Effect of Hydraulic Conductivity Heterogeneity on the Movement of Dense and Viscous Fluids in Porous Media

Thesis

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By

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Abstract

Currently, many remediation approaches are financially prohibitive or unrealistic to remediate deep, persistent dilute plumes of chlorinated ethylenes. This thesis outlines a new remediation approach designed to increase the residence time of in-situ dense chemical oxidants. This will be accomplished through the manipulation of the viscosity of the remediation chemicals and by taking advantage of natural aquifer heterogeneities. Dense chemical oxidants have advantages over more traditional remediation systems because they are relatively affordable, they require little maintenance, and they can be placed in targeted areas to maximize their effectiveness. Because they can be used to target specific areas, dense chemical oxidants have the ability to mitigate large, deep volatile organic compound (VOCs) plumes in aquifers. I postulate that the use of dense chemical oxidants can be enhanced further with the development of methods that will allow for the slow release of remediation chemicals over an extended period of time.

The first chapter identifies the problems addressed in this thesis. The second chapter analyzes the effect of heterogeneities on the movement of hypersaline solutions and demonstrates the modeling of dense, viscous solutions. The third chapter investigates the movement of dense solutions by gravity alone. The final chapter provides a general conclusion to the thesis. This thesis is part of a larger body of work funded by the Strategic Environmental Research and Development Program (SERDP), which is funded
by the United States Department of Defense, Department of Energy, and Environmental Protection Agency.

In chapter 2, it was found that the lenticular media used in the experiments of Schincariol and Schwartz (1990) actually decreased solute residence time due to the high permeability of highly permeable lenses. These high permeability lenses also prevented the downward transport of plumes. One advantage found in this media, however, was that these lenses enhanced solute mixing. This is important because mixing helps spread remediation chemicals throughout larger portions of a contaminated aquifer. Results from chapter 2 also found that the variable-density flow and transport numerical model, MITSU3D (Ibaraki, 1998), was appropriate to model the dense, viscous solutions created by silica grout and that a long-term source of oxidant could be produced using silica grout to increase the viscosity of the remediation chemicals.

Results of chapter 3 analyzed the importance of permeability, instabilities, heterogeneous lenses, and source zone size on the movement of dense solutions by gravity alone in a media with alternating high and low permeable layers. It was found that the permeability of the less permeable layer played a significant role in plume development by slowing the downward transport of dense fluid. Lenses were also shown to significantly affect results by acting as conduits for the mixing and guidance of dense fluid. Instabilities and source zone size were shown to have only marginal effects on plume development.
Dedication

To my mom, my grandparents, Chingas, Kevtron5000, Deadmau5, Justin, Olivia, and Erin.
Acknowledgments

First and foremost, I would like to thank my graduate committee: My advisor, Dr. Franklin Schwartz, whose help, patience, and willingness to take a chance on me is one of the main reasons I’m here; Dr. Motomu Ibaraki, whose patience and help with MITSU3D is one of the key reasons I am graduating; and Dr. Garry McKenzie, who’s friendliness and cordiality rounded out a committee of otherwise ball-busting professors. I would also like to thank the Department of Earth Sciences Chair, Dr. Barry Lyons and Graduate Chair, Dr. William Ausich for their work and dedication in keeping the department afloat and a viable place to work and learn.

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Next, I would like to thank the professors who taught some of the best courses I’ve had the privilege of taking, which include the aforementioned Drs. Frank Schwartz, Motomu Ibaraki, and Dr. Barry Lyons, along with Dr. Nick Basta, Dr. Ann Carey, and Dr. Scott Bair – the best teacher I’ve ever had.
I would also like to thank Penny Winkle for her professional help and guidance through one of the most trying times ever created by my head.

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Chapter 1: Introduction

Contamination of aquifers by volatile organic compounds (VOCs) is a common problem affecting hundreds of aquifers nationwide. These solvents are organic cleaning agents used mostly in the fabrication, cleaning and degreasing of metal. They are examples of dense, non-aqueous phase liquids (DNAPLs), which have specific gravities much higher than water. Common examples of VOCs are trichloroethylene [TCE] and dichloroethylene [DCE]. TCE has been manufactured and used since the 1930s, but it wasn’t identified as a harmful contaminant in groundwater until the 1970s (Doherty, 2000). As a result of this time gap, use and disposal was not regulated for about 40 years. Thus there are thousands of legacy TCE contamination sites that are still problematic today. Although, TCE is still widely used in the United States today, regulations largely prevent new problems from developing.

Particularly because of its use as a metal degreaser, the United States Department of Defense has taken a particular interest in methods of predicting the location of decades-old contaminant plumes as well as the best strategies for cleaning affected aquifers near current and defunct military bases. Moreover Barton and Whitfield (2007) state there are at least 24 active military installations with TCE contamination in groundwater used for municipal/public drinking water. At three of these facilities (Camp Lejeune in North Carolina, New Brighton/Arden Hills Army Base in Minnesota, and Wurtsmith Air Forces Base in Michigan), TCE was discovered in tap water.
A variety of remedial strategies have been developed for cleaning up DNAPL occurring as residual or pure phase product at the source, or dissolved phase contaminants in plumes (Figure 1.1). Typically, remedial strategies work to remove total mass (i.e., source reduction) or to control spreading (i.e., plume control).

Experience has shown that conducting mass removal in DNAPL source zones is extremely difficult. Pumping typically removes only a small fraction of the total mass (Domenico and Schwartz, 1990) and is ineffective for residually saturated DNAPLs. Solvent or oxidant flooding have shown promise but are usually unable to achieve appropriately high efficiencies (Domenico and Schwartz, 1990). Thus source zones are typically treated by physical removal and off-site disposal or in-situ encapsulation by caps and low permeability barriers (Domenico and Schwartz, 1990).

Examples of technologies for plume control are slow release and reactive barriers (Schwartz and Zhang, 2003). Given that active sources containing DNAPLs are often
very long-lived (Schwartz and Zhang, 2003) strategies involving plume control may need to be operated for many decades or centuries. Pump-and-treat systems are often economically infeasible because both installation and operating costs are high. Passive systems are often more desirable because of lower, more predictable costs. For instance, the main cost of zero-valent iron walls is the excavation of a trench to the bottom of a contaminated aquifer. Ongoing costs are relatively small although the lifetime of walls may be less than the required time for treatment. However, zero-valent iron walls have practical constraints on the depth to which they can be installed.

Slow release reactive barriers of potassium permanganate (KMnO$_4$) provide another alternative for passive plume control. Preliminary testing shows promise (Lee et al, 2009); however, at the present time, the approach is limited by the need to place one dimensional forms very close to each other.

Large, deep and dilute plumes of chlorinated solvents are a special problem. Pump-and-treat systems are prohibitively expensive, zero-valent iron walls have practical depth limitations, and controlled release systems are prohibitively expensive give the close spacing required for the solid one-dimensional forms comprising the reactive barriers. There is a need then for strategies to address this common class of problems.

This thesis intends to investigate aspects of a new approach that will address this need. It is part of a larger project funded by the Strategic Environmental Research and Development Program (SERDP) (a program supported by the US Department of Defense, Department of Energy, and Environmental Protection Agency) focusing on specific problems of large, deep, dissolved, low-concentration solvent plumes. The following research investigates methods to maximize the local distribution and residence
time of dense chemical oxidants using natural aquifer characteristics, the properties of the remediation chemicals themselves, and the density of viscous solutions containing chemical oxidants.

Density-dependent flow and mixing in porous media has been the subject of study for several decades for its applications in several different fields. Information on these subjects is pertinent when studying salt water intrusion (Huyakorn et al, 1987; Kopsiaftis et al, 2009), contaminant hydrogeology (Shikaze et al, 1998; Koch and Zhang, 2005), waste disposal (Pruess et al, 2002), aquifer storage and geothermal systems (Misut and Voss, 2007; Ward et al, 2007), and, specific to this study, the use of dense aquifer remediation chemicals (Schnarr et al, 1998; Swartz and Schwartz, 1998; Ibaraki et al., 2000).

Aquifer remediation using dense chemical oxidants is a well-known strategy. In these systems, a dense chemical oxidant (e.g. KMnO₄) reacts and destroys chlorinated ethylenes (Yan and Schwartz, 1999). These systems have advantages over more traditional remediation techniques, including relatively lower costs, less ongoing maintenance and upkeep, and the speed of the cleanup (Schnarr et al, 1998; Yan and Schwartz, 1999; McDade et al, 2005). In addition, density contrasts allow for the delivery of remediation chemicals to deeper and less permeable areas of a contaminated aquifer. Despite the speed of the reaction documented by Yan and Schwartz (1999), DNAPLs are highly persistent as a result of very low solubilities. Thus increasing residence time is essential to the efficiency of in-situ chemical oxidant remediation systems to remove persistent contaminants located in low permeability clay layers. Aquifer properties could
potentially be used to sequester treatment chemicals and enhance their residence time in a zone of reaction.

