

Remediation of Dense Nonaqueous Phase Liquids from Contaminated Subsurface Systems Using a Class of Brine-Based Remediation Technologies

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ABSTRACT

DEONA JOHNSON WRIGHT: Remediation of Dense Nonaqueous Phase Liquids from Contaminated Subsurface Systems Using a Class of Brine-Based Remediation Technologies. (Under the direction of Cass T. Miller)

Concerted efforts to remediate subsurface systems contaminated with dense non-aqueous phase liquids (DNAPLs) have achieved limited success when measured by comparing solute concentrations to drinking water quality standards. A novel treatment technology using a class of brine barrier remediation technologies (BBRTs) based on surfactant- and gravity-induced mobilization, dense brine containment and collection, and a vapor-phase extraction polishing step is utilized to remediate such systems. A series of investigations were conducted using one- and three-dimensional laboratory experiments, a field-scale experiment, and modeling to investigate the impact of BBRTs, the effectiveness of source-zone remediation, and to investigate the establishment, persistence, and rate of removal of a brine layer in a controlled system.

Laboratory and field-scale experiments are performed using the suggested methodology. It is shown that under certain conditions, less than 1% of the original DNAPL mass remained in the laboratory system. DNAPL mobilization and recovery in the field-scale experiment was relatively ineffective due in part to the low saturation levels of the DNAPL. The results show that essentially complete removal of a DNAPL is required to reach typical cleanup standards and that details of the morphology and topology of a DNAPL distribution, in addition to the saturation, play an important role in determining the rate of mass transfer.

The behavior of dense, viscous calcium bromide brine solutions used to remediate these experimental systems consists of a density of 1.7 times, and a corresponding viscosity of 6.3 times, that of water is obtained at a calcium bromide mass fraction of 0.53. The results show that a dense brine layer can be established, maintained, and recovered to a significant extent. Regions of unstable density profiles are shown to develop and persist in the field-scale experiment, which we attribute to regions of low hydraulic conductivity. The saturated-unsaturated, variable-density ground-water flow simulation code SUTRA is modified to describe the system of interest, and used to

compare simulations to experimental observations and to investigate certain unobserved aspects of these complex systems.

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LIST OF ABBREVIATIONS AND SYMBOLS

$^{\circ}\text{C}$	degrees Celsius
α	fitting parameter
α_l	longitudinal dispersivity
α_t	transverse dispersivity
α_{VG}	van Genuchten model parameter
β	fitting parameter
γ	density fitting parameter
γ_x	horizontal correlation length scale
γ_y	vertical correlation length scale
θ	volumetric fraction of the aqueous phase
μ	viscosity
ϕ	porosity
ρ	density
ρ_0	reference density
ω	mass fraction
ω_{min}	minimum mass fraction
A	viscosity fitting parameter
Aerosol AY	sodium diamyl sulfosuccinate
Aerosol OT	sodium dioctyl sulfosuccinate
A.F.S	American Foundry Society
a_{na}	specific interfacial area
B	viscosity fitting parameter
B1-B6	brine ports
BBI	brine barrier interface
BBRTs	brine-based remediation technologies
bgs	below ground surface
C	viscosity fitting parameter

C_{aq}	aqueous phase concentration
CaBr_2	calcium bromide
cm	centimeters
cm^3	cubic centimeters
CO_2	carbon dioxide
cP	centipoise
C_s	aqueous phase solubility
d_{50}	mean grain diameter
d_{60}/d_{10}	uniformity coefficient
DDI	distilled, deionized
D_h	hydrodynamic dispersion coefficient
D_m	effective molecular diffusion coefficient
DNAPL	dense nonaqueous phase liquid
DNTS	Dover National Test Site
DS	Dover sand
E1-E4	extraction ports
EPA	Environmental Protection Agency
E_v	volumetric extraction rate
E_m	mass extraction rate
F1-F3	permeability simulations
g	grams
GB	glass beads
H_2O	water
HPLC	high performance liquid chromatography
K_0	fitting parameter
kg	kilograms
k_l	mass transfer rate coefficient
K_l	mass transfer coefficient
K_s	hydraulic conductivity

L	liters
L1-L4	lower brine ports
ln	natural log
m	meters
M	DNAPL mass
m^2	square meters
M_0	initial DNAPL mass
MCLs	maximum contaminant levels
min	minute
ml	milliliter
MLS	multi-level samplers
mm	millimeters
mPa	millipascals
MS	mixed sand
N	Newtons
n_{VG}	van Genuchten model parameter
NAPL	nonaqueous phase liquid
ORO	Oil-Red-O
PCE	tetrachloroethylene
PV	pore volume
q	Darcy velocity
QS	quartz sand
s	seconds
SGSIM	sequential Gaussian simulation
Sh	Sherwood number
Sh'	modified Sherwood number
s_n	NAPL saturation
SRF	spatial random field
SUTRA	<i>Saturated-Unsaturated Transport</i>

t	time
T1-T3	dispersivity simulations
TCE	trichloroethylene
TDS	total dissolved solids
U.S.	United States
WG	Wagner sand

Chapter 1

Introduction

Groundwater is a vital water resource supplying 51% of the United States population's and 99% of the rural population's potable water supply. It serves 30% of industrial water needs and half of agricultural irrigation water needs (USEPA, 1990). However, the widespread production, transportation, utilization, and disposal of hazardous chemicals have created numerous sites of subsurface contamination jeopardizing groundwater supplies (Cohen and Mercer, 1993). Overuse and application of pesticides and fertilizers has led to penetration of these substances into the subsurface and contaminant infiltration of groundwater supplies (USEPA, 1993a, 1999). Spills and improper disposal of chemicals have resulted in leaks and seepage of hazardous chemicals into the subsurface at industrial sites (USEPA, 1999). Poor construction of landfills and sewer systems have further attributed to chemical and biological contamination of groundwater (USEPA, 1999).

Over 70,000 hazardous waste sites have been discovered in the United States. Of these sites, more than 1,500 have been identified and placed on the National Priority List, which consists of the nation's most serious sites of subsurface contamination (Kavanaugh et al., 2003; USEPA, 2004) and are referred to as Superfund sites. The most prevalent class of contaminants at these sites involves dense nonaqueous phase liquids (DNAPLs), such as chlorinated solvents (Cohen and Mercer, 1993; Fountain, 1998; NRC, 1994; Palmer and Fish, 1992; USEPA, 1993a). These DNAPLs penetrate the unsaturated zone and continue to migrate downward due to gravitational forces. They infiltrate the saturated zone by overcoming buoyancy forces and continue to migrate downward until an impermeable layer is reached, or the contaminant mass is distributed throughout the system due to trapping by capillary forces (Mercer and Cohen, 1990).

While hundreds of billions of dollars have been spent to remediate DNAPL contamination of subsurface environments, it remains a difficult and largely unsolved problem

and it is estimated that a similar amount more will be spent in the future (NRC, 1994, 1999). The remediation of sites contaminated with DNAPLs has proven to be an especially difficult problem due to the multiphase nature of these systems (Mercer and Cohen, 1990; Pankow and Cherry, 1996; Villaume, 1985), the heterogeneity of subsurface environments (Brusseau et al., 2000; Dekker and Abriola, 2000; Illangasekare et al., 1995a,b; Imhoff et al., 1995; Mayer and Miller, 1992a; Mercer and Cohen, 1990; Pankow and Cherry, 1996; Saenton et al., 2002; Schnarr et al., 1998; Waduge et al., 2004), the sensitivity of flow patterns to medium properties (Fu and Imhoff, 2002; Held and Illangasekare, 1995; Illangasekare et al., 1995a,b; Imhoff et al., 2003, 1995; Imhoff and Miller, 1996; Imhoff et al., 1996; Kueper and Frind, 1988; Kueper and Gerhard, 1995; Morrow and Songkran, 1981; Saenton et al., 2002; Zhang and Smith, 2001), the relatively slow rate of mass transfer of contaminants from entrapped DNAPLs to the gas and aqueous phases that naturally occur in subsurface environments (Geller and Hunt, 1993; Hunt et al., 1988a,b; Imhoff and Miller, 1999; Mayer and Miller, 1996; Miller et al., 1990; Pankow and Cherry, 1996; Powers et al., 1992; Roy et al., 1995), uncontrolled mobilization of DNAPLs that can contaminate previously uncontaminated areas (Kaslusky and Udell, 2002; Pennell et al., 1996; She and Sleep, 1999; Tiehm et al., 1997), and the high cost of implementing remediation technologies (NRC, 1994, 1999; USEPA, 2001).

1.1 Remedial Efforts

Efforts to remediate DNAPL-contaminated sites over the last two decades have led to the development of a variety of new technologies. Most of these technologies rely on converting the contaminant mass from a DNAPL phase to a more mobile phase. Using such an approach, the remediation method may be inefficient or ineffectual if the mass transfer process is slow. Because subsurface systems are highly heterogeneous with respect to the porous media's physical, chemical, and morphological properties, DNAPLs released to a subsurface environment tend to assume stagnant distributions that have a range of length scales and local saturations (Fatt, 1956; Hayden and Voice, 1993), with much of the mass trapped in DNAPL pools. The existence of long length scale, high-saturation DNAPL pools virtually guarantees that mass transfer processes will limit common remediation processes (Byers et al., 1994; Imhoff and Miller, 1999; Schulthess and McCarthy, 1990), such as pump-and-treat (Keely, 1989; Mackay and Cherry, 1989; Mercer and Cohen, 1990; NRC, 1994, 1997, 1999), vapor extraction (Ae-

lion and Kirtland, 2000; Cho et al., 1997; Corbin et al., 1994; Heron et al., 1998; Ji et al., 1993; Johnson et al., 2004; Kyte and Berry, 1975; Martin et al., 1991; Waduge et al., 2004), in situ biodegradation (Tiehm et al., 1997; Vayenas et al., 2002; Yang and McCarty, 2000), cosolvent flushing (Kibbey et al., 2002; Lunn and Kueper, 1999b; Pennell et al., 1996; Ramsburg and Pennell, 2002), and surfactant-enhanced dissolution (Dwarakanath et al., 1999; Dwarakanath and Pope, 2000; Pennell et al., 1994; Tiehm et al., 1997). Remediation of subsurface systems contaminated with DNAPLs continues to pose one of the biggest environmental challenges (NRC, 1994, 1999; Pankow and Cherry, 1996).

Active contaminant source-zone remediation can remove significant fractions of non-aqueous phase liquid (NAPL) mass from the subsurface (Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000; Schnarr et al., 1998). However, the endpoint of concern often is the effect of remediation efforts on contaminant concentration distributions in space and time (Kavanaugh et al., 2003; Stroo et al., 2000; USEPA, 2000). Clearly in the long-time limit, source-zone removal will be universally effective. However, the short-time limit, i.e., immediately after source-zone remediation is completed, is a much more stringent condition to control, but is usually the limit of greatest concern to stakeholders (Kavanaugh et al., 2003). Substantial reductions, often orders of magnitude, in contaminant concentrations and contaminant mass fluxes are necessary in the short-time limit in order for a technology to be deemed effective (Sale and McWhorter, 2001). Such extreme reductions in concentrations and mass fluxes of contaminants and their daughter products are especially difficult to achieve in heterogeneous porous medium systems (Mravik et al., 2003; Saenton et al., 2002). Many technologies that have removed large quantities of mass still fail to achieve drinking water standards (Brown et al., 1999; Fountain, 1998; Hirasaki et al., 1997; Jawitz et al., 2000; Londergan et al., 2001; USEPA, 2004). Therefore, it is important to assess the reduction in mass flux post-remediation to assess the benefits of remediation.

To overcome some of the limitations in remediation of DNAPL-contaminated systems, a novel class of methods was developed by Miller and co-workers (Hill et al., 2001; Miller et al., 2000) for efficiently remediating certain DNAPL-contaminated subsurface systems. This remediation approach is mobilization-based because it is believed that mobilization is needed to remediate DNAPL source zones efficiently. To accomplish mobilization, capillary forces that act to hold the DNAPL in the porous medium by increasing the aqueous phase density with the addition of a dense, viscous brine solution and/or decreasing the interfacial tension using a surfactant solution.

1.2 Research Objectives

Although laboratory results conducted by Miller and co-workers (Hill et al., 2001; Miller et al., 2000) are very promising, there are a number of issues that still need to be addressed in order to advance application of this technology: (1) enhancing brine-based remediation technologies (BBRTs) to approach near complete removal by increasing surfactant volumes or by adding an additional remediation step such as vapor extraction, (2) assessing removal as a function of increasing heterogeneity of the system and scale of the system, (3) analysis of changes in downgradient contaminant concentrations and flux after reductions in source zone mass, (4) developing approaches to optimize the choice and usage of surfactant and brine technologies, and (5) investigating the ability to inject and recover dense, viscous brine from subsurface environments.

The open issues are broad and there are years of research that remains to be done before a mature state of knowledge is achieved. Consequently, for this work the scope has been narrowed to the following specific aims:

1. to investigate the performance of a three-fluid-phase brine barrier technology on removal of chlorinated solvents in heterogeneous porous media systems;
2. to evaluate the extent and impact of source-zone removal of chlorinated solvents on contaminant concentration and flux; and,
3. to investigate dense, viscous brine behavior in heterogeneous porous medium systems.

1.3 Organization

Chapters 2 through 4 address the specific aims, respectively, related to the objectives listed in the previous section. Each of these chapters is a reproduction of manuscripts from individual papers, which have been published or submitted for publication. Chapter 2 describes experiments conducted using brine-based technologies and a three-fluid phase approach to achieve near complete removal of contaminant mass from heterogeneous porous medium laboratory systems. Chapter 3 investigates the extent and impact of source zone mass removal on downgradient contaminant concentrations and the factors that influence these concentrations. Chapter 4 demonstrates the ability to effectively establish, maintain, and recover brine from multiple scale subsurface systems. Chapter 5 concludes this research with a summary of findings from the previous

chapters and a discussion of open issues that require of further research. A bibliography of the manuscripts associated with Chapter 2 through Chapter 4 is listed as follows:

Chapter 2: Johnson, D.N., Pedit, J.A., and Miller, C.T. Efficient, Near-Complete Removal of DNAPL from Three-Dimensional, Heterogeneous Porous Media Using a Novel Combination of Treatment Technologies, *Environmental Science & Technology*, 38(19): 5149–5156.

Chapter 3: Wright, D. Johnson, Birak, P.S., Pedit, J.A., and Miller, C.T. Effectiveness of Source-Zone Remediation of DNAPL-Contaminated Subsurface Systems, *Journal of Environmental Engineering*, in print.

Chapter 4: Wright, D. Johnson, Pedit, J.A., Gasda, S.E., Farthing, M.W., Murphy, L.L., Knight, S.R., Brubaker, G.R., and Miller, C.T. Dense, Viscous Brine Behavior in Heterogeneous Porous Medium Systems, *Journal of Contaminant Hydrology*, in print.

Chapter 2

Efficient, Near-Complete Removal of DNAPL from Three-Dimensional, Heterogeneous Porous Media Using a Novel Combination of Treatment Strategies

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2.1 Introduction

The remediation of subsurface systems contaminated with DNAPLs has proven to be an extremely difficult problem—one that is far from solved despite significant efforts over the last two decades (Edwards et al., 1992; Hill et al., 2001; Hunt et al., 1988a,b; Kibbey et al., 2002; Lunn and Kueper, 1999b; Mercer and Cohen, 1990; Miller et al., 2000; Pennell et al., 1996; Ramsburg and Pennell, 2002; Renshaw et al., 1997; She and Sleep, 1999; Tiehm et al., 1997; USEPA, 1995, 2000; Vayenas et al., 2002; Yang and McCarty, 2000, 2002). These efforts have led to an improved understanding of the physics of transport phenomena in multiphase systems, including the reasons why DNAPL remediation is so difficult. Chief among these reasons is the heterogeneity of natural porous medium systems and the resultant complexity of DNAPL flow patterns and entrapment (Blunt, 1997; Hilpert et al., 2000; Hunt et al., 1988b; Lowry and Miller, 1995; Mayer and Miller, 1992b; Mercer and Cohen, 1990; Morrow and Songkran, 1981;

Pankow and Cherry, 1996; Pennell et al., 1996; Powers et al., 1992, 1996; Willson et al., 1999), mass transfer limitations (Hunt et al., 1988a,b; Kaslusky and Udell, 2002; Miller et al., 1990; Powers et al., 1992; Rao et al., 1997; She and Sleep, 1999; Yang and McCarty, 2000; Zhou and Rhue, 2000), and DNAPL dissolution instabilities (Imhoff et al., 1996; Mercer and Cohen, 1990).

Despite this improved understanding, there is not a promising course that can realistically be expected to solve this problem in the near future. One reason for this situation is that many technologies rely on mass transfer from the DNAPL to a mobile fluid phase. This approach requires long time scales for near-complete DNAPL removal because the mass transfer rates are slow (Hunt et al., 1988a,b; Kaslusky and Udell, 2002; Miller et al., 1990; Powers et al., 1992; Rao et al., 1997; She and Sleep, 1999; Yang and McCarty, 2000; Zhou and Rhue, 2000). Other technologies rely on mobilization of free phase DNAPL (Fu and Imhoff, 2002; Heron et al., 2002; Hill et al., 2001; Hofstee et al., 2003; Hunt et al., 1988a; Imhoff et al., 1995; Kaslusky and Udell, 2002; Kibbey et al., 2002; Lunn and Kueper, 1997, 1999a,b; Miller et al., 2000; Okuda et al., 1996; Oostrom et al., 1999; Pennell et al., 1996; Ramsburg and Pennell, 2002; Ramsburg et al., 2003; She and Sleep, 1999; Tiehm et al., 1997; Van Valkenburg and Annable, 2002; Yan et al., 2003). Unfortunately, the mobilized DNAPL may enter previously uncontaminated portions of the subsurface environment (Brandes and Farley, 1993; Imhoff et al., 1995; Kaslusky and Udell, 2002; Okuda et al., 1996; Pennell et al., 1993, 1994, 1996). Although the goal of density conversion technologies is to combat this problem, experiments with this approach have been limited to predominantly one- and two-dimensional studies in homogeneous systems or systems with lenses (Brandes and Farley, 1993; Hofstee et al., 2003; Kibbey et al., 2002; Lunn and Kueper, 1997, 1999a,b; Pennell et al., 1996; Ramsburg and Pennell, 2002; Ramsburg et al., 2003; Yan et al., 2003). Unexpected downward mobilization may still occur at a contaminated field site with density conversion technologies if surfactants are present (Lunn and Kueper, 1997; Pennell et al., 1996; Rao et al., 1997; Van Valkenburg and Annable, 2002).

Heterogeneity and flow instabilities limited DNAPL recovery in a field investigation using a density conversion technology (Rao et al., 1997) and they may similarly limit any technology's ability to recover DNAPL. Natural systems are heterogeneous and this is at the root of the problem; however, little work has been done to investigate DNAPL remediation technologies in heterogeneous, three-dimensional laboratory systems (Hill et al., 2001; Oostrom et al., 1999). While such studies are extremely difficult and time

consuming to perform, they are needed to aid the rate of advancement of more effective DNAPL removal technologies.

Relatively large fractions of DNAPL must be removed from most contaminated systems to reach health-based standards (Mercer and Cohen, 1990; Pankow and Cherry, 1996). However, no laboratory study is known of that has demonstrated a high fraction of DNAPL removal in a realistic heterogeneous three-dimensional system using any technology. Considerable effort along these lines seems both highly challenging and necessary for resolution of this important problem.

Previously, several related technologies based upon the use of dense brines and surfactants to effect DNAPL mobilization and recovery in one-, two-, and three-dimensional systems were investigated (Hill et al., 2001; Miller et al., 2000). While the results have been promising, it has also noted that many open issues remain for this class of problem. Three-dimensional experiments of this sort, while unique in the research community, have been preliminary in nature and no technology capable of efficiently achieving anything approaching near-complete removal of DNAPL from heterogeneous, three-dimensional systems has been found.

The overall goal of this work is to develop and demonstrate a technology that is capable of efficient, near-complete removal of DNAPL from three-dimensional heterogeneous porous medium systems. The specific objectives of this work are: (1) to investigate DNAPL entrapment and removal in heterogeneous, three-dimensional systems; (2) to evolve a technology that is capable of near complete removal of DNAPL; (3) to demonstrate that near complete removal of DNAPL from a realistic porous medium system is possible; and (4) to assess open issues that must be resolved before a mature DNAPL remediation technology is available.

2.2 Approach

2.2.1 Conceptual Model

To meet the objectives of this work, a novel DNAPL removal technology is proposed based upon the following components: surfactant- and gravity-motivated DNAPL mobilization, a dense brine containment strategy, and vapor-phase extraction to remove residual DNAPL remaining after mobilization. It is hypothesized that this strategy may be effective in achieving a high fraction of removal and be efficient based upon previous results with surfactant-brine methods (Hill et al., 2001; Miller et al., 2000)

and the observation that the residual DNAPL remaining after such treatment has a relatively high specific DNAPL-gas phase interfacial area, which should lead to efficient vapor-phase extraction.

Because of the dominant importance of dimensionality and heterogeneity on remediation of natural systems and the scarcity of such controlled laboratory investigations, the studies are restricted to a heterogeneous, three-dimensional system. Because such studies are difficult to perform, the investigations are restricted to a single realization of a random field. A brief overview of the experimental methods follows, with details given in subsequent sections.

Each experiment was conducted in a three-dimensional cell that was packed with uncontaminated sands. DNAPL was injected into the initially water-saturated system. A dense brine barrier was established beneath the contaminated zone by injecting brine into the bottom corners of the cell. A downward surfactant flush was then performed to reduce the interfacial tension between the nonwetting and wetting phases. Reducing the interfacial tension promoted downward mobilization of the DNAPL. Further mobilization was achieved by draining the system to reduce buoyancy forces (Hill et al., 2001; Miller et al., 2000). In some experiments, an attempt was made to remove residual DNAPL by vapor-phase extraction.

2.2.2 Materials

The three-dimensional cell used in these experiments, as depicted in Figure 2.1, was a glass container fitted with an aluminum lid. The glass container was 22.5-cm long, 16.5-cm wide, and 24-cm high. Glass tubing was used to inject brine into the four bottom corners of the cell. Glass coated needles were used to inject DNAPL and to extract effluent.

The porous media in this work consisted of six quartz sands: Accusands A12/20, A20/30, A30/40, and A40/50; American Foundry Society (AFS) Silica 50/70; and United States (U.S.) Silica F-125. The relevant physical properties of these sands are listed in Table 2.1.

The fluids used in these experiments were distilled, deionized (DDI) water, trichloroethylene (TCE) as the DNAPL, a surfactant flushing solution, and a dense brine made of a calcium bromide (CaBr_2) solution. The properties of these solutions are listed in Table 2.2. The brine was chosen based on its density, viscosity, and low health risk compared to other suitable brines. The CaBr_2 solution has a density (1.75 ± 0.01

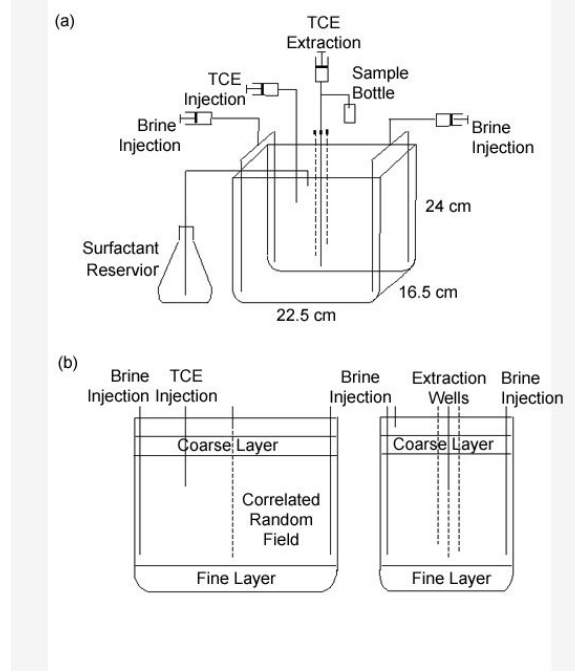


Figure 2.1: Three-dimensional experimental apparatus; (a) Cell schematic for surfactant flushing and TCE extraction and (b) layout of front and side of glass cell.

g/cm^3) greater than the density of TCE ($1.4639 \pm 0.0002 \text{ g/cm}^3$), which is necessary for the brine to form an effective barrier against downward migration of TCE. The brine's viscosity was $6.652 \pm 0.033 \text{ mPa}\cdot\text{s}$, as measured by a Haake falling ball viscometer (www.haake.com). The brine's viscosity relative to water's viscosity indicates that the brine will spread slowly in the subsurface and allow for the recovery of a large percentage of brine solution through hydraulic control (Bond, 2000).

The TCE solution was prepared using high pressure liquid chromatography (HPLC)-grade TCE, ^{14}C -labeled TCE, and 0.01% by weight Oil-Red-O (ORO), a certified biological stain (www.sigma-aldrich.com). The red stain made it possible to observe the TCE during the experiments. The density of the TCE solution was previously determined to be $1.4639 \pm 0.0002 \text{ g/cm}^3$ at 20°C (Hill et al., 2001; Miller et al., 2000). The viscosity of the TCE was $0.577 \pm 0.004 \text{ mPa}\cdot\text{s}$ (Lide, 1997).

The surfactant solution was prepared by dissolving 0.5% by weight each of sodium diamyl sulfosuccinate (Aerosol AY) and sodium dioctyl sulfosuccinate (Aerosol OT) into DDI water. Aerosol AY and Aerosol OT were both from Cytek (www.cytex.com). Three drops of green food coloring were added to each liter of surfactant solution so it could be seen during the experiments. Interfacial tension between TCE and surfactant

Table 2.1: Porous media properties for TCE laboratory cells.

Property	Accusand A12/20 (Schroth et al., 1996)	Accusand A20/30 (Schroth et al., 1996)	Accusand A30/40 (Schroth et al., 1996)	Accusand A40/50 (Schroth et al., 1996)	AFS Silica 50/70	U.S. Silica F-125
d_{50} (mm)	1.105 ± 0.014	0.713 ± 0.023	0.532 ± 0.003	0.359 ± 0.010	0.256	0.108
Uniformity Coefficient (d_{60}/d_{10})	1.231 ± 0.043	1.190 ± 0.028	1.207 ± 0.008	1.200 ± 0.018	1.207	1.753
Particle Density (g/cc)	2.665	2.664	2.665	2.663	2.664	2.653
Hydraulic Conductivity (cm/s)	0.503 ± 0.017	0.250 ± 0.0052	0.149 ± 0.0052	0.0722 ± 0.0018	0.00966	0.00210
Air Entry Pressure (cm H ₂ O)	5.42	8.66	13.03	19.37	35.00	80.2

Table 2.2: Physical properties of the fluids for TCE laboratory cells.

Property	CaBr ₂ Solution	TCE w/ORO	1% Aerosol AY/OT
Composition (by mass)	55.7% CaBr ₂ , 44.3% H ₂ O	99.99% TCE, 0.01% ORO	1% Aerosol AY/OT, 99% H ₂ O
density at 20°C (g/cm ³)	1.75 $\pm$ 0.01	1.4639 $\pm$ 0.0002	0.9987 $\pm$ 0.0002
viscosity at 20°C (mPa·s)	6.652 $\pm$ 0.033	0.577 $\pm$ 0.004 (Lide, 1997)	0.989 $\pm$ 0.007 at 26°C (Hall, 1997)

was previously determined to be $1.40 \times 10^{-3} \pm 0.03 \times 10^{-3}$ N/m, and the critical micelle concentration of the surfactant was determined to be 0.233% by weight (Hill et al., 2001). The density of the surfactant was 0.9987 ± 0.0002 g/cm³ (Hill et al., 2001).

2.2.3 Three-Dimensional Experiments

The cell was packed with sands in three sections: (1) a fine sand at the bottom of the cell, (2) a 14-layer heterogeneous packing based on a correlated random field model in the middle of the cell, and (3) a coarse sand layer on top of the random field. The bottom 4 cm of the cell was filled with fine sand (U.S. Silica F-125). The relatively high entry pressure of this homogeneous layer promoted TCE pool formation on top of this

layer. The 14 layers above the fine sand layer were packed heterogeneously based on an indicator random field model assuming anisotropic exponential covariance conditions and a log normal particle size distribution (Christakos, 1992b; Deutsch and Journel, 1992). Each layer was 1-cm thick and comprised of cubes of homogeneous sands and of lengths and widths of 1.5 cm. Correlation lengths of 7.5 and 2.5 cm for the horizontal and vertical planes, respectively, were used to match the scale of the experiments. The mean and standard deviation were $-0.698 \ln(\text{mm})$ and 0.4, respectively. The relatively narrow distribution was used so that the vast majority (98.5%) of the model-generated particle diameters fell within the range of sands used in the experiments. The final layer above the random field consisted of coarse sand (Accusand A12/20). The packing was consistent for all experiments.

Needles and glass tubing were inserted into the packed cell, and the system was sealed with a gasket-lined aluminum lid. The cell was then vibrated to consolidate the media, confirmed to be air-tight, flushed with carbon dioxide (CO_2) gas, and lastly saturated and flushed with deaired DDI water in an upwards-flow manner. Following complete saturation, the injection of water was halted and a syringe pump was used to inject approximately 104 ml of TCE into the center of the tenth layer from the bottom of the random field at a rate of 0.15 ml/min. This volume of TCE was sufficient to result in a TCE pool on top of the low permeability layer at the bottom of the cell. Once injection was complete, the system was undisturbed for 12 hours to allow the fluids to redistribute to a quasi-static distribution.

Syringe pumps were then used to inject brine into the cell through the four bottom corner ports at a combined rate of 2 ml/min. The addition of brine caused the water level to rise above the sand's surface. The water above the sand's surface was extracted from the cell and its dissolved TCE content quantified. The brine flow rate was reduced to 0.25 ml/min once a brine barrier was established above the bottom fine sand layer. The reduced brine flow rate helped maintain the brine layer during the surfactant flush and dewatering of the system.

Once the brine barrier was established, surfactant was pooled above the top layer of coarse sand. The surfactant was flushed downward through the system by extracting the remediation stream from the bottom of the random field. The volume of surfactant flushed through the system increased with subsequent experiments to increase the amount of TCE recovered through dissolution. Actual volumes were 1.8, 2.6, and 5.3 pore volumes (PVs), respectively, as shown in Table 2.3. A PV is defined here as the volume of pore space over which the majority of the contaminant existed. TCE was

Table 2.3: Summary of Experimental Results for TCE Recovery.

	TCE Injected (ml)	PV (ml)	Surfactant (PV)	Well Recovery (%)	Vapor Recovery (%)	Porous Media Recovery (%)	Total Mass Balance (%)
Experiment #1	104.3	1326	1.8	76.5	n/a	14.7	91.2
Experiment #2	103.3	1471	2.6	83.5	5.7	1.0	90.2
Experiment #3	103.1	1379	5.3	86.2	8.2	0.4	94.8

injected into the tenth layer from the bottom of the random field, and it pooled on top of the bottom fine sand layer, so a PV was taken to be the pore space volume of the bottom 10 layers of the random field.

