial tension (IFT) has to be reduced to an extent that the pressure gradient created by the flow of continuous phase of hot water or steam is sufficient to overcome the capillary force in the direction of flow (Lam et al., 1983). The degree of removal of the residual NAPL through viscous fluid displacement depends on the ratio of viscous forces to capillary forces, defined as the capillary number, $N_{ca}$ (dimensionless), (Larson et al., 1981):

$$N_{ca} = \frac{V_w \mu_w}{\sigma \cos \theta}$$

where $V_w$ is Darcy velocity of the displacing fluid (water) (m/s), $\mu_w$ is the viscosity of the displacing fluid (water) (cP), $\sigma$ is the IFT between NAPL and water (mN/m), and $\theta$ is the contact angle between the fluid-fluid interface and the soil surface. Figure 2.6 shows the variation of IFT with temperature for PCE.
The higher the $N_{ca}$ is, the more NAPL will be removed. If $\theta = 0$, then $\cos\theta = 1$. If the Darcy velocity of injected water in a typical aquifer is assumed to be $3.8 \times 10^{-5}$ m/s (3.3 m/d) the $N_{ca}$ for a PCE-contaminated aquifer decreases from $8.3 \times 10^{-7}$ to $6.5 \times 10^{-7}$ when the temperature is increased from 20 to 90 °C. Thus, in the case of PCE clean-up by hot water and steam flushing, the hydrodynamic removal of PCE will not be significantly enhanced by the increase of temperature. The steam distillation of PCE is the primary mechanism for the decontamination of soil (Ma and Sleep, 1995).

Figure 2.6 The properties of PCE vs. temperature (Ma and Sleep, 1995).
Figure 2.6 also shows the thermal variation of PCE density, viscosity and solubility. The small decrease of PCE density with increasing temperature indicates that the additional recovery of NAPL by thermal swelling would be small, while the increase of the buoyancy force would be minor as well.

The solubility of PCE increases by a factor of two when the temperature increases from 0 to 120 °C indicating that additional PCE would be recovered in the water collected from the extraction well. However, the amount of PCE recovered would be small because of the low aqueous solubility of PCE.

2.3 Summary

The majority of tertiary oil produced worldwide has been recovered by steam injection in the modes of steamflooding, cyclic stimulation, and steam assisted gravity drainage. Research on soil and groundwater remediation by steam flushing is still in the initial stages. The laboratory experiments reported in the groundwater remediation literature are all one-dimensional with no measurements on the variation of organic contaminant concentrations, water saturations, and water pressures in the porous medium. The major steam flushing mechanisms are steam distillation of organic contaminants and steam drive of the mobile NAPLs. Other minor steam flushing mechanisms include solvent drive of organic contaminants, thermal swelling of NAPLs, and increased aqueous NAPL solubilities.
CHAPTER 3 EFFECT OF TEMPERATURE ON $P_c$-$S_w$ RELATIONS

3.1 Literature Review

Many experiments have been performed on various soils to study the effect of temperature on air-water capillary pressure curves ($P_c$-$S_w$ relations), typically in the temperature range of 0-55 °C (Chahal, 1965; Haridasan and Jensen, 1972; Cary, 1975; Constantz, 1982; Hopmans and Dane, 1986; Nimmo and Miller, 1986; Davis, 1994). When steam injection became popular as a tertiary oil recovery method in the 1960's, there were some experiments performed measuring the oil-water capillary pressure curves on rock cores over a wider temperature range than those investigated by soil scientists (Poston et al., 1970; Sinnokrot et al., 1971; Constantz and Herkelrath, 1984). However, so far, no experiments have studied the effect of temperature on capillary pressure curves for chlorinated solvent-water systems.

It is usually assumed that there is a capillary pressure corresponding to a given water saturation which corresponds to a particular effective mean radius of the undrained portion of a porous medium. Performing the mechanical and energy balance results in the Laplace equation (Sinnokrot et al., 1971):

$$ P_{aw} = \frac{2\sigma_{jw} \cos \theta_{jw}}{r} $$

where $j = a$ for air, or $j = o$ for oil or organic chemicals or non-aqueous phase liquids (NAPLs), $\sigma_{jw}$ is the interfacial tension (IFT) between phase $j$ and $w$ (N/m), and $\theta_{aw}$ and $\theta_{ow}$ are the contact angles formed by the interfaces of air-water and organic-water with the solid soil surface, respectively. $r$ is the effective mean soil pore radius (m).

In addition,

$$ P_{caw} = P_a - P_w \quad 3.2 \text{ (a)} $$

$$ P_{cow} = P_o - P_w \quad 3.2 \text{ (b)} $$
Chapter 3. Effect of Temperature on $P_c-S_w$ Relations

where $P_{caw}$ and $P_{cow}$ are the capillary pressures (Pa) for an air-water system and organic-water system, respectively. $P_a$, $P_o$, $P_w$ are air, organic, and water pressures (Pa), respectively.

The wetting coefficient, $\cos \theta_{jw}$, can be expressed as

$$\cos \theta_{jw} = \frac{\sigma_{js} - \sigma_{ws}}{\sigma_{jw}}$$

where $\sigma_{js}$ is air-soil ($\sigma_{as}$) or organic-soil ($\sigma_{os}$) IFT and $\sigma_{ws}$ is water-soil IFT. Equation 3.3 is obtained from Young's equation:

$$\sigma_{js} = \sigma_{ws} + \sigma_{jw} \cos \theta_{jw}$$

Gardner (1954) measured the effect of temperature on the air-water capillary pressure curves of various kinds of soils and found that the capillary pressure decreased significantly when temperature increased. Philip and De Vries (1957) derived an expression for $(\partial P_{jw}/\partial T)_w$, termed the temperature coefficient of capillary pressure:

$$\left( \frac{\partial P_{jw}}{\partial T} \right)_w = \frac{P_{jw}}{\sigma_{jw}} \left( \frac{\partial \sigma_{jw}}{\partial T} \right)$$

They assumed that the wetting coefficient, $\cos \theta_{jw}$, did not change with temperature (i.e. $\partial (\cos \theta_{jw})/\partial T = 0$). Since air-water or organic-water IFT decreases with increasing temperature (Figure 2.6), capillary pressures should decrease with increasing temperature.

Many experimental results (Chahal, 1965; Haridasan and Jensen, 1972; Constantz, 1983; Nimmo and Miller, 1986) could not be explained on the basis of changes in air-water IFT alone, because the temperature effect was larger than at predicted by the Philip and De Vries (1957) theory by one to five orders of magnitude (Nimmo and Miller, 1986). The hypothesis offered by Nimmo and Miller (1986) was that the temperature dependence of the IFT of soil solution was greater than that of pure water since the concentration and effectiveness of dissolved surfactants (such as fulvic and humic acids) increased when temperature increased. Solutions of such fatty acids have been shown to have IFT as low as 44 mN/m (Nimmo and
 Chapter 3. Effect of Temperature on $P_c$-$S_w$ Relations

Miller, 1986). The $\sigma_{aw}$ values measured for soil water are somewhat less than the 72 mN/m of pure water, but are considerably greater than 44 mN/m of the fatty acid solution. It is likely that the concentrations of surfactant in soil solutions were significantly less than the concentration at which the surfactants have their maximum effect (the critical micelle concentration, or CMC). The possible significance of this mechanism is difficult to assess because the identity of surfactants and the chemical environment of the soil are not well known.

Another hypothesis offered by Chahal (1965) was that the effect of volume change of the entrapped air or the nucleation of air in the soil with increasing temperature would cause the larger than predicted temperature effect due to IFT changes alone. The entrapped air was defined as the air in the discontinuous pores or in the pores isolated by water from the continuous free air phase. He showed that the temperature coefficient of capillary pressure was larger than expected from Equation 3.5 immediately following air entry and decreased back to the values calculated from Equation 3.5 at higher capillary pressure during the drainage process. Hopmans and Dane (1986) set up a system to measure the entrapped air volume and drainage-imbibition capillary pressure curves simultaneously and found that the entrapped air volume decreased with increasing temperature, which was in apparent contradiction with the concept that the entrapped air volume should increase due to thermal expansion. This decrease in entrapped air volume may have been caused by an increase in pressure of entrapped air bubbles, which resulted in an increased flow rate of air from the entrapped region to the free air phase. They concluded that a complete explanation for the discrepancy between the measured and calculated temperature effects on air-water capillary pressure curves remains unknown. The work of Chahal (1965) and Hopmans and Dane (1986) were based on the concept of adding one term accounting for the effects of entrapped air volume on the air-water capillary pressure curves to Equation 3.5 by introducing the apparent volumetric water saturation ($S_w$) as defined in Equation 3.27. This resulted in the following equation:
Chapter 3. Effect of Temperature on $P_c$-$S_w$ Relations

The fact that the change of contact angle $\theta_{jw}$ with the change of temperature may cause the discrepancy between the measured temperature coefficient and that calculated from Philip and De Vries (1957) theory was pointed out by petroleum engineers (Poston et al., 1970; Sinnokrot et al., 1971). Poston et al. (1970) measured the contact angle $\theta_{ow}$ (in the range of 20 - 35°) for three different refined oils (80, 99, 600 cP) over the temperature range of 25 - 88 °C in an oil-water-glass system and found that all the $\theta_{ow}$ decreased with an increase of temperature. This means that the capillary pressure for a given water saturation should increase with increasing temperature. This would increase the discrepancy between the measured temperature coefficient and that calculated from Philip and De Vries (1957) theory. However, the effect of contact angle may be small since the temperature coefficients of contact angle are small. For example, the change was -0.27 °/°C for an organic-water-glass system of Poston et al. (1970), -0.29 °/°C for a bayol-water-siliconed glass system of Phillips and Riddiford (Sinnokrot et al., 1971), and -0.13 °/°C for an air-water-naphthalene system of Jones and Adamson (Sinnokrot et al., 1971). The measured contact angle for an air-water-silica system is near zero (Davis, 1994).

Liu and Dane (1993) developed a new theory based on the hypothesis that when temperature increases, water flows from isolated packets to the continuous water phase which results in an additional temperature effect on the capillary pressure curves. It was assumed that the total water saturation $S_{wt}$ equals the sum of continuous water saturation $S_{wc}$ and isolated water saturation $S_{wis}$ (that is, $S_{wt} = S_{wc} + S_{wis}$) and $S_{wc}$ changes linearly with $S_{wt}$. The theory did predict a larger temperature coefficient than that calculated by Equation 3.5 and produced a closer match with the experimental drainage curves of a Norfolk sandy loam at 20 and 44.5 °C than those produced by Philip and De Vries (1957) theory.
Grant and Salehzadeh (1996) extended the theory of Philip and De Vries (1957) by including temperature dependence of the contact angle. They derived the following equation from Equation 3.1:

\[
\left( \frac{\partial P_{cw}}{\partial T} \right)_{sw} = \frac{P_{cw}}{\sigma_{jw}} \left( \frac{\partial \sigma_{jw}}{\partial T} \right) + \frac{P_{cw}}{\cos \theta_{jw}} \left( \frac{\partial \left( \cos \theta_{jw} \right)}{\partial T} \right)
\]

Grant and Salehzadeh (1996) assumed that the effect of temperature on air-water or organic-water interfacial tension can be described by the linear relation:

\[
\sigma_{jw} = a + bT
\]

where \( \sigma_{jw} \) is in mN/m and T is in K. Constants a (mN/m) and b (mN/m-K) are given in Equation 3.38 and 3.39 for calculating the air-water and PCE-water IFTs, respectively. The temperature derivative of the wetting coefficient can be expressed in terms of independently measurable physical-chemical quantities:

\[
\frac{d \cos(\theta_{jw})}{dT} = \frac{1}{\sigma_{jw}} \left( \frac{\sigma_{jw} \cos(\theta_{jw}) + \Delta_{v}''h'}{T} - \cos(\theta_{jw}) \frac{d \sigma_{jw}}{dT} \right)
\]

where \( \Delta_{v}''h' \) is the enthalpy of immersion per unit area and “s” refers to “soil” or “solid”. A differential equation for \( \cos(\theta_{jw}) \) can be obtained by combining Equations 3.8 and 3.9:

\[
(aT + bT^2) \frac{d \cos(\theta_{jw})}{dT} - a \cos(\theta_{jw}) = \Delta_{v}''h'
\]

which, for \( d(\Delta_{v}''h')/dT = 0 \), has the solution:

\[
\cos(\theta_{jw}) = \frac{-\Delta_{v}''h' + TC_{1}}{a + bT}
\]

where constant \( C_{1} \) is a reference temperature.

When the wetting coefficient is independent of temperature, Grant and Salehzadeh (1996) obtained the following expressions for \( P_{cw} \) and \( \partial P_{cw} / \partial T \) from Equation 3.1 and 3.5 using
Chapter 3. Effect of Temperature on $P_c$-$S_w$ Relations

\[ \sigma_{jw} = a + bT \quad \text{(Equation 3.8)} \quad \text{and} \quad \partial \sigma_{jw} / \partial T = b : \]

\[ P_{cjw} = \frac{2(a + bT) \cos \theta_{jw}}{r} \quad \text{(Equation 3.12)} \]

\[ \left( \frac{\partial P_{cjw}}{\partial T} \right)_{S_w} = \frac{bP_{cjw}}{a + bT} \quad \text{(Equation 3.13)} \]

Rewriting Equation 3.13 gives:

\[ \left( \frac{\partial P_{cjw}}{\partial T} \right)_{S_w} = \frac{a}{b} + T \quad \text{(Equation 3.14)} \]

When the wetting coefficient is temperature sensitive and enthalpy of immersion is independent of temperature, that is, $d(\Delta_y^{\text{w}}h^+)/dT = 0$, Grant and Salehzadeh (1996) derived the following expression from Equation 3.1 and 3.11:

\[ P_{cjw} = \frac{2(-\Delta_y^{\text{w}}h^* + C_1 T)}{r} \quad \text{(Equation 3.15)} \]

The temperature derivative of $P_{cjw}$ is:

\[ \left( \frac{\partial P_{cjw}}{\partial T} \right)_{S_w} = \frac{C_1 P_{cjw}}{-\Delta_y^{\text{w}}h^* + C_1 T} \quad \text{(Equation 3.16)} \]

Rewriting Equation 3.16 gives:

\[ \left( \frac{\partial P_{cjw}}{\partial T} \right)_{S_w} = -\frac{\Delta_y^{\text{w}}h^*}{C_1} + T \quad \text{(Equation 3.17)} \]

The following linear equation can be used to represent both Equation 3.14 and 3.17 for a given $S_w$:

\[ \left( \frac{\partial P_{cjw}}{\partial T} \right)_{S_w} = \beta_0 + \beta_1 T \quad \text{(Equation 3.18)} \]
where $\beta_0 = a/b \text{ (in K)}$ for constant $\theta_{jw}$ or $\beta_0 = -\Delta\theta' h'/C_1 \text{ (in K)}$ for Grant and Salehzadeh (1996) theory and $\beta_1 = 1$. If the estimated values of $\beta_0$ are near $a/b$, then $\cos(\theta_{jw})$ is constant. Otherwise, it is suggested that $\cos(\theta_{jw})$ does change with increasing temperature and affects the $P_c-S_w$ relationships.

In order to fit the data for the drainage or imbibition events for a porous medium to an analytical model, Equation 3.18 was rewritten and integrated by Grant and Salehzadeh (1996) to give the following equation

$$P_{cijw} = P_{cijw} \left( \frac{\beta_0 + T_f}{\beta_0 + T_r} \right) \quad 3.19$$

where $P_{cijw}$ and $P_{cijw}$ are the capillary pressures at a given temperature $T_f$ and reference temperature $T_r$, respectively. Equation 3.19 can be incorporated into any empirical capillary pressure functions such as those of van Genuchten (1980), as is discussed in detail in the next section.

A number of studies summarized in Table 3.1 provide experimental data on the effect of temperature on residual water saturation $S_{wr}$, residual air saturation $S_{ar}$, residual organic saturation $S_{or}$, and displacement pressure $P_d$ of the capillary pressure curves for the air-water and organic-water systems in the literature. One can observe that for the air-water systems, in almost all studies the residual water saturation $S_{wr}$ and displacement pressure $P_d$ of different porous media (soil, sand, glass beads) decreased with an increase in temperature for both static equilibrium and transient flow methods. Only the experiments of Haridasan and Jensen (1972) and Constantz (1983) showed an increase of residual air saturation $S_{ar}$. For the organic-water systems, residual water saturation $S_{wr}$ increased and residual organic saturation $S_{or}$ decreased with an increase in temperature.

Demond and Roberts (1991) pointed out that the factors affecting the $S_{wr}$ may be attributable to the change in pendular moisture, to the pore size distribution of the porous medium, and to
the drainage rate of water from the porous medium. They stated that pendular moisture is of the order of 4.2% - 5.5% so changes in pendular moisture due to changes in interfacial tension do not likely have a significant effect on $S_{wr}$. Sinnokrot et al (1971) pointed out that the increase in $S_{wr}$ with decreasing interfacial tension due to increasing temperature may lead to a small reduction in $S_{or}$. The reason is that the water wetness of the solid surface is increased with increasing temperature since the contact angle is decreased with increasing temperature as discussed before. The trapped organic exists as pendular rings (Wilson and Conrad, 1984) and may be squeezed out by water since either the surface active agents in the organic film are desorbed or the aqueous solubility of organic is enhanced. Demond and Roberts (1991) observed that the difference between $S_{wr}$ of the o-xylene-water and the air-water systems was much more significant in unvonctionated sands than in a sand pack of mesh size 60-120. Morrow (1970) found that $S_{wr}$ in a 3 mm porous glass beads varied over a small range, 8%-8.5%, even though the organic-water interfacial tension ranged from 22 to 71.2 mN/m. The dependence of wetting and non-wetting phase residual saturations on displacement rate may be due to increased bypassing of the displaced phase since the viscous fingering and channeling is increased when the displacement rate is increased (Peters and Flock, 1979). This results in higher $S_{wr}$ in the drainage processes and higher $S_{or}$ or $S_{ar}$ in the imbibition processes.

In summary, the effect of temperature on the capillary pressure curves of air-water and organic-water systems is significant and may be attributed to the effect of temperature on the air-water and organic-water IFT, dissolved surfactants or impurities, changes in entrapped air volume in the porous media, the flow of water from isolated packets to continuous water phase in the porous media, and changes in contact angles between the fluids and between fluids and the solid surface. For a given water saturation in the air-water and organic-water systems, the measured capillary pressure decreases with an increase in temperature. The Grant and Salehzadeh model (1996) is used in this study to analyze the effect of temperature on the capillary pressure curves at various temperature levels for the air-water-silica and organic-water-silica systems.
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<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Media</th>
<th>Fluid pair</th>
<th>Method</th>
<th>$T$ (°C)</th>
<th>$S_w$</th>
<th>$S_{ur}$</th>
<th>Hysteresis</th>
<th>$P_d$</th>
<th>Explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1965</td>
<td>Chahal</td>
<td>fine silt soil</td>
<td>air-water</td>
<td>static, drainage</td>
<td>5-55</td>
<td>↓</td>
<td>$S_w$</td>
<td>↓</td>
<td>↓</td>
<td>↑↑, ↓, trapped air↑</td>
</tr>
<tr>
<td>1970</td>
<td>Poston et al</td>
<td>quartz, oilsand</td>
<td>oil-water</td>
<td>24-135</td>
<td>↑</td>
<td>$S_w$</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑↑, ↓</td>
</tr>
<tr>
<td>1971</td>
<td>Sinnenkrot et al</td>
<td>sandstone, limestone</td>
<td>oil-water</td>
<td>static, drainage, imbibition</td>
<td>21-163</td>
<td>↑</td>
<td>$S_w$</td>
<td>↓↑, sandstone only only</td>
<td>↓</td>
<td>unknown</td>
</tr>
<tr>
<td>1972</td>
<td>Haridas-san &amp; Jensen</td>
<td>silt loam soil</td>
<td>air-water</td>
<td>static, transient, drainage</td>
<td>15-35</td>
<td>↓</td>
<td>transient only</td>
<td>↑</td>
<td>↓↑, transient only only</td>
<td>↑↑, ↓↑, unknown factors</td>
</tr>
<tr>
<td>1983</td>
<td>Constantz</td>
<td>Tipperary sand</td>
<td>air-water</td>
<td>static, drainage, imbibition</td>
<td>25-95</td>
<td>↓</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↑↑, ↑↑↑, bubble ↑, sand compaction ↑</td>
</tr>
<tr>
<td>1986</td>
<td>Nimmo &amp; Miller</td>
<td>glass beads, sand, silt loam</td>
<td>air-water</td>
<td>transient, drainage, imbibition</td>
<td>4-50</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑↑, surfactant ↑, bubble formation ↑</td>
</tr>
<tr>
<td>1994</td>
<td>Davis</td>
<td>silica sands</td>
<td>air-water, oil-water</td>
<td>static, drainage, imbibition</td>
<td>10-30</td>
<td>$S_w$</td>
<td>$S_{ur}$</td>
<td>↓↑, air-water only only</td>
<td>↓</td>
<td>↑↑, ↓↑, ↓ impurity ↑</td>
</tr>
</tbody>
</table>

*S$_w$ (for air-water systems) was constant for 20/30 sand and increased for mixed sand.