An alternative method of increasing residence time for in-situ treatment chemicals is manipulating both the density and viscosity of the fluid. Use of dense, viscous fluids in a remediation context was investigated by Wright et al (2010). The authors established and maintained a dense, viscous solution in specific area. Their results suggest the possibility of generating a dense, viscous solution with a long residence time in an aquifer. The viscosity of their solutions, however, did not approach that of the current study (the viscosity of their solution was six times larger than water, while the current study involved solutions with a viscosity 180 times larger than water).

This thesis seeks to provide information to help adapt current in-situ chemical oxidation approaches to deal with deep, persistent contaminant plumes. To this end, the development and implementation of long-term, low-maintenance passive remediation systems using in-situ chemical oxidants will be investigated. The overall goal of this work is to provide information about increasing the residence time of dense remediation chemicals and increase system efficiency.

This thesis consists of four chapters. This first chapter seeks to provide general background information and the structure of the overall work. In chapter 2, I provide modeling results demonstrating the use of aquifer heterogeneity to increase residence time and guide transport of dense remediation chemicals. I will also provide modeling results showing the efficacy of manipulating the viscosity of solutions of remediation chemicals to increase residence time. Chapter 3 examines the transport of dense fluids through low permeability materials by gravity. In this way, I hope to elucidate the effect
that changes in fluid density, solute source zone size, and media permeability have on the mixing and delivery of remediation chemicals to effected parts of contaminated aquifers.

In addition, I will investigate the effect that fluid instabilities have on solute mixing.

Chapter 4 provides a summary of general findings and the overarching conclusions of the entire thesis.

1.2 References:


Chapter 2: The Role of Aquifer Heterogeneity in Dense and Viscous Fluid Mixing

2.1: Introduction

This chapter sets out to examine variable-density and variable-density/viscosity flows in heterogeneous media. Over the past several decades, there have been numerous studies examining the movement of dense fluids in porous media, but only a few have considered how viscosity affects flow. The main goal of this chapter is to develop an improved understanding on how heterogeneity, density, and viscosity influence flow.

Early experimental and modeling work on free convection (i.e. density driven flow) and mixed convection (combined density driven flow coupled with ambient flow) was conducted by List (1965) and Paschke and Hoopes (1984), who worked primarily with homogeneous systems. Schincariol and Schwartz (1990) provided the first detailed study of variable density flow in heterogeneous porous media. Their studies focused on the flow of dense fluids through layered and lenticular media. They observed that a complex field with varying hydraulic conductivities yielded a complicated, dispersed plume but suppressed lobe-shaped plume instabilities.

Instability development is an important consideration in the study of variable-density fluid flow. In many studies (especially those in simple heterogeneous or layered media) lobe-shaped instabilities develop as the result of unstable density stratifications between resident and invading fluids (Schincariol et al, 1994). Schincariol et al (1994)
studied the conditions that lead to instability development using numerical modeling. Instability development can develop from a small perturbation in flow, which may be triggered numerically by truncation errors or time variations in concentrations or by perturbations of an interface between fluids of different density. More recent studies have focused on the complexities involved in dense solute transport through heterogeneous hydraulic conductivity fields (Simmons et al, 2001; Wright et al, 2010). Simmons et al (2001) studied the role of heterogeneity on instability development using the SUTRA transport code (Voss, 1984). They concluded that heterogeneity triggers and determines the growth or decay of instabilities and that the structure of the heterogeneities was the single most important factor determining whether instabilities grew or dissipated. Wright et al (2010) conducted a field and a laboratory experiment to investigate the behavior of dense, viscous brine in porous media. Instabilities were shown to develop in field scale tests – a phenomenon attributed to low permeability heterogeneities in the hydraulic conductivity field.

The broader hypothesis of the overall study is that dense fluids offer prospects for spreading and eventually sequestering treatment fluids (e.g. KMnO$_4$) within a plume. In effect, the density and the viscosity of the fluid, working in connection with the heterogeneous medium, provide for a slow, targeted release of the treatment chemical. Thus a better understanding of the behavior of dense, viscous solutions is required in order to determine what conditions tend to maximize fluid residence time.

Highly viscous solutions in the current study were created by using sodium silicate, which is used as grout. This inexpensive, readily available liquid has the capability to dramatically increase the viscosity of solutions (van der Denck, 1993). It is
environmentally safe and has been used in other industries for the stabilization of soil (Gallagher and Lin, 2009) and in the in-situ containment of contaminant plumes (Persoff et al, 1999). Because of the widespread use of silicate, information about its viscosity (van der Denck and Stein, 1993) and pH dependent solubility (Alexander et al, 1954; Gunnarsson and Arnorsson, 2000; Chida et al, 2004) is widely available. The present study examines the efficiency of using sodium silicate as an agent to increase viscosity, and thereby increasing the residence time of treatment chemicals.

The objectives of this study are to model the behavior of dense fluids in the test aquifer geometry described by Schincariol and Schwartz (1990) using MITSU3D, to use an experiment to describe the inflow of a dense viscous fluid through a complex heterogeneous medium, and finally verify the capability of modeling the flow of a dense, viscous fluid with MITSU3D. I address the objectives first by verifying the capabilities of the MITSU3D code (Ibaraki, 1998) using the experimental data provided by Schincariol and Schwartz (1990). Next, I present the first results of experiments with dense, viscous fluids in heterogeneous media. In hydrological studies, it is uncommon to model the flow of a dense, variable-viscosity fluid because viscosities of natural waters do not vary significantly with increasing salinity. Although MITSU3D is able to model variable viscosities, the large viscosities associated with sodium silicate provide a special challenge.

2.2 Methods:

This study employs existing data and modeling to study the flow of dense fluids. Two sets of experimental data are used here. First, I use experimental results described by
Schincariol and Schwartz (1990). This data is unique in the heterogeneous character of the porous medium and is used to further verify the MITSU3D code. The second experiment was run as part of this study and specifically involved a fluid that was made both extremely dense and viscous through the addition of sodium silicate. These experiments were used to verify the MITSU3D code.

2.2.1: Flow and transport modeling

The flow and transport code, MITSU3D, was first described by Ibaraki (1998). MITSU3D models flow and solute transport by simultaneously solving equations describing groundwater flow (equation 1) and mass transport (equation 3) (Ibaraki, 1998). The transient groundwater flow equation can be written mathematically as:

\[
\frac{\partial q}{\partial t} = \frac{k}{n \rho} \frac{\partial \rho}{\partial t} + \frac{k}{n \rho} \frac{\partial^2 \rho}{\partial Z^2} - \frac{k}{n \rho} \frac{\partial \rho}{\partial t} (\rho + \mu_f \frac{\partial \rho}{\partial Z}) + \frac{k}{n \rho} \frac{\partial \rho}{\partial Z} (\rho + \mu_f \frac{\partial \rho}{\partial Z})
\]

where \( t \) [T] is time, \( n \) [L \( L^{-3} \)] is porosity, \( \rho \) [M \( L^{-3} \)] is fluid density, and \( q \) [L T\(^{-1}\)] is groundwater velocity, described by:

\[
q = \frac{k}{\mu_f} \frac{\partial P}{\partial Z} - \rho g Z
\]

where \( k \) [L\(^2\)] is intrinsic permeability, \( \mu_f \) [M L\(^{-1}\) T\(^{-1}\)] is fluid viscosity, \( P \) [M L\(^{-1}\) T\(^{-2}\)] is pressure, \( g \) [L T\(^{-2}\)] is the gravitational constant and \( Z \) [L] is distance from the datum. The advection-dispersion equation is written as:

\[
\frac{\partial c}{\partial t} + \frac{\partial (\rho c)}{\partial Z} = \frac{\partial}{\partial Z} \left( D_{ij} \frac{\partial c}{\partial Z} \right)
\]

where \( c \) [M \( L^{-3} \)] is solute concentration and \( D_{ij} \) [L\(^2\) T\(^{-1}\)] is the dispersion coefficient, described by (Bear, 1972):
where \([L]\) and \([L]\) are longitudinal and transverse dispersivity respectively, \([\text{unitless}]\) is the Kronecker delta, \([\text{unitless}]\) is tortuosity, and \([L^2 T^{-1}]\) is the diffusion coefficient.

Function of parameters provided in an input file. Parameters include values of intrinsic permeability, porosity, diffusion coefficient, longitudinal and vertical transverse dispersivities, initial source geometry and loading, source location, initial concentration, and the initial pressure and concentration conditions. The modeling package has three components: Premitsu, which assembles input-files to be read; MITSU3D, which performs the actual calculations; and Posmitsu, which conditions the output for plotting. Simulated concentration maps, velocity fields, and hydraulic conductivity fields were plotted using Tecplot © 360 Build 11.0-1-125 for Windows graphing software package.

In the problems considered here, density and viscosity of fluids vary as a function of concentration, requiring concentration-dependent equations (5 and 6, respectively) to solve for these properties. For systems of varying salinity, the following equations are used.