For the first and second experiments, a syringe pump was used to extract the remediation stream through a single needle in the bottom layer of the random field. The extraction setup was modified for the third experiment. The remediation stream was extracted from needles in each of the bottom three layers of the random field using a stepped approach. Extraction began in the third layer from the bottom of the random field and continued until approximately 1.5 PVs had been extracted from the system. Extraction was then switched to the second layer from the bottom of the random field until an additional PV had been removed. Extraction was then switched to the bottom layer of the random field for the remainder of the experiment. The motivation for this approach was to determine if DNAPL recovery could be improved by minimizing the amount of mobilized DNAPL that reached the bottom layer of the random field.

The remediation stream from all experiments was extracted from the cell at a rate of 2 ml/min into a 50-ml air-tight glass syringe. The contents of the syringe was periodically emptied into glass sample jars. Extraction continued until the syringe pump withdrew more gas than liquid from the system. At this point, the system was partially saturated and in a state conducive to vapor-phase extraction of residual DNAPL.

The first experiment was stopped after the dewatering stage in order to determine the amount of DNAPL remaining in the system. An attempt was made to recover residual DNAPL by vapor-phase extraction after the dewatering stage in the second and third experiments. The brine ports were used to flush nitrogen gas through the system. To prepare the cell for vapor-phase extraction, the connectors linking the side

brine ports were removed and two-way valves were attached to the tubing from each brine port. The two-way valves were used to control the influent and effluent locations of the nitrogen gas. A flow meter was used to inject nitrogen gas at 50 ml/min into the porous medium through one port. The effluent from the vapor-phase extraction process was collected from an adjacent or opposing port. The location of the influent and effluent ports was varied such that all possible combinations were used. Effluent from the cell flowed through a two-stage condenser in an attempt to collect and quantify the DNAPL leaving the system. The first stage of the condenser contained ice water, and its temperature was maintained between 0°C and 1°C by periodic additions of ice. The second stage contained methanol, and its temperature was maintained at approximately -40°C by periodic additions of liquid nitrogen. The vapor-phase extraction stage was stopped when DNAPL was no longer being condensed out of the effluent stream.

The amount of DNAPL remaining in the system was determined by extracting the DNAPL from the porous medium at the end of each experiment (Hill et al., 2001). To provide some vertical resolution of the DNAPL's distribution, the porous medium was collected from the cell one or two layers at a time with an aluminum scoop and placed in glass sample jars.

2.2.4 Analytical Methods

The analytical method for quantifying TCE was similar to the scintillation method of Hill et al. (2001). The liquid samples from the experiments contained aqueous and nonaqueous phases. The porous medium samples also contained sand. The aqueous phase of the samples contained dissolved TCE, CaBr_2 , and surfactant. The nonaqueous phase was predominantly TCE. A known amount of hexane was added to each sample to extract TCE from the aqueous phase into the hexane-TCE organic phase. Three milliliters of the organic phase of each extracted sample was combined with 10 ml of ScintiSafe (www.fishersci.com) scintillation cocktail and the resultant samples counted on a Packard Liquid Scintillation Analyzer Model 1900TR (www.packardinst.com).

Extracted samples from the effluent, condensers, porous media, and the syringe and tubing used for TCE injection were analyzed. The TCE mass recovered from each remediation process was determined, and a material balance was used to determine the amount of TCE remaining in the system and/or that which was lost.

2.2.5 Visualization Methods

Images of one face of the three-dimensional cell were captured every 20 minutes during the experiments. The ORO dye added to the TCE made it possible to see the TCE on the face of the cell. However, the dye is not dissolved or volatilized in the same manner as the TCE so the amount or intensity of the dye is not an indicator of the amount of TCE remaining.

2.3 Results

The experimental conditions and results of the three experiments are summarized in Table 2.3. Table 2.3 lists the volume of TCE injected, PV of the contaminated zone, volume of the surfactant flush, percent of the injected TCE recovered during the well and vapor-phase extraction phases, percent of the injected TCE recovered from the porous medium at the end of each experiment, and the overall TCE mass balance. Experiment #1 used only a surfactant flush to recover TCE. Experiment #2 used a surfactant flush followed by vapor-phase extraction. Experiment #3 used a stepped approach during the surfactant flush followed by vapor-phase extraction.

Images representative of each phase of Experiment #2 are shown in Figure 2.2. The images in Figure 2.2 are from one face of the cell and show (a) initial water-saturated conditions, (b) completion of TCE injection with pooling evident in the bottom layers of the random field, (c) establishment of a brine barrier at the bottom of the cell, (d) surfactant breakthrough with downward TCE mobilization evident midway through the surfactant flush, (e) system prior to dewatering, and (f) system partially saturated prior to vapor-phase extraction. Figure 2.2(b) shows how TCE pooled in the two coarsest sands (Accusands A12/20 and A20/30) due to their low entry pressures. Figure 2.2(d) and other images acquired during the surfactant flush show that TCE preferentially migrated downward through the coarser sands after interfacial tension was reduced. Figure 2.2(e) shows evidence that lateral spreading of TCE into finer sands occurred towards the end of the surfactant flush. Inspection of the images recorded after the dewatering step showed that the TCE remaining in the system was in the form of residual and discontinuous thin layers at the level of the extraction well. Images from the other experiments are similar to those in Figure 2.2 and video files from all three experiments are available through the Supporting Information.

Figure 2.3 shows the cumulative TCE recovery during the surfactant flush as a

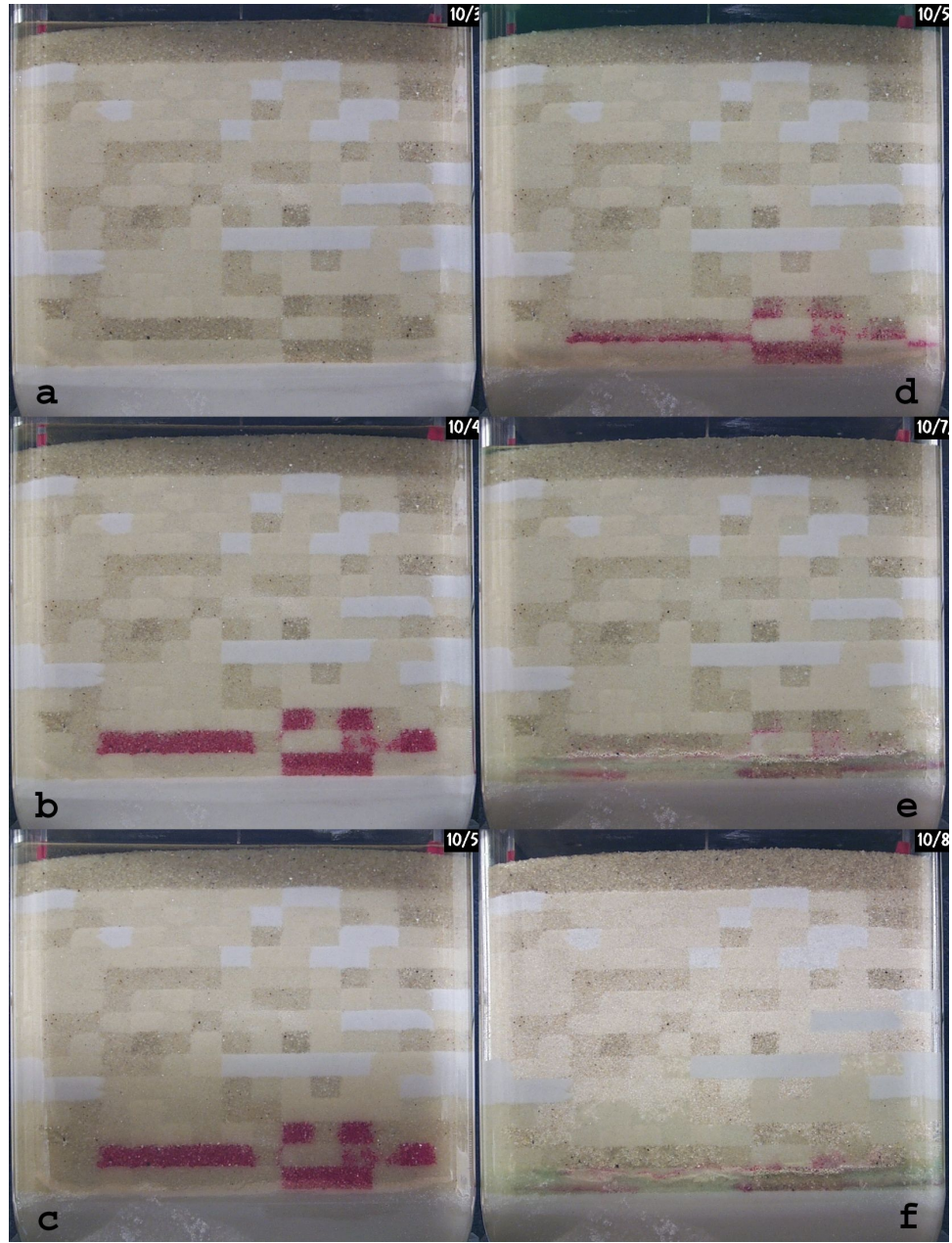


Figure 2.2: Photos depicting Experiment #2: (a) the initial saturated conditions, (b) completion of TCE injection, (c) establishment of a brine barrier at the bottom of the cell, (d) midway through the surfactant flush, (e) the cell prior to dewatering, and (f) the dewatered cell.

function of the volume of fluid extracted from the system. Note that the fluid extracted from the system includes some of the initial water used to saturate the cell, injected TCE, initial brine injected to form the brine barrier, surfactant, and brine injected to maintain the brine barrier level during the surfactant flush. The various fluid sources

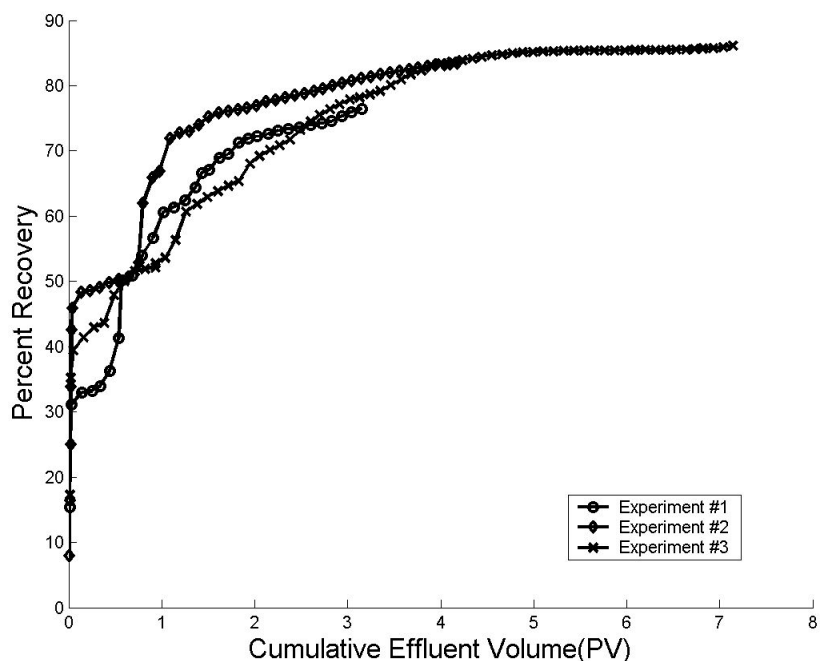


Figure 2.3: Cumulative TCE recovery from extraction well(s)

account for the difference in PVs of surfactant indicated in Table 2.3 and total PVs extracted from the system shown in Figure 2.3.

Figure 2.3 shows that a large fraction (32% to 48%) of the injected TCE was easily recovered at the beginning of the well extraction phase of each experiment. This rapid recovery occurred because the extraction point was located in the large TCE pool in the lower layers of the random field. The variation in initial recovery demonstrates how small variations in the sand packing changed the connectivity of the initial TCE pool. The TCE recovery rate slowed after the initial rapid recovery until the downward surfactant flush reached residual TCE in the middle layers of the random field at about 0.6 to 0.8 PVs. At this point the TCE recovery rate increased as surfactant breakthrough lowered interfacial tension and promoted downward mobilization of residual TCE. DNAPL was evident in the effluent stream until about 2 PVs in Experiments #1 and #2, and about 4 PVs in Experiment #3. TCE recovery after this point and before final dewatering was primarily through dissolution. DNAPL was also evident in the effluent stream in the samples collected at the end of the dewatering stage, and this final DNAPL mobilization can be attributed to a reduction in buoyancy.

Based on the recovery results shown in Table 2.3 and Figure 2.3, increasing the

volume of the amount of surfactant flush increased TCE recovery in Experiment #1 compared to previous work (Hill et al., 2001) as well as in subsequent experiments in this work. Increasing the volume of the surfactant flush increased the amount of desaturation during the dewatering stage. Increased desaturation is beneficial because buoyancy forces are reduced and additional DNAPL mobilization may occur. Well extraction was followed by vapor-phase extraction in Experiments #2 and #3, and the effectiveness of vapor-phase extraction is increased under less saturated conditions (Domenico and Schwartz, 1998; USEPA, 1996). Hence, the additional surfactant used to increase dissolution also assisted in further desaturation of the medium and possibly led to increased efficiency of the vapor-phase extraction stage.

Surfactant precipitated out of solution near the level of the extraction well. This occurred because the solubility of the surfactant was reduced by the brine. These particles formed after surfactant breakthrough, and the volume of particles increased with the volume of surfactant. These particles can potentially lead to pore clogging as well as decreases in hydraulic conductivity.

Experiment #3 had three extraction wells instead of one, each in a different layer of the random field. By introducing surfactant and removing the pool formed at the third and second layers above the bottom fine sand layer, the mass of TCE left to migrate further downward was minimized. However, this does not suggest that the mass of residual remaining using the multilevel extraction approach was less than the mass of residual remaining using one well. Some residual was entrapped in the fine regions in the second and third layers as well as in the first layer. This entrapment is less favorable and may have led to more residual remaining in the system.

The addition of vapor-phase extraction to the remediation scheme in Experiments #2 and #3 increased the recovery of TCE by about 5–8% (Table 2.3). However, tests of the condenser system showed that its efficiency was approximately 85% when no water was present. Therefore, approximately 6–9% was recovered during vapor-phase extraction. A gas leak was detected during vapor-phase extraction in Experiment #2. This leak may explain why TCE recovery during vapor-phase extraction for Experiment #2 was lower than for Experiment #3, and why Experiment #2 had the lowest total TCE recovery.

Figure 2.4 shows the vertical distribution of TCE in the porous medium at the end of each experiment. Recovery results are given in terms of percent TCE saturation. Although the percent TCE saturation is accurate, the distribution with depth is approximate due to the technique used to remove the porous media from the cell.

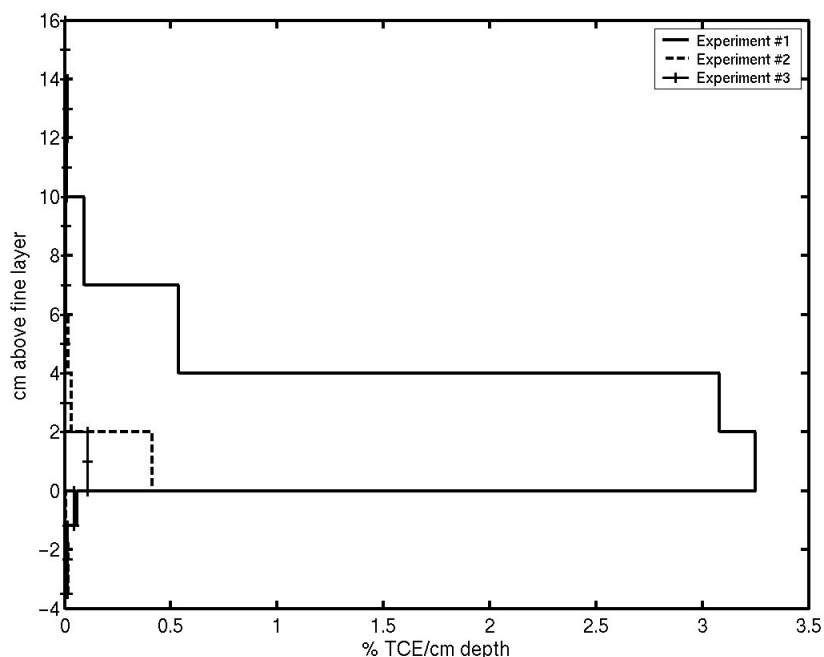


Figure 2.4: Approximate TCE profile at the end of experiments based on porous media extractions.

Therefore, this figure serves primarily to demonstrate how the TCE remaining in the system after well and vapor-phase extraction was approximately distributed as well as how the remaining TCE changed with the addition of vapor-phase extraction to the remediation scheme.

The amount of TCE in the system at the end of each experiment was 14.7% in the absence of vapor-phase extraction and 0.4–1% in the presence of vapor-phase extraction (Table 2.3). Figure 2.4 shows that most of the TCE was distributed over the bottom 4 cm or four layers of the random field in the absence of vapor-phase extraction and over the bottom two layers in the presence of vapor-phase extraction. The impact of vapor-phase extraction on residual recovery is also evident from this figure. Not only was the distribution of mass decreased but also the amount of mass in the overall system.

2.4 Discussion

The first objective of this work was to investigate DNAPL entrapment and removal in heterogeneous, three-dimensional systems. As previously noted, this has received

scarce attention in the literature. This is for good reason, since such experiments are difficult and time consuming to perform. It is essential to conduct such experiments and to continue to work toward systems that mimic a wide range of field conditions.

Images from the experiments show that DNAPL movement and entrapment were strongly affected by heterogeneity in the porous media. This is consistent with previous detailed experiments conducted in the field (Poulsen and Kueper, 1992), and with simulations performed for such systems. Based upon these observations and previous observations, it is expected that the complexity of the DNAPL flow and entrapment will increase as the heterogeneity of the media increases. Evidence of this can be noted from experiments by examining the irregular DNAPL distribution patterns on each of the four exposed faces of the three-dimensional cells. Given this complexity and the resultant complexity of the flow patterns for any flushing technology through such a system, much is to be learned about the relationship between media heterogeneity, entrapment, and remediation. Roughly 85% removal is obtainable at the level of heterogeneity investigated using a combination of a brine-barrier and surfactant/gravity mobilization strategy. However, there is a point at which mass transfer limitations led to a rapid decrease in the rate at which DNAPL was removed from the system by surfactant flushing.

The second objective of this work was to develop a technology capable of near complete removal of DNAPL. To meet this objective, a vapor-phase extraction step was added to the remediation approach taken in previous work (Hill et al., 2001; Miller et al., 2000). This notion was based upon the observation that the surfactant flushing and gravity drainage step of the brine-containment remediation method results in an increased relative interfacial area between the DNAPL and the vapor phase. It is hypothesized that the combined result of mobilization via control of the capillary and gravity forces, containment by the brine barrier, and polishing via DNAPL-vapor phase extraction might accomplish the objective of efficient near-complete removal.

The third objective of demonstration of near complete removal of DNAPL from a realistic porous medium was accomplished through the laboratory experiments performed and documented. Vapor-phase extraction was shown to be effective in removing the remaining residual DNAPL to levels of less than 1% of the original entrapped DNAPL mass. This is the first such laboratory demonstration of DNAPL removals approaching this level for any three-dimensional laboratory system; in addition, removals were accomplished for a system comprised of a correlated random field to mimic realistic heterogeneities. While not the final word, these results are very encouraging.

The fourth objective was to assess open issues remaining before a mature DNAPL remediation technology is available. There are many such relevant issues and that considerable work remains before a mature technology can exist. The following considerations in this list as related to the class of technologies investigated in this work are included, but some of these concerns are also more broadly applicable to the general field of research:

1. *Effects of increased heterogeneity.* Real natural systems can be significantly more heterogeneous than the systems investigated in this work. Clearly, removal of high fractions of DNAPL in such systems might be much less efficient than the results obtained in this work. Such experiments are very time consuming and difficult, but they are important to do in order to make realistic assessments of the performance of any technology under such conditions in the field.
2. *Effect of remediation.* The chief end point for most DNAPL sites is the resulting aqueous phase concentration after remediation, which is an area of significant recent investigation. Experiments should be performed to examine the impact of DNAPL remediation strategies on this endpoint for realistic conditions.
3. *Brine recovery.* The class of strategies used in this work requires the addition of a dense brine to control the movement of DNAPL once it is mobilized. Ideally, a large fraction of this brine should be recovered. The complexity of the systems of concern make the assessment of the brine recovery process in heterogeneous media an open question. Preliminary work has shown this brine can be recovered efficiently (Bond, 2000), but the final word is not yet written since all aspects of these systems were not resolved with a high resolution simulator and no experiments for these systems have been performed.
4. *Larger-scale experimentation.* Remediation technologies often proceed ahead of the resolution of all open scientific questions. This is natural given the complexity of many environmental systems and the need to advance solutions in a timely manner. The standard approach for such cases is to perform a series of successively larger and more realistic experiments. While this can never provide a level of certainty of performance for conditions not specifically analyzed, such activities do increase the empirical knowledge base, give guidance for field-scale applications, and provide additional data to aid the testing of models of such systems that may eventually mature.

Resolution of these open issues for the class of technologies considered in this work will require considerable additional effort. However, such steps should be anticipated for any technology envisioned to remediate DNAPLs. This class of problems has not been resolved for very good reason: they are among the most challenging class of problems facing the environmental sciences community.

2.5 Supporting Information Available

Movies depicting the experiments are available at

http://www.unc.edu/~nomad12/density_motivated.html.

Chapter 3

Effectiveness of Source-Zone Remediation of DNAPL-Contaminated Subsurface Systems

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3.1 Introduction

For more than 25 years, concerted efforts have been made to remediate contaminated subsurface systems. Despite these efforts, few sites have achieved cleanup to drinking water standards, such as the U.S. EPA's MCLs (NRC, 2005). Achievement of maximum contaminant levels (MCLs) is difficult for sites in which contamination has been caused by the release of DNAPL (ITRC, 2002; Kavanaugh et al., 2003; McGuire et al., 2006; NRC, 2005). DNAPL contamination is especially problematic because the contaminant species can pose health concerns at relatively low concentrations, yet the contaminants slowly degrade and are long-lived in the environment (USEPA, 1993b).

The typical pattern of DNAPL contamination is now well understood (NRC, 2005). The release of a DNAPL leads typically to vertical movement below the water table and the establishment of a source zone. The source zone consists of isolated DNAPL residual on the spatial scale of less than 10 pore diameters, and high saturation (e.g., 20%), longer length-scale features that may have a length scale on the order of meters. The DNAPL usually becomes immobile in a relatively short period of time after a release, forming a near-stationary state. As water flows through the contaminated area, the DNAPL dissolves and contaminants spread down-gradient of the source zone. These

general trends have led to the classification of contaminated systems into a source-zone region where the DNAPL is present and a plume region where the contaminant has been transported following dissolution into the water phase. The distribution of mass between a DNAPL source zone and plume zone depends upon many factors, including the length scale of the source zone, the velocity of the aqueous phase, the solubility of the DNAPL constituents of concern, and the age of the spill. For some sites, the majority of the DNAPL mass will be contained in source zone, while for older sites having permeable media and a relatively short length-scale source zone, the majority of the mass originally present in the DNAPL source zone may have already been removed from the source zone.

Remediation of contaminated subsurface systems has frequently been aimed at restoring groundwater quality to levels approaching the standards for drinking water quality. There is near universal agreement that pump-and-treat methods are inefficient for DNAPL removal and cannot be expected to reduce contaminant levels to typical cleanup targets in what most people would consider a reasonable length of time (Kavanaugh et al., 2003; Keely, 1991; Mackay and Cherry, 1989; Mercer and Cohen, 1990; NRC, 1994, 1997, 2005). At DNAPL contaminated sites, any chance for achieving such groundwater standards in a relatively short period of time, say less than a few years, is typically only possible after using more active source-zone remediation (USEPA, 1993b). Unfortunately, efforts to remediate DNAPL source zones have often failed to produce long-term reductions in groundwater concentrations to levels at or below MCLs (McGuire et al., 2006; NRC, 2005).

Because of the way in which mass is distributed at a typical DNAPL-contaminated site and the ineffectiveness of pump-and-treat remediation methods, considerable efforts have been expended to develop more effective source-zone remediation methods. A variety of approaches have been investigated including (1) cosolvent and surfactant flushing (Dong et al., 2004; Gupta and Mohanty, 2001; Jayanti et al., 2002; Londergan et al., 2001; Martel and Gelinas, 1996; Pennell et al., 1993, 1994, 1996; Ramsburg et al., 2005; Shiau et al., 1994; Taylor et al., 2001; Willson et al., 1999; Zhao et al., 2006; Zhong et al., 2003; Zhou and Rhue, 2000; Zhu and Feng, 2003), (2) thermally-based remediation (Burghardt and Kueper, 2008; Gudbjerg et al., 2004; Heron et al., 1998; Hunt et al., 1988a,b; O'Carroll and Sleep, 2007; She and Sleep, 1999; Sleep and Ma, 1997), (3) advanced oxidation processes (Heiderscheidt et al., 2008; Hrapovic et al., 2005; Schnarr et al., 1998; Siegrist et al., 1999; Thomson et al., 2007), and (4) density alteration based remediation methods (Brandes and Farley, 1993; Hill et al., 2001;

Johnson et al., 2004; Miller et al., 2000; Ramsburg et al., 2003). It seems reasonable to conclude that a significant need remains to develop an effective source-zone remediation method, but the path forward is not clear.

At the same time, considerable interest has evolved over the evaluation of the effects of source-zone remediation (Christ et al., 2006; ITRC, 2002, 2004; Kavanaugh et al., 2003; McGuire et al., 2006; NRC, 2005; Soga et al., 2004). The central point of interest is the relationship between mass removal from a source zone and the magnitude of observed changes in concentrations and/or the flux of contaminants downstream of the source zone. Such a relationship is critical because it is typically the basis for evaluating if remediation has successfully met its goal. Interestingly, the relationship between source-zone flux and mass removal has proven elusive, with some even finding that mass removal can lead to increases in down-gradient concentrations or fluxes (McGuire et al., 2006). The lack of a clear understanding of the fundamental processes contributing to this relationship provide an impediment to realistically evaluating the results of active and expensive technologies used for source-zone remediation intended to reduce human and ecological risk (SERDP and ESTCP, 2006).

The overall goal of this work is to advance understanding of the effects of source-zone remediation. The specific objectives of this work are: (1) to evaluate the effect of source-zone remediation on down-gradient concentrations and mass flux, (2) to assess factors that contribute to observed results, (3) to provide guidance on when source-zone remediation should be considered, and (4) to discuss issues that must be resolved before a reliable model of such systems can be advanced.

3.2 Background

A substantial amount of work has been done to develop source-zone remediation approaches to overcome the limitations of pump and treat. While matrix diffusion and sorption play a role in source-zone remediation (Chapman and Parker, 2005; Parker et al., 2008), the focus here is on the role of DNAPL. One class of approaches seeks to remove NAPL by enhancing the rate of mass transfer to either the aqueous or vapor phases. For the aqueous phase, NAPL removal has been achieved through enhanced dissolution via cosolvents (Brooks et al., 2004; Imhoff et al., 1995; Jawitz et al., 2000; Lunn and Kueper, 1997; Rao et al., 1997) or surfactants (Jayanti et al., 2002; Londergan et al., 2001; Martel and Gelinas, 1996; Pennell et al., 1993, 1994; Ramsburg et al., 2005; Shiau et al., 1994; Taylor et al., 2001; Zhao et al., 2006; Zhong et al., 2003; Zhou and

Rhue, 2000; Zhu and Feng, 2003). In the saturated zone, air sparging has been used to increase volatilization (Aelion and Kirtland, 2000; Heron et al., 2002; Ji et al., 1993; Johnson et al., 1999, 1997; Johnston et al., 2002; Kim et al., 2004; Rogers and Ong, 2000). Vapor-phase extraction can enhance the mass flux of volatile DNAPLs in the unsaturated zone or dewatered source zones as a result of the large volumetric flow rates of a gas phase that can be achieved at a relatively low cost compared to liquid phases (Aelion and Kirtland, 2000; Corbin et al., 1994; Johnson et al., 2004; Kirtland and Aelion, 2000). Although these technologies may enhance the rate of mass transfer, they can still require long time frames, albeit shorter than conventional pump-and-treat methods, for complete source-zone removal and attainment of health-based standards.

Separate phase NAPL mobilization and recovery is another class of technologies that has been developed to actively remediate DNAPL source zones. Mobilization of DNAPLs can be achieved by reducing the interfacial tension of residual NAPL using cosolvents (Brandes and Farley, 1993; Fu and Imhoff, 2002; Gauthier and Kueper, 2006; Imhoff et al., 1995; Ramsburg et al., 2005) or surfactants (Dong et al., 2004; Gupta and Mohanty, 2001; Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000; Pennell et al., 1996; Ramsburg et al., 2005; Willson et al., 1999). These methods have the advantages of requiring small volumes of flushing solution to achieve large fractional mass removals and of being relatively fast compared to enhanced dissolution, however, they also have a possible drawback of mobilizing DNAPLs downward into subsurface zones that were previously uncontaminated. In response to this concern, BBRTs have been developed to control downward migration (Hill et al., 2001; Johnson et al., 2004).

An important trend observed in the literature is that the fraction of mass removed is directly related to the value of the initial DNAPL residual saturation. Soga et al. (2004) compiled results from the literature and found that the fraction of mass removed tends to decrease as the initial residual saturation in experiments decreased. This is clearly an important point, since residual saturations are generally lower at field sites compared to conditions typically considered in laboratory experiments. This is due in large part to the natural heterogeneity of subsurface systems, the larger length scales involved, the nature of typical contaminant releases, and the physics that govern multiphase transport phenomena. Mobilization technologies are effective because they reduce interfacial tensions between the water and DNAPL phase sufficiently to mobilize trapped DNAPL, which can in turn lead to a connected DNAPL phase that can move in response to gradients in pressure and gravitational potential. However, when non-wetting phase saturations become very low, capillary forces become increas-

ingly greater, and it becomes less likely that sufficient DNAPL can be mobilized to result in a continuous non-wetting phase. Thus, it appears unrealistic to expect high fractions of DNAPL removal via mobilization alone in field settings with low initial saturations. Though fractional mass removal has traditionally been the metric used to judge success in experimental work, it is not the metric used to judge success in the field. Ultimately the concentration down gradient from a source zone is compared to groundwater standards, such as MCLs, which can be several orders of magnitude lower than the solubility limit of a DNAPL species. However, little relationship has been found between mass removal and the resultant dissolved-phase concentrations (McGuire et al., 2006; Soga et al., 2004). Thus, there has been increased interest over the last several years to understand the effect of source-zone remediation on changes in down-gradient solute concentrations. Overall mass transfer of DNAPL in a source zone to the aqueous phase is the dominant process of interest in understanding the effect of source-zone remediation.