Table 3.1. Summary of previous temperature-dependent capillary pressure curves.

3.2 Two-phase Hysteretic $P_c$-$S_w$ Relationship

Hysteresis in $P_c$-$S_w$ relations of two-phase systems has been well-documented and various theoretically and empirically based models have been developed to describe two-phase
hysteretic $P_c-S_w$ functionals from primary drainage and imbibition path measurements. Parker and Lenhard (1987) presented a parametric model of hysteretic $P_c-S_w$ relations which included the effect of air or organic phase entrapment during imbibition. Entrapped non-wetting fluid saturations at a given point along a saturation path were linearly interpolated between the end points of the primary imbibition scanning curve using maximum trapped saturations estimated by extension of the method of Land (1968). More detail is given at the end of this section.

van Genuchten (1980) presented the following capillary pressure functions to fit both main drainage and imbibition branches of a non-wetting phase (j phase) - water system in a porous medium:

\[ \bar{S}_w = \left[ 1 + \left( \alpha P_c \right)^n \right]^{-m} \quad \text{when } P_{c,j} > 0 \quad 3.20 \text{ (a)} \]

\[ \bar{S}_w = 1 \quad \text{when } P_{c,j} = 0 \quad 3.20 \text{ (b)} \]

where $\bar{S}_w$ is the effective water saturation as defined by Equation 3.24. The parameters $\alpha$, $n$, and $m = 1 - 1/n$ are empirical constants that may be determined from experimental data.

In order to fit all the drainage data of a porous medium at all temperatures to the van Genuchten function, the Grant and Salehzadeh (1996) model can be incorporated into the van Genuchten function by combining Equation 3.19 and 3.20:

\[ \bar{S}_w = \left[ 1 + \left( \alpha P_{c,jf} \frac{\beta_j + T_r}{\beta_j + T_f} \right)^n \right]^{-m} \quad \text{when } P_{c,jf} > 0 \quad 3.21 \text{ (a)} \]

\[ \bar{S}_w = 1 \quad \text{when } P_{c,jf} = 0 \quad 3.21 \text{ (b)} \]

The effective air, organic, and water saturations are defined, respectively, as

\[ \bar{S}_a = \frac{S_a}{1 - S_{wr}} \quad 3.22 \]
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\[ \bar{S}_o = \frac{S_o}{1 - S_{wr}} \]  
\[ \bar{S}_w = \frac{S_w - S_{wr}}{1 - S_{wr}} \]

where $S_a$, $S_o$, $S_w$ are air, organic, and water saturation, respectively. $S_{wr}$ is the irreducible water saturation reached by following a drainage path extrapolated to infinity. The non-wetting phase effective saturation $\bar{S}_j$ consists of the free phase effective saturation $\bar{S}_{jf}$ and trapped phase effective saturation $\bar{S}_{jt}$

\[ \bar{S}_a = \bar{S}_{af} + \bar{S}_{at} \]
\[ \bar{S}_o = \bar{S}_{of} + \bar{S}_{ot} \]

Then the "apparent" water saturations for the air-water and organic-water systems, respectively, are

\[ \bar{S}_w = \bar{S}_w + \bar{S}_{at} \] for air-water
\[ \bar{S}_w = \bar{S}_w + \bar{S}_{ot} \] for organic-water

The capillary heads (m $H_2O$) for the air-water and organic-water systems, respectively, are

\[ h_{aw} = \frac{(p_o - p_w)}{\rho_w} \]  
\[ h_{ow} = \frac{(p_o - p_w)}{\rho_w} \]

where $g$ is the gravitational acceleration constant (m/s$^2$) and $\rho_w$ is the water density (kg/m$^3$).

Parker and Lenhard (1987) developed a primary imbibition scanning curve interpolation method by generalizing the empirical relationship observed by Land (1968). For a two-phase system with main drainage, main imbibition, and primary scanning imbibition curves where the reversal point from drainage to imbibition is $\left( ^\wedge \bar{S}_w, h_{iw} \right)$, the entrapped non-wetting fluid
effective residual saturation corresponding to the primary imbibition scanning curve is \( \bar{S}_{jr} \), and the maximum entrapped non-wetting fluid effective residual saturation corresponding to the main imbibition curve is \( 'S_{jr} \) (Figure 3.1), the \( \bar{S}_{jr} \) of a primary imbibition scanning curve can be estimated as

\[
\bar{S}_{jr} = \frac{1 - 3\bar{S}_w}{1 + R_{jw}(1 - 3\bar{S}_w)}
\]

in which
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\[ R_{jw} = \frac{1}{\bar{S}_{j'}} - 1 \]  
3.32

\( \bar{S}_{j'} \) is predicted to vary linearly with \( \bar{S}_w \) as

\[ \bar{S}_{j'} = \bar{S}_{j'} \left( \frac{\bar{S}_w - \bar{S}_{j'} \bar{S}_w}{1 - \bar{S}_w} \right) \text{ when } \bar{S}_w > \bar{S}_{j'} \]  
3.33

where \( \bar{S}_{j'} = 0 \) at the drainage and imbibition reversal point (when \( \bar{S}_w = \bar{S}_{j'} \)).

Therefore, with \( j = a \) or \( o \), Equation 3.27 and 3.28 become

\[ \bar{S}_w = \bar{S}_w - \bar{S}_{j'} \left( \frac{\bar{S}_w - \bar{S}_{j'} \bar{S}_w}{1 - \bar{S}_w} \right) \]  
3.34

or

\[ S_w = \bar{S}_w (1 - S_{wr}) + S_{wr} - \bar{S}_{j'} \left( \frac{\bar{S}_w - \bar{S}_{j'} \bar{S}_w}{1 - \bar{S}_w} \right) (1 - S_{wr}) \]  
3.35

in which \( S_w \) is the measured water saturation of the primary imbibition scanning curve. The "apparent" water saturation, \( \bar{S}_w \), is used for the capillary pressure calculation. It was assumed that \( S_{wr} \) and \( \bar{S}_{j'} \) varied linearly with temperature \( T \) (K):

\[ S_{wr} = a_r + b_r T \]  
3.36

\[ \bar{S}_{j'} = c_r + d_r T \]  
3.37

3.3 Experimental Apparatus

3.3.1 Experimental Setup

The experimental setup consisted of a water bath (Brinkmann Instrument, Inc., Model Super RMT-20, -15 to +120 ±0.1 °C) to regulate the temperature of the pressure cell, a temperature
control chamber to regulate the temperature of the pressure transducers (Sensotec™ differential pressure transducers, Model WD-Z, $\pm 2 \pm 0.005$ psid or $\pm 140 \pm 0.35$ cm H$_2$O), a nitrogen cylinder to provide gas pressure, a data acquisition system (Sciematic Instruments. Inc., System 200 series, Model 231, 251B, 802) controlled by a computer to record the capillary pressure, and a syringe pump (Cole Parmer Instrument Company, Model 230 series, flow range: 0.001 $\mu$l/h - 70.5 ml/min (60 ml syringe)) to inject or withdraw water from the pressure cell (Figure 3.2).

The water bath has a built-in cooling coil, built-in water circulation pump, and digital temperature control panel. The surface of water in the bath was covered with plastic balls to reduce heat loss. An automated level control system was set up, using the data acquisition...
system to maintain the water level in the water bath and replace evaporated water.

Even though a two-stage pressure regulator was mounted on the nitrogen cylinder to control the air pressure of the pressure cell, it was still very difficult to set the air pressure of the cell. A glass “U” tube half-way filled with water and equipped with two one-meter rulers was used to set the air pressure for the cell.

3.3.2 Pressure Cell

Many types of cells have been developed over the past decades to measure the moisture content of soils by soil scientists. One typical cell used in the early days and still in use today is made from a Buchner-type funnel which has a fritted porous glass disc welded in the lower part of it (Chahal, 1965; Lin et al., 1982; Kueper, 1989; van Geel, 1994). The porous glass disc has fine pores with very high air entry pressure. Manometers or burettes filled with water or mercury were used to measure the water pressure or water suction. This type of cell was open to the air and only allowed the measurements of air-water capillary pressure curves. Care must be taken to avoid the harmful vapor of toxic organic liquids to the experimenter if such a cell is used to measure the water-organic capillary pressure curves at elevated temperatures.

Other types of pressure cells (Topp et al., 1967; Haridasan and Jensen, 1972; Cary, 1975; Constantz and Herkelrath, 1984; Nimmo and Miller, 1986; Stonestrom and Rubin, 1989; Salehzadeh and Demond, 1994) designed to measure only the drainage capillary pressure curves, can not be used to measure the imbibition capillary pressure curves of organic-water systems since they only have hydrophilic semi-permeable barriers (such as porous ceramic, porous fritted glass, and porous polyethylene membrane). Hydrophobic semi-permeable barriers (such as porous teflon membrane), in addition to hydrophilic semi-permeable barrier, are needed to measure the drainage and imbibition capillary pressure curves to prevent imbibed water from leaving the cell.
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Figure 3.3 Pressure cell (top); top view of the stainless steel disc (bottom).
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A new pressure cell was designed and constructed with a heavy-wall glass pipe (Figure 3.3). An extra-fine porous fritted glass disc of 5 \( \mu \)m pore size was welded into the glass pipe and one flange was added at each end making the 5.5 cm-diameter glass cylinder a total of 7 cm long. A 0.5-cm thick stainless steel (SS) disc drilled with 0.3 cm diameter holes, spaced 0.2 cm apart, was used to support two layers of porous teflon membrane (Cole Parmer Instrument Company, PTFE membrane, 0.2 \( \mu \)m pore size) on top of silica sand. The SS disc was sealed against the glass cylinder by one Viton™ “O” ring. The glass cylinder was closed with two pieces of 1/4” thick square SS metal with Viton™ “OoC” rings as the gaskets and was held together by four threaded SS rods bolted at the ends. Five 1/8” Swagelok™ brass male connectors were installed on the SS squares to connect the pressure cell to the syringe containing water, to the air pressure (\( N_2 \)) cylinder, and to a pressure transducer by 1/8” teflon tubing. A segment of the teflon tubing was connected to the water chamber below the porous fritted glass disc to allow the removal of air bubbles from time to time.

3.3.3 Sand Packing

In order to pack the sand tightly and uniformly, a simple and consistent method to pack the sand is needed. The usual methods of packing involve some kind of tamping, shaking, or vibrating techniques which are either non-uniform or mechanically unstable (Wygal, 1963). Wygal (1963) constructed a sand packer based on the law of deposition proposed by Kolbuszewski (1965; Kolbuszewski and Jones, 1961). The law states that a low velocity of fall of granular material (as for example, in water) leads to high porosity, independent of the intensity of deposition. A high velocity of fall (as for example, from heights of several inches or feet in air) produces a low porosity with low intensity of deposition. However, with increasing intensity of deposition the porosity increases progressively until, with a high intensity of deposition corresponding to the free fall of a mass of sand, the porosity is of the same order as that obtained by deposition in water. Kolbuszewski and Jones (1961) reported experimental results from the deposition apparatus based on the law of deposition for two types of sands and obtained excellent reproducibility of porosity. Motion pictures at 3,000
frames /s of the surface of a growing pack of 2.74 mm glass beads showed that the glass beads with proper velocity and intensity were observed to hit the surface singly at well spaced points of impact and the growing surface appeared fluid and alive for a depth of two to three particle diameters. The energy was transferred to the surface beads which were knocked into more stable positions.

![Figure 3.4 Column sand packer.](image)
A sand packer similar to Wygal’s (1963) particle distributor was built with a 5 cm diameter plexiglass tube and 25 mesh nylon screens (Figure 3.4). Five evenly spaced layers of nylon screens were inserted between the plexiglass pipe segments at intervals of 4 cm. Silica sand introduced with a funnel at the top of the column sand packer passed through and collided with the screens falling a total distance of 60 cm to the pressure cell. The flow rate of sand was 0.023 g/cm²-s, which was found by 5 tests to give excellent repeatable results, and was controlled by the size of the opening of the funnel. The porosity of F75 silica sand was 36.7 ± 0.5%. The sand surface in the cell could be leveled by slightly tilting the column toward the direction needing more sand. The column sand packer was able to produce homogeneous and reproducible sand samples simply and quickly.

3.3.4 Temperature Control Chamber

The temperature in the laboratory where the capillary pressure curve experiments were conducted changed by more than 10 °C over a 24-hour period. This caused serious problems for measuring the capillary pressure since the pressure transducers were very sensitive to temperature. A change of 10 °C in room temperature would change the pressure reading as much as 20 cm H₂O. However, most of the organic-water capillary pressure curves had capillary pressure values less than 20 cm H₂O (Figure 3.7). The main cause of capillary pressure change with temperature is that air volume in the pressure transducer chamber changes when temperature changed.

A temperature control chamber was built for the pressure transducers to regulate their temperature (Figure 3.5). A small computer fan was used to uniformly distribute the heat generated by a 40 watt light bulb which was turned on or off by a computer through a solid state relay. With the thermocouple (Thermo-Electric, T-type, maximum 399 °C) monitoring air temperature in the chamber, the computer turned the light bulb off if the temperature was more than 30 °C and on otherwise. The temperature of 30 °C was chosen since it was always
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higher than the laboratory temperature. The variation of air temperature in the chamber was less than 0.5.

![Diagram of temperature control chamber]

Figure 3.5 Temperature control chamber.

3.4 Experimental Procedure

Using the column sand packer, 135 g of F75 silica sand (see Chapter 4.10 for sieve analysis and physical properties) was packed into the glass pressure cell over 5 minutes for all the experiments. The SS disc with the porous teflon membranes attached at the bottom was pushed into the cell from the top until it sat on the sand and left no gap between the membrane and sand. The 1/8" thick SS squares were assembled and the cell was checked for leakage. A vacuum of 61 cm Hg (818 cm H$_2$O) was applied at the top of the cell for 20 minutes and then distilled, deaerated water was drawn in slowly from the bottom until the
sand was fully saturated which was verified by weighing the cell before and after the saturation (assuming porosity was known). A total 30 ml of PCE was introduced into the cell at the top if PCE-water capillary pressure curves were to be measured.

The cell was then placed into the water bath and left over night to raise the cell temperature to the required level and to equilibrate the air and water pressures. A constant air pressure of 110 cm H2O was applied at the top and the cell was closed and left over another night for pressure equilibration. Then, a small amount of water (0.1 - 2 ml) was withdrawn with the syringe pump and the cell was closed again until the capillary pressure remained constant. The procedure was repeated until no more water could be withdrawn even at extremely slow rates, marking the end of drainage process. The imbibition process was started by injecting water back into the cell, step by step, until the capillary pressure reached zero. Only about half of all experiments were repeated since a complete drainage-imbibition experiment took about 2 to 4 months to finish. The static method was used in the experiments.

3.5 Experimental Results

The experimental results of drainage and imbibition capillary pressure curves for the F75 silica sand at temperatures of 20, 40, 60, and 80 °C are plotted in Figures 3.6 and 3.7 for air-water and organic-water, respectively, where "air" means nitrogen gas and "organic" means PCE. Replicate experiments were conducted for air-water drainage curves at 20, 60, and 80 °C, air-water imbibition curves at 20 °C, and organic-water drainage and imbibition curves at 20 °C.

With increasing temperature, the air-water capillary pressure decreased uniformly over most of the water saturation range for the drainage process. However, as the irreducible water saturations were approached the curves for 20, 40, and 60 °C approached similar capillary pressures. It appears that $S_{w,r}$ is decreasing slightly as the temperature increases from 20 °C to 60 °C. This is consistent with the results of Davis (1994) for air-water systems in well graded
silica sand and the temperature range of 10-30. However, for a uniform 20/30 silica sand Davis (1994) found no changes in $S_{wr}$. The curve for 80 °C shows a large increase in $S_{wr}$. The change of capillary pressure with temperature for the imbibition process did not follow any trend (Figure 3.6). The hysteresis of the capillary pressures between the drainage and imbibition curves decreased for all the temperatures. The residual air saturation $S_{ar}$ and displacement pressure $P_d$ decreased with increasing temperature.

When temperature increased, the organic-water capillary pressure for a given water saturation decreased for the drainage process while it increased for the imbibition process (Figure 3.7). This resulted in a decrease in hysteresis between the drainage and imbibition processes. The increase of water saturation at the reversal point, the decrease of residual organic saturation $S_{or}$, and the decrease of displacement pressure $P_d$ (which is estimated as the inflection point of the drainage curve near complete water saturation) can be seen in Figure 3.7. The resultant trend is quite similar to the sandstone case of Sinnokrot (1971). They used a different fluid pair (CHEVRON 15 white oil-water) and different porous medium (consolidated natural sandstone).

The experimental data for each temperature were fitted with various models using a non-linear least square method with the Levenberg - Marquardt scheme (Press et al., 1987). The air-water results are shown in Figure 3.8 - 3.11 and organic-water results are shown in Figure 3.14 - 3.17. The VG-GS (Van Genuchten-Grant and Salehzadeh) and VG-PL-GS (Van Genuchten-Parker and Lenhard-Grant and Salehzadeh) model curves were obtained by fitting all the experimental data of all the temperatures. The VG (Van Genuchten) and VG-PL (Van Genuchten-Parker and Lenhard) models gave slightly better fits than VG-GS and VG-PL-GS models (see Table 3.2 (a) - (f)). The VG-GS model results for all the temperatures were plotted for air-water in Figure 3.12 and for organic-water in Figure 3.18 while VG-PL-GS model results for all the temperatures were plotted for air-water in Figure 3.13 and for organic-water in Figure 3.19.
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Figure 3.6 Air-water experimental data at 20, 40, 60, and 80 °C ("D"=drainage; "I"=imbibition).

Figure 3.6 Air-water experimental data at 20, 40, 60, and 80 °C ("D"=drainage; "I"=imbibition).
Figure 3.7 PCE-water experimental data at 20, 40, 60, and 80 °C ("D"=drainage; "I"=imbibition).
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Figure 3.8 Air-water experimental and fitted data at 20 °C ("D"=drainage; "I"=imbibition).

Figure 3.9 Air-water experimental and fitted data at 40 °C ("D"=drainage; "I"=imbibition).
Figure 3.10 Air-water experimental and fitted data at 60 °C ("D"=drainage; "I"=imbibition).

Figure 3.11 Air-water experimental and fitted data at 80 °C ("D"=drainage; "I"=imbibition).
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Figure 3.12 Predicted air-water drainage curves of VG-GS model for 20, 40, 60, and 80 °C ("D"=drainage).
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Figure 3.13 Predicted air-water imbibition curves of VG-PL-GS model for 20, 40, 60, and 80 °C ("I"=imbibition).

Figure 3.13 Predicted air-water imbibition curves of VG-PL-GS model for 20, 40, 60, and 80 °C ("I"=imbibition).
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Figure 3.14 PCE-water experimental and fitted data at 20°C ("D"=drainage; "I"=imbibition)

Figure 3.15 PCE-water experimental and fitted data at 40°C ("D"=drainage; "I"=imbibition)
Chapter 3. Effect of Temperature on $P_c-S_w$ Relations

Figure 3.16 PCE-water experimental and fitted data at 60 °C ("D"=drainage; "I"=imbibition)

Figure 3.17 PCE-water experimental and fitted data at 80 °C ("D"=drainage; "I"=imbibition)
Figure 3.18 Predicted PCE-water drainage curves of VG-GS model for 20, 40, 60, and 80 °C ("D"=drainage)
Chapter 3. Effect of Temperature on $P_c-S_w$ Relations

Figure 3.19 Predicted PCE-water imbibition curves of VG-PL-GS model for 20, 40, 60, and 80 °C ("I"=imbibition)
3.6 Discussion

The linear relationships between interfacial tension and temperature for air-water and PCE-water, as shown in Equation 3.8, are

\[
\sigma_{aw} = 117.66 - 0.1535T \quad 3.38
\]

\[
\sigma_{ow} = 57.28 - 0.042T \quad 3.39
\]

where \( \sigma_{aw} \) and \( \sigma_{ow} \) are in mN/m and \( T \) is in K (Ma and Sleep, 1995 and Grant and Salehzadeh, 1996). The coefficients of determination \( (R^2) \) were 0.99899 and 0.994 for Equation 3.38 and 3.39, respectively. Then, \( \beta_0 = a/b \) is -766.5 (K) for air-water systems and -1363.8 (K) for organic-water systems. The values of \( \beta_0 \) from curve-fitting of the experimental data for air-water drainage and imbibition are -448.6 (K) and -496.5 (K), respectively, which are much larger than -766.5 (K), while the \( \beta_0 \) for organic-water drainage and imbibition are -413.0 (K) and -848.8 (K), respectively, which are also much larger than -1363.8 (K) (see Table 3.2 (e) and (f)). Therefore, from the Grant and Salehzadeh (1996) theory discussed before, we know that the effect of temperature on the drainage and imbibition capillary pressure curves of the air-water and PCE-water systems cannot be explained by the effect of temperature on the IFTs alone since the experimental values of \( \beta_0 \) are quite different from the theoretical values of \( \beta_0 \).