These relationships were developed using data from *CRC Handbook of Chemistry and Physics, 91st Ed.*

Several previous studies of variable-density flow systems have been conducted with MITSU3D. For example, Ibaraki (1998) modeled dense fluids injected into homogeneous and layered media patterns to establish its utility in modeling variable-density flow systems. Ibaraki et al (2000) used MITSU3D to model instabilities observed
in experiments described by Swartz and Schwartz (1998). Their conclusions were that, while MITSU3D successfully modeled instability development, it was difficult to predict the size, shape, and propagation of the instabilities because of the complexities involved in their creation.

Table 2.1: Important Parameters of dense sodium silicate solutions manufactured by PQ Corporation (Industrial Chemicals Division) (PQ Corp, 2006).

<table>
<thead>
<tr>
<th>Conc. g/L</th>
<th>Density g/cm³</th>
<th>Viscosity Pa•s</th>
</tr>
</thead>
<tbody>
<tr>
<td>628.7</td>
<td>1.41</td>
<td>0.4</td>
</tr>
<tr>
<td>602.6</td>
<td>1.38</td>
<td>0.18</td>
</tr>
<tr>
<td>569.9</td>
<td>1.37</td>
<td>0.1</td>
</tr>
<tr>
<td>529.1</td>
<td>1.36</td>
<td>0.06</td>
</tr>
<tr>
<td>357.2</td>
<td>1.27</td>
<td>0.011</td>
</tr>
<tr>
<td>291.3</td>
<td>1.234</td>
<td>0.0055</td>
</tr>
<tr>
<td>231.5</td>
<td>1.198</td>
<td>0.0025</td>
</tr>
<tr>
<td>177.0</td>
<td>1.15</td>
<td>0.0021</td>
</tr>
<tr>
<td>127.1</td>
<td>1.114</td>
<td>0.002</td>
</tr>
</tbody>
</table>

As yet, MITSU3D has not been used to model the flow of dense, viscous fluids like that created with the sodium silicate solution. Thus, it was necessary to develop and verify a specific concentration-dependent equation to solve for viscosity. To this end, data relating silicate solution concentration to solution density and viscosity were developed from PQ Corp (2006) and included in table 2.1. This information allowed the
derivation of equations (7) and (8) relating silicate solution concentration to density and viscosity, respectively. The density equation (7) is similar to the concentration-dependent density equation for typical saline solutions (equation 5) used to model previous experiments. The viscosity equation (8) is different from normal saline solutions (equation 6), providing the possibility of accommodating viscosities much larger than typical saline waters.

Figure 2.1 shows the difference between the solutions for equations 5 and 6 with those of 7 and 8 over the range of applicable concentrations. Because it is an exponential equation, the differences between equations 6 and 8 are especially noticeable at high concentrations.

During early modeling trials, I created a source zone of five 1 cm$^2$ nodes with maximum concentration in each. It was quickly observed, however, that the high viscosity, resulting from the large concentrations at the continuous source zone, inhibited the development of the plume. Thus, it was necessary to construct a source zone geometry duplicating an early experimental time step. The experimental time of 1.5 hours was chosen as a suitable simulation start time. Because of this adjustment, the simulation start time was adjusted to match the experimental time (i.e. 1.5 hours was added to each simulation time).
2.2.2: Experimental Work

Concentration data for the heterogeneous flow tank experiments came from experiments originally described by Schincariol and Schwartz (1990). Figure 2.2 depicts the lenticular media used in their experiments. The lenticular porous media was constructed from glass beads of uniform mil sizes. Four different mil sizes were used (mil #3, mil #5, mil #7, and mil #10). Table 2.2 summarizes various properties for each of these media types.

Schincariol and Schwartz (1990) presented the results for a set of experiments involving three different saline solutions (2 g/L, 5 g/L, and 10 g/L NaCl). Table 2.3 summarizes the concentration and important properties of the dense solutions used in each of the experiments. These results were modeled using MITSU3D with the methods described previously.

As a collaborative part of this study, a scoping experiment with a sequence of glass columns was undertaken by Solpuker (2011a) using a set of PQ Corporation dense, viscous sodium silicate solutions called “Ru Solution” (viscosity 2.8 Pa•s) and “KASIL6” (viscosity 1.068 Pa•s). This experiment was designed to investigate the change in viscosity due to the dilution of sodium silicate solutions caused by their addition to and mixing with a KMnO₄ solution. It was found the KMnO₄ solution significantly reduced the viscosity of silicate solutions (Figure 2.3). This experiment suggested that silicate solutions with a high initial viscosity were desirable so the resulting KMnO₄ solution would also be viscous. The PQ Corporation N® Clear sodium silicate solution (viscosity 0.18 Pa•s) was chosen for further experimentation.
The actual experimental data for a dense, viscous solution was provided in an unpublished report by Solpuker (2011b). This experiment was conducted using a layered medium (Figure 2.4) set in a glass tank. A silicate solution with an initial concentration of 602.9 g/L was injected into the flow-tank for 8 hours. The viscosity and density of this fluid were 0.18 Pa\(\cdot\)s and 1.38 g/cm\(^3\), respectively. This solution was marked with a 300 mg/L concentration Rhodamine Wt tracer using a method described and successfully employed by Schincariol and Schwartz (1990). Uniform horizontal flow with a seepage velocity of 0.3 m/d was created from left to right through the tank using peristaltic inflow and outflow pumps (Ismatec BV-GE). Like Schincariol and Schwartz (1990), glass beads
(manufactured by Potters Industries, Inc.) served as porous media (see Table 2.2 for hydraulic properties).

![Figure 2.2: Lenticular media used by Schincariol and Schwartz (1990) for the flow-tank experiments. Dotted box indicates location of dense fluid injection. Ambient flow is from left to right.](image)

**Table 2.2: Median Grain Size and intrinsic permeability of glass beads (from Schincariol and Schwartz, 1990).**

<table>
<thead>
<tr>
<th>Bead Size</th>
<th>Median Grain Size ($D_{50}$) (mm)</th>
<th>Intrinsic Permeability ($m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mil #3</td>
<td>0.650</td>
<td>2.97x$10^{-10}$</td>
</tr>
<tr>
<td>Mil #5</td>
<td>0.310</td>
<td>6.75x$10^{-11}$</td>
</tr>
<tr>
<td>Mil #7</td>
<td>0.210</td>
<td>3.07x$10^{-11}$</td>
</tr>
<tr>
<td>Mil #10</td>
<td>0.150</td>
<td>1.64x$10^{-11}$</td>
</tr>
</tbody>
</table>
Table 2.3: Properties of the solutes in the experiments described by Schincariol and Schwartz (1990)

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Conc. NaCl g/L</th>
<th>Conc. RWt mg/L</th>
<th>Density g/cm³</th>
<th>Total Time Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2</td>
<td>500</td>
<td>1.002142</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
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<td>4</td>
<td>10</td>
<td>500</td>
<td>1.007111</td>
<td>2</td>
</tr>
</tbody>
</table>

Figure 2.3: The effect of KMnO₄ solution on the viscosity of sodium silicate solutions
Figure 2.4: Schematic design of flow-tank used for dense, viscous solution experiments. Solute was injected via an inlet made from PVC pipe embedded at the top of the tank into the upper mil #3 layer. Flow was generated from the right portion of the tank to the left.

Image analysis was conducted on digital photographs of the experiments. Images were collected hourly using a Sony Handycam video camera with 15 MP resolution. Data were transferred to a PC for processing. Photos were preprocessed using Adobe® Photoshop® CS2, version 9. Preprocessing included changing image mode from 8 to 16 bits/channel and making green-scale images by turning off red and blue channels. The process outlined in Figure 2.5 is described by McNeil et al (2006). Here, it was implemented in MATLAB version 7.8 (R2009a, 2009 The MathWorks, Inc.).

The data collected by Schincariol and Schwartz (1990) came from digitized color photographs originally collected in 1990. Because their experiment did not explicitly include an optical calibration like the present experiment, the photos were processed using a different method (Schincariol et al, 1993). This process requires using an equation relating grain size of the porous medium to photo optical density values (equation 9):
where D is optical density [unitless] and $\beta$ is media grain size [L]. Again, image processing was conducted using MATLAB.

![MATLAB IMAGE ANALYSIS FLOWCHART]

**Figure 2.5:** Step diagram showing the process by which photos are analyzed. Diagram is adapted from the photo processing approach described by McNeil et al (2006).

**2.2.3: Approach to model calibration**

The calibration for the different experimental runs was accomplished by a series of trial-and-error runs designed to compare simulated plumes with experimental results. The calibrations compared the shapes and concentrations of the three plumes. A mass balance was also performed for further comparisons.

Plume shapes were compared by two different methods. First, comparisons were made of both the distance the plume traveled laterally as well as the depth to which it
sank. Next, outlines of the simulated and experimental plumes were superimposed over each other for comparison. Differences in plume shape were identified, shaded, and qualitatively compared.

Figure 2.6: Example of grid system containing a plume calculated using MITSU3D. The point in the center of each box represents the node used to find simulation concentration (The vertical direction is denoted by the y-axis in MITSU3D).