The traditional mass transfer model represents mass transfer flux as a first-order process that is dependent upon the product of a mass transfer coefficient and the difference between the equilibrium concentration of DNAPL dissolved in the aqueous phase and the aqueous phase concentration. This model is used to represent observed deviations from equilibrium that result from complexities in the flow system across a range of scales. If this model is a reasonable representation of the process, then the issue becomes the determination of the mass transfer coefficient. It is important to note that many important aspects of the physics of interphase mass transfer must be represented by this coefficient if the model is to be of use, and the magnitude of the mass transfer coefficient varies with space and time for most systems. Because of this, approximating the value of this coefficient in terms of other system properties that are known and evolved in time in a mechanistic model is necessary to provide a realistic, long-term simulation of DNAPL dissolution. Such relationships often take the form of empirical correlations of non-dimensional forms of the mass transfer coefficient as a function of other non-dimensional parameters. Because the candidate set of potentially important parameters is large and mass transfer experiments are time consuming even at the laboratory scale, only the variables of a presumed leading order have been investigated, such as NAPL saturations (Imhoff et al., 1994; Miller et al., 1990; Powers et al., 1992, 1994) and aqueous-phase velocities (Imhoff et al., 1997, 1994; Miller et al., 1990; Powers et al., 1992, 1994). From this experimental work, overall mass transfer coefficients (K_l) have been determined and represented non-dimensionally by the mod-

ified Sherwood number ($Sh' = K_l d_{50}^2 / D_m$), where d_{50} is a mean grain diameter of the porous medium, and D_m is the molecular diffusion coefficient. Experimental data have provided a basis for non-dimensional empirical correlations that relate the Sherwood number to other parameters including the Reynolds number, Schmidt number, and the residual saturation (Miller et al., 1990). Though these correlations may be successful for certain experimental conditions, the coefficients in these expressions cannot be universally applied and may require fitting when applied to new systems (Imhoff et al., 1998). This is so because of the incomplete characterization of the underlying physicochemical mechanisms leading to mass transfer that can be characterized by the small set of macroscale variables typically examined. Put another way, mass transfer coefficient correlations, even at the laboratory scale, are rough approximations based upon incomplete characterizations of the underlying mechanisms.

In the last 10 years, research has been conducted to develop upscaled models that attempt to account for increased dimensionality and complexity of field-scale conditions (Fure et al., 2006; Park and Parker, 2005; Parker and Falta, 2008; Saba and Illangasekare, 2000; Saenton et al., 2002). For example, an expression has been developed to approximate Sh' considering the length scale for a given system (Saba and Illangasekare, 2000; Saenton et al., 2002). Similar to the correlations developed from one-dimensional data, this correlation still requires experimental data to determine the coefficients for a given system. Mass transfer correlations have also been posited at the field scale (Park and Parker, 2005; Parker and Falta, 2008). These approaches have shown promise at being able to describe dissolution fluxes at the field scale but require parameterization based on field-scale observations.

A somewhat more pleasing approach is to represent the mass transfer coefficient as the product of a mass transfer rate coefficient and the specific interfacial area ($k_l a_{na} = K_l$). This approach has appeal because of the leading order importance of interfacial area in the process. However, this approach is only of practical use for cases in which the interfacial area is known. In recent experimental studies, MRI imaging has been used to determine interfacial area and has shown that mass transfer models using the interfacial area provide the best agreement to measured mass transfer rates (Zhang et al., 2008). Recent work has also evolved a computational approach to model dissolution from first principles at the pore scale (Pan et al., 2007). This pore scale modeling has shown good agreement with laboratory experiments and confirmed that the Sherwood number ($Sh = k_l d_{50} / D_m$) is insensitive to changes in residual saturation (Pan et al., 2007). An approach has also been developed to estimate the effective interfacial area

(Grant and Gerhard, 2007a), which requires the capillary pressure-saturation function and has been used to simulate effluent concentrations from two-dimensional laboratory dissolution experiments (Grant and Gerhard, 2007b).

The current understanding is that mass transfer is fundamentally driven by the distribution of DNAPL in the source zone, which is controlled by heterogeneity and plays a central role in the dissolution process across all scales (Page et al., 2007; Park and Parker, 2005; Parker and Park, 2004; Sale and McWhorter, 2001; Soga et al., 2004). The DNAPL distribution in a porous medium has been termed the source-zone architecture, but it can more precisely be referred to as the morphology and topology of the DNAPL distribution (Pan et al., 2007).

Not surprisingly, recent work on mass transfer has focused on factors that play a key role in affecting DNAPL morphology and topology. For example, heterogeneity has been shown to greatly influence the rate of dissolution (Mayer and Miller, 1996; Page et al., 2007; Parker and Park, 2004; Powers et al., 1994; Soerens et al., 1998). A primary reason for the importance of heterogeneity is its effect on the distribution of DNAPL, which forms both regions of small length scale residual saturation and longer length scale pools. Recent attention has been paid to the differentiation of residual DNAPL and pooled DNAPL via the ganglia-to-pool ratio (Christ et al., 2006; Lemke and Abriola, 2006; Lemke et al., 2004). However, this ratio is an imprecise statement of the importance of the fluid morphology and topology, as embodied in such measures as the specific interfacial area. Other recent work, using partitioning tracers to parameterize a stream-tube-based dissolution model, has demonstrated some of the limitations of the ganglia-to-pool ratio (Basu et al., 2008).

It has also been shown that the dissolution process is unstable and can lead to the formation of so-called dissolution fingering under certain, commonly occurring circumstances (Imhoff et al., 2003, 1996). When dissolution fingers do form, the effective rate of dissolution can be greatly reduced compared to systems in which such features do not form (Imhoff et al., 2003; Imhoff and Miller, 1996). Because of the disparity between the complexities of model experimental systems traditionally studied and the motivating natural systems of concern, there is a growing sentiment that DNAPL dissolution cannot be quantitatively understood using standard small-scale laboratory approaches. In other words, understanding the initial DNAPL morphology and topology and the evolution of these features across the range of length and time scales of concern are open issues impeding the development of a meaningful understanding of DNAPL dissolution. Hence a fundamental understanding of the remediation of con-

taminated DNAPL systems is elusive. To close this gap, more realistic experiments across a range of saturations, scales, and media complexity, as well as more realistic models are needed.

Developing a fundamental understanding of the effect of DNAPL remediation on mass transfer at the field scale is of even greater complexity. This requires understanding the effect of the remedial strategy on the DNAPL morphology and topology and assessment of the system evolution during remediation. Achieving this final goal will require a substantial amount of additional work, but clearly understanding the issues involved can serve to redirect experimental, theoretical, and computational efforts.

3.3 Approach

3.3.1 Methods

The results from a series of experiments were examined, including (1) one-dimensional column experiments measuring the mass flux of TCE by flushing water to the point of near-complete dissolution (Imhoff et al., 1998), (2) a pilot-scale study of tetrachloroethylene (PCE) remediation conducted at the Dover National Test Site (DNTS), and (3) a three-dimensional tank experiment conducted to mimic conditions in the pilot study. Both the pilot study and the tank experiment used a class of BBRTs (Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000) to control the mobilization of DNAPL caused by surfactant flushing. The portions of the pilot-scale study of focus in this work are restricted to the PCE aspects of the study. Other aspects of this study, such as the brine portion of the study, are not of central importance to this work and will be reported elsewhere.

All of these experiments provide some information about the mass flux changes with reductions in residual saturation. Using data from the one-dimensional columns, the changes in mass flux were directly correlated with orders of magnitude reductions in residual saturation. The well configuration in the pilot study did not allow for a uniform flow field across the extent of the cell, thus, estimates of mass transfer rates corresponding to uniform flow were not possible. Instead, measurements of pre- and post-remediation concentrations were obtained using multi-level samplers throughout the pilot-study test cell under quiescent conditions. In the tank experiment, the mass flux was measured pre- and post-remediation. Each experiment is further described in the following sections.

One-Dimensional Dissolution Experiments

Data collected from one-dimensional dissolution experiments described in detail by Imhoff et al. (1998) were used to determine mass transfer rates of TCE as a function of residual saturation. The media used in the one-dimensional column experiments included glass beads (GB), a mixed sand (MS), and a treated Wagner soil (WG). DNAPL saturations were computed by a mass balance approach based upon an integration of effluent data and neglecting sorption.

The experimental data from the column experiments were used to estimate the overall mass transfer rate, K_l , by assuming quasi-static conditions in the column and solving the following standard one-dimensional advective-dispersive transport equation,

$$0 = D_h \left(\frac{\partial^2 C_{aq}}{\partial x^2} \right) - \frac{q}{\theta_a} \left(\frac{\partial C_{aq}}{\partial x} \right) + \frac{K_l}{\theta_a} (C_s - C_{aq}) \quad (3.1)$$

where C_{aq} is the aqueous phase concentration, C_s is the aqueous phase solubility, $D_h = D_m + \alpha_l q / \theta_a$ is the hydrodynamic dispersion coefficient, D_m is the effective molecular diffusion coefficient, α_l is the longitudinal dispersivity, q is the Darcy velocity, $\theta_a = \phi(1 - s_n)$ is the volumetric fraction of the aqueous phase, ϕ is the porosity, and s_n is the residual DNAPL saturation. Previous work for similar advective-dominated systems has shown that the inverse solution of Equation 3.1 for K_l is insensitive to the value of α_l (Miller et al., 1990; Pan et al., 2007). In this analysis, α_l was set to zero and solved for K_l by rearranging the semi-infinite analytical solution to Equation 3.1 (van Genuchten and Alves, 1982).

Pilot-scale Study

The pilot-scale demonstration was conducted similarly to previous laboratory-scale BBRTs experiments (Johnson et al., 2004). This technology uses a combination of approaches to remove DNAPLs. The general steps in the BBRTs experiments involve (1) injection of the DNAPL into porous media directly below the water table, (2) lowering and raising of the water table to smear the DNAPL in the source zone, (3) injection of a dense brine over an underlying confining layer, (4) flushing the system vertically with a surfactant solution to mobilize residual DNAPL downward to the brine layer, (5) removal of DNAPL in effluent collected above the brine layer, (6) removal of brine by dewatering and flushing with freshwater, and (7) removal of additional DNAPL using vapor extraction.

Key differences between the pilot scale demonstration and previous BBRTs studies include: (1) contaminating the system with PCE instead of TCE and at much lower starting residual saturation, (2) using a new surfactant flushing solution, which was designed for PCE removal, and (3) applying the technology in a naturally heterogeneous porous medium. Because PCE was the selected DNAPL ($\rho = 1.623 \text{ g/cm}^3$), the density contrast with CaBr_2 brine ($\rho = 1.70 \text{ g/cm}^3$) was much lower than in previous work using TCE ($\rho = 1.46 \text{ g/cm}^3$). Due to the change in DNAPL, a new surfactant mixture was formulated that exhibited favorable phase behavior with PCE and with a higher tolerance for high concentration brine. The surfactant solution consisted of 1.425 wt % Aerosol MA-80, 1.575 wt % Triton X-100, 3.0 wt % isopropanol, and 1.55 wt % calcium chloride dihydrate. The purpose of the isopropanol was to promote destabilization of macroemulsions that may lead to pore clogging, the salt lowered interfacial tension with PCE.

The pilot scale study was conducted at the DNTS in Dover, DE. The DNTS consists of a water table aquifer, the Columbia Formation, overlying an extensive clay formation, the Calvert Formation. The Columbia Formation forms a water table aquifer under the site that varies in depth beneath the ground surface from 11 to 14 m over the facility. It is comprised of fine to medium sands with occasional discontinuous clay and silt lenses. The vertically averaged hydraulic conductivity of the Columbia formation is $3 \times 10^{-3} \text{ cm/s}$. The Calvert Formation consists of gray, firm, dense marine clays. This confining layer is approximately 6 m thick and has a hydraulic conductivity between 2×10^{-8} and $3 \times 10^{-7} \text{ cm/s}$ (ARA, 1996).

DNTS had designated areas, or test cells, in which permitted and contained DNAPL releases were conducted. Contaminant releases were contained by several mechanisms: double-walled sheet piles, maintenance of an inward hydraulic gradient between inner and outer barriers, and monitoring wells that were used to extract contaminants in the unlikely event of containment failure. The test cells were enclosed using double-walled sheet piles driven into the subsurface and keyed into a confining aquitard approximately 14 m below the surface (ARA, 1996). The confining aquitard and the sheet piles allowed controlled emplacement of brine similar to the laboratory-scale experiment.

Each test cell was equipped with injection/extraction wells, multilevel micro-samplers, and contaminant injection points. The layout of these locations is displayed in Figure 3.1. The test cell area was covered to prevent groundwater infiltration from precipitation. The test cell for this work was $4.6 \times 3.0 \text{ m}$. The depth to the clay layer was approximately 12.3 m. During the study, the saturated zone had a maximum thickness

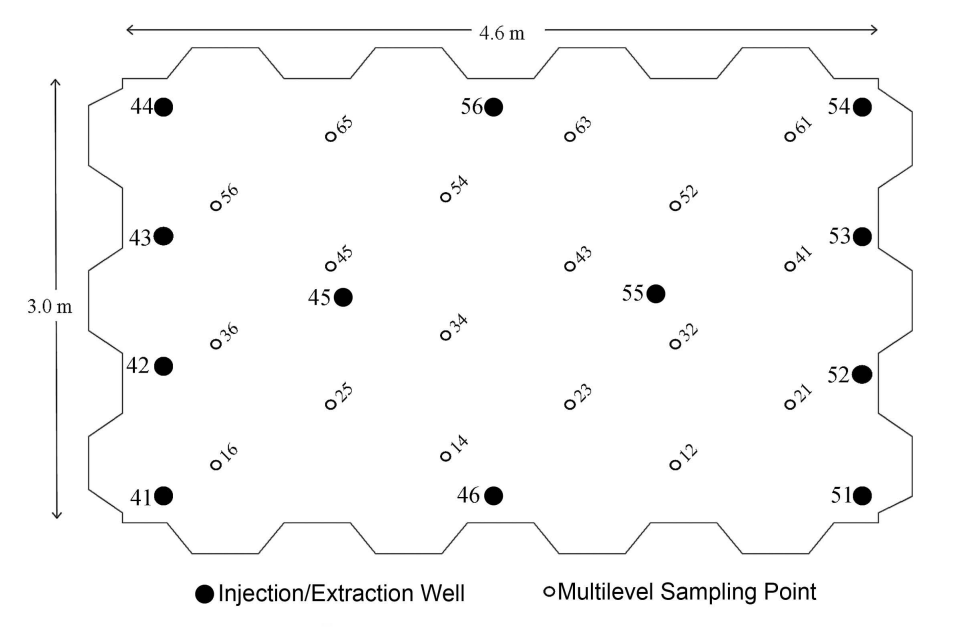


Figure 3.1: Dover Test Cell 3 layout.

of approximately 3.8 m at its maximum height with the water table at approximately 8.5 m below ground surface (bgs).

The DNTS cell was permitted to contain a maximum of 100 L. Site data from previous studies indicated that as much as 36 L of PCE might already be in the cell. However, the actual amount of PCE initially present is believed to be less due to losses through degradation and volatilization. Prior to the BBRTs study, the aqueous phase concentrations were measured for PCE and its degradation products as well as aqueous species introduced in flushing solutions from previous demonstrations, including surfactants, cosolvents, and cyclodextrin. All of these species can serve as food sources for indigenous bacteria leading to degradation of PCE. Losses due to volatilization are also possible because the covered test cell was not airtight.

The water table was adjusted to 11.0 m bgs prior to PCE injection. Approximately 64 L of PCE were added to the cell 10.7 m bgs using six of the contaminant injection points. Injection volumes were 8 L into three points, 12 L into two points, and 14 L into one point. The PCE injection protocol involved lowering the water table to about 11.6 m bgs and raising it back to its initial level to spread PCE downwards. The average initial PCE saturation in the saturated zone was no greater than 0.007 based on an assumed initial PCE volume of 100 L, a source zone thickness of 2.9 meters (i.e., the average distance from the PCE injection points to the clay layer), and a porosity

of 0.32. A pre-remediation sampling round from the cell's multi-level samplers was conducted after PCE injection to establish the starting conditions. All samples were collected in 40 ml Environmental Protection Agency (EPA) volatile organic analysis vials with zero headspace and stored at 40°C. Prior to analysis, samples were diluted at a 1:1 ratio with isopropyl alcohol to dissolve any DNAPL present and minimize volatilization losses. PCE and its daughter products were analyzed using HPLC with a method based on Field and Sawyer (2000).

Brine was injected just above the clay layer to achieve an in-place density of the aqueous phase that was greater than that of the PCE with an approximate thickness of 0.3 m. This equated to about a 0.15-m depth at the shallowest part of the clay-confining unit and approximately 1-m depth at the deepest part of the clay-confining unit. To mobilize PCE downward toward the brine barrier, approximately 0.54 PVs of surfactant were added to the cell near the top of the water table. Following the surfactant flush, the test cell was partially dewatered to the brine barrier at approximately 12 m bgs. The brine was removed by further dewatering and flushing with freshwater.

Vapor extraction began during brine removal to recover trapped DNAPL in the unsaturated zone and continued throughout the dewatering phase. After vapor extraction and brine barrier flushing, the water table was raised to 11 m bgs and post-remediation characterization was performed corresponding to the analyses conducted prior to remediation. A final sampling event from the cells multi-level samplers was conducted three months later and analyzed. It is important to note that during these sampling events no flow was induced through the cell. Therefore, the pilot-scale demonstration addresses changes in concentrations collected from multi-level samplers instead of mass flux.

Three-dimensional Tank Experiment

The three-dimensional tank experiment was designed to mimic the conditions in the pilot study. Specifically, key variables in the pilot-scale study were scaled down in accordance with the size of the laboratory experiment. The laboratory experiment differed from the pilot study in that radiolabeled PCE was used as the DNAPL. Further details of the tank experiment are provided below.

As depicted in Figure 2.1, the experiment was conducted in a glass container that was 22.5-cm long, 16.5-cm wide, and 24-cm high. The tank was packed with media obtained from the DNTS, referred to as Dover Sand (DS), for which the properties are summarized in Table 3.1. The DS was sieved and sorted into 12 different fractions with

Table 3.1: Porous media properties for flux experiments.

Material	d_{10} (mm)	d_{50} (mm)	d_{60}/d_{10} (-)	Porosity (-)
Glass beads (GB) (Imhoff et al., 1998)	0.237	0.277	1.2	0.36
Mixed sand (MS) (Imhoff et al., 1998)	0.170	0.400	2.8	0.35
Wagner soil (WG) (Imhoff et al., 1998)	0.250	0.710	4.0	0.36
Dover sand (DS)	0.200	0.460	2.7	0.44

no diameter greater than 2 mm. Next, it was packed into the laboratory cell using a 21-layer heterogeneous packing based on a correlated random field model assuming anisotropic exponential covariance conditions and a log normal particle size distribution (Christakos, 1992a; Deutsch and Journel, 1992). Each layer consisted of cubes of homogeneous sands obtained from the sieved fractions of 1.5-cm length and width and 1-cm height. Correlation lengths of 7.5 and 5.0 cm for the horizontal and vertical planes, respectively, were used to match the scale of the experiment. The mean and standard deviation of the sieved fractions were $-0.7890 \ln(\text{mm})$ and 0.6326, respectively.

Once the cell was packed, all ports were inserted, and the cell was sealed using a gasket-lined aluminum lid. Stainless steel tubing lined with heat shrunk Teflon tubing was used for all injection and extraction ports. The layout of the ports is shown in Figure 3.2, such that the injection ports have the prefix "PCE" and the extraction ports have the prefix "E". The cell was vibrated to consolidate the media, checked for airtightness and flushed with carbon dioxide. The cell was then saturated using the deepest ports by injecting de-aired deionized (DDI) water. Once air bubbles were removed from the medium, approximately 9.6 ml of ^{14}C -labeled PCE (American Radiolabeled Chemicals, St. Louis, MO) was injected into various ports located in the ninth layer from the bottom of the cell.

Prior to injection, the water table was dropped to just above the injection ports. Injection ports PCE-1, PCE-5, and PCE-6 each received approximately 1.3 ml of PCE. Ports labeled PCE-2, PCE-3, and PCE-4 received approximately 1.8 ml, 2 ml, and 1.85 ml, respectively, of PCE injected at a rate of 0.5 ml/min followed by approximately 2 ml of water to make sure PCE had cleared the tubing and entered the media.

Additional dewatering of the system promoted spreading of PCE downward. During this time, water was extracted from the cell using the extraction ports (E1 and E2) at a combined rate of 2 ml/min. After removing approximately 200 ml, the system was resaturated with DDI water using the deepest ports (B3 and B4) at a combined rate

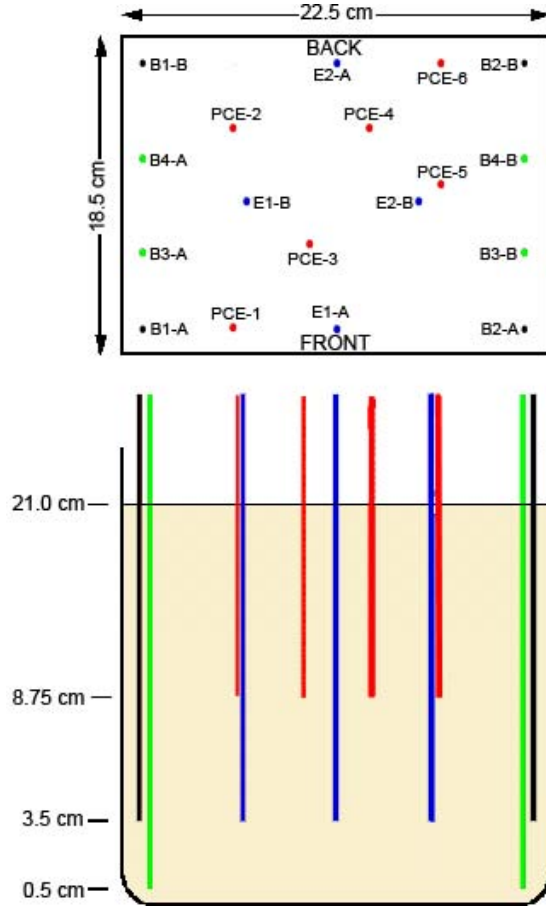


Figure 3.2: Three dimensional laboratory tank for source-zone mass flux analysis.

of 4 ml/min. The resaturated cell was allowed to rest for 12 h to reach a quasi-static state.

Prior to remediating the system, the pre-remediation mass flux was determined. Specifically, DDI water was flushed across the cell using the four ports on the left side of the cell (B1-A, B1-B, B3-A, and B4-A) and collecting the effluent stream from the two corner ports on the right side of the cell (B2-A and B2-B). Effluent samples were collected until the mass flux approached steady state.

Syringe pumps were used to inject brine into the cell through the four bottom corner ports (B3 and B4) at a combined rate of less than 1 ml/min to reduce the degree of mounding of the viscous brine around injection ports. The brine flow rate was reduced to 0.25 ml/min once a brine barrier was established. The reduced brine flow rate helped maintain the brine layer during the surfactant flush and dewatering of the system. Surfactant was pooled on top of the medium and flushed downward through

the system by extracting from locations E1 and E2 at a combined rate of 2 ml/min. Approximately 0.39 PVs of surfactant were flushed through the system. Extraction continued until the effluent flow rate decreased significantly. At this point, the system was only partially saturated and in a state conducive to vapor-phase extraction of the remaining residual DNAPL. Vapor extraction was performed similarly to previous BBRTs laboratory experiments (Johnson et al., 2004).

When vapor-phase DNAPL recovery diminished significantly, the system was resaturated and post-remediation flux measured in the same manner as before remediation, except that the flow rate was varied. Once the effluent concentration approached the detection limit, the system was drained and the amount of DNAPL remaining in the system was determined by extracting the DNAPL from the porous medium.

3.4 Results

A multiscale approach was taken to investigate the effect of source-zone remediation on contaminant concentrations and mass flux as a function of DNAPL remediation. This approach included the reinterpretation of previously conducted one-dimensional laboratory experiments, a pilot-scale field investigation, and a three-dimensional laboratory investigation intended to resemble the pilot-scale study. A multiscale approach was taken to elucidate the level of understanding and improve the mechanistic interpretation of the dominant aspects of this important relationship.

3.4.1 One-Dimensional Column Experiment

The first data sets published in which complete dissolution of a DNAPL was accomplished were re-examined in this work to determine mass transfer coefficient characteristics over a wide range of saturations. This new interpretation of existing data was performed to assess the expected result of source-zone remediation over a range of length scales. The column experimental results are an indicator of what would be expected during source-zone remediation of a system at residual saturation, where changes in concentration or mass flux with mass removal is a central concern. If one-dimensional behavior is assumed, which is a simplification of natural systems, the Sh' can be used to assess the downgradient concentration or mass flux given knowledge of the groundwater velocity and the dispersivity of the system as a function of residual saturation. It is emphasized that such an analysis is a simplistic first-cut approach, but

nonetheless is an indicator of the challenges being faced in source-zone remediation.

Figure 3.3 shows the data from Imhoff et al. (1998) that have been re-analyzed to show Sh' as a function of TCE saturation. Saturations during an experiment were estimated based on the mass of TCE extracted from the system at the end of the dissolution experiment and backward-in-time integration of the TCE mass leaving the column in the effluent. This approach ignores the mass of TCE dissolved in the aqueous phase and sorbed to the solid phase and column apparatus, so it provides a biased estimate of the average saturation in the system, particularly at the lowest saturations. Figure 3.3 also shows the predicted Sh' using three empirical correlations and the coefficients derived by Imhoff et al. (1998). Notably, these relationships are able to represent the mass transfer characteristics of the experimental systems reasonably well. The predicted modified Sherwood numbers are less accurate for the Wagner soil experiments, which may be an artifact of reported analytical difficulties due to desorption from the column apparatus.

Figure 3.4 uses the empirical relationship derived by Imhoff et al. (1994) to evaluate the resulting dissolved-phase concentration that would be expected as a function of source zone length and saturation for a case in which the groundwater velocity is 1 m/day and the dispersivity is 10% of the travel distance. The striking point from this analysis is that if the column results are a representation of source-zone remediation, then the results show clearly that concentrations remain well above typical drinking water standards until DNAPL saturations are reduced several orders of magnitude. In the case of TCE, the MCL is over five orders of magnitude below its solubility limit, C_s . Even for very small scale systems (e.g., 1^{-10} cm), the dissolved phase concentrations approach C_s as the DNAPL saturation increases, and a DNAPL saturation of less than 10^{-6} is required to reach the MCL. Reaching these low concentrations becomes increasingly difficult as the length scale increases.

3.4.2 Pilot-Scale Experiment

The scope of the results for the pilot-scale study is limited to addressing changes in PCE concentrations in the cell resulting from redistribution of NAPL and the resulting changes in morphology and topology of the DNAPL after application of the described remedial approach. As noted previously, the pilot-scale demonstration monitored changes in concentrations collected from multi-level samplers within the cell. These samples provided concentrations at various depths throughout the cell and were

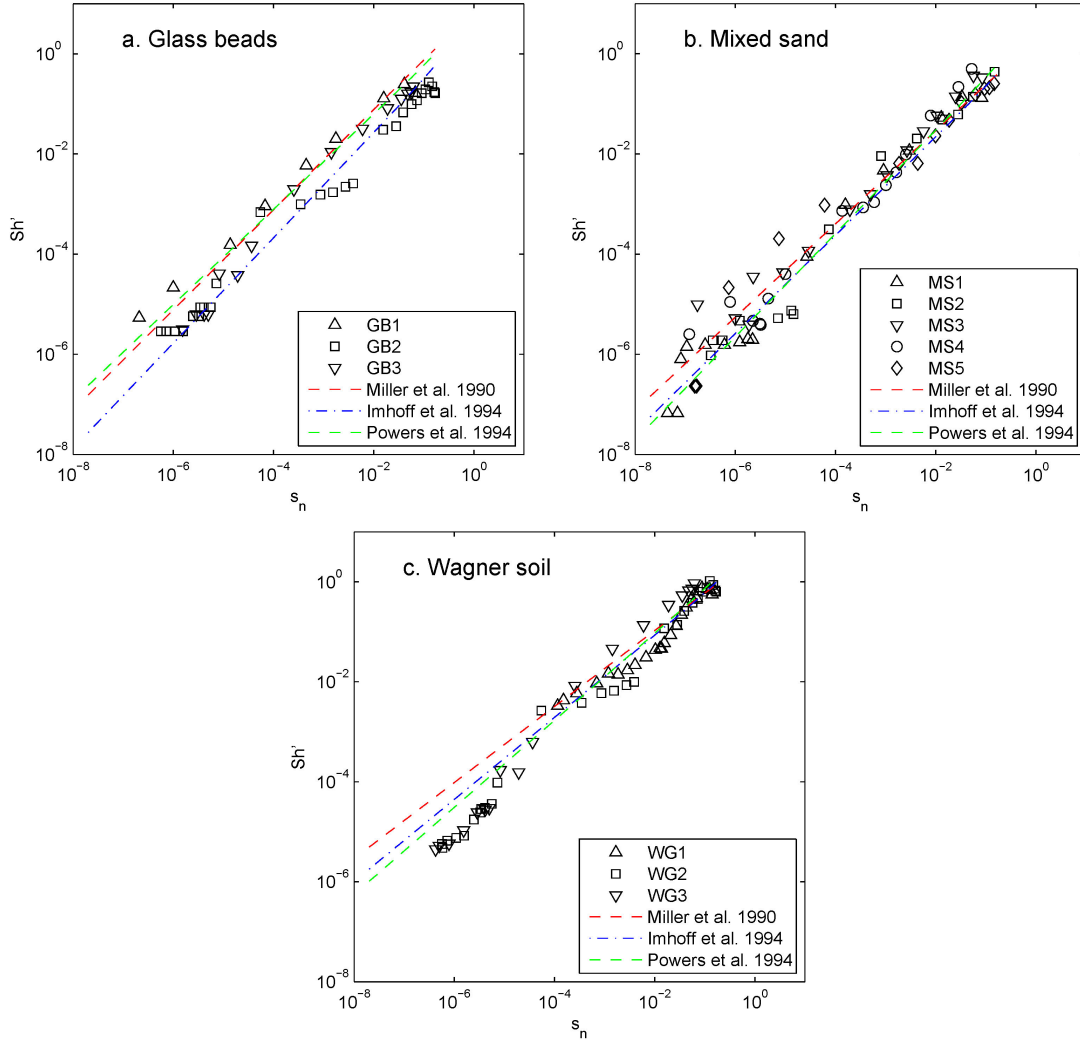


Figure 3.3: Comparison of experimental Sh' and predicted Sh' versus s_n for one-dimensional column experiments.

taken at key points in the pilot project. In Figure 3.5, average concentrations at various depths in the cell are presented for samples taken prior to the remediation, immediately after the remediation, and three months after the remediation. Several samples taken prior to the remediation were at or near the solubility limit. Immediately after the remediation, the average concentrations at some depths dropped as much as two orders of magnitude. At the three-month post remediation sampling event, aqueous-phase concentrations of PCE increased at most locations compared to those values measured immediately after remediation but were still generally well below the values measured prior to remediation. Note that no further flushing of the cell was conducted

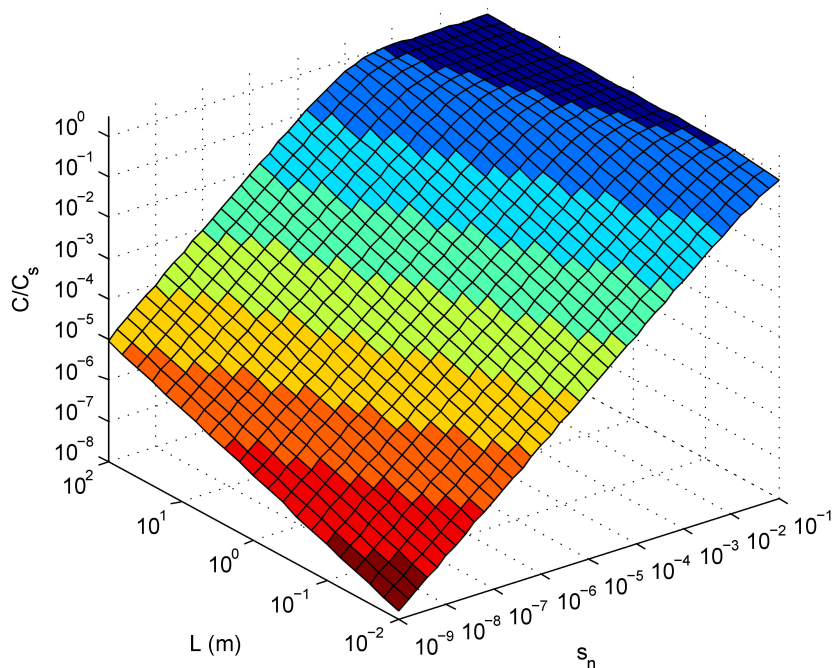


Figure 3.4: DNALP concentration as a function of length and s_n using a Darcy velocity of 1 m/s.

between the samples taken immediately after the remediation and those taken three months after the remediation. Thus, this increase in concentration was likely due to further dissolution of NAPL from isolated residual regions and slow diffusion within the aqueous phase.