However, if the ratios of wetting coefficients, \( \cos(\theta)_T / \cos(\theta)_{T_0} \), of air-water and PCE-water drainage data are plotted against temperature (Figure 3.20) and against water saturation (Figure 3.21), the Grant and Salehzadeh (1996) theory predicts that the ratios of wetting coefficients decreased, i.e., the contact angles increased, for both air-water and PCE-water drainage data when temperature increased. Even though there are no contact angle data obtained directly from the air-water-silica and PCE-water-silica systems at different temperatures to verify the prediction, the contact angle data from the literature (Neumann, 1978; Poston et al., 1970; Davis, 1994) often showed a decrease of contact angle with increasing temperature, or at most very small increases. Neumann and Spelt (1996) reported
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that the contact angle increased from 106.5° to 109° for a air-water-siliconized glass system when temperature changed from 5 °C to 50 °C (i.e., +0.056 °C). If we assume that the contact angle of the air-water-silica system increased from 0° to 3.5° over the temperature range of 20-80 °C, $\cos(3.5^\circ)/\cos(0^\circ)$ is only 0.998, which is larger than even the highest value of the wetting coefficient ratios (0.88 for air-water-silica at $S_w = 0.3$; Figure 3.21, top graph). Therefore, it is obvious that physically reasonable changes in contact angle can not account for the difference between the measured capillary pressures and calculated capillary pressures not accounted for by changes in interfacial tension.

The factors that may be responsible for the decrease of capillary pressures with increasing temperature, in addition to the reduction of the air-water and PCE-water interfacial tension and increase of contact angle, are the increase of impurity (surfactant) concentration, the change of entrapped air volume, the increased flow of water from isolated packets to the continuous water phase, and the change of sand compaction (see Table 3.1). The F75 silica sand used was not washed so it was possible that there may have been some impurities left on the sand surface, even though the amount was very likely insignificant. The volume of entrapped air would be zero, or at most negligible, since high vacuum was used to pull the air out before the water was sucked in. Therefore, the effect of change in entrapped air volume should have been negligible. The effect of the increase of flow of water from isolated packets to the continuous water phase was hard to evaluate since the experiments were not set up to measure this flow. The change of pore sizes due to the change of sand compaction with increasing temperature might happen because of the thermal expansion of the sand and cell materials. According to the Laplace equation (Equation 3.1), the effective mean soil radius, $r$, would have to be increased with increasing temperature in order to reduce the capillary pressure. However, the thermal expansion would be negligible for the sand, glass, and stainless steel 304 since the linear thermal expansion coefficients 4.68 X $10^{-6}$ / °C for silica sand and glass and 1.73 X $10^{-15}$ / °C for 304 stainless steel (Lide and Frederikse, 1996).
Chapter 3. Effect of Temperature on $P_c-S_w$ Relations

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>Confidence Level (95%)</th>
<th>$n$</th>
<th>Confidence Level (95%)</th>
<th>$S_{wr}$</th>
<th>Confidence Level (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.01860</td>
<td>±0.00025</td>
<td>8.62</td>
<td>±0.83</td>
<td>0.132</td>
<td>±0.030</td>
</tr>
<tr>
<td>40</td>
<td>0.02147</td>
<td>±0.00033</td>
<td>8.41</td>
<td>±0.93</td>
<td>0.126</td>
<td>±0.035</td>
</tr>
<tr>
<td>60</td>
<td>0.02473</td>
<td>±0.00050</td>
<td>7.30</td>
<td>±0.82</td>
<td>0.117</td>
<td>±0.044</td>
</tr>
<tr>
<td>80</td>
<td>0.03002</td>
<td>±0.00054</td>
<td>7.00</td>
<td>±0.73</td>
<td>0.244</td>
<td>±0.023</td>
</tr>
</tbody>
</table>

Table 3.2 (a) Drainage: air-water, VG model fitting results.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>Confidence Level (95%)</th>
<th>$n$</th>
<th>Confidence Level (95%)</th>
<th>$S_{wr}$</th>
<th>Confidence Level (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0556</td>
<td>±0.0012</td>
<td>4.76</td>
<td>±0.44</td>
<td>0.076</td>
<td>±0.035</td>
</tr>
<tr>
<td>40</td>
<td>0.0665</td>
<td>±0.0027</td>
<td>4.09</td>
<td>±0.53</td>
<td>0.086</td>
<td>±0.069</td>
</tr>
<tr>
<td>60</td>
<td>0.0834</td>
<td>±0.0048</td>
<td>3.89</td>
<td>±0.70</td>
<td>0.152</td>
<td>±0.064</td>
</tr>
<tr>
<td>80</td>
<td>0.1090</td>
<td>±0.0047</td>
<td>2.77</td>
<td>±0.29</td>
<td>0.193</td>
<td>±0.051</td>
</tr>
</tbody>
</table>

Table 3.2 (b) Drainage: PCE-water, VG model fitting results.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>Confidence Level (95%)</th>
<th>$n$</th>
<th>Confidence Level (95%)</th>
<th>$S_{ar}$</th>
<th>Confidence Level (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0294</td>
<td>±0.0011</td>
<td>4.94</td>
<td>±0.51</td>
<td>0.133</td>
<td>±0.024</td>
</tr>
<tr>
<td>40</td>
<td>0.0425</td>
<td>±0.0028</td>
<td>4.02</td>
<td>±0.55</td>
<td>0.060</td>
<td>±0.040</td>
</tr>
<tr>
<td>60</td>
<td>0.0387</td>
<td>±0.0022</td>
<td>4.47</td>
<td>±0.76</td>
<td>0.087</td>
<td>±0.043</td>
</tr>
<tr>
<td>80</td>
<td>0.0450</td>
<td>±0.0060</td>
<td>3.45</td>
<td>±0.73</td>
<td>0.101</td>
<td>±0.049</td>
</tr>
</tbody>
</table>

Table 3.2 (c) Imbibition: air-water, VG-PL model fitting results.
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<table>
<thead>
<tr>
<th>T ($^\circ$C)</th>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>Confidence Level (95%)</th>
<th>$n$</th>
<th>Confidence Level (95%)</th>
<th>$S_\alpha$</th>
<th>Confidence Level (95%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.207</td>
<td>$\pm 0.020$</td>
<td>2.21</td>
<td>$\pm 0.11$</td>
<td>0.244</td>
<td>$\pm 0.018$</td>
</tr>
<tr>
<td>40</td>
<td>0.180</td>
<td>$\pm 0.015$</td>
<td>2.21</td>
<td>$\pm 0.11$</td>
<td>0.162</td>
<td>$\pm 0.017$</td>
</tr>
<tr>
<td>60</td>
<td>0.131</td>
<td>$\pm 0.014$</td>
<td>2.79</td>
<td>$\pm 0.31$</td>
<td>0.147</td>
<td>$\pm 0.029$</td>
</tr>
<tr>
<td>80</td>
<td>0.157</td>
<td>$\pm 0.024$</td>
<td>2.29</td>
<td>$\pm 0.22$</td>
<td>0.084</td>
<td>$\pm 0.031$</td>
</tr>
</tbody>
</table>

Table 3.2 (d) Imbibition: PCE-water, VG-PL model fitting results.

<table>
<thead>
<tr>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>$n$</th>
<th>$a_r$</th>
<th>$b_r$</th>
<th>$p_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-Water</td>
<td>0.0186</td>
<td>8.0742</td>
<td>-0.5514</td>
<td>-448.6</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0003$</td>
<td>$\pm 0.5590$</td>
<td>$\pm 0.2032$</td>
<td>$\pm 0.0061$</td>
</tr>
<tr>
<td>PCE-Water</td>
<td>0.0552</td>
<td>4.0570</td>
<td>-1.2740</td>
<td>-413.0</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0017$</td>
<td>$\pm 0.3245$</td>
<td>$\pm 0.2971$</td>
<td>$\pm 0.0088$</td>
</tr>
</tbody>
</table>

Table 3.2 (e) Drainage: air-water and PCE-water, VG-GS model fitting results (for all the temperatures: 20, 40, 60, and 80 $^\circ$C).

<table>
<thead>
<tr>
<th>$\alpha$ (1/cm H$_2$O)</th>
<th>$n$</th>
<th>$c_r$</th>
<th>$d_r$</th>
<th>$p_0$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air-Water</td>
<td>0.0318</td>
<td>4.05</td>
<td>0.128</td>
<td>-0.000071</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0019$</td>
<td>$\pm 0.43$</td>
<td>$\pm 0.328$</td>
<td>$\pm 0.001024$</td>
</tr>
<tr>
<td>PCE-Water</td>
<td>0.1587</td>
<td>2.35</td>
<td>1.279</td>
<td>-0.003449</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.0186$</td>
<td>$\pm 0.15$</td>
<td>$\pm 0.261$</td>
<td>$\pm 0.000816$</td>
</tr>
</tbody>
</table>

Table 3.2 (f) Imbibition: air-water and PCE-water, VG-PL-GS model fitting results (for all the temperatures: 20, 40, 60, and 80 $^\circ$C).
Table 3.2 (g) Air-water system, residual water saturations ($S_{wr}$'s) and residual air saturations ($S_{ar}$'s).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$S_{wr}$ (VG) ±95% C.L.</th>
<th>$S_{wr}$ (VG-GS)</th>
<th>$S_{ar}$ (Measured)</th>
<th>$S_{ar}$ (VG-PL) ±95% C.L.</th>
<th>$S_{ar}$ (VG-PL-GS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.132 ±0.030</td>
<td>0.098</td>
<td>0.110</td>
<td>0.133 ±0.024</td>
<td>0.107</td>
</tr>
<tr>
<td>40</td>
<td>0.126 ±0.035</td>
<td>0.142</td>
<td>0.076</td>
<td>0.060 ±0.040</td>
<td>0.106</td>
</tr>
<tr>
<td>60</td>
<td>0.117 ±0.044</td>
<td>0.187</td>
<td>0.058</td>
<td>0.087 ±0.043</td>
<td>0.104</td>
</tr>
<tr>
<td>80</td>
<td>0.244 ±0.023</td>
<td>0.231</td>
<td>0.046</td>
<td>0.101 ±0.049</td>
<td>0.103</td>
</tr>
</tbody>
</table>

Table 3.2 (h) PCE-water system, residual water saturations ($S_{wr}$'s) and residual air saturations ($S_{ar}$'s).

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>$S_{wr}$ (VG) ±95% C.L.</th>
<th>$S_{wr}$ (VG-GS)</th>
<th>$S_{or}$ (Measured)</th>
<th>$S_{or}$ (VG-PL) ±95% C.L.</th>
<th>$S_{or}$ (VG-PL-GS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.076 ±0.035</td>
<td>0.008</td>
<td>0.226</td>
<td>0.244 ±0.018</td>
<td>0.268</td>
</tr>
<tr>
<td>40</td>
<td>0.086 ±0.069</td>
<td>0.096</td>
<td>0.151</td>
<td>0.162 ±0.017</td>
<td>0.199</td>
</tr>
<tr>
<td>60</td>
<td>0.152 ±0.064</td>
<td>0.183</td>
<td>0.115</td>
<td>0.147 ±0.029</td>
<td>0.130</td>
</tr>
<tr>
<td>80</td>
<td>0.193 ±0.051</td>
<td>0.271</td>
<td>0.060</td>
<td>0.084 ±0.031</td>
<td>0.061</td>
</tr>
</tbody>
</table>
Chapter 3. Effect of Temperature on $P_c - S_w$ Relations

Figure 3.20 The ratios of wetting coefficients of air-water (AW) and PCE-water (OW) drainage data at different water saturations vs. Temperature ($T_0 = 20$ °C).

Figure 3.21 The ratios of wetting coefficients of air-water (AW) and PCE-water (OW) drainage data at different temperatures vs. water saturation.
Chapter 3. Effect of Temperature on $P_c-S_w$ Relations

The residual water saturations, residual air saturations, and residual PCE saturations are summarized in Table 3.2 (g) and (h). The $S_{wr}$ values in the second column and the $S_{ar}$ values in the fifth column of Table 3.2 (g) and the $S_{wr}$ values in the second column and the $S_{or}$ values in the fifth column of Table 3.2 (h) were taken from Table 3.2 (a) - (d). The $S_{wr}$ values in the third column of Table 3.2 (g) and (h) were calculated using $a_r+b_rT$ (Equation 3.37) with the $a_r$ and $b_r$ values in Table 3.2 (e). The $S_{ar}$ values in the last column of Table 3.2 (g) and the $S_{or}$ values in the last column of Table 3.2 (h) were calculated using $c_r+d_rT$ (Equation 3.38) with the $c_r$ and $d_r$ values in Table 3.2 (f). The $S_{ar}$ and $S_{or}$ values in Table 3.2 (g) and (h), respectively, were determined directly from the experimental data.

The $S_{wr}$ values of air-water drainage curves from the VG model decreased from 0.132 to 0.117 and then jumped to 0.244 while the $S_{wr}$ values from the VG-GS model increased from 0.098 to 0.231 over the temperature range of 20-80 °C. In fitting the VG-GS model with $S_{wr} = a_r + b_rT$, a statistically significant, positive value of $b_r$ was obtained, indicating that $S_{wr}$ increases with temperature in the air-water system. However, the data suggest that the influence of temperature on $S_{wr}$ is not linear, nor monotonic and that a more complex functional relationship is appropriate. For the PCE-water drainage curves, the $S_{wr}$ values for both VG and VG-GS models increased. The $S_{wr}$ values for the VG model increased from 0.076 to 0.193 while the $S_{wr}$ values for the VG-GS model increased from 0.008 to 0.271. The VG-GS model predicted a wider range of change of $S_{wr}$ than the VG model and may not be true since it assumed that the $S_{wr}$ varied linearly with temperature.

The measured residual air saturations decreased from 0.110 to 0.046 over the temperature range of 20-80 °C. The VG-PL-GS model predicted the same trend as the measured $S_{ar}$ values. However, the temperature dependence of $S_{ar}$ was not significant since $d_r$ (-0.000071 ± 0.001024, Table 3.2 (f)) was not significantly different than zero. The VG-PL model predicted a decrease of the residual air saturation from 0.133 to 0.060 when temperature increased from 20 °C to 40 °C and an increase of the residual air saturation from 0.060 to
Chapter 3. Effect of Temperature on $P_c$-$S_w$ Relations

0.101 when temperature increased from 40 °C to 80 °C. The VG-PL model did not fit the experimental data very well however, especially at the higher temperatures.

The residual PCE saturation from the experimental results, the VG-PL model calculations, and VG-PL-VG model calculations decreased over the temperature range of 20-80 °C. The values of the residual PCE saturations obtained from the VG-PL and VG-PL-GS models at each temperature were quite close to the measured values of residual PCE saturations.

The analysis of the effects of temperature on capillary pressure-water saturation curves have the following implications with respect to steam flushing: a) The undesirable downward mobilization of a DNAPL can happen due to the decrease in capillary pressure with increasing temperature since the DNAPL will flow downward and enter the smaller pores, which can not be entered at lower temperatures, if the capillary pressure is decreased below the entrance pressure of the DNAPL into the smaller pores. The magnitude of the decrease of PCE entry pressure into F75 silica sand, which could be as high as 50 % over the temperature range of 20 to 80 °C (see Figure 3.7), may be comparable with the magnitude of changes of entry pressure in a surfactant flooding. b) More hydraulic removal of organic contaminants from the subsurface by hot water during steam flushing is possible, in addition to the organic contaminants removed by cold water ahead of the steam front, due to the decrease in residual organic phase saturations with increasing temperature. That is, a portion of the immobile organic contaminant phase would be mobile at higher temperatures and could be displaced by hot water or steam. c) The $P_c$-$S_w$ model accounting for the change of capillary pressures with temperature could be incorporated into a steam flushing numerical model. The predictions made by such steam flushing simulator may be more realistic than those steam flushing simulators not accounting for the effect of temperature on capillary pressures-water saturation curves since the magnitude of the decrease of capillary pressures with increasing temperature could be as high as 50 % over the temperature range of 20 to 80 °C.
3.7 Conclusions

A $P_c$-$S_w$ model accounting for the decrease of capillary pressure with increasing temperature, based on an extensive literature review, was presented and fitted very well to the experimental data. A glass pressure cell, column sand packer, and temperature control chamber were designed and constructed. Very good repeatability was obtained for the capillary pressure curves by using the glass pressure cell.

From the experimental measurements of air-water and PCE-water drainage and imbibition curves of F75 silica sand at temperatures of 20, 40, 60, 80 °C and parameter estimation trials, the following conclusions on the effect of temperature on capillary pressure curves ($P_c$-$S_w$ relations) can be drawn:

1. Temperature had a considerable effect on air-water and PCE-water capillary pressure-water saturation drainage and imbibition curves.

2. The capillary pressure and hysteresis of air-water-silica and PCE-water-silica systems decreased when temperature increased from 20 °C to 80 °C.

3. The residual water saturations in the PCE-water-silica system increased when temperature increased from 20 °C to 80 °C. Residual water saturations in the air-water-silica system decreased slightly over the temperature range of 20 - 60 °C and then increased significantly from 60 °C to 80 °C.

4. The residual PCE saturations in the PCE-water-silica system decreased when temperature increased from 20 °C to 80 °C. The measured residual air saturations in the air-water-silica system decreased when temperature increased from 20 °C to 80 °C. The fitted residual air saturations for the air-water-silica system decreased when temperature increased from 20 °C to 40 °C and increased when temperature increased from 40 °C to 80 °C.

5. The magnitude of the effect of temperature on $P_c$-$S_w$ curves can not be fully explained by thermal variation of air-water and organic-water interfacial tensions.
and contact angles. Other possible factors are increases of impurity (surfactant) concentrations, changes of entrapped air volumes, increased flow of water from isolated packets to the continuous water phase, and changes of sand compaction.

The above findings from the analysis of the effects of temperature on capillary pressure-water saturation curves have the following implications with respect to steam flushing:

1. When temperature is increased, the undesirable downward mobilization of a DNAPL can happen if the capillary pressure is decreased below the entrance pressure of the DNAPL into the smaller pores which can not be entered at lower temperatures.

2. In addition to the removal of organic contaminants by cold water ahead of the steam front, more hydraulic removal of organic contaminants from the subsurface by hot water during steam flushing is possible due to the decrease in residual organic phase saturations with increasing temperature.

3. The $P_c$-$S_w$ model accounting for the change of capillary pressures with temperature could be incorporated into a steam flushing numerical model. The predictions made by such steam flushing simulator may be more realistic than those steam flushing simulators not accounting for the effect of temperature on capillary pressures-water saturation curves.
CHAPTER 4 LABORATORY SETUP FOR STEAM FLUSHING

4.1 Introduction

The purpose of the steam flushing experiments is to investigate NAPL removal efficiency, steam gravity override, remobilization of NAPLs, as well as the effects of well orientations, soil layering, soil saturation conditions, and NAPL compositions on NAPL removal. The experiments also provide data for numerical model testing. The steam flushing system consisted of five components (see Figure 4.1):

1. A sand chamber equipped with pressure sensors, temperature sensors, water saturation sensors, sampling ports, and wells for injection and extraction
2. A chemical spill system consisting of syringe pump and chemical spill distributor
3. A steam generating system in which the steam temperature was regulated and steam pressure was monitored and controlled
4. A water and NAPL collecting, condensing, and separating system
5. A process control and data collection system including a data acquisition system, a cable tester, gas chromatography, and two personal computers

The majority of the equipment was designed and constructed in the groundwater laboratory of the Department of Civil Engineering of the University of Toronto during this thesis work. The rest of this chapter explains the construction and testing of these devices.

4.2 Parallel Plate Sand Chamber

The parallel plate sand chamber represents a vertical-cross section of subsurface and holds a volume of sand 110.5 cm wide, 57.5 cm high, and 10 cm thick. The two-dimensional (2D) model consists of one 1/2” thick tempered glass plate at the front and one 1/4” stainless steel (SS) plate at the back supported by an aluminum frame (Figure 4.2). Two vertical iron bars
were placed at the front side of the model to support the glass and withstand the force generated during the steam flushing process. The Viton™ gaskets were placed between the glass and aluminum frame, between the SS plate and aluminum frame, and between two SS lids and the top aluminum frame forming the two windows which measured 44.7 cm long and 5.2 cm wide. A drainage port was placed at the bottom near the right side. One inch thick fiberglass insulating material was wrapped around the parallel plate sand chamber to reduce heat loss from it.

Figure 4.1 Setup for steam flushing experiments.
Chapter 4. Laboratory Setup for Steam Flushing

Figure 4.2 Two-dimensional vertical-cross section sand chamber.
4.3 Temperature Measurement

A total of 24 T-type thermocouples (Thermo-Electric) were installed on the back at various locations (Figure 4.2, 4.3). The tips of the shielded thermocouples were placed in the center of the sand chamber (5 cm from the inside face of the SS plate). A thermistor inside the data acquisition system provided a reference temperature measurement for all the experiments. The error of temperature measurements is less than ±0.5 °C.