Concentrations estimated at specific points in the flow-tank experiments were compared with concentration from the MITSU3D simulations. To facilitate comparisons, a grid was placed over each plume map so that the entire plume was contained (Figure 2.6). A 5 cm² grid was used for this purpose. Because the simulation contained 1 cm nodes, the concentration values obtained by this method reflect the concentration of 1 cm² of the grid-block area. Therefore, experimental concentration values were obtained by calculating the average concentration over a 1 cm² area surrounding the corresponding
point on the processed images. The area by area comparisons yielded a measure of the goodness of fit.

2.3. Results:

The results section provides a description of experimental and simulated plume comparisons. As mentioned, comparisons involve plume shape, concentration, and overall mass balance. Experiments described by Schincariol and Schwartz (1990) and unpublished data provided by Solpuker (2011b) are both included in this analysis.

2.3.1: Simulations of the Schincariol and Schwartz (1990) dataset

Figure 2.7 provides a comparison of the experimental and modeling results. Matches for the 2 g/L and 5 g/L trials are visually good. As Figure 2.7a shows, the 2 g/L plumes have a similar lateral and vertical extents between with the same prominent features (a lower lobe that stops at 0.6 m and upper lobe with a lateral extent that stops at about 0.9 m). The plume at its thickest point is about 8.4 cm in the experimental results and about 10.3 cm in simulated trials. The plume at its thinnest point is about 3.2 cm in the experimental results and about 5.5 cm in the simulated results. Figure 2.8 shows the goodness-of-fit for plume outlines. For this trial (Figure 2.8a), the simulated plume has a slightly larger area than the experimental plume. There was only one small area in this trial where the experimental plume is larger than the simulated plume.

For the trial with 5 g/L (Figure 2.7b), the simulation provides a plume of comparable lateral extent and prominent features (a lower lobe that stops and an upper lobe with lateral extents that stop at about 0.88 m). The maximum plume thickness is about 15.2 cm in the experimental results and about 14.8 cm in the simulated trials. The
thinnest zones are about 2.3 cm in the experiment and about 3.5 cm in the simulated plume. Figure 2.8b provides a comparison of the outlines of the experimental and simulated plumes. Similar to the 2 g/L trial, the simulated plume has a slightly larger area than the experimental plume. There are only two small areas where the experimental plume is larger than the simulated plume.

The comparisons for the 10 g/L trial are not as strong as the other two. The main deviations lay in the difference in the vertical extent of simulated and experimental plumes. The maximum thickness of the plume is about 23.4 cm in the experimental results and only about 16.1 cm in simulated results. There are similarities in key shape elements. These include a small lobe at the top, a prominent middle lobe, and a wide dilute lower lobe. The outline of the experimental plume is larger than the simulated plume (Figure 2.8c). The experimental plume sank further between the 0.15 m and 0.45 m designations in the x-direction. This created a large zone where the simulated plume deviated from the experimental plume in this trial. Another area where only the experimental plume was present is the top upper lobe, a region where the concentration was low.

Differences in plume shape might be explained by three-dimensional effects within the experimental flow-tank, small differences from lens to lens in the experimental hydraulic conductivity field, no explicit provision to create instabilities in simulations, or lighting differences across the surface of the experimental tank.

Next, I provide a qualitative point-by-point comparison in concentration between the simulations and experimental observations (Figure 2.9). Because minor differences in the shape of the plume translated into possibly major differences in concentration in
Figure 2.7: Comparison of Schincariol and Schwartz (1990) and simulated plumes for 2 g/L (a), 5 g/L (b), and 10 g/L (c). Plume concentrations below 0.1 g/L for 2 g/L, below 0.25 g/L for 5 g/L, and below 0.5 g/L for 10 g/L were not plotted for both experimental and simulated plumes.
Figure 2.8: Comparison of the outlines of experimental and simulated results for 2 g/L (a), 5 g/L (b), and 10 g/L (c). Plume concentrations below 0.1 g/L for 2 g/L, below 0.25 g/L for 5 g/L, and below 0.5 g/L for 10 g/L were not plotted for both experimental and simulated plumes.

target areas, care was taken watch that the areas from which concentrations were obtained on the experimental images with the corresponding areas on the simulated fields.

For the 2 g/L trial, 56% of the points have differences in the range from 0 to 25%, 39% of the points were between 25 to 50%, and 5% of the points are greater than 50% (Figure 2.9a). For the 5 g/L trial, 54% of the points have differences in the range of 0 to 25%, 41% of the points are between 25 to 50%, and only 5% are greater than 50%
(Figure 2.9b). For 10 g/L, 31% of the points have differences in the range of 0 to 25%, 48% of the points are between 25 to 50%, and 21% are greater than 50% (Figure 2.9c).

Figure 2.9: Graph comparing concentration found using experimental methods with simulated results. Concentrations are: 2 g/L (a), 5 g/L (b), and 10 g/L (c).

The results of the mass balance analysis followed the same trend as the other analyses with a tendency for the densest trial results to exhibit the largest deviations. The results were 19% difference for 2 g/L, 16% difference for 5 g/L, 48% difference for 10 g/L.

2.3.2: Simulation of the small tank experiments

In the small flow-tank experiments, the injected fluid was denser and more viscous than the background solution. The capability of MITSU3D in simulating this
experiment was assessed using methods described in the previous section. Figure 2.10 provides a visual comparison of modeled and experimental results for three different time steps. The 6 and 8 hour simulated concentration distributions compare quite well with the experimental plumes in terms of width and height. At 2 hours the shapes are poorly matched.

Figure 2.11 compares the outlines of simulated and experimental plume shapes. The modeled plumes at 6 and 8 hours exhibit modest differences in shape as compared to corresponding experimental plumes (Figure 2.11b and c). At 2 hours, the experimental plume is larger than the simulated plume. This result is partially the result of a thin layer of solution on the boundary of the top mil#3 layer with the mil #10 layer beneath, between 0.4 and 0.55 m in the x-direction (Figure 2.11a). This layer disperses and is negligible in later time-steps.

Figure 2.12 provides a qualitative point-by-point comparison of concentration between the simulated and observed trials. The simulated plumes exhibited consistently higher concentrations than the experimental plumes. For the plume at 2.0 hours, none of the points have differences in the range from 0 to 25%, 31% of the points are between 25 to 50%, and 69% of the points are greater than 50% (Figure 2.12a). For the plume at 6.0 hours, 11% of the points exhibit differences in the range of 0 to 25%, 39% of the points are between 25 to 50%, and only 50% are greater than 50% (Figure 2.12b). For the plume at 8 hours, 13% of the points have differences in the range of 0 to 25%, 26% of the points are between 25 to 50%, and 61% are greater than 50% (Figure 2.12c).
Figure 2.10: Comparison of dense, viscous fluid experimental and simulated plumes.
Times steps are: 2 hours (a), 6 hours (b), and 8 hours (c). Plume concentrations below 60 g/L were not plotted for both experimental and simulated plumes.
Figure 2.11: Comparison of dense, viscous fluid experimental and simulated plume outlines. Times steps are: 2 hours (a), 6 hours (b), and 8 hours (c). Plume concentrations below 60 g/L were not plotted for both experimental and simulated plumes.

Figure 2.12: Graph comparing time-step concentrations found using experimental methods with simulated results for dense, viscous fluids experiments. Times steps are: 2 hours (a), 4 hours (b), and 6 hours (c).
2.4 Discussion:

These two sets of comparisons of simulated versus experimental results highlight the difficulties in simulating experiments. As stated in the Results section, potential sources of error in modeling include three-dimensional effects within the experimental flow-tank, small differences from lens to lens in the experimental hydraulic conductivity field, no explicit provision to create instabilities in simulations, or lighting differences across the surface of the experimental tank.

Three dimensional effects could either be the solute plume moving differently in the unobservable middle of the tank or slight imperfections in lens construction (i.e. the lenses may not be the same shape throughout). These effects may have been more noticeable in the 10 g/L trial because of the relative importance of density effects with this concentration (e.g. quicker sinking leading to faster exploitation of unobservable three-dimensional causeways and imperfections) as opposed to the 2 and 5 g/L trials.

Small differences in the local hydraulic conductivity field could be caused during emplacement of the porous media in the experiments. Because media is placed through ports located at the top of the tank, it is difficult to eliminate all undulations and imperfections in lenses. Additionally, it is possible that when water was added to the tank, loose, fine sand grains shifted into the pore spaces of coarse grains. These variations could lead to variations in the hydraulic conductivity field that would be impossible to account for in the simulations. These variations would be most likely to occur near the bottom of the tank (where the water is added to the tank) and could help explain why the majority of the problems occurred in the 10 g/L trial (i.e. the trial in which the plume sank the farthest).
No explicit steps were taken to trigger the formation of instabilities during simulations. This action may have led to some of the differences between simulated and experimental plumes. Specifically, some of the small features present in experimental but not simulated plumes might have been the result of not producing instabilities. This difference could explain why larger features were simulated well while smaller features were difficult to capture in simulations.