Both sets of post-remediation data suggest a change in the distribution of the NAPL mass within the cell between the first sampling event and the latter two sampling events. Specifically, post remediation sampling showed an increase in PCE concentrations with depth with the greatest observed concentration in both cases measured at the deepest locations in the cell. These changes in concentration are especially interesting since only 10.9 L out of a maximum of 100 L of PCE was recovered from the cell and correspondingly remediation had a relatively small effect on the average saturation in the cell. These results serve as evidence that a redistribution of DNAPL mass can dramatically impact resulting concentrations. Presumably, this change in concentration was a result of changes in morphology and topology of the DNAPL source zone due to the downward mobilization of DNAPL. For example, specific interfacial area may have been reduced as the thickness of the source zone was reduced, judging this based upon the range of elevations at which DNAPL was recovered in the multilevel samplers during

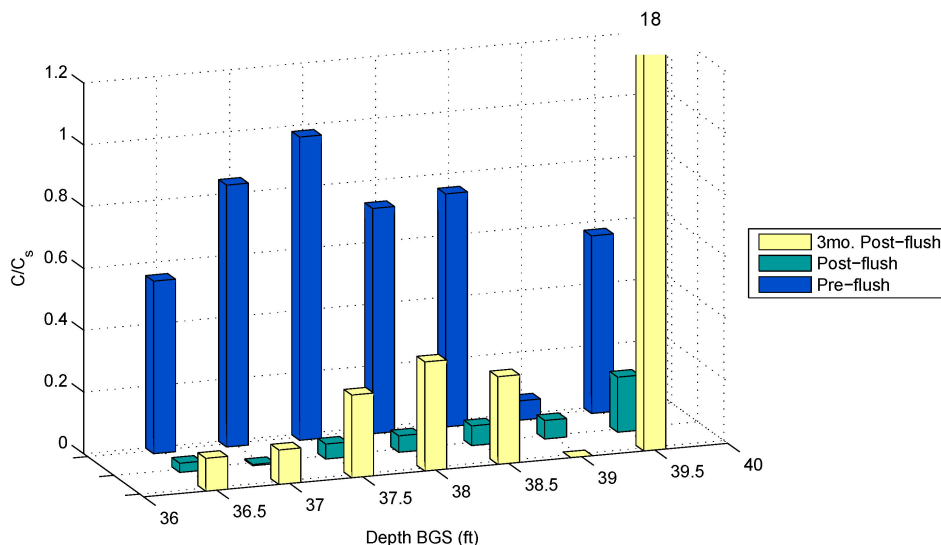


Figure 3.5: PCE concentration as a function of depth bgs in the DNTS test cell. The average relative concentration was 18 at 39.5 feet for the 3-month post-flush measurements. This high value occurred because DNAPL was present in one or more of the samples that made up the average.

the course of the experiment. The change in concentration profiles occurred despite the relatively small change in the average residual saturation over the contaminated region.

3.4.3 Three-Dimensional Laboratory Experiment

The three-dimensional tank study was designed to mimic the conditions in the field study. This allowed us to evaluate changes in mass flux as a function of source-zone remediation in a heterogeneous, three-dimensional cell, which was not possible from the field data. Specifically, the well configuration in the field study did not allow for a uniform flow field across the extent of the cell. In the tank, the well locations were used to purposefully form a relatively continuous flow field across the tank. Thus, effluent concentrations from the three-dimensional tank were found to be representative of the concentrations leaving a source zone due to groundwater flow. The laboratory cell also provided a much more controlled environment in which the initial DNAPL mass was accurately known and the DNAPL saturation could be determined as source-zone removal progressed during the study. Pre-flush saturations were estimated based on the known mass of PCE injected into the cell at the beginning of the experiment and integration of the PCE mass leaving the cell in the effluent. All of the post-flush

saturations were estimated based on the mass of PCE extracted at the end of the experiment and backward-in-time integration of the PCE mass leaving the cell in the effluent. This approach provides a biased estimate of the saturation, particularly at the lowest saturations.

The dependence of the mass transfer coefficient on Darcy velocity and DNAPL mass was determined using the correlation relationship

$$K_l = K_0 \left(\frac{q}{K_s} \right)^\alpha \left(\frac{M}{M_0} \right)^\beta \quad (3.2)$$

where M is the current DNAPL mass in the system, M_0 is the initial mass in the system, K_s is the hydraulic conductivity, and K_0 , α , and β are fitting parameters (Christ et al., 2006; Park and Parker, 2005; Parker and Park, 2004; Soga et al., 2004). Similarly to others, the value for α was assumed to be equal to 1 (Park and Parker, 2005; Parker and Park, 2004; Soga et al., 2004). This assumption implies that the mass transfer coefficient is directly proportional to the Darcy velocity. Due to the changes in Darcy velocity during the experiment, it is useful to rewrite the above equation as

$$\frac{K_l}{q} = \frac{K_0}{K_s} \left(\frac{M}{M_0} \right)^\beta \quad (3.3)$$

As noted in Figure 3.6, effluent concentrations were measured from the tank before and after the surfactant flush. The samples labeled "post-flush" in Figure 3.6 were collected just after the surfactant flush. These samples contained CaBr_2 and surfactant, which could impact PCE's solubility. Thus, these samples were not used to determine the system mass transfer coefficient relationship. The samples labeled "post-flush fitted" were collected after the CaBr_2 and surfactant concentrations declined (e.g., aqueous density was less than 1.000 g/ml and less than 0.4% of the injected brine remained in the system). These samples were used to determine the system mass transfer coefficient relationship. They also correspond to the point where the effluent concentrations began to monotonically decrease after the surfactant flush, which corresponds to a PCE saturation of 1.1×10^{-4} . Based on these data, the value for β was 1.43 and the value for K_0 was $0.128 \times 10^{-3} \text{ s}^{-1}$. In Figure 3.7, this prediction of K_l was used to determine the relationship between s_n and C_{aq}/C_s . in the limit of extrapolation corresponding to low concentrations characteristic of a typical MCL cleanup standard. Similar to the one-dimensional case, these data clearly show the considerable reduction in DNAPL mass that is required to achieve reductions in concentration of the magnitude typically

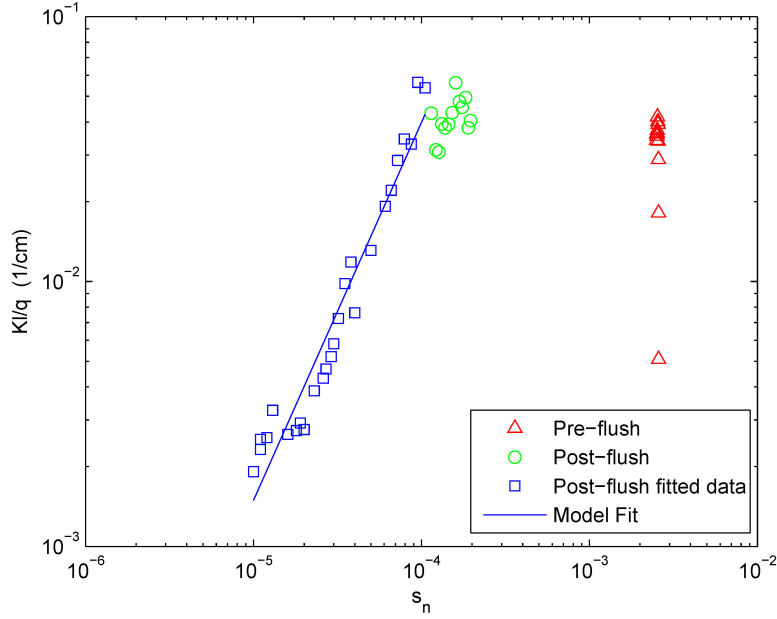


Figure 3.6: Model fit for three-dimensional mass flux tank experiment.

sought for field-scale cleanups.

3.5 Discussion

Both the one-dimensional and three-dimensional, heterogeneous porous medium laboratory experiments analyzed in this work show that essentially complete removal of DNAPL was necessary to approach an aqueous-phase concentration close to an MCL. It is believed that this result will hold for essentially all systems independent of how the DNAPL residual is reduced since it is the morphology and topology of the DNAPL distribution that determines the nature of the mass transfer process and not how this state was achieved. This result is significant because it affects remediation in several ways.

The literature has abundant accounts of relatively high fractions of DNAPL removal in laboratory settings (Soga et al., 2004). For example, in previous BBRTs work about 85% removal was achieved through surfactant flushing and more than 99% removal when surfactant flushing was followed by vapor extraction (Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000). While this is an impressive fractional removal of DNAPL compared to other competing technologies, the results show that orders of magnitude more removal would have been necessary to achieve downstream concentra-

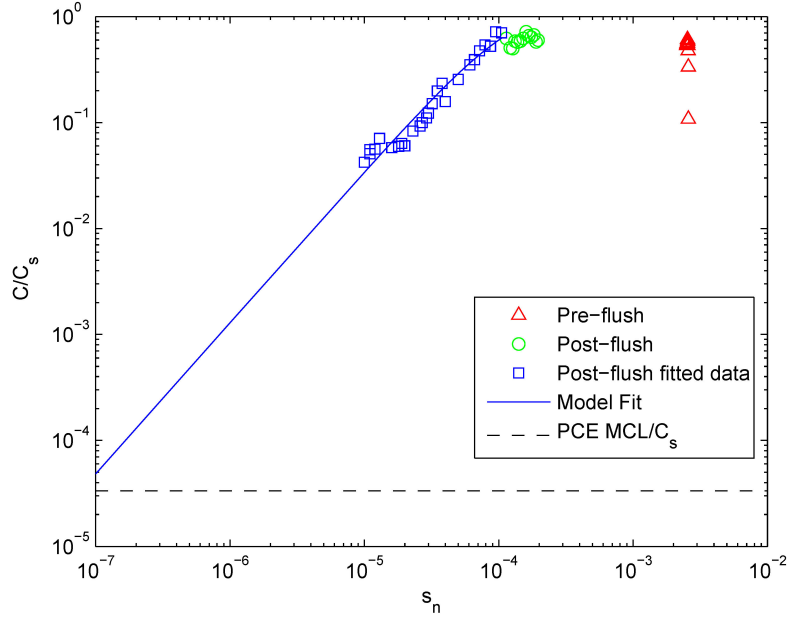


Figure 3.7: Concentration as a function of DNAPL s_n for three-dimensional mass flux tank experiment.

tions near the MCL. So from the perspective of mass removal, aggressive source-zone removal can be very successful, while compared to an MCL, the same source-zone remediation result would likely be interpreted as a failure. While appearing to be a contradiction, such results are consistent with a significant body of research. The take-away messages of this observation are that an MCL is an extremely difficult endpoint to achieve after a short period of source-zone remediation, and MCL drinking water levels are likely not easily attainable for most natural systems due to a variety of factors. In short, attainment of aqueous-phase concentrations less than MCLs following short-duration source-zone remediation is not a realistic goal. Therefore, either the goal or the remediation process must change to improve the probability of success.

While impressive fractional removals can be achieved for active source-zone remediation, this is an incomplete measure of the state of the system. Source-zone flux depends upon the morphology and topology of the pore space and fluid distributions, and the net macroscale effects of microscale advection, diffusion, and dispersion. The fraction of removal alone does not provide sufficient information regarding the underlying physicochemical processes that are operative. More meaningful measures of the state of the system are the porosity, volume fractions, fluid saturations, permeabilities, densities, fluid viscosities, specific interfacial areas, interfacial tensions, contact

angles, interfacial curvatures, specific common curve lengths, curvilinear tensions, and the invariant curvatures of the common curves. Such measures, especially when appropriately averaged from the pore scale, convey important information about the state of the system that is lacking from a fractional removal measure alone. Correspondingly, developing correlations for mass transfer coefficients based upon fractional mass removal measures are destined to be of limited benefit and at best of an application-specific nature. As a corollary to the limitations noted on assessing the state of a system using a fractional mass removal approach, general correlations for mass transfer should be cast in dimensionless form and include parameters that are integral measures of the net microscale state of the system that influences processes contributing to mass transfer. It is emphasized that no such correlation accomplished to date has satisfied this criteria, and typical models do not resolve and evolve many of the above-noted features that are expected to bear on the overall mass transfer coefficient for a system at all scales. More work is clearly needed in this regard.

If the notion of fractional mass removal as an important measure of source-zone remediation is abandoned, then leading order effects are related to the volume fractions, interfacial areas, interfacial tensions, water velocity, solute diffusivity, dispersion characteristics, fluid viscosities, fluid densities, and contact angles. For a given water-wet system consisting of a fixed DNAPL and reasonably consistent aqueous-phase solution, interfacial tension, diffusivity, fluid viscosities, fluid densities, and contact angles are essentially invariant. The remaining system variables will embody the dominant transient effects on the rate of mass transfer and correspondingly the aqueous-phase concentrations down-gradient of a source zone (e.g., volume fractions, interfacial areas, water velocity, dispersion characteristics). These remaining measures should be used to quantify the state of a system, in non-dimensional form of course. For example, it follows then that the DNAPL volume fraction is a key variable rather than a fractional mass removal. This conclusion is consistent with the literature that shows that fractional mass removal is dependent upon the initial residual volume fraction of the NAPL (Soga et al., 2004).

Active source-zone removal through mobilization can lead to the rapid removal of a large fraction of the mass in a heavily contaminated system because lowering the interfacial tension between the fluids can mobilize a trapped DNAPL, lead to a connected DNAPL phase over increasingly long length scales, and thus bulk fluid mobilization. At low saturations, DNAPL recovery becomes increasingly difficult (Soga et al., 2004). The results are consistent with this general observation. High fractional removals were

achieved in previously published BBRTs laboratory studies, while a low fractional removal was achieved in the DNTS pilot study. The leading order reason for this sharp contrast was the initial DNAPL volume fraction, which was much greater in the laboratory studies than the relatively small value used in the pilot study. The mobilization that did occur in the pilot study was primarily vertical in nature in response to reductions in interfacial tension and an increase in gravity forces due to dewatering. The driving forces were not sufficiently large to yield significant horizontal mobilization of DNAPL in the pilot study. This result is consistent with previous laboratory studies because mobilization in the laboratory ceased after 85% fractional removal, which was still at a residual saturation level greater than the initial value of DNAPL saturation in the field (Johnson et al., 2004). In both field and laboratory experiments, mobilization of DNAPL was not a dominant transport mechanism at low residual saturation levels. The implication is that DNAPL mobilization approaches should be expected to leave DNAPL residual saturations on the order of up to a few percent, even when successful. As shown, this level of DNAPL saturation is sufficient to result in aqueous-phase concentrations significantly greater than MCLs.

Because significant DNAPL residual saturation will remain after active DNAPL mobilization for source-zone remediation in virtually all instances, a secondary remediation process will be necessary to affect the essentially complete DNAPL removal needed to approach typical MCL limits. Candidate secondary processes would include vapor extraction, or enhanced solubilization using surfactant or cosolvent flushing solutions, although mass transfer limitations apply to these processes as well and vapor extraction requires dewatering of the saturated zone. Once the majority of DNAPL mass is removed from a system, bioremediation or reactive barriers become technologies of increasing viability and decreasing cost. The majority of DNAPL remediation results suggest that in many cases a combination of remediation process technologies may be the most advantageous approach. In heavily contaminated cases in which DNAPL mobilization is attempted, a rapid removal of DNAPL will occur typically. As shown, the resultant DNAPL residual remaining will preclude the immediate attainment of aqueous-phase concentrations approaching drinking water standards. However, the mobilization of a significant fraction of the DNAPL mass originally present does lessen the remediation burden on alternative technologies used to reach a final cleanup standard. From this perspective, active source-zone remediation using mobilization will be a success in most heavily contaminated systems.

Academic considerations aside, practitioners must make decisions on issues related

to source-zone remediation now and cannot wait for the modeling advancements advocated for in this work. Guidance can be given to such individuals based upon this work. First, it is not reasonable to expect that active source-zone remediation will meet a typical drinking water standard in a short period of time, so expectations must be adjusted accordingly. Second if source-zone remediation is pursued, it should be expected that a mobilization strategy, such as surfactant flushing, will need to be followed with a secondary treatment strategy to remove DNAPL residual that cannot be mobilized. Third, if the constituents are soluble, and the site is permeable and relatively old, mobilization may not be an effective source-zone remediation strategy because DNAPL residual saturation levels would likely be sufficiently low that mobilization would not be effective. Fourth, because typical cleanup standards require essentially complete DNAPL removal from a source zone and contaminants sorbed or diffused into low permeability layers will still remain, a contaminant containment system, such as a chemical or biological reactive barrier, may be needed to protect downstream water quality for an extended period of time even at sites that have had source-zone remediation. Fifth, realize the mass transfer coefficient that appears in the standard mass transfer model is affected by many properties of the system, which makes estimates of this coefficient based upon other studies and other scales inherently unreliable.

Two other topics that have been debated in the literature in recent years are related, although not the focus, of this investigation: (1) the importance of contaminant concentrations versus contaminant fluxes from source zones, and (2) the characterization of the dissolution process. These two topics are related in that both are affected by issues of scale. While records of decision are typically based upon sampling from monitoring wells, it has been argued that a more sensible management variable is contaminant flux exiting a source zone (Soga et al., 2004). The laboratory results included both concentrations and fluxes, while the field investigation did not include flux measurements and instead relied upon a series of multi-level sampler data. In an ideal situation, small-scale characterization of concentrations and velocities and overall measures of contaminant flux would be available and such data would yield the most complete insight about the state of a system and its response to a remedial effort because it could be upscaled to deduce larger scale measures, such as the overall flux from a source zone. Inadequately resolved fine-scale concentration data cannot be used to reliably estimate an overall flux from a source zone. If the overall flux is of concern, then it should be measured. On the other hand, typical records of decision are based upon concentration measured in some set of monitoring wells, which is a different criterion than source-zone flux.

The second topic that bears upon this investigation is the way in which the mass transfer process is characterized. Confusion exists over whether mass transfer is an equilibrium or rate controlled process. This issue bears directly on issues of scale. At the interface between an aqueous phase and a DNAPL, the aqueous phase approaches a concentration equivalent to the aqueous-phase solubility limit of the DNAPL over a time scale that is considered short compared to the time scale at which groundwater flows. From this perspective, it is reasonable to say that DNAPLs can be assumed to be in equilibrium with the aqueous phase. This conclusion is consistent with results reported in the literature nearly two decades ago and the scale at which laboratory experiments are typically done (Miller et al., 1990). However, an equilibrium state suggests that the aqueous-phase concentration is equivalent to the solubility limit. This condition is rarely observed in multidimensional systems and only occasionally observed in one-dimensional systems where NAPL saturation and hydraulic residence time are favorable (e.g., (Imhoff et al., 1998)). The reason for this is that even if concentrations at the boundary of the fluid phases are at solubility at the microscale, these concentrations get averaged over regions that are well below solubility due to the complexities of the flow system in a multiphase porous media at the macroscale. The same notions apply as one moves up the hierarchy of scales present in a natural porous medium system. Overall mass transfer at the field scale has been shown to be affected by the heterogeneity of the media and DNAPL distributions and concentrations rarely approach equilibrium (Parker and Falta, 2008; Parker and Park, 2004; Powers et al., 1992). However, if one knew the morphology and topology of the fluid distributions and velocities at a sufficiently fine scale, equilibrium between the DNAPL and the aqueous phase could be assumed and the state of the system averaged up accordingly. Thus, more information is needed about the morphology and topology of a DNAPL distribution than just the DNAPL saturation to realistically describe and evolve the mass transfer coefficient.

3.6 Conclusions

Several conclusions can be drawn from this work:

1. Source-zone remediation based upon mobilization can result in a rapid reduction in the fraction of DNAPL present in some systems and affect little fractional removal in other systems, because fractional removal is not a meaningful metric of a system.

2. At best, mobilization approaches are expected to leave percent level DNAPL residual saturations after source-zone remediation, which is much larger than the value needed to produce downgradient aqueous-phase concentrations that meet typical drinking water standards.
3. DNAPL mobilization technologies are increasingly more effective and efficient at removing contaminant mass as the initial DNAPL volume fraction increases, and for systems in which low saturations of DNAPL exist, controlled mobilization will be relatively ineffective.
4. To achieve multiple log-scale reductions in aqueous-phase concentration will in most cases require either a very long period of remediation or a series of treatment technologies, such as mobilization followed by an enhanced mass transfer process to remove residual DNAPL and perhaps a tertiary step of treatment as well.
5. While active source-zone remediation of heavily contaminated sites via mobilization alone cannot render down-gradient aqueous-phase concentrations that approach drinking water standards, removals of a large fraction of the DNAPL mass via mobilization does lessen the remediation burden on alternative technologies used to reach a final cleanup standard.
6. A widely applicable correlation for the mass transfer coefficient as a function of other system variables and parameters does not exist because efforts to date at all scales have not included a sufficiently rich set of variables to characterize accurately the dominant processes that affect mass transfer. This situation is in part a result of traditional models and experiments excluding important characteristics such as interfacial areas. More fundamental approaches will be required to resolve this long-standing problem.

Chapter 4

Dense, Viscous Brine Behavior in Heterogeneous Porous Medium Systems

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4.1 Introduction

The effective, efficient, and economical remediation of subsurface systems contaminated with DNAPL remains a significant environmental challenge. Over the last several years, the use of dense-brine methods have been explored as a means to control DNAPL movement during mobilization-based remediation approaches. These approaches are collectively referred to as BBRTs. The basic premise behind BBRTs is that a dense brine can be used to increase the density of the aqueous phase and inhibit downward migration of DNAPL in the presence of DNAPL mobilizing flushing solutions, such as surfactants, or to induce upward mobilization of brine by increasing buoyancy forces.

An example application of BBRTs involves the establishment of a dense brine layer above a low permeability layer and beneath a DNAPL-contaminated region, lowering of the water table to increase gravity forces acting on the DNAPL to mobilize the DNAPL downward, vertical flushing with a surfactant solution to further mobilize the DNAPL downward, collection of the mobilized DNAPL from the top of the brine layer, and secondary treatment of the residual DNAPL remaining in the unsaturated zone

using, for example, vapor extraction. Such an approach has proven effective in three-dimensional, heterogeneous laboratory systems (Johnson et al., 2004).

Laboratory experiments to investigate a range of BBRTs have been performed in one-, two-, and three-dimensional porous medium systems, and heterogeneous systems have been the focus of these experiments (Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000). Encouraging results have been reported based upon these experiments, including the efficient removal of high fractions of DNAPL from heterogeneous, three-dimensional systems (Hill et al., 2001; Johnson et al., 2004).

The encouraging results of laboratory investigations of BBRTs notwithstanding, many open fundamental issues must be resolved before a determination of the feasibility of using BBRTs for active source-zone remediation at the field scale can be made. One set of these open issues deals with the behavior of the dense brine solutions of which relatively little is known. For example, the viscosity of CaBr_2 solutions has not been carefully measured and functionally described for a complete range of mass fractions. In addition, relatively little work has been done to understand flow and transport phenomena in porous medium systems for solutions that have the range of density and viscosity variations of interest for BBRTs. It is known that non-ideal dispersion behavior exists for other non-dilute brine systems, although the appropriate model to describe such systems is an open issue (Hassanizadeh and Leijnse, 1995; Landman et al., 2007b). As with any system that exhibits the range of density and viscosity variations characteristic of BBRTs, both gravity and viscous fingering instabilities are a potential concern depending upon displacement patterns and medium characteristics. As a result of these complexities, no mechanistic simulation model has been developed to simulate brine behavior during the application of BBRTs.

The fundamental open issues with dense brine behavior are more than intellectual curiosities if one wishes to carefully assess the practicality of BBRTs. For example, it is important to understand: the expected density of a brine layer that can be achieved, which affects the DNAPLs for which movement can be controlled; the time scale of the stability of a brine layer, which impacts methods needed to maintain the integrity of a brine barrier; the fraction of the brine that can be recovered as a function of mass fraction, which impacts economical efficiency and the potential for reuse; the rate of removal of relatively dilute brine solutions, which may not be reusable but may be required to ensure environmental compliance; and strategies and limitations for emplacing and removing brine effectively in complex systems, which will determine the number, configuration, and use schedule of injection and removal wells.

The overall goal of this study is to investigate some of the open scientific and practical issues associated with dense, viscous brine behavior in heterogeneous porous medium systems. The specific objectives of this work include: (1) to determine the density and viscosity of CaBr_2 solutions over a wide range of mass fractions; (2) to determine the feasibility of establishing and maintaining a high density layer in a heterogeneous porous medium at the laboratory scale; (3) to assess the rate of brine recovery from a heterogeneous laboratory system; (4) to assess the scalability of experimental results achieved in the laboratory to a heterogeneous field-scale system; (5) to evaluate the role of instabilities in brine layer emplacement, maintenance, and removal at the field-scale; (6) to develop a numerical simulation model to describe dense brine movement; (7) to apply the numerical model to support the understanding of laboratory and field observations; and (8) to assess remaining issues requiring resolution to achieve a mature level of understanding of dense brine behavior in heterogeneous porous medium systems.

4.2 Background

4.2.1 Overview

The dense, viscous fluids of concern in this work can exhibit complex patterns of flow and transport in porous medium systems that depend upon fluid properties, solid medium properties, and displacement patterns (Schincariol and Schwartz, 1990; Schincariol et al., 1994; Sudicky, 1986; Voss and Souza, 1987; Welty and Gelhar, 1991, 1992). While such systems are of significant recent interest due to applications that include waste disposal (Nordbotten et al., 2004; Rumynin et al., 2005), DNAPL remediation (Hill et al., 2001; Johnson et al., 2004; Miller et al., 2000), and saltwater intrusion (Abarca et al., 2007; Brovelli et al., 2007; Goswami and Clement, 2007; Held et al., 2005; Zhang et al., 2001), the understanding of such systems is not complete. In the sections that follow, the state of knowledge regarding equations of state, density effects, viscous effects, porous medium property effects, model formulation, and simulators are briefly summarized.

4.2.2 Equations of State

Fluid flow through a porous medium depends on the density and viscosity of the fluid. In systems with a wide range of variability in these properties, equations of state have to be established to effectively model the system. Although there is a lack of

published data for CaBr_2 , several functional forms for density, ρ , and dynamic viscosity, μ , have been proposed for sodium chloride. The most commonly used non-dilute forms are for density (Diersch and Kolditz, 2002; Kolditz et al., 1998; Watson et al., 2002),

$$\rho = \rho_0 \exp(\gamma\omega) \quad (4.1)$$

where ρ_0 is the reference density, γ is a fitting parameter, and ω is the salt mass fraction; and for viscosity (Johannsen et al., 2006; Watson et al., 2002; Zhou et al., 2005)

$$\mu = \mu_0(1 + A\omega + B\omega^2 + C\omega^3); \quad (4.2)$$

where ω is the salt mass fraction and A , B , and C are fitting parameters.

However, several other studies have used laboratory or field data to fit a range of empirical expressions for density and viscosity relations (Batzle and Wang, 1992; Gill, 1982; Kemp et al., 1989; McCain Jr., 1991; Mercer et al., 1975; Palliser and McKibbin, 1998; Phillips et al., 1981; Rowe and Chou, 1970). These functional forms, all of which were derived for sodium chloride with the exception of Gill (1982) and McCain Jr. (1991), were compared by Adams and Bachu (2002). They found that several different functional forms for density and viscosity represented the available data for sodium chloride adequately for a range of conditions depending on salinity, pressure, and temperature. They also found that both density and viscosity differences between estimated values increased with increasing mass fraction with a difference in density of up to 20%, and a difference in viscosity of up to 50% noted between different estimation methods at high mass fractions. Such differences suggest that care must be taken in choosing an appropriate equation of state. The density and viscosity properties of CaBr_2 , and their respective equations of state, have not been reported over the wide range of mass fractions of interest for BBRTs.

4.2.3 Density Effects

Fluid densities change as a function of fluid pressures, temperatures, and chemical composition. The primary causes of density-dependent flow are due to temperature changes and compositional effects. Both of these motivating conditions have been the source of a substantial amount of recent research (Ackerer et al., 1999; Dentz et al., 2006; Diersch and Kolditz, 2002; Flowers and Hunt, 2007; Graf and Therrien, 2007; Jiao and Hotzl, 2004; Landman and Schotting, 2007; Nigam and Woods, 2006; Prasad and

Simmons, 2003; Schotting et al., 1999; Simmons et al., 2001, 2002; Wood et al., 2004). When nonuniform densities exist in a porous medium system, a gravitational driving force gives rise to preferential flow of a more dense fluid overlying a less dense fluid in the vertical direction and can result in gravity fingering (Prasad and Simmons, 2003; Schincariol et al., 1994, 1997; Simmons et al., 2001; Simmons and Narayan, 1997; Welty and Gelhar, 1991; Woods and Carey, 2007). Density-dependent flow will occur until either an impermeable boundary is encountered or the fluid properties, hence density, change to remove the density gradient. In other words, such systems tend toward a stable state. For the non-isothermal case, this implies stability when an isothermal condition has been obtained, or conversely that unstable conditions and fluid motion can persist in certain cases, such as in a classical Raleigh-Bernard convection system (Gebhart et al., 1988).