![Figure 4.3 Temperature sensors.](image)

4.4 Pressure Measurement

A total of 12 pressure transducers (Micro Gauge Inc., model: P102, pressure range: 0 - 15 psig, accuracy: 0.25% full scale = 2.6 cm H₂O) were connected to various locations on the
back of the model. In order for the pressure transducers to maintain water contact with the sand inside the model, a pressure tensiometer similar to Van Geel’s (1994) was designed and made (Figure 4.4). It consisted of a 3/8” brass Swagelok™ fitting with a 1-bar bubble pressure ceramic cup (from Soil Moisture Corporation) glued into the hole drilled at the end of the Swagelok™ fitting. The glue of choice was epoxy (LePage) since it is compatible with the chemicals used. The pressure transducers were re-calibrated after each experiment since they drifted away from zero by as much as 5 cm of water, which is about 0.5% of their range.

![Figure 4.4 Pressure tensiometer.](image)

Serious errors in pressure measurement or damage to the pressure transducers could be caused by the hot SS plate surface during the steam flushing process if the pressure transducers were too close. Therefore, three metal strips were mounted on the back of the model 25 cm from the stainless steel plate to hang the 12 pressure transducers outside of the insulating fiberglass. The 1/8” Teflon™ tubing connecting the pressure transducers to the ceramic tensiometers were filled with room temperature deaerated and distilled water.
4.5 Water Saturation Measurement

Time domain reflectometry (TDR) was used in the experiments to measure the volumetric water saturation as an inexpensive, non-destructive, fast, and accurate method compared with gamma ray sensor, x-ray sensor, and neutron sensor methods. TDR is based on the theory that the propagation velocity of a high frequency electromagnetic wave through three parallel SS rods in a wet soil is highly dependent on the soil’s dielectric constant which in turn is highly sensitive to the water saturation of the soil (Topp et al. 1980; Topp et al. 1982; Topp and Davis, 1985; Topp et al. 1988; Zegelin et al. 1989) (see Figure 4.5). A cable tester (Tektronix 1502C, Metallic TDR Cable Tester), which has been used in the telecommunication industry for locating faulty coaxial cables, was used by Topp et al. (1980) to determine the propagation velocity. The cable tester displays a wave form which shows the dielectric response corresponding to an electromagnetic pulse traveling inside the soil. Once the travel time of the electromagnetic pulse along the rods in the soil has been read directly from the wave form, the propagation velocity, \( v \), can be easily calculated since the length of the three parallel SS rods is known. Then the apparent dielectric constant, \( K_a \), can be calculated from the formula

\[
v = \frac{c}{(K_a)^{0.5}}
\]

where \( c \) (300,000 km/s) is the electromagnetic wave propagation velocity in free space.

Topp et al. (1980) also found that the dielectric constant was highly sensitive to water saturation and weakly sensitive to soil type, texture, and density. The salt concentration only affected the attenuation of the dielectric constant. A “universal” empirical formula, which is not dependent on soil type, was obtained by fitting their data to a third degree polynomial. The formula is slightly modified to express the volumetric water saturation instead of volumetric water content as followed

\[
S_w = (-5.3 \times 10^{-2} + 2.92 \times 10^{-2} K_a - 5 \times 10^{-4} K_a^2 + 4.3 \times 10^{-6} K_a^3) / \phi
\]

where \( \phi \) is the soil porosity.
Zegelin et al. (1989) showed that a three-wire sensor can adequately represent a coaxial cell (Topp, 1980) and has much better accuracy than a two-wire sensor (Herkerlath et al., 1991; Brisco et al., 1992). The three 304 SS rods used in this study are 10.7 cm length and 1/16" diameter. The central rod was screwed directly to the central conductor of the coaxial connector. The two side rods were screwed into the threaded central holes of two screws mounted on each side of the coaxial conductor on the SS plate which is in direct contact with the outer conductor of the coaxial connector. Viton™ "O" rings were used on the screws and coaxial connectors to prevent the leaking of water and chemicals from the model.

The cable tester, used to measure the 12 volumetric water saturations, was connected through a 50-pin ribbon cable to a 486 personal computer to read, store, and analyze the wave forms. The variation of the water saturation measurements was less than 2%.
Chapter 4. Laboratory Setup for Steam Flushing

Tests were done by Milko (1995) to study the effect of temperature on the water saturation reading for the air-water and water-transformer oil (ESSO Petroleum Canada, Voltesso 35) fluid pairs in F75 Ottawa silica sand over the temperature range of 20 - 80 °C. Negligible temperature effect was found. Experiment results also showed that this method can not be used to accurately measure the oil saturation in an air-oil system since the air and oil have similar dielectric constants (e.g. air: 1; nonane: 1.972; water: 78.54 (Lide and Frederikse, 1995); soils: 2 to 5 (Pepin et al. 1995)).

After the measurement of the variation of the dielectric constant (K_w) with temperature for a range of soil types (sand, loam, and peat) with the water content (i.e. $S_w$) ranging from 0 to 0.8 and soil temperature ranging from 5 to 50 °C, Pepin et al. (1995) reported that the absolute error of water saturations was $0.00175\phi S_w$ 1/°C. The relative error of water saturations was 2.6% for a soil with an average water content of 0.15 and a temperature change of 15 °C. The same error was found for a peat with an average water content of 0.8 and a temperature change of 15 °C. The absolute error of water saturations for the F75 silica sand used in this thesis research would be from 1.4% when $S_w = 10\%$ to 14% when $S_w = 100\%$ with a temperature change of 80 °C (from 20 to 100 °C) if we assume that the absolute error of water saturations of $0.00175\phi S_w$ 1/°C could be used.

### 4.6 Concentration Measurement

A total of 24 sampling ports were made with 1/8" brass Swagelok™ male connectors screwed into the SS plate (Figure 4.2). Two septum discs were placed in the hollow of each Swagelok™ connector and were held in place by screwing on the nut (Figure 4.6). The septum discs can hold more than 20 psig pressure prevent the leaking of steam and other fluids. A side port needle was used with a 0.5 ml Hamilton gas-tight™ glass syringe to take samples from each port by piercing the needle through the septum discs.
Chapter 4. Laboratory Setup for Steam Flushing

Figure 4.6 Sampling port.

A Hewlett Packard 5890 Series II Gas Chromatography (GC) equipped with a flame ionization detector (FID) and a 7673 auto-sampler was used to analyze all the samples. The column used was a 6-foot 3% ov-1 packed column and the carrier gas was helium with a flow rate of 60 ml/min. Hydrogen with a flow rate of 30 ml/min. and air with a flow rate of 300 ml/min. were used for FID. The 486 personal computer connected to the GC collected, analyzed, and stored the results. The retention time was less than 6 minutes with a multi-level temperature program (210 °C for the injector, 220 °C for the detector, and 90 °C during the first 1 minute and 120 °C during the final 4.5 minutes for the oven) of the GC since the vapor pressures of both perchloroethylene (PCE) and n-nonane (nonane) are low. PCE and nonane had retention times of 3 and 4.5 minutes, respectively.

A GC standard for PCE was prepared by injecting a mass of 5.01 mg of PCE into 100 ml of water sealed in a 100 ml volumetric flask to produce a solution with a PCE concentration of 50 mg/L. The flask was shaken by hand for sufficient time (30 minutes) to mix the chemicals with water. After complete dissolution of the PCE, a volume of 0.5 ml of aqueous solution was withdrawn with a syringe and injected into a 2-ml vial containing 0.5 ml
dichloromethane (DCM) (BDH Laboratory Reagents, 99.5% pure) which was used as a liquid solvent to extract the PCE. The vial was shaken sufficiently (3 minutes) and put into the auto-sampler tray for analysis. The 10 µl syringe on the auto-sampler took 1 µl of DCM solution from the bottom of the 2-ml vial (DCM is heavier than water) and injected it into the GC. The concentration was automatically calculated based on the area under the and identified by the retention time. A 4-point (50.0, 250.9, 752.8, and 1505.7 mg/L) GC calibration was used. The replicates of four points showed excellent repeatability and the GC standard was checked with a single point (50 mg/L) after each experiment. Relative variation of the concentrations was less than 4%. A 0.5 ml water sample was withdrawn from each sampling port and was analyzed the same way as the standard was analyzed. A concentration of 0 mg/L was assumed when the PCE concentration was below 0.0001 mg/L which is the detection limit of the method used.

For the nonane or the mixture of PCE and nonane, the GC standard was prepared in a different way since the aqueous solubility of nonane was quite low (0.122 mg/L). Two DCM solutions with different concentrations of PCE and nonane were prepared by injecting known volume ratios of PCE and nonane into two 45 ml vials containing 41.8 ml of DCM. The first volume ratio of PCE to nonane was 2.5 µL : 1.0 µL, which gave a DCM solution with a PCE concentration of 97.24 mg/L-DCM and a nonane concentration of 17.17 mg/L-DCM. The second volume ratio of PCE to nonane was 5.5 µL : 3.5 µL, which gave a DCM solution with a PCE concentration of 213.93 mg/L-DCM and a nonane concentration of 60.08 mg/L-DCM. After the two 45-ml vials were shaken for 30 minutes, a volume of 0.5 ml sample was taken from each of these two DCM solutions by syringe and injected into a 2-ml vial. A volume of 0.5 ml of distilled water was added to each of the 2-ml vials. After each of the two 2-ml vials was shaken for another 30 minutes, the two 2-ml vials were put into the auto-sampler on the GC for analysis with the same setup and procedure described before. Variation of the concentrations in repeated tests was less than 4%.
4.7 Organic Chemicals Utilized

The chemicals used were perchloroethylene (PCE) and n-nonane (nonane) (Caledon Laboratory Ltd., PCE: 99.0%, nonane: 99.0%) which are semi-volatile organic chemicals (Table 4.1). PCE is called a DNAPL (dense non-aqueous phase liquid) since it is heavier than water and nonane is called a LNAPL (light non-aqueous phase liquid) since it is lighter than water. Magdala Red (Allied Chemical Corporation) was chosen to dye PCE red since it was soluble in PCE and insoluble in water.

<table>
<thead>
<tr>
<th>Perchloroethylene (PCE)</th>
<th>n-nonane (nonane)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>CCL₂=CCL₂</td>
</tr>
<tr>
<td>Molecular mass (g/mol)</td>
<td>peak 165.83</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>121</td>
</tr>
<tr>
<td>Solubility @ 25 °C (g/m³)</td>
<td>150-1503</td>
</tr>
<tr>
<td>Solubility (g/m³)</td>
<td>299 (@ 100 °C)</td>
</tr>
<tr>
<td>Vapor pressure (Pa)</td>
<td>1866^a</td>
</tr>
<tr>
<td>Viscosity (cP, @ 25 °C)</td>
<td>0.844</td>
</tr>
<tr>
<td>Specific density^a</td>
<td>1.626</td>
</tr>
</tbody>
</table>

Note: ^a Mackay et al. (1993); ^b Lide (1995); ^c Lide and Frederikse (1995); ^d Montgomery (1991); ^e Ma and Sleep (1994); Temperature =20 °C except noted.

Table 4.1 Chemical properties.

4.8 Chemical Spill Distributor

In order to run the steam flushing experiments, organic chemicals have to be spilled into the parallel plate sand chamber to create a plume of LNAPL or DNAPL which is uniform across
the thickness as the initial condition. It is very important to ensure the uniformity of the plume along the thickness so that the experiment is two-dimensional rather than three-dimensional.

A spill distributor was assembled with brass Swagelok™ fittings and 3/8” stainless steel (SS) porous tubing (Cole Parmer Instrument Company) (Figure 4.7). The porous SS tubing which has a pore size of 5 micron was sealed at the end. When PCE or nonane was injected into the tubing breakthrough along the tubing occurred at a pressure of 2 psig. Once the chemical broke through the porous tubing, it spread out laterally about 2 cm from the center of the tubing to each side. Therefore, the three porous tubes were able to cover 12 cm, which was enough to cover the whole thickness of the model.

![Diagram of chemical spill distributor](image)

Figure 4.7 Chemical spill distributor.

The chemical spill distributor is 17 cm long and was placed in the sand chamber 5 cm from the top of the sand starting 30.5 cm from the right end of the sand chamber (Figure 4.8). Figure 4.8 (a) is for Experiment #1,2, and 3. Figure 4.8 (b) is for Experiment #4.
Chapter 4. Laboratory Setup for Steam Flushing

4.9 Wells

All wells were constructed with 3/8” stainless steel (SS) 304 tubing (Figure 4.9). Many holes with a diameter of 1/16” were drilled along the tubing and covered with a SS screen of sieve size of 200. The use of screens prevented the sand from entering the well during sand packing and NAPL recovery. The wells placed horizontally or vertically were connected to the steam generator and condenser for steam injection and NAPL recovery, respectively (Figure 4.8). The vertical wells were 30 cm long and were divided into two segments of 15 cm by a central plug in the wells. They were located 7 cm from the side of the sand chamber and were centered vertically. The horizontal wells were 65 cm long and were located 1 cm from the top of the sand chamber and 18 cm from the bottom of the sand chamber.
Chapter 4. Laboratory Setup for Steam Flushing

Two types of Ottawa silica sand (US Silica), F75 and F110, were used for all the experiments. The sieve analysis for the two sands are listed in Table 4.2. The physical properties are listed in Table 4.3.

4.11 Sand Packing and Packer

It is very important to pack the sand into the two-dimensional model tightly and uniformly to ensure a homogenous porous medium. Since the front of the two-dimensional model was made of glass and was fragile, and TDR sensors, thermocouples, and ceramic pressure sensors were placed in the chamber before sand was added, portable vibrators and floor top shakers could not used. The Kolbuszewski and Jones (1961) method (as discussed in Chapter 3) was used to pack the sand.
Table 4.2 Typical sieve analysis of the sands.

<table>
<thead>
<tr>
<th>Mesh Size</th>
<th>F75 Silica sand % Retained</th>
<th>F110 Silica sand % Retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 mesh</td>
<td>0.3%</td>
<td>50 mesh</td>
</tr>
<tr>
<td>50 mesh</td>
<td>6.0%</td>
<td>70 mesh</td>
</tr>
<tr>
<td>70 mesh</td>
<td>25.4%</td>
<td>100 mesh</td>
</tr>
<tr>
<td>100 mesh</td>
<td>39.9%</td>
<td>140 mesh</td>
</tr>
<tr>
<td>140 mesh</td>
<td>22.0%</td>
<td>200 mesh</td>
</tr>
<tr>
<td>200 mesh</td>
<td>5.6%</td>
<td>&gt;270 mesh</td>
</tr>
<tr>
<td>&gt;200 mesh</td>
<td>0.8%</td>
<td>&gt;270 mesh</td>
</tr>
</tbody>
</table>

Note: Data were from US Silica Corporation.

Table 4.3 Physical properties of the sands.

<table>
<thead>
<tr>
<th>Property</th>
<th>F75 Silica sand</th>
<th>F110 Silica sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>36.7%</td>
<td>34%</td>
</tr>
<tr>
<td>Permeability (m²/s)</td>
<td>1.07 X 10⁻¹²</td>
<td>5.32 X 10⁻¹³</td>
</tr>
<tr>
<td>Bulk density (kg/m³)</td>
<td>1670</td>
<td>1700</td>
</tr>
<tr>
<td>Heat capacity (kJ/kg·°C)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Thermal conductivity (W/m²·°C)</td>
<td>2.86</td>
<td>2.86</td>
</tr>
</tbody>
</table>

*Measured data; ° F7a et al., 1992. Other data were from US Silica Corporation.

A two-dimensional sand packer, 105 cm long by 60 cm high by 11 cm wide, was built (Figure 4.10). Five layers of evenly spaced 25-mesh screens, at intervals of 4 cm, were placed inside the two-dimensional sand packer. A pattern of 0.2 cm holes was drilled with the same intervals of 4 cm in both directions on a wooden board, which was placed 4 cm above the top screen in the two-dimensional sand packer to serve as a metering board controlling the flow rate of the sand.
Sand was added to the top of the metering board continuously and packed into the two-dimensional model in about 4 hours. The porosity of the silica sand in the two-dimensional model was assumed to be 36.7% for the F75 silica sand and 34% for the F110 silica sand (Table 4.3). The values of the sand porosity were found by measuring the volumes of water and sand after a known volume of sand was deposited into a beaker containing water. The permeabilities of the silica sands were measured with a constant head permeameter made from a 55 cm length of 1.5” pipe and a ±2 psid Sensotec™ pressure transducer (Table 4.3).
Chapter 4. Laboratory Setup for Steam Flushing

4.12 Steam Generator

In order to control the temperature and flow rate of steam precisely and have negligible heat loss, a conventional boiler is not adequate. Sanchez and Schechter (1990) developed an adiabatic steam generator. A 46 cm length of 1/8” SS tubing, which was bent as a “U” shape and wrapped with a 0.476 cm diameter electrical heating cord, was wrapped with fiberglass insulation and pressed into a Dewar flask. The thermocouple inserted at the outlet end measured the temperature of steam and fed it back to the computer for monitoring and controlling. They reported that the adiabatic conditions were maintained at the ambient operating temperature even at low flow rates and high exit temperature.

Encouraged by their results, a similar adiabatic steam generator was constructed. However, a number of problems were encountered even though the steam generator worked. The power supplied by the electrical heating cord was insufficient and the fiberglass insulation material burned. The Dewar flask was not large enough to hold a longer and larger diameter SS tube. Consequently, a second adiabatic steam generator was constructed (Figure 4.11). 316 SS tubing of 1/4” diameter and 610 cm length was bent into a coil shape and wrapped tightly with 5 high power electrical heating tapes (Cole Parmer Instrument Company). Each electrical heating tape was 366 cm long and could generate 628 watts of heat. Five electrical heating tapes generating a total of 3140 watts required that 3 separate electric outlets and a relay box be built (Figure 4.12). The coil was placed into a barrel and insulated with ceramic cloth which could withstand temperatures up to 1000 °C. A thermocouple was inserted into the ceramic cloth to monitor the temperature. Another thermocouple was inserted into the outlet of the coil to measure the steam temperature which was fed back to the data acquisition system (DAS) for monitoring and controlling. Two pressure gauges (30 psig) were installed to monitor the water and steam pressure. Two in-line spring-type pressure-cracking valves (Cole Parmer Instrument Company, Nupro C Series, 3-50 psig cracking pressure) were used as safety valves to release the steam pressure when it went up to a preset value (20 psig for all the experiments).
Figure 4.11 Steam generator system.

The inlet of the steam generator was connected to a gear type pump (Cole Parmer Instrument Company gear pump (Model # 7144-00) with Micropump head (Model # 120-000)) which delivered small flow rates of deaerated and distilled water from a 55-liter container to the steam generator. The SS tubing between the outlet of the steam generator and the sand chamber was wrapped with several layers of insulating tape to reduce heat loss. The power input to the steam generator could be calculated from the computer displayed power level and the capacity of the electrical heating tapes.
Chapter 4. Laboratory Setup for Steam Flushing

To heating tapes of steam generator

<table>
<thead>
<tr>
<th>Channel</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>To 12 V</td>
<td>+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DC</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td></td>
<td>SSR</td>
<td>SSR</td>
<td>SSR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td>To DAS &amp; PC</td>
<td></td>
<td>SSR</td>
<td>SSR</td>
<td>SSR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>SSR</td>
<td>SSR</td>
<td>SSR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Switch 1 2 3 4 5 6 A B C

a) Whole box of 6-SSR connection diagram.

12 V DC

+

Diode

Transistor

Resistor 1

Pulse

Resistor 2

DAS & PC

Ground

115 V AC

SSR Switch 1 Switch A

Resistor 3

b) One SSR connection diagram.

Figure 4.12 Solid state relay (SSR) box.

The proportion-integration-derivation scheme (PID) in the WinGen™ software (Sciemetric Instrument Inc.) was used to regulate the steam temperature. The temperature from a thermocouple installed at the outlet of the steam generator was fed back to the computer.
which controlled the power level of the heating tapes by turning them on or off through the relay box. The control parameters had to be conditioned for the particular steam generator before the steam generator could actually be used.

4.13 Condenser

In order to handle the steam safely and capture all the organic contaminants, a steam condenser was needed. A condenser was constructed with SS tubing of 610 cm length and 1/4" diameter which was rolled into a coil and installed in a Plexiglass™ container of 40 cm long, 35 cm wide, and 40 cm high (Figure 4.13). Room temperature tap water was circulated through the Plexiglass™ container. The SS tubing was covered by cool tap water all the time with the warm water drained constantly from the top of the container.

![Figure 4.13 Steam condenser.](image-url)
Chapter 4. Laboratory Setup for Steam Flushing

4.14 Chemical and Water Separator

The NAPL and water phases removed from the extraction well had to be separated continuously in order to measure the cumulative amount of organic contaminants recovered during steam flushing. One of the difficulties associated with the separation of chemical and water was how to measure the amount of chemicals accurately since the volume of water was much larger than the volume of chemicals. Another difficulty was that DNAPLs are heavier than water and LNAPLs are lighter than water.