The difference in lighting across the tank could explain some of the differences in experimental and simulated concentration. Schincariol and Schwartz (1990) reported problems in lighting the surface of the experimental tank evenly. Any darker or lighter areas on the tank relative to the Kodak color bar used to convert intensity to optical density values would lead to an over- and underestimation of concentration, respectively. A visible shadow was noticeable throughout the bottom half or third of the tank. This could have affected the 10 g/L trial, which was the only trial where the plume was present in this portion of the tank.

The comparisons of the simulated and observed plumes of the dense, viscous solutions were mixed. There was success in reproducing the shape of experimental plumes, especially in latter times of the experimental trial; however, at 2 hours significant differences existed between simulated and experimental plumes (Figures 2.10 and 2.11), and the model was less successful at predicting the concentration profile of experimental plumes (Figure 2.12). With the large density contrasts in this experiment, long, narrow instabilities were generated. The simulations did not capture these – likely leading to poor fits.
2.5 Conclusions:

Modeling the results of the Schincariol and Schwartz (1990) flow-tank experiment suggests that while this particular pattern does not increase residence time, varying high and low permeability lenses helps enhance mixing. Alternating lenses of higher and lower hydraulic conductivity within the background media provide conduits and barriers that produce complex concentration distributions. Increases in fluid density only enhance this effect. High permeability lenses lead to quicker lateral flow of dense fluids.

There are, however, inherent difficulties in working with a system with high permeability lenses relative to background media. Because the background media has an intrinsic permeability over five times less than that of the high permeability lenses, the lenticular pattern acts to decrease the residence time relative to a more homogeneous media consisting solely of background media. Another disadvantage is high permeability lenses can impede the downward transport of dense fluids. In this system, an almost continuous mil #3 lens present between -0.52- and -0.54-m (figure 2.2) suppressed the flow of any remediation chemical to further aquifer depths. This effect is amplified when mixing occurs and causes lower density chemicals to enter these high permeability lenses.

Currently, more work needs to be done to compare the transport of contaminants with that of remediation chemicals. It is possible that the advantages and disadvantages of the flow of dense remediation fluid in lenticular media will mirror those of actual contaminants. If this is the case, the contaminant will only be present in areas that remediation chemicals are present because aquifer heterogeneity will have controlled
contaminant transport in the same ways that it does remediation chemicals. If contaminants move in a way that does not mimic remediation chemical flow, remediation approaches must be carefully designed to deliver chemicals to deeper areas of a contaminated aquifer.

2.6 References:


Chapter 3: Movement and Mixing of Dense Solutions by Gravity Alone

3.1 Introduction:


Because fluids are miscible, an invading fluid can mix with the resident pore fluid. Mixing can be due to convective dispersion caused by unstable stratification (Gebhardt et al, 1988; Shincariol and Schwartz, 1990; Schincariol et al, 1994) or mechanical dispersion caused by porous media heterogeneity (Schincariol and Schwartz, 1990; Swartz and Schwartz, 1998). Mixing is important because it provides a mechanism for the spreading contaminants and remediation chemicals (e.g. dense chemical oxidants) (Schincariol et al, 1994; Swartz and Schwartz, 1998; Ibaraki, 2001).

The tendency for diffusion to transport solutes into low permeability media is of particular interest because it provides yet another mechanism for mixing (Schincariol and Schwartz, 1990; Swartz and Schwartz, 1998). This process is also important because of its contribution to the so-called “tailing” phenomenon – known to create a long-term
persistence of contaminants due to their slow release from low permeability layers (Keeley, 1989). This effect can cause problems for the rapid cleanup of dissolved plumes. Thus, it must be considered when remediating DNAPLs. A lack of knowledge aquifer heterogeneity can lead to the selection of improper remediation techniques and an underestimation of the amount of time and cost of cleanup (Keeley, 1989). For instance, the “tailing” effect can drastically reduce the effectiveness of “pump-and-treat” systems, which must remain in operation for longer periods of time to clean increasingly dilute contaminants after the initial contaminants are removed (Keeley, 1989; Cohen et al, 1994).

This study is focused particularly on potassium permanganate (KMnO₄), a widely used chemical oxidant capable of destroying chlorinated ethylenes. For example, the reaction of KMnO₄ with TCE can be described by the following equations (Yan and Schwartz, 2000):

\[
\text{KMnO}_4 + 2 \text{TCE} \rightarrow \text{MnO}_2 + 2 \text{CO}_2 + 2 \text{H}_2\text{O} + 2 \text{CA} + 2 \text{I}^\bullet
\]

where I is cyclic complex and CA are carboxylic acids. The half-life of TCE reacting with 1 mM MnO₄ is less than 20 minutes (Yan and Schwartz, 1999).

Although low permeability zones have proven to be a challenge in the remediation of contaminated aquifers, they also represent an opportunity as well. I hypothesize that aquifer heterogeneity could be exploited to provide a slow-release mechanism for a treatment chemical like KMnO₄. In effect, low permeability lenses and inclusions could sequester the treatment chemical within a zone of reaction. Like a zero-
valent iron wall, this zone of reaction could provide the basis for preventing the further spread of a dissolved plume.

The purpose of this chapter is to investigate the possibility of using dense fluid to penetrate low permeability porous media through density effects alone. I will conduct a modeling study to investigate the effect of solute density differences as well as the effect of changing the ratio intrinsic permeability in a simple layered system. I will also investigate the effect of varying source zone size on flow and transport. Finally I will determine the relative importance that each of these changes has on flow and transport.

3.2 Materials and Methods:

This study was conducted using MITSU3D, a flow and transport code that has been used successfully in similar applications (Ibaraki, 1998; Ibaraki et al, 2001). The following sections describe the code and the setup for the illustrative modeling exercise.

3.2.1: Description of MITSU3D

MITSU3D simulates fluid flow and solute transport by simultaneously solving the transient groundwater flow equation (12) and the advection-dispersion (13) equation. The following equations describe fluid flow:

\[ \frac{\partial h}{\partial t} + \nabla \cdot (v h) = S_f \]

where \( t \) [T] is time, \( n \) [L \( L \)] is porosity, \( \rho \) [M \( L \)] is fluid density, \( k \) [L \( L \)] is intrinsic permeability, \( \mu_f \) [M \( L \) \( T \)] is fluid viscosity, \( P \) [M \( L \) \( T \)] is pressure, \( g \) [L \( T \)] is gravity, \( Z \) [L] is distance from datum.
where \( c \) [M L\(^{-3}\)] is solute concentration, \( \alpha_l \) [L] is longitudinal dispersivity, \( \alpha_t \) [L] is transverse dispersivity, \( D_d \) [L\(^2\) T\(^{-1}\)] is dispersion, \( \tau \) [unitless] is tortuosity, and \( \delta_{ij} \) [unitless] is a Kronecker delta.

3.2.2: Hypothetical porous medium description

The model was applied in an idealized layered medium. The simulation domain was 20 m long and 0.6 m high. Various patterns of layering were used in the simulations. In order to provide details near the source, a variable sized model grid was used. Grid cells were 1 cm long in the x-direction within the so-called central area (1.0 m x 0.6 m) of the domain and 1.0 m long in the x-direction outside this area. All grid cells in the y-direction were 1 cm high. All boundaries were no-flow and there was no ambient or background flow. During all trials except those with larger and smaller source zones, solute was introduced in a source zone that encompassed twelve 1 cm cells in the top center of the model. Table 3.2 provides the density of the four different solutions used in the simulation trials.

Those model parameters that were kept constant in all model trials are summarized in Table 3.1. Table 3.3 provides parameters of each specific trial. The Base Case scenario (Figure 3.1a) was a simple layered system to provide a basis for comparisons to other trials. The first variation from the Base Case involved reducing the permeability of the low permeable layers. Secondly, I examined the increasing complexity along the boundary between the top high- and low-permeability layers (Figure 3.1b-d). These patterns were designed to trigger instabilities to study their
importance on transport behavior. Thirdly, the most complex pattern involved lenticular bodies in low-permeability layers (Figure 3.1e). Lastly, I examined the effects of halving and doubling the source zone size in the simplest layered medium (Figure 3.1a).

Concentration distributions for the Base Case were compared with results from the four other trials. Mass accounting was used to provide a sense of how much mass flowed into the system during a given simulation trial and compared to that of the Base Case (in % mass difference). These results were used to determine the effect of the changes between each trial on the total mass entering the model.

Table 3.1: Table of hypothetical medium parameters

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<thead>
<tr>
<th>$a_L$ (m)</th>
<th>$a_{TV}$ (m)</th>
<th>$D_d$ (m$^2$/day)</th>
<th>$\theta$</th>
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Table 3.2: The density of saline solutions used in the simulation trials.

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<tr>
<th>Concentration (g/L)</th>
<th>Density (g/cm$^3$)</th>
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</thead>
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Figure 3.1: Simulated media patterns of layering: Panel (a) is the Base Case, panel (b) a 1x1 sawtooth, panel (c) a 3x1 sawtooth, panel (d) an irregular sawtooth, and panel (e) is a case with lenticular inclusions in the low permeability layers. The Base Case pattern was used for trials investigating permeability contrasts and source zone sizes.
Table 3.3: Summary of parameters for each simulation trial. A description of each trial is given by the letters in the code and can be deciphered using the key stated below.