For compositionally-motivated density-dependent flow, a different situation results. The thermodynamic equilibrium condition for a closed system is a solution of uniform composition and density. However, gravitational forces result in a quasi-stable distribution, which can be a relatively sharply stratified system with a thin transition region for cases in which the pore space is filled with sources of two fluids that differ substantially in density. The time scale to achieve a quasi-stable stratified configuration are in general much shorter than the time scale needed to achieve thermodynamic equilibrium typified by uniform composition, since diffusive and dispersive transport is relatively slow in such non-ideal systems.

4.2.4 Viscous Effects

The standard Darcy approximation of the momentum equation predicts that specific discharge is inversely proportional to the viscosity. The generally small change in viscosity that result from compositional changes in most systems has led to a tendency to consider viscosity constant, even in systems for which density variation are of concern (Fried, 1975; Ophori, 1998). This seems reasonable for many systems and is a convenient assumption.

Viscosity variations can be important and give rise to both interesting and complex issues. For certain compositional systems, such as the dense brines of focus in this work, viscosities can be several times that of water, which greatly exceeds the contrasts observed in typical saltwater intrusion applications. Changes in viscosity of this magnitude can significantly affect flow and transport phenomena. Viscosity variations lead

to the potential to develop unstable fingering when a less viscous solution displaces a more viscous solution (Heller, 1966; Juanes and Blunt, 2006; Nagatsu et al., 2007; Paterson, 1985; Welty and Gelhar, 1991; Wooding, 1969). In addition, when compositional variations lead to significant changes in both density and viscosity, interactions between viscous and gravity instabilities will result (Flowers and Hunt, 2007; Jiao and Hotzl, 2004). The nature of these interactions has not been completely elucidated for dense viscous brines.

4.2.5 Porous Medium Property Effects

The effects of density gradients on groundwater flow have been widely studied in recent years, so have the effects of heterogeneity in hydraulic properties of porous media on flow and transport (Elfeki and Dekking, 2001; Juanes and Blunt, 2006; Prasad and Simmons, 2003; Scanlon et al., 2003; Schincariol, 1998; Schincariol and Schwartz, 1990; Shikaze et al., 1998; Simmons et al., 2001; Simmons and Narayan, 1997; Smith and Freeze, 1979). Investigations of the effects of heterogeneity on density-dependent flow have demonstrated a dependence of instability onset and growth or decay on the magnitude of spatial variability in subsurface characteristics, such as hydraulic conductivity (Schincariol and Schwartz, 1990; Simmons et al., 2001).

The onset and growth of density instabilities in heterogeneous media is complex. While local perturbations in the permeability field may induce the formation and growth of instabilities, continued flow through heterogeneous media may in turn reduce growth and increase stabilization of perturbations due to mixing caused by dispersion (Schincariol and Schwartz, 1990; Schincariol et al., 1997). In addition, the existence of low permeable regions such as clay lenses can dampen instability growth and in cases where the density contrast is low stabilize perturbations (Schincariol et al., 1997). In addition, simulations conducted by Schincariol et al. (1997) suggested that low permeability regions can dampen the upward migration of freshwater. Comparatively, much less is known about systems for which both large changes in density and viscosity occur in heterogeneous systems.

4.2.6 Model Formulation

While mechanistic macroscale models based upon phase and species conservation of mass equations are well established and the standard basis for formulations involving density-dependent flow in porous medium systems (e.g., Bear and Bachmat (1991);

Hassanizadeh and Gray (1979); Voss (1984); Voss and Souza (1987)), the adequacy of the closure of such models is in question. As noted above, relations for densities and viscosities as functions of mass fractions are not well established and have yet to be detailed for the CaBr_2 solutions of focus in this work. Without accurate relations for such key variables, model formulations and the resultant simulations will be inaccurate as well.

In addition, high concentration brine solutions are non-ideal solutions. The significance of this observation is manifest in the failure of traditional advective-dispersive models to describe the observed movement and dispersion of brine fronts. Formal averaging (Hassanizadeh and Leijnse, 1995; Schotting et al., 1999; Watson et al., 2002) and homogenization approaches (Landman et al., 2007b) have been used to advance models to describe such systems, but the appropriate model formulation is considered an open issue. Recent work by Gray and Miller (2009) has advanced a new class of models that appear promising, but these models have not yet been compared to experimental data.

Experimental observations have been made to support the non-ideal nature of dense brine porous medium systems and to provide a basis for the development of improved model formulations. High concentration brines have been shown to deviate from Fickian dispersion. Gravitational effects have been shown to have a stabilizing effect on upward displacement of brine in column studies decreasing the observed amount of dispersion relative to an ideal, dilute tracer. This phenomena results in a decrease in the length of the mixing zone (Hassanizadeh and Leijnse, 1995). Changes in dispersive properties have been shown to depend upon flow rates (Landman et al., 2007b; Schotting et al., 1999; Watson et al., 2002), density, viscosity, and concentration gradients (Welty and Gelhar, 1991), porous medium properties (Landman et al., 2007b; Watson et al., 2002), and the magnitude of the density contrast (Landman et al., 2007b).

4.2.7 Simulators

Several production-level finite-element- and finite-volume-based simulators have been developed to model variable-density subsurface flow and transport. These include, but are not limited to, SUTRA (Voss, 1984), FEFLOW (Diersch, 2005), TOUGH2 (Oldenburg and Pruess, 1995), FEMWATER (Lin et al., 1997), and ROCKFLOW (Kolditz et al., 2001). Nonlinear compositional effects and their interaction with heterogeneous porous media mean that analytical or semi-analytical solutions are available in only limited, highly idealized cases (van Duijn et al., 1998; Verruijt, 1968). As a result,

a series of benchmark problems are typically used to evaluate model performance for some subset of the challenges associated with density-dependent flow and transport.

Available benchmarks range from stable displacements with low-density contrasts (Henry, 1964) to highly unstable free-convection problems (Elder, 1967). To be more specific, common test problems include the classical Henry saltwater intrusion problem (Henry, 1964), the HYDROCOIN salt dome problem (Konikow et al., 1997; Oldenburg and Pruess, 1995), and the low-density version of the three-dimensional salt pool problem (Oswald and Kinzelbach, 2004). Stable displacement configurations with high density-contrasts are considered in column experiments (Hassanizadeh and Leijnse, 1995; Schotting et al., 1999) as well as a high-density saltpool experiment (Oswald and Kinzelbach, 2004). On the other hand, benchmarks like the salt lake (Simmons et al., 1999) and Elder (Elder, 1967) problems involve configurations with dense fluid overlying less dense fluid and so exhibit highly unstable fingering and solutions that are qualitatively different depending on the mesh resolution and numerical approximation (Diersch and Kolditz, 2002; Frolkovic and De Schepper, 2001).

Collectively these benchmarks highlight the particular challenges of modeling density dependent flow and transport. In addition to the basic complication of nonlinear closure relations for density and viscosity and potentially non-ideal dispersion behavior, density-dependent coupling places a premium on accurate, stable resolution of solution fronts and accurate velocity approximations (Ackerer and Younes, 2008; Diersch and Kolditz, 2002; Mazzia and Putti, 2002). For problems with gravity or viscous fingering instabilities, mesh resolution has proven critical. In comparisons among multiple simulators, a number of discrepancies have come to the forefront. Discretization effects have resulted from different mesh types and refinement levels. For the Elder problem, several researchers have found varying results on whether the central flow element is upwelling or downwelling due to changes in mesh resolution (Ackerer et al., 1999; Diersch and Kolditz, 2002; Kolditz et al., 1998; Oldenburg and Pruess, 1995; Park and Aral, 2007; Voss and Souza, 1987; Woods et al., 2003). Similar influences of mesh discretization on the speed of propagating density fingers and the number of these perturbations have been found with the salt lake problem as well (Diersch and Kolditz, 2002; Simmons et al., 1999; Wooding et al., 1997). Some have even concluded that the Elder problem is not an appropriate benchmark problem due to the influence of the boundary conditions (Simpson and Clement, 2003).

Recent efforts have been aimed at improving numerical methods to more accurately simulate the Elder problem as a benchmark (Ackerer and Younes, 2008). More broadly,

unstable systems and problems with sharp interfaces continue to challenge and motivate research into improved numerical methods (Gotovac et al., 2007; Johannsen et al., 2006; Landman et al., 2007a; Younes et al., 2009). It seems clear that high-resolution simulation of dense, viscous fluids in complex porous medium systems remains difficult and that care is needed in applying existing simulators to such systems.

4.3 Approach

4.3.1 Overview

The work undertaken to meet the objectives of this study included characterization of solution properties, selecting and characterizing porous media, performance of three-dimensional laboratory cell experiments of brine emplacement and recovery, performance of a field-scale experiment of brine emplacement and recovery, and the modification and application of a numerical model to simulate density and viscosity dependent flow and transport phenomena in heterogeneous porous medium systems. The approach used for each of these components are summarized in the subsections that follow.

4.3.2 CaBr_2 Equations of State

CaBr_2 was chosen as the brine source because it is readily available in large quantities in a concentrated form of 53% by weight (Synergy Fluids, Houston, Texas). In addition, the density of concentrated CaBr_2 solutions can exceed the density of most DNAPLs, which allows the use of such solutions for controlling bulk DNAPL movement. This property is essential for BBRTs.

The objective of this aspect of the study was to develop equations of state for density and viscosity of high-concentration CaBr_2 solutions. To do this, measurements of both properties were made for a range of mass fractions. The density of CaBr_2 solutions with mass fractions up to 0.53 was measured using an Anton Paar DMA 48 density meter. The meter measures density from $0-3 \pm 0.0001 \text{ g/cm}^3$. All samples were measured at 20°C . Viscosity was measured with a Haake Model B falling ball viscometer. All samples were measured at 20°C and at mass fractions that corresponded with the measured density values. Several measurements were collected for each mass fraction sample due to measurement variations. The standard deviation ranged from 0.0074 cP at a mass fraction of zero to 0.0108 cP at a mass fraction of 0.53.

Table 4.1: Porous medium properties of laboratory cell for brine analysis.

Property	Dover sand (DS)	Quartz sand (QS)
d_{50} (mm)	0.47	0.30
Uniformity coefficient (d_{60}/d_{10})	2.79	4.30
Particle density (g/cm^3)	2.63	2.66
Porosity	0.44	0.33
PV	3.775 L	2.604 L
Packing	corr. random field	homogenized

4.3.3 Laboratory Cell Experiments

Laboratory experiments were undertaken to meet two objectives: (1) to determine the feasibility of establishing and maintaining a high density brine layer with minimal dilution effects, and (2) to assess the rate at which brine can be removed from a system. The importance of the first objective is that the density of the brine layer that can be established determines the range of DNAPLs for which free-phase flow can be controlled. The importance of the second objective is that the brines are expensive so it is advantageous to recycle these brines, and most field-scale applications of BBRTs will require removal of a substantial fraction of the brines after remediation is accomplished. The rate and mass fractions at which these brines can be recovered bear upon the efficacy of recycling of the brine and the overall cost of such technologies. Because such aspects of these systems have not been investigated to date, it was appropriate to start with controlled laboratory studies.

Two laboratory experiments were conducted in a three-dimensional cell that measured 22.5-cm long $\times$ 16.5-cm wide $\times$ 24-cm tall and was fitted with an aluminum cover. The cell was filled with porous media to a height of approximately 21 cm. Each experiment was packed with a different medium. One experiment consisted of a mix of quartz sand (QS), which was based on sieve analysis of the DS and consisted of several Accusands (12/20, 20/30, 30/40, and 40/50) and two U.S. Silica sands (AFS 50/70 and F95), and was packed as a homogenized mix. The other experiment was packed as a correlated random field with DS collected from the DNTS in Dover. The properties of each porous medium are provided in Table 4.1.

To create a correlated random field for the DS experiment, the DS was sieved into 12 different sized fractions, all with a diameter less than 2 mm. The DS was packed into the laboratory cell using a 21-layer heterogeneous packing based on a correlated random field model assuming anisotropic exponential covariance conditions and a log-

normal particle size distribution (Christakos, 1992b; Deutsch and Journal, 1992). Each layer consisted of cubes of homogeneous sands obtained from the sieved fractions of 1.5-cm length and width and 1-cm height. Correlation lengths of 7.5 and 5.0 cm for the horizontal and vertical planes, respectively, were used to match the scale of the tank used in the experiment. The mean and standard deviation of the log of particle size were $-0.789 \ln(\text{mm})$ and 2.39, respectively.

Both experiments contained a series of injection and extraction ports as well as sampling ports for monitoring in situ density during all phases of the BBRTs. Stainless steel tubing (2.21-mm i.d., 3.05-mm o.d.) was used for injecting and extracting brine from locations 0.5 and 4.5 cm above the bottom of the cell. The layout of the port locations is represented in Figure 4.1. All injection and extraction ports were point sources and sinks, respectively. All boundaries of the cell were no flow boundaries, but the top of the cell was vented to the atmosphere. Ports labeled with a “B” in Figure 4.1 were located 4.5 cm from the bottom of the cell and ports labeled with a “L” were located 0.5 cm from the bottom of the cell. Stainless steel tubing (0.51-mm i.d., 0.82-mm o.d.) was used as sampling ports. The cell was packed with sand, the ports inserted, the system sealed using a gasket-lined aluminum lid, and the cell vibrated to consolidate the media. The system was flushed with CO_2 gas prior to injecting de-aired DDI water through the deepest ports to saturate the system.

The phases of the BBRTs emulated in the laboratory experiments included establishing a brine barrier by injecting brine with a mass fraction of 0.53 g/g ($\rho=1.7098 \text{ g/cm}^3$) near the bottom of the cell and displacing freshwater upward, pumping near the brine barrier interface (BBI) as it would be done during implementation of a remedial strategy, dewatering of the cell and bulk brine removal, and flushing of the residual brine remaining with freshwater to reduce in situ densities and the total dissolved solids (TDS) concentrations. Table 4.2 provides a summary of injection and extraction locations, PV, as well as sampling locations during each stage of the implemented BBRTs. Effluent and in situ density samples were collected and analyzed during the entire process.

For the QS experiment, fluid was extracted through an upper port (E1) until air was present in the effluent. Fluid extraction was continued through the lower ports (L1–L4), again until air was present in the effluent. The system was partially refilled with DDI water through the lower ports until the medium surrounding the upper ports appeared to be fully saturated. The system was then flushed by injecting DDI water into the lowest ports on one side of the tank (L3–L4) and extracting from the lowest

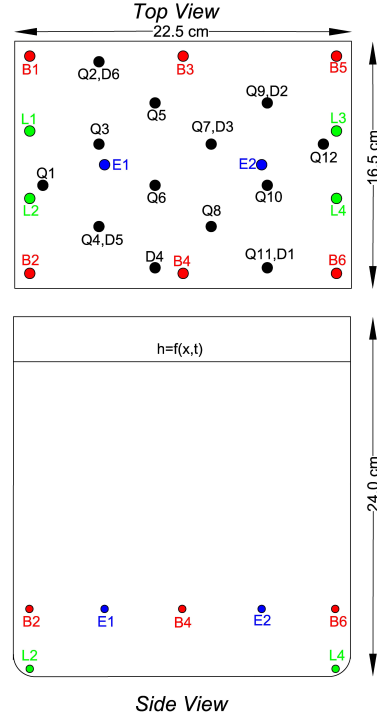


Figure 4.1: Top and side view layout of brine injection and extraction ports for the three-dimensional laboratory cell.

ports on the other side (L1–L2). Additional flushing was conducted by injecting DDI water into the upper ports (B1–B6) and extracting from the lower ports (L1–L4).

Brine was injected into the lowest ports of the DS cell to minimize mixing due to density inversions and establish the brine layer more efficiently. Once the brine layer was established, the CaBr_2 was recovered in each experiment in a different manner. For the DS experiment, fluid was initially extracted through E1, E2, B3, and B4 during the pumping and the initial dewatering stage then extracted through the lower ports (L1–L4) and the system partially refilled and flushed from side to side.

A volume fraction of less than 0.005 of tetrachloroethylene was injected into the DS cell. This low volume fraction of organic liquid was confined to the upper portions of the cell and was assumed to have a negligible effect on the brine aspects of this work, which is the focus of this work.

4.3.4 Field Experiment

A field-scale experiment was performed at the DNTS to assess the scalability of experimental results achieved in the laboratory to a heterogeneous field-scale system.

Table 4.2: Summary of laboratory experiments during brine barrier establishment and maintenance.

Stage	Brine Barrier Establishment		Pumping and Dewatering	
Medium	QS	DS	QS	DS
Injection ports	B1–B6	L1–L4	B1–B6, L3–L4	L1–L4
Extraction ports	—	—	E1, L1–L4	E1–E2, B3–B4, L1–L4
Sample locations	Q1–Q12	D1–D6	Q1–Q7	D1–D6
Injection/extraction (PV)	0.65	0.42	0.30	0.16

Of special interest was an assessment of the brine barrier density that could be achieved and maintained, and the nature of brine mass recovery as a function of mass fraction. While PCE was injected in the field study, this aspect of the work is not a focus of this manuscript. Because the volume fraction of PCE injected was less than 0.005, it had a negligible effect on the brine aspects of the study.

The DNTS site consists of a water table aquifer overlying an extensive clay formation. The permeable sands extend from the ground surface to a depth of 11- to 14-m bgs and are comprised of fine to medium sands with occasional discontinuous clay and silt lenses (ARA, 1996). The ambient water table is approximately 8- to 11-m bgs, giving a saturated thickness of the water table aquifer of about 3 m. The vertically averaged hydraulic conductivity of the aquifer is 2.6 m/day. Organic matter, soluble salts, and clay contents of the aquifer are low. The clay formation consists of gray, firm, dense marine clays and is approximately 6-m thick with a hydraulic conductivity of 2.6×10^{-3} m/day (ARA, 1996).

Test Cell 3 was used in this study and was enclosed using double-walled W275 Waterloo BarrierTM Sheet Piles driven into the subsurface and keyed into a confining aquitard approximately 14-m bgs. Test Cell 3 was equipped with injection/extraction wells, multilevel samplers (MLS), and contaminant injection points. The layout of these locations is displayed in Figure 4.2. The test cell area was covered to prevent precipitation from infiltrating into the cell. The cell was 4.6 m $\times$ 3 m in the horizontal plane. The average depth to the clay layer was approximately 12.3-m bgs with the highest clay elevation at 11.7-m bgs. The elevation of the top of the clay layer was irregular as is shown in Figure 4.3, adding complications to both the physical experiment and computer simulations. Previous studies in this cell included a cosolvent tracer study (Brooks et al., 2002), a cosolvent solubilization study (Brooks et al., 2004), a surfactant

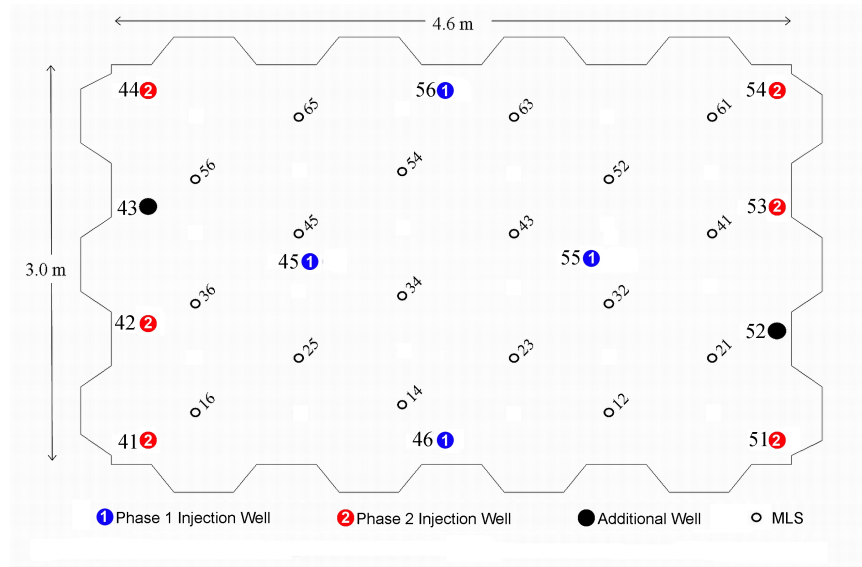


Figure 4.2: Dover Test Cell 3 layout during brine injections.

solubilization study (Childs et al., 2006), and a cyclodextrin solubilization study (Tick et al., 2003).

A CaBr_2 solution was injected into the test cell using two injection phases to establish a brine barrier at approximately 11.6-m bgs. The BBI is terminology used to represent the region in which a transition from a relatively dilute solution to a concentrated brine solution occurs; the BBI varied in location in response to injection and withdrawal. The intended design location for the BBI was 0.9 m above the average clay layer elevation and 0.3 m above the highest clay elevation.

The establishment of the brine barrier was divided into two phases using a series of screened wells that had been packed off and relying on the clay layer and sides of the cell as no flow boundaries to control flow of brine. Brine was primarily injected below 11.58-m bgs into the center of the test cell during Phase 1. Brine was injected at the same depth but on the left and right sides of the test cell during Phase 2. Details of the set up of each stage is summarized in Table 4.3, which contains information on the location of injection and extraction wells during brine barrier establishment. Phase 1 of the field study involved injecting brine into four locations to concentrate brine into the center, deeper part of the cell. Wells 45, 46, 55, and 56 (refer to Figure 4.2 for well locations) were chosen for Phase 1. Brine was injected into the bottom of these wells, which were packed off at 11.4-m bgs. Packing off the wells forced brine into the deepest portions of the cell, which promoted a stable displacement of freshwater upward and

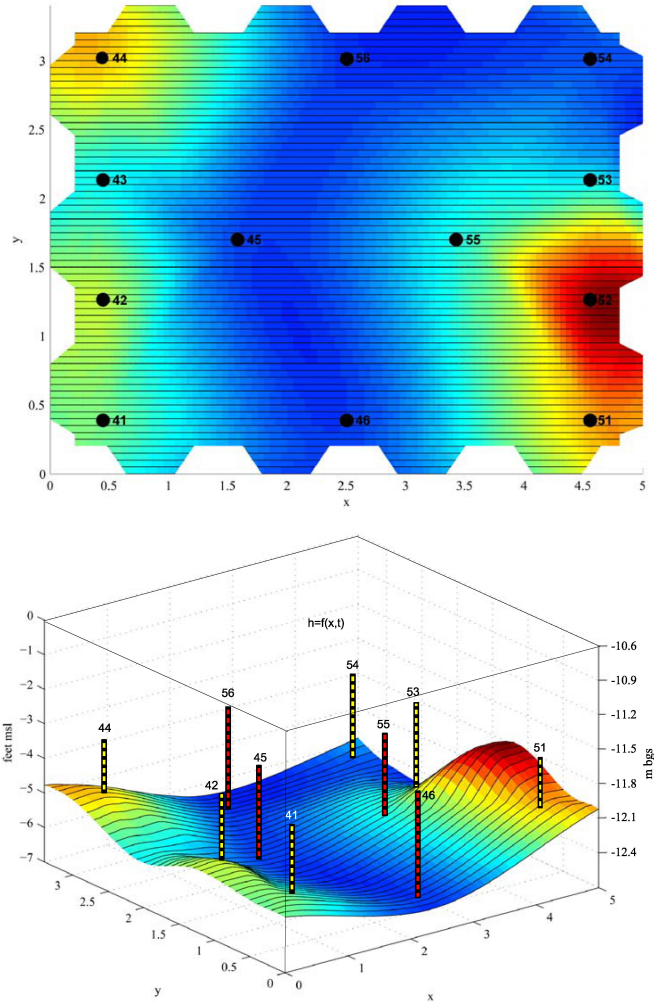


Figure 4.3: Geometry of the confining clay layer beneath Test Cell 3 and line sources for brine injection, where red locations represent Phase 1 and yellow locations Phase 2 injections.

limited brine mixing and dilution, which would decrease the efficiency of brine injection. The displaced water was then removed using wells 41, 42, 44, 51, 53, and 54 by placing pumps at approximately 10.3-m bgs. The water table at the beginning of brine injection was located at 9.3-m bgs.

After injecting approximately 2,440 L of brine over nine days during Phase 1, the brine injection/water extraction locations were reversed such that brine was injected below 11.4-m bgs into wells 41, 42, 44, 51, 53, and 54 and displaced fluids were removed at 10.3-m bgs from wells 45, 46, 55, and 56. This switch to Phase 2 of the brine injection strategy allowed the perimeter of the cell to fill with brine and provided time

Table 4.3: Summary of DNTS study during implementation of a BBRTs.

Stage	Barrier Phase 1	Establishment Phase 2	Pumping	Dewatering & Bulk Brine Removal	Barrier Flushing
Injection wells	45–46, 55–56	41–42, 44,51, 53–54	41–42, 44,51, 53–54	various	various
Extraction wells	41–42, 44,51, 53–54	45–46, 55–56	45–46, 55–56	various	various
CaBr ₂ injected (PV)	0.15	0.40	0.17	0.08	—
CaBr ₂ removed (PV)	0.002	0.11	0.33	0.18	0.12

for relaxation of hydraulic mounds formed around Phase 1 injection wells. Phase 2 continued until another 6,440 L of brine was injected, which occurred over a period of 27 days. During both brine injection phases, and the rest of the study, the fluid density was monitored in situ using multilevel samplers, through effluent sampling from wells, and through periodic bailing of wells. These data assisted in understanding how the brine propagated through the system, as well as determining the temporal profile of brine recovery.

Once the brine barrier was adequately established, brine continued to be injected to maintain the brine barrier in the cell. Brine injection was accomplished using the Phase 2 injection wells, however these wells were simultaneously pumped by packing off locations above the BBI. To minimize brine loss, packers were installed below the pumped portion of the well screens to prevent excess brine depletion. During this 48-day period, approximately 4,000 L of brine was injected to maintain the brine barrier.

At the end of the injection period, pumps were lowered to the bottom of the wells to remove bulk brine. To achieve an efficient removal of fluids, pumps were relocated to more productive wells when fluid recoveries from wells diminished due to low water levels. The remainder of the study was devoted to flushing the residual brine by adding freshwater to the system. Based on density measurements from the multi-level samplers, pumps and freshwater injection locations were rotated to target high fluid density regions.

4.3.5 Modeling Approach

The intent with the modeling was to determine if the brine recovery process could be simulated to mimic the laboratory experiment and to use the model to evaluate the effects of density and viscosity variations and heterogeneity of the intrinsic permeability at the field scale. Another purpose of the simulations, although not discussed herein, was to assist the execution of the field experiment by running preliminary and real-time simulations to guide the brine injection and removal design that was implemented. Because of the difficulty of modeling dense brine behavior, the simulation work is viewed as preliminary in nature.

SUTRA, a simulator distributed by the United States Geological Survey, was selected to carry out these objectives. SUTRA can be used to simulate saturated or unsaturated density-dependent groundwater flow and transport in three-dimensional systems. It uses a hybrid finite-element mesh discretization and an implicit, first-order, finite-difference time-stepping method to approximate the conservation equations (Voss and Provost, 1981). There is a user option of solving either (1) the conservation of mass of a fluid and mass of a solute or (2) the conservation of mass and energy of a fluid, where the first option was chosen in this study. The code solves for fluid pressures and solute mass fractions as they change with time. As is true with all discretization-based groundwater modeling applications, the method is approximate in nature and the accuracy depends upon the spatial and temporal discretization, error tolerances of the solvers, and accuracy of the parameter estimates. An additional consideration for these simulations is that, as noted before, the appropriate mathematical model formulation for such systems is considered an open issue. For all of these reasons, the expectation was that SUTRA was an approximate tool to give a semi-quantitative indication of fluid flow and species transport.

An assumption made in developing the SUTRA simulator is that solute concentrations do not affect viscosity. The equation of state for density in SUTRA is also of a form that does not match the dense brines of concern in this work. Therefore, modified equations of state for density and viscosity that accurately described concentrated CaBr_2 solutions were implemented in the modified SUTRA simulator. The functional form of these equations is discussed later.

A further modification to the SUTRA source code involved altering extraction specifications. This change was essential for the brine recovery simulations. The SUTRA model requires a mass rate of input or removal for any external source or sink. How-

Table 4.4: SUTRA model parameters for brine simulations of laboratory and field experiments.

Model Parameter	Units	Lab Value	Field Value
Freshwater density	g/cm ³	0.9982	0.9982
Freshwater viscosity	cP	1.0019	1.0019
Brine source mass fraction	g/g	0.53	0.53
Brine source density	g/cm ³	1.70	1.70
Brine source viscosity	cP	6.1	6.1
Porosity	[-]	0.33	0.35
Mean intrinsic permeability	m ²	8.3×10^{-12}	3×10^{-12}
Longitudinal dispersivity	m	0.0048	0.48
Transverse dispersivity	m	0.0016	0.16
Molecular diffusivity	[m ² /s]	1.22×10^{-9}	1.22×10^{-9}
n_{VG} (van Genuchten)	[-]	2.0	2.0
α_{VG} (van Genuchten)	[-]	5×10^{-5}	5×10^{-5}

ever, in the field-scale experiment, volumetric injection and extraction rates were used to control the level of the water table in the test cell. Because the mass recovery rate from a well varied with time, it was not convenient to convert a desired volume extraction rate to a mass extraction rate necessary for SUTRA input.

Source code modifications were made such that a volume extraction rate could be specified in the simulation. To make this change, the mass fraction output at each time step in SUTRA, ω^t , and the density equation of state were utilized. From a given volumetric extraction rate (E_V), the mass extraction rate required by SUTRA at each time step (E_m^t), was approximated by:

$$E_m^t = E_V [\rho^{t-1} \omega^{t-1}] \quad (4.3)$$

Because the time steps were relatively small compared to the time rate of change of the density, this approach provided an accurate approximation for the desired mass extraction rate. This change allowed the amount of fluid in the system to be easily controlled in the simulator to match the field conditions.

A laboratory system and a field-scale system were simulated. Some of the relevant model parameters used in the SUTRA simulations for both the laboratory and field-scale simulations are given in Table 4.4.

The laboratory simulation was designed to mimic the laboratory experiment that contained a homogenized mix of quartz sand. Location of injection, extraction, and sampling ports were selected based upon the corresponding locations in the experiment.

Table 4.5: Dispersivity coefficients for laboratory experiment simulations.

Simulation	α_l	α_t
T1	0.048 m	0.016 m
T2	0.0048 m	0.0016 m
T3	0.00048 m	0.00016 m

Initial conditions used in the simulation correspond to the sharp concentration gradient observed in the experiment once the dense brine layer had been established. The initial mass in place in the simulation was approximately 750 g of CaBr_2 . Hydrostatic pressure was set to zero at the top of the domain. The simulation included system dewatering, partial refilling with freshwater, and both horizontal and vertical flushing to remove the residual brine.

Because of the non-ideal dispersion behavior of dense brines, the effect of different dispersivity coefficients was explored for this system. Three sets of longitudinal and transverse dispersivity coefficients were tested, as shown in Table 4.5, with the range varying over three orders of magnitude. The dilute tracer longitudinal dispersivity for this system was estimated to be on the order of 0.1 cm.