Figure 4.14 Chemical and water separator.
Chapter 4. Laboratory Setup for Steam Flushing

A chemical and water separator was constructed with the combination of a 2-liter glass funnel, a 45 cm length of 1” diameter glass pipe, and 2-liter and 20-liter glass bottles (Figure 4.14). The glass funnel, pipe, and 20-liter bottle were marked with volume accuracy of 0.5-2, 0.5, and 5 ml, respectively. All the openings were covered with plastic film with a small hole in the center to minimize the loss of organic chemicals. The DNAPL was drained from the bottom of the funnel from time to time. The LNAPL was drained from the pipe by syringe from time to time. The volume of water was read from the mark on the bottle directly. The outlet was switched to another empty 20-liter bottle once the 20-liter bottle was full.

4.15 Data Acquisition System

A Data acquisition system (DAS) (Sciemetric Instrument Inc.) was used to collect temperature, pressure data and control the steam temperature. The DAS consists of one analog to digital converter board (Model 231), one 16 channel analog expansion transducer interface card (Model 251 B), one 16 channel analog expansion thermocouple interface card (Model 251), and one 8 channel TTL compatible timer and counter card (Model 240). The DAS was connected to a interface card (Model 802) installed in a 486 DX II - 66 IBM compatible personal computer by a 50-pin ribbon cable to communicate with the computer. Window™ based software WinGen™ was used to set up the system, monitor and store the temperature and pressure data, and control the steam temperature.

4.16 Measurement of \( P_c - S_w \) Curves for F110 Silica Sand

The air-water drainage and imbibition \( P_c - S_w \) curves for F110 silica sand were measured with the same devices and procedures described in Chapter 3. The experimental data are presented in Figure 4.15.

The PCE-water drainage curves for the F110 silica sand at the temperatures of 20, 40, 60, and 80 °C were calculated by using the VG-GS model described in Chapter 3 (Figure 4.16).
Chapter 4. Laboratory Setup for Steam Flushing

Figure 4.15 The experimental air-water drainage and imbibition curves of F110 silica sand at 20 °C.

Figure 4.16 PCE-water drainage curves of the VG-GS model for F110 silica sand at 20, 40, 60, and 80 °C.
Additional information is presented in Appendix B. The $\beta_0$ of F110 silica sand is assumed to be the same as the value of F75 silica sand, which may be justified since the theoretical value of $\beta_0$ is only dependent on the IFT of the fluid pair. The PCE entry pressures of the water saturated F110 silica sand at the temperatures of 20, 40, 60, and 80 °C, which were estimated from the inflection points of the curves near 100% water saturation, were 45, 35, 30, and 22 cm H$_2$O, respectively. The PCE entry pressures decreased from 45 cm H$_2$O to 22 cm H$_2$O when temperature increased from 20 °C to 80 °C. From Figure 3.7 (Chapter 3), the PCE entry pressures of the water saturated F75 silica sand at the temperatures of 20, 40, 60, and 80 °C were estimated as 12, 10, 7, and 5 cm H$_2$O, respectively. The PCE entry pressures decreased from 12 cm H$_2$O to 5 cm H$_2$O when temperature increased from 20 °C to 80 °C.

4.17 Summary

Nearly a dozen devices and apparatuses, which are the parallel plate sand chamber, tensiometers, time domain reflectometry probes, sampling ports, chemical spill distributor, wells, two-dimensional sand packer, steam generator, condenser, and finally, chemical and water separator, were designed and constructed. They were tested and modified until satisfactory performances were obtained. Some of the problems encountered and solved for these devices and apparatuses were leakage, temperature and chemical incompatibility, and sand clogging.
Chapter 5. Steam Flushing Experimental Results and Discussion

CHAPTER 5 STEAM FLUSHING EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Introduction

The steam flushing experimental results, obtained from the two-dimensional sand chamber described in Chapter 4, are presented in this chapter. All the experiments were started by injecting a certain amount of PCE or nonane or a mixture of PCE and nonane with a syringe pump into the sand chamber and allowing the chemical(s) to flow laterally and downward. The maximum duration of injection for all the experiments was less than one hour. The water saturations were measured in time intervals from one hour to one day for a period of three days to one month. No measurable change was noticed after three days from the start of each spill. Subsequently, the steam injection was started at least three days after the time of the spill in each experiment.

Distilled and deaerated water was pumped from a 55-liter reservoir to the steam generator at a rate of 58 ml/min. Once the temperature of the steam generated reached a pre-set temperature (105 -125 °C), the steam was introduced into the sand chamber through a vertical or horizontal well. The concentrations and saturations were measured at time intervals from one to six hours while pressures and temperatures were recorded every 2 minutes. The hot water and steam collected from the extraction well were cooled down by a condenser to approximately room temperature. Then the cooled stream went through the chemical and water separator, which separated the LNAPL (nonane), DNAPL (PCE), and water. The volumes of LNAPL, DNAPL, and water were measured.

The steam injection was terminated when all water samples taken from the 24 sampling ports did not indicate any NAPL left in the sand chamber. Hot water was pumped into the sand chamber to lower the sand temperature and prevent any damage from formation of an
extreme vacuum due the condensation of steam in a very short time period. The collected water was analyzed for LNAPL and DNAPL concentrations from time to time.

For the four steam flushing experiments, the stratification of silica sand porous medium, well orientation and configuration, composition of pollutants, steam injection rates, steam temperatures at the injection points, and steam injection pressures at the injection points are summarized in Table 5.1.

<table>
<thead>
<tr>
<th>Description</th>
<th>Experiment # 1</th>
<th>Experiment # 2</th>
<th>Experiment # 3</th>
<th>Experiment # 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand chamber</td>
<td>Coarser sand (F75)</td>
<td>Coarser sand (F75)</td>
<td>Vadose zone (F75)</td>
<td>Vadose zone (F75)</td>
</tr>
<tr>
<td></td>
<td>Finer sand (F110)</td>
<td>Finer sand (F110)</td>
<td>Finer sand (F110)</td>
<td>Finer sand (F110)</td>
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<tr>
<td></td>
<td>Coarser sand (F75)</td>
<td>Coarser sand (F75)</td>
<td>Coarser sand (F75)</td>
<td>Coarser sand (F75)</td>
</tr>
<tr>
<td>Wells</td>
<td>Right vertical injection well</td>
<td>Right vertical injection well</td>
<td>Right vertical injection well</td>
<td>Bottom horizontal injection well</td>
</tr>
<tr>
<td></td>
<td>Left vertical extraction well</td>
<td>Left vertical extraction well</td>
<td>Left vertical extraction well</td>
<td>Top horizontal extraction well</td>
</tr>
<tr>
<td>Contaminant(s)</td>
<td>PCE</td>
<td>PCE &amp; nonane</td>
<td>nonane</td>
<td>nonane</td>
</tr>
<tr>
<td>Injection rates</td>
<td>58 ml H₂O/min. (100 %)</td>
<td>58 ml H₂O/min. (100 %)</td>
<td>58 ml H₂O/min. (100 %)</td>
<td>58 ml H₂O /min. (100 %)</td>
</tr>
<tr>
<td>(% steam quality)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam temperatures</td>
<td>110 °C</td>
<td>125 °C</td>
<td>110 °C</td>
<td>105 °C</td>
</tr>
<tr>
<td>Steam pressures</td>
<td>6 - 8 psig (4.22-5.63 mH₂O)</td>
<td>4.7 psig (2.82-4.93 mH₂O)</td>
<td>5 - 8 psig (3.52-5.63 mH₂O)</td>
<td>3 - 7 psig (2.11-4.93 mH₂O)</td>
</tr>
</tbody>
</table>

Table 5.1 Experimental conditions and variables of the four steam flushing experiments.

As discussed in Chapter 4, the errors of the temperature measurements with the thermocouples and the pressure measurements with the pressure transducers were ± 0.5 °C and ± 2.6 cm H₂O (± 0.25 % of 15 psig), respectively. The variation of repeated water saturation measurements with the time domain reflectometry probes was less than 2 %. The variation of repeated organic chemical concentration measurements on the gas chromatography was less than 4%.
5.2 Saturated Three layer System with Two Vertical Wells and DNAPL
(Experiment # 1)

In this experiment the main goals were to study the possibility of downward remobilization of DNAPL during the steam flushing process and to assess the severity of steam overriding water. PCE was injected into the upper coarser sand layer through a chemical spill distributor (Figure 4.7) over a duration of 25 minutes (Figure 4.8 a)). The injection rate was 3.2 ml/min. or $5.33 \times 10^{-8}$ m$^3$/s. The volume of PCE injected is shown in Table 5.2.

<table>
<thead>
<tr>
<th>Description</th>
<th>Experiment # 1</th>
<th>Experiment # 2</th>
<th>Experiment # 3</th>
<th>Experiment # 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam flushing duration</td>
<td>8 h. 50 min.</td>
<td>11 h. 34 min.</td>
<td>9 h. 20 min.</td>
<td>11 h. 10 min.</td>
</tr>
<tr>
<td>Steam breakthrough time</td>
<td>3 h. 30 min.</td>
<td>3 h. 40 min.</td>
<td>2 h. 42 min.</td>
<td>2 h. 28 min.</td>
</tr>
<tr>
<td>NAPL injected (PCE)</td>
<td>80 ml</td>
<td>160 ml</td>
<td>150 ml</td>
<td>150 ml</td>
</tr>
<tr>
<td>NAPL injected (PCE:nonane=1:1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NAPL recovered</td>
<td>67.3 ml</td>
<td>126.5 ml</td>
<td>132 ml</td>
<td>134 ml</td>
</tr>
<tr>
<td>% NAPL recovery</td>
<td>84 %</td>
<td>79 %</td>
<td>88 %</td>
<td>89.3 %</td>
</tr>
<tr>
<td>Water injected</td>
<td>30.7 L</td>
<td>40.3 L</td>
<td>23.0 L</td>
<td>37.0 L</td>
</tr>
<tr>
<td>Water recovered</td>
<td>45.5 L</td>
<td>41.2 L</td>
<td>34.8 L</td>
<td>22.4 L</td>
</tr>
<tr>
<td>NAPL in waste water</td>
<td>115 mg/L</td>
<td>65.6 mg/L (PCE)</td>
<td>0.4 mg/L (nonane)</td>
<td>0.0229 mg/L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0137 mg/L</td>
</tr>
</tbody>
</table>

Table 5.2 Summary of results of the four steam flushing experiments.

Seven days after start of the DNAPL spill, steam at a temperature of $110 \, ^\circ C$ was injected into the sand chamber with a constant injection rate of $1.16 \times 10^{-3}$ m$^3$/s over a duration of 8 hours
50 minutes. Steam was injected through the top half of the injection well while the fluids were recovered through the top half of the extraction well. PCE (dyed red) was observed at the outlet after 3 hours 20 minutes of steam injection. The DNAPL looked opaque and foamy. After 6 hours of steam injection, the top half of the extraction well was closed while the bottom half of it was opened to collect the DNAPL in the lower coarser sand layer.

A total volume of 67.3 ml of PCE was recovered at the end of Experiment #1 while there was no indication of any PCE left in the water samples taken from the 24-sampling ports on the back of the sand chamber (Table 5.2). A volume of 12.7 ml of PCE is not accounted for. This PCE may have moved down to the bottom near extraction well where no sampling port was available. Another possible explanation could be that the PCE was trapped in the tubing between the extraction well and the chemical/water separator (a small volume of PCE was found in the vertical tubing outside the sand chamber at a later time). The raw data are in Appendix C.

The PCE concentration at the start of steam injection showed the location of the separate DNAPL phase (concentrations more than 150 mg/L) and the dissolved aqueous phase DNAPL plume (concentration less than 150 mg/L) (Figure 5.1). The raw concentration data of Experiment #1 (Appendix C) were from sampling ports and TDR probes. A concentration of 200 mg/L was assigned to a TDR probe location if there was separate PCE phase there (same for Experiment #2). The value of "200 mg/L" was chosen since it was the average aqueous PCE solubility over the temperature range of 20 to 100 °C (see Figure 2.6). Other values could be chosen since there is large variation of reported PCE solubilities even at one temperature (e.g. 150-1503 mg/L at 25 °C, see Table 4.1). For the purpose of plotting water phase concentrations any GC measurements extraction of PCE concentrations that were above the 200 mg/L were reduced to the solubility limit of 200 mg/L. At 20 minutes after the steam injection started, the whole DNAPL plume spread toward the left (Figure 5.2). At 50 minutes, the plume had moved further to the left (Figure 5.3). However, at 98 minutes after steam injection started, a portion of PCE had moved downward past the middle finer sand
layer to the lower coarser sand layer (Figure 5.4). This is not desirable since it contaminated the lower coarser sand layer. The concentration contour map at 218 minutes after steam injection started, shows that significant liquid PCE and dissolved aqueous phase PCE was present in the lower coarser sand layer near the bottom half of the extraction well (Figure 5.5). Eventually, the PCE was almost completely removed at 390 minutes (Figure 5.6).

Since there was a relatively limited number of experimental data points and a relatively small NAPL plume due to the limitation of speed of the data acquisition system and computer, the contours near the boundaries and corners may not represent the true values. The plotting software (Spyglass™) interpolated and extrapolated the limited experimental data points to generate the data for a finer regular grid across the whole domain with the method of kriging. According to the plotting software (Spyglass™) manual, kriging is the most accurate method for the interpolation of data points from true data values (especially for a small number of data points) compared with other methods such as linear interpolation and weighted fill. A detailed analysis of kriging is given by Journel and Huijbregts (1978).

The initial PCE saturation profile can be observed from the initial water saturation contours (Figure 5.12) since there were only two phases (NAPL and water) present before the steam injection started. The highest initial PCE saturations were 40% (i.e. 100% minus 60% of water saturation) and were located right above the finer sand layer. PCE did not enter the finer sand layer since the entry pressure for the finer sand layer pore (F110 silica sand) was 45 cm H₂O at 20 °C (Figure 4.16, see Appendix B for more detail). Liquid PCE could not enter the water saturated finer sand layer at higher temperatures since the entry pressure was only reduced to 22 cm H₂O at 80 °C. However, once the finer sand layer became desaturated PCE could displace the gas phase and enter the finer sand layer. The water saturation contours after 20 minutes of steam injection (Figure 5.13) did not change much compared to the initial condition (Figure 5.12). The PCE saturation contours did not change much either. At 50 minutes, a steam chamber had formed near the upper right hand corner (Figure 5.14). A PCE bank was formed ahead of the steam chamber with the saturation range of 10% to 70%
(water saturation ranged from 30% to 90%). These contours must be interpreted with help of concentration contours and temperature contours (Figure 5.18) to avoid the confusion as to whether there is NAPL or steam in the particular region. At 98 minutes, about 2/3 of the sand was swept by steam (Figure 5.15). The PCE bank was between x=0.4 to x=0.6 m with the PCE saturation of 10%-90% based on comparing the water saturation contours with the temperature contours (Figure 5.19 (a)). Water saturation contours at 218 minutes (Figure 5.16) showed that the residual water saturation was about 10% and steam was everywhere.

The water pressure contours at various times (Figure 5.7 - 5.11) showed that there were large pressure changes at the steam front. The pressure increased during the steam injection processes. The water pressures measured in the steam zone might not be as accurate as those outside the steam zone since some of the water in the porous ceramic cups connecting with the pressure transducers could have evaporated. However, the amount of water evaporated would be small since the ceramic cups still had contact with the residual water saturations. The soil temperature contours (Figure 5.17 - 5.19 (b)) showed more or less a tilted steam front moving from the steam injection well to extraction well, which was comparable with the visual observation of the front through the glass (see the photograph in Figure 5.20). No sharp steam channeling was observed, as expected. This was due to the condensation of steam at the steam front, which damped any steam channeling. The steam front also moved through the F110 sand layer to the lower F75 sand layer. This shows that both heat advection and conduction were important mechanisms of heat transfer. The temperature contours at 170 minutes (Figure 5.19 (b)) showed that more steam override happened at later times of steam injection compared with the earlier times (Figure 5.18 and 5.19 (a)).

5.3 Saturated Three layer System with Two Vertical Wells, LNAPL and DNAPL

(Experiment # 2)

This experiment studied the removal of a 1:1 volume mixture (0.6367:0.3633 mole fraction) of PCE and nonane from a saturated three layer system with vertical wells. The vapor
pressure of PCE is higher than that of nonane, so that it was expected that the former would be removed preferentially. The setup was the same as in Section 5.2 except that two components and different well screen sections were used.

The experiment was initiated by injecting a miscible mixture of PCE and nonane into the sand chamber over a period of 28 minutes, which gave an injection rate of 5.71 ml/min. or $9.52 \times 10^{-8}$ m$^3$/s. Twenty-seven days after the start of the DNAPL spill, steam at a temperature of 125 °C was injected into the sand chamber through the top half of the injection well while the fluids were recovered though the bottom half of the extraction well. Steam was injected at a constant rate of $7.66 \times 10^{-4}$ m$^3$/s. The mixture of PCE and nonane as a DNAPL was observed at the outlet after 2 hours and 56 minutes of steam injection. The DNAPL looked opaque and foamy due to emulsification. At 4 hours and 16 minutes when 31 ml of DNAPL had been collected, the extracted DNAPL was colorless, which meant the red dye lagged behind the evaporation of DNAPL. A volume of 1.8 ml of a mixture of PCE and nonane, as a colorless LNAPL, was collected at the outlet at 5 hours 15 minutes. After 6 hours and 15 minutes of steam injection, the bottom half of the steam injection well and the top half of the extraction well were opened to allow the full steam sweep of the sand chamber.

In a total, 126.5 ml (2.3 ml LNAPL plus 124.2 ml DNAPL) of PCE and nonane was removed from the sand chamber. The 126.5 ml of pure NAPL consisted of 73.6 ml (92% recovery) of PCE and 52.9 ml (66% recovery) of nonane. The raw data are in Appendix C.

The raw nonane and PCE concentration data of Experiment #2 were from sampling ports and TDR probes (see Appendix C). Reported aqueous solubilities of nonane range from 0.071 to 1.7 mg/L at 25 °C (Table 4.1). For the mixture of nonane and PCE, assuming Raoult’s Law (Reid, 1977) can be applied to dissolution, then, the aqueous PCE and nonane solubilities would have been 127.34 mg/L (i.e. 200 X 0.6367) and 0.73 (i.e. 2 X 0.3633) mg/L, respectively, since the mole fractions of PCE and nonane of a 1:1 mixture by volume were
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0.6367 and 0.3633, respectively. Therefore, at TDR probe locations where saturations indicated the presence of NAPL, PCE concentration of 127.34 mg/L and nonane concentration of 0.73 mg/L were assigned. For the purpose of plotting water phase concentrations any GC measurements of PCE and nonane concentrations that were above the solubility limits were reduced to the solubility limits of 127.34 and 0.73 mg/L.

The nonane concentration contour map at start of the steam injection (Figure 5.21) showed that nonane was as spread out as the PCE (Figure 5.26). At 55 minutes, both nonane and PCE moved downward past the finer sand layer to the lower coarser sand layer (Figure 5.22 and 5.27, respectively) as was observed in Experiment #1. The nonane concentration contours at 140 and 245 minutes (Figure 5.23 and 5.24, respectively) showed a wide spread of nonane plume across the whole domain while PCE concentration contours at 140 and 245 minutes showed much less spread and faster removal (Figure 5.28 and 5.29, respectively). Eventually, the PCE was almost completely removed at 245 minutes. It took as twice as much time (490 minutes, Figure 5.25) for nonane to be nearly completely removed.

The water saturation contour map at 30 minutes (Figure 5.35) did not change much compared to the initial condition (not shown). A steam chamber formed near the upper right hand corner at 55 minutes (Figure 5.36). A NAPL bank was formed near the upper center to upper left corner where the NAPL saturation ranged from 10 to 40% (water saturation ranged from 90 to 60%). This interpretation was aided by the associated temperature contours (Figure 5.40). At 140 minutes (Figure 5.37), the NAPL saturation at NAPL bank ahead of the steam front ranged from 10 to 30%. Water saturation contours at 245 minutes (Figure 5.38) showed that the residual water saturation was about 10%.

The water pressure contours at various times (Figure 5.30 - 5.34) showed that there were large pressure changes at the steam front. The pressure increased with time which meant that the whole steam injection processes was in a transient state. The soil temperature contour maps (Figure 5.39 - 5.43) at different times showed the movement of steam fronts. A tilted
steam front moved from the injection well at the right to the well at the left, which was also observed through the glass at the front. The temperature contours showed the steam override in this experiment was less severe than in Experiment #1. No steam channeling was observed through the front glass of the sand chamber.