<table>
<thead>
<tr>
<th>Code</th>
<th>Concentration (g/L)</th>
<th>Time (days)</th>
<th>Media Pattern</th>
<th>High Perm. k (m²)</th>
<th>Low Perm. k (m²)</th>
<th># of Source Zone Cells</th>
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Key: A = Base Case, B = 1x1 Sawtooth, C = 3x3 Sawtooth, D = Irregular Sawtooth, E = Lenticular Inclusions, I = 1-order of magnitude lower permeability, J = 1-order of magnitude lower permeability, X = Source Zone Width Increase, and Y = Source Zone Width Decrease

*Media patterns can be found in figure 3.1.
+Two other permeability values exist in these trials the k-values are 5.71x10⁻¹¹ and 2.24x10⁻¹¹ for mil #5 and #7, respectively.
3.3 Results:

This section describes the results from the modeling experiments. The discussion in this section first examines results for the Base Case and then the four variations. The Base Case set of simulations includes concentrations distributions for four different fluid densities (5 g/L, 10 g/L, 25 g/L, and 50 g/L NaCl) at three different times (0.5 days, 1.0 day and 2.0 days). The other sets of simulations involving varying permeability contrasts and source zone size also include the same four fluid densities but only at 2.0 days. The remaining simulations with varying saw-tooth patterning and lenticular heterogeneities include the same four different fluid densities at 1.0 day.

3.3.1: Base Case

Figure 3.2 displays the simulation results for the Base Case. At early times in all four simulations trials, mass moves vertically downward, tending to pile up and to spread laterally once the first low-permeability unit is encountered. Vertical flow continues downward to the bottom no-flow layer with a continuing tendency for lateral mass spreading as the dense plume encounters low permeability layers.

As density increases (e.g., Figure 3.2, 50 g/L), a greater quantity of dissolved mass enters the system through the upper boundary and penetrates deeper in a given period of time. Although downward vertical flow is pervasive, mass spreading becomes even more extensive laterally as the plume encounters low permeability layers. As is evident, downward mass flow occurs more quickly as density increases. At 0.5 days, the 25 g/L plume entered the second high permeability layer while the 50 g/L plume is entered the third low permeability layer. This behavior contrasts with the 5 g/L plume, which is only present in the first high permeability layer. As will become apparent, this
behavior is consistent amongst all simulations with this general pattern of layering until mass reaches the bottom no-flow boundary. Other interesting results are worth noting. A plume that is double the concentration of any other plume will develop nearly the same shape over half the length of time if all other conditions are held constant. For example, the 5 g/L plume at 1.0 day (Figure 3.2) has the same shape as the 10 g/L plume at 0.5 days (Figure 3.2). Similarly, the 25 g/L plume at 2.0 days has the same shape as the 50 g/L plume at 1.0 days. These results imply that the relationship between increasing density and increasing velocity of plume propagation is linear, given this rather simple geometry and only density driving forces.

3.3.2: Further reduction in permeability in lower permeability layers

The next set of simulations results (Figure 3.3 and 3.4) examine a pattern of layering comparable to the Base Case but with lower permeability layers ten times and 100 times lower, respectively (Problem Sets I and J). Again, these systems are investigated with fluids of four different densities. The figures show concentration distributions after 2 days of simulation.

For the patterns of layering with a ten times reduction in permeability of the lower permeability media (Figure 3.3), downward transport of mass is less extensive as compared to the Base Case for all fluid densities. The 5 g/L and 10 g/L plumes spread laterally in the initial high permeability layer and only a rather small quantity of mass enters the lowered permeability layer after 2 days. The 25 g/L plume tends to spread laterally but a larger quantity of mass enters the first low permeability layer after 2 days. The 50 g/L plume with the greatest density contrast of all analyses provides the deepest
Figure 3.2: Concentration distributions for the Base Case Simulations: 5 g/L, 10g/L, 25 g/L, and 50 g/L solute concentration after 0.5, 1.0, and 2.0 days of elapsed time.
Figure 3.2 (continued)

Concentration (g/L)

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Concentration (g/L)

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Concentration (g/L)

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Distance (m)

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Concentration (g/L)

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solute penetration. After considerable lateral flow in the initial high permeability layer, the plume is transported through the first low permeability layer and reaches the second high permeability layer after 2 days.

With the 100 times lower permeability case (Figure 3.4), downward transport of mass is essentially nonexistent irrespective of density. In each case, the plume spreads laterally in the initial high permeability layer (Figure 3.4). Both of these trials demonstrate that the amount of mass entering the system increases with solute concentration as with the Base Case.

3.3.3: Varying the size of the source zone

The next set of simulations examine a pattern of layering comparable to the Base Case but with a wider (Figure 3.5) and narrower (Figure 3.6) source zone (Problem Sets X and Y). This effect is investigated with four different fluid densities. Results are depicted after 2 days of simulation.

The wider source zone produced concentration distributions qualitatively similar to those of the Base Case (Figure 3.5). After two days, the 5 g/L plume begins to enter the second high permeability layer, the 10 g/L plume begins to enter the second low permeability layer, the 25 g/L is beginning to enter the final low permeability layer, and the 50 g/L plume reaches the bottom no-flow barrier and begins to spread laterally.

Doubling the width of the source zone relative to the Base Case results in instabilities for all concentrations even though no specific variations of the simple layered system were provided to trigger their formation (Figure 3.1a). While these instabilities are relatively minor, they did produce slightly different concentration distributions as
Figure 3.3: Concentration distributions for simulations with low permeability layers one order of magnitude lower than the Base Case. Solute concentration at the source were: 5 g/L, 10 g/L, 25 g/L, and 50 g/L. All simulation times are 2 days.
Figure 3.4: Concentration distributions for simulations with low permeability layers two order of magnitude lower than the Base Case. Solute concentration at the source were: 5 g/L, 10 g/L, 25 g/L, and 50 g/L. All simulation times are 2 days.
compared to the Base Case, especially at the lateral and vertical ends of the plumes. The extent of these differences seems to be dependent on density; in other words, the higher the starting fluid density, the more closely the plume resembles the Base Case. Likely, any instabilities associated with the larger density case formed much earlier and were not captured in the time step at 2.0 days.

The narrower source zone produces concentration distributions almost identical to those of the Base Case (Figure 3.6). The pattern of downward transport for each of the plumes is comparable to equivalent trials in the Base Case. The only noticeable difference in any of the plumes occurs at the source zone itself, which, of course, is narrower than the Base Case.

3.3.4: Saw-tooth layer boundaries

The next set of simulations examines patterns of layering with three types of “saw-tooth” boundaries between the initial high permeability layer and the first low permeability layer (Problem Sets B-D). The first boundary (Figure 3.1b) is created with a 1 cm x 1 cm saw-tooth pattern (Figure 3.7). The next boundary (Figure 3.1c) is a more irregular 3 cm x 1 cm saw-tooth pattern (Figure 3.8). The third boundary (Figure 3.1d) is an irregular sawtooth pattern (Figure 3.9). These complex boundaries were added to trigger the growth of instabilities with the unstable system create using four different fluid densities.

Figure 3.7 shows the concentration profiles associated with the 1 x 1 cm sawtooth grid. The patterns of downward transport are nearly identical to that of the Base Case. The only instabilities to form occurred at the vertical nose of the 5 g/L and 10 g/L plumes and early in the development of the 25 g/L plume where lateral spreading was first
Figure 3.5: Concentration distributions for simulations with source zone double the size of the Base Case. Solute concentrations at the source were: 5 g/L, 10 g/L, 25 g/L, and 50 g/L. All simulation times are 2 days.
Figure 3.6: Concentration distributions of simulations with source zone half the size of the Base Case. Solute concentrations at the source were: 5 g/L, 10 g/L, 25 g/L, and 50 g/L. All simulation times are 2 days.
evident. The extent of the differences seems to be related to places where the largest concentration gradients have developed.

The 3 x 1 sawtooth grid produces more noticeable concentration differences as compared to the Base Case (Figure 3.8). Although the general pattern of downward transport for all plumes is similar to that of the Base Case, instabilities forming at the vertical nose of the 5 g/L and 10 g/L plumes are larger and more noticeable. These instabilities grew through time, creating a plume that is skewed slightly to the right for the 25 g/L and 50 g/L cases. This tendency to favor the right side of the domain is also noticeable with the 5 g/L and 10 g/L results because after one day, the instabilities on the right side of the plume are larger and more developed than those on the left.

The irregular sawtooth boundary creates the largest and most noticeable instabilities in this set of simulations (Figure 3.9). Overall, these simulations have similar patterns of vertical spreading as those of the Base Case; however, there are large and noticeable instabilities in all of the plumes except the 50 g/L trial. This complex pattern is also the only trial producing instabilities beyond the first low permeability layer in the 25 g/L plume. In spite of large concentration gradients, instabilities triggered by the complex patterning only tend to grow locally. To a large extent, the presence of low permeability layers causes them to dissipate. These results confirm conclusions of Schincariol et al (1994) that heterogeneities tend to interfere with the growth of instabilities.