Field-scale laboratory simulations were designed to represent the DNTS test cell during the brine emplacement period. The elevation of the top of an irregularly shaped clay layer was interpolated based on well installation data. The locations of wells and sampling points were based on their locations within the test cell. Minimal information on the heterogeneity of the domain was available, so as a first approximation it is assumed that the effects of heterogeneity could be evaluated by treating permeability as a log-normally distributed spatial random field (SRF) (Freeze, 1975; Simmons et al., 2001). Realizations of three-dimensional permeability fields were generated using sequential Gaussian simulation (SGSIM) (Deutsch and Journel, 1992). It was assumed that changes in permeability were gradual and that the domain could be approximated by a Gaussian covariance model. Correlation length scales could not be determined because of a lack of permeability data. The vertical and horizontal correlation length scales (γ_y and γ_x , respectively) were assumed to be 0.5 m and 2.5 m, respectively. SGSIM was used to create two permeability fields: a domain heterogeneous in three dimensions, and a vertically layered domain with each layer having a homogeneous permeability. In the latter case, SGSIM was used to generate a packing with a desired vertical correlation length and vertical covariance structure. Information on permeabil-

Table 4.6: Permeability fields for field-scale simulations.

Simulation	Domain	Variance	γ_x	γ_y
F1	Homogeneous	0	-	-
F2	Gaussian SRF	1	2.5 m	0.5 m
F3	Layered	2	-	0.5 m

ity fields used in each brine simulations are available in Table 4.6.

Initial conditions for the DNTS cell simulations consisted of a solute mass fraction set to zero, and a hydrostatic pressure profile with the top of the water table equal to zero. All boundaries were set as no flow boundaries, which matched the physical system that was contained with sheet piling. Brine was injected into the model system below 11.58-m bgs based on the strategy implemented in the field study such that Phase 1 occurred at an average injection rate of 5.34×10^{-3} kg/s over a 9-day period and Phase 2 occurred at an average injection rate of 4.75×10^{-3} kg/s over a 27-day period. Fluids were extracted from the top of the domain over the 36-day period at an average rate of 2.95×10^{-6} m³/s.

4.4 Results

4.4.1 Equations of State

The density and viscosity of CaBr₂ solutions were measured as a function of mass fraction yielding the results shown in Figure 4.4. Both relationships exhibited nonlinear behavior that was not well described by standard equations of state. The change of viscosity for CaBr₂ was substantial, therefore such changes must be accounted for to model transport phenomena accurately in the systems of concern in this work and for BBRTs in general.

An empirical equation of state for fluid density as a function of CaBr₂ mass fraction was estimated from the data using nonlinear least-squares analysis. The third-degree polynomial that accurately describes the measured data is

$$\rho(\omega) = 0.8319\omega^3 + 0.4958\omega^2 + 0.8417\omega + 0.9982 \quad (4.4)$$

where density is given in g/ml, and 0.9982 is the reference density.

An empirical equation of state for fluid viscosity as a function of CaBr₂ mass fraction

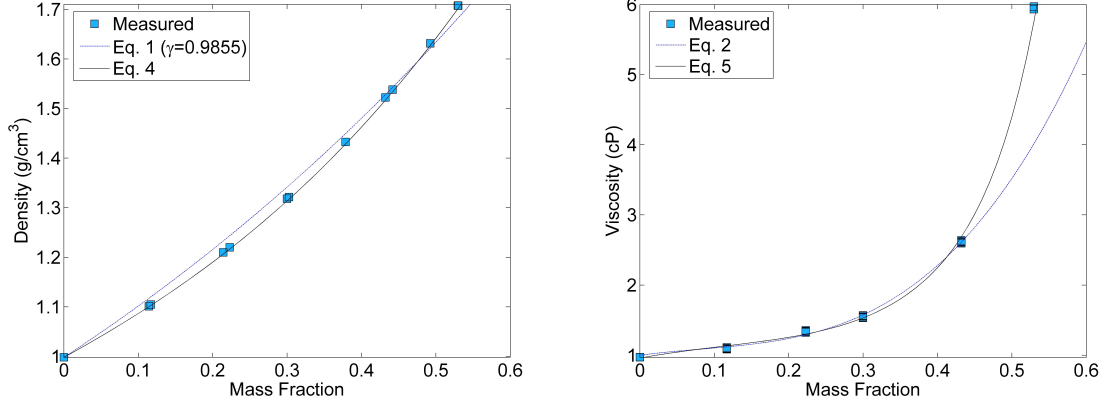


Figure 4.4: Density (*left*) and viscosity (*right*) of CaBr_2 as a function of mass fraction.

was estimated from the data and is of the form

$$\mu(\omega) = 1.0019e^{[16.43\omega^3 - 5.190\omega^2 + 1.552\omega]} \quad (4.5)$$

where viscosity is given in cP.

Using Equation 4.1 for the density relationship with a γ value of 0.6923, a value that was originally derived from sodium chloride solution data, would lead to an under prediction of the density of a CaBr_2 solution. Estimating the fitting parameter from the CaBr_2 data yields a γ value of 0.9855 and improves the model fit for Equation 4.1. However, the improved relationship over and under predicts density when the mass fraction is less than and greater than 0.4, respectively. The viscosity relationship typically used to model groundwater systems (Equation 4.2), which was fitted to the CaBr_2 data such that $A=1.43$, $B=-6.77$, and $C=27.98$, under predicts viscosity for mass fractions greater than 0.42 relative to the data and the empirically derived Equation 4.5.

4.4.2 Laboratory Study

Laboratory Cell Experiment Results

In situ density samples were collected at elevations from 2.0 to 7.0 cm from the bottom of the tank during the QS experiment. Figure 4.5 shows density as a function of depth and number of PVs of brine injected during the establishment of the brine barrier. At early times, sampling locations in close proximity to injection ports had the highest density measurements. This led to large variations in density at a given elevation as can be seen in the data collected after injecting 0.23 PV of brine. For

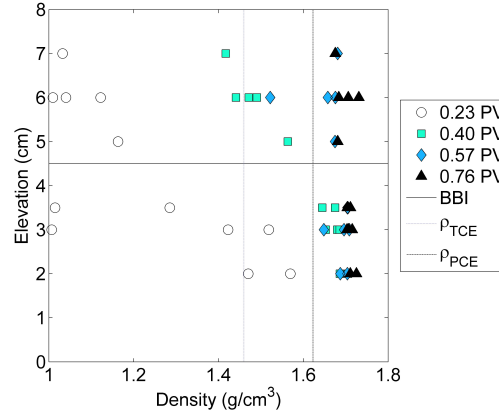


Figure 4.5: Density as a function of elevation during the establishment of the brine barrier for the QS laboratory experiment.

example, the density ranged from 1.01–1.52 g/cm³ at an elevation of 3.0 cm. Density variations at a given elevation greatly diminished after the addition of 0.40 PV of brine. After 0.40 PV, observed densities from the bottom of the tank to the extraction port at 4.5 cm (i.e., the designated BBI) exceeded the density of TCE, which has a density of 1.46 g/cm³. After 0.57 PV, observed brine densities from the bottom of the tank to the extraction port at 4.5 cm exceeded the 1.62 g/cm³, which corresponds to the density of one of the denser DNAPLs of interest, PCE.

Density sampling during the DS experiment was limited compared to sampling during the QS experiment. Samples were only collected at elevations from 1.0 to 3.0 cm from the bottom of the tank. Density as a function of depth after the establishment of the brine barrier are shown in Figure 4.6. Markers in this figure represent the average brine density and lines represent the range of observed densities. There was little variation in density in the lower portion of the cell after the addition of 0.42 PV of brine.

After establishing a brine barrier, pumping began at the BBI, as it would during implementation of a BBRTs. During pumping, brine continued to be injected into the cell through the deepest ports to maintain the brine barrier and counter losses due to pumping. Pumping induced mixing around the extraction wells. Therefore, in situ densities were measured to determine the effect of pumping in the vicinity of the BBI. Densities measured near the end of pumping are shown in Figure 4.6 for the DS medium. After significant pumping from an elevation of 4.5 cm, densities measured at an elevation of 3.0 cm ranged from 1.3 to 1.7 g/cm³. The lowest densities were observed

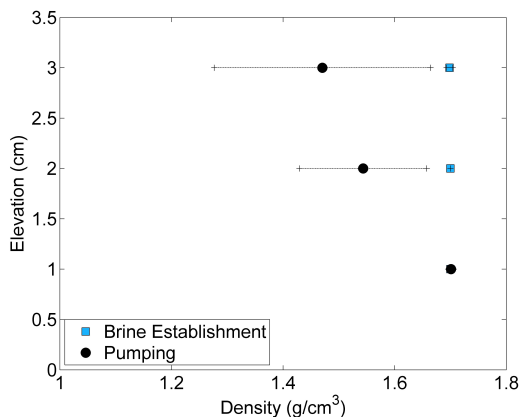


Figure 4.6: Average density as a function of elevation after the establishment of the brine barrier and during pumping for the DS laboratory experiment.

near the extraction locations. The average density in the brine barrier increased and the variability decreased closer to the bottom of the cell. The results suggests that capillary forces will need to offset the loss of buoyancy to prevent DNAPLs with densities similar to TCE and PCE from migrating below the extraction elevation, particularly near the extraction points.

In an effort to recover the CaBr_2 from the QS experiment, the cell was partially drained, partially refilled, and then flushed with DDI water. In situ densities were measured during various stages of brine recovery and the results are shown in Figure 4.7. Dewatering the cell resulted in densities ranging from 1.14 g/cm^3 at an elevation of 7 cm to 1.67 g/cm^3 near the bottom. The DDI water injected to partially resaturate the cell mixed with the residual brine and resulted in a lower vertical density gradient with densities ranging from 1.22 g/cm^3 at an elevation of 7 cm to 1.45 g/cm^3 near the bottom. Flushing with less than two PVs of DDI water reduced density to less than 1.00 g/cm^3 throughout the cell.

Although reducing in situ density is important, the ability to reduce the TDS of the effluent stream is equally important in terms of waste treatment and restoration of the system to its original state. The TDS of the effluent stream are shown in Figure 4.8. The Secondary Drinking Water Standard for TDS is 500 mg/L (USEPA, 2009). In the experiment using the QS medium, a TDS concentration of 789 mg/L was achieved after flushing approximately 2.5 PV of DDI water through the portion of the cell originally containing the brine barrier. The QS experiment exhibited a log-linear decrease in TDS with cumulative flushing volume. The experiment using

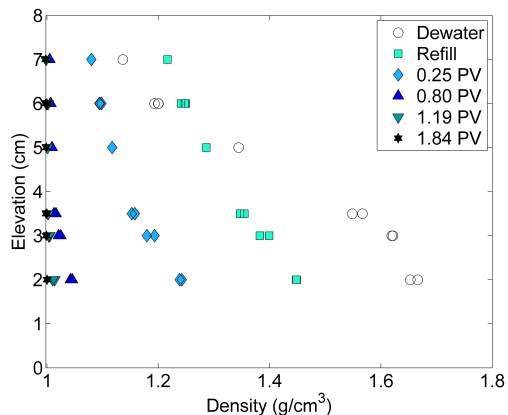


Figure 4.7: Density as a function of elevation during the recovery of the brine barrier for the QS laboratory experiment.

the DS medium also exhibited this log-linear nature, but with slight deviations due to changes in flow rates during flushing. The TDS in the effluent samples from the DS experiment were less than 300 mg/L after flushing with 3.3 pore volumes. Flushing was performed throughout the cell in the DS study whereas flushing was limited to the lower half of the cell in the QS study. In addition, the majority of the flushing in the QS study consisted of flushing from the upper ports to the lower ports while flushing in the DS study consisted of flushing between lower ports. As a result of the differences in flushing strategy and media heterogeneity, less freshwater was needed to reduce the TDS effluent concentrations in the DS study than the QS experiment. Flushing of approximately 3.3 PVs of freshwater after draining the DS medium resulted in recovery of approximately 98.9% of the injected brine from the DS medium. The mass fraction of 91% of the recovered brine exceeded 0.1, which is the approximate limit for recycling brines economically after reconcentration.

Model Results

The modified SUTRA simulator, which accounts for density and viscosity as functions of CaBr_2 mass fraction using Equations 4.4 and 4.5, was used to simulate the brine recovery process of the QS laboratory experiment. To evaluate the model results, the concentration data in Figure 4.8 were converted to fraction of mass removed and compared with the simulated data.

Examination of Figure 4.9 shows that all three simulations with different values of dispersivity (T1, T2, and T3) overestimate mass removal for the first 0.2 PVs re-

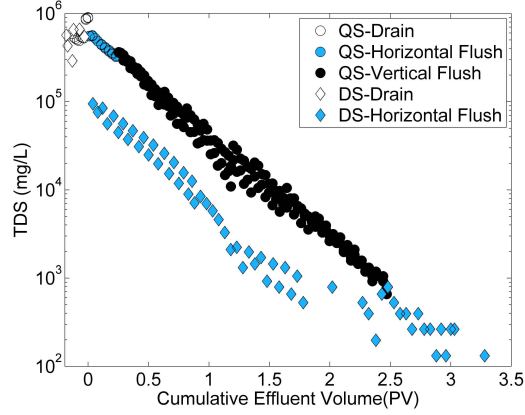


Figure 4.8: Effluent TDS concentration during CaBr_2 removal from the laboratory experiments, where $\circ$ represents the QS medium and $\diamond$ represents the DS medium.

moved, but then diverge from each other as they progress to the end. As expected, the simulation with the highest dispersivity values (T1) leads to excessive dispersion and dilution of the dense brine layer that results in significant underprediction of overall mass removal. The simulation with dispersivity values closest to dispersivity for a dilute system (T2) shows good agreement with the experimental data until approximately 1 PV flushed, but then begins to underpredict mass removal for the remainder of the simulated period. The final simulation (T3) with the lowest dispersivity values shows overprediction for much of the simulation, however by the end, the total mass removal is less than the experimental value by an order of magnitude.

The simulated results indicate that the model is only adequate in predicting accurate mass removal rates at the very beginning of the flushing period. However, the differences in slope after 1.5 PVs flushed suggests that dispersion is an issue. As the simulations progress, the model is not able to maintain a sharp density gradient in the vertical and the dense brine layer becomes diluted, thus hampering effective mass removal. This observation is confirmed by the model result of vertical density profile not shown here. Even with an arbitrarily low dispersivity, the mass removal does not match the overall experimental data.

Numerical diffusion in the model results is controlled to the extent possible using a converged grid. However, some of the poor match to the laboratory data can be attributed to numerical diffusion that cannot be completely eliminated, due to the methods employed in the simulator. Despite the presence of some numerical effects, the model results also suggest that the SUTRA model formulation of dispersion, which

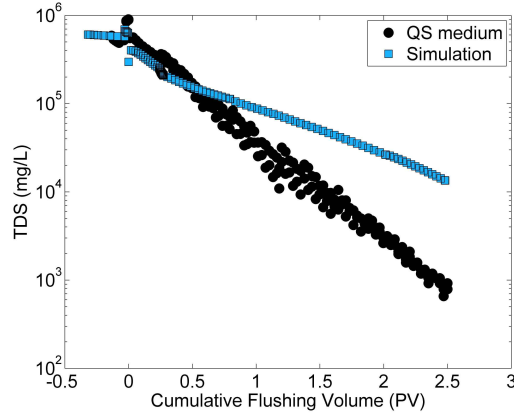


Figure 4.9: Experimental and simulated fraction of CaBr_2 remaining in the laboratory experiment with quartz sand medium.

assumes a dilute system and Fickian dispersion, is not appropriate for modeling high-concentration brines with non-ideal dispersive behavior. Further work is needed to develop appropriate simulators for these types of non-dilute systems.

4.4.3 Field Study

Field Experiment Results

Density samples collected from the multilevel samplers were used to investigate the spatial and temporal distribution of brine within the test cell. In addition, samples were also collected from the effluent stream to maintain a mass balance of the brine during each stage of the BBRTs including brine barrier establishment, pumping and dewatering, bulk brine removal, and flushing of the residual brine. There was considerable variation in density at all depths at the end of Phase 1 as is shown in Figure 4.10. Densities were greatest near the injection wells and decreased with distance from the injection wells. Phase 2 resulted in an increase in density in regions that were low in density at the conclusion of Phase 1. Density variation at all depths decreased by the end of Phase 2.

Density measurements during and at the end of Phase 2 indicted that there were regions in the lower portion of the cell where density inversion developed. The localized regions where apparent instabilities persisted were between wells 42 and 44 and between wells 51 and 53. These results suggest there was some heterogeneity effect that lead to a density inversion in these areas. Utilization of extraction wells in the vicinity of these

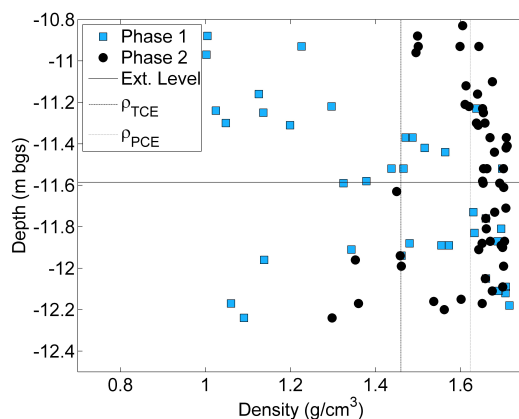


Figure 4.10: In situ densities after Phase 1 and Phase 2 brine additions for the pilot-scale study. The depth of extraction is indicated on the plot as a solid horizontal line. The densities of PCE and TCE are provided as a point of reference.

regions did not occur during the pumping and dewatering stage. However, wells were used as extraction wells in regions where sufficient brine had been injected to achieve the required density to impede the vertical movement of PCE. Selection of wells away from the unstable regions decreased the possibility of brine barrier deterioration due to mixing induced by pumping in the unstable regions.

To minimize the development of instabilities, extraction pumps were initially placed above the proposed BBI and slowly lowered during the course of pumping until the extraction pumps were at the level of the BBI. This strategy decreased brine losses, reduced mixing at the BBI, and promoted continued stabilization of the brine barrier. After removing 0.68 pore volumes—with a PV being based on the maximum saturated zone extending from the clay layer to 8.5-m bgs and yielding an approximate fluid volume of 16,200 L of fluid—from the test cell, densities below the BBI were essentially unchanged compared to densities at the end of Phase 2 as shown in Figure 4.11. The average brine density and range of densities within the brine barrier held relatively constant during vertical flushing of the upper portion of the cell. The observed densities over a several month period showed that the brine barrier was a stable feature that could be maintained. Densities above the brine barrier decreased as fluid was flushed downward towards the extraction locations. The large range of densities that existed above the BBI suggest that all areas were not uniformly flushed, resulting in the persistence of localized high concentrations of brine above the BBI.

After partial dewatering of the test cell, multilevel sampler data revealed results similar to laboratory observations in that densities in the brine barrier zone were still

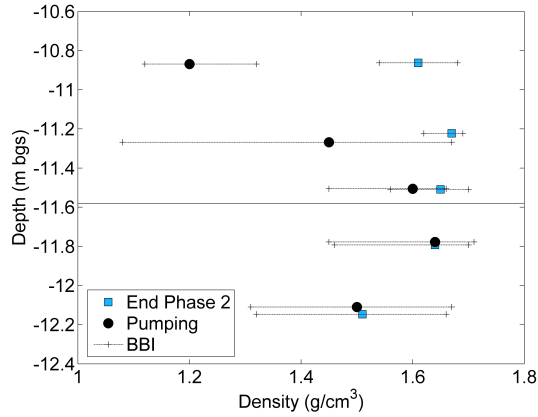


Figure 4.11: Average density as a function of depth during implementation of the BBRTs remediation strategy in the pilot-scale study. The solid horizontal line represents the BBI.

relatively high (i.e., exceeded 1.3 g/cm^3). Residual brine from the brine establishment phase that had been bypassed during the flushing stage contributed to elevated density readings in the upper regions of the domain, but, in general, densities decreased with elevation above the BBI.

Samples collected after refilling the cell with water indicated that densities above 12.0-m bgs ranged from 1.01 to 1.32 g/cm^3 with the results shown in Figure 4.12. Below 12.0-m bgs, the density increased with depth with the exception of the local regions of lower density observed earlier. The test cell was undisturbed for three months after the completion of the primary study. Density samples collected at the end of this period indicated that the wide variation in density at a given depth observed earlier diminished and that the overall vertical density gradient also diminished. Apparent density instabilities in the lower portion of the cell persisted, but were less pronounced. The reductions in variability and vertical gradient were due to diffusion and small-scale flow driven by local density instabilities. Drainage from above the water table increased the water level in the cell by 0.63 m during the three month period and the drainage, depending on its density, may have also impacted the density profile.

Effluent samples collected throughout the study revealed changes in the composition of the effluent stream depending on the stage of the BBRTs as shown in Figure 4.13. As brine was injected into the system during establishment of the brine barrier, the thickness of the barrier increased and brine migrated upward toward the extraction elevation leading to an increase in the density of the effluent stream. The extraction pumps were lowered during the addition of the flushing solution which resulted in an

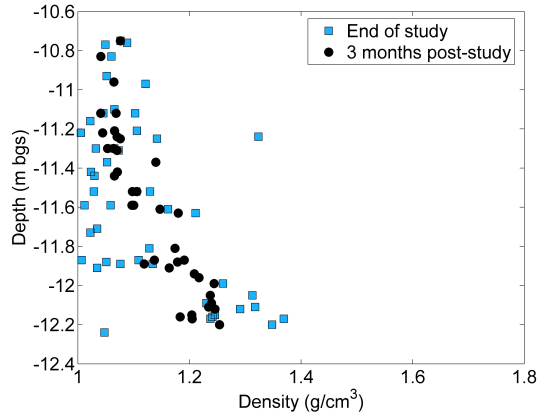


Figure 4.12: Density as a function of depth at the end of the primary pilot-scale study and three months post-study.

initial increase in the density of the effluent stream, followed by a slight decline. Further lowering of the extraction pumps during dewatering and bulk brine removal resulted in an increase in the effluent density from 1.3 to 1.6 g/cm³. A 0.4 PV flush with water resulted in a decrease in the density of the effluent to 1.1 g/cm³.

The overall process recovered 92% of the CaBr₂ injected into the system. The number of PVs of water flushed through the field-scale system was only a small fraction of the PVs that were flushed through the laboratory systems. In addition the rate of flushing was higher in the test cell than in the laboratory systems. Laboratory systems were refilled at a slow rate to try to re-saturate the cell. Further flushing could have removed additional CaBr₂ mass as in the laboratory experiments, but time constraints did not make further flushing possible.

It may be possible to recycle brine during the application of a BBRTs if the contaminants can be removed and the brine reconcentrated. It is assumed that the cost of such a recycling process would be inversely related to the CaBr₂ mass fraction of the effluent. Assessing the potential for economic brine recycling includes examining the volume of brine effluent that exceeds a minimal mass fraction (ω_{min}) that is defined as the mass fraction below which the cost of recycling becomes uneconomical. Figure 4.14 shows that, for example, if $\omega_{min} = 0.25$ then more than 50% of the effluent that was collected could be recycled economically. Similarly, if $\omega_{min} = 0.10$, then more than 88% of the collected effluent could be feasibly recycled. The exact mass fraction at which it becomes uneconomical to reconcentrate the brine would likely be project-dependent.

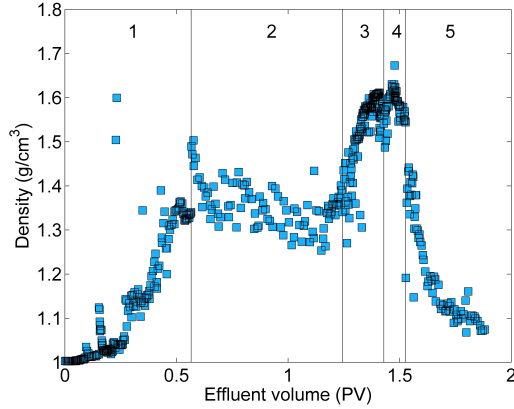


Figure 4.13: Effluent density in the pilot-scale study as a function of effluent volume during (1) brine injection, (2) flushing solution addition, (3) dewatering, (4) bulk brine removal, and (5) brine barrier flushing.

Model Results

Field-scale simulations were also conducted to investigate the formation of a density inversion (or instability) during the injection of brine to form the brine barrier. Since minimal information was available on the porous media properties, three permeability fields were used in the simulations: a homogeneous field, a field based on a Gaussian covariance model, and a layered permeability field (see Table 4.6). The areally-averaged results of the simulations are shown in Figure 4.15. The completion of Phase 1, which corresponds to brine injection into the center 4 wells and deeper zone of the test cell (see Figure 4.3), shows a stable and relatively sharp density profile in the simulations with homogeneous and Gaussian permeability fields. However, the simulation with the layered permeability field developed a density inversion early in this phase. Inspection of the permeability field in the instability region for the layered system indicates that the permeability decreases by more than two orders of magnitude between 12-m bgs and the bottom of the domain (see Figure 4.15). The low permeability inhibited the migration of brine into this region.

Density instabilities were found to develop in each of the simulated systems by the end of Phase 2. The inversion that developed during Phase 1 for the layered permeability system persisted through Phase 2. In addition, the simulations for the homogeneous and Gaussian permeability fields also developed slight density inversions beneath 12-m bgs, although not as pronounced as the layered permeability field system. The initiation and persistence of the density inversion during this phase for the homogeneous and

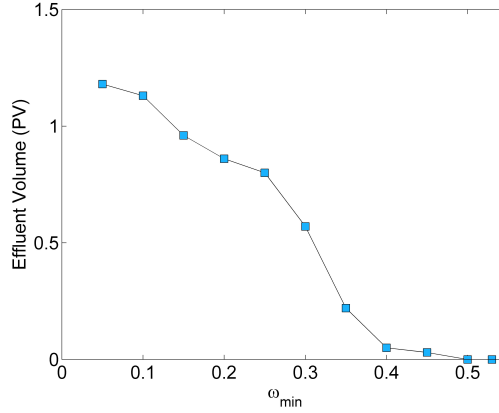


Figure 4.14: The volume of effluent from the pilot-scale study exceeding a minimum mass fraction (ω_{min}).

Gaussian cases is largely due to the location of the Phase 2 injection wells, which were along the outer edges of the cell where the topography of the bottom surface becomes shallower (Figure 4.3). In addition, Phase 2 injection was three times as long as Phase 1, which resulted in most of the total CaBr_2 mass being injected in shallower zones. This also caused circulation of fresh water into the deeper zones, diluting the dense brine injected during Phase 1. Thus, stable density gradients existed locally but at different elevations, and therefore the apparent density inversion in Figure 4.15 is an artifact of averaging. Additional simulations showed that after the system equilibrates for a number of days, the brine migrates slowly into the deeper zones for the simulations with homogeneous and Gaussian permeability fields, and the apparent density instability in Figure 4.15 for these two cases stabilized. The density instability for the layered permeability field persisted as expected due to the strong permeability contrast in the deeper region.

Compared with the field-scale experiment observations shown in Figure 4.11, the simulated results with the layered permeability field best approximates the observed average density gradient at the end of Phase 2. This indicates that a low permeability zone likely exists along the top of the clay layer as discussed earlier. Near the top of the observed BBI between -10.8 and -11.8 m bgs, the simulated results show a density gradient not as sharp as observed in the test cell and with lower average concentrations. Despite the use of a converged grid, this is likely due to numerical dispersion, and the underlying assumption of Fickian diffusion. These results further reveal the overall inadequacy of the simulator to maintain sharp density gradients over time as observed

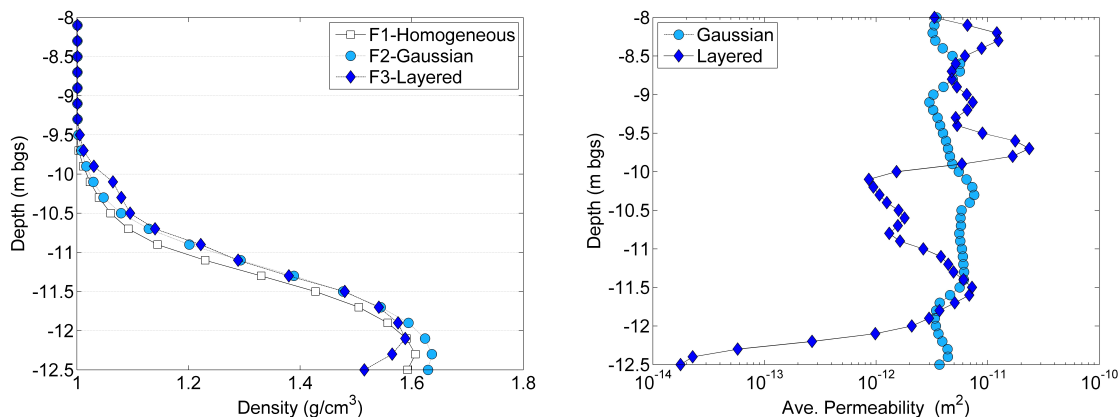


Figure 4.15: (*left*) Simulated average densities with depth for different permeability fields in the field-scale simulations, where F1 is the homogeneous, F2 is the Gaussian, and F3 is the layered permeability field. (*right*) Average permeability with depth for the Gaussian and layered permeability fields.

in both the laboratory and field experiments.

4.5 Discussion

Knowledge of the fluid properties of a high-concentration CaBr_2 solution is essential for understanding the dynamics of a BBRTs based upon such a solution. This was of particular importance because the density was 1.7 times and the viscosity was 6 times that of water at the mass fraction used in the BBRTs studies. Changes in the density and viscosity over the range of mass fractions experienced during implementation of a BBRTs can result in a 72% decrease in hydraulic conductivity.

Although laboratory studies conducted to date have implemented brine barrier strategies, the properties of such brine barriers have not been investigated. In situ brine densities during all stages of a BBRTs implementation were monitored. Laboratory studies showed effective establishment of dense brine barriers that achieved densities in excess of a variety of chlorinated solvents. These densities were maintained with some localized reductions in density near extraction wells. With adequate brine barrier thickness, localized reductions in density due to mixing near extraction wells should not affect the effectiveness of a brine barrier at arresting downward migration of most DNAPLs.

With adequate flushing, more than 98% of the injected brine was recovered from the laboratory systems. High recoveries are needed if in situ CaBr_2 concentrations are going

to be substantially reduced. The ability to reduce CaBr_2 concentrations is particularly important in natural systems that may eventually serve as sources for drinking water.

Some of the primary differences between the laboratory and field studies, other than the domain size, were the degree of heterogeneity, the source and sink type (i.e. the laboratory experiments had point sources and sinks while the field experiment had line sources and sinks), and the presence of residual fluids from previous studies in the field test cell. Obstacles that arose during brine injection and maintenance in the field setting included brine mounding around wells and density instabilities within the medium, which were investigated in more detail using a modified SUTRA simulator. Any remnants remaining from the prior studies had a minimal effect on density and viscosity in comparison to the brine solution since initial measurements were found to be comparable to water. A more likely influence of the remnants would be pore clogging as the solutions serve as food for bacteria, which would inhibit brine migration in such areas if it occurred.