5.4 Unsaturated Three layer System with Two Vertical Wells and LNAPL (Experiment #3)

This experiment studied the steam flushing of nonane from unsaturated soil with vertical wells. The water table was at $Z = -0.425$ m (0.15 m from the bottom of the sand chamber). The main goal was to study the effectiveness of steam injection for the remediation of low vapor pressure LNAPLs in the vadose zone and to determine the potential for LNAPL in the upper layer to contaminate the lower coarser sand layer during the steam flushing process. The experimental setup was the same as Experiment #1 except that in this experiment the contaminant was a LNAPL (nonane) and the water table was lower.

The nonane was injected into the upper layer over a period of 47 minutes. The injection rate was 3.19 ml/min. or $5.32 \times 10^{-8}$ m$^3$/s. The temperature of steam injected was set at 110 $^\circ$C. The top half of the extraction well was closed while the bottom half of it was opened after 7 hours and 45 minutes of steam injection. The injection rate of steam was $1.17 \times 10^{-3}$ m$^3$/s. The raw data are in Appendix C.

For the purpose of plotting water phase concentrations any GC measurements of nonane concentrations that were above the solubility limit were reduced to the solubility limit of 2 mg/L. There was no concentration data from the TDR probes due to the presence of three phases at the beginning (air, water, NAPL phases). Initially, the nonane was in the upper-right-hand corner above the middle finer sand layer (Figure 5.44). Steam was injected into the sand chamber through the top half of the injection well and the fluids were recovered through the top half of the extraction well. Seventy-five minutes after the start of steam
injection, the plume had moved toward the left boundary (Figure 5.45). Some nonane moved downward past the middle layer of F110 finer silica sand contaminating the lower F75 coarser sand layer. At 135 minutes, the nonane plume reached the extraction well while there was still substantial nonane left near the right boundary (Figure 5.46). At 365 minutes, the whole pure phase plume had moved to the left side where the extraction well was located (Figure 5.47). No nonane was detected at 540 minutes at any of the 24 sampling ports when 88% nonane was recovered.

Comparing the water saturation contour maps at 0 and 75 minutes (Figure 5.53 and 5.54, respectively), shows that a water bank formed at the center after 75 minutes of steam injection. The water saturation in the bank was up to 80%. At 135 minutes (Figure 5.55), the water bank moved to the left and disappeared at 195 minutes (Figure 5.56). At 365 minutes (Figure 5.57), most of the sand had water saturations slightly higher than the residual water saturation of 12%.

At 30 minutes after steam injection started, the water pressure was 90 cm H₂O (the highest) at the steam front, while the water pressure was 40 cm H₂O (the lowest) at the condensation front (Figure 5.48). These pressure contours and later pressure contour maps should be analyzed with the help of the temperature contours at corresponding times to locate the steam and condensation fronts. The same trend could be seen at 60 minutes (Figure 5.49). At 90 minutes (Figure 5.50), there was a large increase in water pressure (710 cm H₂O) in the coarser sand layer near the lower-right-hand corner while the steam front moved to the center in the vadose zone where the water pressure was 530 cm H₂O. The steam front moved to the upper-left-hand corner where water pressure was 420 cm H₂O while the water pressure in the lower-right-hand corner was unchanged after 140 minutes of steam injection (Figure 5.51). Water pressures were quite high (the highest was 840 cm H₂O) everywhere compared to the early time (Figure 5.48) when steam was everywhere (Figure 5.52).
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The soil temperature contour maps (Figure 5.58 to 5.62) showed more or less a tilted steam front moving from the steam injection well to extraction well, which was comparable with the visual observation of the front through the glass. The temperature showed the same trend as the saturated case, however, the temperature front moved faster than the saturated case. This is because air has much smaller heat capacity (1.0 kJ/kg-K) than water (4.184 kJ/kg-K), and there was less water to be evaporated. The steam override was about the same as in the saturated case.

5.5 Unsaturated Two layer System with Two Horizontal Wells and LNAPL
(Experiment # 4)

This experiment studied the steam flushing of nonane from unsaturated soil using horizontal wells. The water table was at \( Z = -0.525 \) m (0.05 m from the bottom of the sand chamber). The main goal was to assess the performance of horizontal wells for use in steam flushing.

The horizontal well setup was shown in Figure 4.8 (b). The nonane was injected into the upper layer through the chemical spill distributor over a period of 40 minutes. The injection rate was 3.75 ml/min. or \( 6.25 \times 10^{-8} \) m\(^3\)/s. Steam was injected from the bottom horizontal well while the extraction well was the top horizontal well. The temperature of steam injected was set to 105 °C. The injection rate of steam was \( 1.39 \times 10^{-3} \) m\(^3\)/s. A volume of 6.3 ml of nonane was collected at the extraction well after 2 hours and 2 minutes of steam injection. The nonane recovered looked opaque and foamy. The raw data are in Appendix C.

For the purpose of plotting water phase concentrations any GC measurements of nonane concentrations that were above the solubility limit were reduced to the solubility limit of 2 mg/L. There was no concentration data from the TDR probes due to the presence of three phases at the beginning (air, water, NAPL phases). Initially the nonane (Figure 5.63) was located at the center above the bottom finer sand layer. Sixty-five minutes after the steam injection started the plume moved toward the right boundary (Figure 5.64). At 160 minutes,
the nonane plume was spread all the way to right boundary (Figure 5.65). At 325 minutes, the whole plume became smaller since 93.6 ml of nonane was collected (Figure 5.66). There was still nonane left after 590 minutes of steam injection (Figure 5.67). No nonane was found in the finer sand layer below the horizontal steam injection well.

The water saturation map at the start of steam injection showed that the initial water saturations were from 20% to 70% (Figure 5.73). The contours at 65 minutes showed an increase of water saturation to a range of 63 % to 75% (Figure 5.74). The water saturations were lower in the center above the injection well. The water saturations at 160 minutes (Figure 5.75) had a lower water saturation region in the middle where steam had passed from the bottom horizontal well. The water saturations were in the range of 40% to 75%. At 325 minutes all the sand chamber had been swept by steam and the water saturations ranged from 24% to 40% (Figure 5.76). After 640 minutes of steam injection the water saturations in the sand chamber had not changed much (22% - 34%) from conditions at 325 minutes. The residual water saturation (22%) at the end of this experiment (Figure 5.77) was twice as much as the residual water saturations in all the vertical well experiments (Experiment #1, #2 and #3). The total volume of water collected was 22.4 L which was only 50% of the water collected in Experiment #1 (Table 5.2). The higher residual water saturation may be caused by the lower steam injection temperature (105 °C), compared to steam injection temperatures of 110 °C to 125 °C used in other experiments (Table 5.1). Another reason could be that the steam front had an early breakthrough (2 h 28 min., comparing to 3 h 40 min. in Experiment #2, Table 5.2) in the center of the chamber, resulting in higher water saturations at the left and right sides of the chamber (Figure 5.77).

Water pressures were still negative in the vadose zone after 60 minutes of steam injection (Figure 5.68). At 120 minutes the water pressure had increased to as high as 140 cm H₂O in the vadose zone (Figure 5.69). The water pressures were higher in the center (330 cm H₂O) at 210 minutes of steam injection showing that the steam front had moved from the bottom injection well to the top extraction well (Figure 5.70). The water pressure profile had not
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changed much at 300 minutes (Figure 5.71) compared with that at 210 minutes. The steam swept all the vadose zone and finer sand layer after 480 minutes of steam injection and the highest water pressure was 390 cm H$_2$O (Figure 5.72).

The temperature contour maps at 60, 120, and 210 minutes (Figure 5.78, 5.79, and 5.80, respectively) showed that the steam chamber formed at the bottom, expanded, and reached to the top. The steam chamber expanded all the way to the left boundary after 300 minutes of steam injection (Figure 5.81). The steam front swept all the vadose zone and finer sand layer after 480 minutes of steam injection (Figure 5.82), taking more than double the time required for the vertical well cases (Experiment #1, #2, and #3).

5.6 NAPL Removal Rate

In order to compare the efficiency of different well setups and water saturation conditions, a plot of percent oil recovered vs. time was presented in Figure 5.83 (top). The vertical well cases (Experiment #2 and #3) reached 75 - 85% NAPL recovery before 300 minutes while the horizontal well case (Experiment #4) reached 85% NAPL recovery before 650 minutes. The vertical well cases were more efficient than the horizontal well case since they required less time to produce the same amount of NAPL. However, the horizontal well case is more efficient than the vertical well cases in producing the first 25% NAPL.

The pore volume of the sand chamber was in the range of 22.84 to 22.95 liters. The cumulative amount of water produced in the unit of pore volume was plotted against time in Figure 5.83 (bottom). The vertical well cases produced more water than the horizontal well case over the entire steam injection process. Therefore the trade-off was that even though the vertical well cases were more efficient, they required treatment of more water than the horizontal well case.
5.7 Conclusions

1. The steam flushing method has been shown as a promising technique for the removal of volatile and semi-volatile NAPLs from soils.

2. Complete removal of PCE and nonane from zones swept by steam was achieved. The highest overall removal measured was 84 % for PCE in the saturated three-layer system with two vertical wells and 89.3% for nonane in the unsaturated two-layer system with two horizontal wells, due to the trapping of the organic chemicals at the bottom of the sand chamber and in the outlet tubing.

3. Some steam override occurred in the vertical well cases.

4. Steam channeling was insignificant in the steam flushing experiments.

5. Downward mobilization of DNAPL and LNAPL past a finer grained silica sand layer happened in the vertical well cases.

6. The vertical well design was more efficient than the horizontal well design. However, the trade-off was that there was more contaminated water to be treated in the vertical well system.
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Figure 5.1 Experiment # 1: PCE concentration (mg/L) at the start of steam flushing.

Figure 5.2 Experiment # 1: PCE concentration (mg/L) at 20 minutes of steam flushing.
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Figure 5.3 Experiment #1: PCE concentration (mg/L) at 50 minutes of steam flushing.

Figure 5.4 Experiment #1: PCE concentration (mg/L) at 98 minutes of steam flushing.
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Figure 5.5 Experiment #1: PCE concentration (mg/L) at 218 minutes of steam flushing.

Figure 5.6 Experiment #1: PCE concentration (mg/L) at 390 minutes of steam flushing.
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Figure 5.7 Experiment #1: Water pressure (cm H₂O) at the start of steam flushing.

Figure 5.8 Experiment #1: Water pressure (cm H₂O) at 20 minutes of steam flushing.
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Figure 5.9 Experiment #1: Water pressure (cm H₂O) at 50 minutes of steam flushing.

Figure 5.10 Experiment #1: Water pressure (cm H₂O) at 98 minutes of steam flushing.
Figure 5.11: Experiment #1: Water pressure (cm H₂O) at 218 minutes of steam flushing.

Figure 5.12: Experiment #1: Water saturation (%) at start of steam flushing.
Figure 5.13 Experiment #1: Water saturation (%) at 20 minutes of stem flushing.

Figure 5.14 Experiment #1: Water saturation (%) at 50 minutes of stem flushing.
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Figure 5.15 Experiment #1: Water saturation (%) at 98 minutes of steam flushing.

Figure 5.16 Experiment #1: Water saturation (%) at 218 minutes of steam flushing.
Figure 5.17 Experiment #1: Soil temperature (°C) at 20 minutes of steam flushing.

Figure 5.18 Experiment #1: Soil temperature (°C) at 50 minutes of steam flushing.
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Figure 5.19 (a) Experiment #1: Soil temperature (°C) at 98 minutes of steam flushing.

Figure 5.19 (b) Experiment #1: Soil temperature (°C) at 170 minutes of steam flushing.
Figure 5.20 Experiment # 1: Photographs of the front side of the sand chamber. Top photograph: taken at 95 minutes of steam flushing; bottom photograph: taken at 210 minutes of steam flushing (steam breakthrough).
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Figure 5.21 Experiment # 2: Nonane concentration (mg/L) at start of steam flushing.

Figure 5.22 Experiment # 2: Nonane concentration (mg/L) at 55 minutes of steam flushing.
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Figure 5.23 Experiment #2: Nonane concentration (mg/L) at 140 minutes of steam flushing.

Figure 5.24 Experiment #2: Nonane concentration (mg/L) at 245 minutes of steam flushing.
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Figure 5.25 Experiment #2: Nonane concentration (mg/L) at 490 minutes of steam flushing.

Figure 5.26 Experiment #2: PCE concentration (mg/L) at start of steam flushing.
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Figure 5.27 Experiment # 2: PCE concentration (mg/L) at 55 minutes of steam flushing.

Figure 5.28 Experiment # 2: PCE concentration (mg/L) at 140 minutes of steam flushing.
Figure 5.29 Experiment #2: PCE concentration (mg/L) at 245 minutes of steam flushing.

Figure 5.30 Experiment #2: Water pressure (cm H₂O) at 30 minutes of steam flushing.
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Figure 5.31 Experiment # 2: Water pressure (cm H₂O) at 60 minutes of steam flushing.

Figure 5.32 Experiment # 2: Water pressure (cm H₂O) at 90 minutes of steam flushing.
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Figure 5.35 Experiment #2: Water saturation (%) at 30 minutes of steam flushing.

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Figure 5.37 Experiment # 2: Water saturation (%) at 140 minutes of steam flushing.

Figure 5.38 Experiment # 2: Water saturation (%) at 245 minutes of steam flushing.
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Figure 5.40 Experiment #2: Soil temperature (°C) at 60 minutes of steam flushing.
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Figure 5.46 Experiment #3: Nonane concentration (mg/L) at 135 minutes of steam flushing.
Figure 5.47 Experiment # 3: Nonane concentration (mg/L) at 365 minutes of steam flushing.

Figure 5.48 Experiment # 3: Water pressure (cm H₂O) at 30 minutes of steam flushing.
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Figure 5.49 Experiment # 3: Water pressure (cm \( \text{H}_2\text{O} \)) at 60 minutes of steam flushing.

Figure 5.50 Experiment # 3: Water pressure (cm \( \text{H}_2\text{O} \)) at 90 minutes of steam flushing.
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Figure 5.51 Experiment #3: Water pressure (cm H₂O) at 140 minutes of steam flushing.

Figure 5.52 Experiment #3: Water pressure (cm H₂O) at 170 minutes of steam flushing.
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Figure 5.53 Experiment # 3: Water saturation (%) at start of steam flushing.

Figure 5.54 Experiment # 3: Water saturation (%) at 75 minutes of steam flushing.
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Figure 5.55 Experiment # 3: Water saturation (%) at 135 minutes of steam flushing.

Figure 5.56 Experiment # 3: Water saturation (%) at 195 minutes of steam flushing.
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Figure 5.57 Experiment #3: Water saturation (%) at 365 minutes of steam flushing.

Figure 5.58 Experiment #3: Soil temperature (°C) at 30 minutes of steam flushing.
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Figure 5.59 Experiment # 3: Soil temperature (°C) at 60 minutes of steam flushing.

Figure 5.60 Experiment # 3: Soil temperature (°C) at 90 minutes of steam flushing.
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Figure 5.62 Experiment # 3: Soil temperature (°C) at 170 minutes of steam flushing.
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Figure 5.68 Experiment # 4: Water pressure (cm H₂O) at 60 minutes of steam flushing.
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Figure 5.74 Experiment # 4: Water saturation (%) at 65 minutes of steam flushing.
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Figure 5.75 Experiment # 4: Water saturation (%) at 160 minutes of steam flushing.

Figure 5.76 Experiment # 4: Water saturation (%) at 325 minutes of steam flushing.
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Figure 5.78 Experiment # 4: Soil temperature (°C) at 60 minutes of steam flushing.
Figure 5.79 Experiment #4: Soil temperature (°C) at 120 minutes of steam flushing.

Figure 5.80 Experiment #4: Soil temperature (°C) at 210 minutes of steam flushing.
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Figure 5.81 Experiment # 4: Soil temperature (°C) at 300 minutes of steam flushing.

Figure 5.82 Experiment # 4: Soil temperature (°C) at 480 minutes of steam flushing.
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Figure 5.83 Steam flushing experimental results: Percent NAPL recovered (top); Pore volume water extracted (bottom).
CHAPTER 6 STEAM FLUSHING MODELING RESULTS AND DISCUSSION

6.1 Introduction

The numerical model described in Appendix D was used to simulate the steam flushing of Experiments #1 and #2 (Chapter 5). The constants and model parameters for PCE, nonane, and water are summarized in Table 6.1. The values of \( \alpha \), \( n \), and \( \beta_0 \), which are the van Genuchten \( P_e-S_w \) parameters, were 1.86 l/m-H\(_2\)O, 8.0742, and -448.6 (K), respectively, for air-water drainage curves of the F75 silica sand and 1.3281 l/m-H\(_2\)O, 6.643, and -448.6 (K), respectively, for air-water drainage curves of the F110 silica sand. The \( a \), and \( b \) values for the calculation of residual water saturations from Table 3.2 (e) were also used. No capillary hysteresis (entrapment) was assumed in the model. The sand chamber was represented by 600 small blocks with 20 blocks in the X-direction (horizontal direction) and 30 blocks in the Z-direction (vertical direction).

Initially, the model simulated the NAPL spill with exactly the same volume of PCE and injection rate as in Experiment #1 and the same amount of PCE and nonane and injection rate as in Experiment #2 to generate the initial PCE and nonane saturation and aqueous PCE and nonane concentration profiles. Then, the steam flushing simulations were started by injecting steam at a liquid water flow rate of 58 ml/min. (9.66 \( \times 10^{-4} \) kg/s). A total enthalpy of 620,131 Cal/kg (Himmelblau, 1974) is needed to transform 1 kg of water to steam from 20 °C to 110 °C of temperature. The energy required for the steam generator to evaporate the water fed at the rate of 58 ml/min. to 100% steam was 2502 Watts. Four out of five heating tapes (648 Watts per tape) were connected. These could deliver a total of 2592 Watts if fully turned on. However, the 4 heating tapes were turned on and off on a periodic basis to maintain the steam temperature set point. The fraction of the time the power was on was not recorded by the data acquisition system. In addition, it is difficult, if not impossible, to measure the heat loss from
the steam generator and the heat loss from the tubing between the steam generator and the injection well. So the steam quality could not be measured. An attempt was made to estimate steam quality (fraction of the volume which is the water vapor) from the conditions in the sand chamber at 170 minutes of steam flushing during Experiment #2.

<table>
<thead>
<tr>
<th>Constants</th>
<th>PCE</th>
<th>nonane</th>
<th>Water</th>
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<tr>
<td>Critical temperature $T_c$ (K)</td>
<td>620.0</td>
<td>594.65</td>
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<td>Critical pressure $P_c$ (atm)</td>
<td>44.0</td>
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<td>Critical volume (cm$^3$/g-mol)</td>
<td>290.0</td>
<td>555.0</td>
<td>56.0</td>
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<td>Liquid viscosity $\mu_{ll}$ (cP):</td>
<td>B</td>
<td>313.66</td>
<td>517.30</td>
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<tr>
<td>$T_0$</td>
<td>182.48</td>
<td>271.21</td>
<td>283.16</td>
</tr>
<tr>
<td>Gas viscosity $\mu_{lg}$ (kg/m-s):</td>
<td>$\mu^*$</td>
<td>1.92X10^-5</td>
<td>1.09X10^-5</td>
</tr>
<tr>
<td>Latent heat (Cal/g-mol)</td>
<td>8067.0</td>
<td>8740.8</td>
<td>9717.0</td>
</tr>
<tr>
<td>Thermal conductivity (J/m-s-K)</td>
<td>0.12</td>
<td>0.131</td>
<td>0.26</td>
</tr>
<tr>
<td>Vapor pressure (mm Hg): A</td>
<td>16.16</td>
<td>15.97</td>
<td>18.30</td>
</tr>
<tr>
<td>B</td>
<td>3259.29</td>
<td>3291.45</td>
<td>3816.44</td>
</tr>
<tr>
<td>C</td>
<td>-52.15</td>
<td>-71.33</td>
<td>-46.13</td>
</tr>
<tr>
<td>Liquid diffusion coefficient (m$^2$/s)</td>
<td>2.81X10^-9</td>
<td>1.76X10^-7</td>
<td>1.0X10^-9</td>
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<tr>
<td>Gas diffusion coefficient (m$^2$/s)</td>
<td>1.08X10^-5</td>
<td>8.49X10^-6</td>
<td>2.45X10^-5</td>
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</tbody>
</table>

Table 6.1 Constants and model parameters for PCE, nonane, and water.a

From the water added and water produced it was possible to estimate the volume of steam in the sand chamber (10.3 L). From the temperature profile and water saturation profile at 170 minutes of steam flushing for Experiment #2, the volume of the steam chamber was determined to be 14.4 L. From the porosity and the volume of steam the volume of water in the steam zone was estimated to be 4.1 L. The average steam zone water saturation was

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*a Reid et al. (1977); Lide and Frederikse, 1995.*
28.5% at 170 minutes of steam flushing. For the section of the sand chamber that was fully water saturated the average temperature was estimated to be 60 °C. The increase in heat content in the sand chamber was estimated from the volume of steam and the latent heat of steam, the increased sand chamber temperatures, and heat capacity of water and sand. The increase in enthalpy at 170 minutes, relative to initial conditions, was 12, 400 KJ which is equivalent to a power input of 1150 Watts. For the water input rate of 58 ml/minute this represents a steam quality of 28%.