3.3.5: Lenticular inclusions

The final set of simulations examines the influence of a more complex permeable field on the patterns of plume evolution. In this trial, lenticular inclusions (Figure 3.1e) have been added to the low permeability layers. Again, the set of simulations involves
Figure 3.7: Plumes created by a 1x1 saw-tooth boundary pattern. Source concentrations are: 5 g/L, 10 g/L, 25 g/L, and 50 g/L with a simulation time of 1.0 day.
Figure 3.8: Plumes created by a 3x1 saw-tooth boundary pattern. Source concentrations are: 5 g/L, 10 g/L, 25 g/L, and 50 g/L with a simulation time of 1.0 day.
Figure 3.9: Plumes created by an irregular saw-tooth boundary pattern. Source concentrations are: 5 g/L, 10 g/L, 25 g/L, and 50 g/L with a simulation time of 1.0 day.
the same four different fluid densities. Results after one day of simulation are shown in Figure 3.10.

This complex permeability field produces results that are the most different from the Base Case. The 5 g/L plume migrates about 6 cm downward into the first lenticular layer. The concentration distribution is marked by irregular lobes of several different sizes, with two larger prominent lobes on both sides of the plume and a smaller lobe in the middle of the plume. The 10 g/L plume spreads into the second lenticular layer after one day. Like the 5 g/L plume, this plume also has two larger prominent lobes on both sides and a smaller, less prominent lobe in the middle. The 25 g/L plume features two large lobes that reflect transport in different directions and to different depths. The left portion of the plume has been transported to the lowermost lenticular layer, while the right portion of the plume only reached the second lenticular layer. The total mass in each of these major lobes is also quite different, with the left lobe with more mass and covering a greater amount of surface area than the right lobe. The 50 g/L plume has migrated to the bottom no-flow layer after 1 day. Here the mass begins to move laterally, preferentially favoring the left side of the domain, similar to other trials.

3.3.6: Mass distributions in time

The analysis of mass distributions as a function of time, like concentration, provides a useful parameter for assessing system response. Ultimately from a remediation perspective, it will be important to add as much mass as possible.

Table 3.4 shows the calculated mass balance for simulations at specific times. For all problem sets, the total mass in the system did not increase over time in a linear manner but tended to decline slightly with time. For example, in the 05A trial, the initial rate of
Figure 3.10: Plumes created by a media with lenticular forms added to the lower permeability layers. Source concentrations are: 5 g/L, 10 g/L, 25 g/L, and 50 g/L with a simulation time of 1.0 day.
mass inflow to the system was calculated at 0.5 days to be 1020 g/day. This rate decreased to 836 and 727 g/day at 1 and 2 days, respectively. The decrease occurs because the maximum density gradient occurs with no mass in the system. As the plume spreads toward the bottom of the domain, the density gradient declines.

In the 50A trial, the initial mass inflow rate over the first 0.5 days is 64,600 g/day. This rate decreases as the others do to 63,496 g/day; however, there is an increase in the rate to 64,872 g/day at 2 days. This increase occurred once the mass reached the bottom no-flow boundary causing it to spread beyond the area of interest. With a large density, it is less likely for mass to pile up with more capacity to spread into otherwise unaffected areas. This behavior would tend to maintain some initial density gradient.

Interestingly, simulations with the exact same shape in problem set A (e.g. 5 g/L at 1 and 10 g/L at 0.5 days) did not have correspondingly similar mass balances. The mass in lower density trials at later times (e.g. 5 g/L at 1 day) was always slightly greater than the higher concentrations at earlier times (e.g. 10 g/L at 0.5 days).

Permeability contrasts had a greater effect on plumes of higher concentrations (i.e. 25 and 50 g/L). 25I and 50I had 23.37% and 36.14% less mass, respectively than plumes in the Base Case compared with 05I and 10I, which had 2.59% and 8.21% less mass than the Base Case, respectively. Increasing the permeability contrast even further amplified this effect. Compared to the Base Case, 25J and 50J had 26.98 and 43.13 % less mass, respectively. Again, these results were more significant than 05J and 10J, which had 2.95% and 9.38% less mass, respectively.

Varying the width of the source zone, not surprisingly, varied the amount of solute present. This effect was more significant for lower concentrations (i.e. 5 and 10
Table 3.4: Total mass of solute (in grams) in each simulation

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Table 3.5: Percent difference of Problem Set B-E, I, J, X, and Y versus “Base Case”

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<th>10</th>
<th>25</th>
<th>50</th>
<th>Time (days)</th>
</tr>
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<td>-0.59%</td>
<td>-0.70%</td>
<td>0.37%</td>
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<tr>
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<td>0.73%</td>
<td>-0.11%</td>
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<td>9.27%</td>
<td>9.10%</td>
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</tr>
<tr>
<td>Y</td>
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<td>-7.19%</td>
<td>-4.41%</td>
<td>-3.14%</td>
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</table>
g/L) than higher concentrations (i.e. 25 and 50 g/L). 5X and 10X had 36.8% and 19.8% more mass than the Base Case, respectively, while 25X and 50X had only 8.22% and 3.28% more mass than the Base Case, respectively. Similarly, 5Y and 10Y had 10.8% and 7.19% less mass than the Base Case, respectively, while 25Y and 50Y had only 4.41% and 3.14% less mass than the Base Case, respectively. This could be because less dense plumes were not as large as denser plumes, thus constant concentration source zone cells had a proportionally greater significance to the total mass of less dense plumes.

In general, Problem Sets B-D contained boundary patterns designed to trigger the formation of instabilities. They all resulted in decreased mass entering the system compared with the Base Case. Changes of mass were slight and ranged between 2.13% less mass and 2.28% more mass with an average of 0.58% less mass than the Base Case (table 3.5). There were exceptions, including C50 and D50, which had 0.4% and 2.3% more mass, respectively. Again, this is probably due to the solute reaching the bottom and thus influencing the flow.

Problem Set E (lenticular inclusions) had more mass than the Base Case for all source concentrations. While 05E had only slight more mass (0.81%), 10E had a significantly greater quantities of mass (4.52%) and 25E and 50E has almost 10% more mass (9.27% and 9.10%, respectively). It is likely that the particular choice of permeability values for the lenticular inclusions actually created a slightly more permeable layer, promoting a greater downward transport.
3.4 Discussion:

These simulations highlight the complexity of dense solute transport in porous media. The factors controlling plume development that were explored in this study are permeability values, source zone size, instability development, and the effects of lenses.

One of the more important controlling factors is the permeability value of the lower permeable layers. In the Base Case, the 50 g/L plume migrated to the bottom of the simulation domain in about one day. Lowering the permeability value of the less permeable layer by one order of magnitude slowed plume development so that it was only able to migrate to the first less permeable layer after 2.0 days. Plumes of lower density were unable to migrate through the less permeable layer after the same amount of time. Similarly, when the permeability value of the less permeable layers was reduced an additional order of magnitude, none of the plumes were able to migrate beyond the initial high permeability layer.

These results suggest that in order to take advantage of low permeable lenses in a slow release remedial system, careful preparation is necessary to assure that remediation chemicals are dense enough to migrate through low permeable layers. These results also suggest the importance of knowing where low permeable media are so they will not act as barriers to the movement of remediation chemicals to affected areas.

Lenses of varying hydraulic conductivity also significantly affected the development of the plume. The lenses in this experiment acted as conduits that promoted solute mixing and guided plume transport. The resulting plumes were more dispersed and irregularly shaped than any other plume in the study. The results of these simulations
suggest the importance of knowledge of aquifer heterogeneity in the design of a remediation system because lenses have the ability to mix and divert plumes.

The presence of instabilities in these experiments only marginally affected plume development. The 1 x 1 cm saw-tooth pattern produced the least amount of instabilities. These instabilities were relatively short-lived, and the resulting plumes were similar to the Base Case. The 3 x 1 cm saw-tooth pattern produced more noticeable instabilities. Again, these were short lived and did not affect long-term plume development. The irregular saw-tooth pattern produced the most significant instabilities. These instabilities were more important than those of the other two patterns, but only marginally affected long-term plume development. These results suggest that the presence of instabilities is not as an important consideration as media hydraulic conductivity and media heterogeneity.

Finally, source zone size also did not produce significantly different results. When the source zone width was doubled, there were instabilities that developed, despite the lack of low permeability inclusions designed to generate them. Despite these instabilities, however, the resulting plumes were not significantly different than those in the Base Case. When the width of the source zone was halved, the plume was almost identical to the Base Case.

3.5 Conclusion:

In general, the results point to the possibilities of using dense fluids for spreading treatment chemicals downward and into low permeability units. The downward transport of a plume is particularly susceptible to the intrinsic permeability of lower permeability
units. Decreasing the intrinsic permeability relative to the Base Case by only one order of magnitude virtually eliminated the rapid transport of mass into deeper layers except for the densest solute. Even in this case, the transport of solute was restricted to only one additional layer after 2 days. These results suggest that changes of intrinsic permeability of only an order of magnitude relative to surrounding media can significantly restrict the amount of dense solute flowing in an aquifer. Longer simulations will be required to fully assess the prospects with 100 times lower permeabilities.