Hydraulic issues were encountered during the dewatering and bulk brine removal phase of the field-scale study. The same degree of dewatering of the brine barrier in the laboratory systems was not achieved, which made removal of the residual brine more difficult. Based on its areal extent and porosity, the test cell had approximately 4,850 L of pore space volume per meter of depth. Lowering the water table resulted in the fluid recovery of water that corresponded to approximately a third of the pore space volume per thickness of medium. This inefficient fluid recovery was partly due to the slow drainage of the unsaturated zone relative to the time frame of the field experiment. Reductions in the thickness of the saturated zone diminished the efficiency of the bladder pumps used in the wells, which also contributed to the inefficient fluid recovery. Although reductions in fluid recovery occurred, a high fraction of the injected brine was not recovered and it is expected that with further freshwater flushing additional mass removal was feasible.

SUTRA was modified to include the density and viscosity relationships for CaBr_2 . SUTRA's mass-based extraction scheme was converted to a volume-based extraction scheme, which made simulating BBRTs easier. There was general agreement between the SUTRA simulation and effluent measurements from the laboratory system during the early period of brine-barrier flushing. However, excessive numerical dispersion, even for very low dispersivity values, led to excessive mixing and poor brine recovery in the latter part of the simulation. SUTRA simulations also provided insight to field-scale observations including the role of density- and viscosity-dependent flow, and the

interaction of the two properties during brine barrier flushing.

Density inversions were observed in the field study as well as in simulations of the field study. Simulated density instabilities were found near areas of low permeability, which were found in the deeper portions of the system. Density instabilities may have arose from decreased permeability because such conditions existed in the deeper portions of the test cell that were in close proximity to the clay layer. These instabilities persisted in both the field and simulated studies further suggesting their existence was due to areas of low permeability. The formation of localized density inversions in low permeability regions may not pose a problem with respect to the performance of BBRTs. If the permeability is low enough to limit migration of brine, the low permeability regions are likely not accessible to a DNAPL either, at least prior to a DNAPL coming into contact with a solution that promotes mobilization.

The ability to accurately monitor and predict in situ densities in a field setting is difficult. Fluids in wells stratify quickly relative to fluids in the adjoining medium so monitoring density in wells can be unreliable, particularly when density inversions exist in the medium. Discrete interval sampling within wells or multilevel samplers can be used to alleviate density sampling difficulties. Model simulations can be used to describe the density within a brine barrier, but modeling requires detailed knowledge of the porous medium properties, particularly if it is hoped that the model will capture localized inversions. A conservative brine barrier strategy would be to increase the thickness of the barrier to ensure control of mobilized DNAPL, but such an approach may lead to significant amounts of DNAPL trapped below the BBI where recovery would be difficult.

Although insight into the behavior and application of brine barriers was gained, there are still a number of relevant issues that should be considered to reach a mature understanding of brine barriers. These issues include the following items:

1. *Model Development and Simulators.* Density-dependent models and simulators are still an active area of research. As the theory, model, and numerics continue to develop, so will a more mature scientific understanding of the systems of concern, the role of sharp fronts, and density and viscosity induced instabilities.
2. *Behavior in the Absence of Hydraulic Controls.* Installation of sheet piles may be unrealistic at some sites so wells must be used to control brine migration. Well placement would have to be optimized to minimize migration and loss of brine outside of the contaminated region. Such systems would require larger volumes of

brine, which emphasizes the importance of being able to recycle and reuse brine on site.

3. *Horizontal Flushing of Remedial Fluids.* The impact of horizontal flushing with remedial fluids, such as surfactants and cosolvents, on brine barrier stability has not been investigated. Horizontal flushing is more common than vertical flushing, but it may increase mixing at the BBI. The impact of such a flushing strategy on brine barrier maintenance needs some consideration.
4. *Barrier Thickness.* Persistent density inversions were observed during the field experiment. Consequently, the brine barrier thickness in some locations was less than the desired thickness. The minimal thickness of a brine barrier needed to control mobilization needs to be assessed. It is expected that this thickness will be a function of distance from an extraction or injection well, flow rates, density difference between the brine and the DNAPL, and the DNAPL and medium properties.
5. *Clay Effects.* Due to the length of time a brine barrier may overlay a clay layer, it is important to determine the impact of brine on the structural integrity of the clay layer. In addition, the rate of loss of brine into the underlying clay layer needs to be investigated. Diffusion of brine back out of the clay layer after removal of the bulk brine is also a concern as it could pose a long-term source of dissolved salt into the aquifer.

Resolution of these issues will require substantial work, but such a resolution would benefit future applications of BBRTs.

4.6 Conclusions

The relationship of the density and viscosity of CaBr_2 solutions was characterized and defined over a range of mass fractions that were observed during implementation of a BBRTs. Commonly used approaches for representing these relationships were unable to adequately describe the data over the entire mass fraction range. Therefore, equations of state were developed to better represent the relationships between density and viscosity as a function of CaBr_2 mass fraction.

Changes in the density within a brine barrier were observed as a function of space and time while establishing and maintaining a brine barrier in laboratory cells. A brine

barrier could be effectively established by injecting about 0.4 PVs of brine into the confined cell. The brine barrier could also be maintained during the course of a BBRTs experiment.

It is feasible to recover high percentages of brine at the end of a BBRTs. In the laboratory setting, more than 98% of the injected brine was recovered, of which more than 90% had a mass fraction exceeding 0.1, which is the lower limit at which it is economically viable to re-concentrate and recycle the effluent. Focusing flushing on the lower portion of the laboratory cell, or primarily the region where the brine barrier existed, is more efficient in reducing CaBr_2 concentrations than flushing the entire cell. Freshwater flushing of the brine barrier region was found to require less than half of the PVs of freshwater needed to reduce the CaBr_2 concentration to a similar level when flushing the entire system.

A BBRTs was implemented at the field-scale. A brine barrier was successfully established and maintained. Approximately 92% of the injected brine was recovered. Instabilities were encountered in the field due to the complex heterogeneities that existed near an underlying clay layer. These instabilities were persistent through the course of the study. It is not believed that the instabilities posed a major problem because they existed in locations that were not likely to be easily penetrated by mobilized DNAPL.

Chapter 5

Conclusions

Remediation of DNAPLs using a three-fluid phase remedial strategy and incorporating a novel class of BBRTs was applied successfully to three-dimensional heterogeneous laboratory experiments and resulted in near complete removal of TCE. Solely mobilization-based remediation methods, using surfactants and a BBRT strategy, were shown to reduce contaminant mass by 85% for these laboratory systems. Further mass recovery resulted from relying on mass-transfer of DNAPL into the aqueous phase through solubilization. Since mass recovery through solubilization is relatively inefficient, a three-fluid phase approach was utilized to incorporate dewatering of the laboratory cell and application of a vapor-phase extraction step to reduce any remaining TCE mass in the laboratory cell to less than 1% of the injected contaminant mass.

While mobilization-based results from the TCE-contaminated systems were very encouraging, the effectiveness of mobilization-based strategies was found to be system-dependent. For systems with low residual saturations, mobilization-based strategies were not as effective at reducing contaminant mass. The effectiveness of mobilization-based strategies increases with DNAPL saturation. Mobilization-based strategies leave sufficient residual behind after source-zone remediation that downgradient aqueous phase concentrations do not meet MCLs. Even in the absence of achieving MCLs after source-zone remediation, removal of significant source-zone mass will ultimately decrease the long-term impact of DNAPL contamination.

Mass transfer processes governing aqueous-phase concentrations are dependent on the DNAPL topology and morphology resulting from complex migration of DNAPL through heterogeneous subsurface environments. The resulting topology and morphology of DNAPL residual influences the final time frame to achieve MCLs. Mass transfer processes are governed by key measures of state including porosity, volume fractions,

fluid saturation, permeabilities, densities, viscosities, specific interfacial areas, and interfacial tensions.

Although detailed laboratory studies have been conducted investigating BBRTs, to date, the behavior of such dense, viscous brines in porous media had not been investigated. While laboratory experiments showed very effective brine barrier establishment that would exceed densities of most chlorinated solvents, field-scale experiments resulted in the development of density instabilities within the brine barrier. A study of simulated density instabilities demonstrated that density instabilities are influenced by decreases in the permeability of the porous medium. It is feasible that density instabilities at the field-scale may have similarly resulted from decreases in permeability. The permeability may have decreased as a result of clay mixing with sands in the deeper portions of the pilot test cell in close proximity to the clay layer. If brine could not penetrate these low permeability areas, it is not expected that DNAPL would migrate readily into these regions without being assisted by a change in the balance of forces that control DNAPL migration.

High fractions of brine were removed from both laboratory systems and the field-scale system. In laboratory systems, 98% of the injected brine was recovered with more than 90% exceeding the mass fraction required for economical recycling of brine from the effluent stream. The fraction of brine removal from the field-scale system decreased to 92% of the injected mass. Several factors may have influenced the reduction in brine recovery at the field-scale including inefficient drainage of the test cell and a relative short time frame for brine barrier flushing. Higher levels of brine recovery are feasible and would be expected with further freshwater flushing.

While several issues have been addressed for BBRTs, there are a significant set of open issues remaining. Resolution of these issues will require substantial work, but such a resolution would benefit future applications of BBRTs as well as advance the understanding of DNAPL migration in the subsurface and the impact of remediation strategies in general. Some of these issues are listed and discussed briefly below.

1. *Development of a New Mass Transfer Coefficient.* A mass transfer coefficient that is a function of state variables, such as interfacial areas and contact angles, and can be applied to multiple scales is needed to accurately characterize mass transfer processes. Current definitions of mass transfer coefficients cannot be applied to multiple scales due to inadequate characterization of the system variables that contribute to the mass transfer process.

2. *Model development.* A complete mathematical model for complex systems does not exist to describe the observed behavior with adequate accuracy. The lack of such a model is in part due to the complexity of the system of concern, which includes many unresolved scientific and numerical aspects such as movement of disconnected phases, films, very complex composition, the potential for gravitational-, viscous-, and dissolution-induced instabilities, and sharp fronts. In addition, there is a gap in the complete understanding and incorporation of the role of state variables such as described above for mass transfer processes.
3. *Behavior in the Absence of Hydraulic Controls.* Systems to date have all utilized hydraulic controls to control brine migration, whether via laboratory cell walls or sheet piles for the field-scale application. Such controls may be unrealistic at some sites. Therefore, control of brine and any flushing fluids will rely on a series of injection and extraction wells. Such a system would likely involve horizontal flushing that may decrease the efficiency of the brine barrier through increased mixing at the BBI.
4. *Barrier Thickness.* Persistent density inversions were observed during the field experiment. Consequently, the brine barrier thickness in some locations was less than the desired thickness. The minimal thickness of a brine barrier needed to control downward mobilization of DNAPL needs to be assessed. It is expected that this thickness will be a function of distance from an extraction or injection well, flow rates, flushing strategy, density difference between the brine and the DNAPL, and the DNAPL and medium properties.
5. *Clay Effects.* Due to the length of time a brine barrier may overlay a clay layer, it is important to determine the impact of brine on the structural integrity of the clay layer. In addition, the rate of loss of brine into the underlying clay layer needs to be investigated. Diffusion of brine back out of the clay layer after removal of the bulk brine is also a concern as it could pose a long-term source of dissolved salt into the aquifer.

BIBLIOGRAPHY

- Abarca, E., Carrera, J., Sanchez-Vila, X., and Dentz, M. (2007). Anisotropic dispersive Henry problem. *Advances in Water Resources*, 30(4):913–926.
- Ackerer, P. and Younes, A. (2008). Efficient approximations for the simulation of density driven flow in porous media. *Advances in Water Resources*, 31:15–27.
- Ackerer, P., Younes, A., and Mose, R. (1999). Modeling variable density flow and solute transport in porous medium I. Numerical model and verification. *Transport in Porous Media*, 35:345–373.
- Adams, J. and Bachu, S. (2002). Equations of state for basin geofluids: Algorithm review and intercomparison for brines. *Geofluids*, 2(4):257–271.
- Aelion, C. and Kirtland, B. (2000). Physical versus biological hydrocarbon removal during air sparging and soil vapor extraction. *Environmental Science & Technology*, 34(15):3167–3173.
- ARA (1996). Groundwater remediation field laboratory–GRFL: Hydrogeology characterization and site development. Volume I: Site characterization and development. Technical report, Prepared by Applied Research Associates, Inc. for Armstron Laboratory.
- Basu, N., Fure, A., and Jawitz, J. (2008). Predicting dense nonaqueous phase liquid dissolution using a simplified source depletion model parameterized with partitioning tracers. *Water Resources Research*, 44(7).
- Batzle, M. and Wang, Z. (1992). Seismic properties of pore fluids. *Geophysics*, 57:1396–1408.
- Bear, J. and Bachmat, Y. (1991). *Introduction to Modeling of Transport Phenomena in Porous Media*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Blunt, M. (1997). Pore-level modeling of the effects of wettability. *SPE Journal*, 2:494–510.
- Bond, R. (2000). An analysis of density enhanced remediation of DNAPLs. Technical report, University of North Carolina at Chapel Hill, Chapel Hill, NC.
- Brandes, D. and Farley, K. (1993). Importance of phase behavior on the removal of residual DNAPLs from porous media by alcohol flooding. *Journal of Water Environment Research*, 65(7):869–878.
- Brooks, M., Annable, M., Rao, P., Hatfield, K., Jawitz, J., Wise, W., Wood, A., and Enfield, C. (2002). Controlled release, blind tests of DNAPL characterization using partitioning tracers. *Journal of Contaminant Hydrology*, 59(3–4):187–210.

- Brooks, M., Annable, M., Rao, P., Hatfield, K., Jawitz, J., Wise, W., Wood, A., and Enfield, C. (2004). Controlled release, blind test of DNAPL remediation by ethanol flushing. *Journal of Contaminant Hydrology*, 69(3-4):281-297.
- Brovelli, A., Mao, X., and Barry, D. (2007). Numerical modeling of tidal influence on density-dependent contaminant transport. *Water Resources Research*, 43:Art No. W10426.
- Brown, C., Delshad, M., Dwarakanath, V., Jackson, R., Londergan, J., Meinardus, H., McKinney, D., Oolman, T., Pope, G., and Wade, W. (1999). Demonstration of surfactant flooding of an alluvial aquifer contaminated with DNAPL. In *Demonstration of Surfactant Flooding of an Alluvial Aquifer Contaminated with DNAPL*. American Chemical Society, Washington, D. C.
- Brusseau, M., Nelson, N., Oostrom, M., Zhang, Z., Johnson, G., and Wietsma, T. (2000). Influence of heterogeneity and sampling method on aqueous concentrations associated with NAPL dissolution. *Environmental Science & Technology*, 34(17):3657-3664.
- Burghardt, J. and Kueper, B. (2008). Laboratory study evaluating heating of tetrachloroethylene impacted soil. *Ground Water Monitoring and Remediation*, 28(4):95-106.
- Byers, W., Meyers, M. B., and Mooney, D. E. (1994). Analysis of soil from a disused gasworks. *Water Air and Soil Pollution*, 73(1-4):1-9.
- Chapman, S. and Parker, B. (2005). Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research*, 41(12).
- Childs, J., Acosta, E., Annable, M., Brooks, M., Enfield, C., Harwell, J., Hasegawa, M., Knox, R., Rao, P., Sabatini, D., Shiauc, B., Szekeres, E., and Wood, A. (2006). Field demonstration of surfactant-enhanced solubilization of DNAPL at Dover Air Force Base, Delaware. *Journal of Contaminant Hydrology*, 82(1-2):1-22.
- Cho, J., DiGiulio, J., Wilson, J., and Vardy, J. (1997). In situ air injection, soil vacuum extraction and enhanced biodegradation: A case study in a JP-4 jet fuel contaminated site. *Environmental Progress*, 16(1):35-42.
- Christ, J., Ramsburg, C., Pennell, K., and Abriola, L. (2006). Estimating mass discharge from dense nonaqueous phase liquid source zones using upscaled mass transfer coefficients: An evaluation using multiphase numerical simulations. *Water Resources Research*, 42(11).
- Christakos, G. (1992a). Certain results on spatiotemporal random fields and their applications in environmental research. *Probabilistic and Stochastic*, 372:287-322.

- Christakos, G. (1992b). *Random Field Models in the Earth Sciences*. Academic Press, San Diego, CA.
- Cohen, R. and Mercer, J. (1993). DNAPL site evaluation. Technical Report EPA/600/SR-93/022, US EPA Robert S. Kerr Environmental Research Laboratory, Ada, OK.
- Corbin, M., Metzger, N., and Kress, M. (1994). Field investigation of effectiveness of soil vapor extraction technology: Project summary. Technical Report EPA/600/SR-94/142, US EPA Risk Reduction Engineering Laboratory, Cincinnati, OH.
- Dekker, T. and Abriola, L. (2000). The influence of field-scale heterogeneity on the infiltration and entrapment of dense nonaqueous phase liquids in saturated formations. *Journal of Contaminant Hydrology*, 42:187–218.
- Dentz, M., Tartakovsky, D., Abarca, E., Guadagnini, A., Sanchez-Vila, X., and Carrera, J. (2006). Variable-density flow in porous media. *Journal of Fluid Mechanics*, 561:209–235.
- Deutsch, C. and Journel, A. (1992). *GSLIB: Geostatistical Software Library and User's Guide*. Oxford University Press, New York.
- Diersch, H. and Kolditz, O. (2002). Variable-density flow and transport in porous media: Approaches and challenges. *Advances in Water Resources*, 25(8-12):899–944.
- Diersch, H.-J. G. (2005). *FEFLOW Finite Element Subsurface Flow & Transport Simulation System Reference Manual*. WASY GmbH, Berlin, Germany.
- Domenico, P. and Schwartz, F. (1998). *Physical and Chemical Hydrogeology*. John Wiley & Sons, New York, second edition.
- Dong, J., Chowdhry, B., and Leharne, S. (2004). Investigation of the wetting behavior of coal tar in three phase systems and its modification by poloxamine block copolymeric surfactants. *Environmental Science & Technology*, 38(2):594–602.
- Dwarakanath, V., Kostarelos, K., Pope, G., Shotts, D., and Wade, W. (1999). Anionic surfactant remediation of soil columns contaminated by nonaqueous phase liquids. *Journal of Contaminant Hydrology*, 38(4):465–488.
- Dwarakanath, V. and Pope, G. (2000). Surfactant phase behavior with field degreasing solvent. *Environmental Science & Technology*, 34(22):4842–4848.
- Edwards, D., Liu, Z., and Luthy, R. (1992). Enhancing polynuclear aromatic uptake into bulk solution with amphiphilic colloidal aggregates. *Water Science and Technology*, 26(9-11):2341–2344.
- Elder, J. (1967). Transient convection in a porous medium. *Journal of Fluid Mechanics*, 27(3):609–623.

- Elfeki, A. and Dekking, M. (2001). A markov chain model for subsurface characterization: Theory and applications. *Mathematical Geology*, 33(5):569–589.
- Fatt, I. (1956). The network model of porous media: III. dynamic properties of networks with tube radius distribution. *AIME*, 207:164–181.
- Field, J. and Sawyer, T. (2000). High-performance liquid chromatography-diode array detection of trichloroethene and aromatic and aliphatic anionic surfactants used for surfactant-enhanced aquifer remediation. *Journal of Chromatography A*, 893(2):253–260.
- Flowers, T. and Hunt, J. (2007). Viscous and gravitational contributions to mixing during vertical brine transport in water-saturated porous medium. *Water Resources Research*, 43(1):Art No. W01407.
- Fountain, J. (1998). Technologies for dense nonaqueous phase liquid source zone remediation. Technical Report TE-98-02, Ground-Water Remediation Technologies Analysis Center, Pittsburgh, P.A.
- Freeze, R. (1975). A stochastic-conceptual analysis of one-dimensional groundwater flow in nonuniform homogeneous media. *Water Resources Research*, 11(5):725–741.
- Fried, J. (1975). Groundwater pollution. In Fried, J. J., editor, *The Experimental Determination of Groundwater Pollution Parameters*, pages 59–113. Elsevier Scientific Publishing Co., Amsterdam.
- Frolkovic, P. and De Schepper, H. (2001). Numerical modelling of convection dominated transport coupled with density driven flow in porous media. *Advances in Water Resources*, 24(1):63–72.
- Fu, X. and Imhoff, P. (2002). Mobilization of small DNAPL pools formed by capillary entrapment. *Journal of Contaminant Hydrology*, 56(1–2):137–158.
- Fure, A., Jawitz, J., and Annable, M. (2006). DNAPL source depletion: Linking architecture and flux response. *Journal of Contaminant Hydrology*, 85(3–4):118–140.
- Gauthier, M. and Kueper, B. (2006). Removal of PCB-DNAPL from a rough-walled fracture using alcohol/polymer flooding. *Journal of Contaminant Hydrology*, 84(1–2):1–20.
- Gebhart, B., Jaluria, Y., Mahajan, R., and Sammakia, B. (1988). *Buoyancy Induced Flows And Transport*. Hemisphere, New York.
- Geller, J. and Hunt, J. (1993). Mass transfer from nonaqueous phase organic liquids in water-saturated porous media. *Water Resources Research*, 29(4):833–845.
- Gill, A. (1982). *Atmosphere-Ocean Dynamics*. Academic Press, New York.

- Goswami, R. and Clement, T. (2007). Laboratory-scale investigation of saltwater intrusion dynamics. *Water Resources Research*, 43(4):Art No. W04418.
- Gotovac, H., Andricevic, R., and Gotovac, B. (2007). Multi-resolution adaptive modeling of groundwater flow and transport problems. *Advances in Water Resources*, 30(5):1105–1126.
- Graf, T. and Therrien, R. (2007). Variable-density groundwater flow and solute transport in 2D fracture networks. *Advances in Water Resources*, 30(3):455–468.
- Grant, G. and Gerhard, J. (2007a). Simulating the dissolution of a complex dense nonaqueous phase liquid source zone: 1. Model to predict interfacial area. *Water Resources Research*, 43(12):W12410.
- Grant, G. and Gerhard, J. (2007b). Simulating the dissolution of a complex dense nonaqueous phase liquid source zone: 2. Experimental validation of an interfacial area - based mass transfer model. *Water Resources Research*, 43(12):W12409.
- Gray, W. and Miller, C. (2009). Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 5. Single-fluid-phase transport. *Advances in Water Resources*, 32(5):131–144.
- Gudbjerg, J., Sonnenborg, T. O., and Jensen, K. H. (2004). Remediation of NAPL below the water table by steam-induced heat conduction. *Journal of Contaminant Hydrology*, 72(1–4):207–225.
- Gupta, D. and Mohanty, K. (2001). A laboratory study of surfactant flushing of DNAPL in the presence of macroemulsion. *Environmental Science & Technology*, 35(13):2836–2843.
- Hall, J. (1997). *Surfactant Enhanced Mobilization of Nonaqueous Phase Liquids in Porous Media*. PhD thesis, University of North Carolina at Chapel Hill, Chapel Hill, NC.
- Hassanizadeh, S. and Gray, W. (1979). General conservation equations for multi-phase systems: 1. Averaging procedure. *Advances in Water Resources*, 2(3):131–144.
- Hassanizadeh, S. and Leijnse, A. (1995). A non linear theory of high-concentration-gradient dispersion in porous media. *Advances in Water Resources*, 18(4):203–215.
- Hayden, N. J. and Voice, T. C. (1993). Microscopic observation of a NAPL in a 3-fluid-phase soil system. *Journal of Contaminant Hydrology*, 12(3):217–226.
- Heiderscheidt, J., Siegrist, R., and Illangasekare, H. (2008). Intermediate-scale 2D experimental investigation of in situ chemical oxidation using potassium permanganate for remediation of complex DNAPL source zones. *Journal of Contaminant Hydrology*, 102(1–2):3–16.

- Held, R., Attinger, S., and Kinzelbach, W. (2005). Homogenization and effective parameters for the Henry problem in heterogeneous formations. *Water Resources Research*, 41(11):Art No. W11420.
- Held, R. and Illangasekare, T. (1995). Fingering of dense nonaqueous phase liquids in porous media 1. Experimental investigation. *Water Resources Research*, 31(5):1213–1222.
- Heller, J. (1966). Onset of instability patterns between miscible fluids in porous media. *Journal of Applied Physics*, 37(4):1566–1579.
- Henry, H. (1964). Effects of dispersion on salt encroachment in coastal aquifers. In *Sea Water in Coastal Aquifers*, Water Supply Paper 1613-C, pages 70–84. U.S. Geological Survey.
- Heron, G., Gierke, J., Faulkner, B., Mravik, S., Wood, L., and Enfield, C. (2002). Pulsed air sparging in aquifers contaminated with dense nonaqueous phase liquids. *Ground Water Monitoring and Remediation*, 22(4):73–82.
- Heron, G., van Zutphen, M., Christensen, T., and Enfield, C. (1998). Soil heating for enhanced remediation of chlorinated solvents: A laboratory study on resistive heating in a silty, low-permeable soil contaminated with trichloroethylene. *Environmental Science & Technology*, 32(10):1474–1481.
- Hill, E., Moutier, M., Alfaro, J., and Miller, C. (2001). Remediation of DNAPL pools using dense-brine barrier strategies. *Environmental Science & Technology*, 35(14):3031–3039.
- Hilpert, M., McBride, J., and Miller, C. (2000). Investigation of the residual-funicular nonwetting-phase-saturation relation. *Advances in Water Resources*, 24(2):157–177.
- Hirasaki, G., Miller, C., Szafranski, R., Tanzil, D., Lawson, J., Meinardus, H., Jin, M., Londergan, J., Jackson, R., Pope, G., and Wade, W. (1997). Field demonstration of the surfactant/foam process for aquifer remediation, paper SPE 39292. In *SPE Annual Technical Conference and Exhibition*, San Antonio, T.X.
- Hofstee, C., Ziegler, C., Trotschler, O., and Braun, J. (2003). Removal of DNAPL contamination from the saturated zone by the combined effect of vertical upward flushing and density reduction. *Journal of Contaminant Hydrology*, 67:61–78.
- Hrapovic, L., Sleep, B., Major, D., and Hood, E. (2005). Laboratory study of treatment of trichloroethene by chemical oxidation followed by bioremediation. *Environmental Science & Technology*, 39(8):2888–2897.
- Hunt, J., Sitar, N., and Udell, K. (1988a). Nonaqueous phase liquid transport and cleanup 1. Analysis of mechanisms. *Water Resources Research*, 24(8):1247–1258.

- Hunt, J., Sitar, N., and Udell, K. (1988b). Nonaqueous phase liquid transport and cleanup 2. Experimental studies. *Water Resources Research*, 24(8):1247–1258.
- Illangasekare, T., Armbruster, E., and Yates, D. (1995a). Non-aqueous-phase fluids in heterogeneous aquifers - Experimental-study. *Journal of Environmental Engineering-Asce*, 121(8):571–579.
- Illangasekare, T., Ramsey, J., Jensen, K., and Butts, M. (1995b). Experimental study of movement and distribution of dense organic contaminants in heterogeneous aquifers. *Journal of Contaminant Hydrology*, 20(1-2):1–25.
- Imhoff, P., Arthur, M., and Miller, C. (1998). Complete dissolution of trichloroethylene in saturated porous media. *Environmental Science & Technology*, 32(16):2417–2424.
- Imhoff, P., Farthing, M., and Miller, C. (2003). Modeling NAPL dissolution fingering with upscaled mass transfer rate coefficients. *Advances in Water Resources*, 26(10):1097–1111.
- Imhoff, P., Frizzell, A., and Miller, C. (1997). An evaluation of thermal effects on the dissolution of a nonaqueous phase liquid in porous media. *Environmental Science & Technology*, 31(6):1615–1622.
- Imhoff, P., Gleyzer, S., McBride, J., Vancho, L., Okuda, I., and Miller, C. (1995). Cosolvent-enhanced remediation of residual dense nonaqueous phase liquids: Experimental investigation. *Environmental Science & Technology*, 29(8):1966–1976.
- Imhoff, P., Jaffé, P., and Pinder, G. (1994). An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media. *Water Resources Research*, 30(2):307–320.
- Imhoff, P. and Miller, C. (1996). Dissolution fingering during the solubilization of nonaqueous phase liquids in saturated porous media 1. Model predictions. *Water Resources Research*, 32(7):1919–1928.
- Imhoff, P. and Miller, C. (1999). Nonaqueous phase liquids in the subsurface: Effects of nonaqueous-aqueous mass transfer limitations. In Katsifarakis, K., editor, *Groundwater Contamination Control*. in press, Computational Mechanics Publications, Southampton, UK.
- Imhoff, P., Thyrum, G., and Miller, C. (1996). Dissolution fingering during the solubilization of nonaqueous phase liquids in saturated porous media 2. Experimental observations. *Water Resources Research*, 32(7):1929–1942.
- ITRC (2002). DNAPL source remediation: Facing the challenge. Technical report, Interstate Technology and Regulatory Council. <http://www.itrcweb.org/Documents/DNAPLS-2.pdf>.

- ITRC (2004). Strategies for monitoring the performance of DNAPL source zone remedies. Technical report, Interstate Technology Regulatory Council, [http:// www.itrcweb.org/Documents/DNAPLs-5.pdf](http://www.itrcweb.org/Documents/DNAPLs-5.pdf).
- Jawitz, J., Sillan, R., Annable, M., Rao, P., and Warner, K. (2000). In situ alcohol flushing of a DNAPL source zone at a dry cleaner site. *Environmental Science & Technology*, 34(17):3722–3729.
- Jayanti, S., Britton, L., Dwarakanath, V., and Pope, G. (2002). Laboratory evaluation of custom-designed surfactants to remediate NAPL source zones. *Environmental Science & Technology*, 36(24):5491–5497.
- Ji, W., Dahmani, A., Ahlfeld, D., Lin, J., and Hill, E. (1993). Laboratory study of air sparging: Air flow visualization. *Ground Water Monitoring and Remediation*, 13(4):115–126.
- Jiao, C. and Hotzl, H. (2004). An experimental study of miscible displacements in porous media with variation of fluid density and viscosity. *Transport in Porous Media*, 54(2):125–144.
- Johannsen, K., Oswald, S., Held, R., and Kinzelbach, W. (2006). Numerical simulation of three-dimensional saltwater-freshwater fingering instabilities observed in a porous medium. *Advances in Water Resources*, 29(11):1690–1704.
- Johnson, D., Pedit, J., and Miller, C. (2004). Efficient, near-complete removal of DNAPL from three-dimensional, heterogeneous porous media using a novel combination of treatment technologies. *Environmental Science & Technology*, 38(19):5149–5156.
- Johnson, P., Das, A., and Bruce, C. (1999). Effect of flow rate changes and pulsing on the treatment of source zones by in situ air sparging. *Environmental Science & Technology*, 33(10):1726–1731.
- Johnson, P. C., Johnson, R. L., Neaville, C., Hansen, E. E., Stearns, S. M., and Dortch, I. J. (1997). An assessment of conventional in situ air sparging pilot tests. *Ground Water*, 35(5):765–774.
- Johnston, C., Rayner, J., and Briegel, D. (2002). Effectiveness of in situ air sparging for removing NAPL gasoline from a sandy aquifer near perth, western australia. *Journal of Contaminant Hydrology*, 59(1–2):87–111.
- Juanes, R. and Blunt, M. (2006). Analytical solutions to multiphase first-contact miscible models with viscous fingering. *Transport in Porous Media*, 64:339–373.
- Kaslusky, S. and Udell, K. (2002). A theoretical model of air and steam co-injection to prevent the downward migration of DNAPLs during steam-enhanced extraction. *Journal of Contaminant Hydrology*, 55(3–4):213–232.