The heat loss from the sand chamber to surroundings was assumed to be proportional to the area of the sand chamber and the differences between the sand chamber temperature and room temperature. The proportionality constant (i.e. heat loss coefficient) was related to the heat conductivity and thickness of the fiberglass insulation material used and the boundary effects. The proportionality constant was estimated to be 1.2 (Watt/m²-K) by the formula of 1/(L/K+B) where L = 0.0254 m is the thickness of insulation material, K = 0.036 Watt/m-K is the heat conductivity of the insulation material, and B = 0.12 m²K/Watt is the boundary effect.

Experimentation with the model showed that the rate of movement of the steam front was most sensitive to steam quality, heat loss to the surroundings, and soil permeability. A large number of runs were performed to determine the combination of these parameters that produced the best matches with experimental results. Matching the experimental temperature profiles was given the highest priority. Modeling was started using 100% steam quality, the measured sand permeabilities given in Chapter 4 (1.0714 X 10⁻¹² m² for F75 silica sand; 5.32 X 10⁻¹³ m² for F110 silica sand, see Table 4.3), and a heat loss coefficient of 1.2 Watt/m²-K (detail showed at the end of this section).

The intrinsic permeabilities of the F75 and F110 silica sand layers in the X-direction were increased by a factor of two to 2.1428 X 10⁻¹² m² and 1.064 X 10⁻¹² m², respectively, in numerical simulation of Experiments #1 and #2. This increase produced more realistic
pressure profiles than the measured permeabilities. It is very difficult to produce the same sand permeability in packing the two-dimensional sand chamber as was produced in the column used to measure the permeability. As the sand was added in layers it is expected that some anisotropy would exist. The intrinsic permeabilities of the F75 and F110 silica sands and relative permeabilities for water, gas, and organic phase (as defined by Equations D.13 to D.15 in Appendix D) were assumed to be independent of temperature in the model.

A value of 5 Watt/m²-K for the proportionality constant in combination with 25% steam quality was found to give good results in the model. The maximum heat loss from the sand chamber was 720 Watts (5 Watt/m²-K X 1.6 m² X (383.15 K - 293.15 K)), which was 27.8% of the maximum heat produced by all the 4 heating tapes. Higher values of the heat loss coefficient resulted in steam zone growth that was too slow, while lower values of the heat loss coefficient resulted in steam zone growth that was too rapid.

6.2 Results and Discussion

6.2.1 Simulation of Experiment #1

The results of aqueous PCE concentrations, water pressures, water saturations, and soil temperatures from the numerical simulation at various times were presented with contour maps. The results from Experiment #1 were posted on all the contour maps. Very good agreement was observed between the model contours and experimental data points.

The numerical simulation results of aqueous PCE concentrations at 20 minutes of steam flushing (Figure 6.1) showed a pure phase PCE plume which covered the 3 data points of 200 mg/L (pure phase). One datum point of 200 mg/L was on the contour line of 110 mg/L. The predicted area of the pure phase PCE plume and the dissolved phase PCE plume was larger than the area of experimental results (Figure 6.2). Part of the PCE plume near the injection well was cleaned and part of the pure phase PCE plume moved downward and reached the
lower aquifer after 50 minutes of steam flushing (Figure 6.2). This remobilization of PCE into the lower aquifer was not shown in the experimental data at 50 minutes of steam flushing. It should be noted that the model ignores hysteresis and entrapment of the organic phase. This results in over estimation of the mobility of the organic phase. The pure phase PCE plume at 98 minutes of steam flushing showed a very good agreement with the experimental data points. At 218 minutes of steam flushing, the pure phase PCE lagged behind the 3 experimental data points of 200 mg/L probably due to the lack of "wellbore effect" in the model. "Wellbore effect" includes the non-ideal packing of the sand around the well casing in the sand chamber which might increase the permeability of sand around the well.

The simulation results of water pressures at 50 minutes of steam flushing (Figure 6.5) show higher values than most of the experimental data. However, simulation results of water pressures at 218 minutes of steam flushing (Figure 6.6) show lower values than most of the experimental data. The simulation results of the water saturations at 50 minutes of steam flushing (figure 6.7) show the detail of water saturations in the steam zone. The simulation results of the water saturations at 98 minutes of steam flushing (figure 6.8) show a better agreement with the experimental data points than at 50 minutes. The simulation results of soil temperatures at 20 and 50 minutes of steam flushing (Figure 6.9 and Figure 6.10, respectively) show excellent agreement with the experimental data points. The simulation results of soil temperatures at 98 minutes of steam flushing (Figure 6.11) show very good agreement with the experimental data points in the steam zone while the predicted steam front slightly lagged behind the experimental data points.

Figure 6.24 shows the percentage of PCE recovered and PV (pore volume) water extracted with time for the first 360 minutes of steam flushing for the simulation of Experiment #1. No experimental data of percent PCE recovered and PV water extracted with time for Experiment #1 were available for the comparison except the total percent of PCE recovered. The percent of PCE recovered after 360 minutes of steam flushing was 73 % from the
simulation results while the PCE recovered after 530 minutes of steam injection was 84% from the results of Experiment #1.

6.2.2 Simulation of Experiment #2

The results of aqueous PCE concentrations, water pressures, water saturations, and soil temperatures from the numerical simulation at various times were presented with contour maps. The results from Experiment #2 were posted on all the contour maps. Assuming Raoult’s Law can be applied to dissolution, then, the aqueous PCE and nonane solubilities would have been 127.34 mg/L and 0.73 mg/L, respectively, since the mole fractions of PCE and nonane of a 1:1 mixture by volume were 0.64 and 0.36, respectively.

The numerical simulation results of aqueous PCE concentrations at 55 minutes of steam flushing (Figure 6.12) show a pure phase PCE plume which covers the 5 data points of 127.34 mg/L. The model predicts a slightly larger extension of pure phase PCE plume in the middle of the sand chamber. Part of the PCE plume near the injection well was removed. The pure phase PCE plume at 140 minutes of steam flushing moved to the left of the sand chamber and matched most of the experimental data points except one near the injection well at the right of the sand chamber. The measured PCE concentration of 4.12 mg/L from the sampling port near the right boundary might have been the result of contamination of the syringe needle used to take the sample. At 245 minutes of steam flushing, the predicted pure phase PCE plume was larger than the experimental measurements. Again, the PCE concentrations near the right boundary might have been due to the needle contamination.

The nonane concentration contours after 55 minutes of steam flushing agreed very well with the experimental measurements (Figure 6.15). At 140 minutes of steam flushing, the model results also matched the experimental concentration contours (Figure 6.16). The measured nonane concentration data points near the right of the sand chamber might have been from the contamination of the needle used for sampling. The pure phase nonane plume predicted
by the model at 245 minutes of steam flushing (Figure 6.17) is to the right of measured nonane data points indicating that the predicted nonane plume moved slightly faster than the measured nonane plume.

The simulation results of water pressures at 60 minutes of steam flushing (Figure 6.18) predicted lower values at the left and higher values at the right of the sand chamber than the experimental data. However, simulation results of water pressures at 140 minutes of steam flushing (Figure 6.19) show lower values than most of the experimental data.

The model predicted much higher water saturations at 55 minutes of steam flushing (figure 6.20) in the upper middle region than were measured. The simulated water saturations at 140 minutes of steam flushing (figure 6.21) show better agreement with the experimental data and indicate the effect of the F110 sand layer on the water saturation. The predicted water saturation in the middle layer within the steam chamber was over 55%, which is much higher than the measured value of 14.1%. Part of the difference of about 41% might be caused by the uncorrected effects of temperature on the time domain reflectometry measurements in steam flushing experiments (see Chapter 4, section 4.5). However, the possible measurement error due to the temperature effect is only in the range of 1.4% to 14%.

Another possible explanation could be that the assumption of steam quality of 25% in the model might be too low so that there was not enough energy to evaporate the extra water, even though the assumed steam quality is only slightly lower than the estimated steam quality (28%). The predicted total pore volume water production was 0.7 at 170 minutes of steam flushing (Figure 6.24). The measured total pore volume water production was 0.9 at 170 minutes of steam flushing (Figure 6.83). The discrepancy of the pore volume water produced was 0.2 at 170 minutes of steam flushing. An extra 0.2 PV water, that is 4.6 L of water (0.2 X 22.95 L), would be equivalent to 40% more water saturation in the steam chamber if the steam chamber was assumed to be half of the sand chamber (Figure 6.21)!
Chapter 6. Steam Flushing Modeling Results and Discussion

The simulation results of soil temperatures at 60 minutes of steam flushing (Figure 6.22) show excellent agreement with the experimental data points. The simulation results of soil temperatures at 140 minutes of steam flushing (Figure 6.23) show very good agreement with the experimental data points in the steam zone while the predicted steam front slightly lagged behind the experimental data points.

Figure 6.24 shows the percentage of NAPLs recovered and PV (pore volume) water extracted with time for the first 360 minutes of steam flushing for the simulation of Experiment #2. The percent of PCE and nonane recovered after 360 minutes of steam flushing was 83 % from the simulation result of Experiment #2 while the PCE and nonane recovered after 530 minutes of steam injection was 79 % from the result of Experiment #2. Therefore, the numerical simulation predicts a more efficient and better NAPL recovery even in the first 360 minutes of steam flushing than the measurement of Experiment #2.

6.3 Conclusions

The model predictions and experimental results for temperature profiles and concentration profiles were in close agreement. Reasonably good matches of water saturation and water pressure profiles were obtained. The parameters of the steam flushing numerical model, which were adjusted to give better predictions, were the injected steam quality (steam injection rate), horizontal intrinsic permeability, and heat loss from the system. The model predicted somewhat higher removal efficiency and NAPL recovery in the simulation of Experiment #2 than the experimental measurements. This may be due to the lack of capillary hysteresis and non-wetting fluid entrapment in the model.
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Figure 6.1 Numerical simulation #1: PCE concentration (mg/L) at 20 minutes of steam flushing.

Figure 6.2 Numerical simulation #1: PCE concentration (mg/L) at 50 minutes of steam flushing.
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Figure 6.3 Numerical simulation #1: PCE concentration (mg/L) at 98 minutes of steam flushing.

Figure 6.4 Numerical simulation #1: PCE concentration (mg/L) at 218 minutes of steam flushing.
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Figure 6.5 Numerical simulation #1: Water pressures (cm H₂O) at 50 minutes of steam flushing.

Figure 6.6 Numerical simulation #1: Water pressures (cm H₂O) at 218 minutes of steam flushing.
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Figure 6.7 Numerical simulation #1: Water saturation (%) at 50 minutes of steam flushing.

Figure 6.8 Numerical simulation #1: Water saturation (%) at 98 minutes of steam flushing.
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Figure 6.9 Numerical simulation #1: Soil temperature (°C) at 20 minutes of steam flushing.

Figure 6.10 Numerical simulation #1: Soil temperature (°C) at 50 minutes of steam flushing.
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Figure 6.11 Numerical simulation #1: Soil temperature (°C) at 98 minutes of steam flushing.

Figure 6.12 Numerical simulation #2: PCE concentration (mg/L) at 55 minutes of steam flushing.
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Figure 6.13 Numerical simulation #2: PCE concentration (mg/L) at 140 minutes of steam flushing.

Figure 6.14 Numerical simulation #2: PCE concentration (mg/L) at 245 minutes of steam flushing.
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Figure 6.15 Numerical simulation #2: nonane concentration (mg/L) at 55 minutes of steam flushing.

Figure 6.16 Numerical simulation #2: nonane concentration (mg/L) at 140 minutes of steam flushing.
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Figure 6.17 Numerical simulation #2: nonane concentration (mg/L) at 245 minutes of steam flushing.

Figure 6.18 Numerical simulation #2: water pressure (cm H₂O) at 60 minutes of steam flushing.
Figure 6.19  Numerical simulation #2: water pressure (cm H$_2$O) at 140 minutes of steam flushing.

Figure 6.20  Numerical simulation #2: water saturation (%) at 55 minutes of steam flushing.
Figure 6.21 Numerical simulation #2: water saturation (%) at 140 minutes of steam flushing.

Figure 6.22 Numerical simulation #2: soil temperature (°C) at 60 minutes of steam flushing.
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Figure 6.23 Numerical simulation #2: soil temperature (°C) at 140 minutes of steam flushing.

Figure 6.24 Numerical simulation #1 and #2: percent PCE and nonane recovered, PV water extracted.
Chapter 7. Conclusions and Recommendations

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The three objectives in Chapter 1, namely the steam flushing feasibility study, the study of effect of temperature on $P_c$-$S_w$ curves, and the testing of a numerical model, were satisfactorily accomplished. They are summarized in the following three sections.

1. Effect of temperature on $P_c$-$S_w$ relations:

   - Temperature had a considerable effect on air-water and PCE-water capillary pressure-water saturation drainage and imbibition curves.
   - The capillary pressure and hysteresis of air-water-silica and PCE-water-silica systems decreased when temperature increased from 20 °C to 80 °C.
   - The residual water saturations in the PCE-water-silica system increased when temperature increased from 20 °C to 80 °C. Residual water saturations in the air-water-silica system decreased slightly over the temperature range of 20 - 60 °C and then increased significantly from 60 °C to 80 °C.
   - The residual PCE saturations in the PCE-water-silica system decreased when temperature increased from 20 °C to 80 °C. The measured residual air saturations in the air-water-silica system decreased when temperature increased from 20 °C to 80 °C. The fitted residual air saturations for the air-water-silica system decreased when temperature increased from 20 °C to 40 °C and increased when temperature increased from 40 °C to 80 °C.
   - The magnitude of the effect of temperature on $P_c$-$S_w$ curves can not be fully explained by thermal variation of air-water and organic-water interfacial tensions and contact angles. Other possible factors are increases of impurity (surfactant)
concentrations, changes of entrapped air volumes, increased flow of water from isolated packets to the continuous water phase, and changes of sand compaction.

- A $P_c-S_w$ model derived from the Laplace equation accounting for the effect of temperature on the capillary pressure was developed and successfully fitted to the experimental data.

- The undesirable downward mobilization of a DNAPL with increasing temperature could happen if the capillary pressure is decreased below the DNAPL entry pressure of the underlying finer layers or lenses.

- Additional hydraulic removal of organic contaminants from soil and groundwater is possible due to the decrease in residual organic phase saturations with increasing temperature.

2. **Steam flushing experiments**:

- Steam flushing has been shown as a promising technique for the removal of volatile and semi-volatile NAPLs from soils.

- Complete removal of PCE and nonane from zones swept by steam was achieved. The highest overall removal measured was 84% for PCE in the saturated three-layer system with two vertical wells and 89.3% for nonane in the unsaturated two-layer system with two horizontal wells, due to the trapping of the organic chemicals at the bottom of the sand chamber and in the outlet tubing.

- Some steam override occurred in the vertical well cases.

- Steam channeling was insignificant in the steam flushing experiments.

- Downward mobilization of DNAPL and LNAPL past a fine grained silica sand layer happened in the vertical well cases.

- The vertical well design was more efficient than the horizontal well design. However, the trade-off was that there was more contaminated water to be treated in the vertical well system.
3. **Numerical model testing:**

- The model predictions matched the experimental results reasonably well.
- The model is sensitive to the injected steam quality, horizontal intrinsic permeability, and heat loss from the system.

### 7.2 Recommendations

Future research is needed in the following areas in order to extend the current study of the steam flushing technique for the *in situ* remediation of NAPLs contaminated soil and groundwater:

1. Measure contact angle changes of air-water-silica and PCE-water-silica systems over the water saturation range of residual water saturation to 100% and over the temperature range of 20 °C to 80 °C.
2. Investigate other possible factors affecting the decrease of capillary pressures with increasing temperature, such as the increase of impurity (surfactant) concentration, the change of entrapped air volume, the increased flow of water from isolated packets to the continuous water phase, and the change of sand compaction.
3. Investigate different combinations of vertical wells and horizontal wells in order to maximize the NAPL removal efficiency while avoid the downward mobilization of NAPLs and steam override problems.
4. The effect of variation of the steam injection temperatures, pressures, and rates on the NAPL removal efficiency should be investigated.
5. The effect of capillary hysteresis on the NAPL removal efficiency should be investigated.
6. Three-dimensional field scale tests should be performed to provide data for model testing.
7. The analysis of costs of the equipment and operation, as well as the commercialization opportunities should be investigated.
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Bibliography


Appendix A: $P_c-S_w$ Experimental Data of F75 Silica Sand

PCE-Water $P_c-S_w$ Curves of F75 silica sand at 20, 40, 60, 80 °C
($P_{cow}$: cm H$_2$O; $S_w$: volume fraction)

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### Appendix

#### Air-Water $P_c-S_w$ Curves of F75 silica sand at 20, 40, 60, 80 °C

($P_{cw}$: cm H₂O; $S_w$: volume fraction)

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Appendix B: $P_c$-$S_w$ Experimental and Curve-Fitting Data of F110 Silica Sand

Air-water & PCE-Water $P_c$-$S_w$ Curves of F110 silica sand

($P_{caw}$, $P_{cow}$: cm H$_2$O; $S_w$: volume fraction)

<table>
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<tr>
<th>Air-H$_2$O</th>
<th>PCE-H$_2$O 20 °C</th>
<th>PCE-H$_2$O 40 °C</th>
<th>PCE-H$_2$O 60 °C</th>
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<td>$S_w$ (VG-GS)</td>
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Note: The values and 95 % confidence levels of the curve-fitting parameters of Van Genuchten model for F110 silica sand were:

\[ \alpha = 0.013281 \pm 0.000274 \text{ l/cm H}_2\text{O} \]

\[ S_{\text{wr}} = 0.0455 \pm 0.0492 \]

The values of \( P_{\text{cow}} \) in the 4th, 5th, 6th, and 7th column of above table were calculated according to the following formula (derived from Equation 3.22):

\[
P_{\text{cow}} = \frac{1}{\alpha} \left( \frac{\beta_0 + T_f}{\beta_0 + T_r} \right) \left[ \left( \frac{S_{\text{sat}} - S_{\text{wr}}}{1 - S_{\text{wr}}} \right)^{-1/m} - 1 \right]^{1/n}
\]

where \( S_{\text{wr}} = a_r + b_r T = -1.2373 + 0.004376 T \) and \( \beta_0 = -413 \text{ (K)} \) (Table 3.2 (e)).

Assumptions: a) The \( \beta_0 \) of F110 silica sand is the same as that of F75 silica sand.

b) The \( b_r \) of F110 silica sand is the same as that of F75 silica sand.
### Appendix C: Steam Flushing Experimental Data

#### Experiment #1: Water saturation, $S_w$, (%)

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<th>X (m)</th>
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<th>20 (min.)</th>
<th>50 (min.)</th>
<th>98 (min.)</th>
<th>218 (min.)</th>
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#### Experiment #1: Water pressure, $P_w$, (cm H$_2$O)

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#### Experiment #1: Soil temperature, $T$, (°C)

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## Experiment #1: Aqueous PCE concentration, $C_p$, (mg/L)

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**Note:**
200 mg/L means pure PCE phase (TDR data marked with *).
### Experiment #2: Water saturation, $S_w$ (%)

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### Experiment #2: Water pressure, $P_w$ (cm H$_2$O)

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### Experiment #2: Soil temperature, $T$, (°C)

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Experiment #2: Aqueous PCE & nonane concentrations, \( C_{PCE} \), \( C_{n} \) (mg/L)

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*0.380| -0.105| 127.34 127.34| 0          | 0.73       | 0.73       |               |               |               |               |               |               |
*0.150| -0.105| 127.34 127.34 127.34| 0          | 0.73       | 0.73       |               |               |               |               |               |               |
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*0.610| -0.232| 127.34 127.34| 0          | 0.73       | 0.73       |               |               |               |               |               |               |
*0.380| -0.232| 127.34 127.34 127.34| 0          | 0.73       | 0.73       |               |               |               |               |               |               |
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Note:
127.34 mg/L PCE and 0.73 mg/L nonane (TDR data marked with *)
These values were assigned to indicate NAPL phase presence
Appendix

Experiment #3: Water saturation, $S_w$ (%)

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Experiment #3: Water pressure, $P_w$ (cm H$_2$O)

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Experiment #3: Soil temperature, $T$, (°C)

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## Experiment #4: Water saturation, $S_w$ (%)

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## Experiment #4: Water pressure, $P_w$ (cm H$_2$O)

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Appendix D: Steam Flushing Numerical Model (COMPSIM)

D.1 Introduction

The numerical modeling of non-isothermal multi-phase flow (water, gas, and oil phase) first started in the 1960s when the use of steam injection as a tertiary oil recovery method became increasingly popular in the petroleum industry. Over the last three decades, the numerical models improved from the one-dimensional three-phase model introduced by Shutler (1969) to the three-dimensional three-phase steamflood simulators including compositional effects (Sleep, 1990). However, these proprietary models can not be applied directly to simulate the steam flushing of NAPL in soil and ground water. The simulation of organic contaminant transport must include many subtle multi-phase processes that are usually ignored in petroleum reservoir engineering, such as dissolution and transport of organic compounds in the water phase, the diffusion of organic vapors in the gas phase, the capillary pressures between different fluids, the dispersion of the organic phase, and partitioning of organic chemicals into the water phase (Sleep and Sykes, 1993; Forsyth, 1993; Falta et al., 1992).