Trials showed the possibility of creating identical plumes with double the concentration in half the time. This result suggests over modest density ranges, the response of the system scales linearly. Also, for lower concentration plumes can be predicted by simulating a denser plume over a shorter period of time under similar conditions with appropriate scaling in time. This means results could be obtained faster and using less computing power. This same trend was also observed within problem sets with instability patterns, larger or smaller source zone size, and even lenticular inclusions.

Varying the width of the source zone produced unexpected results. When the width of the source zone was doubled, plume shapes were similar to the Base Case except that instabilities exhibited a slightly altered shape. When the width was halved, the plume shape was almost exactly the same and no instabilities were observed. The mass balance revealed the susceptibility of low concentration solutes (i.e. 5 and 10 g/L) to changes in source zone size compared to higher concentration solutes. This result could be of significance with source zone nodes in lower concentration plumes. This effect
diminishes with increased concentration because the larger plumes make mass of the source zone nodes unimportant compared to the plume itself.

While the presence of inclusions in the lower permeability layer caused instabilities, my simple arrangement of low-permeability blocks produced relatively modest effects (e.g. Problem Sets B and C). A more complicated arrangement low and high permeability blocks (Problem Set D) produced more noticeable effects; however, these were short-lived and did little to change the transport of mass as compared to the Base Case. The mass balance revealed instabilities had little effect on total mass, suggesting that instability inclusions do little to change movement of mass.

Lenticular inclusions (Problem Set E) produced more noticeable effects. A noticeably high percentage of mass moved toward one side of the tank or the other depending on the point of injection, an effect exclusive to this Problem Set. This suggests source zone placement is a vital consideration when simulating solute transport. The increase in mass in Problem Set E also suggests that, along with increased mixing, lenticular inclusions augment the movement of mass by exposing additional areas of the domain. The increase of the significance of this effect with increased solute concentration suggests that the more inclusions the plume is exposed to, the greater the change. The finding that 50E had a similar increase in mass as 25E is the result of interaction with the no-flow boundary.

3.6 References:


Chapter 4: Concluding Statement

The preceding work presented modeling results of a study investigating the movement of dense, viscous fluids in heterogeneous porous media. The aim of this thesis was to explore the development of a new passive remediation approach. This approach involves increasing the residence time of dense chemical oxidants by augmenting their viscosity and taking advantage of natural heterogeneities of porous media. These effects were examined by simulating an experiment (Schincariol and Schwartz, 1990) that tracked the movement of dense fluid through a lenticular media in a 1.068 m x 0.71 m flow-tank (Chapter 2), an unpublished experiment (Solpuker, 2011b) that tracked the movement of a dense, viscous solution through a layered media in a 0.8 m x 0.3 m flow-tank (Chapter 2), and a series of idealized layered media with a domain size of 1.0 m x 0.6 m (Chapter 3). This chapter provides conclusions to these studies that explain and relate the results to the development of the new remediation approach.

Chapter 2 demonstrated how fluid density, lens permeability, and groundwater velocity influence vertical transport and lateral spreading of dense solutions in lenticular media. Fluid was guided by preferential flow pathways resulting from high permeability lenses. These lenses were about six times more permeable than the background matrix. The density of the solution significantly affected the amount of vertical transport because denser fluid was able to penetrate deeper into the media. As a result, lateral spreading was also enhanced because fluid moved along more of the high permeability
fluid moved along more of the high permeability preferential pathways as it migrated further downward.

This study also demonstrated the importance of low permeability lenses in the movement of the plume. The two different types of lower permeability lenses were about half and a quarter of the permeability of the background matrix. Low permeability effectively slowed or prevented the downward transport of plumes at certain points in plume development. The 2 and 5 g/L plumes were both restricted to the middle portion of the aquifer, roughly the area they were injected. Additionally, very little mass migrated into the low permeability lenses. While the 10 g/L plume did migrate through the lower permeability lenses, a preferential pathway created by a high permeability lens coupled with a barrier created by a low permeability lenses prevented its transport to the bottom of the simulation domain. These results suggest the necessity of utilizing a fluid with sufficient density to allow delivery of a chemical oxidant to deeper affected portions of a hypothetical contaminated aquifer.

Finding the correct ratio between high and low permeability lenses is important to the success of the in-situ remediation approach. Preferential pathways created by high permeability lenses could effectively divert fluid from contaminated areas of a hypothetical aquifer. The problem could be compounded if this is coupled with barriers created by low permeability lenses. This problem could be overcome by the utilization of a solution with sufficient density to migrate through all high and low permeability lenses. As suggested by the results of the 10 g/L plume in chapter 2, this fluid would have to be much denser than water to be effective.
Along with the importance of lens, ambient fluid velocity is also important to the movement of dense fluids in porous media. Because a constant concentration boundary condition was applied to the solute source zone of all simulations in chapter 2, the higher the ambient fluid velocity, the more mass entered the system. This is because ambient fluid moves mass away from the source zone and more mass is produced at the source zone. However, higher ambient fluid velocity prevented downward plume transport. This is because higher velocities enhance the importance of preferential flow pathways resulting from high permeability layers. At sufficient velocities, this can impede downward transport of plumes. This could be an important consideration to an in-situ remediation approach.

Chapter 2 also demonstrated the success and shortcomings of modeling dense, viscous solutions using MITSU3D (Ibaraki, 1998). Because the code had never been used to simulate the movement of viscous fluids, it was necessary to develop new equations to solve for the density and viscosity of the silicate solutions used in the experiments. The complexity of these equations made simulations complicated, non-linear problems. As a result of these complications, shapes and macro-scale concentrations of the experimental results were produced successfully by the model; however the specific point-by-point concentrations were not produced successfully. This could be because no effort was made to model fingering instabilities observed in experiments. These instabilities often control local-scale concentrations.

The modeling results of dense, viscous solutions suggested that a long-term source of remediation solution can be achieved by manipulating the viscosity of dense, chemical oxidants. The high viscosity of the solution controlled the downward transport
of the plume. This could potentially allow for the controlled, efficient delivery of oxidants to deeper portions of an aquifer at high concentrations. This solution would eventually be diluted by ambient fluid and decrease in viscosity. It would then, ideally, slowly release oxidants over a long period of time.

Chapter 3 investigates the downward transport of dense solutions by gravity alone. Simulations were conducted in a media of alternating high and low permeability layers. Four fluid densities were used and compared in each trial. After modeling a comparative Base Case, the permeability of the less permeable layer was changed to investigate the effects of permeability ratio on plume transport. Next, the size of the source zone was changed to investigate its effect on plume propagation. Additionally, saw-tooth boundaries of varying complexity were added to the interface between the initial higher permeable layer and the first lower permeable layer. This was done to investigate the importance instability development in the plume transport. Finally, lenticular inclusions were added to all lower permeable layers to observe the effects of lenses on plume development.

The permeability ratio of the layers had an extremely important effect on the downward transport plumes. Decreasing the permeability of the lower permeable layer by ten times prevented the downward transport of all plumes except the densest. Decreasing the permeability by 100 times that of the Base Case effectively prevented all downward transport of plumes, regardless of the density. These results suggest that the ratio of permeabilities of the layers is an important consideration for efficient delivery of dense chemical oxidants in layered media. If the ratio is too high, it is possible that remediation chemical will not migrate to deep affected areas. As is suggested by the 50 g/L plume, it
is possible that the density of the fluid could be increased sufficiently to overcome this effect.

The development of instabilities along the boundary of the initial high permeability layer and the first low permeability layer proved to be of little consequence to long-term plume development. While more noticeable instabilities formed by increasing complexity of the saw-tooth boundary, these instabilities were all relatively short-lived and caused only marginal differences in plume development. While it was already known that complex heterogeneities in aquifers prevent the propagation of instabilities (Schincariol et al, 1994), these results suggest that instabilities are unimportant even in simple layered systems.

Lenticular inclusions in the low permeability layer, on the other hand created drastically different solutions. The lenses led to preferential flow paths and barriers. This caused the plumes to spread preferentially toward the left side of the media. These results reinforce the importance of chemical oxidant placement in the design of in-situ remediation systems. Knowledge of the lenticular structure is very important to system success.

Solute source zone size, surprisingly, had very little effect on plume development. When the source zone size was doubled, the plumes did develop instabilities, but they had very little effect on long-term plume development. Halving the width of the source zone had almost no effect on the plume at all.

The development of dense plumes and dense, viscous plumes is an important consideration when working with in-situ chemical oxidants. Dense plumes are significantly affected by groundwater velocity. High groundwater velocity can increase
the significance of preferential flow paths and thus increase the lateral spreading of a plume. In contrast, high groundwater velocity can prevent the downward transport of a plume. These contrasting effects must be considered when designing a remediation approach. Additionally, the permeability of the media in which plumes propagate must also be understood. The importance of accurate permeability measurements increases with the heterogeneity of the media (and thus the complexity of the plume). Careful consideration of both of these effects can lead to the implementation of the best remediation approach.
List of References


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