- Kavanaugh, M., Rao, P., and Wood, A. (2003). The DNAPL remediation challenge: Is there a case for source depletion? Technical Report EPA 600/R-03-143, US EPA.
- Keely, J. (1989). Performance evaluations of pump-and-treat remediations. Technical Report EPA/540/4-89/005, US EPA Robert S. Kerr Environmental Research Laboratory Ground Water Issue, Ada, OK.
- Keely, J. (1991). Performance evaluations of pump-and-treat remediations. Technical Report EPA 540/4-89/005, United States Environmental Protection Agency, Ada, OK.
- Kemp, N., Thomas, D., Atkinson, G., and Atkinson, B. (1989). Density modeling for brines as a function of composition, temperature, and pressure. *SPE Production Engineering*, 4:394–400.
- Kibbey, T., Ramsburg, C., Pennell, K., and Hayes, K. (2002). Implications of alcohol partitioning behavior for in situ density modification of entrapped dense nonaqueous phase liquids. *Environmental Science & Technology*, 36(1):104–111.
- Kim, H., Soh, H., Annable, M., and Kim, D. (2004). Surfactant-enhanced air sparging in saturated sand. *Environmental Science & Technology*, 38(4):1170–1175.
- Kirtland, B. and Aelion, C. (2000). Petroleum mass removal from low permeability sediment using air sparging/soil vapor extraction: Impact of continuous or pulsed operation. *Journal of Contaminant Hydrology*, 41(3–4):367–383.
- Kolditz, O., Habbar, A., Kaiser, R., Rother, T., Thorenz, C., and Moenickes, S. (2001). Rockflow numerical modeling of fluid flow, mass and heat transport in subsurface systems. Technical report, Institute of Fluid Mechanics and Computer Applications in Civil Engineering, University of Hannover, Hannover, Germany.
- Kolditz, O., Ratke, R., Diersch, H., and Zielke, W. (1998). Coupled groundwater flow and transport: 1. Verification of variable density flow and transport models. *Advances in Water Resources*, 21(1):27–46.
- Konikow, L., Sanford, W., and Campbell, P. (1997). Constant-concentration boundary condition: Lessons from the HYDROCOIN variable-density groundwater benchmark problem. *Water Resources Research*, 33(10):2253–2261.
- Kueper, B. and Frind, E. (1988). An overview of immiscible fingering in porous media. *Journal of Contaminant Hydrology*, 2(2):95–110.
- Kueper, B. and Gerhard, J. (1995). Variability of point source infiltration rates for two-phase flow in heterogeneous porous media. *Water Resources Research*, 31(12):2971–2980.
- Kyte, J. R. and Berry, D. W. (1975). New pseudo functions to control numerical dispersion. *Society of Petroleum Engineers Journal*, pages 269–276.

- Landman, A., Johannsen, K., and Schotting, R. (2007a). Density-dependent dispersion in heterogeneous porous media Part I: A numerical study. *Advances in Water Resources*, 30(12):2467–2480.
- Landman, A. and Schotting, R. (2007). Heat and brine transport in porous media: The Oberbeck-Boussinesq approximation revisited. *Transport in Porous Media*, 70:335–373.
- Landman, A., Schotting, R., Egorov, A., and Demidov, D. (2007b). Density-dependent dispersion in heterogeneous porous media Part II: Comparison with nonlinear models. *Advances in Water Resources*, 30(12):2481–2498.
- Lemke, L. and Abriola, L. (2006). Modeling dense nonaqueous phase liquid mass removal in nonuniform formations: Linking source-zone architecture and system response. *Geosphere*, 2(2):74–82.
- Lemke, L., Abriola, L., and Goovaerts, P. (2004). Dense nonaqueous phase liquid (DNAPL) source zone characterization: Influence of hydraulic property correlation on predictions of DNAPL infiltration and entrapment. *Water Resources Research*, 40(1).
- Lide, D. (1997). *CRC Handbook of Chemistry and Physics*. CRC Press, Boston.
- Lin, H.-C. J., Richards, D., Yeh, G.-T., Cheng, J.-R., and Cheng, H.-P. (1997). *FEMWATER: A Three-Dimensional Finite Element Computer Model for Simulating Density-Dependent Flow and Transport in Variably Saturated Media*. U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS.
- Londergan, J., Meinardus, H., Mariner, P., Jackson, R., Brown, C., Dwarakanath, V., Pope, G., Ginn, J., and Taffinder, S. (2001). DNAPL removal from a heterogeneous alluvial aquifer by surfactant-enhanced aquifer remediation. *Ground Water Monitoring and Remediation*, 21(3):71–81.
- Lowry, M. and Miller, C. (1995). Pore-scale modeling of nonwetting-phase residual in porous media. *Water Resources Research*, 31(3):455–473.
- Lunn, S. and Kueper, B. (1997). Removal of pooled dense, nonaqueous phase liquid from saturated porous media using upward gradient alcohol floods. *Water Resources Research*, 33(10):2207–2219.
- Lunn, S. and Kueper, B. (1999a). Manipulation of density and viscosity for the optimization of DNAPL recovery by alcohol flooding. *Journal of Contaminant Hydrology*, 38(4):427–445.
- Lunn, S. and Kueper, B. (1999b). Risk reduction during chemical flooding: Preconditioning DNAPL density in situ prior to recovery by miscible displacement. *Environmental Science & Technology*, 33(10):1703–1708.

- Mackay, D. and Cherry, J. (1989). Groundwater contamination: Pump-and-treat remediation. *Environmental Science & Technology*, 23(6):630–636.
- Martel, R. and Gelinas, P. (1996). Surfactant solutions developed for NAPL recovery in contaminated aquifers. *Ground Water*, 34(1):143–154.
- Martin, E., Fontaine, D., Tillotson, P., and McRae, G. (1991). Global sensitivity analysis in environmental mobility assessment. *Pesticide Science*, 31(3):399–402.
- Mayer, A. and Miller, C. (1992a). The influence of porous medium characteristics and measurement scale on pore-scale distributions of residual nonaqueous-phase liquids. *Journal of Contaminant Hydrology*, 11(3/4):189–213.
- Mayer, A. and Miller, C. (1992b). Interactions between nonaqueous phase liquids and the aqueous phase as a function of observational scale. In *Agronomy Abstracts, Soil Science Society of America Annual Meeting*, Minneapolis, MN. American Society of Agronomy.
- Mayer, A. and Miller, C. (1996). The influence of mass transfer characteristics and porous media heterogeneity on nonaqueous phase dissolution. *Water Resources Research*, 32(6):1551–1567.
- Mazzia, A. and Putti, M. (2002). Mixed-finite element and finite volume discretization for heavy brine simulations in groundwater. *Journal of Computational and Applied Mathematics*, 147:191–213.
- McCain Jr., W. (1991). Reservoir fluid property correlations - State of the art. *SPE Reservoir Engineering*, 6:266–272.
- McGuire, T., McDade, J., and Newell, C. (2006). Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites. *Ground Water Monitoring and Remediation*, 26(1):73–84.
- Mercer, J. and Cohen, R. (1990). A review of immiscible fluids in the subsurface: Properties, models, characterization and remediation. *Journal of Contaminant Hydrology*, 6(2):107–163.
- Mercer, J., Pinder, G., and Donaldson, I. (1975). A Galerkin-Finite element analysis of the hydrothermal system at Wairakei, New Zealand. *Journal of Geophysical Research*, 80:5608–2621.
- Miller, C., Hill, E., and Moutier, M. (2000). Remediation of DNAPL-contaminated subsurface systems using density-motivated mobilization. *Environmental Science & Technology*, 34(4):719–724.
- Miller, C., Poirier-McNeill, M., and Mayer, A. (1990). Dissolution of trapped non-aqueous phase liquids: Mass transfer characteristics. *Water Resources Research*, 26(11):2783–2796.

- Morrow, N. and Songkran, B. (1981). Effect of viscous and buoyancy forces on non-wetting phase trapping in porous media. In *Surface Phenomena in Enhanced Oil Recovery*, pages 387–411. Plenum Press, New York.
- Mravik, S., Sillan, R., Wood, A., and Sewell, G. (2003). Field evaluation of the solvent extraction residual biotreatment technology. *Environmental Science & Technology*, 37(21):5040–5049.
- Nagatsu, Y., Matsuda, K., Kato, Y., and Tada, Y. (2007). Experimental study on miscible viscous fingering involving viscosity changes induced by variations in chemical species concentrations due to chemical reactions. *Journal of Fluid Mechanics*, 571:475–493.
- Nigam, M. and Woods, A. (2006). The influence of buoyancy contrasts on miscible source-sink flows in a porous medium with thermal inertia. *Journal of Fluid Mechanics*, 549:253–271.
- Nordbotten, J., Celia, M., and Bachu, S. (2004). Analytical solutions for leakage rates through abandoned wells. *Water Resources Research*, 40(4):Art No. W04204.
- NRC (1994). *Alternatives for Ground Water Cleanup*. National Academy Press, Washington, D.C.
- NRC (1997). *Innovations in Ground Water and Soil Cleanup: From Concept to Commercialization*. National Academy Press, Washington, D.C.
- NRC (1999). *Groundwater and Soil Cleanup: Improving Management of Persistent Contaminates*. National Academy Press, Washington, D.C.
- NRC (2005). *Contaminants in the subsurface: Source zone assessment and remediation*. National Academies Press, Washington, DC.
- O’Carroll, D. and Sleep, B. (2007). Hot water flushing for immiscible displacement of a viscous NAPL. *Journal of Contaminant Hydrology*, 91(3–4):247–266.
- Okuda, I., McBride, J., Gleyzer, S., and Miller, C. (1996). An investigation of physicochemical transport processes affecting the removal of residual DNAPL by nonionic surfactant solutions. *Environmental Science & Technology*, 30(6):1852–1860.
- Oldenburg, C. M. and Pruess, K. (1995). Dispersive transport dynamics in a strongly coupled groundwater brine flow system. *Water Resources Research*, 31(2):289–302.
- Oostrom, M., Hofstee, C., Walker, R., and Dane, J. (1999). Movement and remediation of trichloroethylene in a saturated heterogeneous porous medium, 1. Spill behavior and initial dissolution. *Journal of Contaminant Hydrology*, 37:159–178.
- Ophori (1998). The significance of viscosity in density-dependent flow of groundwater. *Journal of Hydrology*, 204:261–270.

- Oswald, S. and Kinzelbach, W. (2004). Three-dimensional physical benchmark experiments to test variable-density flow models. *Journal of Hydrology*, 290:22–42.
- Page, J., Soga, K., and Illangasekare, T. (2007). The significance of heterogeneity on mass flux from DNAPL source zones: An experimental investigation. *Journal of Contaminant Hydrology*, 94(3–4):215–234.
- Palliser, C. and McKibbin, R. (1998). A model for deep geothermal brines, II: Thermodynamic properties - Density. *Transport in Porous Media*, 33(1–2):129–154.
- Palmer, C. D. and Fish, W. (1992). Chemically enhanced removal of metals from the subsurface. In *Subsurface Restoration Conference — Third International Conference on Water Quality Research*, pages 46–48, Dallas, TX. National Center for Ground Water Research.
- Pan, C., Dalla, E., Franzosi, D., and Miller, C. (2007). Pore-scale simulation of entrapped non-aqueous phase liquid dissolution. *Advances in Water Resources*, 30:623–640.
- Pankow, J. and Cherry, J. (1996). *Dense Chlorinated Solvents and other DNAPLs in Groundwater*. Waterloo Press, Ontario.
- Park, C. and Aral, M. (2007). Sensitivity of the solution of the Elder problem to density, velocity and numerical perturbations. *Journal of Contaminant Hydrology*, 92(1-2):33–47.
- Park, E. and Parker, J. (2005). Evaluation of an upscaled model for DNAPL dissolution kinetics in heterogeneous aquifers. *Advances in Water Resources*, 28(12):1280–1291.
- Parker, B., Chapman, S., and Guilbeault, M. (2008). Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following tce source-zone hydraulic isolation. *Journal of Contaminant Hydrology*, 102(1–2):86–104.
- Parker, J. and Falta, R. (2008). Comparison of alternative upscaled model formulations for simulating DNAPL source dissolution and biodecay. *Advances in Water Resources*, 31(10):1325–1332.
- Parker, J. and Park, E. (2004). Modeling field-scale dense nonaqueous phase liquid dissolution kinetics in heterogeneous aquifers. *Water Resources Research*, 40(5):W05109, doi:10.1029/2003WR002807.
- Paterson, L. (1985). Fingering with miscible fluids in a hele shaw cell. *Journal of Chemical Engineering Data*, 28(1):26–30.
- Pennell, K., Abriola, L., and Weber, J. (1993). Surfactant-enhanced solubilization of residual dodecane in soil columns. 1. Experimental investigation. *Environmental Science & Technology*, 27(12):2332–2340.

- Pennell, K., Jin, M., Abriola, L., and Pope, G. (1994). Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene. *Journal of Contaminant Hydrology*, 16(1):35–53.
- Pennell, K., Pope, G., and Abriola, L. (1996). Influence of viscous and buoyancy forces on the mobilization of residual tetrachloroethylene during surfactant flushing. *Environmental Science & Technology*, 30(4):1328–1335.
- Phillips, S., Igbene, A., Fair, J., Ozbek, H., and Tavana, M. (1981). A technical data-book for geothermal energy utilization. Technical Report 12810, Lawrence Berkeley Laboratory Report.
- Poulsen, M. and Kueper, B. (1992). A field experiment to study the behavior of tetrachloroethylene in unsaturated porous media. *Environmental Science & Technology*, 26(5):889–895.
- Powers, S., Abriola, L., and Weber, J. (1992). An experimental investigation of non-aqueous phase liquid dissolution in saturated subsurface systems: Steady state mass transfer rates. *Water Resources Research*, 28(10):2691–2705.
- Powers, S., Abriola, L., and Weber, J. (1994). An experimental investigation of non-aqueous phase liquid dissolution in saturated subsurface systems: Transient mass transfer rates. *Water Resources Research*, 30(2):321–332.
- Powers, S., Anckner, W., and Seacord, T. (1996). Wettability of NAPL-contaminated sands. *Journal of Environmental Engineering - ASCE*, 122(10):889–896.
- Prasad, A. and Simmons, C. (2003). Unstable density-driven flow in heterogeneous porous media: A stochastic study of the Elder [1967b] “short heater” problem. *Water Resources Research*, 39(1):1–21.
- Ramsburg, C. and Pennell, K. (2002). Density-modified displacement for DNAPL source zone remediation: Density conversion and recovery in heterogeneous aquifer cells. *Environmental Science & Technology*, 36(14):3176–3187.
- Ramsburg, C., Pennell, K., Abriola, L., Daniels, G., Drummond, C., Gamache, M., Hsu, H., Petrovskis, E., Rathfelder, K., Ryder, J., and Yavaraski, T. (2005). Pilot-scale demonstration of surfactant-enhanced PCE solubilization at the bachman road site. 2. System operation and evaluation. *Environmental Science & Technology*, 39(6):1791–1801.
- Ramsburg, C., Pennell, K., Kibbey, T., and Hayes, K. (2003). Use of a surfactant-stabilized emulsion to deliver 1-butanol for density-modified displacement of trichloroethene. *Environmental Science & Technology*, 37(18):4246–4253.
- Rao, P., Annable, M., Sillan, R., Dai, D., Hatfield, K., Graham, W., Wood, A., and Enfield, C. (1997). Field-scale evaluation of in situ cosolvent flushing for enhanced aquifer remediation. *Water Resources Research*, 33(12):2673–2686.

- Renshaw, C., Zynda, G., and Fountain, J. (1997). Permeability reductions induced by sorption of surfactant. *Water Resources Research*, 33(3):371–378.
- Rogers, S. and Ong, S. (2000). Influence of porous media, airflow rate, and air channel spacing on benzene NAPL removal during air sparging. *Environmental Science & Technology*, 34(5):764–770.
- Rowe, A. and Chou, J. (1970). Pressure-volume-temperature-concentration relation of aqueous nacl solutions. *Journal of Chemical Engineering Data*, 15:61–66.
- Roy, S., Dzombak, D., and Ali, M. (1995). Assessment of in situ solvent extraction for remediation of coal tar sites: Column studies. *Water Environment Research*, 67(1):4–15.
- Rumynin, V., Konosavsky, P., and Hoehn, E. (2005). Experimental and modeling study of adsorption-desorption processes with application to a deep-well injection radioactive waste disposal site. *Journal of Contaminant Hydrology*, 76(1-2):19–46.
- Saba, T. and Illangasekare, T. (2000). Effect of groundwater flow dimensionality on mass transfer from entrapped nonaqueous phase liquid contaminants. *Water Resources Research*, 36(4):971–979.
- Saenton, S., Illangasekare, T., Soga, K., and Saba, T. (2002). Effects of source zone heterogeneity on surfactant-enhanced NAPL dissolution and resulting remediation end-points. *Journal of Contaminant Hydrology*, 59(1-2):27–44.
- Sale, T. and McWhorter, D. (2001). Steady state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields. *Water Resources Research*, 37(2):393–404.
- Scanlon, B., Mace, R., Barrett, M., and Smith, B. (2003). Can we simulate regional groundwater flow in karst system using equivalent porous media models? Case study, Barton Springs Edwards Aquifer, USA. *Journal of Contaminant Hydrology*, 276:137–158.
- Schincariol, R. (1998). dispersive mixing dynamics of dense miscible plumes: Natural perturbation initiation by local-scale heterogeneities. *Journal of Contaminant Hydrology*, 34:247–271.
- Schincariol, R. and Schwartz, F. (1990). An experimental investigation of variable density flow and mixing in homogeneous and heterogeneous media. *Water Resources Research*, 26(10):2317–2329.
- Schincariol, R., Schwartz, F., and Mendoza, C. (1994). On the generation of instabilities in variable density flow. *Water Resources Research*, 30(4):913–927.

- Schincariol, R., Schwartz, F., and Mendoza, C. (1997). Instabilities in variable density flows: Stability and sensitivity analyses in homogeneous and heterogeneous media. *Water Resources Research*, 33(1):31–41.
- Schnarr, M., Truax, C., Farquhar, G., Hood, E., Gonullu, T., and Stickney, B. (1998). Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. *Journal of Contaminant Hydrology*, 29(3):205–224.
- Schotting, R., Moser, H., and Hassanizadeh, S. (1999). High-concentration-gradient dispersion in porous media: Experiments, analysis and approximations. *Advances in Water Resources*, 22(7):665–680.
- Schulthess, C. P. and McCarthy, J. F. (1990). Competitive adsorption of aqueous carbonic and acetic acids by an aluminum oxide. *Soil Sci. Soc. Am. J.*, 54:688–694.
- SERDP and ESTCP (2006). Expert panel workshop on reducing the uncertainty of DNAPL source zone remediation, Final report. Technical report, Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program, <http://docs.serdp-estcp.org/viewfile.cfm?Doc=DNAPLWorkshopReport.pdf>.
- She, H. and Sleep, B. (1999). Removal of perchloroethylene from a layered soil system by steam flushing. *Ground Water Monitoring & Remediation*, 19(2):70–77.
- Shiau, B., Sabatini, D., and Harwell, J. (1994). Solubilization and microemulsification of chlorinated solvents using direct food additive (edible) surfactants. *Ground Water*, 32(4):561–569.
- Shikaze, S., Sudicky, E., and Schwartz, F. (1998). Density-dependent solute transport in discretely-fractured geologic media: Is prediction possible? *Journal of Contaminant Hydrology*, 34:273–291.
- Siegrist, R., Lowe, K., Murdoch, L., Case, T., and Pickering, D. (1999). In situ oxidation by fracture emplaced reactive solids. *Journal of Environmental Engineering-Asce*, 125(5):429–440.
- Simmons, C., Fenstemaker, T., and Sharp, J. (2001). Variable-density groundwater flow and solute transport in heterogeneous porous media: Approaches, resolutions, and future challenges. *Journal of Hydrology*, 52:245–275.
- Simmons, C. and Narayan, K. (1997). Mixed convection processes below a saline disposal basin. *Journal of Hydrology*, 194:263–285.
- Simmons, C., Narayan, K., and Wooding, R. (1999). On a test case for density-dependent groundwater flow and solute transport models: The salt lake problem. *Water Resources Research*, 35(12):3607–3620.

- Simmons, C., Pierini, M., and Hutson, J. (2002). Laboratory investigation of variable-density flow and solute transport in unsaturated-saturated porous media. *Transport in Porous Media*, 47(2):215–244.
- Simpson, M. and Clement, T. (2003). Theoretical analysis of the worthiness of Henry and Elder problems as benchmarks of density-dependent groundwater flow models. *Advances in Water Resources*, 26(1):17–31.
- Sleep, B. and Ma, Y. (1997). Thermal variation of organic fluid properties and impact on thermal remediation feasibility. *Journal of Soil Contamination*, 6(3):281–306.
- Smith, L. and Freeze, R. (1979). Stochastic analysis of steady state groundwater flow in a bounded domain: 1. One-dimensional simulations. *Water Resources Research*, 15(3):521–528.
- Soerens, T., Sabatini, D., and Harwell, J. (1998). Effects of flow bypassing and nonuniform NAPL distribution on the mass transfer characteristics of NAPL dissolution. *Water Resources Research*, 34(7):1657–1673.
- Soga, K., Page, J., and Illangasekare, T. (2004). A review of NAPL source zone remediation efficiency and the mass flux approach. *Journal of Hazardous Materials*, 110(1–3):13–27.
- Stroo, H., Jensen, R., Loehr, R., Nakles, D., Fairbrother, A., and Liban, C. (2000). Environmentally acceptable endpoints for PAHs at a manufactured gas plant site. *Environmental Science & Technology*, 34(18):3831–3836.
- Sudicky, E. (1986). A natural gradient experiment on solute transport in a sand aquifer: Spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research*, 22(13):2069–2082.
- Taylor, T., Pennell, K., Abriola, L., and Dane, J. (2001). Surfactant enhanced recovery of tetrachloroethylene from a porous medium containing low permeability lenses – 1. Experimental studies. *Journal of Contaminant Hydrology*, 48(3–4):325–350.
- Thomson, N., Hood, E., and Farquhar, G. (2007). Permanganate treatment of an emplaced DNAPL source. *Ground Water Monitoring and Remediation*, 27(4):74–85.
- Tick, G., Lourenso, F., Wood, A., and Brusseau, M. (2003). Pilot-scale demonstration of cyclodextrin as a solubility-enhancement agent for remediation of a tetrachloroethene-contaminated aquifer. *Environmental Science & Technology*, 37(24):5829–5834.
- Tiehm, A., Stieber, M., Werner, P., and Frimmel, F. (1997). Surfactant-enhanced mobilization and biodegradation of polycyclic aromatic hydrocarbons in manufactured gas plant soil. *Environmental Science & Technology*, 31(9):2570–2576.

- USEPA (1990). The national water quality inventory - 1988 report to congress. Technical report, United States Environmental Protection Agency.
- USEPA (1993a). Evaluation of the likelihood of DNAPL presence at NPL sites. Technical Report EPA/540/R-93/073, United States Environmental Protection Agency, Washington, D.C.
- USEPA (1993b). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons. Technical Report EPA/600/R-93/089, United States Environmental Protection Agency, Washington, D. C.
- USEPA (1995). In situ remediation technology status report: Treatment walls. Technical Report EPA542-K-94-004, National Center for Environmental Publications and Information, Cincinnati, OH.
- USEPA (1996). Citizen's guide to soil vapor extraction and air sparging. Technical Report EPA/542/F-96/008, U. S. Environmental Protection Agency, Cincinnati, OH.
- USEPA (1999). Enhanced source removal technology demonstrations: Technologies to clean up contaminated soils and groundwater. Technical Report EPA/600/F-99/011, United State Environmental Protectional Agency, Ada, O.K.
- USEPA (2000). Western research institute contained recovery of oily wastes (CROW) process: Innovative technology report. Technical Report EPA/540/R-00/500, EPA, Washington, D. C.
- USEPA (2001). Cost analyses for selected ground water clean up project: Pump and treat systems and permeable reactive barriers. Technical Report EPA/542/R-00/013, U. S. Environmental Protection Agency.
- USEPA (2004). Cleaning up the nation's waste sites: Markets and technology trends. Technical Report EPA/542/R-04/015, United States Environmental Protection Agency, Cincinnati, OH.
- USEPA (2009). MCL National primary drinking water regulations. Technical report, United States Environmental Protection Agency, Washington, DC.
- van Duijn, C., Peletier, L., and Schotting, R. (1998). Brine transport in porous media: Self-similar solutions. *Advances in Water Resources*, 22(3):285–297.
- van Genuchten, M. and Alves, W. (1982). Analytical solutions of the one-dimensional convective-dispersive solute transport equation. Technical report, U.S. Dept. of Agriculture, Washington, DC.
- Van Valkenburg, M. and Annable, M. (2002). Mobilization and entry of DNAPL pools into finer sand media by cosolvents: Two-dimensional chamber studies. *Journal of Contaminant Hydrology*, 59(3–4):211–230.

- Vayenas, D., Michalopoulou, E., Constantinides, G., Pavlou, S., and Payatakes, A. (2002). Visualization experiments of biodegradation in porous media and calculation of the biodegradation rates. *Advances in Water Resources*, 25(2):203–219.
- Verruijt, A. (1968). A note on the Ghyben-Herzberg formula. *Bulletin of the International Association of Scientific Hydrology*, XIII(4):43–46.
- Villaume, J. (1985). Investigations at sites contaminated with dense non-aqueous phase liquids. *Ground Water Monitoring Review*, 5(2):60–74.
- Voss, C. (1984). A finite-element simulation model for saturated-unsaturated, fluid-density-dependent ground-water flow with energy transport or chemically-reactive single-species solute transport. Technical Report U. S. Geological Survey Water-Resources Investigations Report 84-4369, U.S. Geological Survey.
- Voss, C. and Provost, A. (1981). Sutra a model for saturated, variable-density ground-water flow with solute or energy transport. Technical Report 02-4231, U.S. Geological Survey, Reston, VA.
- Voss, C. and Souza, W. (1987). Variable density flow and solute transport simulation of regional aquifers containing a narrow freshwater-saltwater transition zone. *Water Resources Research*, 23(10):1851–1866.
- Waduge, W., Soga, K., and Kawabata, J. (2004). Effect of NAPL entrapment conditions on air sparging remediation efficiency. *Journal of Hazardous Materials*, 110(1–3):173–183.
- Watson, S., Barry, D., Schotting, R., and Hassanizadeh, S. (2002). Validation of classical density-dependent solute transport theory for stable, high-concentration-gradient brine displacements in coarse and medium sands. *Advances in Water Resources*, 25(6):611–635.
- Welty, C. and Gelhar, L. (1991). Stochastic analysis of the effects of fluid density and viscosity variability on macrodispersion in heterogeneous porous media. *Water Resources Research*, 27(8):2061–2075.
- Welty, C. and Gelhar, L. (1992). Simulation of large-scale transport of variable density and viscosity fluids using a stochastic mean model. *Water Resources Research*, 28(3):815–827.
- Willson, C., Hall, J., Imhoff, P., and Miller, C. (1999). Factors affecting bank formation during surfactant-enhanced mobilization of residual NAPL. *Environmental Science & Technology*, 33(14):2440–2446.
- Wood, M., Simmons, C., and Hutson, J. (2004). A breakthrough curve analysis of unstable density-driven flow and transport in homogeneous porous media. *Water Resources Research*, 40(3):Art No. W03505.

- Wooding, R. (1969). Growth of fingers at an unstable diffusing interface in a porous medium or Hele-Shaw cell. *Journal of Fluid Mechanics*, 39(3):477–495.
- Wooding, R., Tyler, S., White, I., and Anderson, P. (1997). Convection in groundwater below an evaporating salt lake: 2. Evolution of fingers or plumes. *Water Resources Research*, 33(6):1219–1228.
- Woods, J. and Carey, G. (2007). Upwelling and downwelling behavior in the elder-voss-souza benchmark. *Water Resources Research*, 43:Art No. W12403.
- Woods, J., Teubner, M., Simmons, C., and Narayan, K. (2003). Numerical error in groundwater flow and solute transport simulation. *Water Resources Research*, 39(6):Art No. WR000586.
- Yan, L., Thompson, K., Valsaraj, K., and Reible, D. (2003). In-situ control of DNAPL density using polyaphrons. *Environmental Science & Technology*, 37(19):4487–4493.
- Yang, Y. and McCarty, P. (2000). Biologically enhanced dissolution of tetrachloroethene DNAPL. *Environmental Science & Technology*, 34(14):2979–2984.
- Yang, Y. and McCarty, P. (2002). Comparision between donor substrates for biologically enhanced. *Environmental Science & Technology*, 36(15):3400–3404.
- Younes, A., Fahs, M., and Ahmed, S. (2009). Solving density driven flow problems with efficient spatial discretizations and higher-order time integration methods. *Advances in Water Resources*, 32(3):303–486.
- Zhang, C., Yoon, H., Werth, C., Valocchi, A., Basu, N., and Jawitz, J. (2008). Evaluation of simplified mass transfer models to simulate the impacts of source zone architecture on nonaqueous phase liquid dissolution in heterogeneous porous media. *Journal of Contaminant Hydrology*, 102(1-2):49–60.
- Zhang, Q., Volker, R., and Lockington, D. (2001). Influence of seaward boundary condition on contaminant transport in unconfined coastal aquifers. *Journal of Contaminant Hydrology*, 49(3–4):201–215.
- Zhang, Z. and Smith, J. (2001). The velocity of DNAPL fingering in water-saturated porous media: Laboratory experiments and a mobile-immobile-zone model. *Journal of Contaminant Hydrology*, 49(3–4):335–353.
- Zhao, B., Zhu, L., and Yang, K. (2006). Solubilization of DNAPLs by mixed surfactant: Reduction in partitioning losses of nonionic surfactant. *Chemosphere*, 62(5):772–779.
- Zhong, L., Mayer, A., and Pope, G. (2003). The effects of surfactant formulation on nonequilibrium NAPL solubilization. *Journal of Contaminant Hydrology*, 60(1–2):55–75.

- Zhou, M. and Rhue, R. (2000). Screening commercial surfactants suitable for remediating DNAPL source zones by solubilization. *Environmental Science & Technology*, 34(10):1985–1990.
- Zhou, Q., Bear, J., and Bensabat, J. (2005). Saltwater upconing and decay beneath a well pumping above an interface zone. *Transport in Porous Media*, 61(3):337–363.
- Zhu, L. and Feng, S. (2003). Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nomonic surfactants. *Chemosphere*, 53(5):459–467.