The steam flushing simulator used here is the latest version of the compositional model developed and coded by Sleep (Sleep and Sykes, 1993; McClure and Sleep, 1996). The simulator is a three-dimensional, three-phase (water, gas, and NAPL), finite difference model designed for simulation of groundwater contamination by organic compounds, and remediation of groundwater contamination by the steam injection method. The model includes simultaneous flow of water, gas (steam) and organic phases, energy transport, temperature, pressure and composition dependent interphase partitioning, and dispersive transport within phases. An arbitrary number of organic and inorganic species may be included in the model. Densities and viscosities are functions of composition, pressure and temperature. Hysteresis in multiphase flow relationships is included. The technique of variable substitution is used to properly handle complex phase change behavior typical of multiphase flow and transport problems. The model includes several numerical options,
ranging from fully implicit with first order upstream weighting to implicit in pressure, explicit in saturations and concentrations (IMPESC) with third order upstream weighting.

D.2 Governing Equations

The equation for the movement of a species $a$ in a phase $\beta$ (Sleep and Sykes, 1993) is

$$\frac{\partial}{\partial t} \left( \phi S_\beta + K_{a\beta,d} \rho_\beta \right) \rho_\beta x_{a\beta} + \nabla \cdot \left( \rho_\beta x_{a\beta} q_\beta \right) + \nabla \cdot \left( \phi S_\beta J_{a\beta}^D \right) - \Gamma_{a\beta} - r_{a\beta} = 0 \quad \text{D.1}$$

where $\phi$ is porosity, $S_\beta$ is phase saturation, $K_{a\beta,d}$ is the linear adsorption coefficient, $\rho_\beta$ is bulk soil density, $\rho_\beta$ is phase molar density, $x_{a\beta}$ is species mole fraction, $q_\beta$ is the Darcy velocity vector, $J_{a\beta}^D$ is the dispersion flux vector, $r_{a\beta}$ represents inter-phase transfer of species $a$ to, or from, phase $\beta$, and $\Gamma_{a\beta}$ represents sinks and sources of species $a$ to phase $\beta$ due to injection or pumping (e.g. a PCE injection at a rate of 1 mole/h). The symbol "del", $\nabla$, is a vector with components $\partial/\partial x$, $\partial/\partial y$, and $\partial/\partial z$. The second term of Equation D.1 is a scalar of dot product of the vectors $\nabla$ and $q_\beta$. The third term of Equation D.1 is a scalar of dot product of the vectors $\nabla$ and $J_{a\beta}^D$. The species molar balance equation is obtained by summing the Equation D.1 for a species over the three phases:

$$\sum_{\beta=1}^{3} \left\{ \frac{\partial}{\partial t} \left[ \phi S_\beta + K_{a\beta,d} \rho_\beta \right] \rho_\beta x_{a\beta} + \nabla \cdot \left( \rho_\beta x_{a\beta} q_\beta \right) + \nabla \cdot \left( \phi S_\beta J_{a\beta}^D \right) - \Gamma_{a\beta} \right\} = 0 \quad \text{D.2}$$

where the $r_{a\beta}$'s sum to zero.

The energy balance equation in a multiphase system, where energy is transported with the flow of water, steam, and NAPL in the soil and as a result of temperature gradients in the soil, is given by

$$\sum_{\beta=1}^{3} \left\{ \frac{\partial}{\partial t} \left[ \phi S_\beta \rho_\beta U_\beta \right] + \nabla \cdot \left( \rho_\beta h_\beta \right) + \sum_{\alpha=1}^{\infty} \left[ \nabla \cdot \left( \phi S_\beta J_{a\alpha}^D h_{a\alpha} \right) - \Gamma_{a\beta} h_{a\beta} \right] ight\} + \frac{\partial}{\partial t} \left[(1 - \phi) U_r \rho_r \right] + \nabla \cdot (\zeta \nabla T) + \Gamma_{en} = 0 \quad \text{D.3}$$
where $U_\beta$ is the internal energy of phase $\beta$, $U_s$ is the internal energy of the soil, $h_\beta$ is the enthalpy of the $\beta$ phase, $h_{a\beta}$ is the enthalpy of the a component in the $\beta$ phase, $T$ is the temperature (K), $\zeta$ is the thermal conductivity of the combined soil and fluids, and $\Gamma_{en}$ represents sinks or sources of energy. The term of $\nabla \cdot (\zeta \nabla T)$ in Equation D.3 is a scalar of dot product of the vectors $\nabla$ and $\nabla T$.

The above balance equations, one for each species and one for energy, have to be solved simultaneously through numerical methods to describe the steam injection process in multiphase flow problems in porous media.

**D.3 Fluid Flow and Dispersion**

It is assumed that the flow obeys Darcy's law since the fluid velocity is generally small enough to be in the laminar range. The molar-averaged Darcy velocity vector for flow in a three-phase system is given by

$$q_\beta = -\frac{k k_{\beta}}{\mu_\beta} (\nabla p_\beta + \gamma_\beta g \nabla z)$$  \hspace{1cm} D.4

where $k$ is the intrinsic permeability tensor, $k_{\beta}$ is the relative permeability of phase $\beta$, $\mu_\beta$ is the viscosity of phase $\beta$, $p_\beta$ is the pressure of phase $\beta$, $g$ is gravitational acceleration, $\gamma_\beta$ is the mass density of phase $\beta$, and $z$ is elevation. Both $\nabla p_\beta$ and $\nabla z$ are vectors.

The hydrodynamic dispersion representing the spread of solute in the soil consists of molecular diffusion and mechanical dispersion. Molecular diffusion is due to the molecular scale mixing while mechanical dispersion is due to the mixing of fluids caused by mixing at the pore scale and larger scales. The dispersive molar flux vector $J_{a\beta}^D$ which is proportional to the concentration gradient, known as Fick's law, is given by:

$$J_{a\beta}^D = -\rho_\beta D_{a\beta} \cdot \nabla c_{a\beta}$$  \hspace{1cm} D.5
where vector $\nabla x_{\alpha\beta}$ is the concentration gradient and $D_{\alpha\beta}$ is the dispersion tensor defined (Bear, 1972) as:

$$D_{\alpha\beta} = \alpha_T |v_\beta| \delta_{ij} + (\alpha_L - \alpha_T) \frac{v_\beta v_{\beta j}}{|v_\beta|} + \delta_{ij} D_{\alpha\beta}^m \tau_3$$  \hspace{1cm} \text{(D.6)}$$

where $\alpha_L$ and $\alpha_T$ are the longitudinal and transverse dispersivities, respectively, representing the mechanical dispersion, $v_{\beta j}$ and $v_{\beta j}$ are the two components of the linear pore-water velocity, $v_\beta$, in perpendicular planes (where $v_\beta = q_\beta / \phi$), $\delta_{ij}$ is the Kronecker delta (which is a 3 X 3 matrix with "1" at diagonal positions and "0" at off-diagonal positions), $D_{\alpha\beta}^m$ is the molecular diffusion coefficient, and $\tau_3$ is the tortuosity factor.

The following constraints apply to Equation D.1, D.4, D.5, and D.6

$$S_w + S_a + S_o = 1.0$$  \hspace{1cm} \text{(D.7)}$$

$$\sum_{\alpha=1}^{n_c} x_{\alpha\beta} = 1.0$$  \hspace{1cm} \text{(D.8)}$$

where $n_c$ is the number of components, $S_w$, $S_a$, $S_o$ are the saturations of water, air (gas), and organic (NAPL) phases, respectively.

**D.4 Three-phase Capillary Pressure and Permeability**

The capillary pressures associated with interfaces between phases, as discussed in Chapter 3.1, are given by:

$$P_{caw} = P_a - P_w$$  \hspace{1cm} \text{(D.9)}$$

$$P_{cow} = P_o - P_w$$  \hspace{1cm} \text{(D.10)}$$

$$P_{cao} = P_a - P_o$$  \hspace{1cm} \text{(D.11)}$$

where $P_{caw}$ is the capillary pressure between the gas (air, steam, and organic vapor) and water phases, $P_{cow}$ is the capillary pressure between the organic (NAPL) and water phases, and $P_{cao}$ is the capillary pressure between the gas and organic phases.
The effective water (w), gas (a), and organic (o) saturations as defined in Chapter 3 (3.22 to 3.24) can be related to capillary pressures defined above through Van Genuchten formulae (3.20 and 3.21).

The relative permeabilities for the three-phase system are defined as:

\[ k_{p\beta} = \frac{k_\beta}{k} \quad \text{D.12} \]

where \( \beta = w, a, \) or o. \( k_\beta \) is the effective permeability of phase \( \beta \). Both \( k_{p\beta} \) and \( k_\beta \) are functions of saturation \( S_\beta \). \( k_{p\beta} \) can be calculated by the following formula proposed by Lenhard and Parker (1987) using the Van Genuchten equations

\[ k_{rw} = \overline{S}_w^{\frac{1}{n}} \left( 1 - \left( \frac{S_w}{\overline{S}_w} \right) \right)^{2} \quad \text{D.13} \]

\[ k_{ra} = C (1 - \overline{S}_a)^{\frac{1}{n}} \left( 1 - \overline{S}_a^{\frac{1}{n}} \right)^{2} \quad \text{D.14} \]

\[ k_{ro} = \left( \overline{S}_o - \overline{S}_w \right)^{\frac{1}{n}} \left( 1 - \overline{S}_w^{\frac{1}{n}} \right)^{2} \quad \text{D.15} \]

where \( C \) is the Klinkenberg factor that accounts for gas slippage and

\[ \overline{S}_i = \overline{S}_w + \overline{S}_o = \frac{S_w + S_o - S_{wr}}{1 - S_{wr}} \quad \text{D.16} \]

**D.5 Phase Equilibrium**

Henry's law states that the partitioning of an organic chemical between the gas and water phases is at a constant ratio termed Henry's constant, \( H \), while the inter-phase mass transfer of the chemical is at equilibrium. When temperatures and pressures are low and organic solubilities in the water phase are small, Henry's Law can be used to calculate the species mole fractions in water and organic phases:

\[ x_{aw} H = x_{ag} P_g = x_{ao} P^v_o \quad \text{D.17} \]

where \( P^v_o \) is the saturation vapor pressure of species \( o \). The \( x_{ag} \) is defined by Equation 2.4.
D.6 Gas and Liquid Viscosities

Gas phase viscosities for pure components, $\mu_{lg}$, may be calculated from the Golubev Method (Reid et al., 1977)

$$
\mu_{lg} = \begin{cases} 
\mu^*_c T_r^{0.965} & T_r < 1 \\
\mu^*_c T_r^{0.71 + 0.29/T_r} & T_r \geq 1 
\end{cases}
$$

D.18

where $\mu^*_c$ is the gas viscosity at the critical temperature, $T_c$, and a low pressure, and $T_r$ is the reduced temperature ($T/T_c$), $\mu^*_c$ is given by

$$
\mu^*_c = \frac{3.5 M^{1/2} P_c^{2/3}}{T_c^{1/6}}
$$

D.19

where $M$ is the molecular weight of the component. Viscosities of multi-component gas phases are calculated from pure component gas viscosity using the formula:

$$
\mu_g = \sum_{i=1}^{n_c} \sum_{j=1}^{n_c} x_{ij} \mu_{ig}
$$

D.20

where the interaction parameters, $\phi_{ij}$, are calculated using the Herning and Zipper approximation

$$
\phi_{ij} = \Phi_{ij} = \left( \frac{M_j}{M_i} \right)^{1/2}
$$

D.21

Pure component liquid viscosities may be approximated from the Van Velzen, Cardozo and Langenkamp Method (Reid et al., 1977):

$$
\log \mu_{il} = B \left( \frac{1}{T} - \frac{1}{T_0} \right)
$$

D.22

where $\mu_{il}$ is the liquid viscosity (cP), $T$ is the liquid temperature (K), and $B$ and $T_0$ are related to molecular structure. Liquid mixture viscosities are calculated from
Appendix

\[
\log \mu_\beta = \sum_{i=1}^{n_c} x_i \log \mu_{iL}
\]  \hspace{1cm} \text{(D.23)}

where \(n_c\) is the number of components in the liquid mixture.

The viscosities of steam condensate over the temperature range of 273.15 to 640 K are calculated by the saturated-steam-property functional correlation (Tortike and Ali, 1989):

\[
\mu_{sc} = -0.0123274 + 27.1038 / T - 23527.5 / T^2 + 1.01425 \times 10^7 / T^3
\]
\[-2.17342 \times 10^9 / T^4 + 1.86935 \times 10^{11} / T^5\]
\hspace{1cm} \text{(D.24)}

where \(\mu_{sc}\) is in Pa-s and T is the temperature in K.

The viscosities of steam vapor over the temperature range of 273.15 to 640 K are calculated by the saturated-steam-property functional correlation (Tortike and Ali, 1989):

\[
\mu_{sv} = -5.46807 \times 10^{-4} + 6.89490 \times 10^{-6} T - 3.39999 \times 10^{-8} T^2
\]
\[+ 8.298842 \times 10^{-11} T^3 - 9.97060 \times 10^{-14} T^4 + 4.71914 \times 10^{-17} T^5\]
\hspace{1cm} \text{(D.25)}

where \(\mu_{sv}\) is in Pa-s and T is the temperature in K.

D.7 Vapor Pressures

Pure component vapor pressures are calculated from the Antoine equation:

\[
\ln P_{vp} = A - \frac{B}{T+C}
\]  \hspace{1cm} \text{(D.26)}

where A, B, and C are empirical constants and T is the temperature (K).

D.8 Liquid and Gas Phase Diffusion Coefficients

The aqueous phase diffusion coefficient, \(D_{AW}\), was calculated using the Hayduk-Laudie correlation:
where $\mu_w$ is the water viscosity in cP, $V_A$ is the solute molar volume at the normal boiling point (cm$^3$/g-mol), and $D_{AW}$ is the binary diffusion coefficient at infinite dilution (cm$^2$/s). Rather than use Equation D.27 directly, the model requires the specification of the diffusion coefficient at reference pressure and temperature ($D_{AW}^{ref}$). $D_{AW}$ is then calculated from the ratio of the viscosities at reference and actual conditions:

$$\frac{D_{AW}}{D_{AW}^{ref}} = \left( \frac{\mu_w}{\mu_w^{ref}} \right)^{-1.14} \tag{D.28}$$

Gas phase diffusion coefficients are assumed to be a function of pressure and temperature according to the Fuller, Schettler, and Giddings method:

$$D_{AB} = 10^{-3} T^{1.75} \left[ \frac{M_A + M_B}{M_A M_B} \right]^{1/2} \frac{1}{P \left( \frac{\sum V}{M_A} + \sum V_{B} \right)} \tag{D.29}$$

where $T$ is the temperature (K), $P$ is pressure (atm), $M_A$ and $M_B$ are the molecular weights of A and B, and the $\Sigma V$ terms are determined from the structure of the molecules (Reid et al., 1977). If $D_{AB}$ is known at a reference pressure and temperature then the diffusion coefficient may be calculated at any other pressure, $P$, and temperature, $T$, by using Equation D.30

$$\frac{D_{AB}}{D_{AB}^{ref}} = \frac{T^{1.75} P_{ref}}{T_{ref}^{1.75} P} \tag{D.30}$$

D.9 Thermal Conductivities

Gas phase pure component thermal conductivities are calculated from reference values using the temperature correction (Reid et al., 1977):

$$\frac{\lambda_2}{\lambda_1} = \left( \frac{T_2}{T_1} \right)^{1.786} \tag{D.31}$$
Appendix

Mixture thermal conductivities are calculated from the Wassiljewa equation:

\[ \lambda_{pL} = \sum_{i=1}^{n} \frac{x_{ri} \lambda_i}{\sum_{j=1}^{n} x_{rj} A_{ij}} \]  \hspace{1cm} (D.32)

Where \( A_{ij} \) is given by the Lindsay and Bromley modification:

\[ A_{ij} = \frac{1}{4} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{3/4} \left( \frac{T + S_i}{T + S_j} \right) \right]^{-2} \]  \hspace{1cm} (D.33)

where \( T \) is the temperature (K), and \( S_i \) is the Sutherland constant, given by

\[ S_i = 1.5T_{bi} \]  \hspace{1cm} (D.34)

where \( T_{bi} \) is the normal boiling point of \( i \) (K). The interaction Sutherland constant \( S_{ij} \) is calculated from:

\[ S_{ij} = C_s (S_i S_j)^{1/2} \]  \hspace{1cm} (D.35)

where \( C_s \) is taken to be 0.73 if water is one of the constituent, and \( C_s \) is taken to be 1.09 for other pairs not involving water.

Liquid phase thermal conductivities (cal/cm-s-K) are calculated from the method of Robbins and Kingrea:

\[ \lambda_L = \frac{(88.0 - 4.94H)(10^{-3})(0.55)}{\Delta S^*} \left( \frac{0.55}{T_r} \right)^{N} C_p P_L^{4/3} \]  \hspace{1cm} (D.36)

where \( H \) and \( N \) are parameters given in Reid et al. (1977) for different compounds, \( C_p \) is the heat capacity (cal/g-mol-K), \( \Delta S^* = \Delta H_{vb}/T_b + R \ln(273/T_b) \) and \( \Delta H_{vb} \) is the molar heat of vaporization at the normal boiling point (cal/g-mol), and \( T_b \) is the normal boiling point (K). Mixture liquid thermal conductivities are calculated from the method of Li (Reid et al., 1977):

\[ \lambda_{BL} = \sum_i \sum_j \phi_i \phi_j \lambda_{ij} \]  \hspace{1cm} (D.37)

where
\[
\lambda_i = 2 \left( \frac{1}{\lambda_i} + \frac{1}{\lambda_j} \right)^{-1}
\]

and

\[
\phi_i = \frac{x_i V_i}{\sum_j x_j V_j}
\]

where \(V_i\) is the molar volume of pure liquid \(i\).

The thermal conductivities of steam condensate over the temperature range of 273.15 to 640 K are calculated from the saturated-steam-property functional correlation developed by Tortike and Ali (1989):

\[
k_{hsc} = 3.51153 - 0.0443602 T + 2.41233 \times 10^{-4} T^2 - 6.05099 \times 10^{-7} T^3 \\
+ 7.22766 \times 10^{-10} T^4 - 3.37136 \times 10^{-13} T^5
\]

Where \(k_{hsc}\) is in W/m-K and \(T\) is the temperature in K.

The thermal conductivities of steam vapor over the temperature range of 273.15 to 640 K are calculated from the saturated-steam-property functional correlation developed by Tortike and Ali (1989):

\[
k_{hsv} = -2.35787 + 0.0297429 T - 1.46888 \times 10^{-4} T^2 + 3.57767 \times 10^{-7} T^3 \\
- 4.29764 \times 10^{-10} T^4 + 2.04511 \times 10^{-13} T^5
\]

Where \(k_{hsv}\) is in W/m-K and \(T\) is the temperature in K.

**D.10 Steam Vapor and Condensate Enthalpy**

Tortike and Ali (1989) presented the following functional correlations of saturated-steam-property over the temperature range of 273.15 to 640 K. The specific enthalpy of steam vapor, \(h_{sv}\), is

\[
h_{sv} = -22026.9 + 365.317 T - 2.25837 T^2 + 0.00737420 T^3 \\
- 1.33437 \times 10^{-5} T^4 + 1.26913 \times 10^{-8} T^5 - 4.96880 \times 10^{-12} T^6
\]
where $h_{sv}$ is in kJ/kg and $T$ is the temperature in K.

The specific enthalpy of steam condensate, $h_{sc}$, is:

$$ h_{sc} = 23665.2 - 366.232 T + 2.26952 T^2 - 0.00730365 T^3 $$

$$ + 1.30241 \times 10^{-5} T^4 - 1.22103 \times 10^{-8} T^5 + 4.70878 \times 10^{-12} T^6 $$

where $h_{sc}$ is in kJ/kg and $T$ is the temperature in K.

Specific enthalpy of vaporization of steam vapor and condensate (latent heat), $L_v$, is

$$ L_v = (7184500 + 11048.6 T - 88.4050 T^2 $$

$$ + 0.162561 T^3 - 1.21377 \times 10^{-4} T^4)^{1/2} $$

where $L_v$ is in kJ/kg and $T$ is the temperature in K.

**D.11 Summary**

The governing equations comprising the species molar balance equations and energy balance equation are highly non-linear partial differential equations which have to be solved numerically. The fluid flow, dispersion, and phase partition obeying Darcy's law, Fick's law, and Henry's law, respectively, are incorporated into the governing equations. The capillary pressures, relative permeabilities, viscosities, vapor pressures, diffusion coefficients, thermal conductivities, and enthalpy are calculated through various experimental measurements, empirical formulae, and correlation functions.